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by

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Abstract

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by

JOSEPH MAZZARESE

Advisor: Professor Orest Popovych

EMF measurements were performed on cells consisting of an alkali-metal amalgam electrode versus a silver-silver chloride electrode in dilute solutions of the alkali-metal chloride. These metals included Li, Na, and K. The ethanol-water and methanol-water solvents ranged from 0% to 100% alcohol by weight.

Transfer activity coefficients and transfer free energies were calculated from the difference between the standard potential of each nonaqueous cell and that of the corresponding aqueous cell. The standard potential of the metal/metal ion electrode versus the standard hydrogen electrode was calculated for the alkali metals in each solvent. Activity coefficients for the alkali-metal chlorides are reported.

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Finally, my thanks and good wishes to all the friendly people who helped me in a variety of ways and who made my graduate years more pleasureable. I shall not attempt to list them here, but they will be long remembered.

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Joseph Mazzarese

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I. Introduction

Historically, chemistry has been studied primarily in aqueous solutions. A vast amount of fundamental data for these systems has been compiled and analyzed. While aqueous investigations are far from complete, our knowledge of nonaqueous solutions is much poorer. Yet, there is great interest in nonaqueous systems. Chemists are increasingly making use of nonaqueous solvents to produce solutions having properties(e.g., solvating ability, pH, dielectric constant) unattainable in water.

For many years, organic chemists have used nonaqueous solvents to dissolve certain compounds or increase reaction rates. Physical chemists use different solvents to study fundamental chemical interactions. Analytical chemists carry out titrations that would be impossible in aqueous solutions and regularly achieve separations based on differences in solvent properties. As more uses for nonaqueous solvents are discovered, the need for fundamental data grows. This work attempts to partially meet that need.

Methanol-water and ethanol-water solvents are among the most commonly used nonaqueous media. In this study, the electrode potential of dilute alkali-metal amalgams versus a silver-silver chloride reference electrode were

measured in dilute solutions of the alkali-metal chloride. These metals included Li, Na and K. The solvents ranged from 0% to 100% by weight for each alcohol at 10% intervals. From these data and the available literature, the following can be calculated:

1) activity coefficients of each salt in each solvent at various concentrations;

2) the potential of the pure metal/metal ion electrode versus the reference electrode in each solvent;

3) the transfer free energy of each salt from water to each nonaqueous solvent;

4) the standard potential of the metal in each solvent versus the standard hydrogen electrode in that solvent.

A. Free Energy and Activity Coefficients

In any given solvent the activity, a_i^*, of solute i is related to its standard state in the solvent by the equation

$$\bar{G}_i = {}_s\bar{G}_i^\circ + RT \ln a_i^* \qquad (1)$$

where $\bar{G}_i$ is the partial molal free energy of the solute and ${}_s\bar{G}_i$ is its standard free energy. The activity is related to solute molality, m, by the salt-effect activity coefficient, ${}_s\gamma_i$, according to the equation

$$a_i^* = m_i \cdot {}_s\gamma_i \tag{2}$$

and ${}_s\gamma_i$ becomes unity at infinite dilution in the solvent. This represents a different standard state for each solvent. We can, however, relate any nonaqueous ${}_s\gamma_i$ to the corresponding activity coefficient on the aqueous scale, ${}_w\gamma_i$, by defining a transfer activity coefficient, or medium effect, ${}_m\gamma_i$, with the expression

$${}_w\gamma_i = {}_s\gamma_i \; {}_m\gamma_i \tag{3}$$

Therefore,

$$a_i = a_i^* \; {}_m\gamma_i \tag{4}$$

and

$$G_i = {}_sG_i^o + RT \ln(a_i / {}_m\gamma_i) \tag{5}$$

where a_i represents aqueous activity.

If we relate the activity of the solute in the nonaqueous solvent to the aqueous standard state we can write

$$G_i = {}_w\bar{G}_i^o + RT \ln a_i \tag{6}$$

where ${}_w\bar{G}_i^o$ is the standard free energy on the aqueous scale. Subtracting equation (5) from equation (6) and rearranging shows that

$${}_s\bar{G}_i^o - {}_w\bar{G}_i^o = RT \ln {}_m\gamma_i \tag{7}$$

This free-energy difference is often called the standard free energy of transfer, $G_t^o(i)$, of solute i from water to the nonaqueous solvent. Clearly, $G_t^o(i)$ can be calculated from ${}_m\gamma_i$, and vice versa.

B. Transfer Activity Coefficients and Electrode Potentials

Standard free energy and standard electrode potential, E^o, are linked by the expression

$$G^o = -nFE^o \qquad (8)$$

where n is the number of equivalents/mole in the electrode reaction and F is the Faraday constant. Combining equations (7) and (8) we find

$${}_sE^o - {}_wE^o = -RT/nF \ \ln {}_m\gamma_i \qquad (9)$$

If the standard potential of an electrolytic cell with solvent s and that of the corresponding aqueous cell are kno the transfer activity coefficient of i can be calculated from equation (9).

C. The Alkali-Metal Amalgam Cell

Consider the cell

$$M(Hg)\,|\,M^+,Cl^-(\text{solvent})\,|\,AgCl;Ag \qquad (I)$$

where M(Hg) is an alkali-metal amalgam and M^+,Cl^- are the ions from the metal chloride. The expression for the cell

potential, E, in the solvent is

$$E = {}_sE^{o}_{AgCl} - {}_sE^{o}_{M(Hg)} - \frac{RT}{nF} \ln \frac{a^{*}_{M} a^{*}_{Cl}}{a_{M(Hg)}} \qquad (10)$$

where $a_{M(Hg)}$ is the activity coefficient of the metal, M, in the amalgam. For convenience we can write

$$k = 2.3026\ RT/nF \qquad (11)$$

and

$$E^{o'} = {}_sE^{o}_{AgCl} - {}_sE^{o}_{M(Hg)} + k \log a_{M(Hg)} \qquad (12)$$

and rewrite equation (10), using activity coefficients, in the form

$$E = E^{o'} - 2k(\log m + \log {}_s\gamma_{\pm}) \qquad (13)$$

To include the possibility of incomplete dissociation, m must be replaced by αm, where α is the degree of dissociation. Expressing $\log {}_s\gamma_{\pm}$ as a function of ionic strength, I, equation (13) can be written

$$E + 2k \log(\alpha m) = E^{o'} + 2kAI^{1/2} \qquad (14)$$

A plot of the left side of equation (14) versus $I^{1/2}$ yields a straight line with a slope of 2kA and intercept $E^{o'}$. Therefore, measurements of the cell potential at

various salt concentrations are sufficient to calculate the standard cell potential and activity coefficients of the salt in the solvent.

D. Calculations from EMF Measurements

Using equation (14), it is possible to determine the cell potential of both aqueous and nonaqueous cells. To find the medium effect for the metal chloride, equation (9) can be used in the form

$$\log {}_m\gamma_{MCl} = \frac{{}_wE^o - {}_sE^o}{k} \qquad (15)$$

Substituting this medium effect into equation (7), the transfer free energy can be calculated.

If we combine cell (I) with

$$M|M^+(\text{aprotic solvent})|M(Hg) \qquad (II)$$

we get

$$M|M^+,Cl^-(\text{solvent})|AgCl;Ag \qquad (III)$$

and $E^o_{III}=E^o_I+E^o_{II}$, since E^o_{II} is solvent-independent. Note that E^o_{III} is the standard potential of the alkali metal versus the reference electrode in the solvent of interest, a quantity not directly measureable for these metals in protic solvents.

If we now add

$$Ag;AgCl|H^+,Cl^-(solvent)|H_2;Pt \qquad (IV)$$

to cell (III) we have

$$M|M^+,H^+(solvent)|H_2;Pt \qquad (V)$$

where $E^o_V=E^o_I+E^o_{II}+E^o_{IV}$, and E^o_V is the standard potential of the metal versus the standard hydrogen electrode in the nonaqueous solvent.

The values of E^o_{II} and E^o_{IV} will be taken from literature sources for combination with the experimentally determined $E^{o'}$.

E. Previous Work at 25 °C

Lithium: The first experimental measurements of the standard reduction potential of lithium in aqueous solutions were carried out by Lewis and Keyes(1), using a cell with liquid junction. Akerlof(2) introduced the nonaqueous double cell to measure activity coefficients of LiCl in methanol-water solutions. As we shall see, the double cell became a popular method for these measurements and took the general form

$$Ag;AgCl|M^+,Cl^-(aq)|M(Hg)|M^+,Cl^-(nonaq)|AgCl;Ag \qquad (VI)$$

with M representing the alkali metal, as before. In this set-up, the amalgam acts as a bridge without liquid junction between the aqueous and nonaqueous side. This is ac-

complished by having twin streams from the same amalgam simultaneously enter each side of the cell. Scrosati, Schiavo and Pecci(3) used this type of cell to measure the standard free energy of transfer of LiCl from methanol to water. This was followed by a similar study in methanol-water mixtures by Feakins and co-workers(4), who also calculated transfer free energies from Akerlof's data.

Butler and Cogley(5) studied the potential of lithium versus lithium amalgams of various concentrations in the cell

$$Li|Li^+,X^-(S)|Li(Hg) \qquad (VII)$$

where $X=Cl^-$ or ClO_4^- and S=DMSO. They calculated the standard potential of lithium versus an infinitel dilute lithium amalgam, as well as the activity coefficient for lithium in lithium amalgams of various concentrations. Butler and Huston(6) measured the standard potential of the cell

$$Pt;H_2|Li^+,OH^-,H_2O|Li(Hg) \qquad (VIII)$$

and combined it with the result of Butler and Cogley to get a value for the standard potential of lithium in aqueous solutions without liquid-junction error. Mussini and co-workers(7) redetermined these potentials and activity

coefficients, using propylene carbonate instead of DMSO in cell (VII) and aqueous solutions in cell (I).

Sodium: Lewis and Kraus(8) determined the aqueous reduction potential of sodium in a cell with liquid junction. Smith and Taylor(9) used a 0.065% sodium amalgam in an aqueous cell (I) and in the cell

$$Na_{(s)}|NaI(dimethylamine)|Na(Hg) \qquad (IX)$$

to measure the same quantity in the absence of any liquid junction.

Akerlof(2) and Feakins(4) made the same measurements and calculations with sodium as they did with lithium, yielding activity coefficients and standard free energies of transfer for NaCl in methanol-water mixtures. Gladden and Fanning(10) used the double cell to measure the standard free energy of transfer of NaCl in pure methanol.

An extensive study of the activity of sodium in sodium amalgams was performed by Bent and Swift(11), using dimethylamine in cell (VII). They developed a formula relating the sodium activity to the mole fraction of sodium in the amalgam.

