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**Liquid-liquid extraction using solvent mixtures with a critical
point of miscibility**

Ullmann, Amos, Ph.D.

City University of New York, 1993

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**300 N. Zeeb Rd.
Ann Arbor, MI 48106**

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**LIQUID-LIQUID EXTRACTION USING SOLVENT MIXTURES
WITH A CRITICAL POINT OF MISCIBILITY**

by

Amos Ullmann

A dissertation submitted to the Graduate Faculty in
Engineering in partial fulfillment of the requirements
for the degree of Doctor of Philosophy,
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11/16/92
Date

Reuel Shinnar
Prof. Reuel Shinnar
Chair of Examining Committee

11/16/92
Date

Gerard J. Bowen
Prof. Gerard Bowen
Executive Officer

Prof. Roberto Mauri

Prof. Irven H. Rinard

Supervisory Committee

The City University of New York

Abstract

LIQUID-LIQUID EXTRACTION USING SOLVENT MIXTURES
WITH A CRITICAL POINT OF MISCIBILITY

by

Amos Ullmann

Adviser: Professor Reuel Shinnar

The isolation and purification of solutes by a novel type of separation, the Phase Transition Extraction (PTE) process, has been developed and studied.

The main idea underlying the PTE process is based on the use of solvents that have a critical point of miscibility. By manipulating the temperature of such solvents across the coexistence curve one can alternately create regions where either the solvents form a homogeneous solution or they separate into two distinct phases. Hence, the mixing and settling sections of the conventional extraction equipment are replaced in the PTE process by heated and cooled sections.

The formation of a single phase in the mixing section results in a substantially superior contact between the solvents, eliminating the need for intense agitation.

The continuous change in the composition of the phases during the phase separation process prevents the formation of stable interface on which solids or emulsion-forming

impurities can adhere. Consequently, the coalescence process is very fast, and the process is not sensitive to the presence of impurities or emulsifiers.

The PTE process allows high efficiency extraction in emulsion forming systems such as fermentation broth without the use of pre-filters, emulsion-breakers, or centrifuges. Moreover, since a high stage-efficiency can be obtained in the PTE process with a minimal or without any mechanical mixing, the degradation of shear sensitive compounds is avoided.

Operating the PTE process in a column with no moving parts incorporates the simplicity of non-agitated columns with the high efficiency of agitated columns. This makes the PTE column an attractive tool for separations that require a large number of theoretical stages. In addition, moving parts, bearing and the like, which are subjected to mechanical wear, can be eliminated. The ability to effectively seal the equipment is particularly important in handling of irradiate compounds where remote operation, low maintenance, and heavy shielding are required.

The above features of the PTE process could allow for separation processes which are at present economically not feasible or difficult to carry out.

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1 INTRODUCTION

Separation processes play an important part in the Chemical Industry. They are especially critical in the new developing biotechnology industries in which separation is a major part of the production cost.

In the present work we present a novel separation process, the Phase Transition Extraction (PTE) process, that could add a valuable and powerful tool to the process designer and could overcome some of the constraints in present solvent-solvent extraction processes.

The objective of this work is to test the feasibility of batch and continuous operation of the proposed PTE process, to study and demonstrate its advantages compared to conventional extraction processes, and finally provide a firm basis for understanding the different features and phenomena involved in this process. Consequently, this work presents a basic scheme from which future designs of the PTE process can be developed for different separation assignments.

Essential Content of The Work

In Section 2.1 we summarize the basic principles of conventional liquid-liquid extraction (LLE) process and describe some of the most widespread LLE equipments in order to show their advantages and limitations. Some specific applications of the LLE process are also listed identifying difficulties in the use of present LLE methods in various

commercial applications.

Emulsion formation is a common problem in industrial LLE processes particularly, in the biotechnology and pharmaceutical industries. Some of the basic mechanisms of emulsion stabilization are summarized in Section 2.2.

As the whole approach of the PTE process is based on using solvents mixtures with critical point of miscibility, we review their properties in Section 2.3.

In Section 3 we introduce the Phase Transition Extraction Process (PTE) and illustrate the basic idea underlying the novel approach. We also give a list of the PTE process advantages when compared with traditional extraction processes.

The novel approach is based on using of solvents that have a critical point of miscibility. By manipulating the temperature of such solvents across the coexistence curve, one can alternately create regions where either the solvents form a homogeneous solution or they separate into two distinct phases.

The formation of a single phase in the mixing section results in a substantially superior contact between the solvents, allowing efficient and rapid mass transfer of solutes between the solvent phases with a minimal or without any mechanical agitation.

In the settler section, where the homogeneous solution is separated into two distinct phases, a continuous change in the

composition of the phases prevents the formation of stable contaminated drop surfaces. Consequently, the coalescence process is very fast and the process is not sensitive to the presence of impurities or emulsifiers.

In Section 4 we describe a series of batch experiments conducted in order to demonstrate the feasibility of the PTE process. These experiments demonstrate that following a temperature quench of the homogeneous solution into the two phase region, the solute in the separated phase is distributed according to the equilibrium state. In addition, the coalescence and phase separation when coupled with the phase transition process are very fast.

The experiments also demonstrate that the phase separation rate following the temperature quench is fast even in the presence of emulsifying substances that cause the formation of stable emulsion when the solvents are mixed isothermally. The absence of stable interfaces during the phase transition process appear to prevent the adsorption of the emulsifiers on the droplets surface and allow a rapid coalescence process. The most convincing demonstration of the rapid phase separation phenomenon is shown in the experiments with the extraction of fermentation broth. Isothermal mixing of the broth with extracting solvents lead to the formation of a very stable emulsion. In contrast, extraction via the PTE process provides a complete phase separation in less than one minute, with improved recovery of the product, and with

obtaining a solvents extract free from solids.

In Section 5 we examine the feasibility of operating the PTE process in a column. We summarize the development and testing of single-stage and three-stage laboratory-scale columns. A model is developed to evaluate the heat requirements and to described the flow pattern in the PTE column. In contrast to conventional columns where two distinct phases at uniform temperature exist throughout the column, in the PTE column the solvents streams are subjected to periodic change of their temperature (and therefore their densities). Furthermore, in the mixing section of the PTE column the solvent streams are mixed together to form virtually a single homogeneous phase. The model predicts successfully the hold-up in the mixing section and the energy consumption of the experimental columns.

The performance of the columns is evaluated by extracting a solute between two countercurrent solvent streams. The experiments show that the PTE column can be operated with high efficiency without any moving parts. The performance test of the column demonstrates that an actual stage (one heating and one cooling section) provides one theoretical stage (100% stage efficiency). In our experimental set-up it is equivalent to 4.5 theoretical stages per meter. Furthermore, it is demonstrated that the stage efficiency is not affected when increasing the total number of actual stages in the column. To evaluate the impact of heating and cooling, which

served as the basis for the PTE process, the columns are also operated isothermally using identical throughput. In comparison to the isothermal operation mode, the PTE column shows 350% stage-efficiency improvement.

Finally in Section 6 we summarize our work and suggest some application for the PTE process.

2 BACKGROUND

2.1 Liquid-liquid Extraction

Liquid-liquid extraction (LLE) has important uses in many industries and has been extensively studied (Harland, 1963, Treybal, 1963, Hanson, 1971, Lo et al., 1983, Akel and King, 1984 and Alegert, 1988). Such processes are used both for the extraction of one compound as well as for the separation between two and more compounds (fractional extraction).

In one sense there is a strong similarity between the distillation and the LLE processes. In both cases the operations generally rely upon the unequal equilibrium distribution of substances to be separated between two phases. However, while in the distillation operation the two phases are generated from the original solution by addition of heat, and the components of the original solution then distribute unequally between the liquid and vapor phases, in the LLE process, the second phase is created by addition of extraction solvent, and the solutes are distributed between two liquid phases.

In general, LLE will be preferred either where distillation fail or where, despite some disadvantages, it provides a less expensive overall process than the distillation process. The following list indicates some typical examples where LLE has demonstrated its unique

abilities as a separation method.

1. As a substitute for distillation process where LLE is less expensive.

1.1 Separation of close-boiling liquids. An example is the separation of butadine (b.p. -4.75°C) from butylenes (b.p. -5 to -6°C).

1.2 Separation of liquids of poor relative volatility.

An example is the separation of acetic acid and water, which, despite their relatively large difference in boiling point, have poor relative volatility.

1.3 For mixtures with very high boiling point where high-vacuum is essential for the distillation process, like long-chain fatty acids and vitamins.

2. As a separation means where distillation process fail.

2.1 Separation of heat-sensitive substances such as antibiotics.

2.2 Separation of solvents that form azeotropes.

3.3 Separation according to chemical type, where boiling points overlap. An example is the separation of aromatic hydrocarbons from paraffin hydrocarbons.

The LLE process procedure is simple in concept and usually requires contacting of a feed containing the solute to be extracted with a solvent, this solvent/feed mixture is usually immiscible but may be partially miscible in some

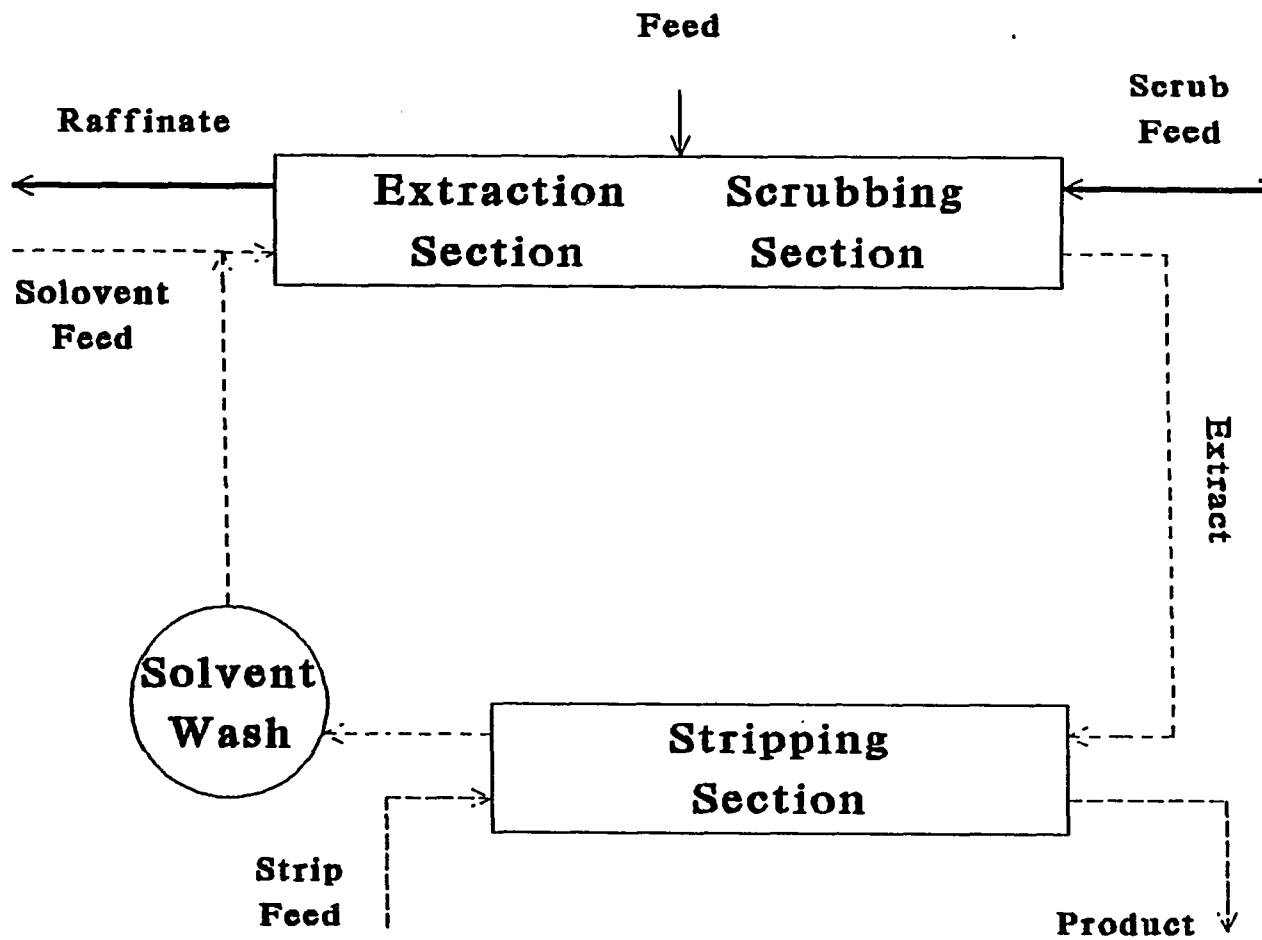


Figure 2.1: Typical solvent extraction process.

cases. After forward extraction, the solute remains in the solvent phase and the depleted feed becomes the raffinate (see Fig. 2.1). In fractional extraction the extract is scrubbed with an immiscible phase (usually involving the same phase type as the original feed) in order to improve the purity of the final product. After scrubbing, the solvent is stripped of its solute and the regenerated solvent returned as solvent feed to the process. Often, the returned solvent is washed to remove breakdown products. The strip solution provides a product stream.

It is important at this stage to recognize certain features of the process which the present work will seek to change.

The extraction and the stripping involves liquid-liquid contacting in which the droplets of one phase are dispersed in a second phase and mass-transfer has to take place across liquid-liquid boundary. There are several types of contact-equipment in industrial use, and a brief review will be given in the following section. Basically, there are two types of units. Those in which each individual stage is a separate unit and those in which several stages are integrated into one column. Multistage-columns, can be simple spray or packed columns, or can have stages equipped with various types of mixing devices separated by coalescence sections. The stage efficiency and the throughput of such devices are, obviously, a strong function of the mass-transfer and the coalescence

rates.

Another important point worth mentioning is the fact that high intensity mixing is required in order to form small drops and good contact between the phases in slow mass-transfer systems. However, the shear stress induced by such a mixing can, in many cases, damage high molecular weight molecules (Hsien-wen, 1980). In addition, the intense mixing forms fine dispersions which reduce the coalescence rate, or, in the presence of surface active impurities, may even cause a "stable emulsion", one of the operating hazards of solvent extraction equipment.

It would be a novel approach with significant advantages to have contacting equipment and solvent systems that will operate with minimal or without any mechanical agitation, and in which there will be no stable boundaries to slow down the mass-transfer and the coalescence rates.

2.1.1 Existing Equipments for Liquid-Liquid Extraction

Detailed descriptions of industrial LLE equipments are given in general works such as the Handbook of Solvent Extraction (Lo et. al., 1983), and by Ritcey and Ashbrook, 1979, and Schweiter, 1979. Some of the most widespread devices are described below in order to show their advantages and limitations.

Mixer-Settlers. This class of device can range from a simple tank with an agitator in which the phases are mixed and then allowed to settle prior to pump-out (Fig. 2.2), to a large, compartmentalized, horizontal or vertical structure. In general settling must be carried out in tanks, unless centrifuges are used. Mixing, however, can be carried out by impingement in a jet mixer; by shearing action, if both phases are fed simultaneously into a centrifugal pump or in-line mixing device; by injectors where the flow of one liquid is induced by another; or in orifice or mixing nozzles.

A major problem in settlers is emulsification, which occurs if the dispersed droplet size falls below 1 to 1.5 μm or in the presence of surface active impurities. When this happens separator membranes, meshes, electrostatic forces, chemical treatment, or other means are required to speed the settling action.

Spray Columns. In spray columns, one phase is dispersed as drops that move through the second, or continuous, phase as result of the difference in phase densities. At the main interface the drops coalesce and leave the column (Fig. 2.3a). There have been relatively few applications of the spray column in industry. Although it can handle high flow rates and is relatively simple and cheap, it suffers from serious back-mixing of the continuous phase. Driving force for mass transfer are reduced, and, as pointed out by Laddha and Degaleesan (1978), a spray column ordinarily is equivalent to

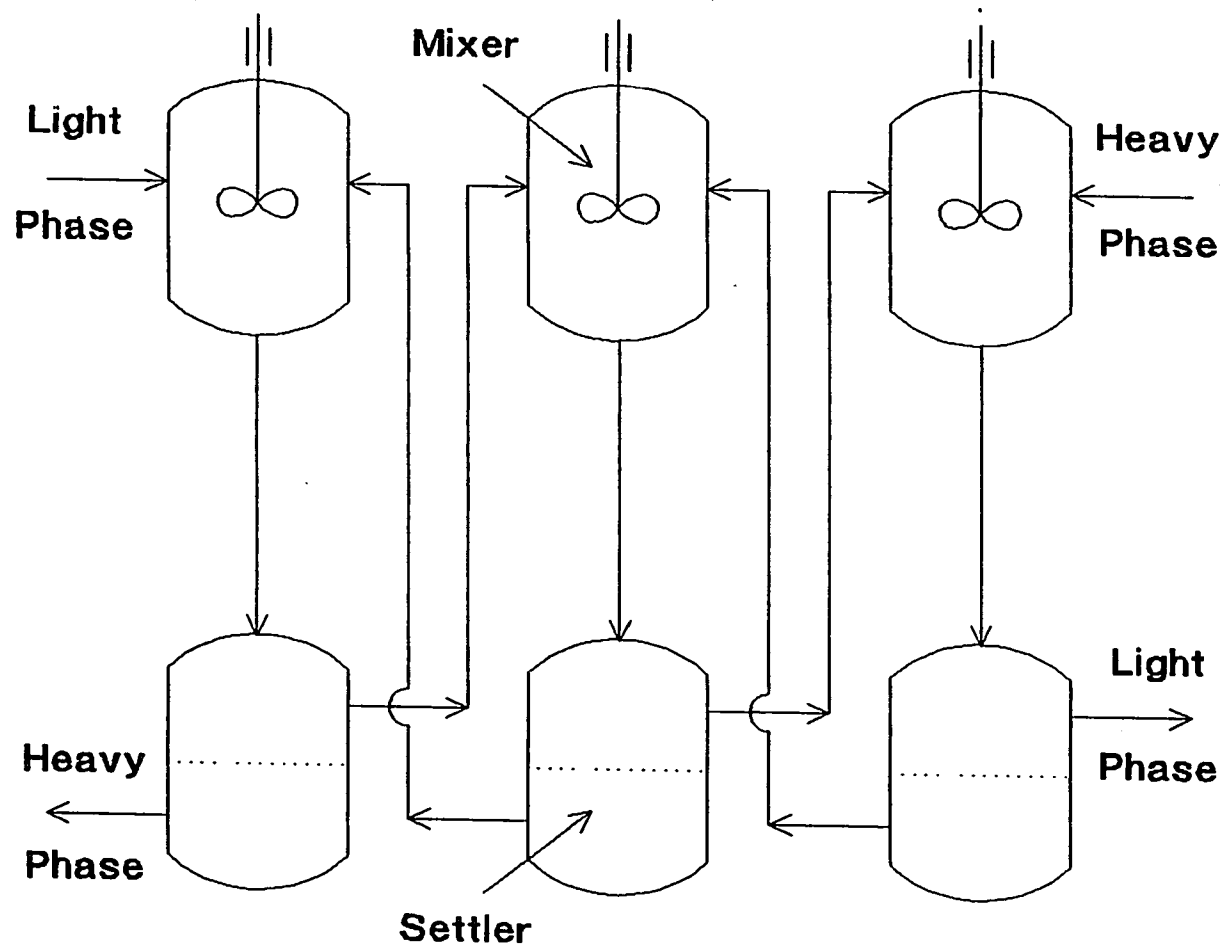


Figure 2.2: Schematic diagram of mixer-settler extractor.

not more than a few theoretical stages. In general, this situation appears to worsen as the diameter of the column is increased (Horvath et al., 1979).

Packed Columns. A spray column becomes a packed tower if its shell is filled with packing pieces (Fig 2.3b). Packing reduces axial mixing, lengthens residence time, and causes distortion of drops; the result is an increase of mass transfer (Eckert, 1976). However, packing reduces the area available for flow, thus lowering capacity.

Although packed columns are not suitable for liquids containing suspended solids or for those of high interfacial tension (Treybal, 1963), they are used in wide range of applications. Normally a packed column is preferred over a spray column, as the reduced flow capacity is less significant than the improved mass transfer. Packed columns should not be used if the ratio of the flow rates is outside the range 0.5-2.0 because of probable flooding when suitable holdup and interfacial area are provided (Treybal, 1968, Lo et al., 1983). Although axial mixing is less severe than in spray column, mass-transfer rates are found to be poor. Therefore, it is recommended (Treybal, 1980) that instead of packed columns, Sieve-tray towers be used for systems of low interfacial tension and mechanically agitated extractors for those of high interfacial tension.

Perforated-Plate (Sieve-tray) Columns. Perforated-plate columns consist of a series of trays, provided with orifices,

and placed one above the other in a vertical shell. Drops of dispersed phase form from the orifices, and flow upward through a layer of continuous phase then coalesce under the next plate of the column. The continuous phase flows horizontally across a plate, and then through a downspout to the plate below (Fig. 2.3c).

Advantages of sieve-tray columns include elimination of axial mixing between trays, and whatever mass-transfer benefits accrue from repeated coalescence and redispersion of drops. However, they are subject to the same limitations as distillation columns: flooding, entrainment, and, to a lesser extent, weeping. Additional problems such as scum formation due to small amounts of impurities are frequently encountered.

Sieve-tray columns are however well established in many different applications, especially in petroleum refining and petrochemical plants.

Mechanically Agitated Extractors. If the surface tension between the two liquid phases is high and/or the density differences are low, gravity forces will be inadequate for proper phase dispersal and the creation of turbulence which are important for high transfer rates. In this case, mechanically agitated extractors are necessary.

This category includes extractors in which mechanically moving parts within the extractor itself serve to stir or agitate the liquids as they pass through, and also those in which the agitation is transmitted hydraulically to the

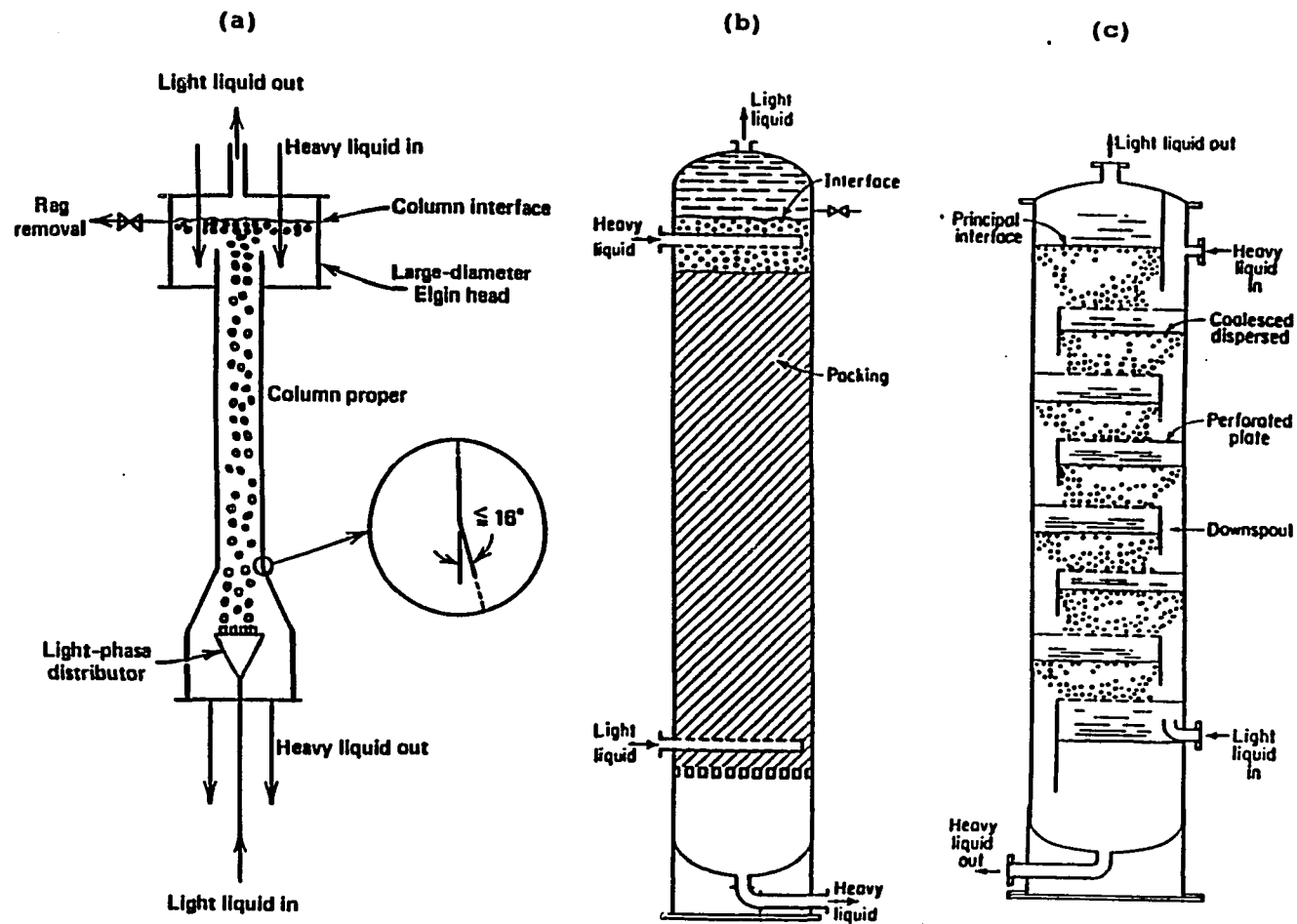


Figure 2.3: Unagitated columns: (a) Spray column of Elgin, (b,) Packed extraction tower and (c) Perforated-plate extractor (Treybal, 1963).

extractor contents.

In the case of mechanically agitated extractors, rotating agitators driven by a shaft that extends axially through the column are used to create shear mixing zones alternating with settling zones in the column. Differences between the various columns lie primarily in the mixers and settling chambers used. Alternatively, agitation can be induced by moving the plates back and forth in a reciprocating motion as suggested by Van Dijck (1935) and developed by Karr (Karr, 1959, and Karr and LO, 1971).

The RDC, rotating disc contactor (Fig. 2.4a), was developed by the Royal Dutch/Shell Group at Amsterdam Laboratory during 1948-1952 and has since found numerous applications. Some hundreds of RDCs are at present in use worldwide, ranging in diameter from less than 1 m to 4.5 m. Rapidly rotating discs provide the power required for mixing, and the annular rings serve the purpose of guiding the flow and preventing back-mixing.

In the original Scheibel (Scheibel, 1948) device, mixing was obtained by unbaffled turbine blades (Fig 2.4b), in later versions (Scheibel, 1956) baffles were added. The wire mesh packing between the turbines promotes settling and coalescence.

The Oldshue-Rushton (Lightnin CM Contactor) (Fig 2.4c), which is no longer widely used, has deep compartments with turbine agitators and no separate settling zones.

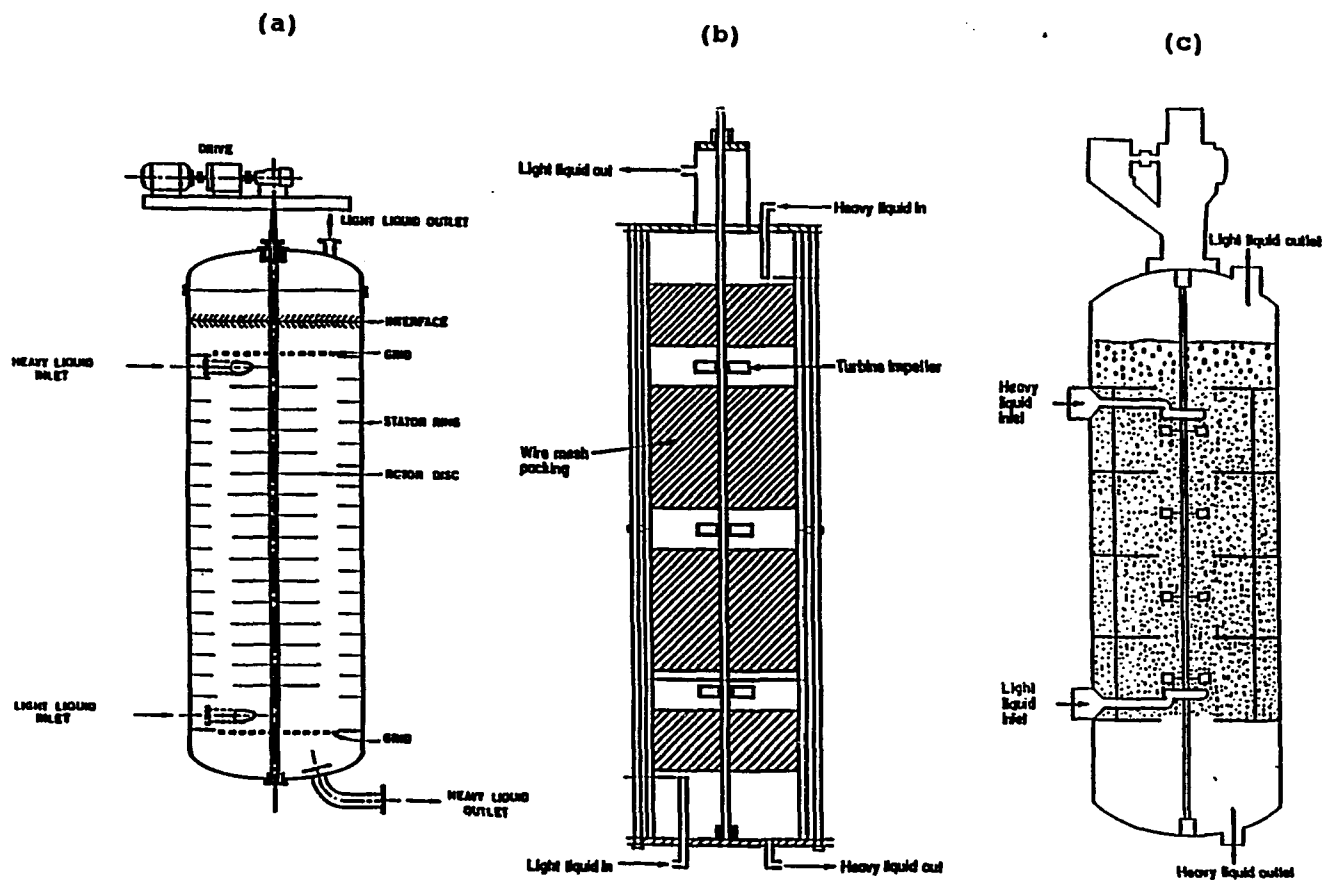


Figure 2.4: Agitated columns: (a) Rotating-disc extractor, (b) Scheibel extractor (first model) and (c) Oldshue-Rushton extractor (Treybal, 1963).

There are two type of extractors which are utilizing the hydraulic agitation principle. The Pulsed Packed Column (PPC) (Fig. 2.5a) in which a pulsator, at the column base, imparts an up-down movement to the total liquid contents through a packing, specifically, Rasching rings, and the Pulsed Plate Column in which the liquid is pulsed through series of perforated plates (Fig. 2.5b). The best known application of these column types have been in the nuclear fuel industry (Judson, 1958). Here, mechanical agitation of some sort is necessary to reduce excessive extractor heights in order to reduce the expense of massive radioactive shielding. At the same time moving parts, bearings, stuffing boxes, and the like, which are subject to mechanical wear and corrosion must be avoided, since in many instances maintenance is impossible.

In general, all the mechanical agitated columns are suffering from operational difficulties in handling systems that easily emulsify, or have small density difference.

Centrifugal Extractors. Centrifugal forces, which can be thousands of times larger than gravity, can greatly facilitate separations where emulsification is a problem, where low-density differences exist, or where very low residence times are required because of rapid product deterioration. Commonly, centrifugal extractors have only one or two stages, however four-stage units have been built (Lo et al., 1983). From mechanical point of view, they are precision equipment and hence expensive to build and maintain.

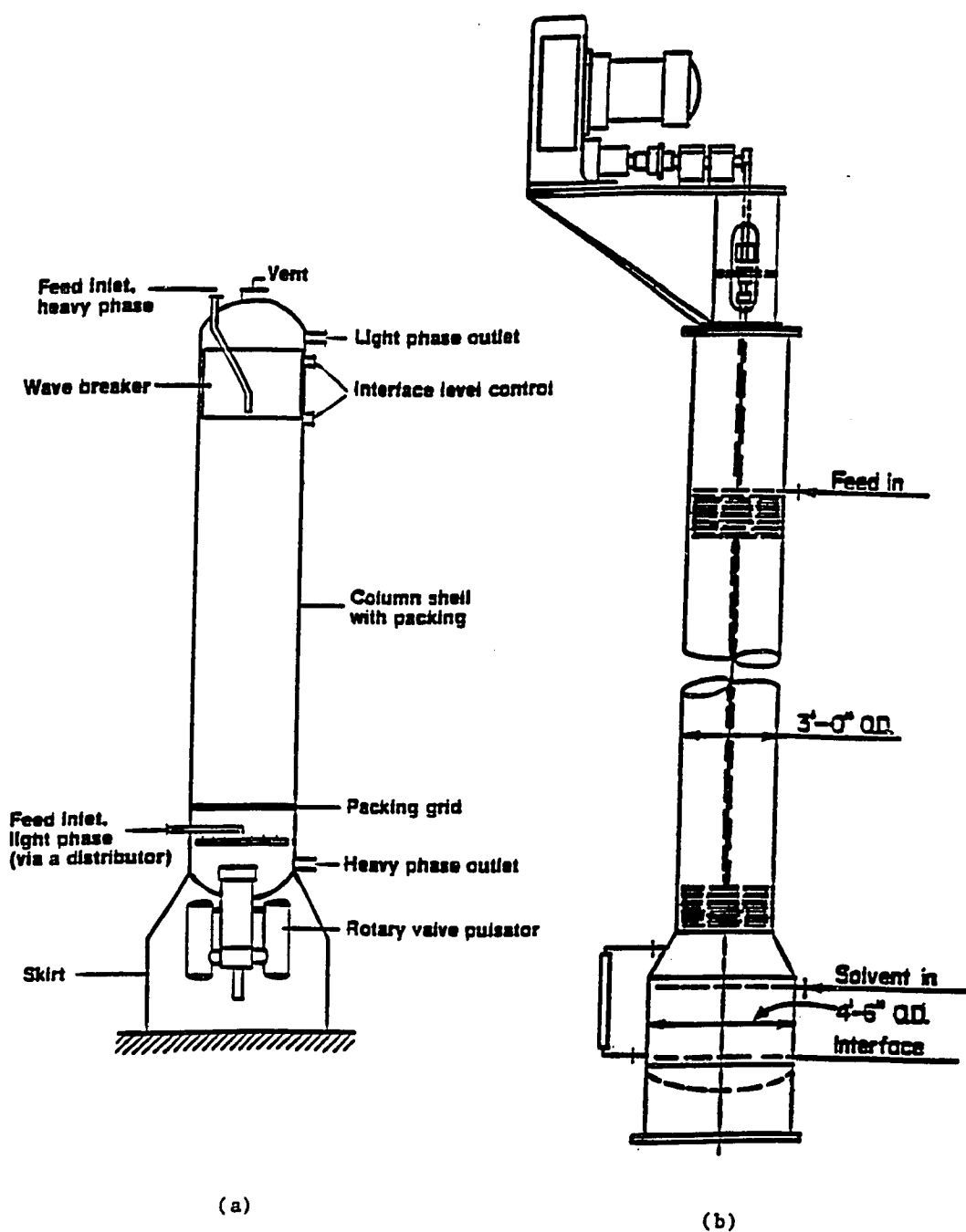


Figure 2.5: Pulsed packed (a) and pulsed sieve-plate (b) columns.

2.1.2 Some applications of Solvent Extraction

There are many applications of LLE, and most of them are summarized in various reviews (Lo, 1983, Ritcey and Ashbrook, 1979, Schweiter, 1979, Alegeret, 1988, and Blumberg, 1988). Some specific applications are listed below in order to point out the range of importance of the LLE process, and to identify difficulties in the use of the present methods of solvent extraction in various commercial applications.

Organic Solutes

The applications of the LLE in the chemical industry can be grouped as follows:

- a) Petroleum and petrochemical industry;
- b) Coal tar industry;
- c) Pharmaceutical and food industry.

a) Petroleum and petrochemical industry - The need to separate mixtures of aliphatic and aromatic hydrocarbons provided the first large-scale applications for LLE. The advantage of solvent extraction was that it represented a physical means for separating groups of components of similar chemical type, so energy intensive processes such as distillation are avoided. Thus a solvent which preferentially dissolved aromatic component from mixtures of hydrocarbons could be used to remove aromatics from kerosene and lubricating oils.

LLE is now used extensively for the production of high-

purity aromatic extracts. Benzene, toluene and xylene (BTX), produced in this manner, are the essential raw materials for products such as polystyrene, nylon and Terylene.

b) Coal tar industry - In the coal tar industry LLE is used to separate tar acids from basic or natural compounds. These processes use the principles of fractional extraction. An example of fractional extraction is the separation of tar acids from crude tar distillate using aqueous methanol and hexane (Newworth et. al. 1951).

c) Pharmaceutical and food industry - The first major, and still by far, the most important use of solvent extraction in the pharmaceutical industry is in the manufacture of penicillin. Penicillin is an umbrella term covering a range of compounds, having the same basic structure but differing slightly, e.g. in the alkyl group. It is produced by a fermentation process and extracted by organic solvent such as butyl or amyl acetate, chloroform, or methyl isobutyl ketone (Souders et al., 1970). In order to increase the solvent to aqueous distribution coefficient of the penicillin, the pH of the broth is typically reduced to about 2-2.5 with sulfuric acid. However, the low pH causes a relatively rapid decomposition of the penicillin so a fast extraction is needed. The need for rapid extraction favors the use of centrifugal contactors, where the residence time is typically of the order of seconds. Some description of various extraction processes using different solvents at different pH

ranges and contact equipments are reviewed by Rowley et. al. 1946, Kansawa et al. 1950, Eisenloher and Schariau 1955, Zhukovskaya 1972, and Radzinskaya et al. 1977.

Emulsion formation is a common problem in the extraction of the penicillin from the fermentation liquor. Current practice to overcome this is to add a precise quantity of deemulsifying agent to the aqueous stream just prior to extraction. An example for such a treatment is given by Stround and Ransley (1956).

The traditional process for the manufacture of penicillin requires that the broth be filtered to remove mycelium prior to solvent extraction. Direct extraction of the unfiltered fermentation broth has the potential of increasing the extraction efficiency by up to 10% since penicillin adsorbed onto the mycelial solid can also be extracted. In addition, there are the advantages that filter aid is not required and the broth is not diluted with wash water from the filtration stage. Extraction processes of unfiltered broth are reported by Anderson and Lau 1955, and Karr and Lo 1977.

Fermentation followed by LLE are employed in the preparation of a number of other antibiotics such as: Erythromycin (Kostareva et al. 1971, 1974, 1977), Tetracyclines (Sobine et al. 1950), Bacitracin (Miescher, 1974) and Cephalosporins (Andrisano, 1976). Like the antibiotics, a number of other pharmaceuticals are produced in the aqueous liquors of fermentation broths and hence are

obtained by LLE. Vitamins A, B₁₂, and C have been recovered in this way. Prednisolone, a steroid compound, can be extracted from a bacterial fermentation by use of chloroform (Nobile, 1958). Actinomycin, used in cancer chemotherapy, is obtained from fermentation broth by use of ether as the organic phase (Waksman and Woodruff, 1945).

The application of LLE in the food industry long predates modern technology. In the eighth century the use of aqueous alcohol as an extraction solvent was known in the Arab world, and before then extraction with water was used to recover aroma-bearing extracts. Presently, some of the applications are extraction of lipids (Foresti and Giuffrida, 1958), the removal of caffeine from coffee (Sivetz, 1963), and the extraction of flavors and aromas (Randall et al., 1971).

Inorganic Solutes

Solvent extraction may be usefully applied to salt-acid reactions. This permits the production of salt and acids from primary raw materials (Baniel and Blumberg, 1957) as the solvent dissolves both acids completely but dissolves the salts only sparingly. In this way, the reaction products may be separated. These methods are well adapted for up-grading the alkali chlorides KCl and NaCl. For example, nitrates and sulphates of sodium, potassium and ammonium cations may be prepared from their chlorides; phosphoric acid can be produced by direct attack of hydrochloric acid on phosphate rock. Israeli Mining Industries have developed several processes of

this type in order to prepare inorganic compounds, mainly for the fertilizer industry (Araten et al., 1967).

Other areas where LLE is successfully used include production boric acid (Brown and Sanderson, 1977) and hydrogen peroxide.

Metal solutes

The field of extractive metallurgy has been one of the most rapidly growing areas in the use of LLE. The solvent extraction of metals, on a large scale, originated in the uranium industry because it was required to produce ultra pure uranium for primary fuel for the reactors, and to separate the uranium and plutonium fission products after burn up of the fuel in the reactor. The atomic energy industry has been the largest user of LLE for metal separation and recovery, and many of the extractant solvents first used in that industry have been later adopted for the recovery of other metals. These solvents include the poly-ethers, ketones, organophosphorus compounds, and long chain amines.

The extraction of irradiated compounds introduces special requirements for the contact equipments. The need for remote routine operation and the difficulties of maintenance in case of breakdown mean that equipment should be as simple as is compatible with other requirements, with as few moving components as possible in contact with radioactive materials.

During the study of LLE for the nuclear industry it was soon realized that the extractants had wider use and that

other valuable cationic metals could be extracted. The value of the metals led to the development of LLE processes for rear earth metals such as: vanadium, zirconium, tantalum and hafnium (Sekine and Hasegawa, 1977). Recent developments include the extraction of metals such as, aluminum (Muhl et al., 1980), boron, gallium (Schepper, 1979), germanium (Cote and Bauer, 1980) and lithium (Epstein et al., 1981).

Another use of the LLE is the removal of metals from liquid effluent streams to environmentally acceptable levels. The type of metals removed and recovered include, zinc, copper, nickel, chromium and mercury (Andersson and Reinhart, 1983).

2.2 Stability of Dispersion and Emulsions Formation

Phase dispersion and coalescence phenomena are important in LLE with either stage-wise or differential contact. Agitation or mixing of two liquid phases that are not or only slightly mutually soluble results in the formation of emulsion or dispersion of one phase in the continuum of the other. Dispersions are generally considered to be unstable or temporary emulsions, and stable dispersions or emulsions are those which remain unchanged for considerable time after preparation.

From the point of view of LLE processes the stability or permanence of the dispersion is its most important property, since it is necessary to separate the phases at each extraction stage. For all practical purposes, the breakup time or the coalescence rate will determine the workable throughput of the extraction equipment. In countercurrent column-type contactors, steady operation is possible when the rate of droplets arrival does not exceed the coalescence rate at the main interface, otherwise the dispersed band will extend over the entire column leading to flooding. In mixer-settler contactors, the dimensions of the settler are designed according to the coalescence rate, and increasing the throughput above the coalescence rate will result in flooding of the settler. It is clear therefore that systems with emulsification tendencies can not be operated by conventional

extractors. Commonly such systems are handled in centrifugal extractors.

Emulsion formation is a common problem in the pharmaceutical industry where the desired products are extracted from the fermentation broth by organic solvents, but virtually it is also common in many other extraction processes where mechanical agitation is used to increase the mass transfer rates. The problem of emulsion formation is more severe for industrial systems than it is in the laboratory because in industry there is a greater opportunity for system contamination, such as by dirt or rust, which later constitute emulsion stabilizer.

Over the last 40 years there has been a growing interest in understanding the factors controlling dispersions stability and breakdown (good reviews are given by Bencher, 1983).

Stability represents the resistance offered by the dispersion to ultimate coalescence of the dispersed phase droplets. In order for dispersion to separate into its phases, the droplets have to undergo the following steps: a) collision, b) flocculation or agglomeration, and c) coalescence (Treybal, 1963).

Collision. For very fine droplets, the rate of collision is dominated by their Brownian movement. For larger droplets, external force fields, usually gravitational, centrifugal, or electrostatic, are acting on the system and causing settling or sedimentation, thus bringing the droplets into contact with

each other to form a closed-packed array.

Flocculation. In this case, aggregates of droplets are formed within the dispersion. This process results from the existence of attractive forces between the droplets.

Coalescence. Flocculated droplets in an aggregate in the bulk of the dispersion, or, alternatively, droplets within a closed-packed array resulting from sedimentation, coalesce to form larger droplets. The limiting case considered here is the complete separation of the dispersion into two bulk liquids. The coalescence process is the combination of two distinct steps: first - drainage of the continuous phase film trapped between the drops, and second - rupture of the lamellar film.

Not every collision of droplets is resulted with coalescence, and if the collisions in the dispersion are completely ineffective the dispersion is said to be stable. Two pure liquids rarely form stable emulsion, and a third substance nearly always must be present. The additional substances are commonly impurities, surface-active agents (surfactant) or finely divided solids which are adsorbed at the liquid-liquid interface. These substances (emulsifiers) stabilize the dispersions against breakdown by preventing either the flocculation or the coalescence of the droplets.

The emulsions can be stabilized by one or more different mechanisms. Basically there are three of these to consider: charge stabilization, steric stabilization, and stabilization by adsorbed solid particles at the liquid-liquid interface.

Charge stabilization is caused by the adsorption of ionic "stabilizer", e.g., an ionic surfactant or a polyelectrolyte, at the droplets interface. The increase in the coalescence time is caused by the formation of electrical double layers on the surface of the droplet. The electrical double layers tend to retard the flow or the draining of the liquid film due to the attraction force of the opposite charges at the interface and the flowing film (electroviscous effect). Furthermore, the repulsion of the equally-charged droplets prevents the flocculation of the droplets (Tadros and Vincent, 1983).

In the presence of nonionic emulsifiers, especially polymers, the steric mechanism of stabilization dominates. Polymer molecules adsorb on the liquid-liquid interface, and form a protective layer (Shinnar 1961). The protective layer comprised of loops and tails extending into the solution phase. These protective layers generate a repulsive force between the droplets and prevent the flocculation (Heeler, 1954). Moreover, the macromolecular film formed at the interface, in view of its viscoelastic properties, can provide a "mechanical" barrier to coalescence. This is particularly the case with many adsorbed protein molecules which denature on adsorption and hence collapse at the interface, forming a fairly rigid film (Bikerman, 1958).