Potassium: Lewis and Keyes(12) determined the aqueous standard potential of potassium by the method used for their lithium work. Armbruster and Crenshaw(13) studied the potential of aqueous cells of the form

$$K(c2)(Hg)|K^+,Cl^-|K(c1)(Hg) \qquad (X)$$

where c1 and c2 are amalgams of different potassium concentration, to calculate the activity of potassium in each of these amalgams. They also measured the potential of their amalgams versus silver-silver chloride and calomel electrodes in aqueous solutions, combining these data with Lewis and Keyes' potential of K versus K(Hg) to obtain the standard potential of potassium without liquid junction. Brauer and Strehlow(14) remeasured the potential of potassium amalgam versus the silver-silver chloride electrode and used the same Lewis and Keyes result to calculate a new aqueous E.

Akerlof(2), Feakins(4), and Gladden and Fanning(10) each reported data for KCl analogous to their work with NaCl. Scrosati, Schiavo and Pecci(3) considered Gladden and Fanning's KCl data too scanty and redetermined the transfer free energy of KCl in methanol, using cell (VI). Malahias and Popovych(15) recently reported two sets of data for the transfer free energy of KCl over the entire range of methanol-water solvents. One set of data was based on their solubility studies and the other on the standard potential of cells using a glass potassium ion-selective electrode versus a calomel reference electrode.

Izmaylov's(16) measurement of E_K^o in ethanol was quickly followed by the extensive work of Dill, Itzkowitz

and Popovych(17), using cell (I) over the whole range of ethanol-water solvents. These workers reported the standard potential of potassium in each solvent and determined the transfer free energy and salt-effect activity coefficients of KCl in the nonaqueous solvents.

F. This Work

The experiments reported here followed the method of Dill, Itzkowitz and Popovych(17), where they studied KCl in ethanol-water solvents. For NaCl and LiCl, however, standard potentials, activity coefficients and transfer free energies in ethanol-water solvents have not been reported elsewhere; these data were prime objectives of this study.

The preceding section shows that transfer free energies of these alkali-metal chlorides in methanol-water solvents have been previously investigated to some extent, but standard potentials in these systems have not been reported. This study complements the transfer free energy data for methanol-water systems and reports the calculation of the standard potential of the alkali metals and activity coefficients of the alkali-metal chlorides.

II. Experimental

A. Preparation of Electrodes

The silver-silver chloride reference electrodes were made according to the procedure for thermal-electrolytic preparation outlined by Bates(18). Briefly, freshly made and well-rinsed silver oxide paste was applied to a platinum wire helix and heated at 450 ^{o}C for 1/2 hour to decompose the brown silver oxide to white silver. Then, the silver was electrolyzed in 1.0 N HCl to convert some silver to silver chloride, turning the electrode dark gray. To prepare HCl free of impurities that could poison the electrodes, the aqueous 20.2 weight % HCl azeotrope was double-distilled in glass and the middle fractions collected. The final product was then diluted to 1.0 N for the electrolysis.

The electrodes aged for at least one day in deaerated 0.05 N HCl and then their voltages were compared. A group of electrodes agreeing within better than 0.1 millivolt was found, along with several electrodes that were several tenths of a millivolt higher or lower than the former and did not agree with any others. The latter were rejected.

B. Materials

Fisher Certified ACS Spectroanalyzed Methanol was

used without further purification to prepare the methanol-water mixtures. The water used was deionized and had a specific conductance of 2×10^{-7} to 4×10^{-7} mho/cm.

Anhydrous methanol was prepared by refluxing four liters of Fisher Spectroanalyzed or Baker "Photrex" Reagent absolute methanol over 25 grams of aluminum powder and 5 grams of mercuric chloride(which form an aluminum amalgam) for 24 hours and then distilling through a 22-cm Vigreaux column, collecting the middle three liters. Each batch of the aluminum amalgam was used for two 4-liter charges. The anhydrous methanol thus prepared had a density of 0.7865g./ml. at 25 ^{o}C, in agreement with literature values of 0.78654g./ml.(19) and 0.7866g./ml.(20).

USP 95% Ethanol was distilled twice in an all-glass still, collecting only middle fractions, before being used for ethanol-water solvents.

Anhydrous ethanol was made from Rossville Gold Shield Reagent 200 proof ethanol in the following manner. A 300-ml portion of the ethanol was refluxed over 24 grams of Mg turnings for three hours, with a crystal of iodine added to initiate the formation of magnesium ethoxide. The Mg was then rinsed with additional ethanol and 5 liters of ethanol were refluxed over it for 24 hours, forming a suspension of white magnesium ethoxide. The ethanol was slowly distilled through a 25-cm vigreux column, collecting only the middle 3 liters. A slow

stream of dry argon gas was bubbled into the ethanol during refluxing and distillation. The ethanol product had a density of 0.7850 g./ml. at 25 ^{o}C, in agreement with literature values of 0.7850 g./ml.(21) and 0.785058 g./ml.(22).

The argon gas(Liquid Carbonic) used for distillation and solution deaeration was 99.998% pure. The hydrogen(Liquid Carbonic) was 99.99% pure and passed through an Engelhard Deoxo Gas Purifier containing a catalyst to remove oxygen by reaction with the hydrogen to form water. The gases were dried by passage through a tube of Linde 5A molecular sieves. When bubbling into a solution, the dried gases were first passed through a bubbling column containing the solvent to avoid evaporation of the solvent from the solution.

Solvent density was measured by using 100-ml. volumetric flasks. They were first calibrated by equilibrating the previously weighed flasks, filled with water, in a 25.00 ^{o}C bath and then adjusting the water level to the mark and weighing them. The procedure was repeated with the flasks filled with each of the nonaqueous solvents. Both the aqueous and non-aqueous measurements were done in triplicate. The density of the solvent was then calculated by comparing the weights of the equal volumes of solvent and water. All weight measurements were corrected to weight in vacuo using standard buoyancy for-

mulas.

Fisher Certified ACS reagent-grade LiCl, NaCL, KCl, LiOH, NaOH and KOH were used without further purification. The chlorides were oven-dried before use.

C. Preparation of Solutions

The solutions were generally prepared by adding accurately weighed(to ±0.2mg) portions of salt(between 0.1g and 0.5g) to the calibrated volumetric flasks and filling each flask to the mark with the solvent. The only exception was the sodium chloride in absolute ethanol, due to the low solubility. In this case, a relatively concentrated solution of NaCl was diluted to prepare the other solutions by pipeting specific amounts into the flasks and filling each to the mark with ethanol. (The pipets were calibrated in quadruplicate.) It was necessary to determine the concentration of the stock solution by gravimetric chloride analysis. Silver nitrate solution was used to precipitate silver chloride following the procedure of Waser(23).

The absolute methanol and ethanol solutions were prepared in an inert dry-box atmosphere to avoid absorption of water.

D. Measurements

The alkali-metal amalgams were prepared as follows. Triple-distilled mercury and a 1.0 N solution of the al-

kali metal hydroxide were poured into a separatory funnel. Platinum wire electrodes were inserted into the mercury and the aqueous phase. Current was passed through, with the mercury acting as the cathode, to reduce the solution's metal ions to atoms in the mercury phase. Argon gas was bubbled into the mercury to stir and deaerate the system during the amalgamation. Immediately after the current was stopped, the bulk of the amalgam was drawn from the bottom of the flask into a dry, evacuated storage vessel.

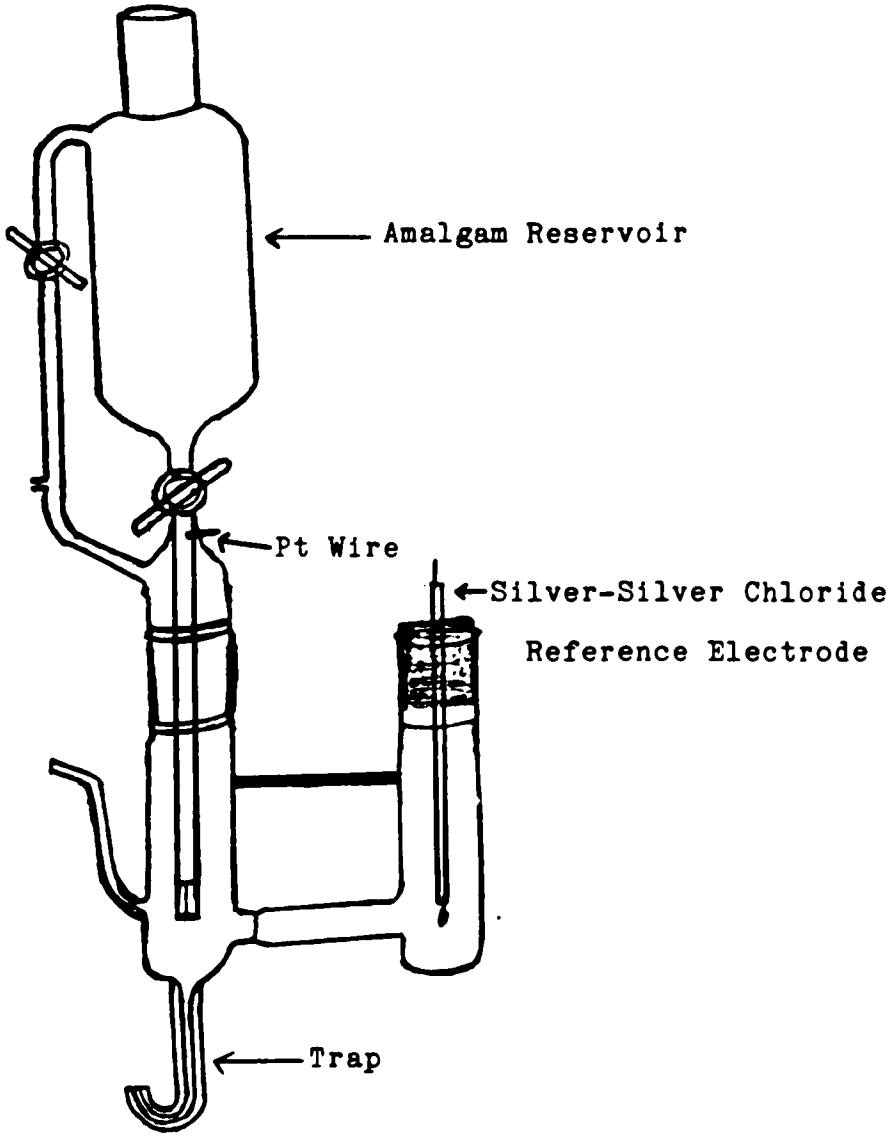
The amalgam was transferred in a dry argon atmosphere directly to the glassware(Figure I) that would serve as the dropping-amalgam electrode. A piece of 1/4" o.d. glass capillary was attached at the bottom by means of a segment of Tygon tubing. A platinum wire sealed into the side of the glass served as the electrical connection between the amalgam and the outside. For sodium and potassium amalgams, a 1.5-cm piece of Sargent-Welch 2-5 sec polarographic capillary(S-29419) was used and produced approximately 2 drops/second. The lithium amalgam required a larger i.d. because it was more reactive and tended to clog the capillary. A Wilmad .005" i.d. glass capillary was used for the lithium amalgams.

The salt solutions were contained in the cell shown in Figure I. A fritted glass disk separated the amalgam side and the reference side, both containing the same

solution, to prevent the solvent-saturated hydrogen gas used to deaerate the amalgam side during the run from affecting chemically the reference electrode. The reference side was deaerated by solvent-saturated argon prior to each measurement. During measurements, the cell was submerged in a constant-temperature bath maintained at 25.00±0.01 ^{o}C with a YSI Model 72 temperature controller and a thermometer graduated in hundredths of a degree.

The voltage was measured with an Electro Scientific Industries potentiometer(Model 300) connected to the reference electrode and the platinum wire of the amalgam electrode. This meter is capable of readings to the nearest tenth of a millivolt in the voltage range used. Readings were taken about every five minutes until two consecutive readings matched within ±0.1mV. This generally took between 20 and 40 minutes. These readings remained stable for at least another 20 minutes.

Figure I : Experimental Cell



III. Results

In this chapter, both experimental and calculated results will be presented. Appendix I lists the experimental data and calculated activity coefficients for each solution. Chapter IV will discuss the uncertainties of these data, and other relevant points.

Most of the systems studied here do not involve ion association. For those that do, values of the degree of dissociation, α, have been calculated for each solution. The calculation of these degrees of dissociation requires values for the association constant, K_a, of the solute in a given solvent, the ion-size parameter, $\underline{a}$, and the Debye-Huckel constants, $\underline{A}$ and $\underline{B}$. The latter are calculated, at 25 ^{o}C, from these equations:

$$A = (354.69/D^{3/2})\ 1.^{1/2}\ \text{mole}^{-1/2} \qquad (16)$$

$$B = (2.9132\text{x}10^{8}/D^{3/2})\ 1.^{1/2}\ \text{mole}^{-1/2}\ \text{cm.}^{-1} \qquad (17)$$

where $\underline{D}$ is the dielectric constant of the solvent. Values of K_a and $\underline{a}$ come from the literature(24,25,26).

The degree of dissociation for each solution is calculated from

$$\alpha = \frac{-1+(1+4cf_{\pm}^{2}K_a)^{1/2}}{2K_a cf_{\pm}^{2}} \qquad (18)$$

where c is the molar concentration, and $f_{\pm}$ the mean molar activity coefficient, of the solute. The latter is estimated by the extended Debye-Huckel equation

$$-\log f_{\pm} = \frac{AI^{1/2}}{1+BaI^{1/2}} \qquad (19)$$

The ionic strength, I, is calculated from

$$I = 0.5 \Sigma m_i z_i^2 \qquad (20)$$

where z_i is the charge, and m_i the molality, of each ion, i. As a first approximation, each $I^{1/2}$ was calculated on the assumption of $\alpha=1$. The α calculated for each solution was then used to compute a more accurate value of $I^{1/2}$; the calculations were repeated using these new values in equation (19) to generate new values of $f_{\pm}$ for equation (18). Additional cycling produced no significant change(<.001 units) in the new α values.

Values of $\log \gamma_{\pm}$, the salt-effect activity coefficient, are listed in Appendix I for each solution and were calculated via equation (13) in the form

$$\log \gamma_{\pm} = \frac{E^{o'}-E}{2k} - \log(\alpha m) \qquad (21)$$

Conversion of molal standard free energies of

transfer for electrolyte i to the molar scale utilized the relationship

$$\text{Molar } G_t^o(i) = \text{molal } G_t^o(i) - 2RT \ln(\rho_s/\rho_w) \qquad (22)$$

where ρ_s and ρ_w are the densities of the solvent and water, respectively.

A. Lithium

Four separate experiments with aqueous lithium chloride solutions in cell (I) were performed to determine the standard cell potential in water. These results and the corresponding results for the ethanol-water and methanol-water systems are listed in Tables I-III. (See Appendix I for data on individual solutions.)

Calculation of the standard cell potential, E_I^o, from the experimentally determined quantity, $E^{o'}$, required the use of literature(7) values for the activity coefficients of lithium in its amalgams as a function of concentration. These activities are referred to a standard state of infinitely dilute lithium amalgam. The average of the four standard aqueous cell potentials is 2.4134 Volts, with a standard deviation of ±0.5 millivolts.

The quantity E_{II}^o=0.8480 Volt(7) was combined with E_I^o to produce E_{III}^o. The average aqueous E_{III}^o=3.2614 Volts. The corresponding E^o's for the nonaqueous solvents are

listed in Table II.

Table I

Parameters of Experimental Lines for LiCl Systems

Solvent	Slope	A	$E^{o'}$ (Volts)
Aqueous			
	0.0562+.0013	0.475	2.2192+.0008
	0.0631+.0044	0.533	2.2184+.0008
	0.0576+.0023	0.487	2.2314+.0004
	0.0552+.0021	0.467	2.2319+.0004
Wt % Ethanol			
10.0	0.1145+.0038	0.968	2.1900+.0007
20.1	0.1254+.0048	1.060	2.1765+.0009
30.4	0.1261+.0077	1.066	2.1708+.0014
40.3	0.1309+.0046	1.107	2.1350+.0009
49.9	0.1195+.0041	1.010	2.1297+.0007
60.3	0.1096+.0055	0.927	2.0845+.0011
70.3	0.1764+.0070	1.491	2.0762+.0013
80.4	0.1353+.0083	1.144	2.0454+.0017
90.4	0.2127+.0062	1.798	1.9752+.0012
100.0	0.3948+.0016	3.338	1.9102+.0014
Wt % Methanol			
30.0	0.0692+.0024	0.585	2.1748+.0005
50.3	0.0772+.0049	0.652	2.1301+.0009
69.9	0.0802+.0013	0.678	2.1081+.0002
90.0	0.1758+.0047	1.486	2.0713+.0009
100.0	0.1800+.0079	1.522	2.0581+.0017

Table II

Standard Cell Potentials for the LiCl Systems

solvent	Wt % Li(Hg)	Log a_{Li}	E^{o}_{I} (V.)	E^{o}_{III} (V.)
Aqueous				
	0.00184	-3.266	2.4126	
	0.00170	-3.301	2.4139	
	0.00284	-3.074	2.4135	
	0.00289	-3.066	2.4135	
Wt % Ethanol				
10.0	0.00132	-3.415	2.3920	3.2400
20.1	0.00159	-3.333	2.3737	3.2217
30.4	0.00276	-3.091	2.3536	3.2016
40.3	0.00135	-3.405	2.3364	3.1844
49.9	0.00210	-3.211	2.3197	3.1677
60.3	0.00081	-3.628	2.2992	3.1472
70.3	0.00196	-3.241	2.2680	3.1160
80.4	0.00248	-3.138	2.231	3.079
90.4	0.00112	-3.487	2.181	3.029
100.0	0.00348	-2.988	2.087	2.935
Wt % Methanol				
30.0	0.00143	-3.380	2.3747	3.2227
50.3	0.00087	-3.597	2.3429	3.1909
69.9	0.00110	-3.495	2.3148	3.1628
90.0	0.0141	-3.386	2.2716	3.1196
100.0	0.00323	-3.021	2.2368	3.0848

Table III

Medium Effects for LiCl in Ethanol-Water and Methanol-Water Solvents

solvent	Log $\gamma_{m_{LiCl}}$	ΔG_t^o	
		Molal	Molar
Wt % Ethanol			
10.0	0.362	0.493	0.513
20.1	0.671	0.915	0.952
30.4	1.011	1.379	1.436
40.3	1.302	1.775	1.857
49.9	1.584	2.160	2.268
60.3	1.930	2.633	2.773
70.3	2.46	3.35	3.52
80.4	3.08	4.20	4.41
90.4	3.92	5.35	5.59
100.0	5.52	7.53	7.81
Wt % Methanol			
30.0	0.654	0.892	0.952
50.3	1.192	1.625	1.731
69.9	1.667	2.273	2.439
90.0	2.397	3.269	3.508
100.0	2.985	4.072	4.353

B. Sodium

The results for the solutions of sodium chloride are shown in Tables IV-VI (and Appendix I). The data(11) for the activity of sodium in its amalgams are referred to sodium metal as the standard state, so that E^{o}_{III} is calculated directly from $E^{o'}$, and the amalgam activities, without requiring a standard potential for cell (II).

The standard potential for the sodium electrode(Na/Na^{+}) in water was reported by Smith and Taylor as -2.7132 Volts(9). This value was used here to calculate medium effects in the nonaqueous systems.

Table IV

Parameters of Experimental Lines for NaCl Systems

Wt % Ethanol	Slope	A	$E^{o'}$ (Volts)
10.1	0.0584+.0012	0.494	1.9927+.0002
20.4	0.0524+.0019	0.443	1.9627+.0004
30.8	0.0633+.0018	0.535	1.9398+.0003
40.6	0.0765+.0031	0.647	1.9202+.0006
50.5	0.0941+.0030	0.795	1.8935+.0006
60.6	0.0986+.0013	0.833	1.8706+.0003
69.9	0.1111+.0010	0.939	1.8394+.0002
80.0	0.1119+.0022	0.946	1.7896+.0005
90.5	0.253+.011	2.14	1.7118+.0019
100.0	0.334+.014	2.83	1.6299+.0011
Wt % Methanol			
69.8	0.0951+.0026	0.804	1.8678+.0004
100.0	0.1645+.0067	1.390	1.7908+.0013

Table V

Standard Cell Potentials for the NaCl Systems

Wt % Ethanol	Wt % Na(Hg)	Log a_{Na}	E^{o}_{III} (V.)
10.1	0.0177	-15.602	2.9157
20.4	0.0124	-15.764	2.8953
30.8	0.0128	-15.749	2.8715
40.6	0.0142	-15.702	2.8491
50.5	0.0138	-15.715	2.8232
60.6	0.0155	-15.662	2.7972
69.9	0.0167	-15.628	2.7640
80.0	0.0112	-15.809	2.7249
90.5	0.0127	-15.753	2.644
100.0	0.0128	-15.749	2.562
Wt % Methanol			
69.8	0.0150	-15.677	2.7953
100.0	0.0165	-15.634	2.7157

Table VI

Medium Effects for NaCl in Ethanol-Water and Methanol-Water Solvents

Wt % Ethanol	Log γ_{mNaCl}	ΔG_t^o	
		Molal	Molar
10.1	0.335	0.457	0.477
20.4	0.680	0.927	0.965
30.8	1.082	1.476	1.534
40.6	1.469	1.992	2.074
50.5	1.898	2.589	2.699
60.6	2.338	3.189	3.300
69.9	2.899	3.954	4.124
80.0	3.560	4.856	5.061
90.5	4.93	6.73	6.97
100.0	6.32	8.62	8.90
Wt % Methanol			
69.8	2.370	3.232	3.396
100.0	3.715	5.068	5.349

C. Potassium

The data on potassium chloride are shown in Tables VII-IX (and Appendix I). The activity coefficients of potassium amalgams are taken from Armbruster and Crenshaw(13), and refer to a standard state of infinitely dilute amalgam. The standard potential of cell (I) in water has been reported(17) as 2.1932±.0005 Volts(molal scale). The E^{o}_{II} for potassium calculated(17) from the data of Lewis and Kraus(12) is 0.9521 Volt.