The mechanism of emulsion stabilization by the presence of finely divided solids at the liquid-liquid interface is far from being understood at present. Presumably, the presence of

solid particles at the liquid-liquid interface plays an important role in preventing the thinning of the liquid film between the droplets. For the solid particles to be effective, they should form a continuous monoparticulate film on the droplet interface, thus making the coalescence more difficult, essentially by keeping the droplets from coming into close contact (Tadros and Vincent, 1983). If, on the other hand, the particles are relatively large compared to the droplets, and they are preferentially wetted by droplet phase, they can act as connecting links across the draining film causing film rupture almost instantaneously, and consequently promoting the coalescence (Charles and Mason, 1960).

As in the case of solid particles, an effective stabilization of dispersions by any of the above mentioned stabilizing substance requires a full coverage of the droplet interface by the adsorbed molecules. If this is not the case, "bare patches" on the two surfaces may come into direct contact leading to coagulation or even coalescence.

The adsorption of the emulsifier molecules on the interface is a dynamic process which includes the diffusion of the molecules from the bulk liquid to the interface and the adsorption on the interface. The adsorption rate is highly affected by the properties of the dispersed and the continuous liquids and the adsorbed molecules, as well as the fluid-dynamic conditions (e.g. laminar or turbulent flow). In some cases the adsorption rate is very low. For example, the

adsorption of macromolecule at the liquid-liquid interface is a very slow process and equilibrium is only reached after a long time (hours or days), depending strongly on the molar mass distribution of the adsorbed molecules (Tadros and Vincent, 1983).

2.3 Properties of Solvent System with Critical Point of Miscibility

As our whole approach, in the present work, is based on using partially miscible liquid solvents, a short review of their properties is in order.

2.3.1 Introduction - Partially miscible solvents system

Two-component liquid system may be classified according to whether the components are completely or only partially miscible. From practical viewpoint, it may be sometimes considered that complete immiscibility occurs, but it should be realized that actually all liquids dissolve in each other if only to a limited extent.

Consider two liquids A and B, exhibiting only partial miscibility. While complete miscibility is obtained whenever a small amount of A is added to B, as more A is added to the solution, eventually the limit of solubility of A in B at the current temperature is reached. Then, further addition of A will result in the appearance of two liquid phases that are saturated solutions of A in B and of B in A. Finally, sufficient addition of A will again bring the system to a condition of one liquid phase. Thus, for a substantial range of the system composition at a given temperature, two liquid phases of constant composition, the saturated solutions, will

coexist. The variation in the composition of these saturated solutions with temperature is conveniently shown graphically in the so called miscibility curves (sometimes also called solubility or coexistence curves).

Figure 2.6 is a plot of the composition of the saturated liquid phases at equilibrium as a function of temperature. The area above the curve represents mixtures that form a single liquid phase, and that below the curve represents mixtures that form two mutually saturating liquid solutions. A mixture whose overall composition and temperature are given by point S will form two saturated solutions of compositions D and E, and the horizontal line DE that joins these is named a tie line.

In the case described in Figure 2.6a, which is typified by the system butanol-water, the solubilities of A in B and B in A increase with increase in temperature, so at some elevated temperature, at point C, the two conjugate solutions become identical and the interface between them consequently disappears. This point is termed as the critical solution temperature (CST), or consolute temperature, and in the case described in Figure 2.6a point C is in fact an upper critical solution temperature (UCST).

There are other systems whose mutual solubility increases with decreasing temperature, as exemplified by the system triethylamine-water, and described in Figure 2.6b. In this case the point, in which the compositions of the two phases

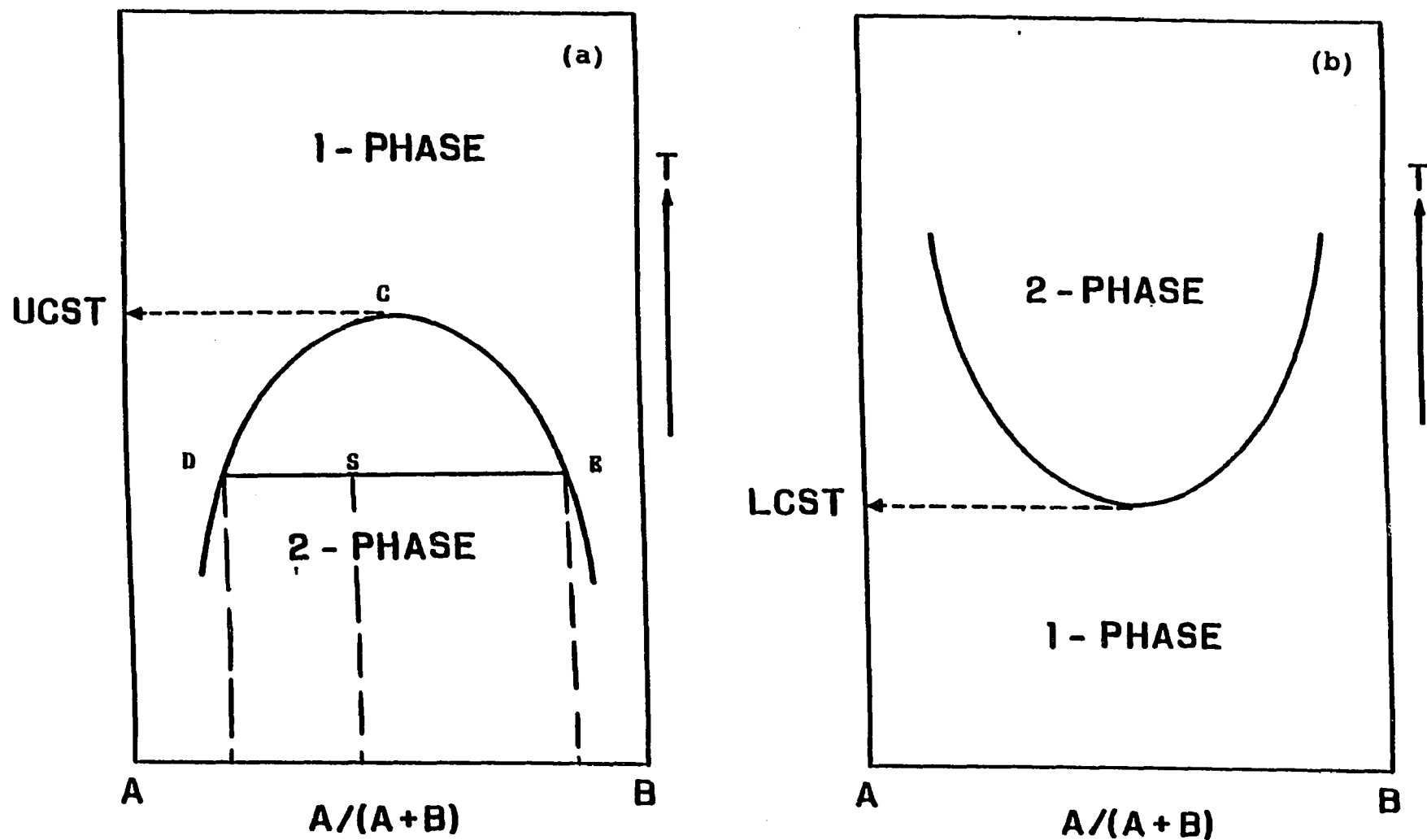


Figure 2.6: Equilibrium composition in a two-component system with an upper critical solution temperature (a), and a lower critical solution temperature (b).

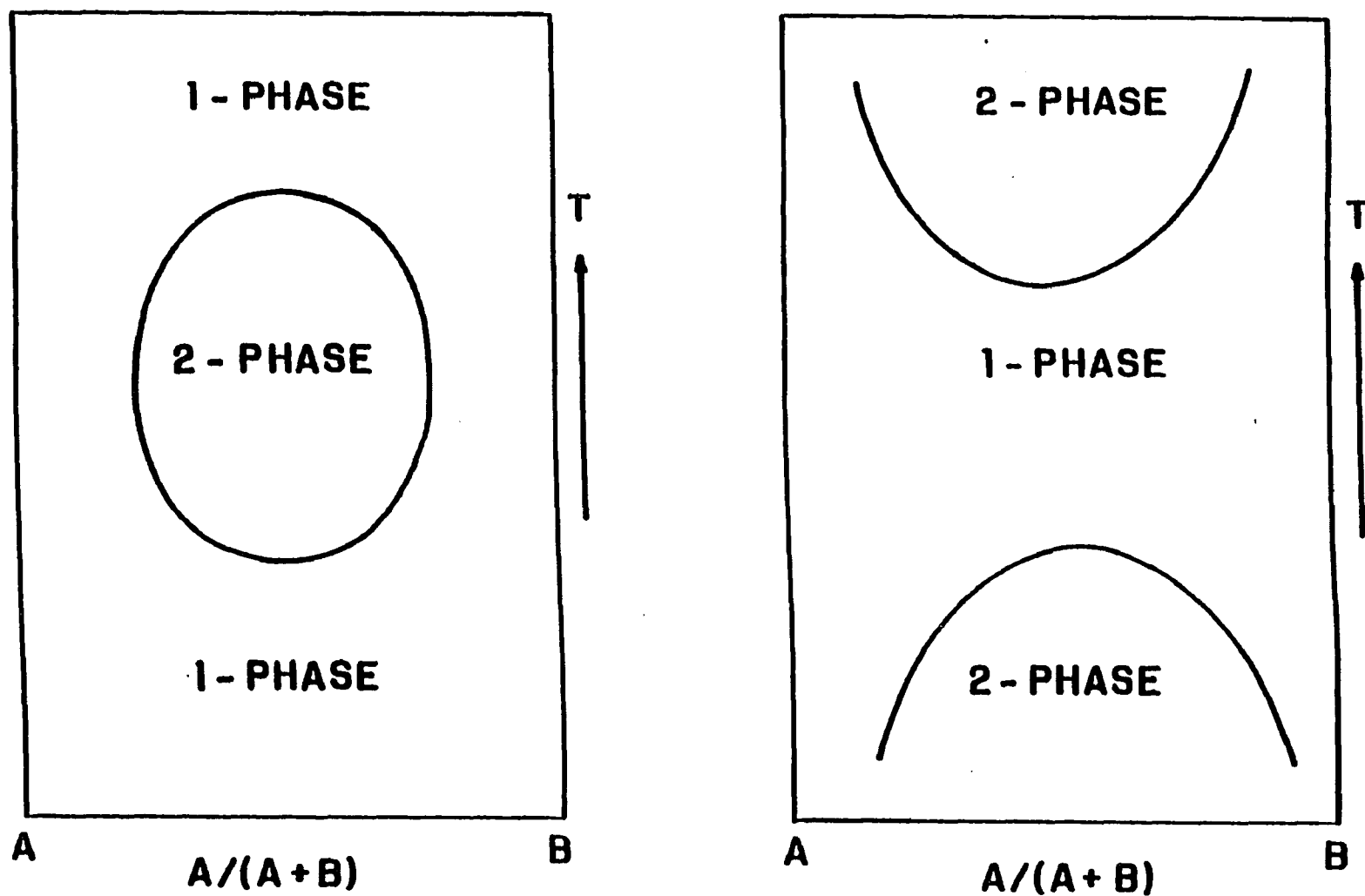


Figure 2.7: Equilibrium composition in a two-component system with both upper and lower critical solution temperature.

approach each other, is a lower critical solutions temperature (LCST). Some examples of two component systems of upper and lower CST are listed in Tables 2.1 (see Appendix III).

Figures 2.7a and b describe two-component systems with both UCST and LCST. Some systems do show a tendency to form a closed two-phase region if a wide enough temperature range is explored (Walas, 1985). As one can see, in the examples in Table 2.1, the temperature difference between the LCST and the UCST is at least 80°C.

A large number of liquid pairs form systems without upper or lower critical points. In these cases vaporization may occur before an UCST or freezing before a LCST can be obtained (Treybal, 1963). However the most unusual behavior is that of sulfur-benzene system, Figure 2.7b, which has an UCST that is lower than a LCST.

2.3.2 Listing of Systems with Critical Point of Miscibility

Several comprehensive collections of liquid-liquid equilibrium data are available, such as Stephen, Stephen, and Silcock (1979) in seven volumes. More than 2,000 binary systems are represented graphically in Landolt-Bornstein (1964) without any correlation or predictive theory. The most comprehensive collection of liquid-liquid equilibria in graphical as well as tabular form is that of Sorensen and Arlt (DECHEMA Chem Data Series V/1,2,3, 1979-1980). More than

6,000 critical solution temperature observations are listed by Francis (Francis, 1961, 1963), and more than 300 involve water as one of the solvents.

2.3.3 The Physical Chemistry of Consolute Systems

The physical explanation of the critical miscibility phenomena is based upon the interplay of intermolecular forces (Rowlinson, 1969, Domb and Green, 1972).

For example, the existence of UCST can be explained assuming that the A - B molecular bond is weaker than the individual interaction A - A and B - B, then at high temperatures (above UCST) the entropy effects are favored, and complete miscibility results. At low temperatures the free energy of interactions is favored and phase separation occurs.

Explanations of the LCST (Domb and Green, 1972) revolve around the highly directional short-range interaction of the entities A and B as in the hydrogen bonding case. At low temperatures the decrease in free energy of solution due to specific interaction of A with B gives rise to miscibility. However, as temperature raises above the LCST the entropy effects take over favoring a more random orientation of the entities. This then destroys the directional bonds resulting in unfavorable free energy of solution and thus phase separation.

2.3.4 Effect of Pressure

The temperature-composition diagrams discussed above were considered to be obtained at the equilibrium vapor pressure of the system, which varies both with temperature and in the one liquid phase region with composition. However, the change in solubility of the relatively immiscible liquids with externally applied pressure is very small and may be neglected in most situations (Treybal, 1963). The nature of the effect may be predicted by the Le-Chatelier's principle, i.e., if the solution of the two components is accompanied by an increase in volume, it follows that an increased pressure will favor a decreased solubility (UCST will be raised, and LCST will be lowered), and vice versa. Table 2.2 in Appendix III indicates the small change that occurs at the critical solution point for several systems.

2.3.5 Effect of Third Component Dissolution on Critical Mixture

The addition of even small amount of a third component to a two-component liquid system may alter the CST considerably. Typically, when the third component is much more soluble in one of the binary mixture components, its addition raises the UCST (Hales et al., 1966). When the third component distributes in roughly equal proportions between the two

components, its addition tends to lower the UCST (Snyder and Eckert, 1973). Therefore, water for example, raises the UCST of methanol/n-hexane mixture (Rogers, 1969), whereas acetone, as a third component, lowers the UCST of methanol/cyclohexane by 3.5°C per percent of acetone dissolved (Cohen and Jacobs, 1984). In similar way, the addition of a third component that is soluble in both liquids raises the LCST, and addition of a third component that is mainly soluble in one of the binary solution mixture components lowers the LCST.

Due to the addition of a third component to a two-liquid system and its distribution between the equilibrium phases, the critical composition will be altered as well. However, for a small amount of third component, the solvents mixture can be regarded as a pseudo two-component system, and the changes in the critical temperature and critical composition can be considered linear (Tveekrem and Jacobs, 1983, Cohn and Jacobs, 1984).

2.3.6 Phase-Equilibria Thermodynamics

The mutual solubility of solvents and the critical solution temperature phenomena can be examined by using the classical phase-equilibria thermodynamics and performing thermodynamic stability analysis.

A state of equilibrium is characterized as having a minimum Gibbs energy at a given temperature, pressure and composition. Thus, a mixture of solvents will split to

separated phases whenever the total Gibbs energy of the heterogeneous solution is less than that of the homogeneous solution. This can be easily demonstrated for the case of binary solutions. In Figure 2.8a the Gibbs energy G of binary mixtures is plotted as functions of the composition x . The convex portion a-d-h of the curve represents an unstable region of which the stable Gibbs energy is along the straight line a-f-h. For any overall mixture composition between "a" and "h" the mixture will split into two coexisting phases with equilibrium compositions of points "a" and "h", and with an equal chemical potential (or partial molal Gibbs energy). Such a curve always has at least one local maxima and two or more minima, and is described as having convex portions. The mathematical condition for convexity and therefore the mixture instability is that

$$\frac{\partial^2 G}{\partial x^2} < 0 \quad (1)$$

The inflection points at which $\partial^2 G / \partial x^2 = 0$ separate the regions of instability and stability (with respect to small concentration fluctuations), and is called "spinodal" point (see Fig 2.8b).

If the range of immiscibility decreases gradually, by reason of temperature change or other factors, eventually it degenerates to a point. This point of incipient immiscibility, or critical solution, is mathematically characterized as having

$$\frac{\partial^2 G}{\partial x^2} = \frac{\partial^3 G}{\partial x^3} = 0 \quad (2)$$

This behavior of binary mixtures, as well as the generalization to multi-component mixtures, was described by Lupis (1983).

When the relations between composition, temperature, and the Gibbs free energy of the mixture are known, the above considerations can be used to evaluate the CST and the equilibrium compositions of the coexisting phases. The former can be determined by using the conditions of Eq. 2 (or their equivalents for multi-component systems), whereas the equilibrium composition can conveniently be evaluated by applying the principle of equality of chemical potentials. Various types of activity coefficient correlations, such as the Van-Larr, NRTL, UNIQUAC, etc. are known in the literature and can be used for this purpose.

The above thermodynamic analysis can serve as an analytical tool to evaluate the behavior of solvent mixtures, namely to predict the existence of a critical point, and to estimate the composition of the coexisting liquid phases. It is particularly important for preliminary screening of solvents, and when performing feasibility study of a new extraction process.

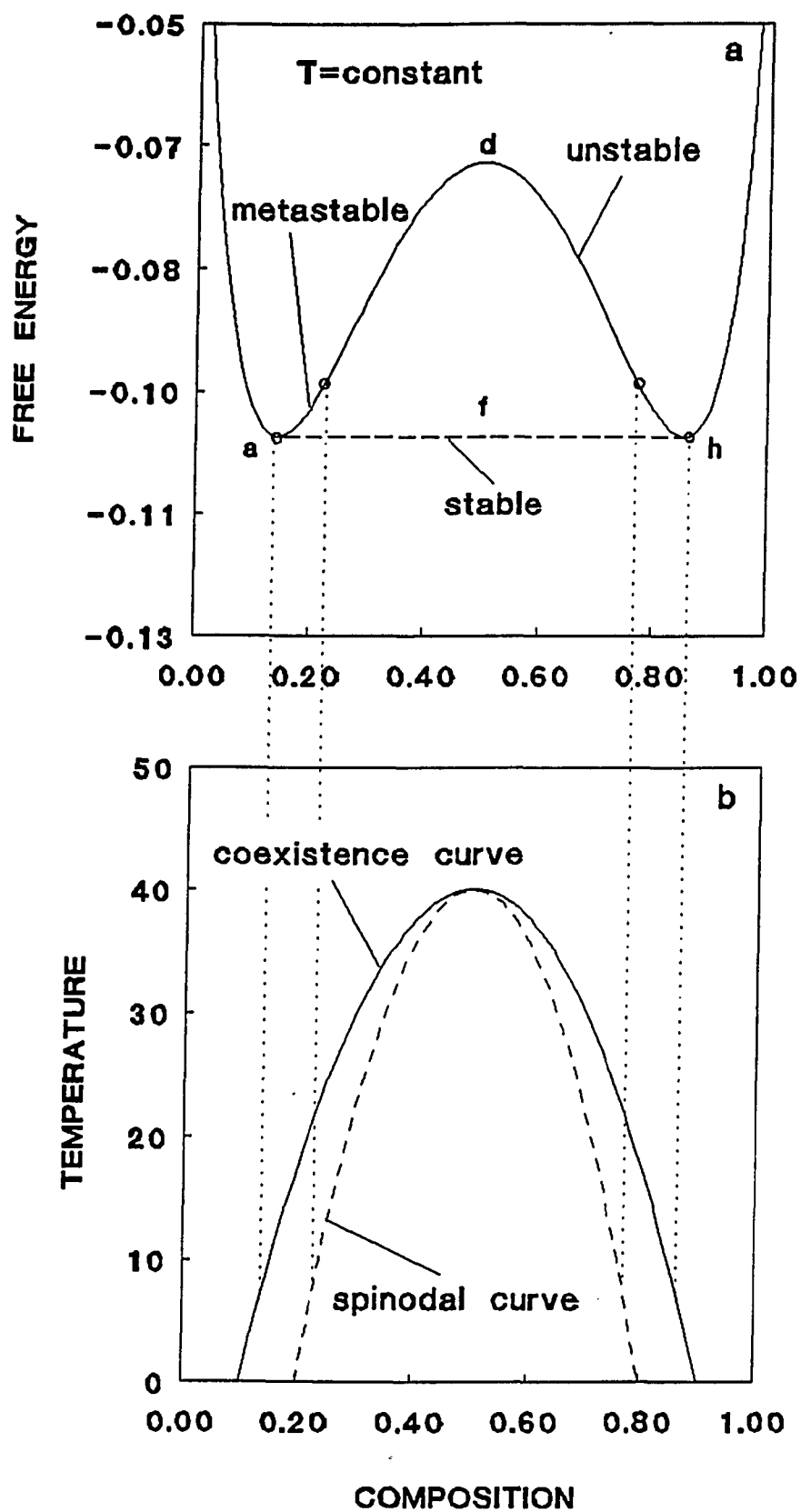


Figure 2.8: Gibbs energy of binary mixtures as function of composition, (a), and coexistence curve and spinodal line of binary mixture, (b).

2.3.7 Dynamics of Phase Transition

Although the study of the kinetics of phase transition in fluids has a long history (Zettlemoyer, 1969), it is only recently that the study has been extended to cases in which a binary mixture is rapidly quenched from a state at temperature T_0 in the one-phase region to a state at temperature T inside its coexistence curve (see Fig. 2.9). In this process the system evolves from the non-equilibrium state to an equilibrium thermodynamic state which consists of two coexisting phases, through a sequence of highly inhomogeneous states which are far from equilibrium (Gunton et. al., 1983). This dynamic evolution is highly non-linear, and in spite of extensive experimental and theoretical studies, a first principle understanding does not yet exist.

According to the classical (mean field) theory of first-order phase transition, the region inside the coexistence curve is divided into two distinct types of instability. The first is the metastable region in which only concentration fluctuations larger than a critical radius are able to grow (nucleation). In the second region, where the system is thermodynamically unstable, non-localized concentration fluctuations of infinitesimal amplitude can grow and reach their equilibrium value. This process is termed "spinodal decomposition". According to the mean field theory, the metastable and the unstable regions are separated by the

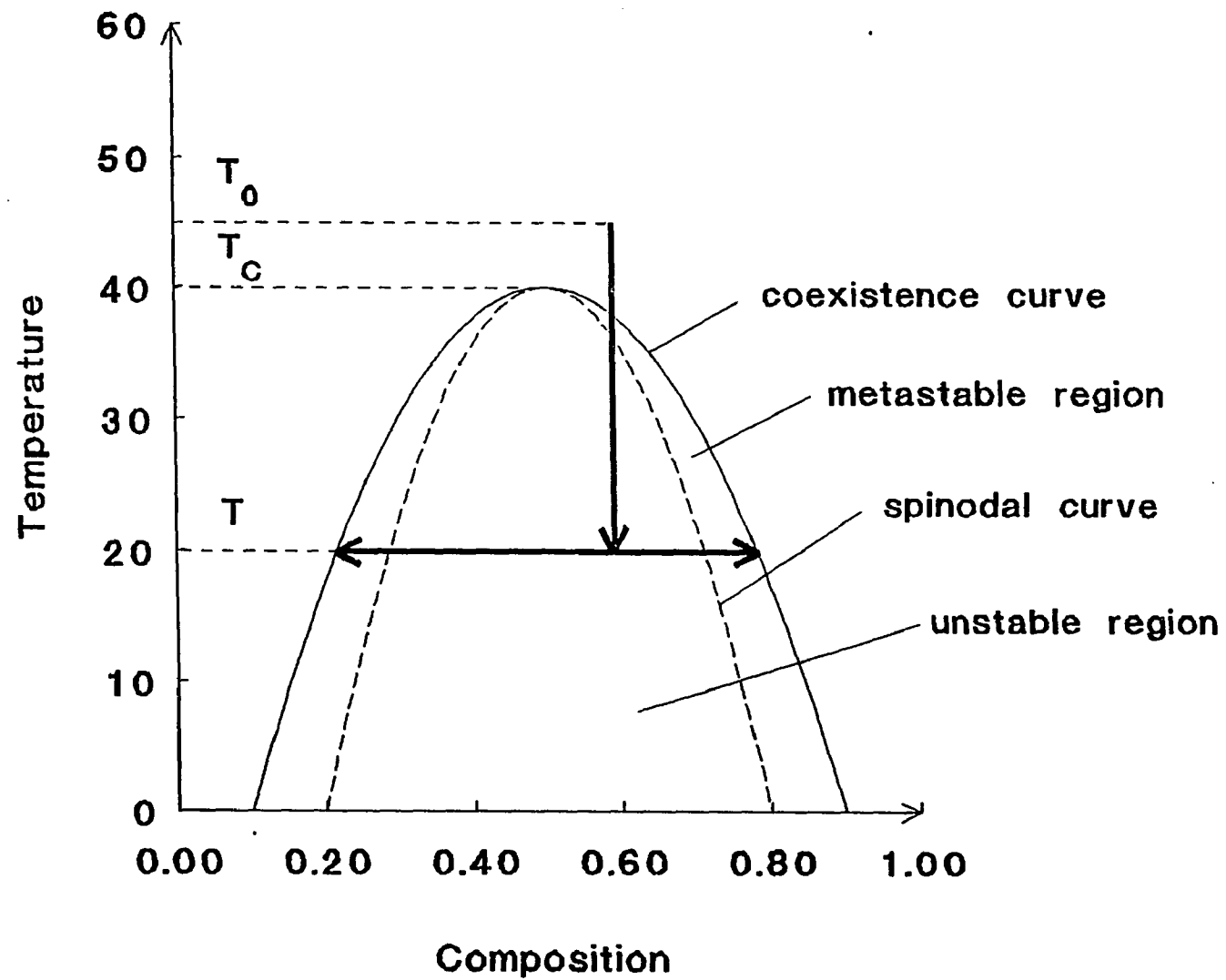


Figure 2.9: Temperature quench into the metastable region of CST forming mixture.

spinodal curve which is the locus of the points inside the coexistence curve for which $\partial^2 G / \partial x^2 = 0$ (see Section 2.3.6). The classical spinodal curve, first introduced by Gibbs in 1906, provides a convenient way to distinguish loosely between the metastable and the unstable states. However, it should not be taken too literally, as in fact recent research suggests that there is a gradual transition in the dynamical behavior of a quenched system as one varies the quench concentration in the vicinity of the classical spinodal curve (Gunton et. al., 1983).

Now, it is clear that following a temperature quench into the spinodal (i.e unstable) region the system will first quickly evolve towards its metastable region (Fig. 2.9), and subsequently slowly reach the point of stable equilibrium on the coexistence curve. Therefore, the process of phase transition can be divided into an early stage, consisting in the exponential growth of long wavelength (delocalized) concentration fluctuations (which is generally referred to as "spinodal decomposition"), and a late stage, characterized by a nucleation of localized microdomains followed by a droplets growth.

The first successful qualitative theory of the structure now thought to characterize the early stages of the phase separation was developed by Hillert (1956). A continuum version of Hillert's model was later developed by Cahn and Hilliard (1958). In this model all interactions are assumed

to be incorporated into the free energy density with no further effects to be considered. Following a linearization of the generalized diffusion equation, and using the Landau-Ginsburg form for the free energy Cahn's model, leads to predicting an exponential growth of the microdomains during the initial stages of the spinodal decomposition. Unfortunately, this process is too fast to be experimentally observed.

The validity of Cahn's linearized theory is now considered by many authors to be at best limited to very short times following the quench (Gunton et. al. 1983). Many attempts have been made to develop a theory of spinodal decomposition which can handle the nonlinear effects in the equation of motion (an example is the statistical theory of Langer, Bar-On, and Miller 1975). However, most of these attempts are rather unsatisfactory.

At longer times, the system is composed of well-defined regions of coexisting phases separated by sharp interfaces. The Lifshitz-Slyozov theory (Lifshitz and Slyozov, 1961) is one of the few reasonably well-established studies in the dynamics of first-order phase transition. Lifshitz and Slyozov argue that in the late stage of spinodal decomposition, when the supersaturation of the solution becomes very slight, the fluctuational formation of new nuclei has practically ceased, and molecular diffusion plays a decisive role in determining the droplet growth. According to

their theory the average droplet size obeys the growth law, $R \propto t^{1/3}$. The physics of this late stage growth is that larger droplets grow at the expense of smaller droplet, a process which is often called Ostwald ripening.

In the Lifshitz-Slyozov theory, hydrodynamic interactions between droplets are neglected. In an important paper, Siggia (1979) examined in detail the influence of hydrodynamic interactions and surface tension on the droplets growth rate. Siggia postulated that when the droplets volume fraction exceeds the percolation limit $v \approx 0.15$, surface tension effects lead to a crossover from $R \propto t^{1/3}$ to $R \propto t$.

First-order phase transitions were first observed in alloys and glasses (a good review is given by Kawasaki, 1976), and only more recently experiments have been conducted on binary liquid mixtures. In the pioneering series of works by Huang et. al. (1974) and Chou and Goldburg (1979 and 1981) and also by Wong and Knobler (1978 and 1981), it was shown that while the initial stage of the phase separation is still too rapid to be observed, during the nucleation process the characteristic droplet radius R grows in time like $R \propto t^m$, where $m=1/3$ in the early, purely diffusive stage, and $m=1$ at later time where surface tension effects become dominant. However, the observed crossover to $m=1$ behavior is only in qualitative agreement with Siggia's predictions (Gunton et. al., 1983). More recently, by using a density-matched solvents system to suppress gravity effect, Beysens, Guenoun, and coworkers

(1987,1988 and 1991) have studied spinodal decomposition patterns near the critical point. They also showed that in the late stage of decomposition under microgravity conditions the droplet radius grows according to $R=t$.

Finally, it should be pointed out that no research has been devoted to study how the presence of surface-active solutes in the solvents will influence the coalescence rate. Moreover, all past experimental investigations have dealt with binary mixtures very near the critical point (few mK below the CST), while we are interested in a much larger temperature quench.

3 Phase Transition Extraction (PTE) - Representation of Concept.

Based on the properties of mixtures with critical point of miscibility discussed in the previous sections, a novel separation process (PTE) is proposed. The novel process capitalizes on the phase transition of such mixtures, especially on the fact that with a relatively small change in temperature one can go from one completely mixed phase to two phases with differing compositions (see Fig. 2.6a).

To illustrate this idea, one can consider a conventional countercurrent solvent extraction process, using mixer-settlers. It could be carried out in a series of individual mixer settlers (Fig. 3.1), as well as in a vertical column in which the mixers are operated by a common shaft (Fig. 3.2), or any similar design based on the same principle.

Now, instead of an immiscible solvent system, we used a solvent pair with an upper critical point of solubility, forming a homogeneous solution above the critical point and two separate phases below the critical point. Ternary and four compound systems that form two phases and have a similar critical point can also be applied. The basic concept of the proposed approach is to perform a phase transition of the solvent system in each stage.

To implement the new separation process, we modify the processes in Figures 3.1 and 3.2 by equipping each mixing

section with a heater and each settling section with a cooler. One can arrange these in a mixer settler type device (Fig. 3.3) or in a column (Fig. 3.4).

In the hot (i.e mixing) section, the temperature is kept higher than the critical temperature, so the mixture forms an homogeneous phase. Therefore, here we achieve a perfect mixing since the solute molecules can be thought of as being in contact with both solvents at the same time. The rate controlling step in the mixing section is the diffusion of the solvents themselves. Above the critical point, in the absence of liquid-liquid interface barriers, the rate at which the two solvents form a homogeneous phase by mixing is much faster than the rate of mass transfer between dispersed droplets and a continuous phase below the critical point.

In the cold (i.e. settling) section, the mixture is cooled below the coexistence curve into a state of thermodynamic instability, leading to coalescence and phase separation. The phases thus separated contain solute and solvents at thermodynamic equilibrium composition corresponding to the system temperature. This phase transition process involves diffusion of the solute as well as diffusion of the solvents, and the transfer of the solute is therefore superimposed by concurrent transfer of solvents. This solvents transfer between the phases also prevents formation of a stable interface which, as mentioned above, can reduce the diffusion rates.

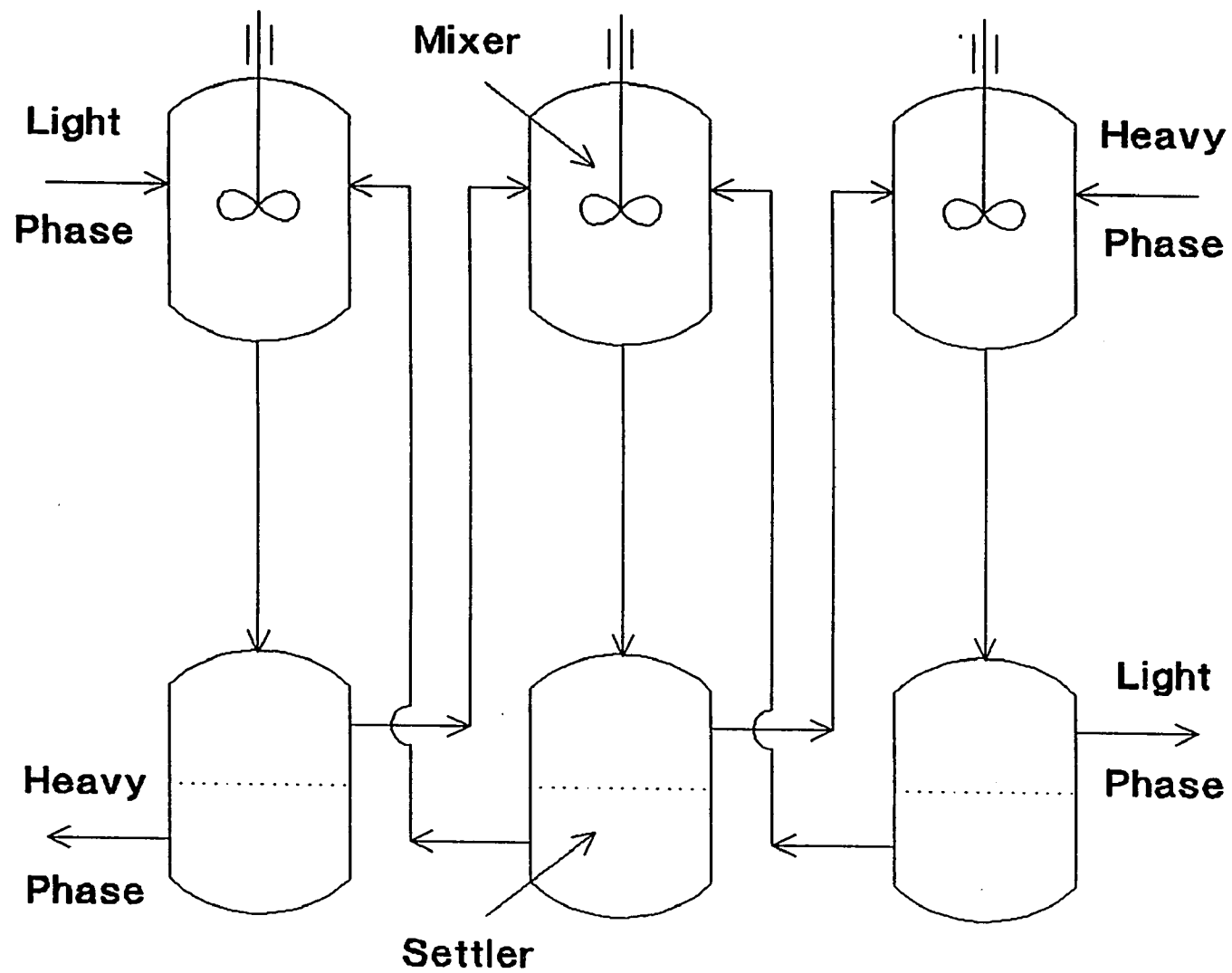


Figure 3.1: Schematic diagram of mixer-settler extractor.

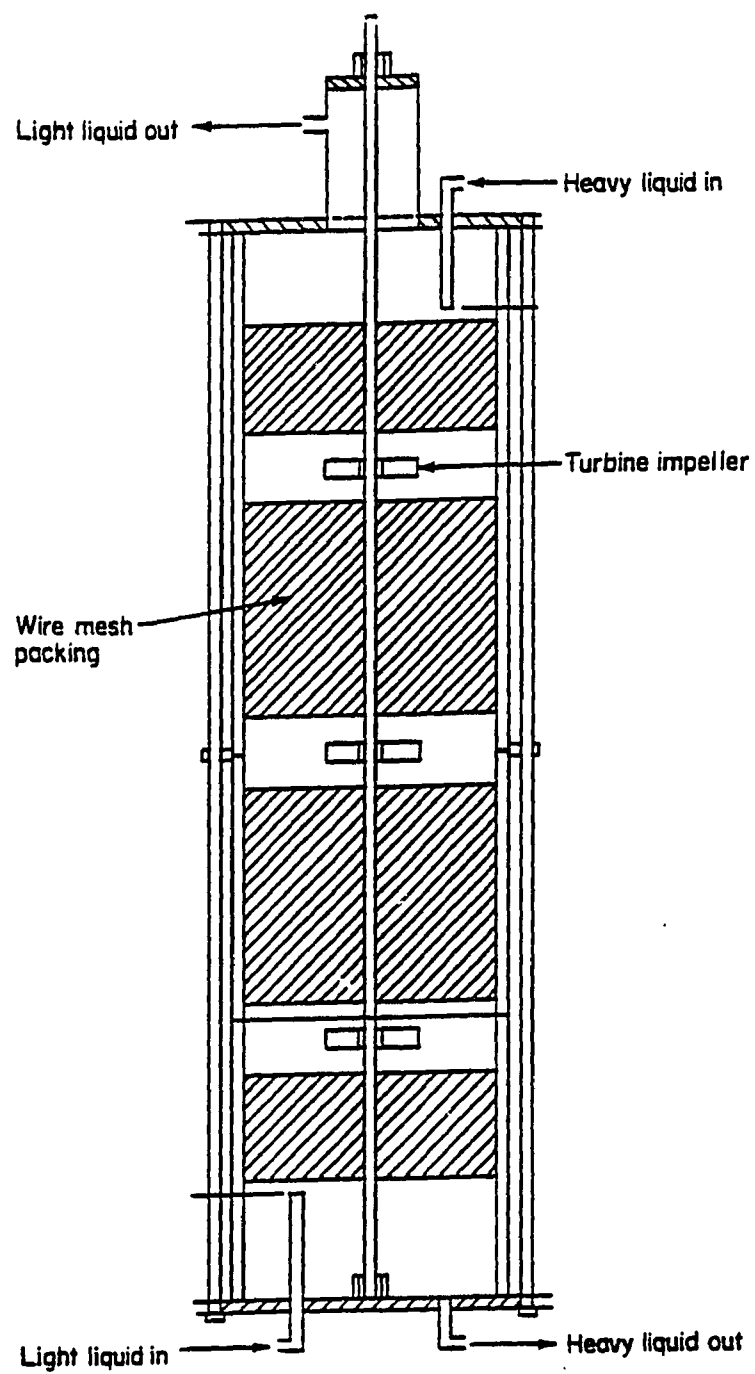


Figure 3.2: Schematic diagram of mixer-settler column extractor.

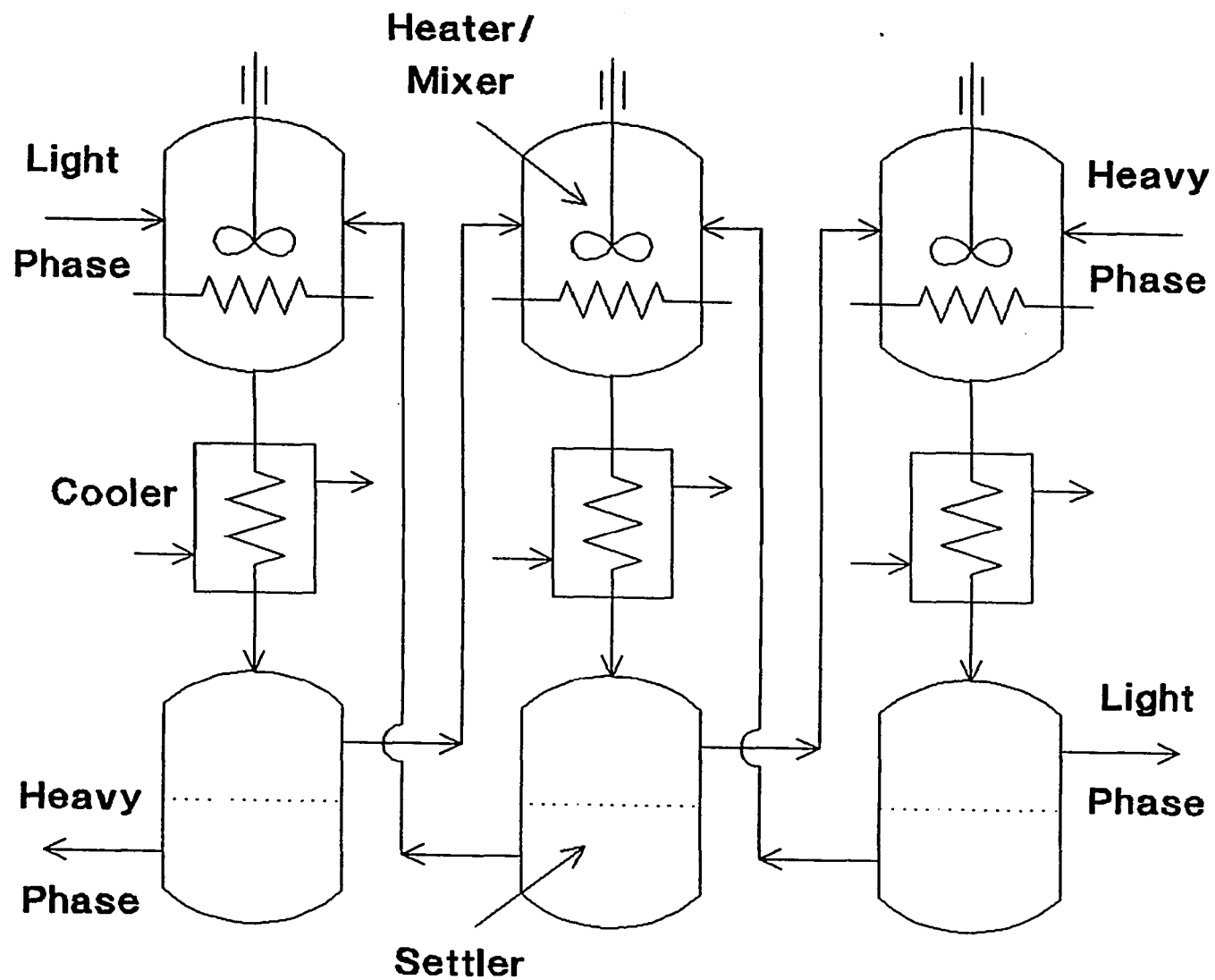


Figure 3.3: Schematic diagram of PTE mixer-settler extractor.

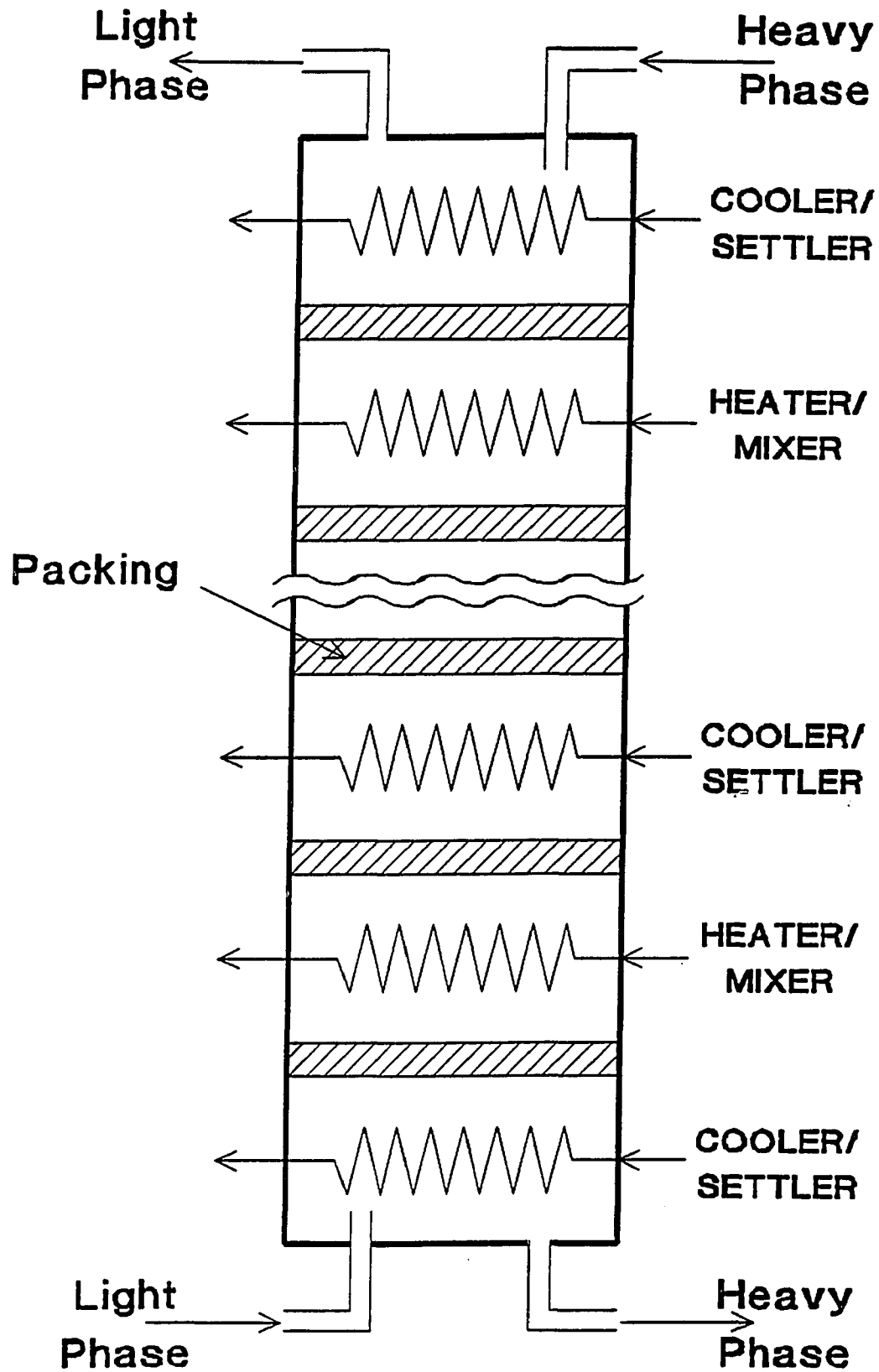


Figure 3.4: Schematic diagram of PTE column.

It is clear, from the above description, that the stage efficiency will be completely dominated by the efficiency of separation in the settler, unlike the conventional system in which mass transfer in the mixer often determines the stage efficiency. Since the diffusion of the solute molecules is not a dominant factor in the above process, one can readily see that the suggested approach has an obvious advantage when high molecular weight molecules have to be extracted.

For all practical purposes the time scale and therefore the throughput will be dominated by the phase separation rate in the settler. Here, it is of interest that when partially miscible liquids undergo a phase transition from a single phase to two phases by cooling, the rate of coalescence is remarkably high even in the presence of impurities that hinder coalescence in conventional extraction. The continuous change of the phase composition during the cooling process prevents the creation of a stable contaminated drop surface which is the main cause of coalescence retardation. The high coalescence rate acquired in the PTE process should have the potential to allow either a large increase in throughput in comparison to existing columns, or a significant reduction in the required settler dimensions in comparison to conventional mixer-settlers.

We also avoid here the need for a compromise that one normally faces in conventional methods. If the mixing intensity is low, mass transfer is slow and inefficient. If

it is high, coalescence is slow and stable emulsion might be formed. By proper use of solvents, one can in our case always achieve fast coalescence.

The PTE method will increase stage-efficiency and the operational throughput, which are important by themselves. But more important, it allows difficult separations, such as the solvent extraction of fermentation-broth which are not feasible in conventional mixer settlers, and require a centrifuge.

Figures 3.3 and 3.4 describe extraction processes using systems with an upper critical point. For systems with a lower critical point, all we have to do is to exchange the positions of heaters and coolers. The mixing section will now contain the cooler and the settler will be heated.

The introduction of heating and cooling in the column (Fig. 3.4), together with the use of solvents with a critical point, allows a further important modification. It is possible to eliminate the mechanical mixer and use the heating element to promote thermal convection. One can do that by proper placement of the heating element in the mixing section.

In one sense there is a strong similarity between the processes described in Figures 3.3 and 3.4 to those in Figures 3.1 and 3.2. In both cases countercurrent solvent streams are successively brought in close contact and separated again. The solutes separation in each case depends on the distribution of solutes between the two solvents and requires

a difference in the distribution coefficients between the two or more solutes that have to be separated.

For some separations the novel separation process described in Figures 3.3 and 3.4 have some very significant advantages:

1) In conventional extraction contactors the stage efficiency is often determined in the mixing sections, especially when the solute has high-molecular-weight and low diffusivity. In addition, surface active impurities or insoluble materials dispersed in the solvents contaminate the droplets stable interfaces, dampen internal circulation within the droplets and reduce the mass-transfer even more. In contrast, in each mixing section of the PTE process we achieve virtually perfect mixing, since the solvents form a single phase, without any of the limitations of the conventional devices.

2) In conventional separation process the mixture is stirred (either directly or through the introduction of perforated-plates) to decrease the droplets size and to increase mass transfer. However, intense mixing will increase the settling time, and in the presence of impurities it will even cause emulsification. On the contrary, in the PTE separation process, after the mixture is cooled below the miscibility curve, the droplet interfaces are unstable, so that the creation of stable contaminated drop surface is prevented and the coalescence process is very fast. Therefore, the

extraction of difficult emulsion-forming systems (e.g. fermentation broth) can be performed easily via the PTE process.

3) The PTE process can be operated with much less intensive or without any mechanical agitation, therefore eliminating any possible shear-stress damage to large solute molecules.

4) The PTE column (Fig. 3.4), having no moving parts, incorporates the simplicity of unagitated columns with the high efficiency of agitated columns. This makes the PTE column an attractive tool for separations that require a large number of theoretical stages. In addition, moving parts, bearing and the like, which are subjected to mechanical wear, can be eliminated. The ability to effectively seal the equipment is particular important in handling of irradiated compounds, where remote operation, low maintenance and heavy shielding are required.

4 BATCH EXPERIMENTS - TESTING THE FEASIBILITY OF THE PTE PROCESS

In the previous Section we have described the concept of the PTE separation process and summarized its anticipated features. We also suggested that the process can be operated either as a mixer-settler or as a column extractor. However, regardless of the operation mode the basic concept is the same: first, a homogeneous solution of solvents and solutes is obtained in the mixing stage and then, in the settling stage, the solution temperature is quenched into the two-phase region. Following the temperature quench, the thermodynamically unstable system evolves toward its stable state of two coexisting phases consisting of solvents and solute at equilibrium. In the settling stage in fact, two processes, the phase transition and the phase separation, are taking place in the same time. In order to complete the extraction process, the desired final state is to get not only two phases in equilibrium but also to achieve a complete separation of the two phases.

Following the above description it is clear that the capacity and the efficiency of the PTE process are determined by the effectiveness and the rate of the phase separation in the settling stage. Where the quality of the solute distribution (the proximity to the equilibrium state) determines the efficiency of the extraction process, the phase

separation rate determines the workable throughput of the extraction equipment and may affect the process efficiency as well.

In mixer-settler operation mode for example, insufficient phase separation at a given throughput will reduce the stage efficiency due to entrainment of either one or both of the phases. In the more severe case when the throughput is higher than the phase separation rate, the settler will be flooded.

Therefore, in order to demonstrate the feasibility of the proposed PTE process, we have to test two critical issues: (a) Whether following the phase transition the solutes are distributed between the two separated phases according to the equilibrium state, and (b) the rate of the phase separation process.

We tested these issues by performing a series of batch experiments in which we measured the compositions of solvents and solutes in the separated phases following a temperature quench. The results then were compared with the equilibrium phase diagrams of the solvents systems and the solute distribution curve, which were obtained separately.

In another set of batch experiments we measured the time needed to complete the phase separation when it was coupled with the phase transition process, and compared the results with the coalescence time following an isothermal mixing of the solvents system.

A special emphasis was given to study the phase

separation rate in the presence of stabilizing substances (emulsifiers). As we already mentioned (see discussion in Section 2.2), the phase separation can be highly affected by the presence of substances that hinder the coalescence of the droplets. Impurities, surface active agents or finely divided solids present in the system tend to collect on the droplets interface and thereby to increase the coalescence time and in some cases even to cause the formation of stable emulsion.

In Section 3 we postulated that when the phase separation is coupled with the phase transition process the continuous change of the phase compositions prevents the formation of stable interfaces on which the emulsifiers can adhere, and consequently the phase separation is fast. Experimental test of this phenomenon is essential to demonstrate the attractiveness of the PTE process in separating difficult emulsion-forming systems.

The formation of stable emulsions is a common problem in the extraction of fermentation broth, a process which is widely used in the pharmaceutical industries. Therefore, the ability of the proposed PTE process to handle such a difficult system was tested via batch extraction of commercial fermentation broth.

4.1 Solvents and Solute Distribution Following Phase Transition

4.1.1 Selection of Solvents and Solute System

Generally, the selection of solvent for liquid-extraction processes involves criteria such as: capacity, selectivity, availability, physical properties, safety and cost. When choosing a solvent for the PTE process two additional features are important. First, the deviation of the critical temperature of the mixture from the ambient temperature should be small, since a large deviation would make the PTE process energy intensive. Secondly, it is advantageous to have as low a solvent concentration in the feed-rich phase as possible; this will minimize the need for solvent separation by distillation, and will also increase the distribution coefficient.

In our experiments, the selection of a solvent system for the experiments was mainly affected by our need for easy and accurate experimental operation.

Although we used several binary and ternary solvent systems, most experiments were conducted with a water-acetonitrile-toluene system.

Water was selected as one of the components of our experimental system since it is frequently used as a feed solvent in many commercial extraction processes.

Acetonitrile, which is commonly used as a solvent for HPLC analysis and to extract fatty acids from animal and vegetable oils, was selected as the second component.

The acetonitrile-water system has an UCST at -0.5°C with 0.36 acetonitrile molar fraction. Toluene has been used as a third component (see chapter 2.3.5) to increase the CST to the desired operational level.

Crystal violet, a non-toxic dye, was chosen as a model solute. The use of a dye as a solute allows an easy, accurate and fast measurement of even very low dye concentration by means of light absorption spectrophotometry. A low solute concentration was preferred because it has a negligible effect on the solvents mutual miscibility and thus simplifies the performance computation of multi-stage extraction processes.

4.1.2 Analytical Techniques

4.1.2.1 Measurement of Solute Concentration

The light absorption spectroscopy method was used to measure the dye concentration in the solvents. A Perkin Elmer UV/VIS spectrophotometer model "Lambda 2", hooked up to a PC computer, has been utilized for this purpose. Absorption spectra of the dye dissolved in methanol showed a maximum absorption at wavelength of 570 nm (see Figure 4.1).

X: SAMPLE03; absc 700.0- 500.0; pts 1001; int 0.20; ord -0.001-0.6735; A
inf: 01:45:05 91/10/08

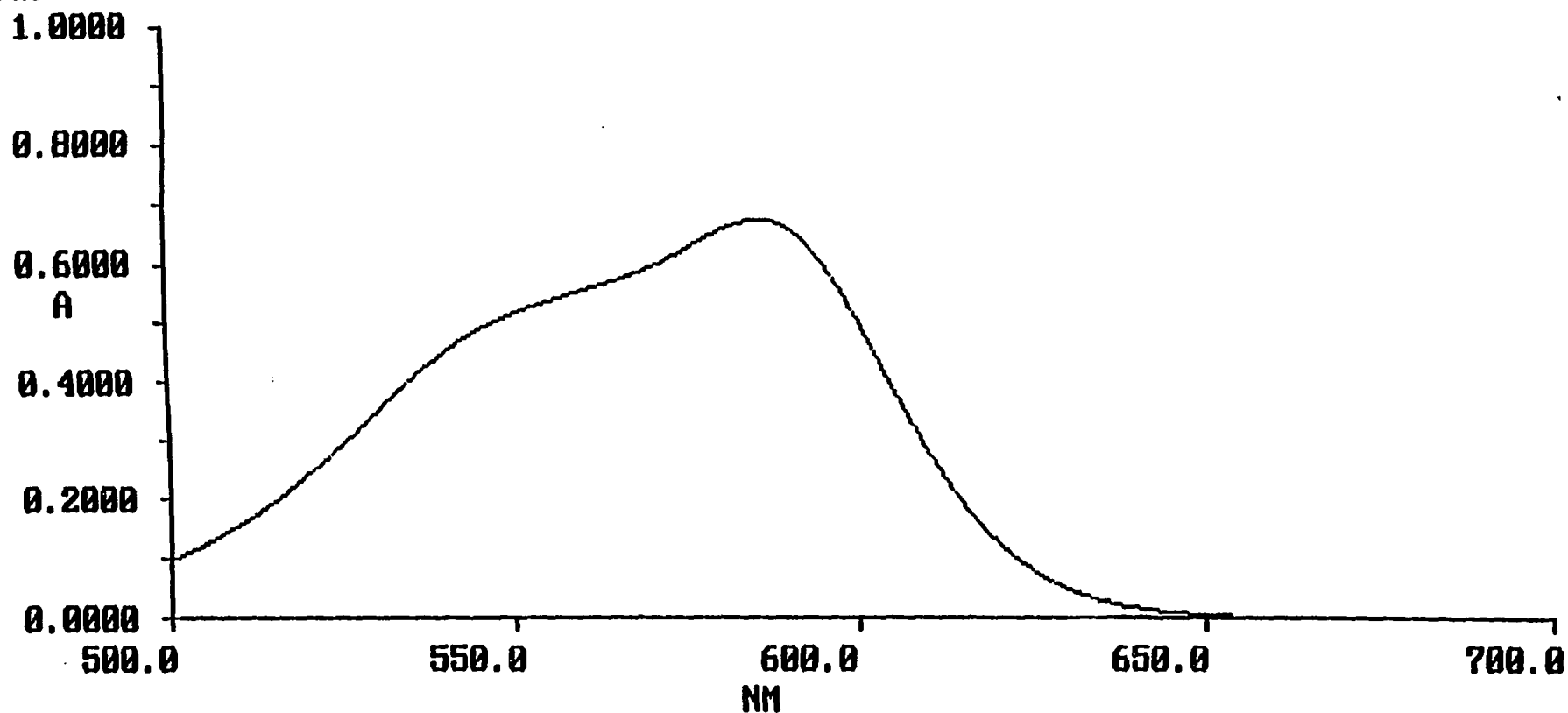


Figure 4.1: Light absorption as a function of wavelength of crystal violet in Methanol.

Z: methn0; absc 0.0- 800.0; pts 501; int 1.60; ord 0.0000-2.2349; A
inf: PRM: 0, 0.279350, 0, 0; RE: 0.00706103

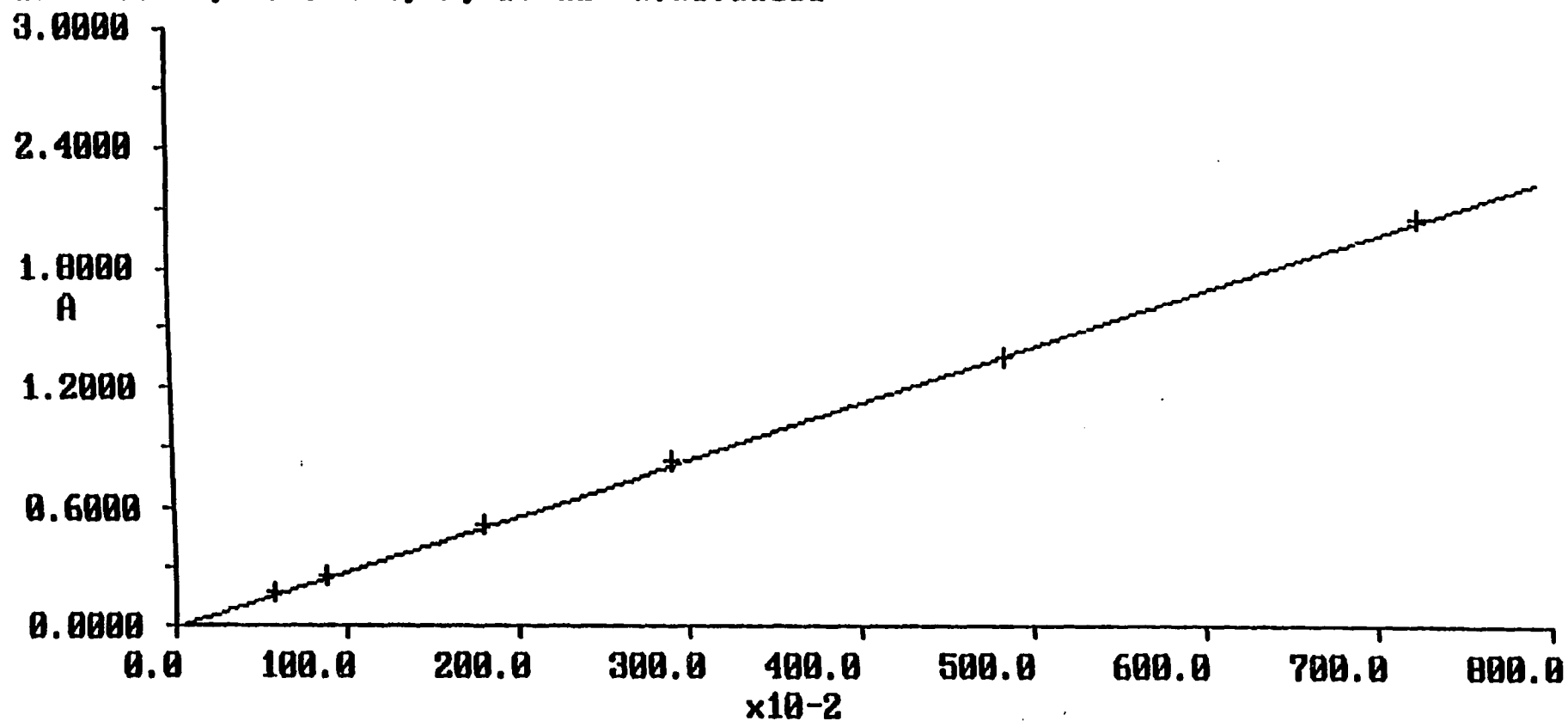


Figure 4.2: Calibration line for crystal violet concentration.

It was also found that this wavelength is unchanged whether the dye is dissolved in the acetonitrile-rich phase or water-rich phase of the acetonitrile-water-toluene system. Thus, the dye concentration, in each of the phases, can be obtained, by diluting the sample with methanol as a reference solvent.

The calibration line of the dye in methanol is presented in Figure 4.2.

4.1.2.2 Analysis of Solvents Composition

The analysis of the solvent composition was conducted with a "Carl Series 400" gas chromatograph (GC) with a thermoconductivity detector, connected to a Spectra Physics model SP4270 integrator.

4.1.2.3 Determination of the Phase Diagram

The phase diagrams were obtained by employing the cloud point method (Treybal, 1963) and by analysis of the solvents compositions in the coexisting phases.

The cloud point method: A test tube was filled with a known ratio of the components. The test tube was then sealed, allowing a vapor space for subsequent expansion of the liquid. The sealed tube was shaken in a bath while the temperature was slowly lowered until the homogeneous solution began to form two separate phases, and the clear solution became opaque.

The temperature at which this occurs was noted, and the experiment provided one point on the phase diagram. A check on the observed temperature was obtained by reversing the temperature effect, allowing the two liquid phases to be replaced by a single liquid solution. Cloud points are typically very sharp and usually reproducible within 0.1°C . This procedure was then repeated with different solvent-ratios and the complete phase diagram was obtained.

Solvents composition analysis: For three-component systems the cloud point method provides only the binodal curve (the boundary between the two-phases and the single-phase regions), and not the tie lines (the composition of the solvents in the coexisting phases). Therefore, solvents composition analysis (with Gas Chromatograph), was used to determine simultaneously both the tie line and the binodal curve of ternary solvent systems. By varying the overall composition and the system temperature the entire phase diagram was measured. The equilibrium state of each data point was confirmed by repeating the procedure of mixing the solvents and analyzing the separated phase till undeviating results were obtained.

The phase diagram of the solvent system is an essential information for the design of extraction processes. In the absence of published data it has to be determined by experimental methods such as the methods described above. However, an analytical prediction method can save a lot of tedious experimental work, at least in the stage of the

solvents screening for a new process. A computational method based on activity coefficient correlations is given in Appendix I.

4.1.3 Equilibrium Distribution of Solvents and Solute

4.1.3.1 Solvents Distribution - Phase Diagrams

Hexane-methanol - The phase diagram of this system is given in Figure 4.3. The critical solution temperature, 34°C , obtained in our experiments is in agreement with the temperature reported by Francis (1963).

acetonitrile-water-toluene - This system was used in most of our experiments and therefore was carefully examined. There is no published data for this three-component system and the only available data is for the acetonitrile-water system which possesses an UCST at -0.5°C . The toluene, as we mentioned before, was added to the acetonitrile-water system to increase the CST of the mixture to the desired operating temperature.

Four different toluene concentrations were examined in order to determine the effect of the toluene concentration on the critical temperature and composition of the solvents system. The results are given in Table 4.1 (see Appendix III). For the simplicity of the graphic representation, and since the toluene is mainly dissolved in the acetonitrile, the system is regarded in the following figures as a pseudo two-

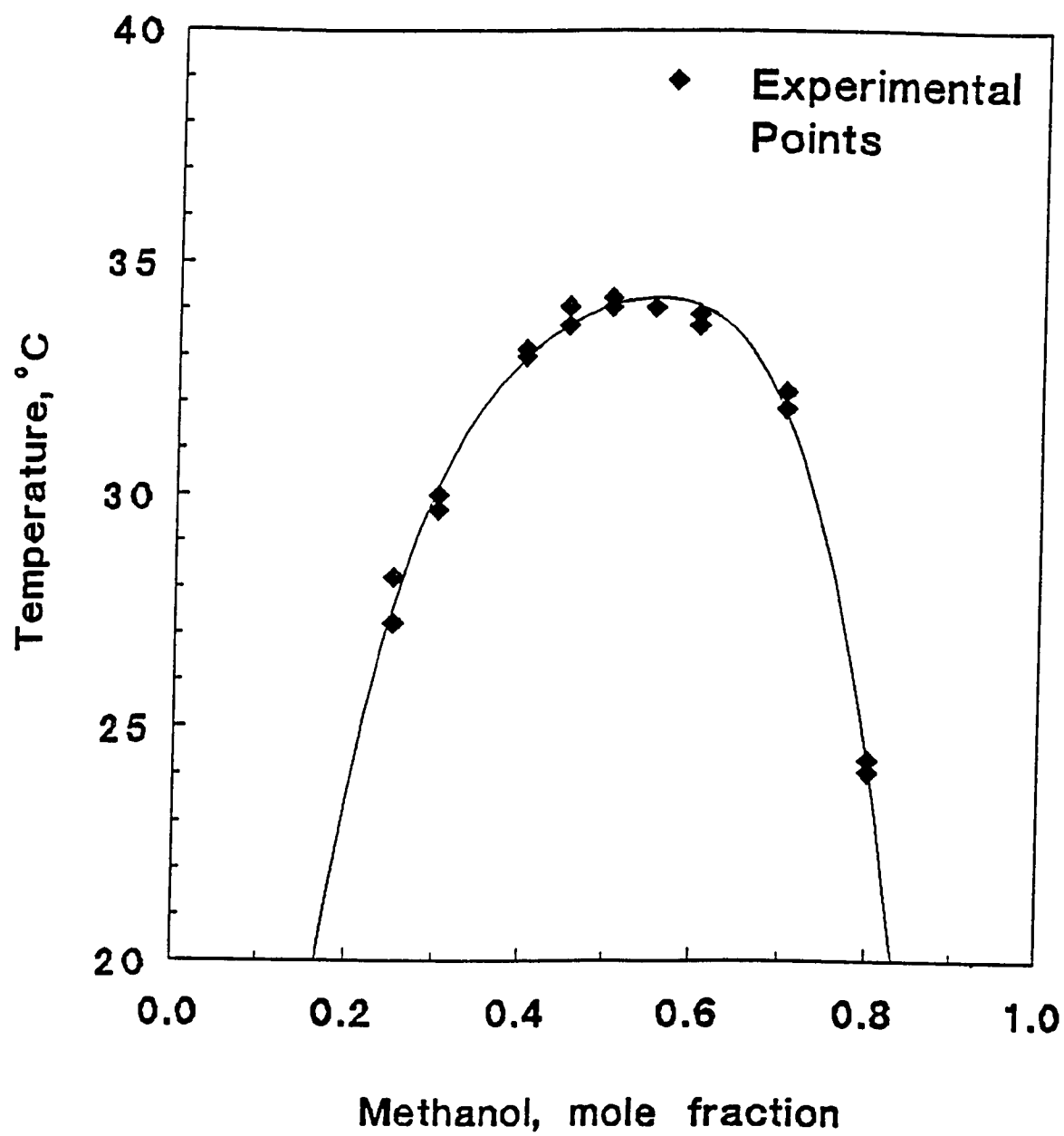
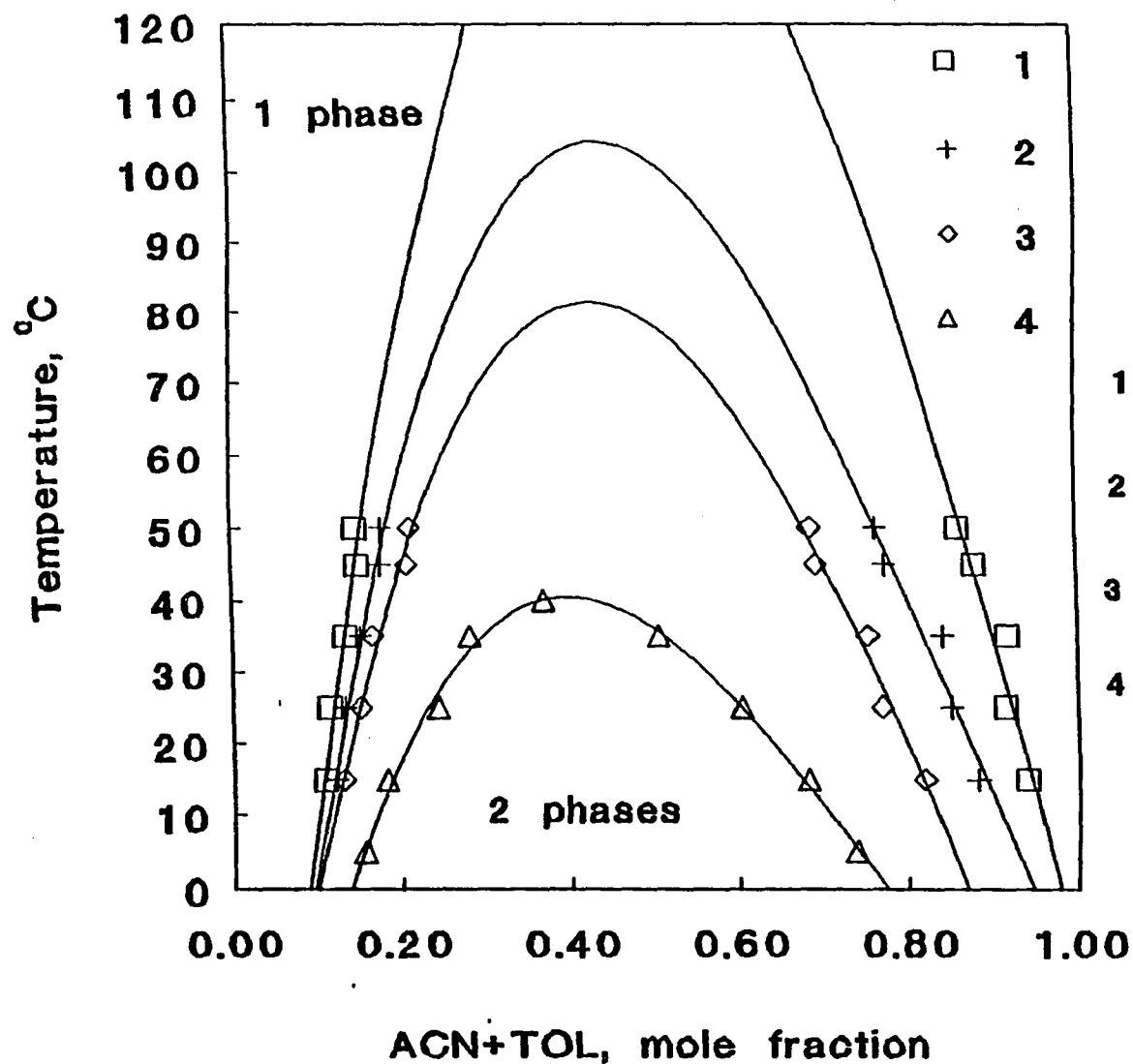


Figure 4.3: Phase diagram of hexane-methanol system.



Overall composition

	ACN	TOL	H ₂ O
1	.3210	.0863	.5927
2	.3344	.0476	.6180
3	.3398	.0305	.6297
4	.3467	.0129	.6404

Figure 4.4: Phase diagram of acetonitrile-water-toluene system (four different toluene concentrations).

component, aqueous and organic, system. The composition of the organic component (toluene + acetonitrile) as a function of temperature for the four different toluene concentration are plotted in Figure 4.4. The experimental results were also correlated by a third order polynomial equation, and extrapolated to include the CST in this figure (for the cases in which the CST was out of the temperature range examined). As one can see in Figure 4.4, the toluene has a minor effect on the critical composition and on the composition of the aqueous phase. Since the toluene is hydrophobic, it concentrates mainly in the organic phase, and its addition causes a shift of the organic portion of the phase diagram to the right. On the other hand, the toluene concentration has a major effect on the critical temperature of the mixture. The CST increases with the increase of the toluene concentration. For low toluene concentration, this change in the CST is nearly linear, about 30°C per percent of toluene dissolved (see Fig. 4.5). For the batch extraction experiments (and for the performance study of the column in Section 5) we chose an overall composition of 0.585 acetonitrile, 0.371 water, and 0.044 toluene (volumetric fraction) which is equivalent to molar fraction of 0.347, 0.640, and 0.013 respectively. This composition of the solvents system gives a convenient UCST at 40°C and a sufficient phase separation at ambient temperature.

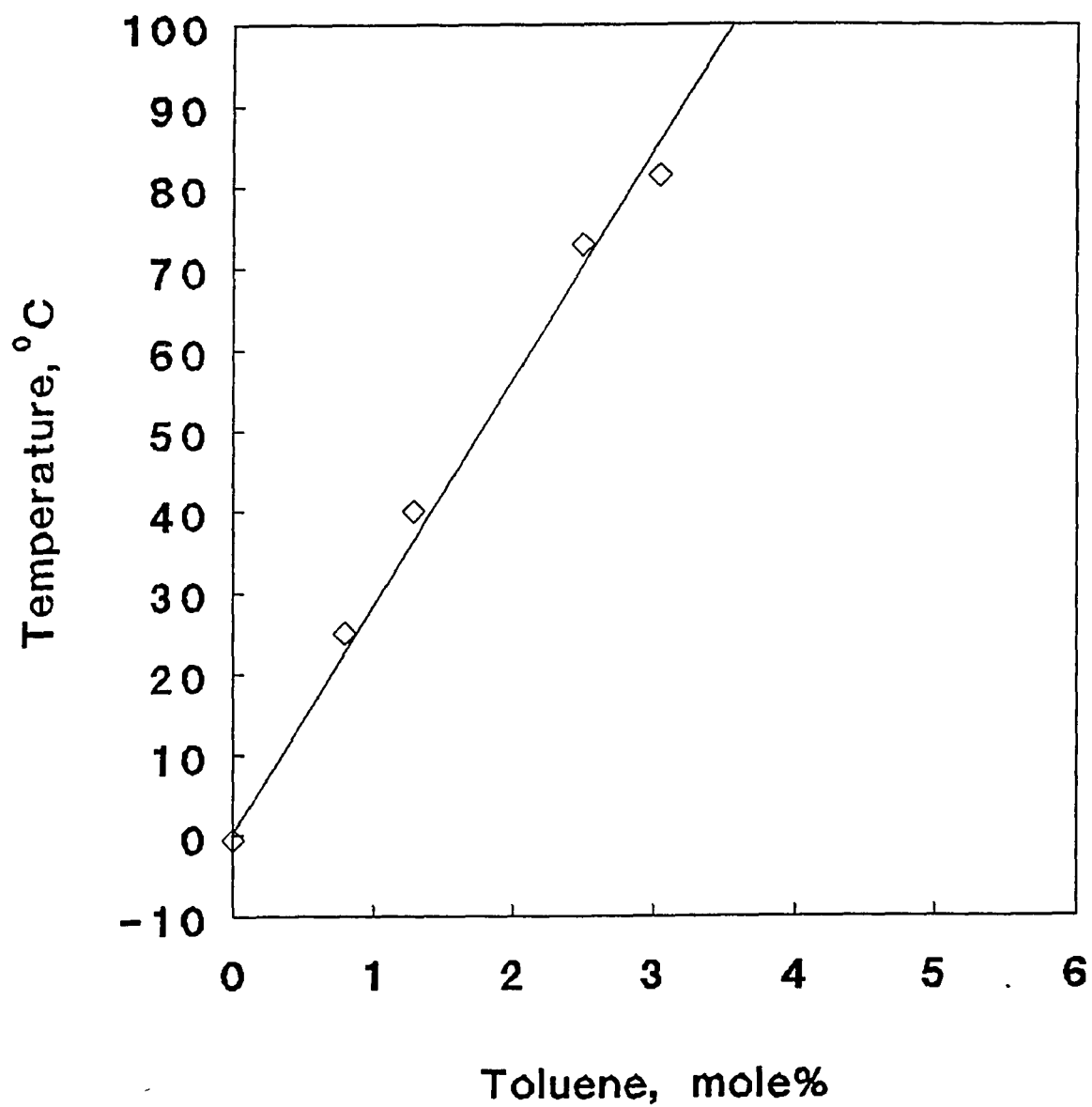


Figure 4.5: Effect of toluene concentration on the critical temperature of acetonitrile-water-toluene system.

The effect of crystal violet, the model solute, on the solvents mutual solubility was tested by dissolving the solute in the above solvent composition. No observable effects on either the CST or the phases composition was detected up to crystal violet concentration of 500 mg/liter, which is more than five times higher than the concentration used in our experiments.

4.1.3.2 Equilibrium Solute Distribution

The distribution of the crystal violet dye between the two phases of the acetonitrile-water-toluene system was determined by dissolving increasing quantities of dye. At first, a sufficient amount of the two phases was prepared. The components of the solvent system (0.585 acetonitrile, 0.371 water and 0.044 toluene) were mixed together to reach equilibrium at room temperature and then separated into acetonitrile-rich and water-rich phases. A measured amount of dye was then added to one of the phases, and the two phases were mixed again in a funnel to reach equilibrium. The concentration of the dye in each phase was measured by the spectrophotometric method described in Section 4.1.2.1.

The total amount of the dye was calculated, based on the concentrations and the phase volumes, and the result was compared to the original measured amount of dye. A discrepancy of less than 2% between the measured and the

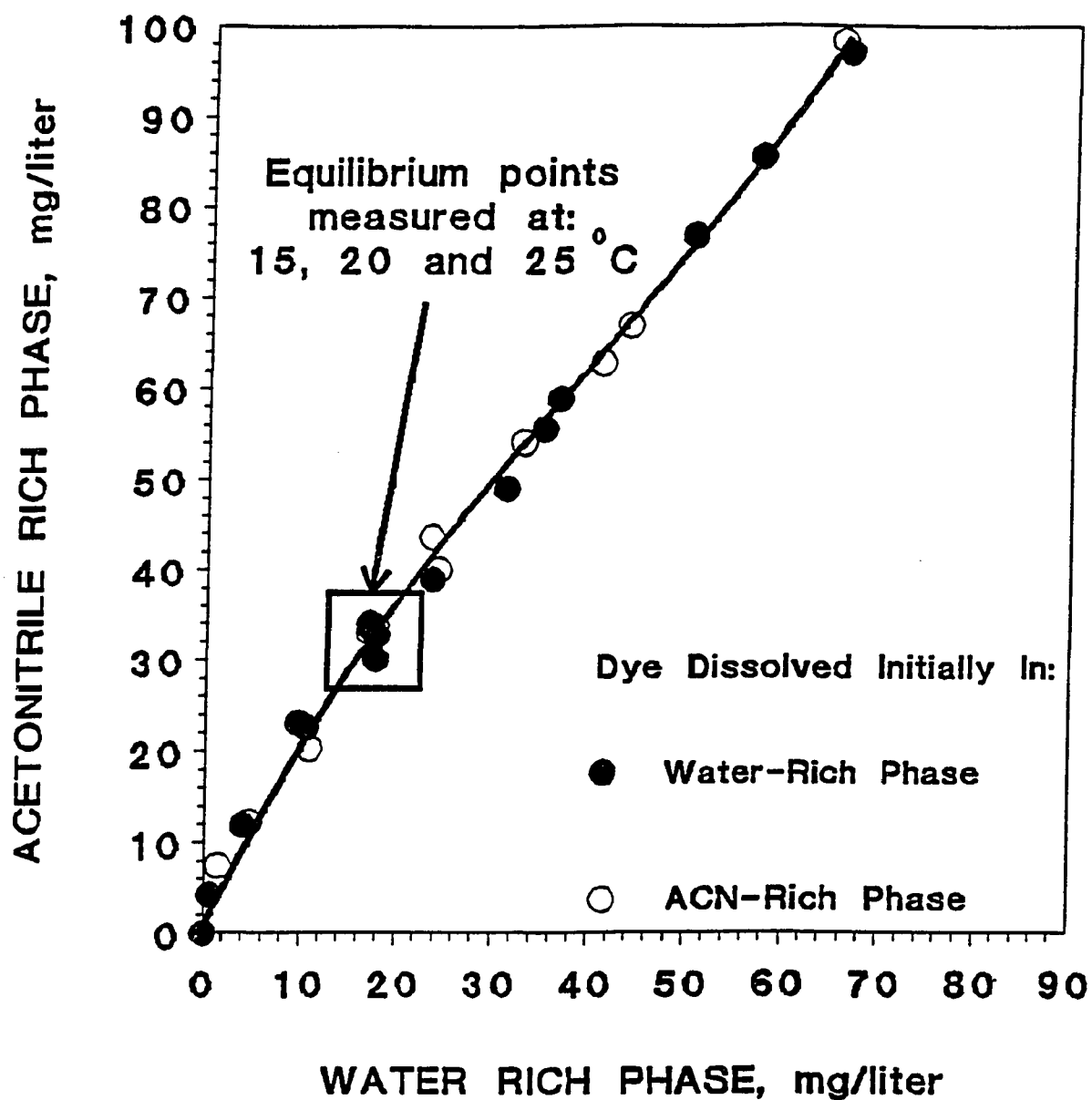


Figure 4.6: Equilibrium distribution of crystal violet between the two phases of acetonitrile-water-toluene solvents system.

calculated values assured the accuracy of the composition measurements. The experiment was repeated with increasing quantities of dye, and the results are given in Table 4.2 (see Appendix III) and Figure 4.6. To confirm that an equilibrium state was really achieved, the dye was dissolved, before the phases mixing, intermittently once in the water-rich and once in the acetonitrile-rich phases. In this way, a deviation from equilibrium in the experiments will magnify the scattering of the results, and two distinct groups of data points will be formed, one above and one below the real equilibrium line. As one can see, the scattering of the data points in Figure 4.6 is random and in the limits of the experimental error. The best-fitting line between the points can be regarded as a good representation of the equilibrium line.

The effect of temperature on the dye distribution was tested by repeating the measurements of one data point at temperatures of 15° and 25°C. Figure 4.6 shows that the temperature effect is very small, and within the limits of the experimental error.

4.1.4 Distribution Following Phase Transition

4.1.4.1 Solvents System

We studied the solvents distribution following a phase transition cycle of two-component and three-component systems. The solvents were first heated to form a homogeneous solution and then cooled rapidly to a temperature below their coexistence curve. As soon as the phase separation was completed, samples were withdrawn from the two phases and analyzed in order to determine the solvents compositions. This procedure was repeated by cooling the mixtures to several different temperatures below the critical temperature. The results obtained in this way are compared with the equilibrium phase diagrams in Figures 4.7 and 4.8 for the hexane-methanol and the acetonitrile-water-toluene systems respectively. These figures demonstrate that, within limits of experimental error, following the completion of a heating and cooling cycle, the separated phases of both the two-component and the three-component systems established a thermodynamic equilibrium composition corresponding to their temperature.

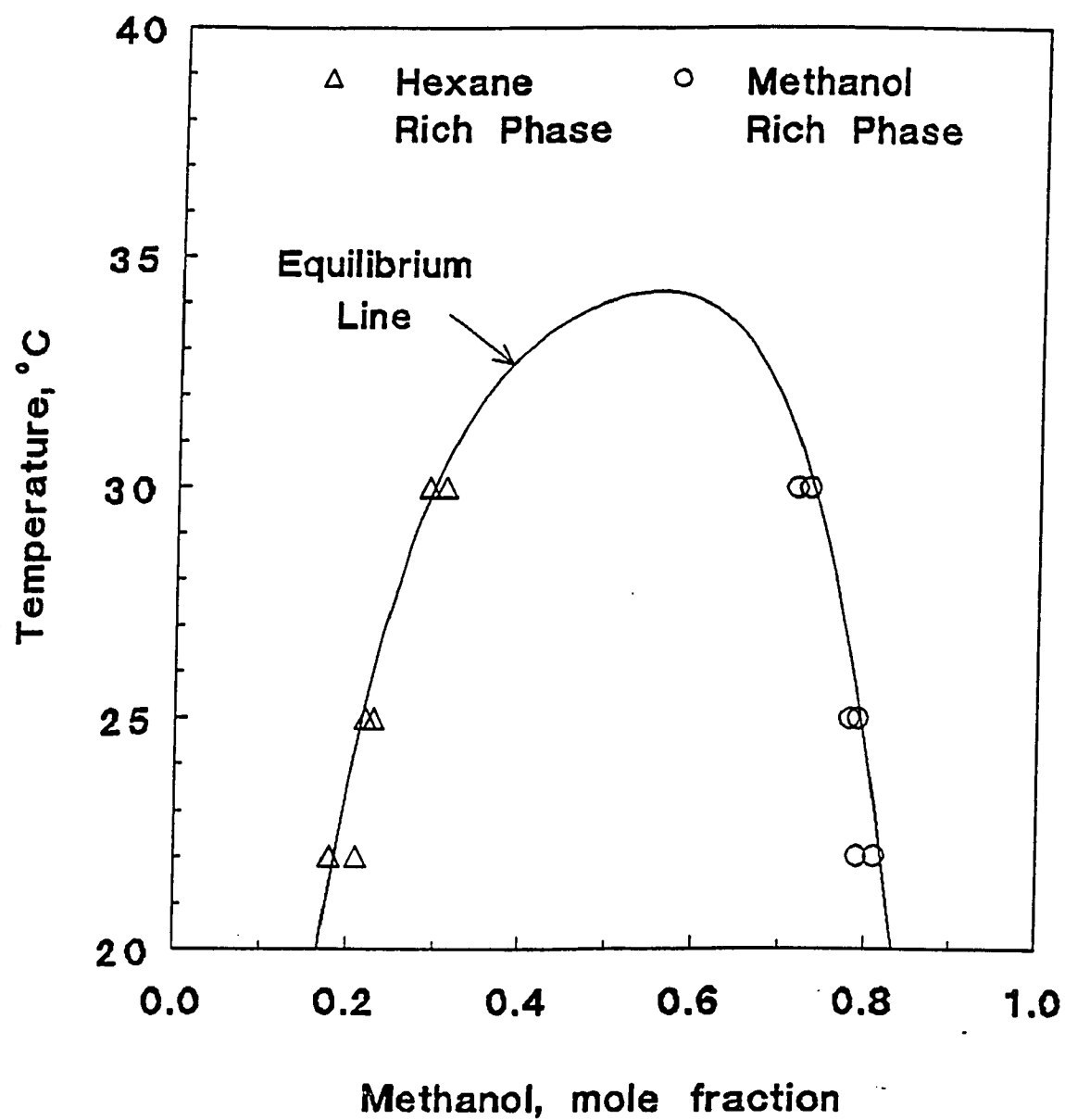


Figure 4.7: A comparison of the solvents composition following a heating and cooling cycle with the equilibrium phase diagram of hexane-methanol system.

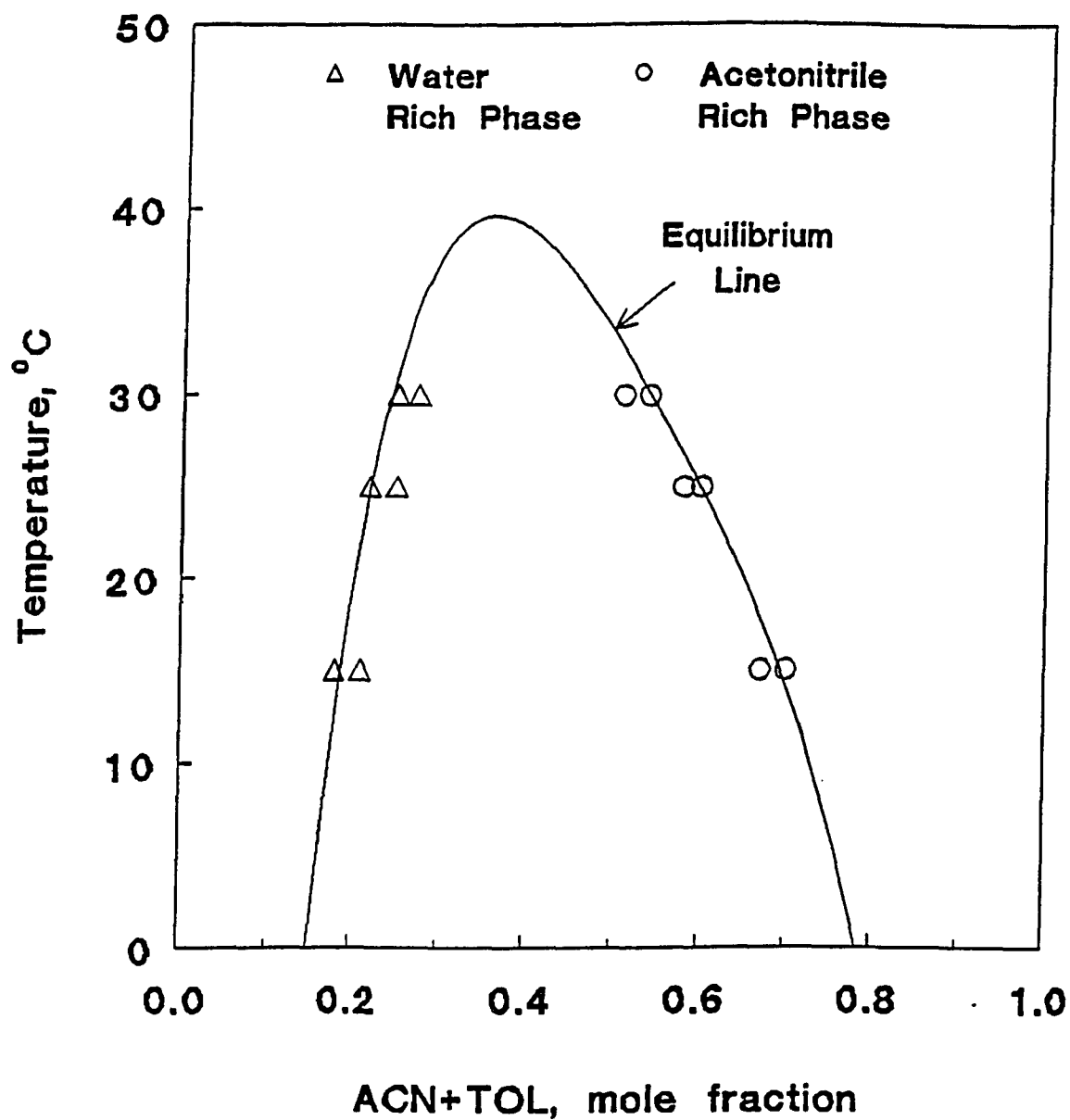


Figure 4.8: A comparison of the solvents composition following a heating and cooling cycle with the equilibrium phase diagram of acetonitrile-water-toluene system.