Table VII

Parameters of Experimental Lines for KCl Systems

Wt % Methanol	Slope	A	$E^{o'}$ (Volts)
28.9	0.0689+.0024	0.582	1.9761+.0005
49.7	0.0647+.0028	0.547	1.9335+.0005
70.1	0.1025+.0013	0.867	1.8779.0003
90.6	0.1277+.0043	1.080	1.8413+.0008
100.0	0.1504+.0052	1.271	1.8012+.0009

Table VIII

Standard Cell Potentials for the KCl Systems

Wt % Methanol	Wt % K(Hg)	Log a_K	E^o_I (V.)	E^o_{III} (V.)
28.9	0.0293	-2.769	2.1399	3.0920
49.7	0.0281	-2.804	2.0994	3.0515
70.1	0.0227	-2.893	2.0490	3.0011
90.6	0.0449	-2.569	1.9933	2.9454
100.0	0.0283	-2.785	1.966	2.918

Table IX

Medium Effects for KCl in Methanol-Water Solvents

Wt % Methanol	Log γ_{mKCl}	ΔG^o_t	
		Molal	Molar
28.9	0.901	1.229	1.286
49.7	1.586	2.163	2.268
70.1	2.438	3.325	3.491
90.6	3.379	4.609	4.850
100.0	3.840	5.238	5.519

IV. Discussion

A. Uncertainties

Voltage Measurements: The silver-silver chloride reference electrode potentials agreed to better than ±0.1mV. and the voltage bridge was accurate to ±0.1mV., so the maximum uncertainty of each reading is ±0.2mV.

Solutions: The uncertainty in the weight of salt for each solution varied from one to two parts per thousand. The solution volumes were ±1ppt. An error of 3ppt in solution concentration produces an error of 1.5ppt in $I^{1/2}$, according to the equation(23)

$$(x + dx)^{1/2} = (1 + dx/2)\ x^{1/2} \qquad (23)$$

where dx is the uncertainty in the quantity, x. The insignificance of this uncertainty, as compared to the accuracy of the voltage measurements, can be shown by consideration of the change in voltage with a change in I. The slopes listed in the Tables of chapter III show these variations. Even for the steepest slope of 0.395 in Table I, and a large $I^{1/2}$=0.2000, a change of 1.5ppt in $I^{1/2}$ would mean a difference of only 0.1mV. For lesser slopes and less concentrated solutions this uncertainty is even smaller.

Solvent Density: The precision of each density meas-

urement was well within ±0.1ppt. The interpolation of the weight percent alcohol from the solvent density is accurate to 0.1 weight % absolute error.

Alpha corrections: The uncertainty of the degree of dissociation stems from the uncertainties in K_a and $\underline{a}$, the ion-size parameter, which were evaluated in the original references(24,25,26). The largest of these uncertainties, in both absolute and relative terms, are those for solutions of LiCl in 100% ethanol.

In order to test the propagation of these errors to $E^{o'}$, the calculation of each α was repeated using values of K_a and $\underline{a}$ that differed from the previous ones by their respective uncertainties. The $E^{o'}$ was then recalculated using these α values. For solutions of LiCl in 100% ethanol, the α values differed from those in Table XI by from 0.013 units to 0.020 units and the $E^{o'}$ varied by 0.5mV. Table X lists the uncertainties of these degrees of dissociation, and the uncertainty of log $\gamma_{\pm}$, which will be discussed below.

For the other associated systems, the uncertainty of every α was <0.003 units, yielding an uncertainty in $E^{o'}$ of only ±0.1mV. in each case.

Table X

Uncertainties - LiCl in 100% Ethanol

M	α	Log $\gamma_\pm$
0.01371	0.915±.013	-0.420±.035
0.01493	0.912±.014	-0.434±.037
0.01960	0.902±.015	-0.505±.041
0.02189	0.897±.016	-0.529±.044
0.02527	0.891±.017	-0.571±.046
0.02869	0.886±.018	-0.598±.048
0.03465	0.878±.020	-0.653±.055

Determination of $E^{o'}$: While the uncertainty of each voltage measurement is only 0.2mV., as noted above, the extrapolation of the experimental line to I=0 leads to a greater error in $E^{o'}$. This error decreases as the number of points, and their internal ageement, increase. The uncertainty of each $E^{o'}$ resulting from the extrapolation is listed with $E^{o'}$ in Tables I, IV and VII.

The additional uncertainties for the associated systems, $d(E_1^{o'})$, can be combined with these errors, denoted by $d(E_2^{o'})$, to determine the total uncertainty in $E^{o'}$, $d(E^{o'})$, from the equation

$$d(E^{o'})=(d(E_1^{o'})^2+d(E_2^{o'})^2)^{1/2} \qquad (24)$$

These uncertainties are listed in Table XI.

Table XI

Uncertainties of $E^{o'}$ and $\log \gamma_{\pm}$

LiCl	Systems	$E^{o'}$ (Volts)	$d(\log \gamma_{\pm})$
10.0%	Ethanol	2.1900±.0007	0.006
20.1%	"	2.1765±.0009	0.008
30.4%	"	2.1708±.0014	0.012
40.3%	"	2.1350±.0009	0.008
49.9%	"	2.1297±.0007	0.006
60.3%	"	2.0845±.0011	0.009
70.3%	"	2.0762±.0013	0.011
80.4%	"	2.0454±.0017	0.014
90.4%	"	1.9752±.0012	0.010
100.0%	"	1.9102±.0015	
30.0%	Methanol	2.1748±.0005	0.004
50.3%	"	2.1301±.0009	0.008
69.9%	"	2.1081±.0002	0.003
90.0%	"	2.0713±.0009	0.008
100.0%	"	2.0581±.0017	0.014

Table XI (continued)

NaCl Systems		
10.1% Ethanol	1.9927±.0002	0.003
20.4% "	1.9627±.0004	0.003
30.8% "	1.9398±.0003	0.003
40.5% "	1.9202±.0006	0.005
50.5% "	1.8935±.0006	0.005
60.6% "	1.8706±.0003	0.003
69.9% "	1.8394±.0002	0.003
80.0% "	1.7896±.0005	0.004
90.5% "	1.7118±.0019	0.016
100.0% "	1.6299±.0011	0.009
69.8% Methanol	1.8678±.0004	0.003
100.0% "	1.7908±.0013	0.011
KCl Systems		
28.9% Methanol	1.9761±.0005	0.004
49.7% "	1.9335±.0005	0.004
70.1% "	1.8779±.0003	0.003
90.6% "	1.8413±.0008	0.007
100.0% "	1.8012±.0009	0.008

Log $\gamma_{\pm}$: From equation (21) it follows that the uncertainty of log $\gamma_{\pm}$, d(log $\gamma_{\pm}$), derives from the uncertainties of $E^{o'}$, E and log (αm) (denoted by d($E^{o'}$), d(E), and d(log (αm)), respectively) in the following manner:

$$d(\log \gamma_{\pm})=[(d(E^{o'})/.1183)^2+(d(E)/.1183)^2+(d(\log(\alpha m))^2]^{1/2} \quad (25)$$

The term $d(\log(\alpha m))$ in equation (25) is negligible for systems without ion association. With the exception of the 100% ethanol - LiCl system, the uncertainty of the product (αm) is ±5ppt for all the associated systems; this results in $d(\log(\alpha m)) = 0.002$. Recalling that $d(E)=$ 0.2mV., and taking each $d(E^{o'})$ from Table XI, $d(\log \gamma_{\pm})$ can be calculated for each system; these values are listed in Table XI. Separate values must be calculated for each solution of LiCl in 100% ethanol since here each α has a different uncertainty; these are shown in Table X.

Amalgam Activities: There are three sources of uncertainty in the determination of amalgam activity: weighing of the amalgam sample; titration of the amalgam sample to determine the number of milliequivalents of the alkali metal; determination of amalgam activity as a function of concentration from literature data.

The first source of error amounts to only ±1ppt(±0.1g./100g.). The titration error is ±0.04ml., which is 20ppt for the more dilute lithium amalgams and 7ppt for the sodium and potassium amalgams. Each determination was done in triplicate and the average value was used. The uncertainty of this average is $[3(dx)^2]^{1/2}/3 = 0.58(dx)$, where dx is the relative error of a single determination. For the lithium amalgams, this uncertainty

is ±1%, or about 0.2mV. in $E^{o'}$. The sodium and potassium amalgam concentration error is ±4ppt, or ±0.1mV. in the standard potential of cell (I) or cell (III).

The additional uncertainty in calculating log a_M from the amalgam concentration with the literature equations for the lithium(7) and sodium(11) amalgams is negligible, since the dominant error in these calculations is the mole fraction(concentration) of the amalgam. Each potassium(13) amalgam activity is interpolated from a plot of activity versus mole fraction; the uncertainty of this interpolation is ±1%, or ±0.004 in log a_K. This propagates to ±0.3mV. for the standard potential of cells (I) and (III).

Standard Potential of Cells (II) and (III): The standard potential of cell (III) for the lithium and potassium amalgams includes the uncertainty of E^o_{II}, which comes from the literature(7,24). In both instances, the uncertainty of E^o_{II} is ±0.2mV.

The total uncertainty of E^o_{III} includes the uncertainties of both E^o_I and E^o_{II}, and the uncertainty of E^o_I is the combined errors of $E^{o'}$ and the amalgam activity. Therefore, the uncertainty of E^o_{III}, $d(E^o_{III})$, can be calculated from

$$d(E^o_{III})=[d(E^{o'})^2+d(E^o_{II})^2+d(.05916\log a_M)^2)^{1/2} \qquad (26)$$

The calculated values of E^{o}_{I} and $E^{o}_{III}+d(E^{o}_{III})$ are shown in Table XII.