4.1.4.2 Solute Distribution - PTE Batch Extraction

Following the experiments conducted with the pure solvent systems we studied the distribution of solute. We did so by performing a batch experiment in which a solute, the crystal violet dye, was extracted between the two phases of the acetonitrile-water-toluene system by performing the proposed PTE process.

The experimental procedure was similar to that employed to determine the solute equilibrium distribution data (see Section 4.1.3.2). However, in the present experiments, the conventional stirring of the feed and the extracting phases was replaced by performing a phase-transition of the solvent system. The solute was extracted from the feed-phase to the extracting-phase by first heating the solvents to form a homogeneous solution and then cooling the mixture back to the original temperature in order to separate the two phases. The concentration of the dye in the two separated phases was measured immediately after the phase separation was completed. The experiment was repeated with different dye concentration and the results are shown in Figure 4.9 where they are also compared with the equilibrium distribution data. The results demonstrate that following the completion of a heating and cooling cycle the solute concentrations obtained in this way are in a good agreement with the equilibrium line obtained by mechanical mixing of the solvents at a fixed temperature.

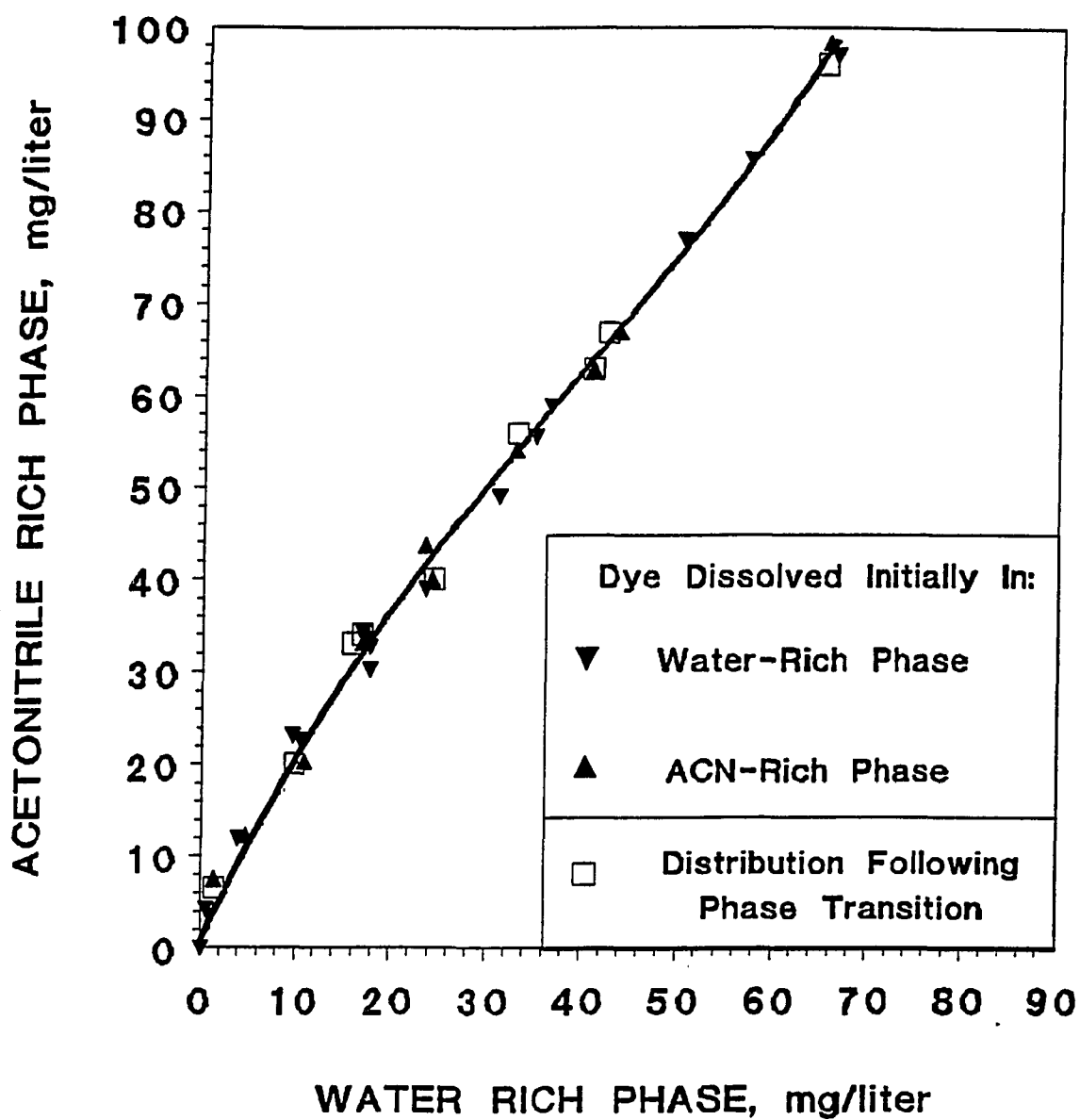


Figure 4.9: Comparisons of the solute distribution line obtained by isothermal mixing of the solvents with the one obtained following a heating and cooling cycle.

The phase-transition batch experiments have also demonstrated another important feature of the PTE process; a low mixing intensity is sufficient to obtain a homogeneous solution in the single phase regime (above the CST).

4.2 Phase Separation Rate During Phase Transition

we tested the phase separation rate by performing a series of batch experiments. In these experiments we measured the time needed to complete a full phase separation of a mixture of solvents following a phase transition, and we compared this time with the separation time of the isothermally-mixed mixture.

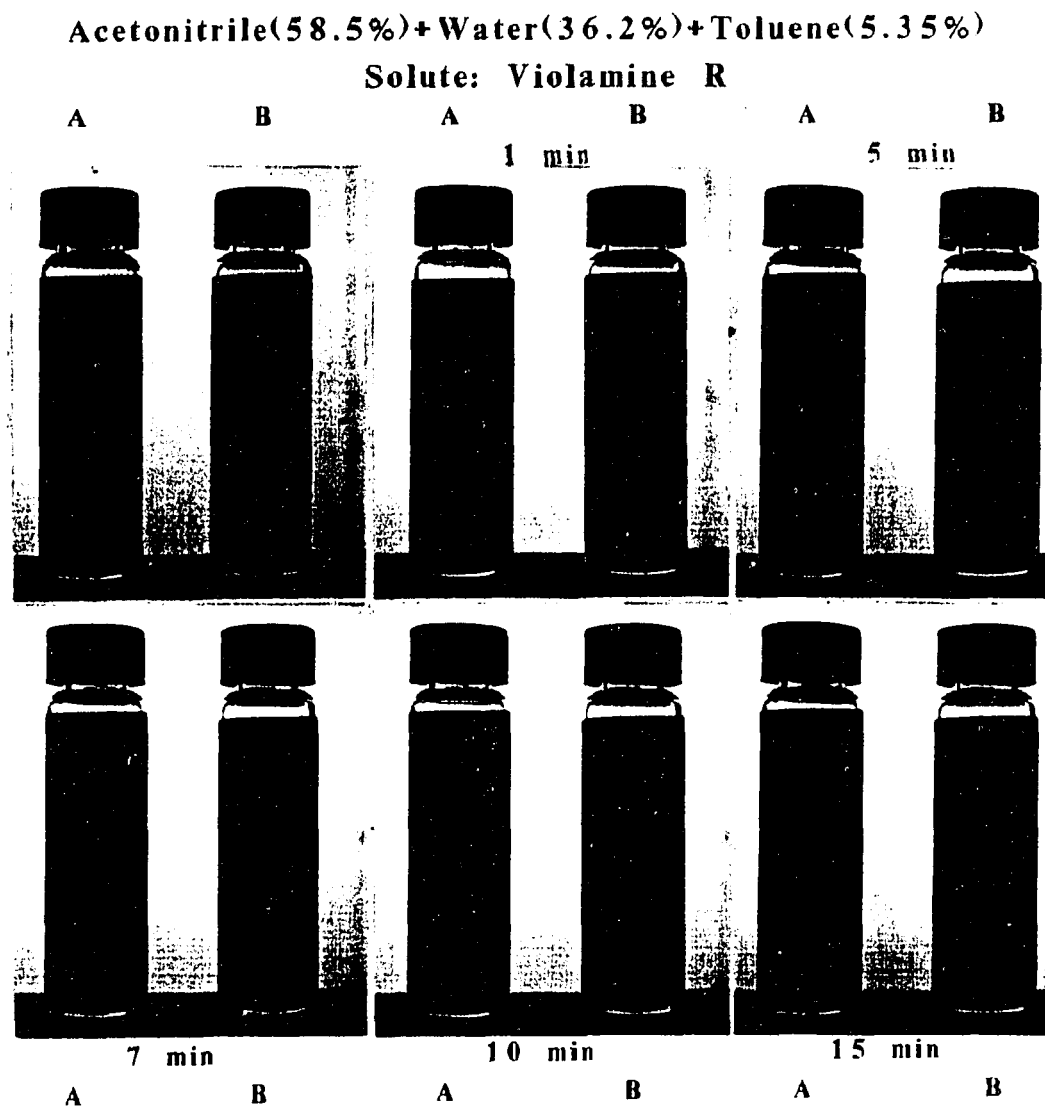
For all the solvent systems studied, two-component as well as three-component, when the homogeneous solvent mixtures were separated by temperature quench, the phase separation was very fast and was completed within one minute. When only pure solvents were used, the phase separation of the isothermally mixed solvents was also fast and virtually the same time was required to complete the phase separation following either isothermal mixing and phase transition processes.

However, a significant difference in the separation rates was observed when the crystal violet was added as a solute to the acetonitrile-water-toluene system. This dye was found to have a strong emulsifying effect on the solvents system. When the solvents were mechanically mixed at ambient temperature

with the solute, a dispersion of very fine droplets was formed, and the phase separation was completed only after seven hours. In comparison, when the heated homogeneous mixture was cooled to the ambient temperature, the primary phase separation was completed within one minute. However, a haze of fine droplets remained and cleared up only after 20 minutes. The total amount of solvent droplets in this haze was less than 1%, and for a practical separation it would have no importance. This haze was caused by a secondary (late) nucleation, a phenomenon that we will further discuss in Section 4.4.

We repeated the experiment with a different dye, i.e. violamine R, using the same solvent system. The violamine R was found to have a weaker emulsifying effect on the solvent system, but still sufficient to demonstrate the rapid coalescence phenomenon. Coalescence under isothermal conditions (25°C), where the phases are in equilibrium, took 15 minutes versus only one minute for the case where coalescence was coupled with phase transition. This experiment is summarized in Figure 4.10. The vial on the left contains the agitated mixture and the one on the right contains the same mixture that was first heated above the critical temperature and then cooled down to the room temperature.

Figure 4.10: Phase separation via temperature quench versus isothermal phase separation in the presence of emulsifying impurities.



A- Stirred for 15 min. at 25c

B- Heated to 50c and cooled rapidly to 25c (CST=48c)

The above experimental results demonstrate a very important feature of the PTE process - when the phase separation is coupled with phase transition the coalescence process is very rapid, and only short time is required to complete the phase separation even when emulsifying substances are present in the system.

4.3 Extraction of Fermentation Broth

One of the most encouraging applications for the rapid phase separation phenomenon presented in the previous Section could be found in the biotechnology and the pharmaceutical industries, namely the extraction of products from fermentation broths.

Today in the pharmaceutical industry many products are made in a fermentation process using either yeasts or microbes. One common way to recover the desired product from the fermentation broth is to use an organic solvent that extract the antibiotic or any other desirable compounds from the broth.

One common problem with such an extraction process, is the formation of stable dispersion or emulsions due to the presence of impurities and finely divided solids in the broth.

The common practice today is to break the stable emulsions by the use of centrifuges. However, this is not only expensive but can also damage some of the desired

products as high molecular weight compounds are often degraded by shear. Alternatively the broth has to be filtered prior to the extraction process, which is also often difficult. Furthermore, the filtration reduces the product yield as part of the products remain in the solids cake.

Performing the extraction of the fermentation broth by the PTE process has a great advantage over the prevailing conventional separation process. Here, the phenomenon of rapid phase separation when the coalescence is coupled with phase transition, even in the presence of impurities and solids, plays a main role.

4.3.1 Experimental

The experiments conducted are similar to the batch experiments described in Section 4.2, and have two major objectives:

- a. To measure the time needed to complete a full phase separation of a mixture of organic solvents with a fermentation broth following a phase transition, and to compare this time with the separation time of isothermally mixed mixtures.
- b. To visually observe the phase separation process.

The unpurified fermentation broth containing water, cells, and an antibiotic product was supplied by "Merck & Co. Inc.". The nature and the concentration of the antibiotic, as

well as the broth composition, are confidential and will not be described here. However, this broth, as any other industrial broth, contains a large amount of impurities and finely divided solids, and was used without any further purification or filtration. In the original process, the extracting solvent used by "Merck" is methyl isobutyl ketone (MIBK), which is a conventional solvent used in many extraction processes. In the original process the mixing of the broth with the MIBK produces a very stable emulsion and the MIBK-broth slurry is separated using a centrifugal decanter.

Two solvent systems were studied: the first was based on the MIBK - the extracting-solvent which is used in the original commercial process, and the second on propylene carbonate (PC).

The MIBK and the broth (which is composed of mainly water) have very low mutual solubility at ambient temperature. Practically, they can be regarded as a system without a CST, and therefore cannot be used to perform an extraction by phase transition. We modified this system by adding acetonitrile, which has good solubility in both water and MIBK, to form a CST-forming mixture (see Section 2.3.5). A system composed of 39.6% broth, 12% MIBK and 48.4% acetonitrile (volumetric composition) with upper CST at 40°C was selected for the experiments.

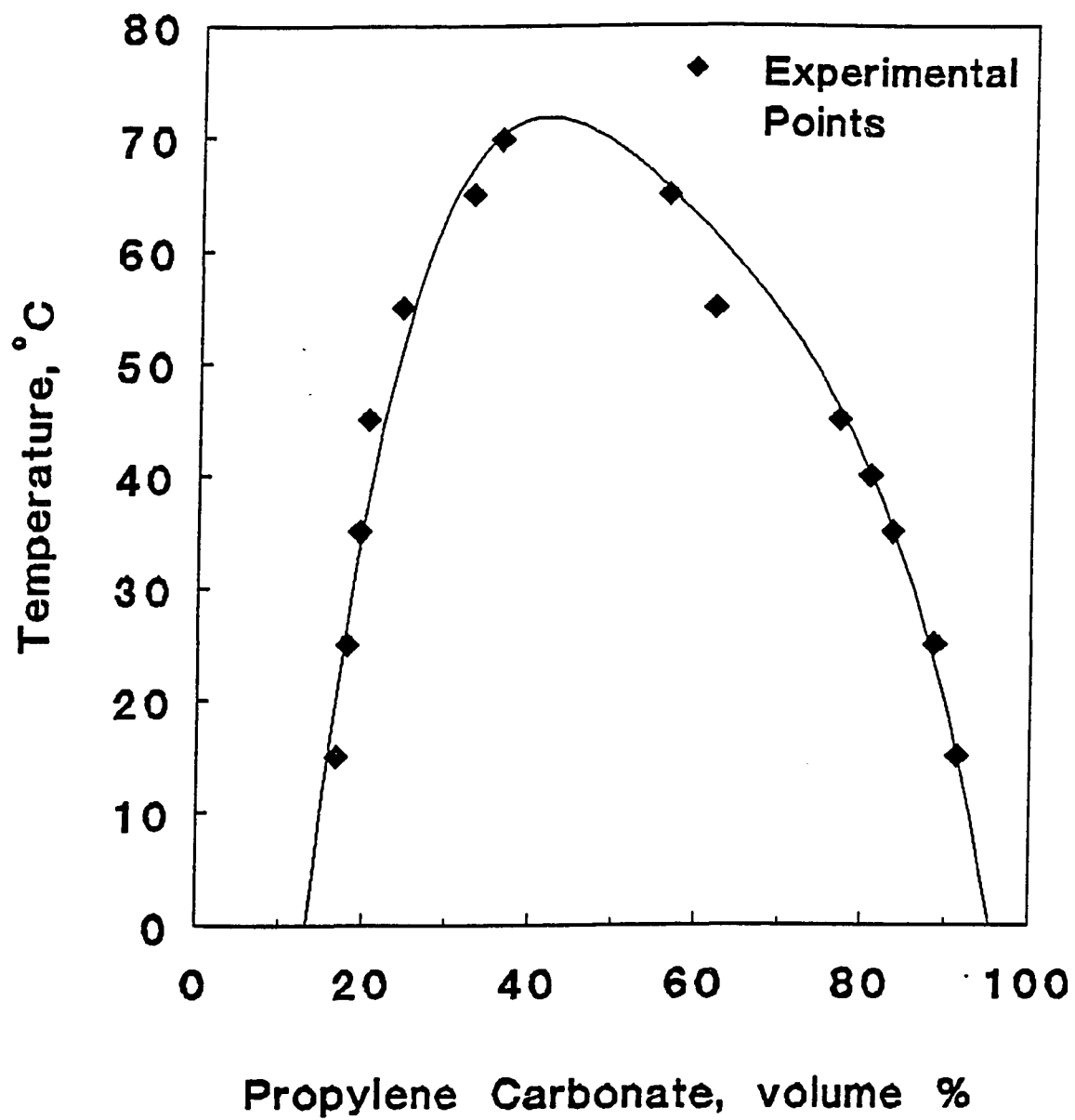


Figure 4.11: Phase diagram of propylene carbonate-water system.

The second solvent studied - the propylene carbonate (PC), possesses an upper CST with water (or broth) at 71°C (the phase diagram is given in Fig. 4.11). By using the PC as an extracting solvent we could perform an extraction by phase transition without the use of any third component as modifier. However, the phase transition temperature of the broth-PC system is too high to be used in most of the commercial processes since many compounds are heat-sensitive and can be damaged at such an elevated temperature. Therefore, we reduced the CST of the system to 44°C by adding methanol as a modifier. The system finally selected was of 43.1% broth, 50% PC and 6.9% methanol (volumetric composition). Conducting the experiments with both the broth-PC and the broth-PC-methanol system also allowed us to compare the phase separation processes of two-component and three-component systems with each other and to examine if the addition of a third component has another effect on the process beside the change of the phase transition temperature.

4.3.2 Results

First system - broth-MIBK and broth-MIBK-acetonitrile

Three cases were compared in this experiment, and the results are summarized in Figure 4.12. Vials A and B contain the critical mixture of broth-MIBK-acetonitrile where vial C contains the broth with the MIBK alone - a non-critical

mixture. The volume ratio of the organic to aqueous phases is the same in the three vials, 1:1, and the organic phase in all cases is the lighter one. The mixtures in vials A and C were mixed vigorously for 15 min. at ambient temperature (20°C), and then allowed to settle, where the mixture in vial B was heated above its critical temperature until one homogeneous phase was formed, and then cooled down to ambient temperature.

The extraction with the MIBK alone led to a dispersion which was very hard to separate (Fig. 4.12 case C). Following the mixing of the broth and the MIBK, the solids from the broth adhered to the droplets interfaces and caused the formation of a very stable emulsion. In fact, the separation of the sample in vial C was incomplete after 30 hours. Furthermore, the emulsions and the solids in this case concentrates in the extracting-solvent phase (the MIBK phase) which also contains the desired products. In order to separate the solids from the extracting solvents for any downstream processing (e.g. precipitation, crystallization etc.), a centrifuge separation is required.

The use of the MIBK-acetonitrile mixture to perform an isothermal extraction of the fermentation-broth leads to two phases: one phase is water rich, whereas the other is rich in MIBK and acetonitrile. The solvent-rich phase is as good an extracting-solvent as the pure MIBK. However, an isothermal mixing of the solvents with the broth still resulted in the formation of very stable dispersion that separated only after

30 hours (Fig. 4.12 case A).

In stark contrast, performing the extraction by heating the mixture (broth-MIBK-acetonitrile) to the single-phase stage and cooling it down to the ambient temperature resulted in a very fast coalescence, and a complete separation of the phases was achieved within one minute (Fig. 4.12 case B). This means that the rate of coalescence increased by more than three magnitudes.

The rapid phase separation in case B is clearly the result of the phase transition process induced by a temperature variation, since, as demonstrated in case A, an isothermal mixing of the same solvent mixture resulted in a stable emulsion. In addition, heating and cooling the emulsified broth-MIBK mixture (case C) in a similar way as in case B (with the critical-mixture), did not bring any appreciable change in the stability of the emulsion. This confirms that the rapid coalescence is a result of the phase transition and not of the temperature variation alone.

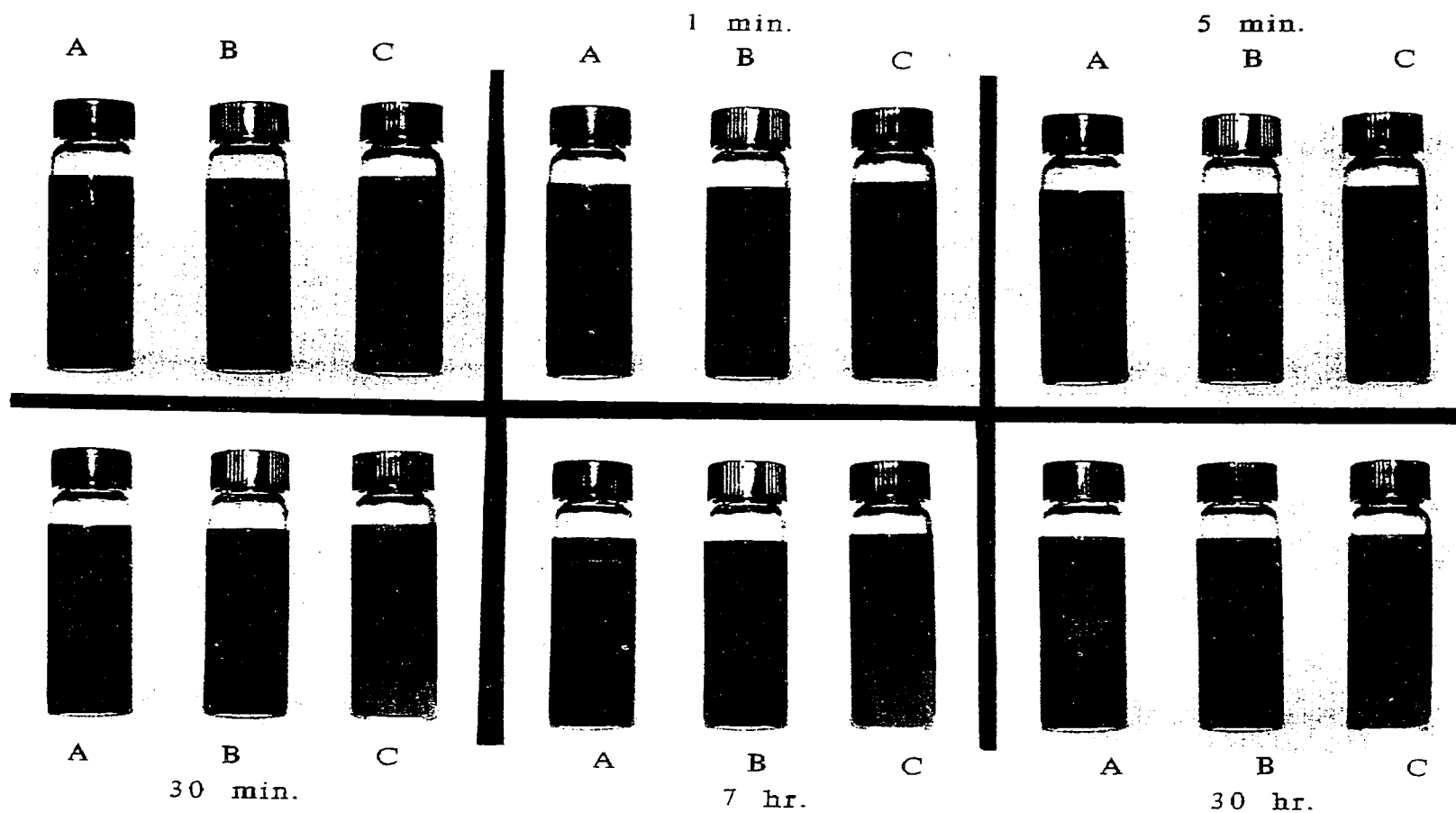
The above experiments demonstrated another advantage in performing the extraction via phase transition. After the coalescence is completed, the solids concentrate in the aqueous phase (see Fig. 4.12 case B). This allows to perform a multi-stage extraction when a single-stage extraction is not sufficient.

The efficiency of the extraction was studied by analyzing¹ the concentration of the products in the organic phase of the broth-MIBK and the broth-MIBK-acetonitrile systems (cases B and C). In both cases the broth was extracted three times by fresh organic solvents. This was a simple procedure in the case of the phase transition extraction, since, as we mentioned above, the solids concentrated in the aqueous phase after every extraction step. However, in the case of extraction by the MIBK, a centrifuge had to be used to separate the phases. The results of the analysis are tabulated in Table 4.3 (see Appendix III). In both cases the extraction was completed after two extraction-cycles, and no traceable amount of products was found in the organic phase after the third extraction-cycle. However, the extraction by phase transition was evidently more efficient than the conventional extraction by the MIBK (see also Fig. 4.13).

The higher products yield of the phase transition process may be explained by the higher capability of this process to extract the products from the interior of the organism cells. By achieving a complete miscibility of the extracting solvent with water in the single phase stage of the process, the extraction of the products from the cells, which contain mostly water, may encounter much less

¹ The work on the MIBK-broth-acetonitrile was conducted in collaboration with Eliahu Nitzan from the Faculty of Agriculture of the Hebrew University in Israel

Figure 4.12: Phase separation during the solvent extraction process (broth-MIBK and broth-MIBK-acetonitrile systems).



A & C - Conventional extraction (isothermal mixing) B - Phase Transition Extraction

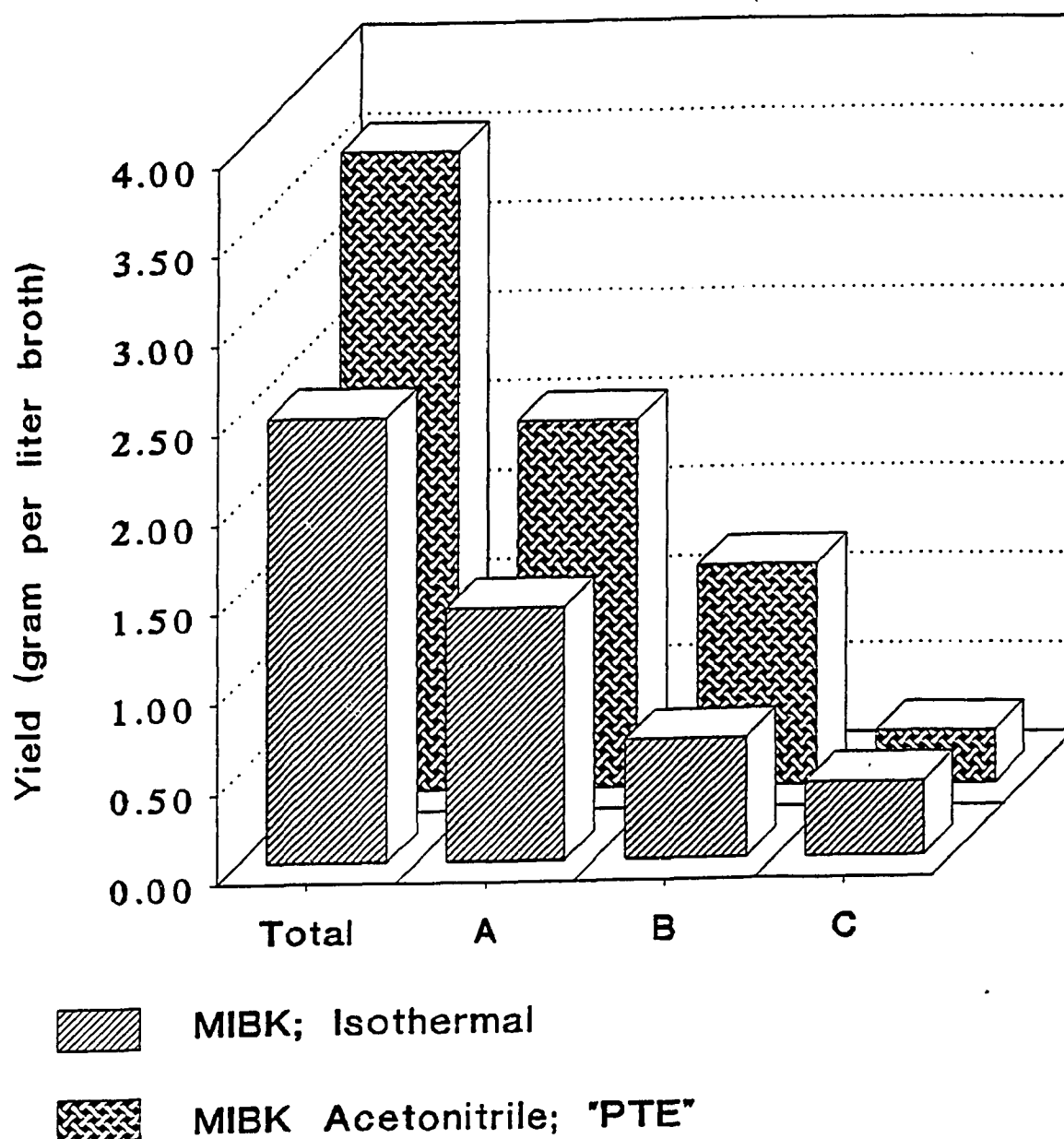


Figure 4.13: Amount of components extracted from the fermentation broth (first extraction), a comparison of the PTE process with the conventional process.

resistance at the cells interface than in the case of two immiscible solvents.

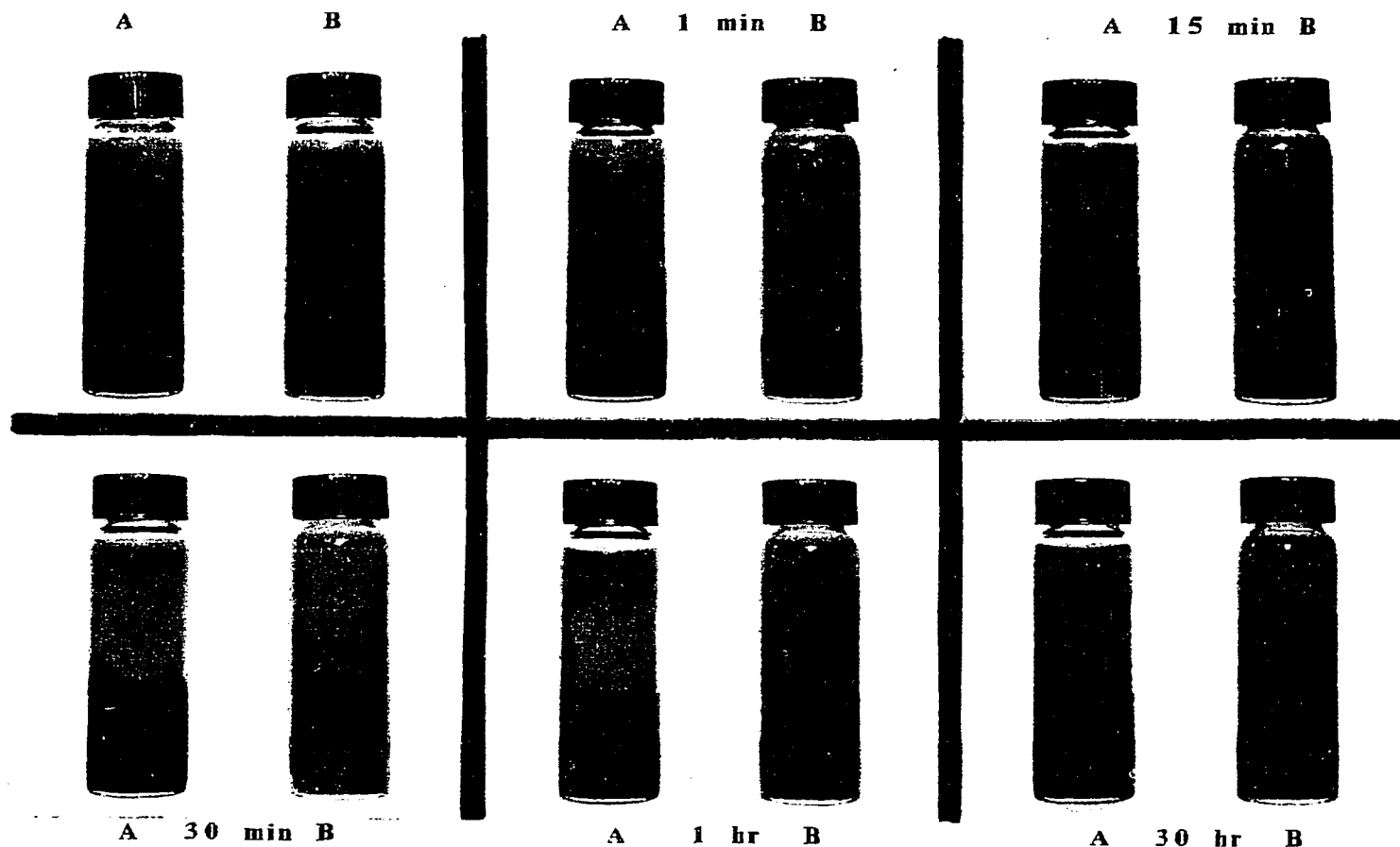
Second system - broth-PC and broth-PC-methanol

The experiments with these solvent systems were conducted in a similar way as the experiments with the first system, and the results are shown in Figures 4.14 and 4.15 for the two-component and the three-component systems respectively. Vials A and B in each case contain the same mixture with 1:1 volume ratio of organic to aqueous phase, but the mixtures in vials A were heated above the CST and then cooled down to the ambient temperature, whereas the mixtures in vials B were mixed at the ambient temperature and then allowed to settle.

The results confirm again the superiority of the phase-transition extraction over the conventional isothermal extraction. An isothermal mixing of both the two-component and the three-components systems led to a very stable emulsion which did not separate even after thirty hours, whereas the phase-transition extraction resulted in a very rapid coalescence, and a complete phase separation was achieved after one minute with all the solids concentrated at the aqueous phase (the light phase in this case).

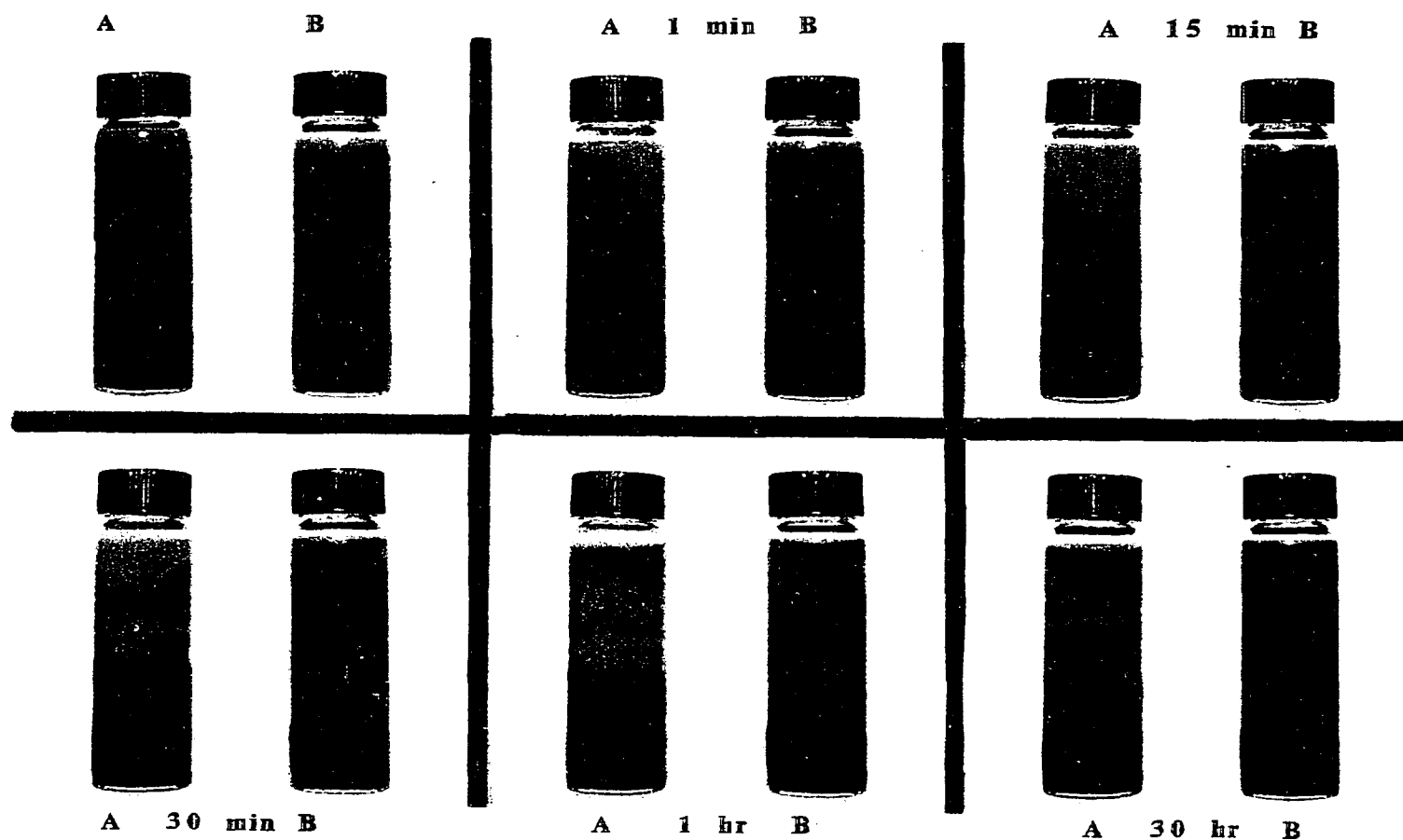
No appreciable differences were observed between the results of the experiments with the two-component and those with the three-component solvent systems (Figs. 4.14 and 4.15). This confirms again that the rapid phase separation

Figure 4.14: Phase separation during the solvent extraction process (broth-propylene carbonate system).



A - Phase Transition Extraction. B - Conventional Extraction (isothermal mixing).

Figure 4.15: Phase separation during the solvent extraction process (broth-propylene carbonate-methanol system).



A - Phase Transition Extraction. B - Conventional Extraction (isothermal mixing).

is a result of the phase-transition process and not of the addition of the third component to the solvents system. The only effect of the third component is the adjustment of the CST of the system to a desired value.

4.4 Discussion - Phase Separation Rate

In the previous Sections we demonstrated that when performing by the proposed Phase Transition Extraction (PTE) process the coalescence rate is very high. The results of our experiments show that for all the solvent systems studied the primary phase separation was completed within one minute. This fast phase separation was common to the pure solvent systems as well as to systems containing dye solutes with emulsifying effects which coalesce very slowly when mixed isothermally. Moreover, the phase separation when coupled with phase transition is fast even for the extraction of fermentation broths that form a stable emulsion under isothermal mixing conditions.

This phenomenon is unknown in the literature to date, and has not received a thorough theoretical investigation. However, some understanding of the phenomenon can be established based on the dynamics of the phase transition process as reviewed in Section 2.3.7.

An essential condition to the emulsion stabilization is the presence of surfactant, polymers, or small solid particles

(emulsifiers) in the liquid-liquid system. The emulsion can be stabilized by different mechanisms, where the stabilizing mechanism is determined by the emulsifier type (see a review in Section 2.2). However, regardless of the emulsifier type or stabilization mechanism, a basic requirement for the stabilization is the adsorption of the emulsifier on the droplet interface. Moreover, an effective stabilization requires a full coverage of the droplets interface by the adsorbed substances. It will be therefore reasonable to assume that if the adsorption of emulsifiers on the droplets interface is prevented, or if the rate of droplet growth is higher than the rate of emulsifiers adsorption, the stabilizing effect will be negligible.

We can now try to determine the effect of emulsifiers on the rate of phase separation of critical mixture during a phase-transition process. As discussed in Section 2.3.7, the phase transition process following a temperature quench of the system from the single-phase region into the two-phase region can be divided into two major steps according to the thermodynamic stability of the system (see Fig 2.9); the first stage - "spinodal decomposition" in the unstable region, and the "late stage" characterized by nucleation of micro-domains followed by a droplets growth, in the metastable region.

In the first stage, the unstable mixture is separated via a very fast exponential growth of non-localized concentration fluctuations. In this stage there are no stable or well

defined boundaries between the different phases, and consequently any adsorption of emulsifiers on the interface is prevented.

In the "late stage" of the phase transition process, the initially very diffused boundaries between the phases are sharpening with time until well defined regions are formed. From now on, the growth mechanism of the separated domains is similar to the one that occurs in the late stage of growth following nucleation events, a process which combines a growth by diffusion and coalescence of the droplets.

When a substantial supersaturation of the solution exists, the growth of the separated domains can be accompanied by the formation of new nuclei (late nucleation) which will grow by a similar mechanism.

Since in the "late stage" of the phase transition the phases are separated by a defined interface, the emulsifiers can start to adsorb on this interface. This is a dynamic process which requires: first - the diffusion of the emulsifiers towards the interface, and second - their adsorption on the droplets surface. The rates of these processes are usually determined by the nature of the emulsifier, the solvents properties, and the fluid dynamics conditions. However, during the phase transition process the adsorption is also affected by the diffusion of the solvents from the continuous phase into the growing droplets. This solvents diffusion prevents the formation of stable interfaces

and thereby slow down the emulsifiers adsorption rate.

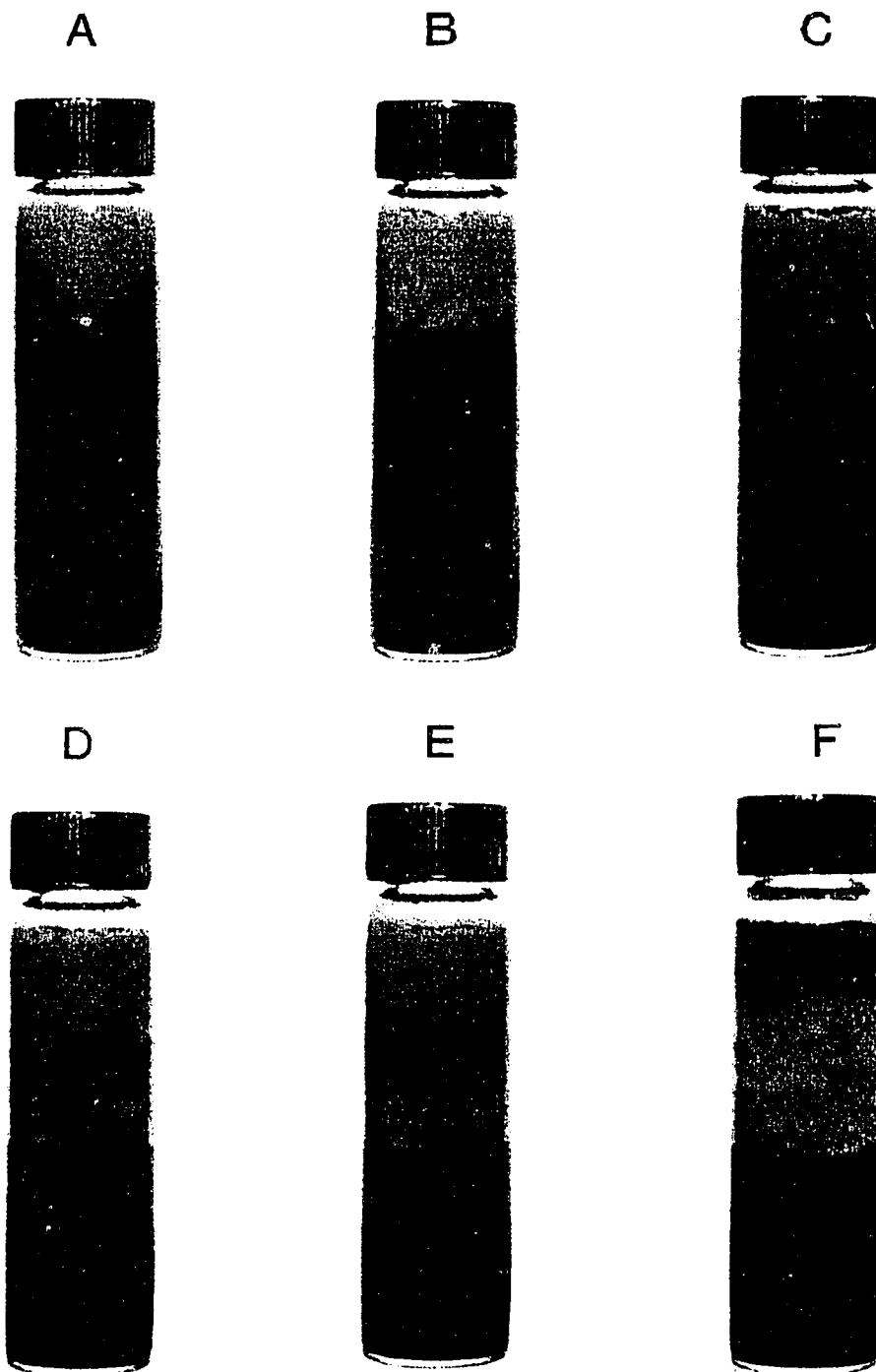
The rate of the droplet interface coverage by the emulsifiers is determined in this stage by the ratio between two competing mechanisms, namely the rate of the emulsifier adsorption on the droplet interface, and the rate of the droplet growth by diffusion which causes an expansion of the droplet surface area. If the rate of droplet growth is sufficiently higher than the rate of the surfactant adsorption, then the coverage of the droplets surface by emulsifiers will be prevented, and consequently the coalescence and the phase separation processes will be fast.