Table XII

Standard Potentials of Cells (I) and (III)

LiCl	Systems	E^{o}_{I}(Volts)	E^{o}_{III}(Volts)
10.0%	Ethanol	2.3920	3.2400±.0008
20.1%	"	2.3737	3.2217±.0009
30.4%	"	2.3536	3.2016±.0014
40.3%	"	2.3364	3.1844±.0009
49.9%	"	2.3197	3.1677±.0008
60.3%	"	2.2992	3.1472±.0011
70.3%	"	2.2680	3.1160±.0013
80.4%	"	2.2310	3.0790±.0017
90.4%	"	2.1815	3.0295±.0012
100.0%	"	2.0870	2.9350±.0015
30.0%	Methanol	2.3747	3.2227±.0006
50.3%	"	2.3429	3.1909±.0009
69.9%	"	2.3148	3.1628±.0003
90.0%	"	2.2716	3.1196±.0009
100.0%	"	2.2368	3.0848±.0017

Table XII (continued)

NaCl Systems		
10.1% Ethanol		2.9157±.0002
20.4% "		2.8953±.0004
30.8% "		2.8715±.0003
40.6% "		2.8491±.0006
50.5% "		2.8232±.0006
60.6% "		2.7972±.0003
69.9% "		2.7640±.0002
80.0% "		2.7249±.0005
90.5% "		2.6437±.0019
100.0% "		2.5616±.0011
69.8% Methanol		2.7157±.0013
100.0% "		2.7157±.0013
KCl Systems		
28.9% Methanol	2.1941	3.0920±.0006
49.7% "	2.0994	3.0515±.0006
70.1% "	2.0490	3.0011±.0005
90.6% "	1.9933	2.9454±.0008
100.0% "	1.9660	2.9181±.0009

Medium Effects: The expressions for the uncertainties of $\Delta G_t^o(MCl)$, dG, and $\log {}_m\gamma_{MCl}$, dm, are derived directly from equations (7) and (15):

$$dm = [(d({}_wE^o)/k)^2+(d({}_sE^o)/k)^2]^{1/2} \qquad (27)$$

$$dG = (2.3026\ RT)(dm) \qquad (28)$$

The uncertainty of the standard potential of cell (I) in water is ±0.5mV. for both the lithium chloride and potassium chloride solutions, as noted in chapter III. The standard potential of the sodium cell (III) in water (2.9355 V.) was calculated from the literature(9) standard potential of the sodium electrode(Na/Na^+) in water and the literature(18) standard potential of the silver-silver chloride reference electrode in water(0.22234 V.). These values introduce an uncertainty of no more than ±0.1mV.

The values of $\log \gamma_m$ and ΔG_t^o for each system, and their uncertainties, are summarized in Table XIII.

Table XIII

Medium Effects

LiCl Systems	$\log \gamma_m$	ΔG_t^o(kcal/mole)	
		Molal Scale	Molar Scale
10.0% Ethanol	0.362±.008	0.493±.011	0.513
20.1% "	0.671±.009	0.915±.012	0.952
30.4% "	1.011±.013	1.379±.017	1.436
40.3% "	1.302±.009	1.775±.012	1.857
49.9% "	1.584±.008	2.160±.011	2.268
60.3% "	1.930±.010	2.633±.014	2.773
70.3% "	2.46 ±.012	3.35 ±.016	3.52
80.4% "	3.08 ±.02	4.20 ±.02	4.41

90.4%	"	3.92 ±.011	5.35 ±.02	5.59
100.0%	"	5.52 ±.02	7.53 ±.02	7.81
30.0%	Methanol	0.654±.007	0.892±.009	0.952
50.3%	"	1.192±.009	1.625±.012	1.731
69.9%	"	1.667±.005	2.273±.007	2.439
90.0%	"	2.397±.009	3.269±.012	3.508
100.0%	"	2.985±.015	4.07 ±.02	4.35
NaCl Systems				
10.1%	Ethanol	0.335±.003	0.457±.004	0.477
20.4%	"	0.680±.003	0.927±.005	0.965
30.8%	"	1.082±.003	1.476±.004	1.534
40.6%	"	1.460±.005	1.992±.007	2.074
50.5%	"	1.898±.005	2.589±.007	2.699
60.6%	"	2.338±.003	3.189±.005	3.300
69.9%	"	2.899±.003	3.954±.004	4.124
80.0%	"	3.560±.004	4.856±.006	5.061
90.5%	"	4.93 ±.02	6.73 ±.02	6.97
100.0%	"	6.32 ±.01	8.62 ±.01	8.90
69.8%	Methanol	2.370±.003	3.232±.005	3.396
100.0%	"	3.715±.011	5.068±.015	5.349
KCl Systems				
28.9%	Methanol	0.901±.007	1.229±.009	1.286
49.7%	"	1.586±.007	2.163±.009	2.268
70.1%	"	2.438±.006	3.325±.008	3.491
90.6%	"	3.379±.008	4.609±.011	4.850
100.0%	"	3.840±.009	5.238±.012	5.519

B. Feakins' Transfer Free Energies

The molar transfer free energies for the methanol-water systems reported by Feakins and Voice(4) are shown in Table XIV. These data were converted to the molal scale via equation (22) and the molal ΔG_t^o's are also shown in Table XIV.

Feakins used the double cell method, as noted in chapter I. This allowed him to calculate ΔG_t^o's without determining standard potentials for the alkali metals. The transfer activity coefficients of these systems can be calculated directly. Furthermore, the corresponding standard potentials in the nonaqueous media can also be calculated from ΔG_t^o values, using the known standard potential in water. These calculations are the reverse of those used to calculate ΔG_t^o's in chapter III. Table XIV lists $\log {}_m\gamma$ and E^o_{III} for each system. The quantity E_I^o is listed for the lithium chloride and potassium chloride systems.

Table XIV

Transfer Free Energies and Standard Potentials from Feakins(4)

Wt. % MeOH	Molar ΔG_t^o	molal ΔG_t^o	$\log_m \gamma$	E^o_{III}(V.)	E^o_I
		LiCl Systems			
10	0.313 kcal.	0.292	0.214	3.2487	2.4007
20	0.623	0.584	0.428	3.2361	2.3881
40	1.268	1.187	0.870	3.2099	2.3619
60	1.992	1.858	1.362	3.1808	2.3328
80	2.845	2.645	1.939	3.1467	2.2987
99	3.901	3.624	2.657	3.1042	2.2562
		NaCl Systems			
10	0.437	0.416	0.305	2.9175	
20	0.883	0.844	0.619	2.8989	
30	1.328	1.268	0.930	2.8805	
40	1.785	1.704	1.249	2.8616	
50	2.291	2.185	1.602	2.8407	
60	2.790	2.656	1.947	2.8203	
80	3.968	3.768	2.762	2.7721	
90	4.600	4.361	3.197	2.7464	
95	4.914	4.654	3.412	2.7336	
99	5.140	4.863	3.565	2.7246	

Table XIV (continued)

KCl Systems

Wt. % MeOH	Molar ΔG_t^o	molal ΔG_t^o	log $_m\gamma$	E^o_{III}(V.)	E^o_I
10	0.428	0.407	0.298	3.1276	2.1755
20	0.876	0.837	0.614	3.1090	2.1569
40	1.804	1.723	1.263	3.0705	2.1185
60	2.866	2.732	2.003	3.0268	2.0747
80	4.174	3.974	2.913	2.9729	2.0208
99	5.437	5.160	3.783	2.9215	1.9694

The reported uncertainty of these transfer free energies is ±.006 kcal. or better, except for solutions of lithium chloride in 60% and 99% methanol and sodium chloride in 90% methanol, which are listed as ±.008 kcal. The former uncertainty results in an error of ±0.2mV. for the standard potential, while the latter leads to an error of ±0.3mV.

C. Results of This Study at Integral Solvent Compositions

The standard potentials of cell (III) were interpolated on a large-scale graph in order to report data at integral solvent compositions. Tables XV - XVII list these standard potentials, plus the medium effects calculated from them. The interpolated values are indicated by an asterisk.

The molal transfer free energies from Tables XIV - XVII are plotted in Figures II - VI, along with other data which will be discussed in Section E.

Table XV

Solutions of Lithium Chloride(This Study-Molal Scale)

Wt. % Ethanol	E°_{III}(V.)	Log $_{m}\gamma_{LiCl}$	ΔG°_{t}(kcal/mole)
10.0	3.2400	0.362	0.493
20.0 *	3.2219	0.668	0.910
30.0 *	3.2023	0.999	1.363
40.0 *	3.1849	1.294	1.763
50.0 *	3.1675	1.587	2.165
60.0 *	3.1478	1.920	2.619
70.0 *	3.1170	2.44	3.33
80.0 *	3.0804	3.06	4.17
90.0 *	3.0314	3.89	5.31
100.0	2.9350	5.52	7.53
30.0	3.2227	0.654	0.892
50.0 *	3.1914	1.184	1.613
70.0 *	3.1626	1.670	2.278
90.0	3.1196	2.397	3.269
100.0	3.0848	2.985	4.07

Table XVI

Solutions of Sodium Chloride(This Study-Molal Scale)

Wt. % Ethanol	E^{o}_{III}(V.)	Log $_{m}\gamma_{NaCl}$	ΔG^{o}_{t}(kcal/mole)
10.0 *	2.9160	0.330	0.450
20.0 *	2.8961	0.666	0.909
30.0 *	2.8734	1.050	1.432
40.0 *	2.8505	1.436	1.960
50.0 *	2.8245	1.876	2.559
60.0 *	2.7987	2.313	3.154
70.0 *	2.7636	2.906	3.963
80.0 *	2.7249	3.560	4.856
90.0 *	2.6473	4.87	6.65
100.0	2.5616	6.32	8.62

Table XVII

Solutions of KCl(This Study-Molal Scale)

Wt. % Methanol	E^{o}_{III}	$\text{Log}\ {}_{m}\gamma_{KCl}$	ΔG^{o}_{t}(kcal/mole)
30.0 *	3.0899	0.937	1.277
50.0 *	3.0508	1.598	2.179
70.0 *	3.0013	2.435	3.320
90.0 *	2.9469	3.354	4.574
100.0	2.9181	3.840	5.238

D. Standard Reduction Potentials of the Alkali Metals

The standard potential of the silver-silver chloride electrode versus the standard hydrogen electrode in each solvent($-E^{o}_{IV}$) is required to calculate the standard potentials for the alkali metals($-E^{o}_{V}$). These data were gathered from literature sources, as indicated in Table XVIII. Tables XIX - XXI show the interpolated values of $-E^{o}_{IV}$, and the calculated values of $-E^{o}_{V}$, for each system. The uncertainties listed with each $-E^{o}_{V}$ indicate the combined errors in both E^{o}_{III} (Table XII) and the interpolation of E^{o}_{IV}.