The prevention of the emulsifiers from adhering to the droplets interface is well demonstrated in the experiments conducted with the fermentation broth. The sequence of pictures in Figure 4.16 display the first steps of the phase separation of the broth-PC-methanol system. The emulsifiers in this case mainly consist of finely divided solids originated in the broth. The first picture (4.16 A) shows the critical mixture heated to a temperature above the CST. The organism-cells and solids from the fermentation-broth are floating in the single-phase solvents mixture which has a specific density $\rho \approx 1.11$. Following the phase separation, the solids become heavier than the light, aqueous phase ($\rho \approx 1.04$), but lighter than the organic phase ($\rho \approx 1.19$). They sink due to the gravity force, and concentrate on the main interface (Figs. 4.16C to 4.16F). However, in Figure 4.16B, which was

taken a short time after the mixture was cooled to ambient temperature, it can be seen clearly that the main phase separation is completed without any appreciable change in the bulk of the solids at the top of the vials. Since the phase separation during the phase-transition is not localized and occurs all over the solvent bulk, any adherence of solids to droplet interface during the phase separation would result in a sweeping of solids to the bulk of the lower (organic) phase or at least to the main interface. The undisturbed solids bulk therefore serves as evidence that during phase-transition the adherence of solids to interface and the consequent stabilizing effect are prevented.

As we have mentioned already, the primary phase separation during the phase transition process was fast for all the systems studied in our experiments. However, in one of the systems, the acetonitrile-water-toluene system with the crystal violet dye, following the primary separation, some fog-like dispersions (secondary dispersions) remained in the bulk of the separated phases and settled down after 20 minutes. A similar phenomenon was also reported for isothermal mixing of immiscible solvents (Treybal, 1963). However, in our experiments the secondary dispersions should

Figure 4.16: The behavior of particulates during Phase Transition Extraction of fermentation broth (broth-propylene carbonate-methanol system).



be related to the presence of emulsifiers, in this case the crystal violet, since it was not observed during the phase separation of the pure solvents.

The secondary dispersions have a minor effect on the extraction efficiency since they contain a very small amount (less than 1%) of the main phase volume. However, the formation of the secondary dispersions at the final stage of the phase transition has a substantial importance in understanding the phase separation phenomenon, since it demonstrates that the presence of emulsifiers in the system may have some effect on the phase separation also during the phase transition process.

Some explanation for the appearance of secondary dispersion following the completion of the primary phase separation can be obtained on the basis of the dynamics of the phase transition process as discussed at the beginning of the present Section. According to this discussion, the adsorption of the emulsifiers during the "late stage" of the phase transition is prevented due to the fast growth of the droplets and by the solvent diffusion into the droplets. However, during the final stage of the phase transition, most of the phase separation has been already completed, and the supersaturation of the separate phases, which is the driving force for the solvent diffusion, becomes low. Consequently, the remaining droplets, most of which were formed by a late nucleation process, are now growing by a slow solvent

diffusion process. The slow droplets growth and the low-rate solvent diffusion allow the coverage of the droplets interface by the emulsifiers which in turn slows down the coalescence of the remaining droplets which emerges as a secondary dispersion.

The above discussion may provide a qualitative explanation for the appearance of the secondary dispersion at the end of the phase transition process. However, it still falls short in explaining why the secondary dispersion was observed only in one of the systems studied, and for only one of the emulsifiers, the crystal violet, and not for the other, the violamine R, when the same solvents system was studied.

A better understanding of all the aspects of the rapid phase separation phenomenon requires a thorough experimental and theoretical work. Such a work is now in progress, but is outside the scope of this thesis. Some preliminary experiments of direct microscopic observation of the phase transition process are given in Appendix II.

4.5 Conclusions - Batch Experiments

The validity of the basic concepts underling our novel process has been proven via a series of batch experiments. In these experiments, a solute was extracted via performing a phase transition of the solvents and solute system. The experiments showed that, within limits of experimental error,

following the completion of a heating and cooling cycle, the separated phases established a thermodynamic equilibrium composition corresponding to their temperature. The solute concentrations and the solvents composition obtained in this way have been found to be in good agreement with the equilibrium line and the phase diagram obtained by mechanical mixing of the solvents at a fixed temperature.

The phase-transition batch experiments have also demonstrated that low mixing intensity is sufficient to obtain a homogeneous solution in the single phase regime (above the CST).

The rapid coalescence and phase separation of solvents systems undergoing a phase transition from a single-phase state to two distinct phases via temperature variation, has been demonstrated. It has also been shown that such a phase separation has very low sensitivity to any presence of emulsifying substances. In the case of isothermal mixing, such emulsifiers usually adsorb on the droplets interface causing the formation of stable dispersions or emulsions. The absence of stable interfaces between the separating phases during the spinodal decomposition stage of the phase-transition prevents any adsorption of emulsifiers during this stage. Later, in the second stage of the phase transition, the relatively rapid growth of the droplets (accompanied by the absorption of solvents from the continuous phase), throughout the metastable stage of the phase-transition,

prevents the adsorption of the emulsifiers on the droplets interface. Consequently, the stabilizing effect of the impurities is neutralized.

The rapid phase separation during the phase-transition process was demonstrated for several two-component and three-component solvents systems, and in the presence of different types of impurities. This phenomenon has a substantial importance in performing extraction of systems which are sensitive to the formation of stable emulsions.

A possible application of this phenomenon was demonstrated by applying the phase-transition process to the extraction of a fermentation-broth. Here, the extraction of the broth by phase transition process has some considerable advantages over conventional extraction processes:

- a) The formation of stable emulsion, one of the crucial problems of broth extraction, is prevented without the need to filter the broth prior to the extraction process, or to use expensive and complicated centrifuges.
- b) The rapid phase separation and the concentration of the solid fraction of the broth in the aqueous phase allows a convenient multi-stage extraction when a single-stage extraction is not sufficient, and simplifies any down-stream processing (e.g. precipitation, crystallization etc.) of the products concentrated in the organic phase.
- c) Since a complete miscibility between the organic (extracting solvent) and water (feed) is obtained during the

phase transition process, the extraction of the product from the organism-cell (which contains water) encounters much less resistance at the cell interface than in the case of extraction with immiscible solvents. Therefore, a high product yield is obtained by the phase-transition extraction process without the need for a prior breaking of the cells and a severe mixing of the broth with the extracting-solvent.

d) Eliminating both the need for intense mixing of the solvents in the contacting stage of the process and the use of centrifuges in the settling stage prevents any possible shear-stress damage to large molecules.

e) The presence of water in the solvent rich phase (the extracting phase) may reduce denaturation of compounds which decompose or change their form in water-free solvents.

At this point, it is important to present answers to problems that may rise regarding the use of the phase transition for the extraction of fermentation broth:

(1) The need for solvents that form a critical mixture with the broth (or water) may restrict the number of available solvents for the extraction process.

Although the process was demonstrated using solvents that possess a CST with water, it is important to emphasize that the process is not based on the use of any particular critical composition (or on any critical phenomenon) but only on the phase transition of the solvents. In fact, there is a considerable number of solvents which form such a partially

miscible system with water (see Section 2.3.2), and therefore can be used for the PTE process. In addition, as we demonstrated for the broth-MIBK system, one can add an appropriate solvent to modify the original solvents system. Thus, almost all solvents that are currently used in centrifuge-base extractions and which are only slightly soluble in water can be integrated into mixtures having a critical point of miscibility.

(2) The temperature variation of the solvents while performing the phase-transition extraction may damage heat-sensitive compounds.

Here again, by the addition of an appropriate solvent, the phase-transition temperature of the solvent system can be adjusted to any desired level (as we demonstrated for the broth-PC system).

(3) The variation of the solvents temperature across the miscibility curve requires a higher energy consumption as thermal energy in comparison to the energy of mixing required in conventional extraction processes.

The energy consumption of the phase-transition extraction process will have to be weighted by the designer against the advantages of the process when deciding upon the preferable extraction for a specific separation. Such a decision will be naturally highly affected by the product's value. However, adjusting the operational temperature to the vicinity of the ambient temperature (as we explained above), may reduce the

cost of the required heating and cooling by permitting the use of low cost and highly available heating and cooling sources. In addition, a significant fraction of the process heat consumption can be recycled through an appropriate heat exchange between the hot and cold streams.

We may conclude here that the rapid phase separation, along with the high efficiency of the phase-transition extraction process, provides a flexible and powerful tool for performing difficult separations in the biotechnological and pharmaceutical industries.

5 COUNTERCURRENT OPERATION OF THE PTE PROCESS - COLUMN EXTRACTOR

5.1 Introduction

In the previous part of this work we described the concept of the novel phase transition extraction process and demonstrated that such a process works by performing a series of batch experiments. The purpose of the following part is to demonstrate the feasibility and to examine the performance of a continuous countercurrent operation of the suggested process.

The basic configuration of mixer-settler extractors, the conventional as well as our novel design, are simple in concept. Such extractors consist of distinct sections used for mixing and for separation of the solvent streams. A cascade of mixer-settlers incorporates separate and independent stages which are controlled and operated autonomously. Therefore, the testing and scale-up of such equipment are relatively simple and can be done as well by batch experiments.

The main advantages of performing the phase transition extraction (PTE) process in mixer-settler operation mode over conventional mixer-settlers - the fast phase separation of emulsifying systems, and the reduction of the required mixing intensity - have been demonstrated via the batch experiments

conducted in Section 4 of this work.

Therefore, we have emphasized, and concentrated on, our experimental work in the following part, demonstrating the feasibility of performing the PTE process in a column, and on studying the mass transfer performance of such a column.

In general, mixer-settler extractors are recommended when only a few stages are required. Otherwise, the hardware cost, space requirement, and the need to control each of the individual units separately become excessive, and column extractors are recommended (Cusack R. W. and Fremeaux P., 1991). The features of the PTE process, as described in Section 3, make a column operated by virtue of phase transition to be a very attractive tool for separation processes that require a large number of theoretical stages. Such a column can operate without any moving parts and still provide a high stage efficiency. The simplicity of the column allows to construct a large number of stages. Furthermore, the fast coalescence that characterizes the phase transition process, allows high throughput in the column even with solvent systems that tend to emulsify.

As any conventional extraction column, the PTE column is based on a vertical countercurrent flow of two liquid phases caused by density difference and gravity. However, in contrast to conventional columns, which usually operate under isothermal conditions, the streams in our column are subjected to periodic change of the solvents density when passing

through the heating and cooling section which are placed intermittently one above the other. Furthermore, in the PTE column the two liquid phases are mixed together to form virtually a single homogeneous phase in the mixing section, before separating again, by virtue of phase transition in the settling section. This may complicate the flow pattern of the solvents in our column in comparison to conventional columns where two distinct phases exist throughout.

In order to demonstrate the feasibility of performing our process in a column, lab-scale single-stage and three-stage columns were designed and built and their performance evaluated. We will show that such columns have unique features and operating constraints that have to be understood.

5.2 Experimental Techniques

5.2.1 Experimental Solvents and Solute System

The selection of a solvent system for the experiments was mainly affected by the need for a solvent system which will allow easy and accurate experimental operation.

In the experiment conducted to study the operation of the lab-scale columns we used a mixture of 0.585 acetonitrile 0.371 water and 0.044 toluene (volumetric fraction) which possesses an UCST at 40°C (see phase diagram in Fig. 5.1). The same system was also used in the batch experiments

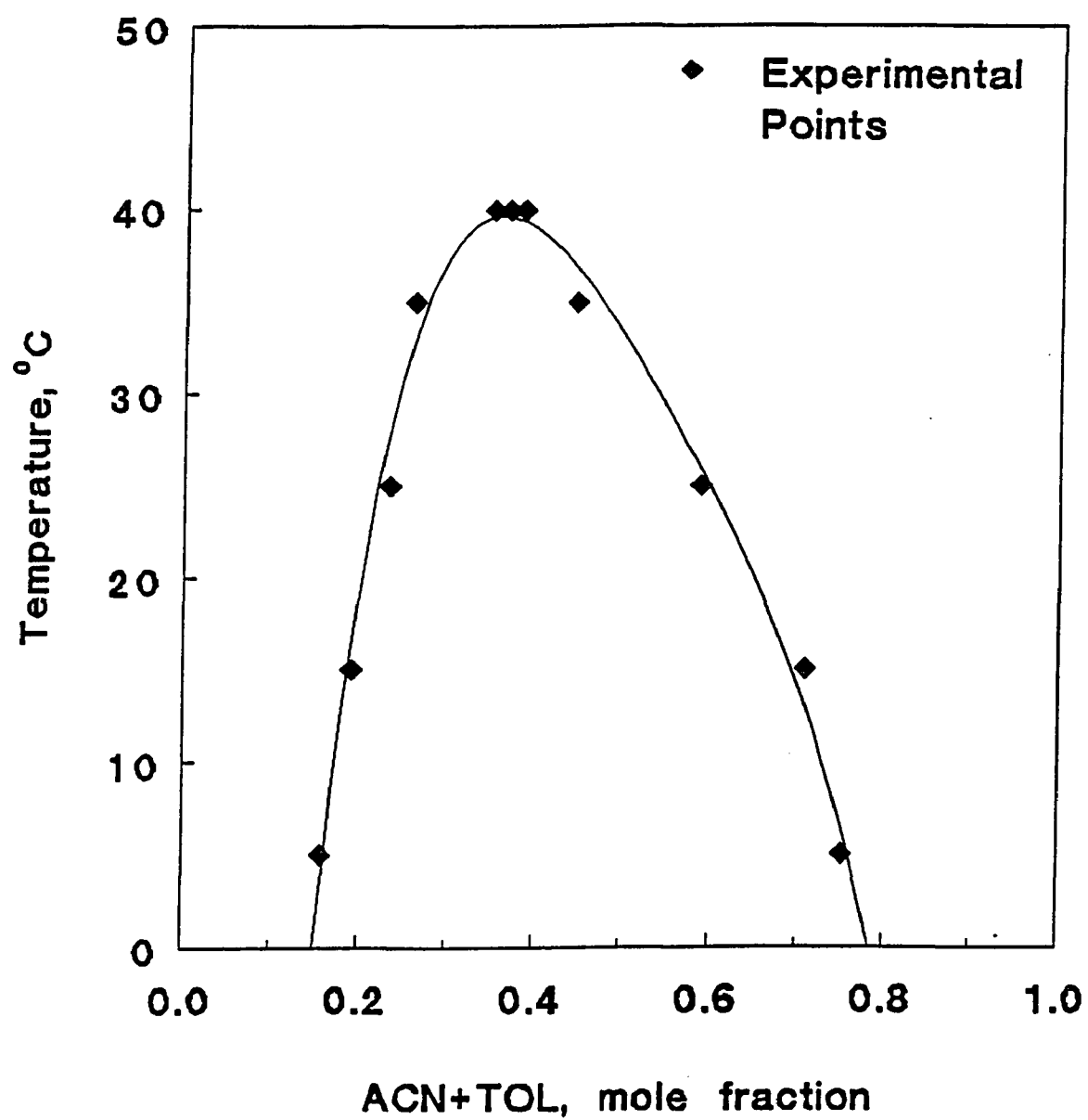


Figure 5.1: Phase diagram of acetonitrile-water-toluene system.

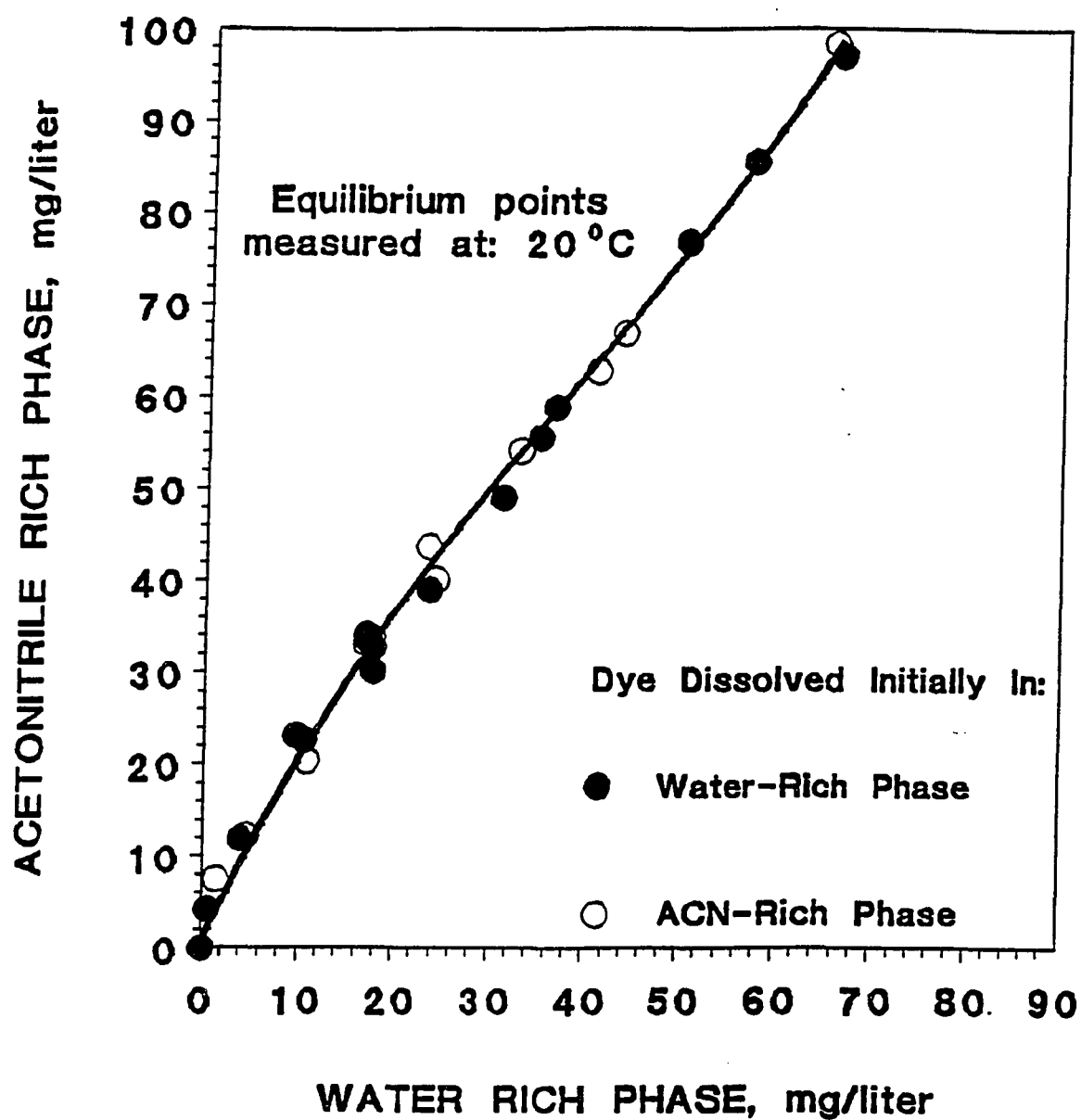


Figure 5.2: Equilibrium distribution of crystal violet between the two phases of acetonitrile-water-toluene solvents system.

described in Section 4, and the considerations in selecting this system, together with the experiments in which the phase diagram of the system was determined are given in Sections 4.1.2 and 4.1.3, respectively.

Crystal violet, which was also used in our previous batch experiments, was chosen as the model solute. The use of a dye as a solute allows an easy, accurate and fast measurement of even very low dye concentration by means of light absorbance spectrophotometry. A low solute concentration was preferred because it has a negligible effect on the solvents mutual miscibility and thus simplifies the computation of the column performance.

The equilibrium distribution of the dye between the two phases of the acetonitrile-water-toluene system was determined in Section 4.1.3.2 and is given in Figure 5.2.

5.2.2 Apparatus for Performance Study

In order to study the performance of the PTE process a modular laboratory-scale column was designed and constructed. The modular structure of the column enables performing changes in the equipment if modifications are necessary, and allows one to alter the number of stages or to replace parts very easily. The performance tests were made on single and three-stage columns operated with simple liquid extraction processes in which a solute is transferred from one liquid phase to

another. The small number of stages was chosen to give representative performance, to allow rapid approach to steady state condition, and to reduce the effect of slight errors in equilibrium data on the stage efficiency evaluation.

5.2.2.1 Description of the Extraction Column

The experimental single-stage column consists of one heated zone and two cold zones. The heater section is a 15 mm inside diameter, 100 mm high glass cylinder, equipped with an electrical heater. The temperature in the heater is controlled by a variable power supplier. The cooling sections are constructed as a shell-and-tube type heat exchanger, where the solvents flow in a 50 mm diameter glass shell 150 mm high, and the coolant in a coil-structured copper tubes. The temperature in the heat exchanger is regulated by changing the coolant flow rate. The coolant, a water-ethylene-glycol mixture, is circulated by pump between a storage tank and the heat exchanger. The coolant in the storage tank is maintained at constant low temperature by means of immersion cooler (PolyScience Inc. Model KR-80A) and temperature controller (Omega Inc.). The solvents inlet and outlet 1/4 inch pipes are inserted through teflon cups into T-shape glass cylinders at the bottom and the top of the column. The various column parts are connected to each other by teflon connectors. Thermocouples are placed in each of the column-sections, and

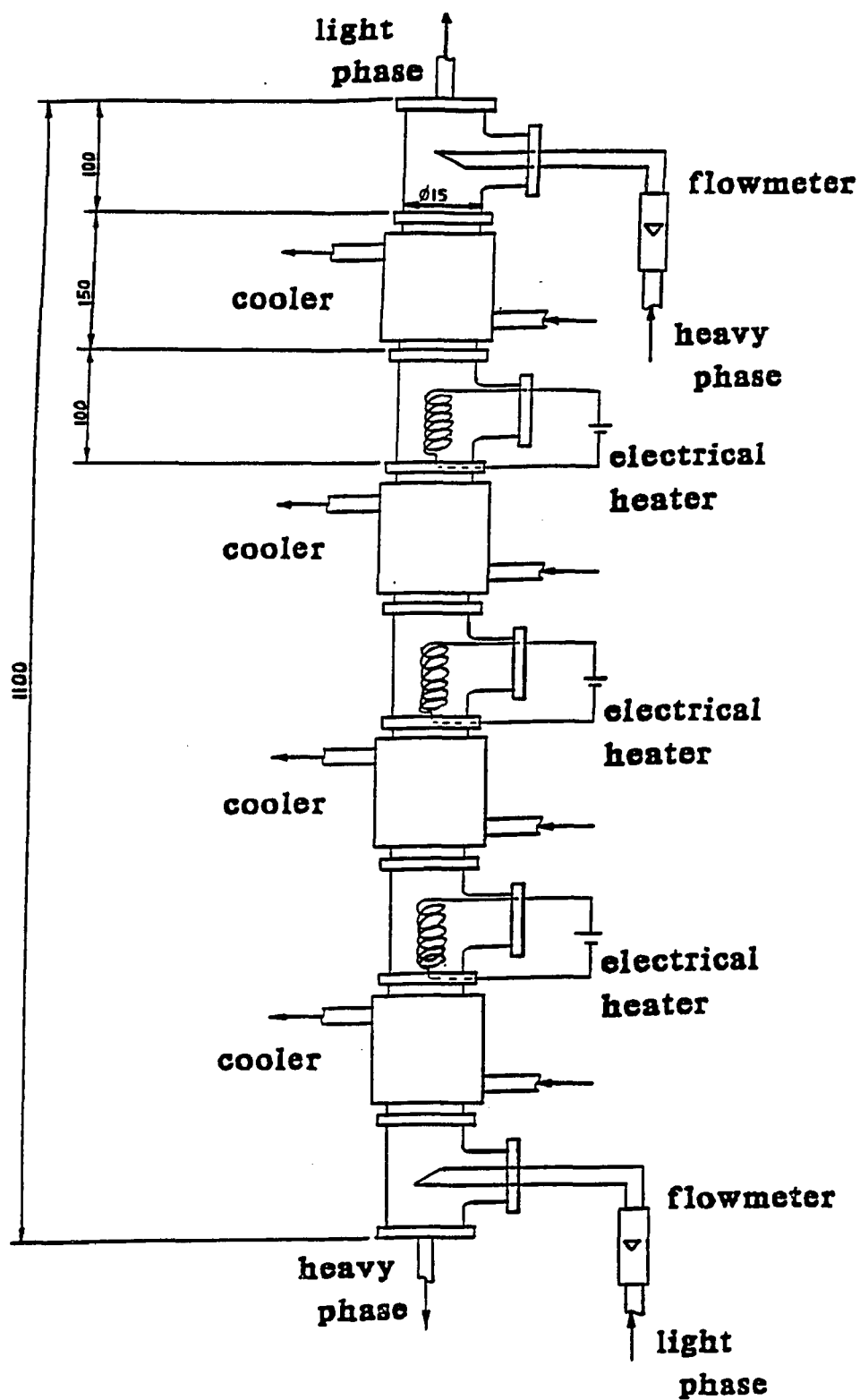


Figure 5.3: Experimental three-stage PTE column.

a data acquisition system (Omega Co.), hooked up to a PC computer, is used to record continuously the temperatures throughout the column.

Special efforts were made to construct a glass-made column, in spite of the technical difficulties involved in placing the heating and the cooling elements in a glass structure. This allows us to follow visually the mixing in the heater, and the phase separation in the coolers.

The same basic elements of the single-stage column were used to assemble the three-stage column described in Figure 5.3. The fragile glass coolers were replaced by stainless steel heat-exchangers, and two heaters and two coolers were added.

The single and the three-stage columns are operated in the same manner. The heavy and the light phases flow by gravity force from storage tanks through rotameters into the top and the bottom of the column, and the flow rates are regulated by needle valves. The light phase overflows from the top of the column, and the heavy phase leaves the bottom of the column through a loop so as to ensure the column being filled with liquid. The interface level in the column is regulated by the heavy phase outlet loop position.

5.2.2.2 Operating Procedure

At the beginning of each experimental run, a sufficient

amount of solvents mixture is prepared. The solvents are mixed together to reach equilibrium at ambient temperature and then separated into the heavy and light phases storage tanks.

In the runs, the column is filled with the continuous phase and a small amount of the dispersed phase to give an interface at the proper end of the column, and the heaters and the coolant-pumps are turned on. The flows of the two phases are adjusted to the proper rates, and the height of the heavy phase outlet loop is adjusted to maintain the interface at the desired level.

It has been found that steady conditions are approached by the time the liquid holdup in the column have been replaced two to three times. A steady state condition is considered when the outlet flow rates and solute concentration are found to be constant through successive measurements along, at least, one more turn over of the liquid in the column. These measurement results are then used for equilibrium stage calculations. A small tube, connected to the heated section of the column, is used to collect a sample of a single-phase liquid. This sample is then allowed to separate into two layers at room temperature, and the volume ratio and the solute distribution between the two phases are measured. The distribution data collected in this way are then used to confirm the equilibrium line and the stage calculation.

5.2.2.3 Performance Evaluation

The material balance and the equilibrium-stage calculations were based on assuming constant flow rate of the solvents along the column. As we will further discuss in Section 5.3.1.1, if all the settlers in the column are kept at the same temperature, and the extracted solute has a negligible effect on the solvents mutual solubilities, then virtually the inter-stage streams have a constant solvents composition, and subsequently have constant flow-rates along the extractor.

The extractor operating line, which relates the solute compositions between stages, is obtained by taking a material balance on solute around the inlet end; this gives (see Fig. 5.4)

$$C_L^{n+1} = \frac{Q_H}{Q_L} C_H^n + (C_L^{N+1} - \frac{Q_H}{Q_L} C_H^N) \quad (3)$$

where the solute concentration is given as mass of solute per unit volume of the solvent. This expression, which represents a straight line of slope Q_H/Q_L , is shown in Fig. 5.5, and is in fact similar to the one obtained for immiscible solvents in conventional extractors (Treybal, 1963, and Lo et. al., 1982). Based on the experimental solute distribution data, the equilibrium curve is also plotted using the same concentration units. The number of theoretical stages required, according to the inlet and outlet solute concentrations, is now

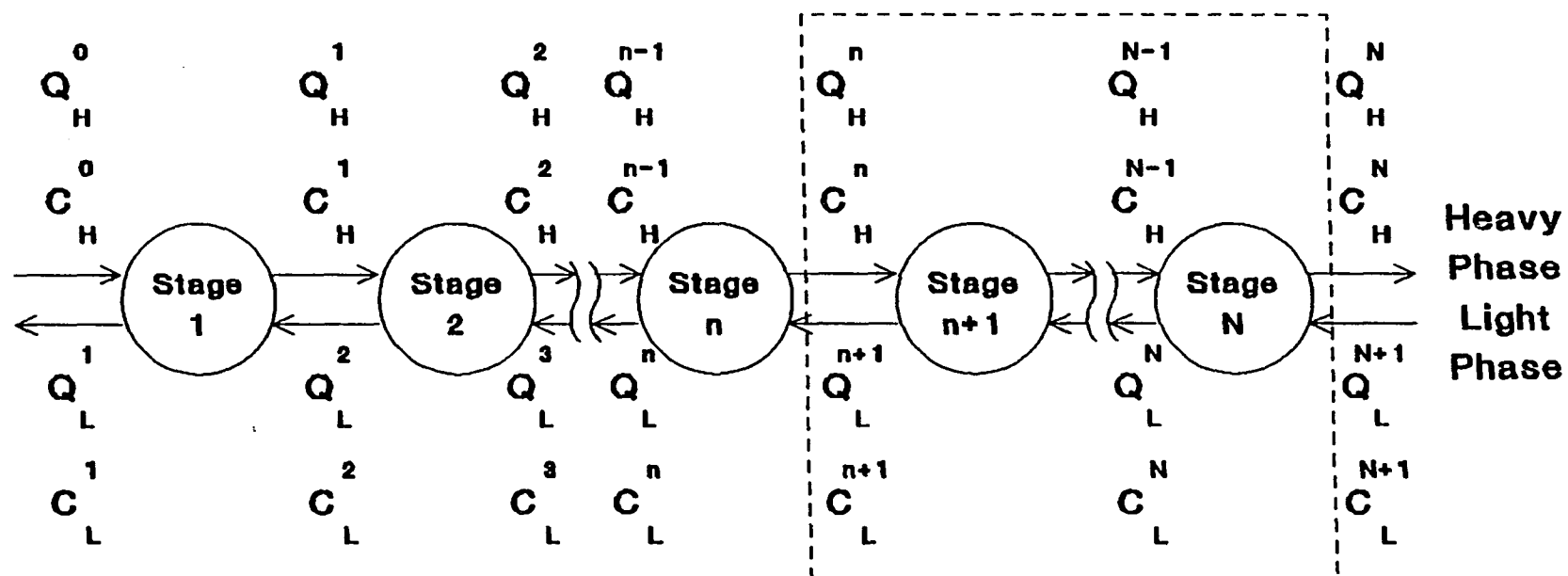


Figure 5.4: Countercurrent extraction in multistage cascade - material balance.

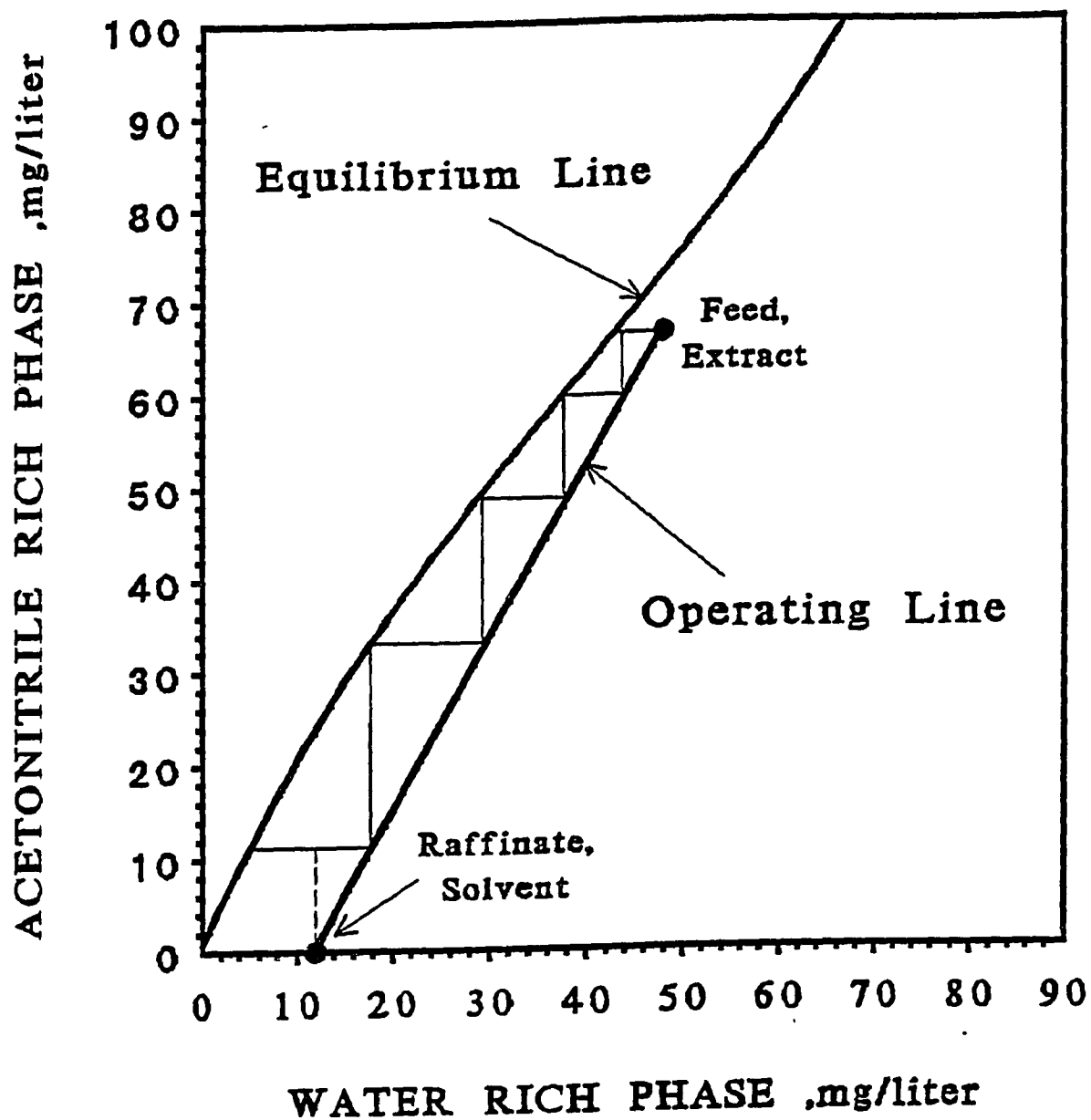


Figure 5.5: Graphical calculation of the number of theoretical stages of multistage countercurrent extractor.

determined by the McCabe-Thiele step-wise construction as shown in Figure 5.6.

5.3 Experimental results

5.3.1 Fluid Dynamic Features and Energy Consumption of The PTE Extractor

In Section 3 we described the concept of the PTE separation process which can be carried out either as a mixer settler cascade or as a column extractor. In contrast to conventional processes, which are generally operated under isothermal conditions, the solvents in our process are subjected to temperature variation when passing from the mixer section to the settler. The estimation of the thermal-energy requirements, and consequently the streams flow rate are essential for an adequate design of our equipment.

5.3.1.1 Fluid Dynamics

Mixer-Settler - In the case of mixer-settler operation mode the flow in our proposed design is similar to the flow in conventional mixer-settlers. The phases are mixed together in the mixing section and then allowed to settle in a separated tank (settler) prior to pump-out into the next section. The flow is possible in just one direction, from the mixer to its

settler and from the settler to the mixers of the next stages. The ratio of the phases in the mixing section is the same as the feed streams flow-rate ratio (Flynn and Treybal, 1955). The energy consumption of this type of operation can be determined simply by the feed streams flow-rate and the temperature variation. However, as we will show in the following section, the situation is quite different in the case of the column extractor where the flow pattern is more complicated, and has a major effect on the process' heat consumption.

Column Extractor - In the countercurrent multistage column, the phases to be contacted enter a series of equilibrium stages from opposite ends. The countercurrent flow of the streams in the column is a result of the density-difference between the two phases. In the PTE column, as well as in conventional agitated columns, in which the mixing and settling sections are placed intermittently one above the other, each settler, excluding the top and the bottom ones, serves as a separator for the mixed phases entering from the mixers above and below, and every mixer has two adjacent settlers, one from each side. Consequently, each section in the column, mixer or settler, has two inlet and two outlet streams. In addition, as we will show later, following the phase separation in the settlers, fractions of the mixer's outlet streams return to the mixer as back-flow streams. This

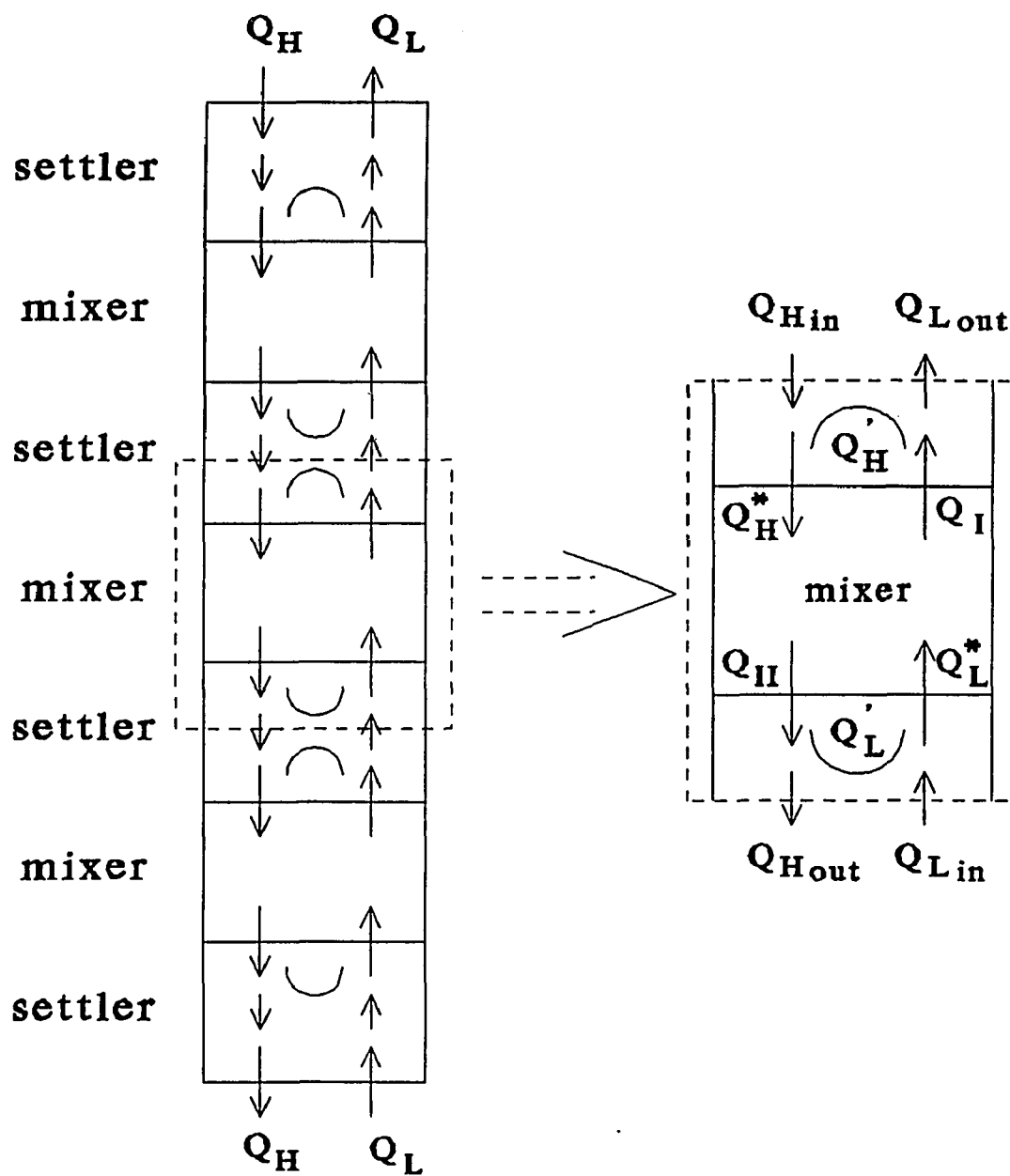


Figure 5.6: Schematic description of the streams in single-stage and three-stage columns.

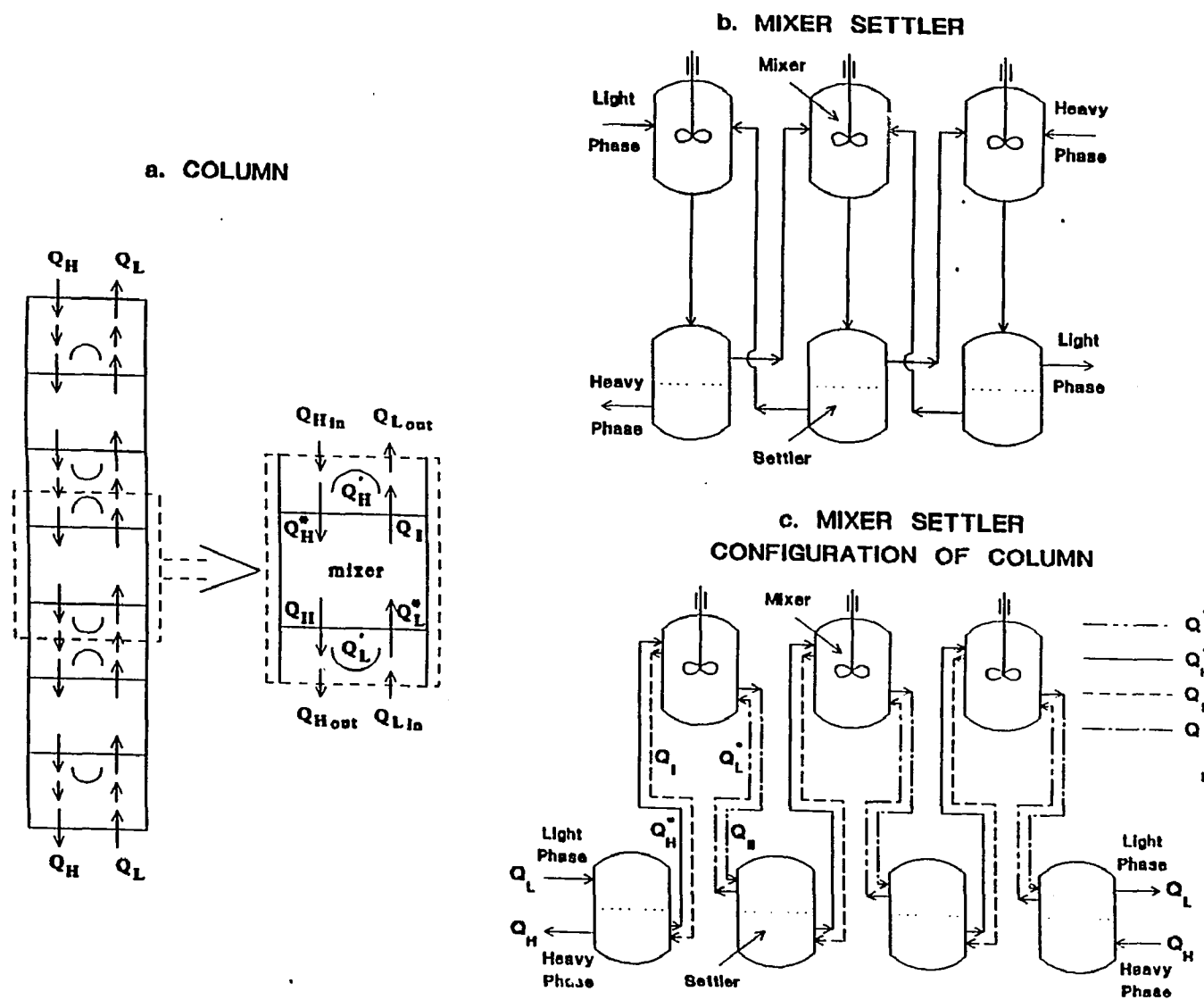


Figure 5.7: The various stream in mixer-settler and column extractors.

only occurs in columns, and in that sense they are hydrodynamically different from mixer-settlers. The various inter-stage and inter-section streams in such columns are diagrammatically represented in Figure 5.6.

To avoid any confusion, it is important at this point to summarize our definitions of the various streams in the column:

Inter-section streams - the streams between any two adjacent sections in the column, from the mixer to the settler or vice versa.

Inter-stage streams - the streams between any two neighboring stages in the column.

Back-flow streams - the streams returning to the mixer section following the phase separation in the settler.

It is clear now that the flow pattern in the column is more complicated than the one that exists in a mixer-settler cascade where each stage consists of only one mixing section and a single settler. Furthermore, the inter-section streams in mixer-settler cascades flow only in one direction, from each mixer to its adjacent settler and from the settler to the mixers of the next stages. The differences between the flow pattern in the mixer-settler and the column are described in Figure 5.7, where, for the simplicity of the comparison, a column is also presented in a mixer-settler-like form (Fig. 5.7c).

In the following section we will develop a model which

will allow us to evaluate the flow rates of the various streams in the column as a function of the solvents physical properties, and the column's operational conditions.

Let us assume that the residence time of the solvents in the settlers is sufficient for a complete phase separation, and that the separated phases are at equilibrium composition corresponding to the temperature in the settler. Furthermore, if all the settlers are kept at the same temperature and the extracted solute has a negligible effect on the solvents mutual solubilities, then the inter-stage streams have a constant solvents composition along the column. In order to have similar streams at the top and the bottom stages, we introduce the heavy and the light phases, $Q_{H,in}$ and $Q_{L,in}$, into the column at an equilibrium composition related to the settlers temperature. It will be of convenience to regard the heavy and the light phases as pure components with physical properties, such as density viscosity etc., related to the equilibrium composition of the constituent compounds in the separated phases at the settlers temperature.