Table XVIII

Standard Potential of the Ag-AgCl Electrode in Ethanol-Water and Methanol-Water Solvents

Wt % Ethanol	$-E^{o}_{IV}$	Reference
10.0	.21467,.21449	27,28
20.0	.20757,.20743	27,28
30.0	.20033,.2003	28,29
40.0	.19454,.1935	28,29
46.0	.1882, .1890	30,31
50.0	.18588,.1842	28,29
65.0	.1647, .16516	29,32
70.0	.1563	29
71.9	.1530, .1511	30,31
80.0	.0282	29
88.5	.1004, .0978	30,31
90.0	.08880,.09166	29,32
93.5	.0687	30
95.8	.0485	30
98.0	.0198	30
98.09	.0179	32
100.0	.08138	33

Table XVIII (continued)

Wt % Methanol	$-E^{o}_{IV}$	Reference
10.0	.21549	34,35
20.0	.2094,.2091,.20901	29,34,35
30.0	.2031	35
33.3	.20103	36
40.0	.1968	29
43.3	.1939	37
45.0	.19414	35
50.0	.1906	38
60.0	.1818	29
64.0	.1765	37
70.0	.16833	35
80.0	.1492	29
84.2	.1319	37
90.0	.1135	29
94.2	.0838,.0841	37,39
100.0	-.0099,-.0101,-.0103	29,35,37

Table XIX

Standard Potentials of the Lithium Electrode(Li/Li^+)

Wt % Ethanol	$-E^o_{IV}$	Reduction Potential($-E^o_V$) in Volts
10.0	.2146	-3.025±.001
20.1	.2074	-3.014±.001
30.4	.2001	-3.002±.001
40.3	.1934	-2.991±.001
49.9	.1848	-2.983±.001
60.3	.172	-2.975±.001
70.3	.155	-2.961±.001
80.4	.127	-2.952±.002
90.4	.088	-2.942±.002
100.0	-.081	-3.016±.002
Wt % Methanol		
10.0	.2155	-3.033±.001
20.0	.2092	-3.027±.001
30.0	.2031	-3.020±.001
40.0	.1968	-3.013±.001
50.3	.1904	-3.001±.001
60.0	.1818	-2.999±.001
69.9	.1684	-2.994±.001
80.0	.1492	-2.998±.001
90.0	.1135	-3.006±.001
99.0	.0062	-3.098±.001
100.0	-.0101	-3.095±.002

Table XX

Standard Potentials of the Sodium Electrode(Na/Na^+)

Wt % Ethanol	$-E^o_{IV}$	Reduction Potential($-E^o_V$) in Volts
10.1	.2145	-2.701±.001
20.4	.2072	-2.688±.001
30.8	.1998	-2.672±.001
40.6	.1932	-2.656±.001
50.5	.1842	-2.639±.001
60.6	.171	-2.626±.001
69.9	.157	-2.607±.001
80.0	.128	-2.597±.001
90.5	.087	-2.557±.002
100.0	-.081	-2.643±.002
Wt % Methanol		
10.0	.2155	-2.702±.001
20.0	.2092	-2.690±.001
30.0	.2031	-2.677±.001
40.0	.1968	-2.665±.001
50.0	.1906	-2.650±.001
60.0	.1818	-2.639±.001
69.8	.1686	-2.627±.001
80.0	.1492	-2.623±.001
90.0	.1135	-2.633±.001
95.0	.0725	-2.661±.001
99.0	.0062	-2.718±.001
100.0	-.0101	-2.726±.001

Table XXI

Standard Potentials of the Potassium Electrode(K/K^+)

Wt % Methanol	$-E^o_{IV}$	Reduction Potential($-E^o_V$) in Volts
10.0	.2155	-2.912±.001
20.0	.2092	-2.900±.001
28.9	.2037	-2.888±.001
40.0	.1968	-2.874±.001
49.7	.1908	-2.861±.001
60.0	.1818	-2.845±.001
70.1	.1682	-2.833±.001
80.0	.1492	-2.824±.001
90.6	.1096	-2.836±.001
99.0	.0062	-2.915±.001
100.0	-.0101	-2.928±.001

E. Comparison with Other Workers

In this section, literature results for ethanol-water and methanol-water systems are compared to the present work. The molal scale is used throughout.

Lithium: The standard (reduction) potentials of the infinitely dilute lithium amalgam electrode, $E^{o}_{Li(Hg)}$, and the Li/Li^{+} metal electrode, E^{o}_{Li}, in water are shown in Table XXII, along with values from literature data. These potentials were calculated by subtracting E^{o}_{I} and E^{o}_{III}, respectively, from ${}_{w}E^{o}_{AgCl}$ (0.2223Volts). The standard potential of cell (II), E^{o}_{II}, used in each case to calculate E^{o}_{Li} from $E^{o}_{Li(Hg)}$ is also listed.

The data from Lewis and Keyes(1) include an estimated liquid-junction correction of unknown accuracy. The values of $E^{o}_{Li(Hg)}$ from references (6) and (7) agree within experimental error, but their other values do not. The E^{o}_{Li} from reference (6) is in agreement with the present study, within experimental error(±0.002V).

Table XXII

Standard Potentials of Li Electrodes in Water(Volts)

Source	$E^{o}_{Li(Hg)}$	E^{o}_{II}	E^{o}_{Li}
This Work	-2.1911	0.8480	-3.0391
Reference (1)	-2.1831	0.8412	-3.0243
Reference (6)	-2.1963	0.8438	-3.0401
Reference (7)	-2.1951	0.8480	-3.0431

A comparison of the available data on the standard potential of lithium in methanol and ethanol is given in Table XXIII. The value from reference (3) was reported in the compilation by Covington and Dickinson(40).

Table XXIII

Standard Potentials of Lithium
in Methanol and Ethanol, Volts(molal scale)

	Methanol	Ethanol
This Study	-3.095	-3.016
Reference (3)	-3.653	
Reference (41)	-3.045	
Reference (42)	-3.0845	
Reference (43)		-3.042

A summary of all the available transfer free energy data for solutions of lithium chloride in methanol-water solvents is presented in Table XXIV. The results from Akerlof's work(2) are based on Feakins' calculations(4). The result of Scrosati(3) at 100% methanol agrees with the value reported here within experimental error. Figure III shows that the data of Feakins fits well with the results reported in this study.

Table XXIV

Standard Free Energies of Transfer for Lithium Chloride from Water to Methanol-Water Solvents(kcal/mole, molal scale)

Wt % MeOH	This Work	Feakins(4)	Akerlof(2)	Scrosati(3)
10		0.292	0.284	
20		0.584	0.584	
30	0.892			
40		1.187	1.206	
50	1.613			
60		1.858	1.91	
70	2.278			
80		2.645	2.72	
90	3.269			
99		3.624		
100	4.07			4.093

Sodium: The available data on the standard potential of sodium in 100% methanol and ethanol are listed in Table XXV. It must be noted that the result from Buckley and Hartley(43) includes a liquid-junction correction of unknown accuracy. The data from references (3) and (10) are taken from reference (40), since these values were not calculated in the original paper.

Table XXV

Standard Reduction Potentials of Sodium in Methanol and Ethanol(Volts)

	Methanol	Ethanol
This Work	-2.726	-2.643
Reference (3)	-2.7152	
Ref. (10)	-2.7132	
Ref. (44)	-2.728	
Ref. (43)		-2.657
Ref. (45)		-2.646

Table XXVI lists the available data for the transfer free energies of sodium chloride from water to methanol-water solvents. The Akerlof results(2) shown here were

calculated from his data by Feakins(4). Figure V illustrates the change in the transfer free energy with changing solvent composition.

Table XXVI

Standard Free Energies of Transfer of Sodium Chloride from Water to Methanol-Water Solvents(kcal/mole, molal scale)

Wt %MeOH	This Work	Feakins(4)	Akerlof(2)	Gladden(10)
10		0.416	0.407	
20		0.844	0.828	
30		1.268		
40		1.704	1.706	
50		2.185		
60		2.656	2.70	
70	3.241			
80		3.768	3.71	
90		4.361	4.59	
95		4.654		
99		4.863		
100	5.068			4.7

The ΔG_t^o reported by Gladden and Fanning(10) for 100% methanol is in poor agreement with the data of the other

workers. The data of Feakins and Voice(4) fit well with the data reported here and with the Akerlof data for solvents of low methanol content. Akerlof estimated that his results in solvents containing >50% methanol have an uncertainty of ±0.06 kcal. (compared with ±0.007 kcal. for the other solvents). Except for 90% methanol, his values agree within this limit with those of Feakins.

Potassium: Table XXVII shows all available data on the standard free energy of transfer of potassium chloride from water to methanol-water solvents. The results of Feakins, Akerlof and the present work fit together very well. Malahias and Popovych(15) reported two sets of results: the first is based on the solubility of KCl and the second, from the EMF measurements of potassium glass vs. calomel electrodes. These results are in excellent agreement with the other values from 50% to 80% methanol, but agreement is poor below 50% methanol.

The agreement among all the data for 99% and 100% methanol is not particularly good. The closest agreement (within 0.07kcal.) for 100% methanol is between the result from Malahias and Popovych(15) based on the solubility of KCl and the result reported in this study. The result from the Malahias and Popovych(15) solubility study for 99% methanol is not far from Feakins'(4) value.

Figure VI displays graphically most of the tabulated data.

Table XXVII

Standard Free Energies of Transfer for Potassium Chloride from Water to Methanol-Water Solvents(kcal/mole, molal scale)

Wt % Methanol	This Study	Feakins(4)	Akerlof(2)
10		0.407	0.413
20		0.837	0.844
30	1.277		
40		1.723	1.739
50	2.179		
60		2.732	2.75
70	3.320		
80		3.974	3.97
90	4.574		
99		5.160	
100	5.238		

(Table XXVII continues on next page.)

Table XXVII(continued)

Wt % Methanol	Malahias and Popovych(15)		Scrosati(3)
	Solubility	Emf	
10	0.250	0.281	
20	0.690	0.554	
30	1.22	1.22	
40	1.65	1.65	
50	2.15	2.15	
60	2.74	2.74	
70	3.26	3.26	
80	3.98	3.93	
90	4.65	4.65	
99	5.25	5.75	
100	5.31	5.90	5.056

Table XXVIII shows the literature values for the standard reduction potential of potassium metal(K/K^+) in methanol. The result reported in this paper falls in the middle of the literature values, and is within 1mV. of the average of these values.

Table XXVIII

Standard Reduction Potential of Potassium in Methanol(Volts)

This Study	-2.928
Reference (3)	-2.9116
Reference (14)	-2.933
Reference (42)	-2.9362

F. Figures II-VII

The symbols used in these Figures indicate the source of the data, as follows:

Symbol :	x	$	o	*	+
Ref. no.:	(this work)	(3)	(4)	(10)	(15)

The results reported in reference (15) for both the solubility and EMF measurements are represented by the same symbol(+). These results are indicated in Figure VI by a single point at each solvent composition from 30% to 80% methanol. In the other solvents, the agreement is sufficiently poor to require two points. In these instances, the higher value is from the EMF study in every solvent except 20% methanol.

Figure VII shows all five curves from Figures II - VI, for comparison. Note that the two highest curves are values in ethanol-water, while the other three are

methanol-water. Each curve in Figure VII is labelled to show which alkali-metal chloride it represents.