In the mixer section, the heavy and the light phases are mixed together, hence the outlet streams, Q_I and Q_{II} , contain both the heavy and the light phase liquids. If the volume fraction of the heavy liquid, $X = V_H / (V_H + V_L)$, is uniform throughout the mixer, then the fraction of the heavy phase in the two outlet streams will be identical and equal to X . Since according to our previous assumption, a complete

separation of the phases is taking place in the settlers, the outlet streams from each stage, $Q_{H,out}$ and $Q_{L,out}$, contain only one of the phases (the heavy or the light phase respectively). Therefore, the liquid of the second phase, Q_L' and Q_H' , are joining the inlet streams and return to the mixing section as Q_L^* and Q_H^* .

In order to evaluate the flow rates of the various streams, we utilize the mass conservation equations of the heavy and light phases at the various sections of a single representing stage.

A mass balance of the heavy and the light phases in the top settler gives:

$$\rho_H \frac{dV_H^I}{dt} = \rho_H Q_{Hin} - \rho_H Q_H^* + \rho_H^T Q_I X \quad (4)$$

$$\rho_L \frac{dV_L^I}{dt} = \rho_L^T Q_I (1 - X) - \rho_L Q_{Lout} \quad (5)$$

A similar mass balance on the bottom settler yields:

$$\rho_L \frac{dV_L^{II}}{dt} = \rho_L Q_{Lin} - \rho_L Q_L^* + \rho_L^T Q_{II} (1 - X) \quad (6)$$

$$\rho_H \frac{dV_H^{II}}{dt} = \rho_H^T Q_{II} X - \rho_H Q_{Hout} \quad (7)$$

and for the mixer section:

$$\rho_L^T \frac{d[V_M(1 - X)]}{dt} = \rho_L Q_L^* - [\rho_L^T(1 - X)](Q_I + Q_{II}) \quad (8)$$

$$\rho_H^T \frac{d(V_M X)}{dt} = \rho_H Q_H^* - (\rho_H^T X)(Q_I + Q_{II}) \quad (9)$$

In the above equations V, with the subscripts H and L, refer to the volumes of the heavy and the light phases, respectively, in settlers I and II, and V_M is the total volume of the mixer section. Since in our extractor, the temperature in the mixer differs from the temperature in the settlers (higher for solvents system with UCST and lower for LCST system) the densities (ρ_H and ρ_L) of the streams living the mixer are marked with the superscript T.

The following expressions for the various streams in the column, at steady-state condition, can be obtained by algebraic manipulations of the above equations:

$$Q_{Hin} = Q_{Hout} = Q_H \quad ; \quad Q_{Lin} = Q_{Lout} = Q_L \quad (10)$$

$$Q_I = \frac{Q_L}{(1 - X)} \frac{\rho_L}{\rho_L^T} \quad ; \quad Q_{II} = \frac{Q_H}{X} \frac{\rho_H}{\rho_H^T} \quad (11)$$

$$Q'_H = Q_L \frac{X}{(1 - X)} \frac{\rho_H^T \rho_L}{\rho_H \rho_L^T} \quad ; \quad Q'_L = Q_H \frac{(1 - X)}{X} \frac{\rho_L^T \rho_H}{\rho_L \rho_H^T} \quad (12)$$

and

$$Q_H^* = Q_H + Q_H' \quad ; \quad Q_L^* = Q_L + Q_L' \quad (13)$$

At this stage, it is clear that the various streams in the column are functions of the inlet streams and the volume fraction of the phases in the mixer section (i.e X). This volume fraction can not be determined by applying only the mass conservation principal. The above equations also emphasize the importance of a correct estimation of the inter-section flow rates. For $X=0.5$, for example, the flow-rates of the streams leaving each of the mixers or the settlers in the column are twice the inlet flow-rates, and therefore the amount of fluid which has to be heated and cooled is doubled. This phenomenon eventually has a significant effect on the estimation of the thermal energy requirements in our process.

Let us now return to the basic model described in Figure 5.6. Through a careful examination of this model, it is clear that the key streams in the column are Q_I and Q_{II} leaving the mixing section. The compositions and flow-rates of these streams determine the rates of the back-flow streams Q_H' and Q_L' , and subsequently the inlet streams to the mixer, Q_H^* and Q_L^* (see Eq. 13). A further analysis of Q_I and Q_{II} streams will, therefore, assist us to evaluate the other streams in the column.

As a result of the phase separation, the bottom of each settler is occupied, mainly, with the heavy phase where the

light phase is accumulating in the top of the settler. Therefore, Q_I passes upward to the settler above and enters into a heavy phase liquid layer, where the Q_{II} stream passes to the settler below into a bulk of light phase liquid. The driving force for these streams is the buoyant force arising from the density difference between the phases mixture in the mixer and the heavy and light phase liquid layers in the settlers above and below the mixer respectively. By applying a momentum balance on the fluid layers, above and below the mixer section, one can estimate the relation between the density-difference driving force and the flow rates of the streams.

The momentum equation for incompressible liquid can be written as

$$\rho \left(\frac{du}{dt} + u \cdot \nabla u \right) + \nabla p = \rho g + \mu \nabla^2 u \quad (14)$$

An order of magnitude analysis of this equation yields

$$O\left(\rho \frac{u^2}{d}\right) \quad ; \quad O\left(\mu \frac{u}{d^2}\right) \quad (15)$$

for the convective and viscous stress terms respectively. For low Reynolds number the convective inertial effects can be neglected and a typical velocity, u , can be obtained as follows

$$\frac{u}{d^2} \approx \frac{\nabla p + \rho g}{\mu} \quad (16)$$

For high Re, on the other hand, the inertial effects prevail and the typical velocity is determined by the inertial effects as

$$\frac{u^2}{d} \approx \frac{\nabla p + \rho g}{\rho} \quad (17)$$

The flow of the streams, Q_I and Q_{II} , leaving the mixer will also be effected by the way the mixer and the settler are separated from each other. Therefore, the characteristic length, d , in the above equations is represented by the diameter of the orifices if perforated plates are used, or by the average voids diameter if a wire-mesh is used to separate the mixer from the settler section. However, if the same separating means are used above and below the mixer, and the pressure gradients in the liquid layers are due solely to the weight of the fluid, then the ratio of the streams leaving the mixer can be evaluated as

$$\frac{Q_I}{Q_{II}} = \frac{(\rho_H - \rho_M^T) \mu_L}{(\rho_M^T - \rho_L) \mu_H} \quad (18)$$

for low Re, or for high Re as

$$\frac{Q_I}{Q_{II}} = \left[\frac{(\rho_H - \rho_M^T) \rho_L}{(\rho_M^T - \rho_L) \rho_H} \right]^{1/2} \quad (19)$$

where ρ_M^T is the density of the solvents mixture in the mixer.

The streams leaving the mixer have the same density which can be calculated based on X , the volume ratio in the mixer

$$\rho_M^T = X\rho_H^T + (1 - X)\rho_L^T \quad (20)$$

Assuming that the thermal expansion of the fluids is linear, and taking the temperature in the settlers as the reference temperature, the densities of each phase in the mixer can be calculated as

$$\rho^T = \rho(1 - \beta\Delta T) \quad (21)$$

where ΔT is the temperature difference between the mixing and the settling sections, and β is the volume expansion coefficient.

Combining equations (11), (18), (20) and (21) and neglecting the effect of temperature on β and μ , gives

$$\frac{Q_L}{Q_H} \frac{1 - \beta_H \Delta T}{1 - \beta_L \Delta T} \frac{X}{1 - X} = \frac{(1 - X) \Delta \rho + \xi \Delta T}{X \Delta \rho - \xi \Delta T} \frac{\mu_L}{\mu_H} \quad (22)$$

for low Re , or by applying Equation (19),

$$\frac{Q_L}{Q_H} \frac{1 - \beta_H \Delta T}{1 - \beta_L \Delta T} \frac{X}{1 - X} = \left[\frac{(1 - X) \Delta \rho + \xi \Delta T}{X \Delta \rho - \xi \Delta T} \frac{\rho_L}{\rho_H} \right]^{1/2} \quad (23)$$

for high Re , where

$$\xi = X(\rho_H \beta_H - \rho_L \beta_L) + \rho_L \beta_L \quad (24)$$

To test our model a set of experiments with single-stage column was conducted. The volumetric fraction of the phases in the mixer, X , was measured as a function of the inlet-streams flow rate fraction $Q_F = Q_{H,in} / (Q_{H,in} + Q_{L,in})$. The inlet streams, consisting of the heavy and the light phases of the acetonitrile-toluene-water solvents system ($UCST = 40^\circ C$) were saturated with each other at the ambient temperature before being introduced into the column. The streams were heated up above the CST at the mixing section and cooled down to the ambient temperature ($25^\circ C$) and separated in the settlers. X was measured by withdrawing samples from the mixer section. The samples then cooled to the ambient temperature and the volume fraction of the separated phases was measured. The physical properties of the phases were evaluated based on the equilibrium compositions of the separated phases and the properties of the pure components.

Figure 5.8 shows the experimental results and the theoretical lines obtained by applying Equations (22) and (23). As one can see, the agreement between the theoretical and the experimental results is remarkably good. The Reynolds number in our experiments (based on the streams superficial velocities and the column diameter) were in the range of 5 to 100 which suggest that Eq. (23) may be more suitable for representing the experimental points. However, the discrepancy between the lines, obtained by the different equations, is relatively small and in the limits of the

scattering of the experimental points. Therefore, either of the equations will be satisfactory in this case.

Figure 5.9 shows the variation of X as a function of Q_F at various temperature differences (ΔT). The temperature difference between the mixing section and the settlers is positive when operating the column with solvents systems exhibiting UCST, and negative for solvents systems with LCST.

It is important to mention at this point that the above discussion is not limited to our column. The line of $\Delta T=0$ in Figure 5.9 can represent any mixer settler column where the phases are mixed together by any conventional mixing device, and the mixing and settling sections are placed one above the other (e.g the "Scheibel" column). These column types, according to our model, are subjected to similar inter-section and back-flow streams. Yet, these streams do not get any attention in the literature perhaps because, as we mentioned above, and will discuss further later on, the main effect of these streams is on the energy consumption. This effect is significant only if the streams are subjected to temperature variation and is therefore negligible, and subsequently overlooked, in the case of isothermal columns.

Figure 5.9 raises an interesting point relating to the existence of limiting values for the solvents volume fraction in the mixer. These limiting values appear in Figure 5.9 as minimum values for X when Q_F approaches 0 for positive ΔT , and as maximum X when Q_F approaches 1 for negative ΔT .

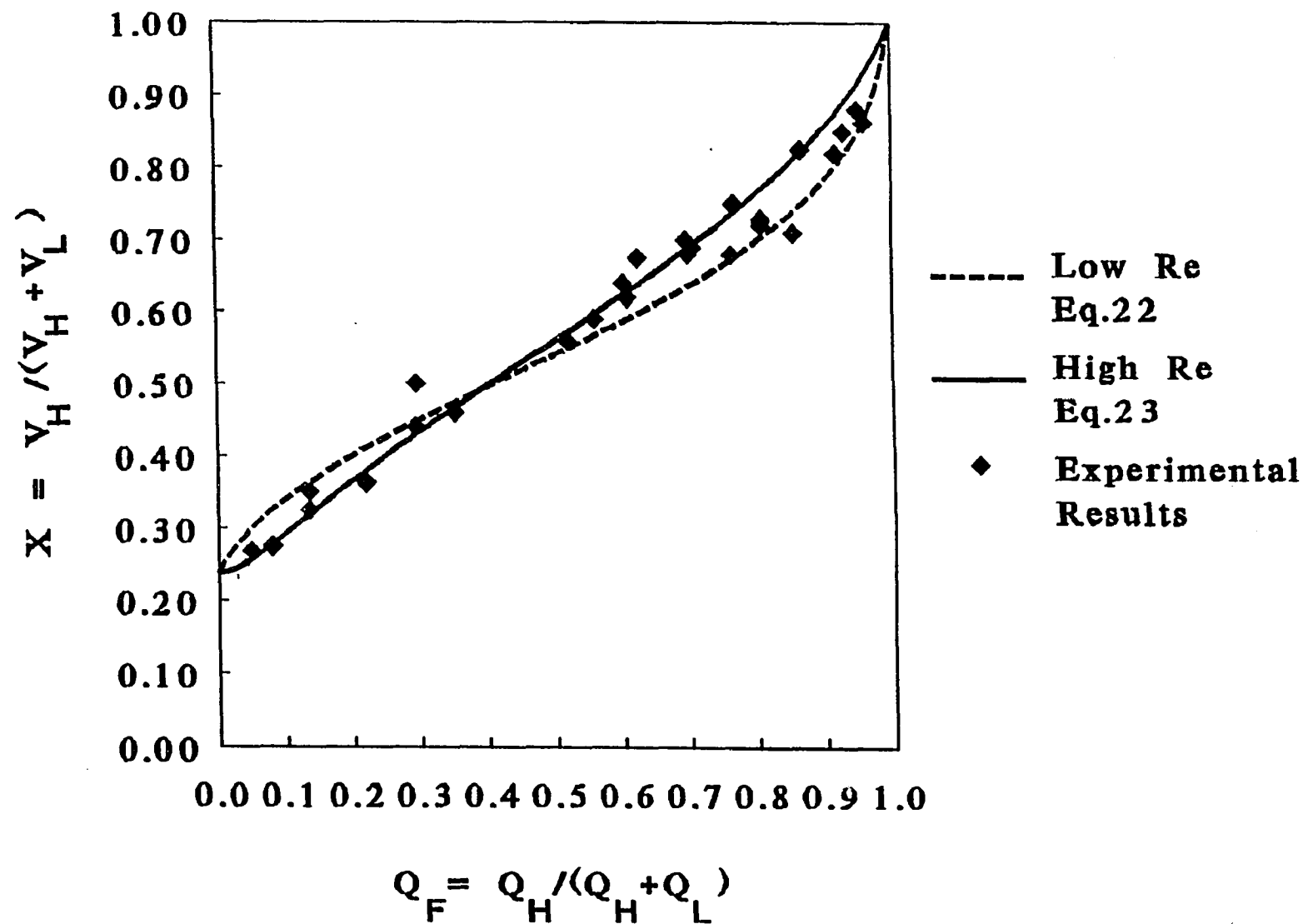


Figure 5.8: Calculated and experimental results of the phases volume fraction in the mixer, X , as a function of the inlet streams flow rate fraction, Q_F .

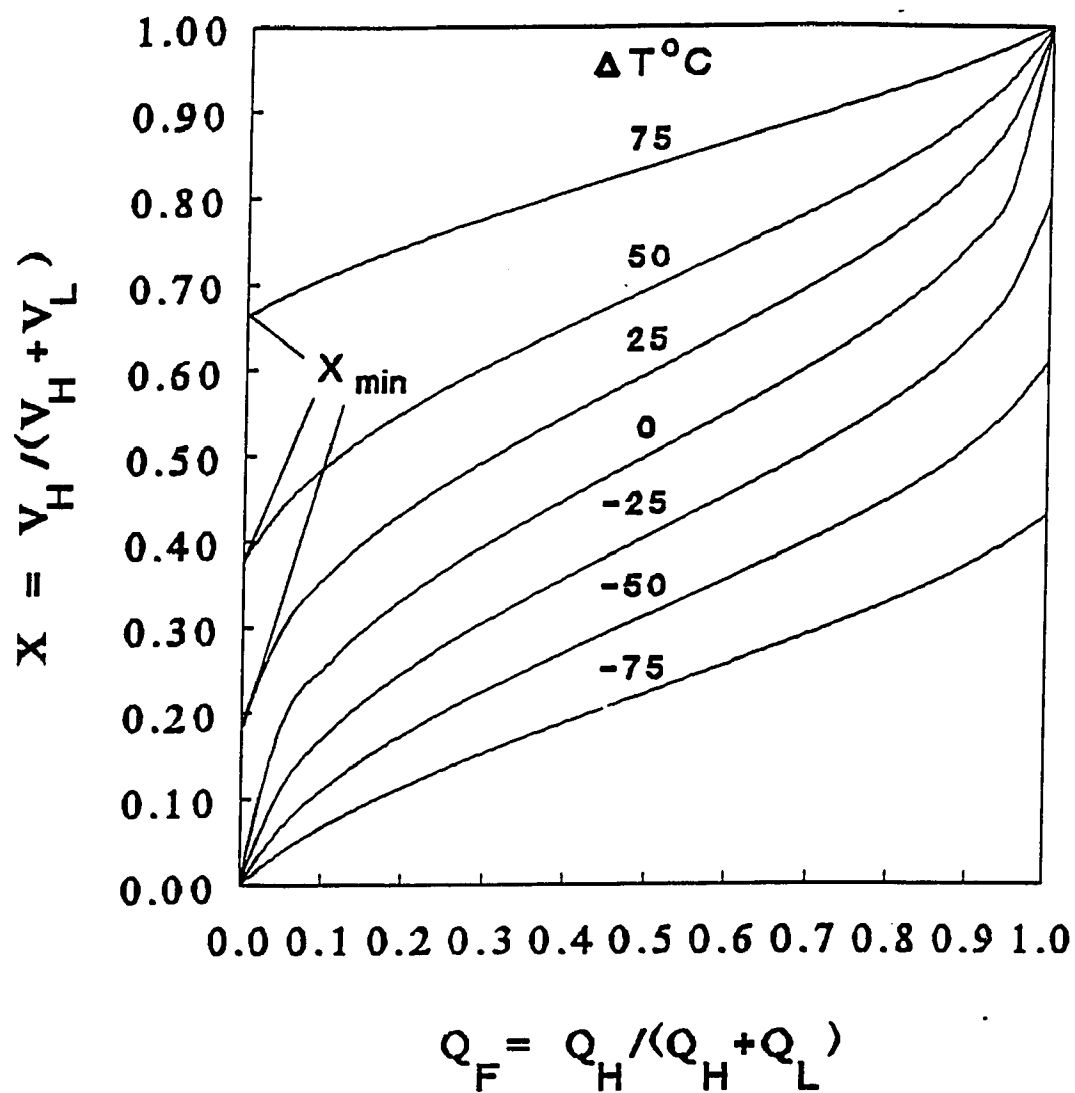


Figure 5.9: Variation of the phases volume fraction in the mixer, X , as a function of the inlet streams flow rate fraction, Q_F , for various temperature differences, ΔT .

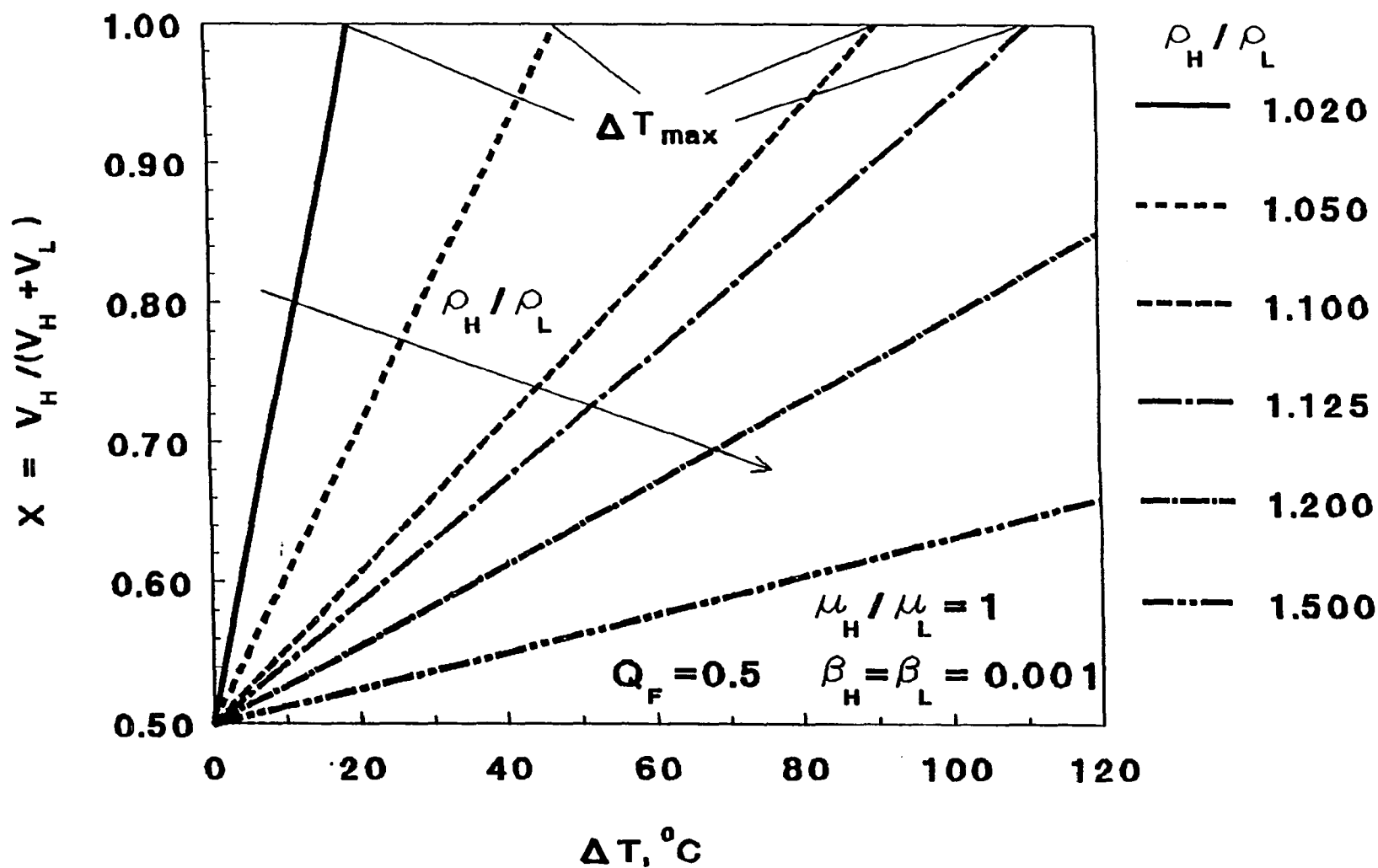


Figure 5.10: Effect of the temperature difference, ΔT , on the phases volume fraction in the mixer, X .

The limiting values are merely a result of the need for a density difference between the mixer and the settler section as a driving force for Q_I and Q_{II} streams (see Fig. 5.6). These values can be easily evaluated by equating to 0 the denominator, for UCST system, or the nominator, for LCST system, in either Equation (22) or (23). The practical significance of these values is limited since, as we will show later, the value of X has no effect on the performance of the column. However, as one can see in Figure 5.8, the experimental results confirm the existence of a minimum value for X as Q_F approaches 0, and thus reaffirm the validity of our model.

Figure 5.10 demonstrates the effect of the temperature difference on the phases volume fraction X for a representing case of equal inlet flow rates ($Q_F=0.5$). The curves were plotted using Eq. (22), for various heavy phase to light phase density ratios (but constant β and μ) of UCST solvents system. As could be expected, X increases as ΔT is increased, and is more sensible to ΔT as the densities of the phases approach each other. Figure 5.10 demonstrates another important point, the existence of a maximum operational temperature difference. This maximum ΔT is shown in Figure 5.10 as the ΔT in which the volume fraction in the mixer reaches its maximum possible value $X=1$ (only heavy phase liquid in the mixer).

The limiting condition on ΔT is a result of the thermal expansion of the fluids. Above the maximum ΔT the density of

the heated heavy phase is reduced below the density of the light phase, and therefore annulling the driving force for the flow between the mixer and the settler below. The maximum operational temperature difference $\Delta T_{\max}$ is, therefore, determined by the densities of the fluids and the expansion coefficients as,

$$\Delta T_{\max} = \frac{(\rho_h - \rho_L)}{\rho_H \beta_H} \quad (25)$$

for UCST solvents system. The same result can be obtained by equating the denominator either of Eq. (22) or (23) to 0 (or $\Delta \rho_{II}=0$) for $X=1$. The variation of $\Delta T_{\max}$ with the heavy to light phase density ratio is shown in Figure 5.11.

For LCST solvents system, where the mixer is cooled below the temperature of the settler, the maximum value of ΔT is reached at $X=0$, and is equal to

$$\Delta T_{\max} = \frac{(\rho_H - \rho_L)}{\rho_L \beta_L} \quad (26)$$

The evaluation of $\Delta T_{\max}$ has a practical importance in the designing of a new process using PTE column. Following the selection of an appropriate solvents system, a preliminary examination of the limiting conditions can be done in order to determine if the process can be performed in a column. The limiting conditions on the operational temperature difference between the mixing and settling sections of the column are schematically described in Figure 5.12.

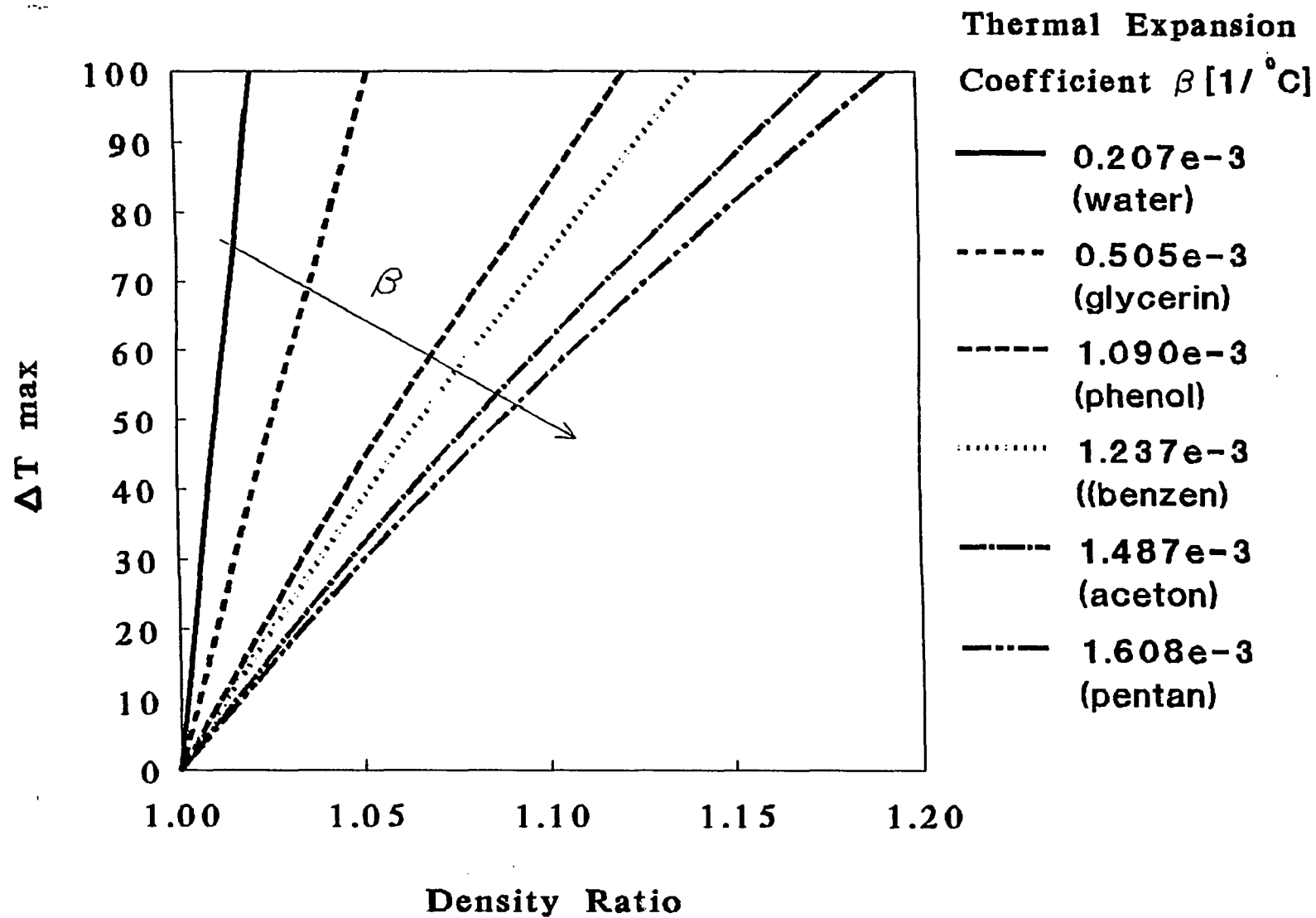


Figure 5.11: Variation of the maximum operational temperature difference, $\Delta T_{\max}$, with the heavy to light phase density ratio.

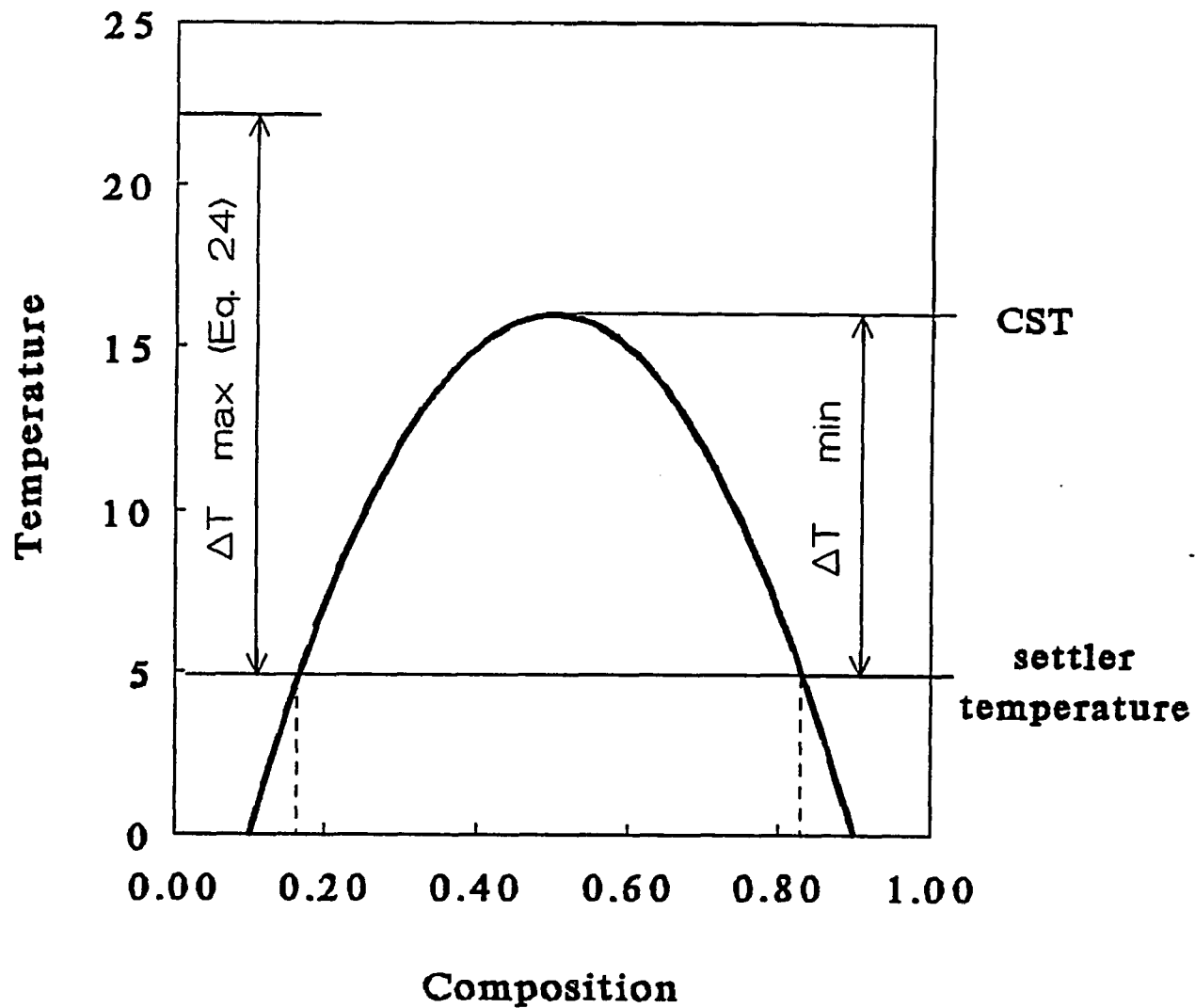


Figure 5.12: Limiting conditions on the operational temperature difference between the mixing and settling sections of the column.

To ensure the formation of a single homogeneous phase in the mixing section, at any flow-rate ratio of the inlet streams, $\Delta T_{\min}$ is determined as the temperature difference between the settler temperature and the CST of the solvent system. Based on the composition of the phases in the settler, the maximum ΔT , which will still allow a countercurrent flow in the column, can be calculated by applying Eq. (25) or (26). Now, the precondition, which has to be met, for safe operation of the extraction process in a column, is simply that $\Delta T_{\max} > \Delta T_{\min}$. If this requirement is not satisfied, one can still try to increase the settler temperature in order to decrease the $\Delta T_{\min}$. However, in most cases, increasing the settler temperature will be of little use since it will cause the reduction of the density ratio (ρ_H/ρ_L), subsequently decreasing the $\Delta T_{\max}$ (see Fig. 5.11). The preferred practice in this case is to perform the extraction process in a mixer-settler contactor. In this type of contactor, the countercurrent flow of the streams is not dependent upon a density difference. Therefore, the operation of such equipment, is not subjected to the $\Delta T_{\max}$ limitation.

5.3.1.2 Energy Consumption

Since our process is based on varying the temperature of the solvents across the critical temperature, the evaluation of the thermal energy requirements of the heating and the

cooling sections is an essential part of the process design. In order to study this operational aspect of the PTE process, we measured in our experiments the actual heat consumption of the heating section in the column and we are also suggesting here a computation procedure to evaluate it.

The evaluation of the energy which has either to be supplied to the heating sections or to be extracted from the cooling sections is based on the same principle. Therefore, we will bring here as an example only the computation procedure of the heat consumption of a representing heating section. The same procedure then can be applied for any section in the column by using its particular conditions (i.e. the flow rates and the temperatures of the section inlet streams and the sections' temperatures). Furthermore, if the temperature difference between the heating and cooling sections is the same along the column, then the energy consumption of all the sections in the column will be the same excluding the bottom and the top sections. These sections are exposed to back-flow streams only from one direction, whereas from the other direction they are exposed to the column's inlet streams (see Fig. 5.6). Therefore, a separate (but still based on the same procedure) calculation of the energy consumption has to be conducted for these sections.

The energy consumption calculation procedure is based on the following principles and assumptions:

a) The flow pattern of the solvents in the column is assumed

to follow the model described in section 5.3.1.1. Thus, the actual streams entering the heating section (Q_H^* and Q_L^*) consists of the original column's inlet streams and the back-flow streams, Q_H' and Q_L' (Eq. 13), and calculated by Eqs. (12) and (22).

b) The heat exchange between the streams leaving and entering the heating section is negligible due to the short contact time between these streams. Therefore, the streams entering the heater are at the measured cooling section temperature.

c) The evaluation of the heat losses from the column is based on a free convection to the ambient air (at atmospheric pressure and the measured ambient temperature). The resistance to the heat-transfer in the column is assumed to be negligible (measurements in the column showed that the temperature in the heating section is uniform across the column). The heat-transfer coefficient ($W/(m^2 \text{ } ^\circ C)$) was computed by the simplified equation given by Holman (1990)

$$h = 1.42 \left(\frac{\Delta T_\infty}{L} \right)^{1/4} \quad (27)$$

where ΔT_∞ is the temperature difference between the heater and the ambient measured temperatures ($^\circ C$), and L is the height of the heating section (m).

d) The physical properties, heat capacity (C_p) and density (ρ), of the heavy phase and light phase streams entering the heater, are evaluated based on the equilibrium compositions of the constituent solvents at the cooler temperature according

to the phase diagram given in Fig. 5.1.

According to these principles and assumptions, the energy consumption of the heater consists of the sum of the sensible heat employed to increase the temperature of the solvents streams from the cooler temperature to the temperature in the heater, and the heat losses to the ambient

$$Q = (Q_L^* \rho_L C_{pL} + Q_H^* \rho_H C_{pH}) \Delta T + hA \Delta T_\infty \quad (28)$$

where A is the surface area of the heating section exposed to the ambient. For solvent-systems with an appreciable mixing-heat, the right side of Eq. 28 should include an additional term to represent the heat added to the system as a result of the solvents solution. The mixing-heat of solvents systems is a function of the system temperature and composition. In PTE columns the composition in the mixing section is a function of the streams flow-rate. In the absence of published data, the mixing-heat as a function of composition has to be evaluated via a separate set of experiments. This may complicate the procedure of evaluating the energy consumption of the process. Therefore, when the mixing-heat is small in comparison with the sensible heat of the mixture, it can be neglected during the preliminary heat consumption calculation.

In the case of the solvent-system used in our experiments, the effect of the mixing-heat was evaluated (via calorimetric measurements for equal inlet streams flow-rates at 45°C) to be less than 5% of the mixer energy consumption.

This value is within our experimental error, and therefore neglected in our calculations.

The actual heating energy consumption was determined by measuring the power-supply to the electrical heating element placed in the mixing (heating) section. The experimental energy consumption data were compared with calculated values, that were computed based on the measured solvents' flow-rates and temperature difference between the heating and cooling sections.

The experimental and the corresponding calculated values of the energy consumption together with the pertinent operation conditions (i.e. the streams flow rates and the temperature difference between the heater and the cooler) are summarized in Table 5.1 (see Appendix III), and the calculated values are compared with the experimental results in Figure 5.13. The good agreement demonstrates that a satisfactory prediction of the heating requirements of the column can be obtained by the above suggested procedure. As a reference, the energy consumption was also calculated in a similar way but solely based on the inlet streams flow-rates neglecting the back-flow streams. As we explained before, these results will also represent the heat consumption for the case of mixer-settler in which back-flow streams do not exist. The results for this case are also plotted in Figure 5.13. As one can see, the values calculated in this way are considerably lower than both the experimental results, and the values

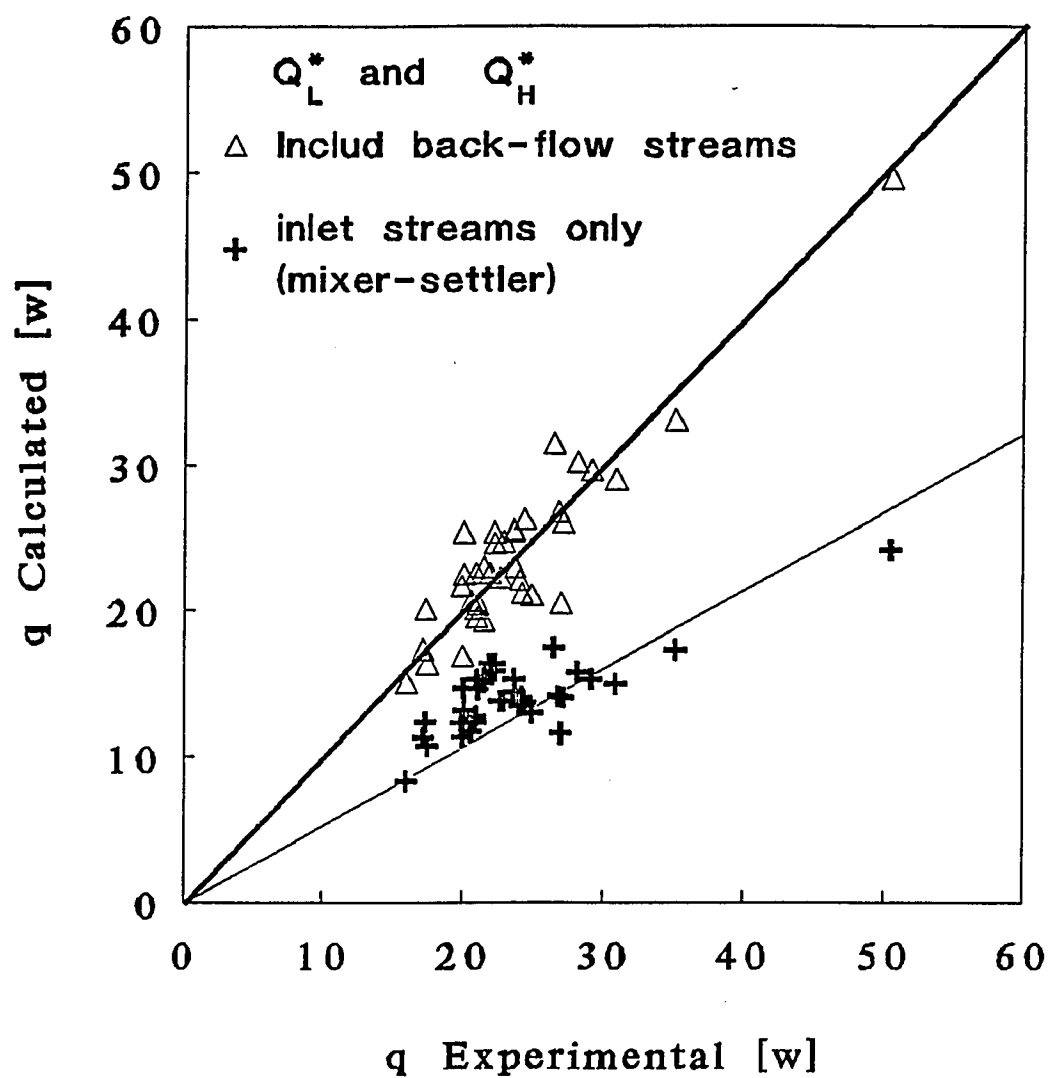


Figure 5.13: Comparisons of the calculated and experimental heat consumptions in the column's mixing section.

calculated where the back-flow streams are included. This result confirms the existence of back-flow streams in the column, and demonstrates their impact on the heating and cooling requirements.

5.3.2 Performance Test of the Column

The potential performance of a column based on the PTE process was tested by operating the single and the three-stage laboratory-scale columns, described in Section 5.2.2. Our test consisted of a simple liquid extraction in which a solute was transferred from one liquid phase to the other.

To evaluate the impact of phase-transition on the performance, the column was also operated isothermally (i.e. the same apparatus, but with the heating and cooling devices turned off) using identical throughputs. The performance of an individual type of apparatus is highly affected by the properties of the solvents and solutes being processed, and by the dimensions and the internal structure of the apparatus. The comparison with the isothermally-operated column provides therefore a direct evaluation of the effect of the solvents phase transition (which is the basis of the PTE process) on the column performance.

The pertinent operating conditions, including the inlet and outlet stream flow rates and solute concentrations, and the temperatures in the various sections of the column are

shown in Tables 5.2 and 5.3 for the single and the three-stage columns respectively (see Appendix III). Tables 5.4 and 5.5 summarize the column performance which includes: the column throughput based on the total flow rate of the solvents and the column diameter, and the number of theoretical stages obtained in each run.

To evaluate the accuracy of the measurements and to confirm the steady state operating condition of the column, the heavy to light phase flow-rate ratio (based on solute mass balance) was calculated, and compared to the actual outlet streams flow-rate ratio. The measured ratios and the deviations from the calculated values are given in Tables 5.4 and 5.5. As one can see, the agreement is remarkably good considering that the effect of slight changes in the holdup or in the interface level will produce a double error in this ratio by simultaneously making one outlet flow rate too high and the other too low.

The mass transfer performance (i.e. the number of theoretical stages obtained) of the single-stage and the three-stage columns are plotted as a function of the total throughput in Figures 5.14 and 5.15. These figures clearly demonstrate the effect of the phase-transition on the performance of the column. For the single-stage column (i.e. one heating section and therefore one cycle of solvents' phase transition) the number of theoretical stages is about 2.8 compared to 1.8 stages for the uniform temperature operation

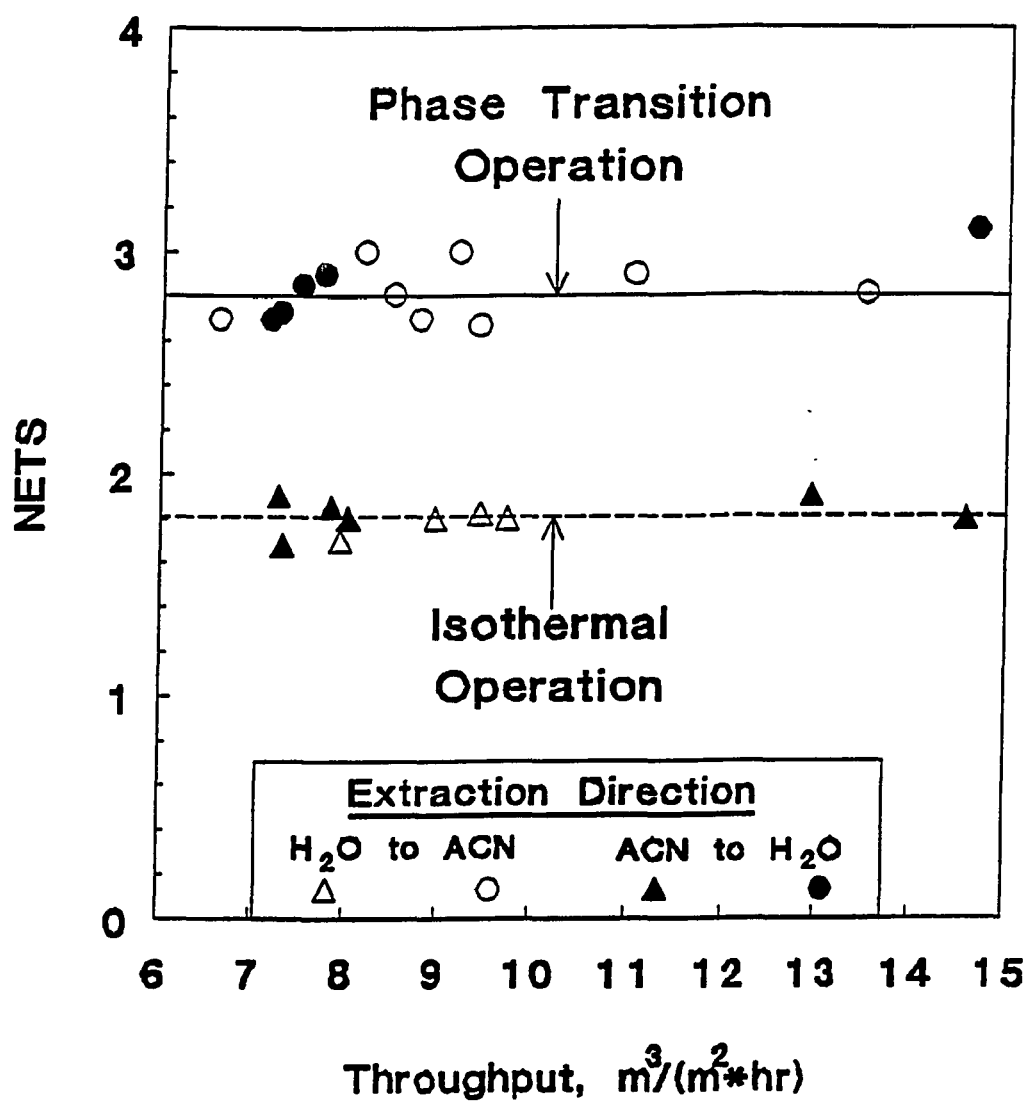


Figure 5.14: Mass transfer performance (NETS) of the experimental single-stage column as a function of the total solvents throughput.