Figure II

Free Energies of Transfer: LiCl in Ethanol-Water Solvents

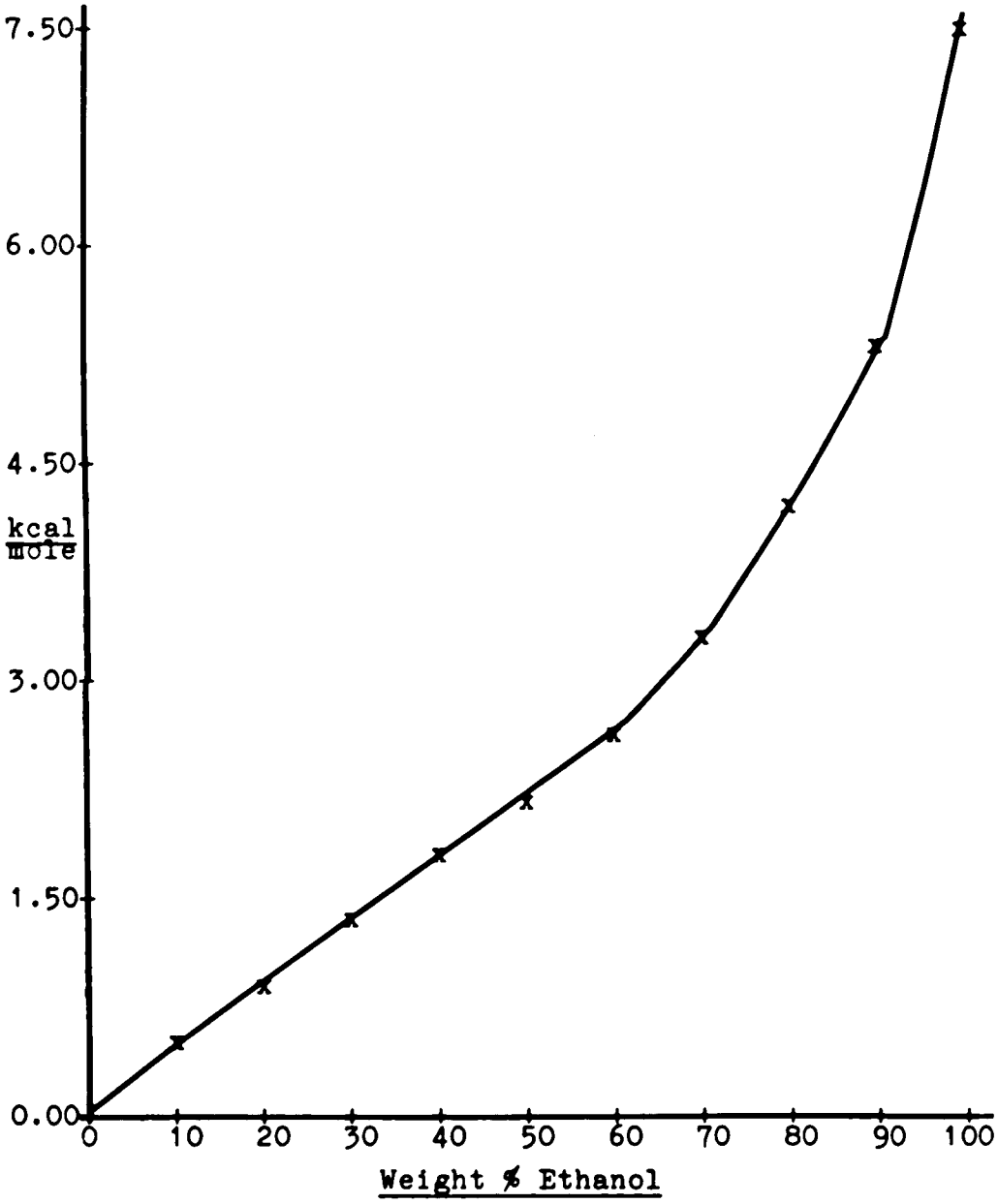


Figure III

Free Energies of Transfer: LiCl in Methanol-Water Solvents

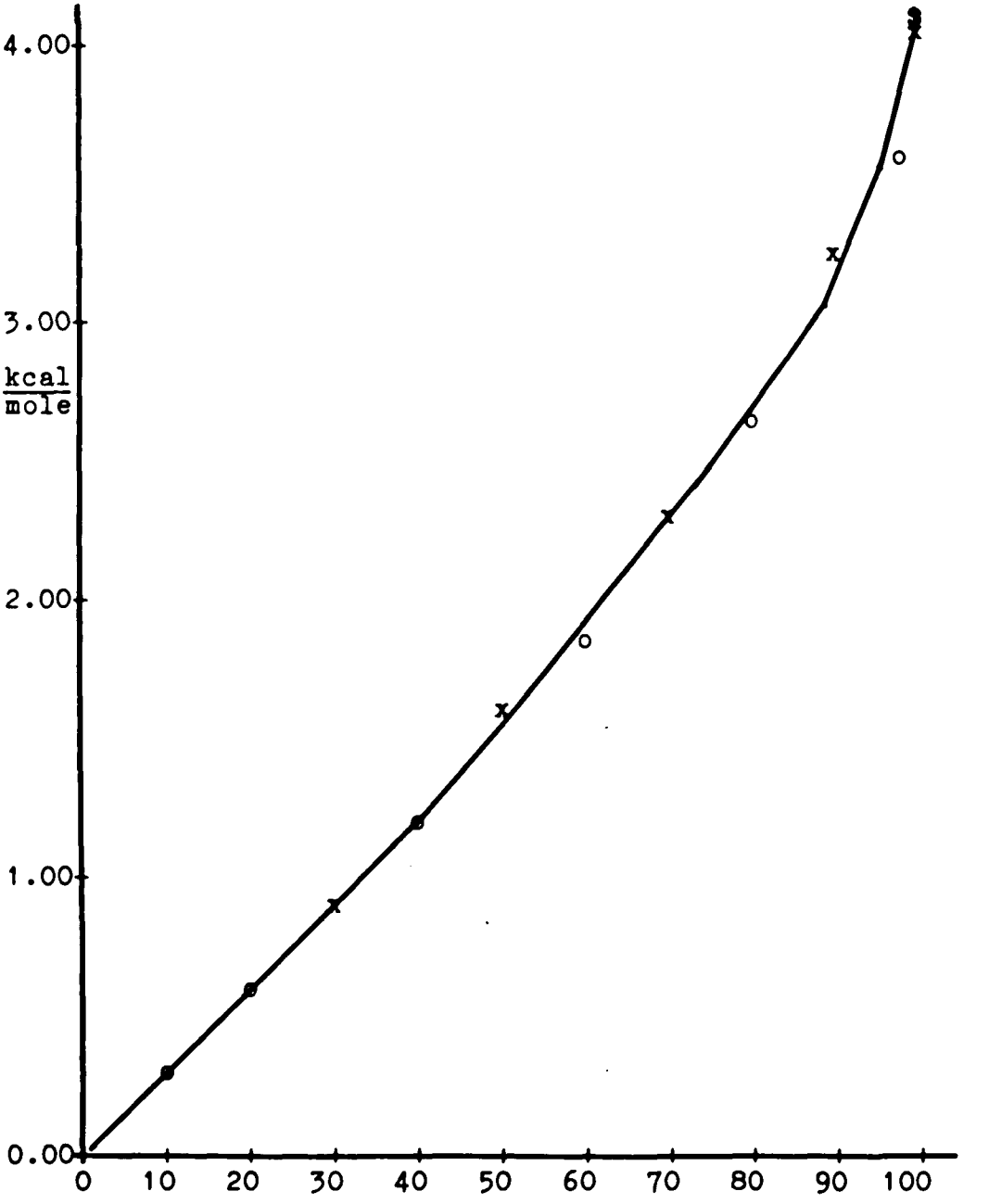


Figure IV

Free Energies of Transfer: NaCl in Ethanol-Water Solvents

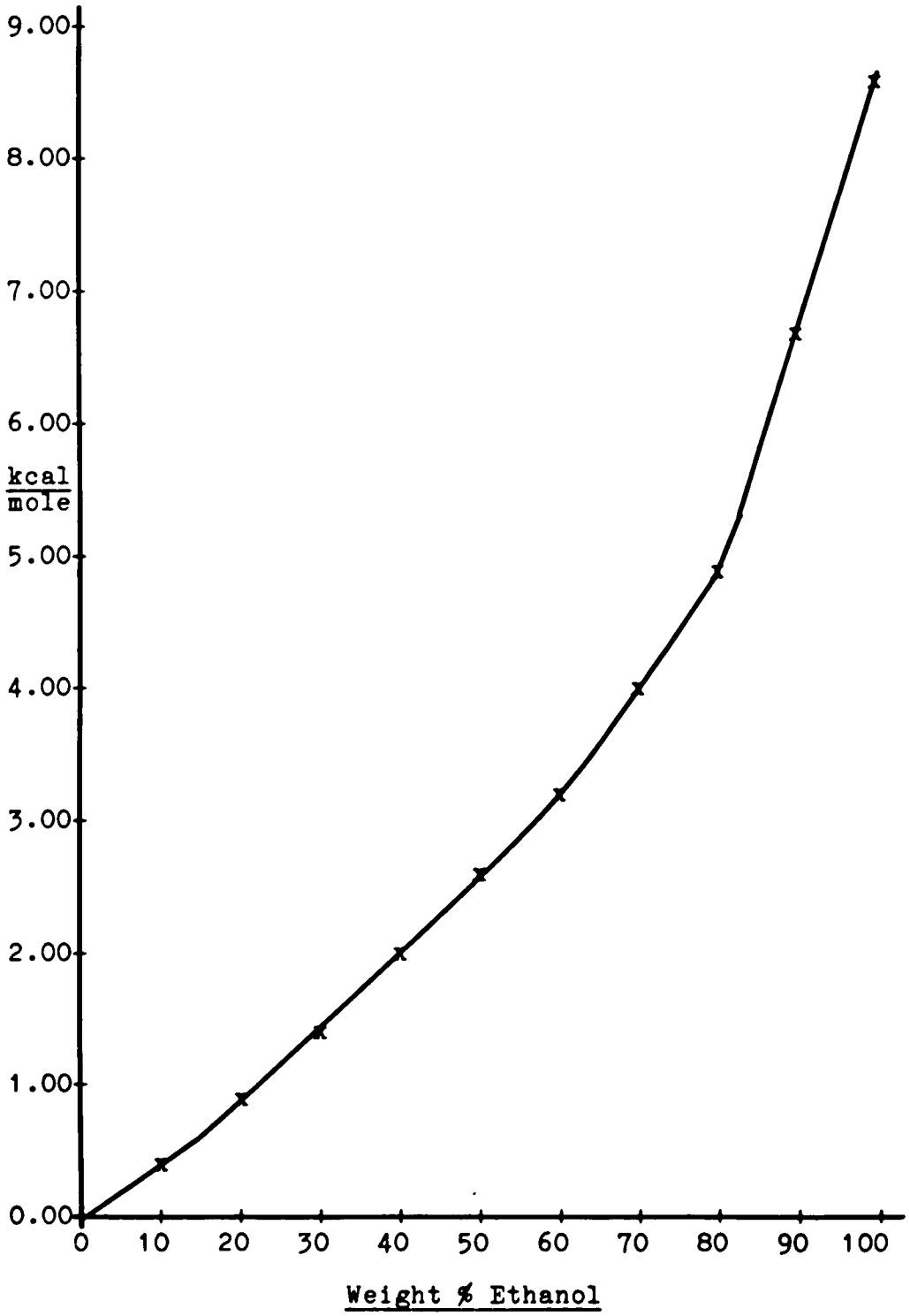


Figure V

Free Energies of Transfer: NaCl in Methanol-Water