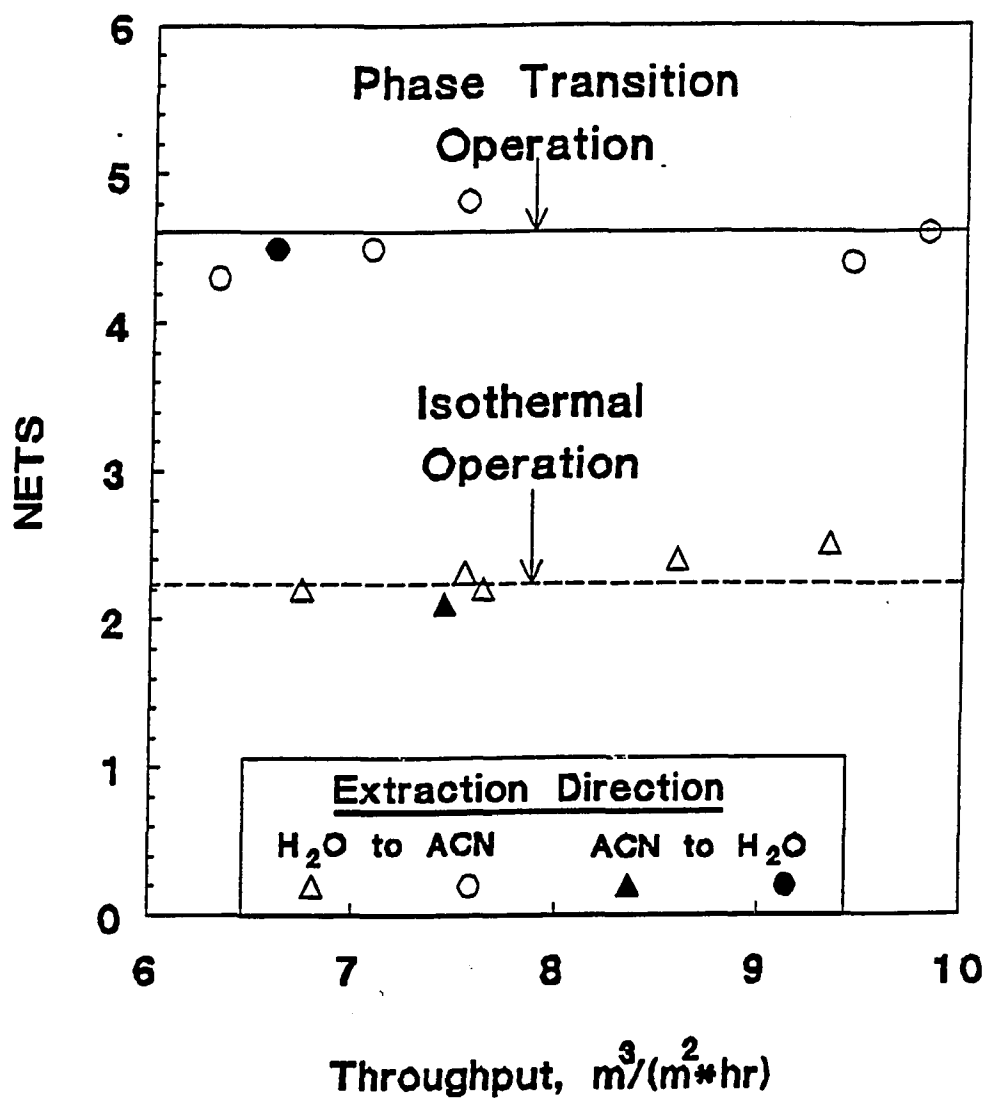


Figure 5.15: Mass transfer performance (NETS) of the experimental three-stage column as a function of the total solvents throughput.

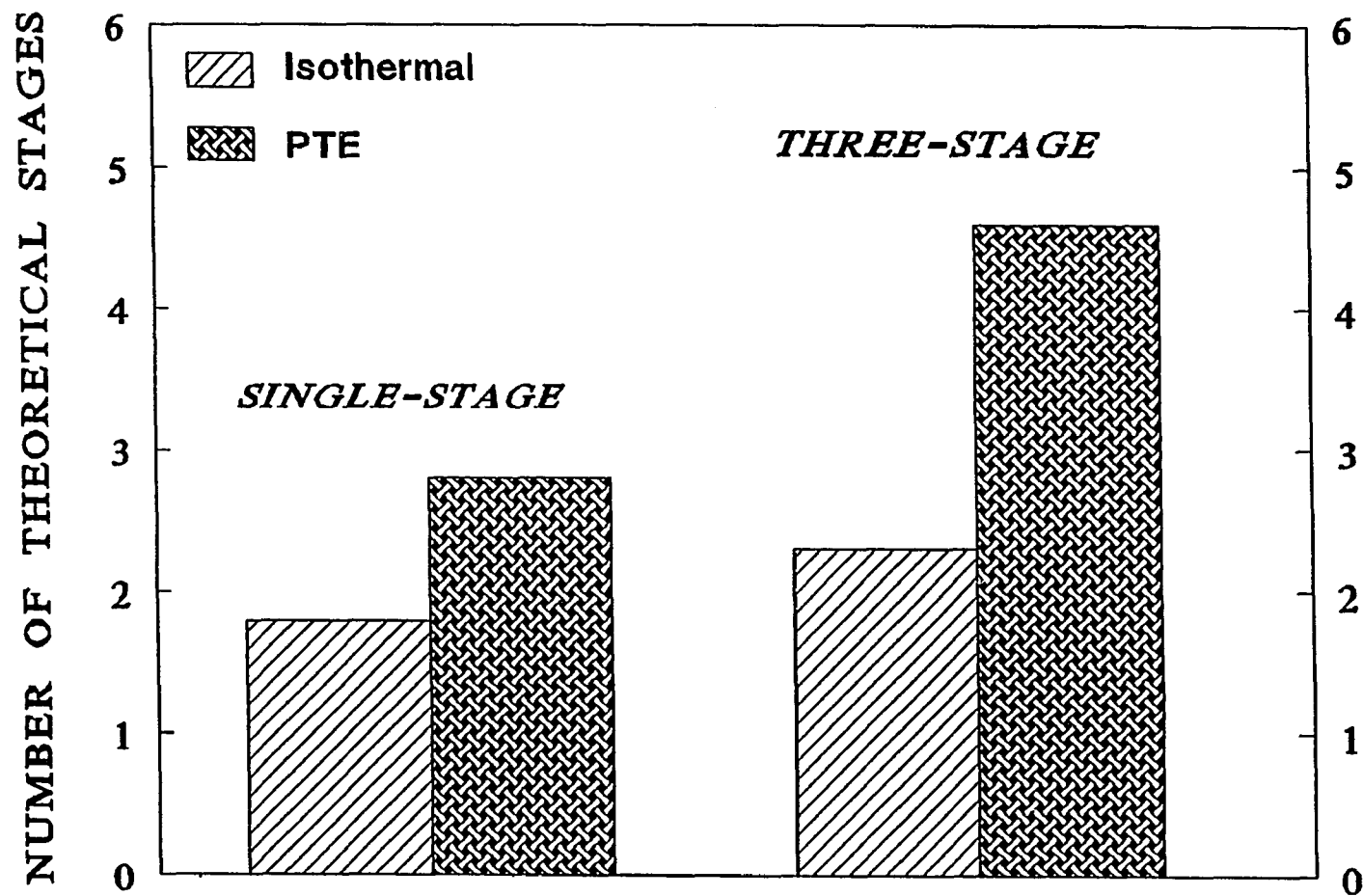


Figure 5.16: Typical results of the performance of the experimental single-stage and three-stage columns.

mode. The effect of the phase-transition operation mode is even more evident for the three-stage column (three cycles of phase transition). Here, the number of theoretical stages of the PTE column is about 4.6 compared to only 2.2 theoretical stages in the isothermal column.

The average results of the mass-transfer performance of the single-stage and the three-stage columns are represented in Figure 5.16. This figure demonstrates that the addition of column height results in an improved additional mass-transfer performance when the column is operated as PTE column, in comparison to the column operated at uniform temperature. For the uniform temperature operation mode, increasing the height of the column from 0.6 m to 1 m resulted in an increase of the average number of theoretical stages from 1.8 to 2.2 (equivalent to 1 NETS/meter). Whereas, in the PTE column, the same additional height has been resulted in an average addition of 1.8 theoretical stages (4.5 NETS/meter), or about one theoretical stage for each additional heating section.

The relatively small contribution of additional height to the mass-transfer performance of the column when operated at uniform temperature, may be attributed to the strong influence of end-effects on the performance of relatively short spray columns. Treybal (1963) showed that an appreciable amount of extraction can occur during the formation of a drop at an orifice or nozzle and when the drop coalesces with the bulk of the same liquid. Based on data by Licht (1950), it can be

shown, that up to 40% of the extraction from single drops in a 0.6 m column can be related to these end-effects. Eventually, the relative contribution of the end effects to the overall performance of the column is reduced as the height of the column is increased.

Similar end-effects are also present in the column's inlet and outlet sections of the PTE columns. These end-effects may explain the excess of the total number of theoretical stages obtained in the experiments beyond the actual number of stages of the column. As our experimental findings show, an excess of between 1.5 to 1.8 theoretical stages was measured when the single-stage and the three-stage columns were operated as PTE columns. The experiments also show that the same number of excess theoretical stages was obtained for both the single-stage and three-stage columns. Thus, we can postulate that this excess can be attributed mainly to the relatively high mass-transfer efficiency related to the end-effects together with the additional countercurrent extraction in the inlet and outlet sections of the columns, and less significantly to the mass transfer between the streams in the cooling sections (the settling sections).

Figures 5.14 and 5.15 show that, within the range of operation studied here, the effect of the throughput on the columns' performance is negligible for both the uniform temperature and the phase-transition operation modes. Regrettably, our design did not allow much higher flow-rates

to test the maximum achievable throughput. These figures also show that the diffusion direction of the solute has no appreciable effect on the performance of the column. The effect of the diffusion direction on the mass-transfer performance was examined by extracting the solute alternately from the aqueous phase and from the organic phase.

The effect of the solute concentration on the performance of the column was studied by varying the concentrations of the solute in the feed streams between 40 mg/l to 80 mg/l. Figures 5.17 and 5.18 show that in this range the performance of the columns was independent of the solute concentration. A change in the column performance due to the solute concentration can be anticipated if the solute concentration can effect the solvents properties (and thereby the diffusion coefficient) or flow-rates. However, as we showed in section 4.1.3.1, the solute concentration in the range studied here has a negligible effect on the mutual solubility of the feed and extract solvents. The solute concentration probably was also low enough to prevent any change in the solvents' properties.

A relatively narrow range of solvents' flow rate ratios have been studied. Most of the results were obtained in the range 0.45 to 0.55 of aqueous (heavy) flow rate fraction. The experiments were conducted in this range of flow rate ratio in order to keep the operation line parallel to the solute's equilibrium curve (in the limits of solute concentration

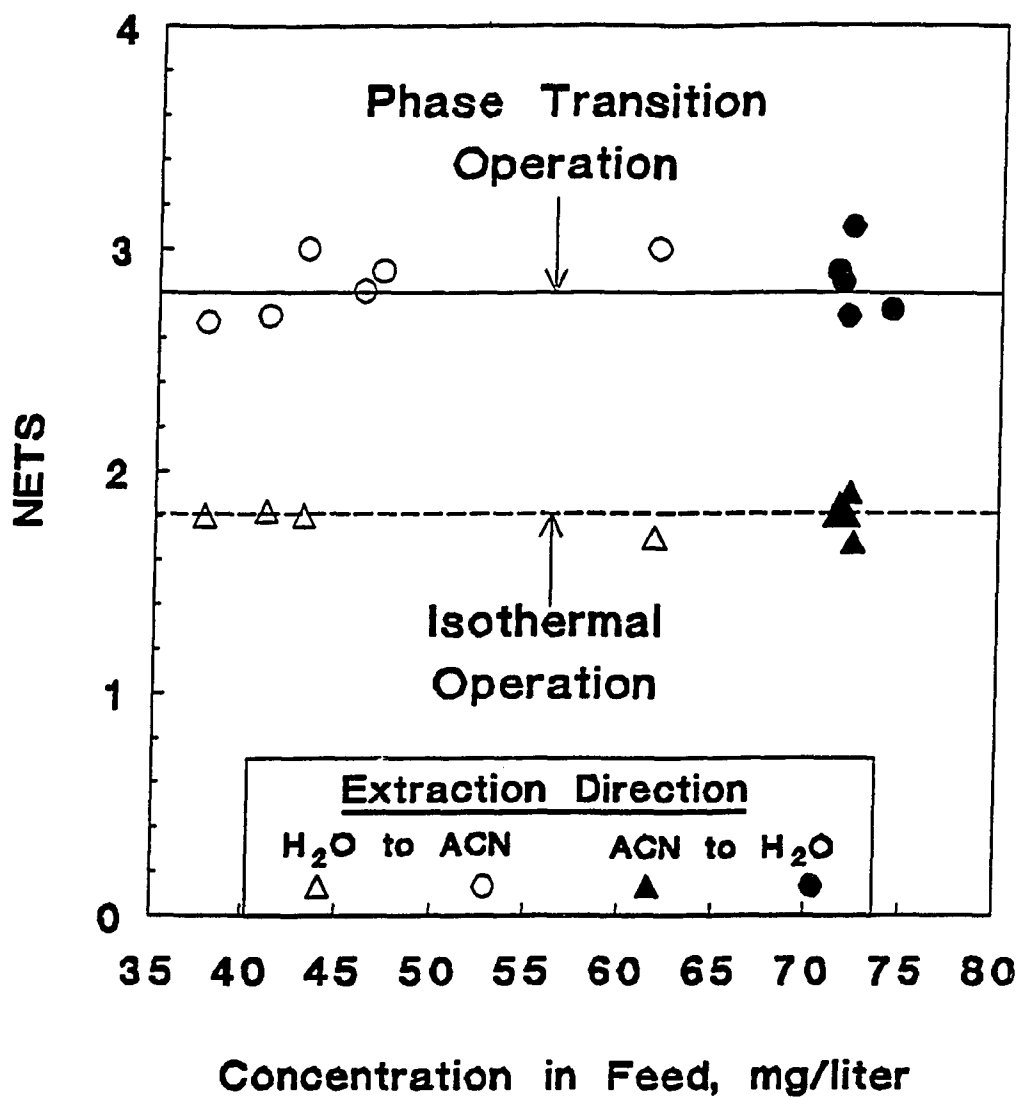


Figure 5.17: Mass transfer performance (NETS) of the experimental single-stage column as a function of the solute concentration.

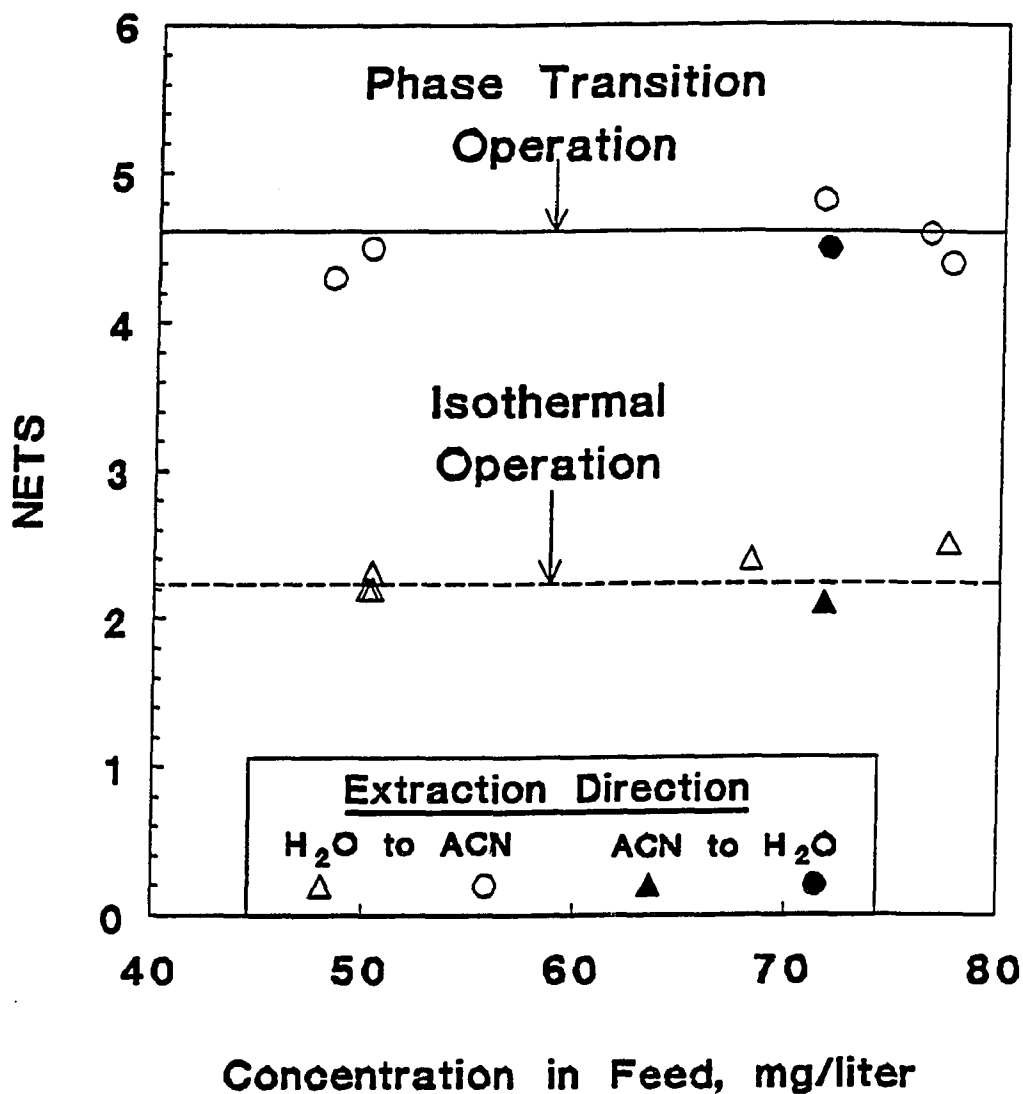


Figure 5.18: Mass transfer performance (NETS) of the experimental three-stage column as a function of the solute concentration.

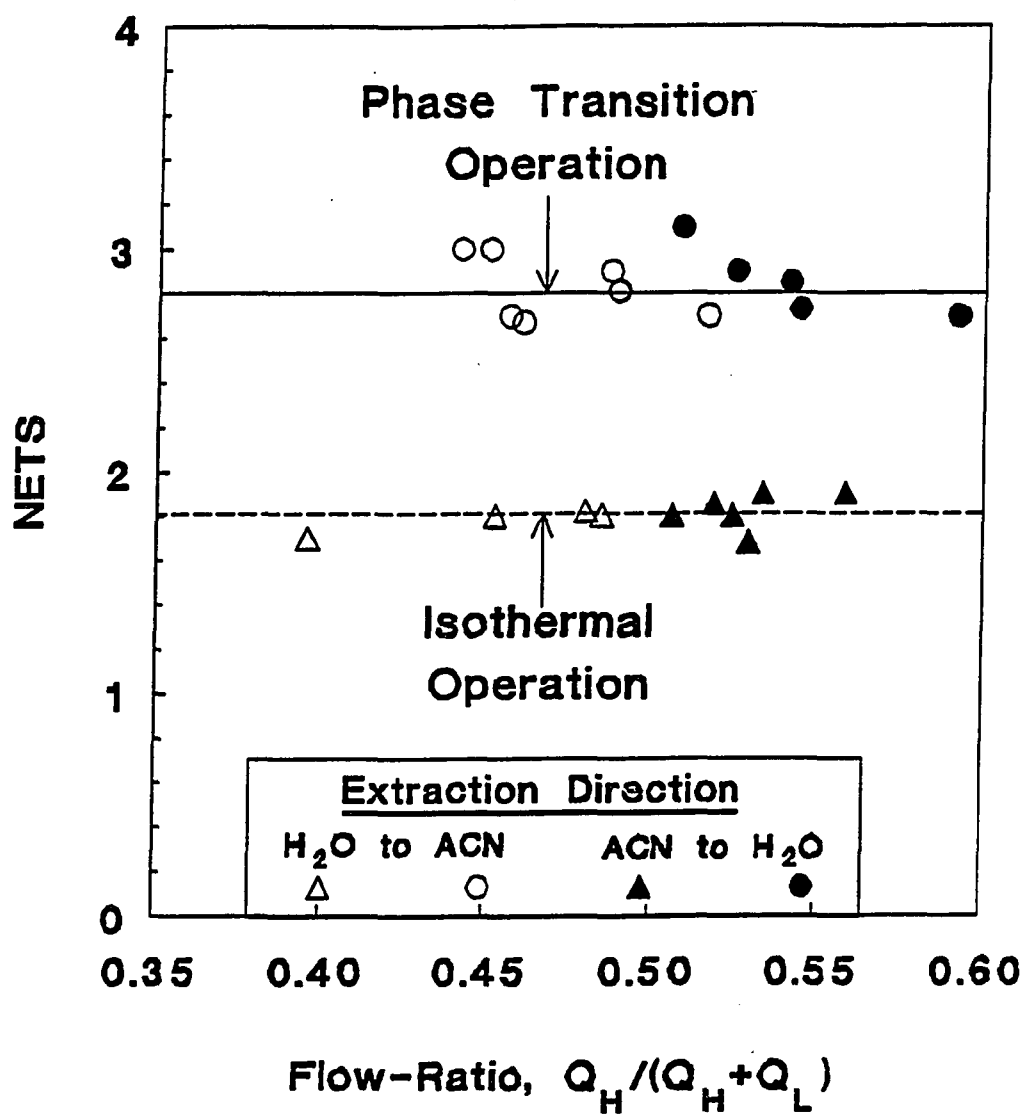


Figure 5.19: Mass transfer performance (NETS) of the experimental single-stage column as a function of inlet-streams flow rate ratio.

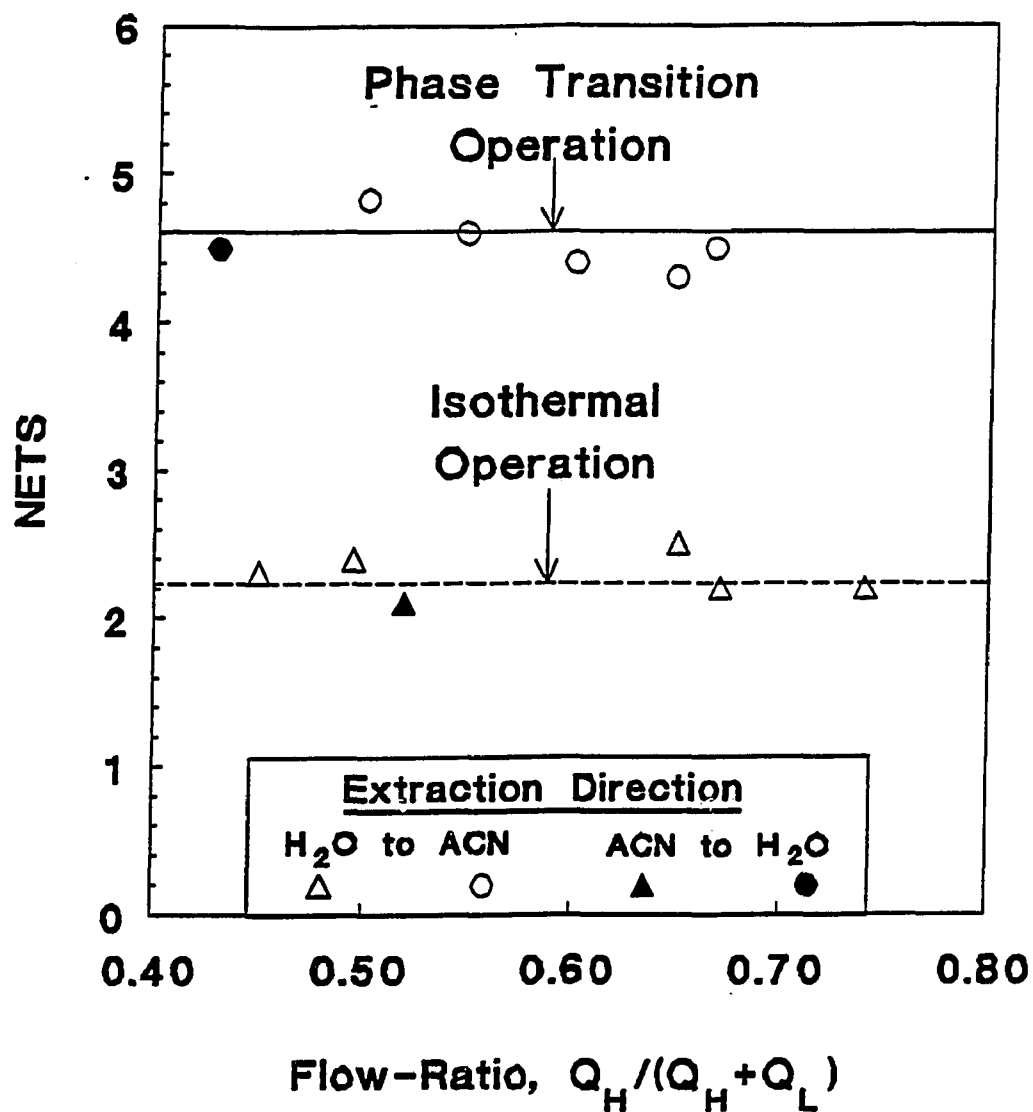


Figure 5.20: Mass transfer performance (NETS) of the experimental three-stage column as a function of inlet-streams flow rate ratio.

studied), and to avoid the development of a "pinch" point in the columns. A pinch point may occur if the extraction factor (i.e. the ratio between the solute's distribution factor and the solvents' flow-rate ratio) is appreciably different from unity. In such cases the liquid leaving one end of the column will be in substantial equilibrium with the stream entering this end. The operating line obtained in this case cannot yield acceptable data for determining the number of stage to which the column is equivalent (NETS) because of the pinch. Figures 5.19 and 5.20 show that in the range of aqueous flow rate fraction studied, the performance of the columns was independent of the solvents' flow rate ratio.

By examining figures 5.14 to 5.20 it seems that the results obtained for the phase-transition operation mode of the column are more scattered than the results obtained when the column was operated under uniform temperature conditions. However, regardless of the operation mode, the scattering of the experimental results are more evident as the number of theoretical stages obtained by the columns are increased. This may be explained by the approach of "pinch" conditions as the extraction process becomes more efficient. As the equilibrium and operation curves get closer to each other in one of the column's ends (depending upon the extraction factor), the evaluation of the number of theoretical stages is more sensitive to any experimental error in the analysis of the stream's concentration or flow rate (see Fig. 5.5) and

this results in a higher scattering of the experimental performance results.

Another important characteristic of the column performance is the coalescence rate in the settling sections. Insufficient coalescence rate at a given throughput will reduce the stage efficiency due to entrainment of either one or both of the phases. Furthermore, if the throughput is too high, then the rate of droplets arrival may exceed the coalescence rate at the interface and the column will be flooded.

During each run of the column, complete phase separation in the bottom and the top coolers was verified by inspecting the outlet streams for the presence of a second phase. The presence of light phase in the heavy phase or heavy phase in the light phase is very easy to inspect since even a trace amount of second phase will cause an opaque appearance of the outlet stream.

We succeeded in maintaining a continuous steady-state of the column without detecting any entrainment in each of the column outlet streams and without reduction in the column efficiency for throughput values of up to $15 \text{ m}^3/(\text{m}^2 \text{ hr})$ (see Figs. 5.14 and 5.15). These throughput values are remarkably high considering the solvent system studied in our experiments. The solvents system of acetonitrile water and toluene with the crystal violet as a solute has shown high emulsifying tendency when mixed isothermally via a mechanical

agitation. In the batch experiment described in Section 4.2, where this system was mixed by mechanical agitation, a dispersion of very fine droplets was formed, and complete separation at isothermal condition was achieved just after seven hours. However, as we demonstrated in the batch experiments, the phase separation of the solvents and solute system was rapid when it was coupled with phase-transition. Therefore, we were able to obtain high mass-transfer performance and high throughputs when we operated the column via phase-transition mode.

When we operated the column isothermally, similar throughputs were possible by maintaining the droplets diameter in the range of 2-4 mm by using appropriate distributor in the inlet of the dispersed phase. This droplets size is commonly used in extractors since it yields a sufficient surface area and still allows oscillation and circulation of the droplet which improve the mass transfer in the droplet. In our case, this droplets size also provided a sufficient coalescence rate at the column's main interface when the column was operated isothermally. However, as our batch experiments showed, any attempt to increase the mass-transfer performance by input of agitation energy will probably result, in an isothermal column, in emulsification and consequently a flooding of the column. It would also be very difficult to operate a conventional mixer-settler with such a system.

5.4 Discussion - Column Performance

The main purpose of our experimental work was to demonstrate the feasibility of a continuous operation of the PTE process in a column, and to examine the performance of such a column. Beside demonstrating the operational feasibility, the data determined in the experimental investigation led to several definite conclusions and also indicated certain other factors involved in the design and operation of the novel PTE process.

The operation of the PTE process in a column is more complex than the performance of an extraction in equivalent mixer-settler or batch equipment. In the column, the solvent streams are successively mixed together to form an homogeneous phase, and then separated again by virtue of temperature variations, in a series of sections located one above the other intermittently. The various sections of the column are connected and therefore affect each other. Accordingly, the solvents flow-pattern in the PTE column is more complicated in comparison to the flow in conventional columns where two distinct phases at constant temperature exist throughout. Our first goal was therefore to establish whether such an intricate flow will occur in our column.

Experiments conducted in a laboratory-scale column showed that a continuous countercurrent flow of the solvents accompanied with phase-transitions induced by temperature-

variations is indeed feasible. Moreover, the experiments also demonstrated that a complete mixing of the solvents in the mixing section can be achieved without the use of any mechanical agitation.

In order to gain more understanding of the flow pattern in the column, we have developed a basic model to predict the flow pattern of the solvent in such a column. The model predicts the existence of back-flow streams between the mixing and settling section of the column as a result of the phase separation in the settling section. The model has been successful in predicting the experimental hold-up of the phases in the mixing sections of the column as well as the energy consumption in the heating sections. Consequently, the validity of the model and its ability to serve as a designing tool has been established. The model also suggests that if a complete phase separation is achieved in the settling sections, then the back-flow streams are affecting mainly the heat consumption, and have only a negligible effect on the column's performance.

The mass transfer performance of the PTE column was studied by extracting a solute from one phase of a solvent system to the other. An evaluation of the impact of phase-transition (via heating and cooling the solvents) on the column performance was conducted by operating the column at uniform temperature using the same solvents and solute and with identical throughput. Since the performance of an

individual type of apparatus is highly affected by the properties of the solvents and solutes being processed, the dimensions, and the internal structure of the apparatus, utilizing the same equipment with the same solvents and solute system for comparison, provided us with direct results regarding the effect of the solvents phase transition on the column performance.

A comparisons of the overall performance of the two operation modes showed that for the single-stage column 2.8 theoretical stages obtained in the PTE column compared to 1.8 stages in the isothermal column. Where, for the three-stage column the PTE column provided 4.6 theoretical stages compared to only 2.2 stages of the isothermal column.

As we explained previously, end-effects play an important role in the performance of short columns. Therefore, more reliable evaluation of the mass transfer performance can be obtained by measuring the contribution of additional actual stages to a single-stage column, and the contribution of additional height to the performance of the isothermally operated column. Here our experiments showed that, for the phase-transition operation mode, an additional actual stage (one heater and one cooler) contributed an approximately one theoretical stage, which is equivalent to contribution of 4.5 NETS/meter. In a similar way, an additional height to the uniform temperature operated column contributed only 1 NETS/meter.

These results demonstrate that the effect of the phase-transition and cooling in our experimental PTE columns is real and not spurious. In addition, the results confirm what we set out to show, namely that each heating-cooling section acts as one theoretical stage. Consequently, one could build a PTE column with a very large number of efficient stages.

Although, a direct evaluation of the heating and cooling impacts on the performance of the column showed a significant stage efficiency improvement, it will still be of interest to compare the PTE process to other extractor types. However, as we mentioned before, the parameters of the materials being processed have highly different effects on the performance of the individual types of apparatus and therefore any reliable comparison between different equipments has to be done by using the same solvents and solute system. Thus, comparisons and evaluations of different extractor types on the basis of data available today is almost impossible. This is especially true when trying to compare our process, in which partially miscible solvents with critical point of miscibility are utilized to perform the extraction, to any other existing extractors, in which one of the basic requirements of the solvents is to have the lowest possible mutual miscibility.

A limited comparison between different extractors is given in a work published by Stichlmair (1980). In this work, the efficiency and the capacity range of small diameter extractors, 50-150 mm dia., have been compared for extracting

acetone from water with toluene as the disperse phase. The performance range of different extractors, taken from Stichlmair work, and our experimental result for the uniform temperature and phase transition operation modes, are plotted in Figure 5.21. As one can see, the PTE column provided good results for both the capacity and the mass transfer performance in comparison to the other extractors.

Although the design of our experimental column is far from being optimal, its efficiency has been found to be higher than most of the other extractors examined. We have reasons to believe that some modifications in our basic model, such as more efficient heat exchangers, can lead to a reduction in the height of the heating and the cooling sections, and consequently result in an improvement of the number of the columns theoretical stages per unit height.

Modifying our column will also improve the column capacity which, as Figure 5.21 shows, is slightly lower than some of the other extractors. Here it is important to indicate the difference between the solvents and solute system used in our experiments, and the system used in the compared equipment. Where no emulsion formation regarding the system used in the conventional extractors was reported by Stichlmair (1980), the system used in our experiments showed a high tendency to form stable emulsions even with moderate agitation (see section 4.2). It is therefore clear that performing extraction with our experimental solvents system in any of the

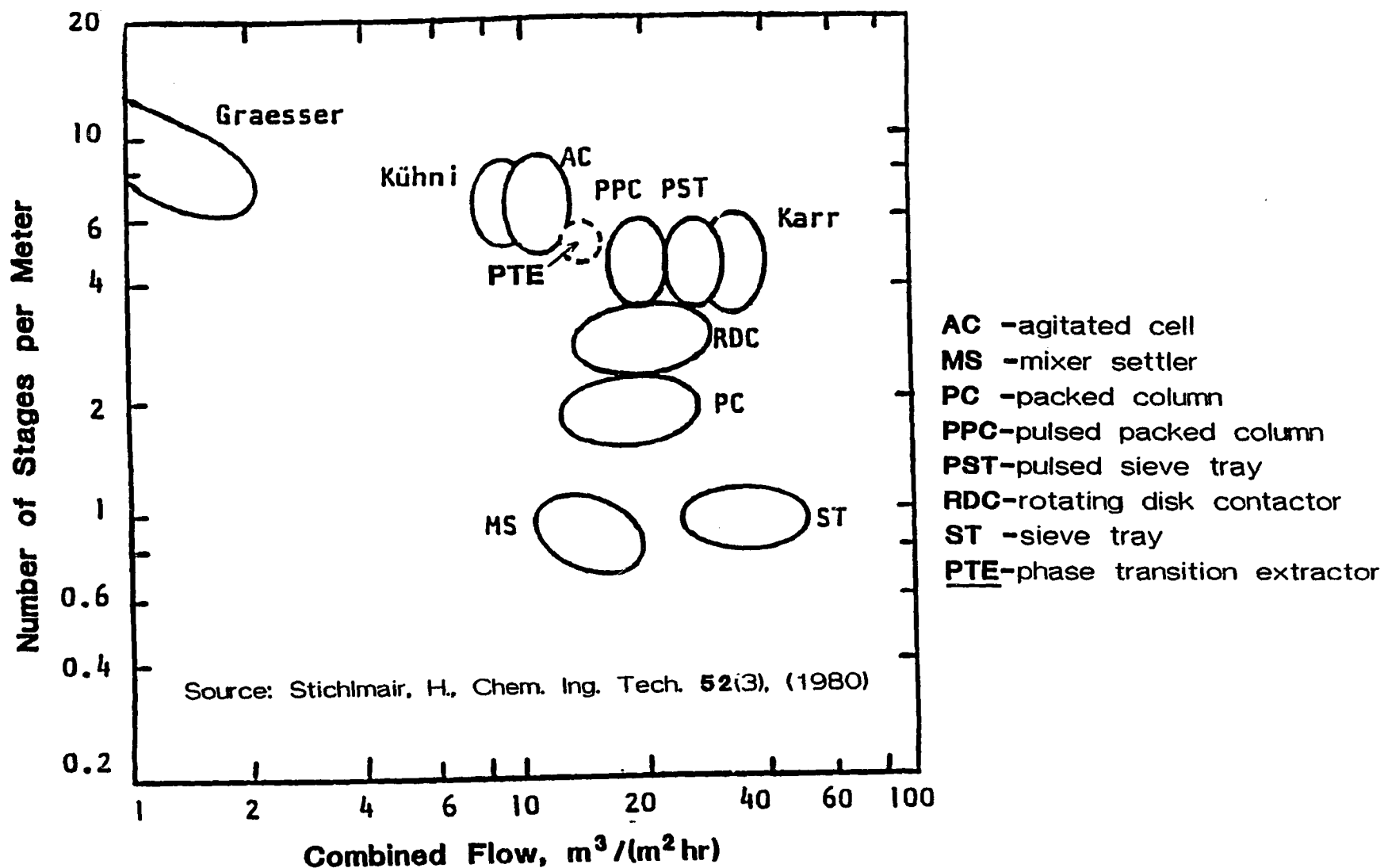


Figure 5.21: Efficiency and capacity range of conventional extractors and the PTE column.

other mechanically agitated extractors, would lead to a considerable reduction in their capacities. This emphasizes the advantage of our process in handling difficult systems that are sensitive to emulsion formation.

The main difference between our process and other conventional extraction processes is the use of thermal energy to accomplish a better contact between the solvents streams. In conventional extractors the streams are contacted by dispersing one of the liquid phases in the other using static or mechanical dispersers and agitators. In contrast, in our process the contact between the solvents is achieved by varying their temperature across the miscibility curve, creating a region of perfect miscibility followed by a region in which the phases are separated. Consequently, the high performance of our process is achieved at the expense of higher energy consumption. However, the liquid-liquid phase transition employed in our process requires significantly less energy than any separation process that utilizes a vapor-liquid phase transition (e.g. distillation). Liquid-vapor phase transition is generally associated with significant input of thermal energy as latent heat, whereas in liquid-liquid phase transition the heat of solution consumed is frequently very low. Therefore, only the input of sensible heat is needed to perform liquid-liquid phase transition in our process. Adjusting the operational temperature to the vicinity of the ambient temperature (see Section 2.3.5, the

effect of third component), may reduce the cost of the required heating and cooling by permitting the use of low cost and available heating and cooling sources from waste heat and ambient cooling water. In addition, in mixer-settlers a significant fraction of the required sensible heat input can be recycled through heat exchange with the mixture as it is cooled down to separate the homogeneous solution.

The recovery of the heat is relatively simple when performing our process in the mixer-settler operation mode. In contrast to the column, in the mixer-settler the streams are entering and leaving the heating and cooling section in different pipes (see the discussion in Section 5.3.1.1). By passing this streams through auxiliary heat-exchangers a substantial fraction of the heating and cooling requirements can be saved.

When operating PTE process in a column, the saving of energy is more difficult. As we demonstrated in Section 5.3.1.2, as a result of the back-flow streams in the column, the energy consumption is considerably higher than in mixer-settlers (see Fig. 5.13). The heat recycling is also more difficult in the column than in mixer-settlers. Our experiments showed that the heat exchange as well as the mass transfer between the streams leaving and entering the heating and cooling sections of our experimental setup were negligible. However, an addition of proper packing material, such as wire-mash, can improve the contact between the

countercurrent streams in the settling section, and consequently enhance both the heat and the mass transfer rates between the solvent streams. This modification can bring a reduction in the heating and cooling requirements of the process, and at the same time, improve the overall column efficiency via the additional extraction in the settling sections.

The addition of packing materials and the effect of packing properties on the performance of the column has not been studied in the present investigation, but, based on the consideration of the factors involved in the performance, it is possible to recognize certain qualitative effects. The less dense packing would have a greater solvents capacity, but would provide less efficient contact between the streams. Thus, an economic study of such a column design requires quantitative comparisons of the effect of packing characteristics on the efficiency capacity and the heat requirements of the column.

Energy consumption is just one of many factors that must be considered by the designer when deciding upon the preferable operation mode for a specific separation. The main advantages of our process, such as the high mass transfer efficiency and the fast phase separation, are common to both the column and the mixer-settler operation modes.

Mixer-settler may be selected when only a few theoretical stages are required and when suspended solid matter are

present in the feed stream. However, the column operation mode will be preferred for separations that require a large number of theoretical stages. As we demonstrated in the present work, our column can be operated with high efficiency without any mechanical agitation. Furthermore, we have shown that we can increase the number of stages and still maintain the high efficiency of each individual stage. Consequently, a large number of efficient stages can be assembled into a tall column whose height is not limited by technical constraints that are involved in constructing tall, mechanical agitated columns.

6 SUMMARY AND CONCLUSIONS

The solvent-solvent separation process described in this work presents a significant advance in separation technology. The novel PTE (Phase Transition Extraction) process is based on manipulating the temperature of solvents that have a critical point of miscibility across their coexistence curve. In this way, the mixing and settling sections of conventional extraction equipments are replaced by heated and cooled sections where either the solvents form a homogeneous solution or they separate into two distinct phases.

In the present work we have demonstrated that the PTE process is feasible, and we have answered all the main critical questions:

- a) Following a phase-transition cycle, the separated phases establish a thermodynamic solutes and solvents composition corresponding to their temperature.
- b) The coalescence and the phase separation following the phase-transition process are rapid and less sensitive to the presence of impurities which tend to stabilize dispersions formed by virtue of isothermal mixing.
- c) High stage efficiency can be achieved with a minimum or without any mechanical agitation.
- d) The choice of the solvents (CST-forming mixtures) for the PTE process is critical. However, it was demonstrated that solvents presently used in conventional processes can be

modified by addition of a second solvent to be used in the PTE process. In a similar way, the temperature range can also be modified over a wide range depending on the specific process needs.

We have demonstrated that by employing the PTE process, an efficient extraction of fermentation-broth can be performed without pre-filtration of the broth and without using centrifuges to separate the phases. Where an isothermal mixing of the broth with extracting solvents resulted with the formation of stable emulsions, the extraction by the PTE process provided a complete phase separation in less than a minute, with higher product yield and with the extracting solvent free from solids.

The feasibility of performing a continuous countercurrent extraction by the PTE process was demonstrated via operating a lab-scale single-stage and three-stage columns. We have shown that high stage efficiency (about 90%) can be obtained without any mechanical agitation of the solvents. This makes the PTE column an attractive tool for separations that require a large number of theoretical stages. As the PTE column is operated without any moving parts, it is possible to assemble a large number of efficient stages into a tall column. In addition, such a column can be effectively sealed and any mechanical wear of moving parts is eliminated.

At this point it is important to recognize that the PTE process is not an energy efficient process. The variation of

the solvents temperature across the miscibility curve in the PTE process requires a higher energy consumption as thermal energy in comparison to the energy of agitation required in conventional extraction process. Therefore, the energy expenses will have to be weighted against the advantages of the process when deciding upon the preferable extraction for a specific separation. Such a decision will be naturally affected by the product's value.

We are not suggesting here that the PTE process aims at substituting existing extraction equipments for any separation process. However, the features of the novel PTE process can open a new avenue of possibilities for difficult separations that have thus far been either economically unfeasible or operationally limited. Such cases include:

1. Separations of systems that easily emulsify (e.g. extraction from fermentation broth).
2. Difficult separations which require a large number of theoretical stages.
3. Separation of large molecules that can be damaged by high shear stress.
4. Separation of irradiate compounds where remote operation, low maintenance, and heavy shielding are essential.

Appendix I: Activity Coefficient Correlations for Predicting Phase Diagrams

When designing a new extraction process, particularly in the stage of the preliminary screening of solvents, it is more advantageous to have an analytical tool to predict the equilibrium compositions of solvent mixtures. Therefore, we have examined the applicability of utilizing activity coefficient correlations. Two activity coefficient correlations, the Van-Laar and the NRTL were tested, and the calculated compositions, based on published binary data (Sorensen, DECHEMA data collections, 1979-1980), were compared with our experimental results of the three-component acetonitrile-toluene-water system equilibrium compositions.

Although the derivation of the Van-Laar equations suggests that they should be used for relatively simple solutions, it has been found (Walas, 1985, Prausnitz, 1986) that these equations can frequently represent more complex mixtures. The Van-Larr equations are widely used in the literature, and we have chosen them here, for their flexibility and mathematical simplicity relative to many other equations.

The NRTL equations, on the other hand, are more complicated, since three parameters are needed for each pair of constituents. However, we selected these equations because they are known to be superior for representing liquid-liquid

equilibria data, especially of aqueous systems (Walas, 1985).

When the parameters of the activity coefficient equations are known, the equilibrium composition can be determined by finding the minimum Gibbs energy corresponding to a given overall composition of the solvents mixture (see Section 2.3.6). However, it is more convenient, in the case of multicomponent system, to apply the principal of the equality of chemical potentials (and therefore the partial fugacities) for each component of the mixture. For two coexisting liquid phases in equilibria the fugacity equality for each component gives

$$\gamma_i x_i = \gamma_i^* x_i^* \quad (1)$$

where γ_i is the activity coefficient of component (i) with composition x_i in the first phase, and the second phase is designated by an asterisk. A computational procedure to solve this nonlinear equation is described by Walas (1985). Based on this procedure, which is similar to the one used for vapor-liquid flash calculation, an iterative computer program was written utilizing the Van Larr and the NRTL correlations for the activity coefficients (the required equations are given in Table I.1). The binary parameters were taken from the DECHEMA data collections (Sorensen and Arlt, 1979-1980), and are summarized in Table I.2.

The calculated phase diagrams (in terms of organic component composition as a function of temperature) are

compared with the experimental results and plotted in Figures I.1-I.4. Based on these results, we can conclude that both the NRTL and the Van-Laar equations show a fairly good agreement with the experimental results only when the temperature of the solvents mixture is far from the critical point. In this range, a comparison between these two equations shows that the NRTL is slightly better in predicting the phase diagram than the Van-Laar equation. However, the Van Laar equation is simpler in use since it requires less parameters, and the convergence of the iterative computation procedure is faster.

Close to the critical point the shape of the phase diagram is extremely sensitive to temperature, as evident in Figure I.4. Clearly, such sensitivity to temperature can be represented only if activity coefficients are known accurately as functions of temperature, which unfortunately is not the situation at present with respect to the usual activity coefficient equations (Walas, 1985). Therefore, caution must be exercised when using activity coefficient correlations as a tool for screening solvents or performing preliminary calculations of new extraction processes. Still, these semi-empirical correlations can save some tedious experimental work in obtaining the phase diagram of the solvent system. However, it is recommended to use these correlations only for estimating the phase compositions in the settling sections of the PTE process, in which the solvents are relatively far from

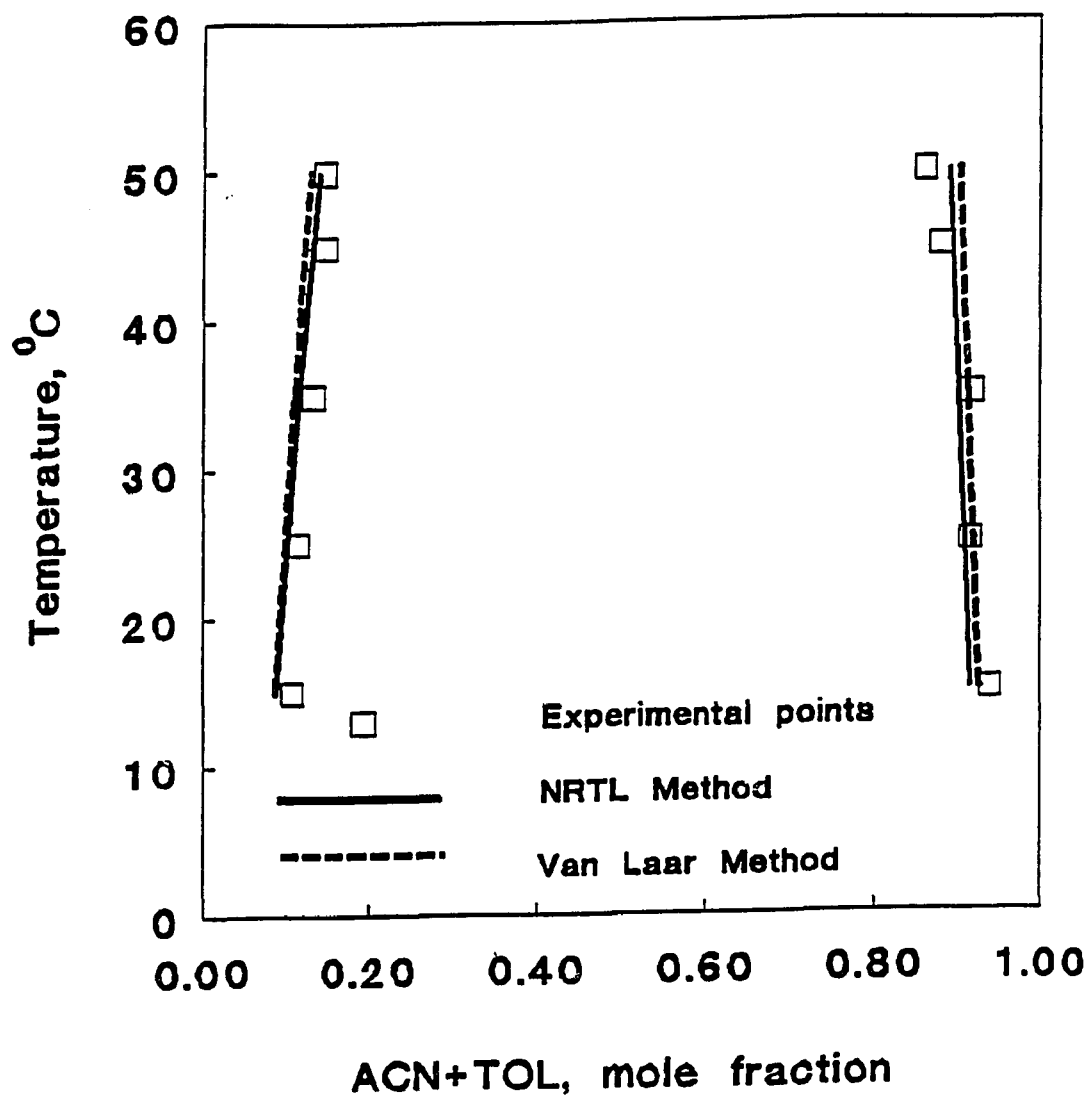


Figure I.1: Experimental and calculated phase diagram of acetonitrile-water-toluene (composition: 0.321/0.593/0.086) system.

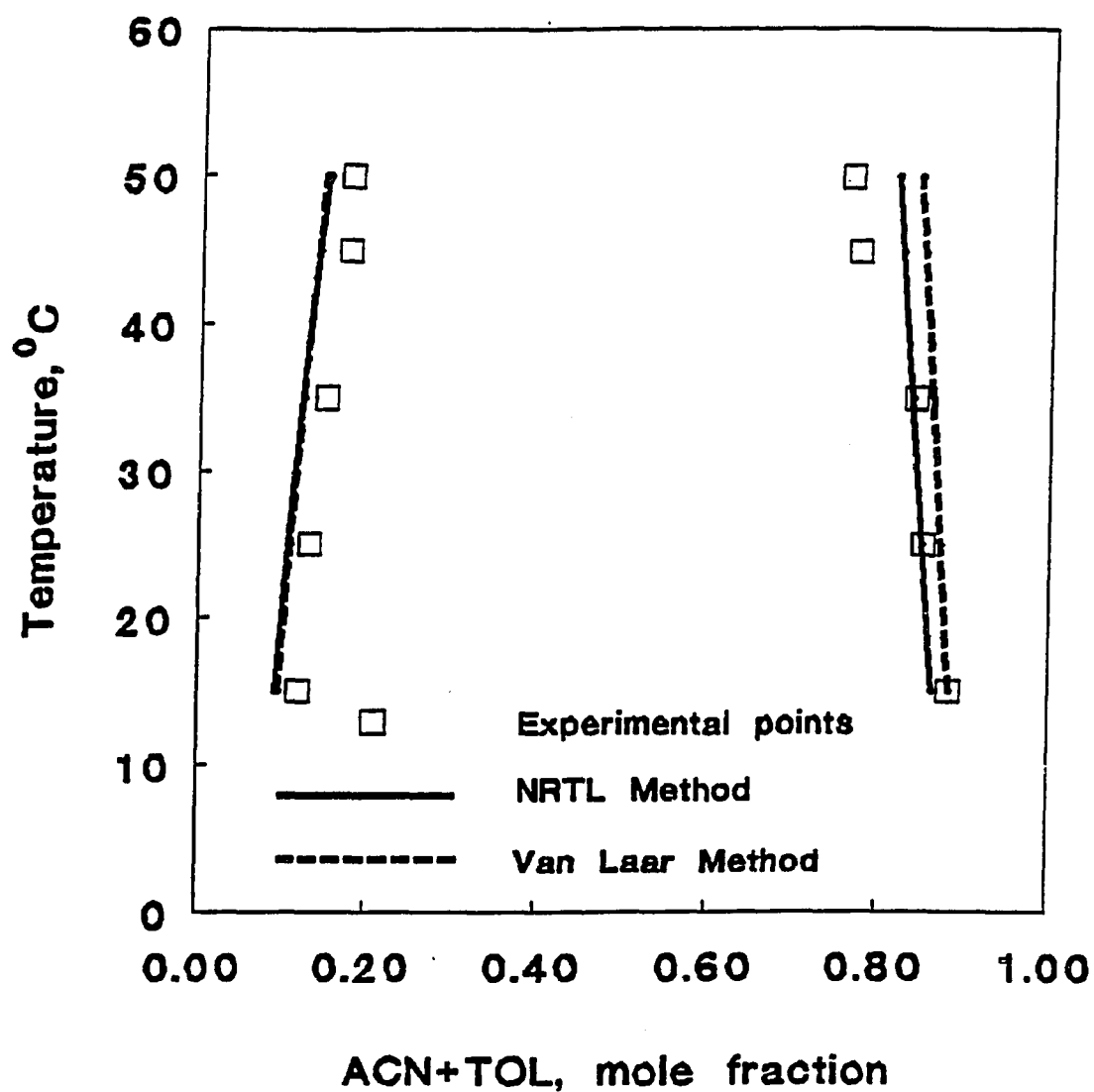


Figure I.2: Experimental and calculated phase diagram of acetonitrile-water-toluene (composition: 0.334/0.618/0.048) system.

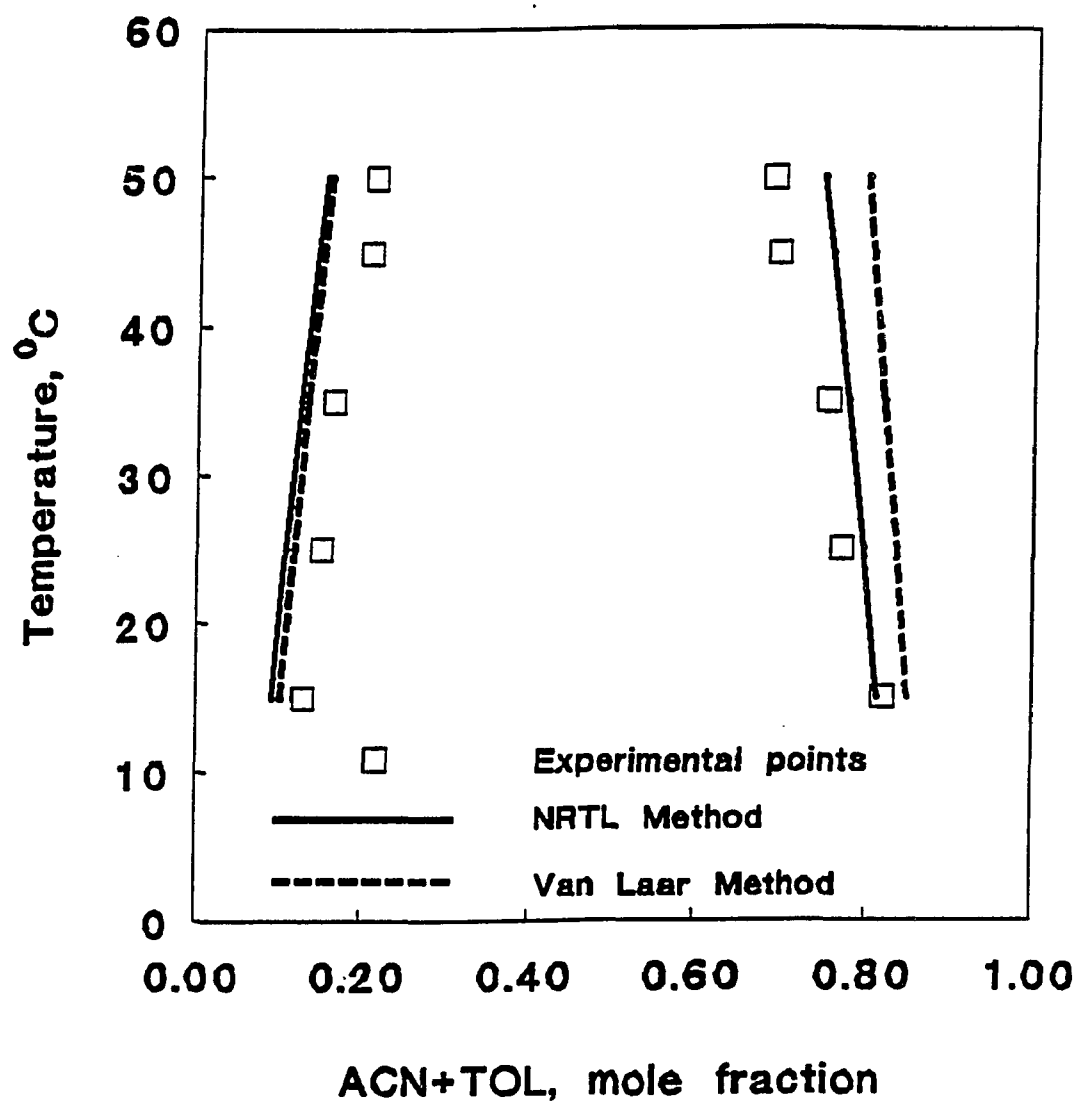


Figure I.3: Experimental and calculated phase diagram of acetonitrile-water-toluene (composition: 0.340/0.630/0.030) system.

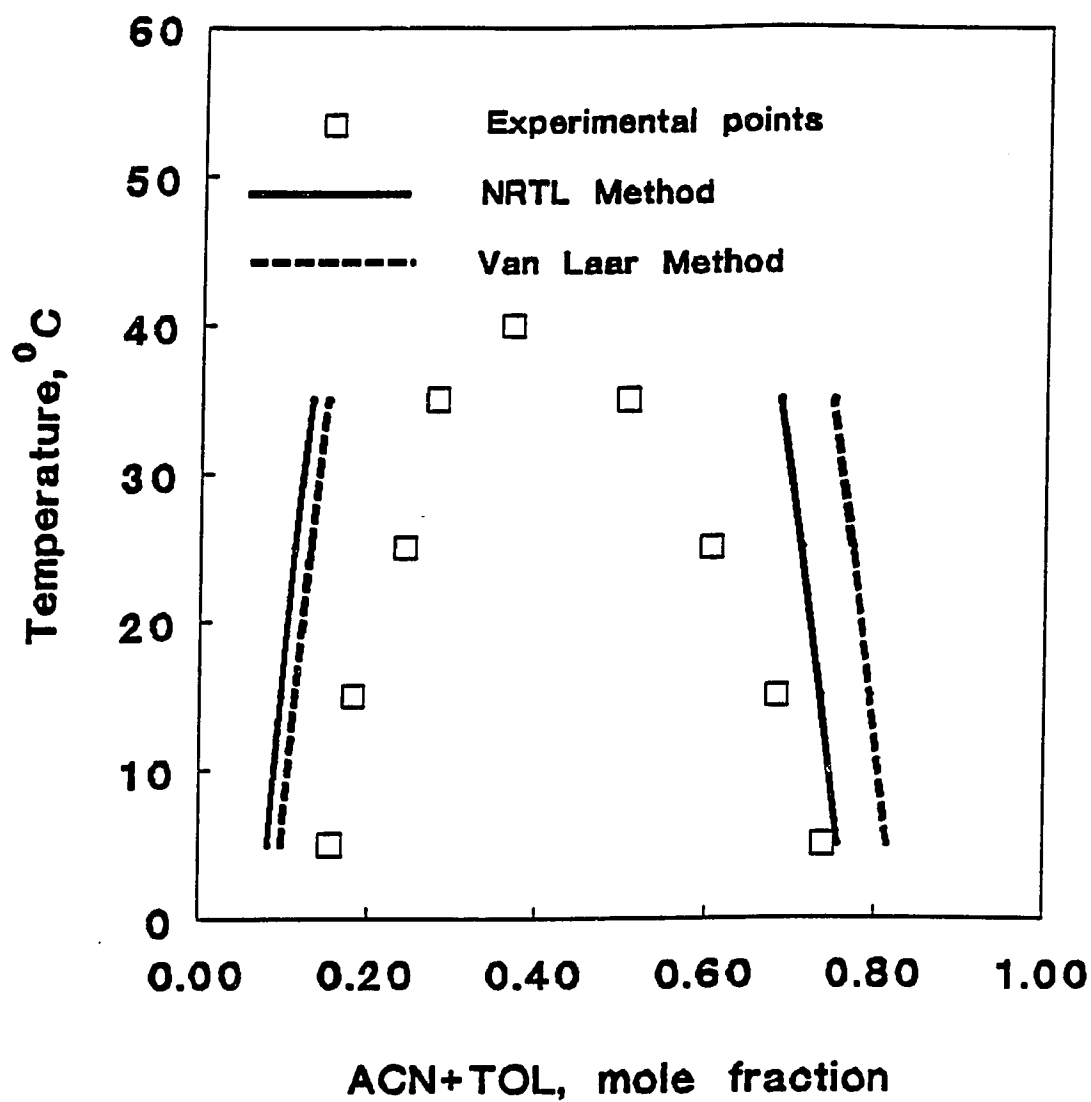


Figure I.4: Experimental and calculated phase diagram of acetonitrile-water-toluene (composition: 0.347/0.640/0.013) system.

their CST. Nevertheless, the critical temperature, which determines the temperature in the mixing section, has to be taken from available published data (Section 2.3.2), or obtained separately by performing the relatively simple cloud point experimental procedure (see Section 4.1.2.3).

Appendix II: Direct Observation of Phase Separation

A direct observation of the phase transition process provides the ability to follow the morphology of the separating solvents phases, and to observe the motion of the droplets and the droplets interfaces throughout the various stages of the phase separation process.

An experimental set-up was designed and built to allow the observation of droplets in the sizes range of 5 to 1000 μm . The experimental setup consists of a temperature-regulated sample-cell, an optical microscope (Nikon SMZ-2T), and a video (Panasonic CCTV Model WV-BD400) or still camera (Nikon N2020) mounted on the microscope. The temperature in the sample-cell is regulated by placing it in a water jacket and circulating water from temperature controlled reservoirs through the water jacket. This arrangement allows us to quench the temperature at the sample-cell up to 30°C within few seconds.

We have used this experimental set-up to follow the phase separation of the acetonitrile-water-toluene system with crystal violet as an emulsifying substance under both isothermal and phase-transition conditions.

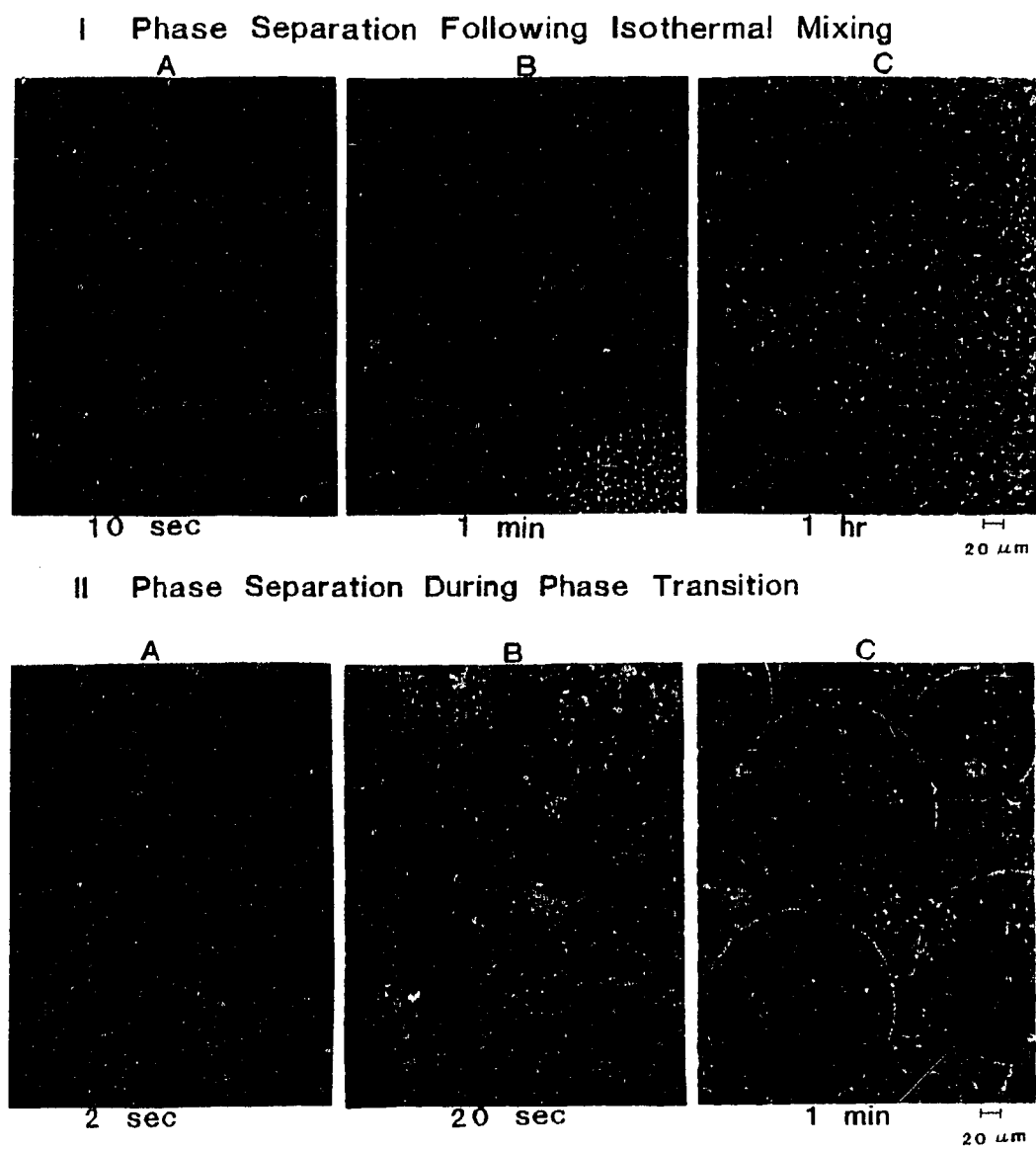
The sequence of pictures at the bottom of Figure II.1 follows the main stages of the phase separation after a 25°C quench of the critical mixture. In order to reduce the effect of gravity, and thereby slow down the separation process, the

sample-cell was placed in a nearly horizontal position.

The most striking feature of the phase separation following a temperature quench is its peculiar morphology. Following the temperature quench, the first stage of the phase separation is characterized by an interconnected pattern of separated domains, which can indicate a spinodal decomposition process (see Section 2.4.7). However, this stage is very short, and soon after the temperature quench a grainy pattern starts to develop (see Fig. II.1, IIA).

The grainy pattern represents the appearance of small droplets which are formed via a nucleation process. At the very beginning of this stage, the droplets are separated from each other and each droplet grows independently by a relatively slow diffusion process. However, as the nucleation and the growth processes proceed, the number and the diameter of the droplets increase. Thus, after a short period of time (about 10 seconds), a pattern of interconnected droplets is formed, and coalescence of the interconnected droplets is observed. Convection starts nearly at the same time. This convection seems to be the result of the onset of instability due to concentration or temperature gradient in the bulk phase and on the droplets interface. The convective motion of the droplets appears to play an important role in increasing the phase separation rate by enhancing the solvents diffusion into the droplets, and by intensifying the collision of the droplets. Consequently, a rapid, hydrodynamically driven

Figure II.1: Direct observation of isothermal phase separation versus phase separation during phase-transition process.



process, of simultaneous growth and coalescence of the droplets is taking place. Within about 20 seconds we observed a droplets' growth of three orders of magnitude (from about 10 μm to 700 μm).

At this stage, the supersaturation of the solvents is still sufficient to cause a nucleation of new droplets. Therefore, the growth of the droplets is accompanied with a formation of new droplets, which, in turn, are growing and coalescing in a process similar to the growth process of the "old" droplets. As a result, droplets with different ages, and therefore different sizes, exist together at every moment, and we observe a wide distribution of droplets sizes (see Fig. II.1, IIB).

As a result of the close-to-horizontal position of the cell, the appearance of well-defined phases at the top and at the bottom of the cell is delayed to a relatively late stage of the phase separation. Following this separation of phases, the growth of the droplets continues in the same manner but in both the upper and the lower phases.

Finally, as the supersaturation of the solvents in both the upper and the lower phases becomes very low, the nucleation of new droplets ceases, and the growth by diffusion of the remaining droplets becomes very slow (Fig. II.1. IIC). These droplets evolve very slowly in time and constitute what we describe as "secondary emulsion".

The whole process of phase separation was completed

within six minutes. A similar order of time was reported by Guenoun et. al. (1987) and Beysens et. al. (1988) for their experiments of phase separation near the critical point (few mK) with density-matched solvents and under micro-gravity conditions. However, in our experiments the main phase separation (excluding the disappearance of the secondary emulsion which was not reported by the above researchers) was completed within two minutes. Hence, it seems that the deeper temperature quench in our experiments raises the supersaturation of the solvents, and consequently accelerates the phase separation process.

Three typical sequence of the isothermal phase separation are shown at the top of Figure II.1. The difference between the morphology of the isothermal phase separation and the phase-transition phase separation is very clear, and is a result of the different phase separation mechanisms. In the isothermal case, the phases are separated mainly via the coalescence of interconnected droplets. Since this process is occurring simultaneously all over the dispersion, the distribution of the droplets size is relatively narrow. Therefore, we observe a continuous growth of the droplets with each droplet having about the same size. This growth process is very slow (after two hours of observation the separation was still far from completion) as a result of the presence of a surfactant - the crystal violet.

We have repeated the above experiments with a vertical

positioning of the sample-cell. In this way the solvents are exposed to the gravitational force which accelerates both the isothermal and the phase-transition phase separation processes.

In general, the phase separation following the temperature quench in the vertical cell includes a similar sequence of events as the phase separation in the horizontal cell. However, the effect of gravity amplifies the convective flow in the vertical cell, and accelerates the sedimentation of the phases. This results in an early appearance of two well-defined phases at the top and the bottom of the cell accompanied by an intense flow activity in the central part of the cell due to the "exchange" of the solvents. In this stage we observe droplets colliding and coalescing, and their behavior appears to be governed by the intensive hydrodynamic forces. In this stage the activity in the cell is so intensive that it was difficult to get a clear image of the droplets and to accurately follow the growth process with our video camera (which needs a time of 40 ms to reset a pixel).

As a result of the gravitational force, the phase separation in the vertical cell was twice faster than the separation in the horizontal cell. The main separation was completed after one minute and the secondary emulsion disappeared within five minutes.

Summary

The direct microscopic observation of the phase transition process shows that the presence of impurities in the system affects only the last stage of the phase separation in which the supersaturation of the phases is small. Excluding this stage, our observations are in a qualitative agreement with observations reported by former researchers. The deeper temperature quench of the system in our experiments (25° K compared to few mK in previous works) resulted in the acceleration of the rate of the phase separation process without changing the characteristics of the various stages of the phase separation. Here it will be of interest to gather quantitative information on the effect of the deep temperature quench and the rate of cooling on the different stages of the phase separation. However, the direct observation via our experimental setup is not accurate enough for this purpose, and we are now modifying our experimental setup to include measurements by light scattering techniques.

However, both the overall break-up time measurements (see Sections 4.2 and 4.3) and the direct observation of the phase separation show that emulsifiers affect the phase separation only during the late stage of the phase transition after most of the separation is completed. A systematic investigation of the effect of various surfactant types with different stabilizing mechanisms and adsorption rates, would be of great

interest, and is now in progress. However, it is out of the scope of this thesis.

Appendix III: TablesTable 2.1: Systems With Critical Solution Temperature

Components		UCST, °C	LCST, °C	Weight % B at CST
A	B			
water	methyl acetate	108.0		52.5
water	n-butanol	125.2		32.5
water	furfural	122.7		51.0
water	phenol	66.0		34.0
water	acetonitrile	-0.5		56.1
methanol	n-hexane	34.0		68.2
water	diethylamine		143.5	37.5
water	triethylamine		18.7	50.0
water	lutidine		34.0	31.4
water	butoxyethanol		48.0	27.8
water	ethylene glycol mono butyl ether	49.1		24.8
			128.0	24.8
water	ethylene glycol mono isobutyl ether	24.5		24.6
			150.4	28.0
water	2,6-dimethyl pyridine	45.3		27.2
			164.9	33.8
water	nicotine	60.8		29.0
			208.0	32.0
water	methyl ethyl ketone	-6.0		31.0
			150.0	45.0

Table 2.2: Variation of Critical Solution Temperature with Pressure

Components		Temperature [°C]	Pressure range [atm.]	$\Delta T/\Delta P$
A	B			
water	nitromethane	103.3	1 - 150	-0.008
water	propionitrile	111.0	5 - 165	-0.020
water	methylal	160.3	20 - 64	-0.210
water	succinonitrile	52.3	10 - 160	-0.003

Table 4.1: Phase Diagram of Acetonitrile-Water-Toluene System

T, °C	Acetonitrile Rich Phase mole fraction			Water Rich Phase mole fraction		
	ACN	TOL	H ₂ O	ACN	TOL	H ₂ O
overall	0.321	0.086	0.593	0.321	0.086	0.593
15	0.694	0.246	0.060	0.109	0.000	0.891
25	0.674	0.241	0.085	0.116	0.000	0.884
35	0.678	0.239	0.083	0.132	0.002	0.866
45	0.642	0.237	0.121	0.148	0.002	0.850
50	0.630	0.232	0.138	0.146	0.002	0.852
overall	0.334	0.048	0.618	0.334	0.048	0.618
15	0.740	0.142	0.118	0.121	0.000	0.879
25	0.711	0.140	0.149	0.133	0.000	0.867
35	0.700	0.141	0.159	0.150	0.001	0.849
45	0.643	0.131	0.226	0.175	0.002	0.823
50	0.636	0.128	0.236	0.176	0.003	0.821
overall	0.340	0.030	0.630	0.340	0.030	0.630
15	0.726	0.093	0.181	0.130	0.000	0.870
25	0.682	0.088	0.230	0.152	0.000	0.848
35	0.663	0.090	0.247	0.167	0.000	0.833
45	0.610	0.083	0.307	0.207	0.002	0.791
50	0.605	0.083	0.312	0.210	0.003	0.787
overall	0.347	0.013	0.640	0.347	0.013	0.640
5	0.703	0.035	0.262	0.156	0.000	0.844
15	0.650	0.031	0.319	0.181	0.001	0.818
25	0.574	0.030	0.396	0.241	0.003	0.756
35	0.481	0.024	0.495	0.276	0.005	0.719
40	0.347	0.013	0.640	0.347	0.013	0.640

Table 4.2: Equilibrium Distribution of Crystal Violet in Acetonitrile-Water-Toluene Solvents System

Dye Dissolved Initially In Water Rich Phase		Dye Dissolved Initially In Acetonitrile Rich Phase	
Concentration: Water Rich Phase, mg/liter	Concentration: Acetonitrile Rich Phase, mg/liter	Concentration: Water Rich Phase, mg/liter	Concentration: Acetonitrile Rich Phase, mg/liter
0.58	4.24	1.41	7.50
3.97	11.91	4.71	12.24
9.69	23.08	10.96	20.33
10.54	22.58	17.02	33.07
17.05	34.08	17.40	33.82
17.20	33.45	23.52	43.65
17.77	30.13	24.28	42.04
17.81	32.67	32.94	54.14
35.00	55.61	41.00	62.90
36.64	58.92	43.77	67.01
50.36	76.91	65.27	98.34
57.18	85.65		
66.00	97.00		

Table 4.3: Product Yield (in mg per liter broth) in Extraction of Fermentation Broth, Comparison of Conventional extraction with the PTE process.

First Extraction			
	BROTH-MIBK ISOTHERMAL	BROTH-MIBK-ACN ISOTHERMAL	BROTH-MIBK-ACN PHASE TRANSITION
COMPONENT A	1.410	1.740	2.050
COMPONENT B	0.660	1.090	1.230
COMPONENT C	0.410	0.360	0.290
TOTAL	2.480	3.190	3.570
Second Extraction			
	BROTH-MIBK ISOTHERMAL	BROTH-MIBK-ACN ISOTHERMAL	BROTH-MIBK-ACN PHASE TRANSITION
COMPONENT A	0.034	0.039	0.046
COMPONENT B	0.027	0.038	0.040
COMPONENT C	0.015	0.000	0.038
TOTAL	0.078	0.077	0.124
TOTAL			
	BROTH-MIBK ISOTHERMAL	BROTH-MIBK-ACN ISOTHERMAL	BROTH-MIBK-ACN PHASE TRANSITION
COMPONENT A	1.444	1.779	2.096
COMPONENT B	0.687	1.128	1.270
COMPONENT C	0.425	0.360	0.328
TOTAL	2.558	3.267	3.964

Table 5.1: Experimental and Theoretical Results of the Holdup and Energy Consumption of the Heating Section in Experimental PTE Columns.

Q_r	ΔT [°C]	Holdup, x		Energy Input, q , [W]		
		Expel.	Calcul. Eq. 22	Exper.	Calcul. Eq. 28	Calcul. (M.8)
0.97	29	0.86	0.88	21.0	19.5	15.3
0.81	37	0.73	0.74	22.3	24.6	15.8
0.81	38	0.73	0.74	22.3	25.4	16.3
0.70	32	0.70	0.66	24.0	22.1	13.4
0.70	33	0.68	0.67	24.9	21.0	13.0
0.60	26	0.64	0.59	23.6	25.4	14.4
0.71	31	0.69	0.66	23.6	25.6	15.3
0.77	27	0.75	0.68	22.6	22.2	13.7
0.61	25	0.62	0.59	26.5	31.5	17.4
0.29	27	0.44	0.46	20.9	22.5	12.7
0.14	32	0.35	0.40	20.9	20.1	12.3
0.05	32	0.27	0.34	20.0	16.9	11.3
0.08	32	0.27	0.37	17.5	16.3	10.7
0.22	33	0.36	0.45	20.1	22.5	13.1
0.14	32	0.33	0.42	17.4	20.1	12.3
0.30	27	0.50	0.46	19.9	21.6	12.3
0.35	28	0.46	0.49	22.9	24.7	13.7
0.63	30	0.67	0.62	20.1	25.4	14.6
0.76	32	0.68	0.70	23.7	23.0	14.3
0.84	30	0.71	0.75	24.2	21.2	14.0
0.81	27	0.72	0.71	17.2	17.3	11.3
0.92	27	0.82	0.81	21.1	20.4	14.6
0.87	28	0.82	0.76	21.5	23.0	15.3
0.96	28	0.88	0.88	21.5	19.3	15.0
0.59	21	0.59	0.57	20.6	20.6	11.6

Q_r	ΔT [°C]	Holdup, X		Energy Input, q , [W]		
		Expel.	Calcul. Eq. 22	Exper.	Calcul. Eq. 28	Calcul. (M.S)
0.93	30	0.85	0.83	21.9	22.6	16.3
0.49	29	0.67	0.63	30.9	29.0	15.0
0.52	29	0.68	0.64	26.8	26.8	14.1
0.59	30	0.72	0.65	27.1	26.1	14.0
0.51	30	0.67	0.62	50.4	49.6	24.2
0.65	27	0.76	0.65	17.2	20.5	11.6
0.50	32	0.57	0.59	29.2	29.7	15.3
0.60	30	0.75	0.62	35.2	33.1	17.2
0.43	32	0.61	0.64	24.4	26.3	13.6

Q_r - Flow-rate fraction $Q_H/(Q_H+Q_L)$

X - Holdup in the mixing section $V_H/(V_H+V_L)$

ΔT - Temperature Difference Between The Heating and Cooling Sections

M.S - Mixer-settler, the heat consumption is calculated as a function of the inlet flow rates (no back-flow streams)

Table 5.2: Operating Conditions of Single-Stage Column

No	Type	Flow-Rate [ml/min]		Solute Concentration [mg/liter]				Temperature [°C]	
		H.P	L.P	Heavy Phase		Light Phase		Hot	Cold
				In	Out	In	Out		
1	ISOT	3.3	5.1	61.7	7.7	0.0	35.6	19.7	19.7
2	PTE	3.8	4.8	61.7	1.7	0.0	49.9	41.0	21.0
3	ISOT	4.8	5.2	41.0	6.5	0.0	33.5	21.0	21.0
4	PTE	4.8	4.5	41.0	3.5	0.0	38.7	48.0	22.0
5	ISOT	5.0	5.3	37.7	5.5	0.0	29.0	20.5	20.5
6	PTE	4.6	5.4	37.7	2.0	0.0	31.7	42.0	20.5
7	ISOT	4.3	5.2	43.0	6.0	0.0	30.8	20.0	20.0
8	PTE	4.4	5.3	43.0	0.8	0.0	34.7	43.0	27.0
9	PTE	3.2	3.8	41.0	1.4	0.0	32.5	42.0	22.0
10	PTE	4.4	4.6	46.0	3.5	0.0	42.5	45.0	16.0
11	ISOT	4.3	4.2	0.0	33.0	71.3	39.0	25.0	25.0
12	PTE	4.3	3.9	0.0	38.0	71.3	29.0	50.0	21.0
13	ISOT	4.3	4.0	0.0	33.0	71.5	38.0	22.0	22.0
14	PTE	4.3	3.7	0.0	37.9	71.5	27.7	43.0	18.0
15	ISOT	4.1	3.7	0.0	33.5	72.3	38.1	24.0	24.0
16	PTE	4.5	3.1	0.0	32.5	71.8	24.1	47.0	22.0
17	ISOT	4.3	3.4	0.0	32.6	72.0	32.6	24.0	24.0
18	PTE	4.3	3.6	0.0	40.5	74.1	27.0	47.0	19.0
19	ISOT	7.3	6.4	0.0	33.0	71.1	33.0	23.5	23.5
20	PTE	7.9	7.7	0.0	40.0	72.0	29.0	42.4	17.0
21	PTE	7.0	7.3	46.0	3.5	0.0	42.5	45.0	16.0
22	PTE	5.7	6.0	47.0	3.5	0.0	43.0	45.0	17.0
23	ISOT	8.1	7.3	0.0	33.0	72.0	34.0	20.0	20.0

ISOT-Isothermal Extraction PTE-Phase Transition Extraction

Table 5.3: Operating Conditions of Three-Stage Column

No	Type	Flow-Rate [ml/min]		Solute Concentration [mg/liter]				Temperature [°C]	
		H.P	L.P	Heavy Phase		Light Phase		Hot	Cold
				In	Out	In	Out		
1	ISOT	4.8	2.4	50.1	18.6	0.0	62.3	20.0	20.0
2	PTE	5.0	2.5	50.1	14.6	0.0	72.0	43.0	22.0
3	ISOT	3.6	4.4	50.3	4.2	0.0	39.0	18.0	18.0
4	ISOT	5.7	2.0	50.3	26.0	0.0	68.5	20.0	20.0
5	PTE	4.3	2.4	48.3	12.2	0.0	66.6	48.0	22.0
6	PTE	4.0	4.0	71.4	1.1	0.0	70.4	53.0	21.0
7	ISOT	6.4	3.5	77.5	27.3	0.0	93.4	23.0	23.0
8	PTE	6.0	4.0	77.5	14.4	0.0	96.0	46.0	20.0
9	ISOT	4.1	3.8	0.0	35.0	71.7	35.0	18.5	18.5
10	PTE	3.0	4.0	0.0	45.0	71.7	37.0	51.0	19.0
11	ISOT	4.5	4.6	68.2	9.0	0.0	60.0	20.0	20.0
12	PTE	5.7	4.7	76.5	5.0	0.0	85.0	45.0	17.5

ISOT-Isothermal Extraction PTE-Phase Transition Extraction

Table 5.4: Performance Data of Single-Stage Column

No	Type	Throughput m ³ /(m ² *hr)	Flow-Ratio Heavy/Light		Number of Theoretical Stages
			Measured	Deviat. %	
1	ISOT	7.94	0.656	0.5	1.7
2	PTE	8.18	0.793	4.8	3.0
3	ISOT	9.44	0.923	5.1	1.8
4	PTE	8.78	1.067	3.3	2.7
5	ISOT	9.72	0.943	4.5	1.8
6	PTE	9.42	0.855	3.8	2.7
7	ISOT	8.96	0.827	0.6	1.8
8	PTE	9.20	0.822	0.1	3.0
9	PTE	6.61	0.842	2.5	2.7
10	PTE	8.49	0.957	4.4	2.8
11	ISOT	8.02	1.024	4.4	1.8
12	PTE	7.74	1.103	0.9	2.9
13	ISOT	7.83	1.075	5.5	1.8
14	PTE	7.50	1.178	2.0	2.8
15	ISOT	7.31	1.123	9.2	1.7
16	PTE	7.17	1.452	1.0	2.7
17	ISOT	7.27	1.265	4.4	1.9
18	PTE	7.45	1.194	2.6	2.7
19	ISOT	12.93	1.141	4.0	1.9
20	PTE	14.67	1.033	4.1	3.1
21	PTE	13.49	0.959	4.2	2.8
22	PTE	11.04	0.950	3.9	2.9
23	ISOT	14.58	1.102	4.5	1.8

Devia. - Deviation of the measured flow ratio from the
calculate values

ISOT - Isothermal Extraction PTE - Phase Transition Extraction

Table 5.5: Performance Data of Three-Stage Column

No	Type	Throughput m ³ /(m ² *hr)	Flow-Ratio Heavy/Light		Number of Theoretical Stages
			Measured	Deviat. %	
1	ISOT	6.75	2.042	3.2	2.2
2	PTE	7.08	2.000	1.3	4.5
3	ISOT	7.55	0.818	3.2	2.3
4	ISOT	7.64	2.850	1.3	2.2
5	PTE	6.32	1.851	0.3	4.3
6	PTE	7.55	1.000	1.5	4.8
7	ISOT	9.34	1.870	0.5	2.5
8	PTE	9.44	1.500	1.5	4.4
9	ISOT	7.45	1.079	2.8	2.1
10	PTE	6.61	0.750	2.9	4.5
11	ISOT	8.59	0.978	3.5	2.4
12	PTE	9.81	1.213	1.9	4.6

Devia. - Deviation of the measured flow ratio from the
calculate values

ISOT - Isothermal Extraction

PTE - Phase Transition
Extraction

Table I1: NRTL and Van-Laar Equations of Activity Coefficient**NRTL**

$$\ln \gamma_i = \frac{\tau_{1i} G_{1i} X_1 + \tau_{2i} G_{2i} X_2 + \tau_{3i} G_{3i} X_3}{G_{1i} X_1 + G_{2i} X_2 + G_{3i} X_3} + \frac{X_1 G_{i1}}{X_1 + G_{2i} X_2 + G_{3i} X_3} \left[\tau_{i1} - \frac{X_2 \tau_{21} G_{21} + X_3 \tau_{31} G_{31}}{X_1 + X_2 G_{21} + X_3 G_{31}} \right] + \frac{X_2 G_{i2}}{G_{12} X_1 + X_2 + G_{32} X_3} \left[\tau_{i2} - \frac{X_1 \tau_{12} G_{12} + X_3 \tau_{32} G_{32}}{X_1 G_{12} + X_2 + X_3 G_{32}} \right] + \frac{X_3 G_{i3}}{G_{13} X_1 + G_{23} X_2 + X_3} \left[\tau_{i3} - \frac{X_1 \tau_{13} G_{13} + X_2 \tau_{23} G_{23}}{G_{13} X_1 + G_{23} X_2 + X_3} \right]$$

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} \quad G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$$

$$\tau_{ii} = 0 \quad G_{ii} = 1$$

$$\alpha_{ij} = \alpha_{ji}$$

Parameters: $g_{ij} - g_{jj}$, α_{ij} ($i = 1..3$, $j = 1..3$)

Van Laar

$$\ln \gamma_1 = \frac{x_2^2 A_{12} \left(\frac{A_{21}}{A_{12}} \right)^2 + x_3^2 A_{13} \left(\frac{A_{31}}{A_{13}} \right)^2 + x_2 x_3 \frac{A_{21}}{A_{12}} \frac{A_{31}}{A_{13}} (A_{12} + A_{13} - A_{32} \frac{A_{13}}{A_{31}})}{\left(x_1 + x_2 \frac{A_{21}}{A_{12}} + x_3 \frac{A_{31}}{A_{13}} \right)^2}$$

To obtain $\ln \gamma_2$: Replace 1 with 2; replace 2 with 3; and replace 3 with 1.

To obtain $\ln \gamma_3$: Replace 1 with 3; replace 2 with 1; and replace 3 with 2.

Parameters: A_{ij} ($i = 1..3$, $j = 1..3$)

Equations for determining binary constants.

$$\frac{A_{ij}}{A_{ji}} = \frac{\left(\frac{x_i}{x_j} + \frac{x_i^*}{x_j^*}\right) \left(\frac{\ln(x_i^*/x_i)}{\ln(x_j/x_j^*)}\right)}{\frac{x_i}{x_j} + \frac{x_i^*}{x_j^*} - \frac{2x_i x_i^* \ln(x_i^*/x_i)}{x_j x_j^* \ln(x_j/x_j^*)}}$$

$$A_{ij} = \frac{\ln(x_i^*/x_i)}{\frac{1}{\left(1 + \frac{A_{ij}}{A_{ji}} \left(\frac{x_i}{x_j}\right)\right)^2} - \frac{1}{\left(1 + \frac{A_{ij}}{A_{ji}} \left(\frac{x_i^*}{x_j^*}\right)\right)^2}}$$

Glossary

g_{ij} parameter for interaction between components i and j;

$g_{ij} = g_{ji}$.

α_{ij} nonrandomness parameter; $\alpha_{ij} = \alpha_{ji}$.

γ_i activity coefficient of component i.

A_{ij} parameter of Van Laar equation for component i and j.

x_i solubility of component i in the first phase of the two phases at equilibrium.

x_i^* solubility of component i in the second phase of the two phases at equilibrium.

Table I2: Constants for Activity Coefficient Correlations

NRTL Constants						
i j	g_{ij} [cal/mole]	g_{ji} [cal/mole]	α_{ij}	T [°C]	P [mm Hg]	Refer
1 2	790.725	724.096	0.935		760	(1)
1 3	422.154	1340.492	0.287		760	(2)
2 3	1313.300	2185.800	0.200	25		(3)
Van-Laar Constants						
i j	A_{ij}	A_{ji}		T [°C]	P [mm Hg]	Refer
1 2	1.2623	1.2008		40		(4)
1 3	2.3864	1.7693		50		(5)
2 3	8.865	6.7667		0		(6)

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