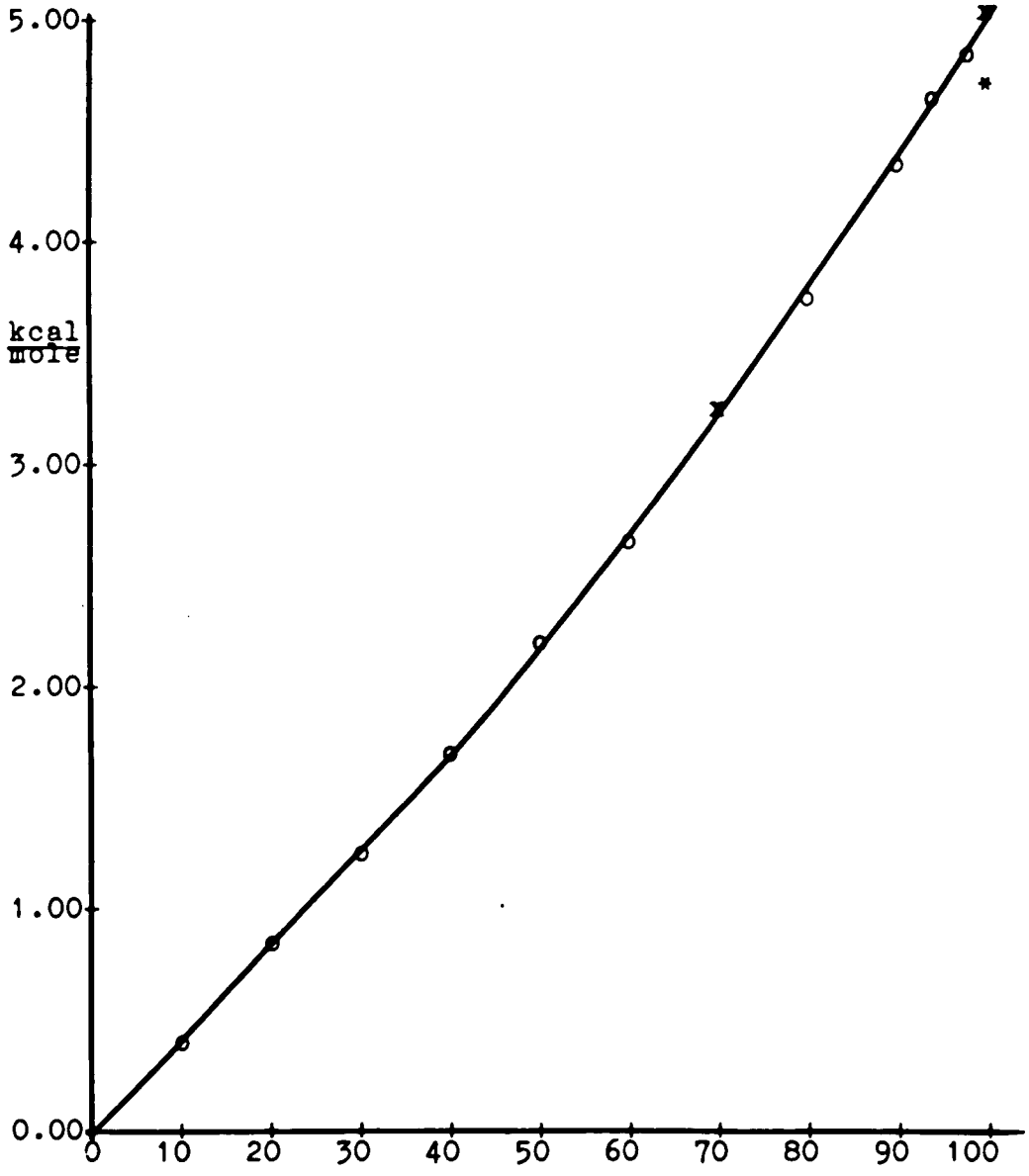


Figure VI

Free Energies of Transfer: KCl in Methanol-Water

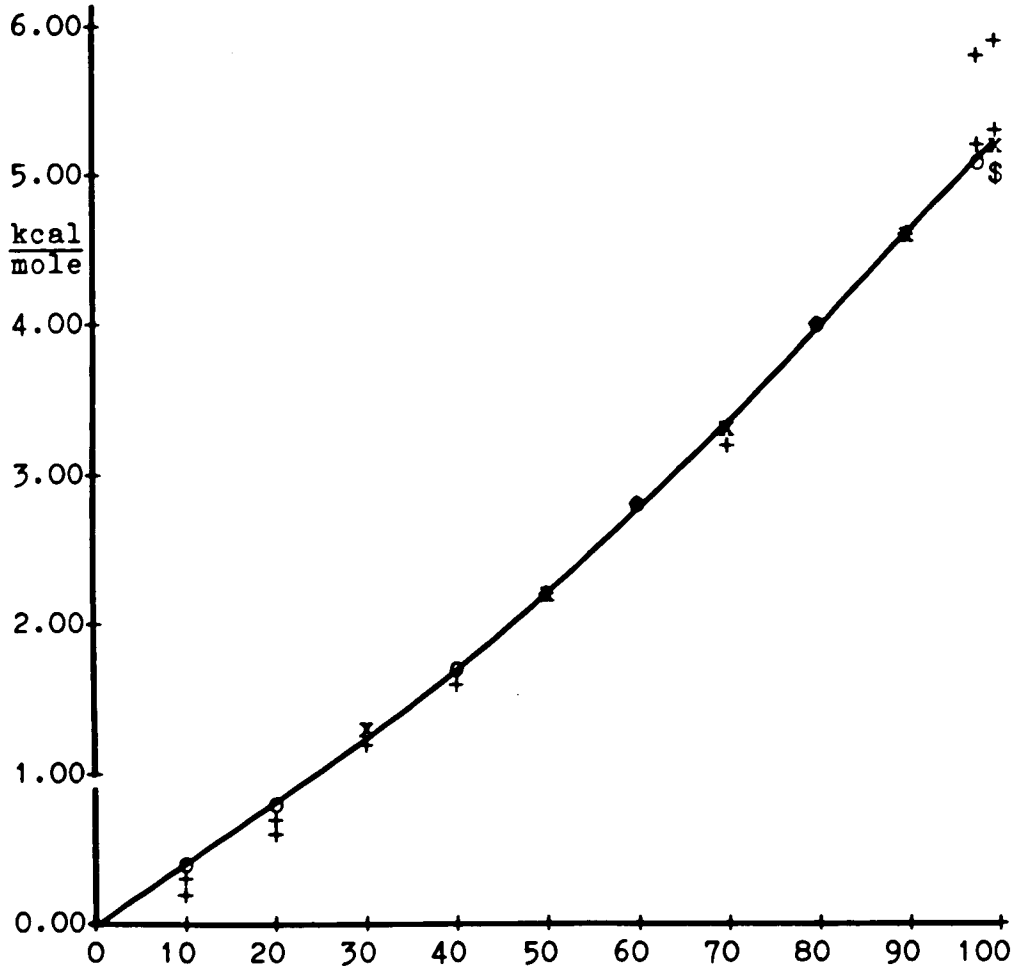
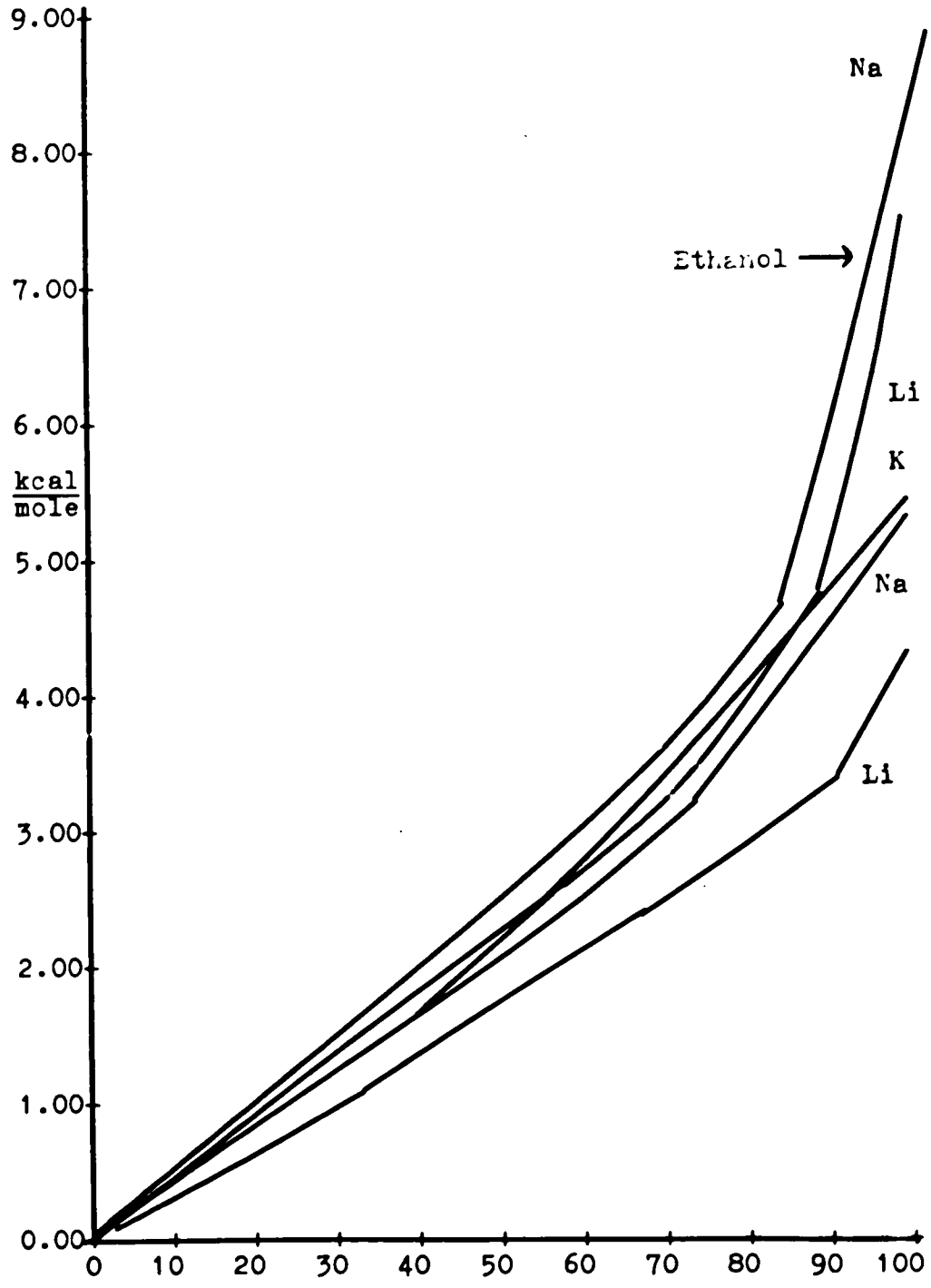


Figure VII

Free Energies of Transfer: All Systems



G. Cation Transfer Activity Coefficient Differences

The difference in the standard potential of the metal/metal ion electrode versus the standard hydrogen electrode, $-E_V^o$, upon changing from aqueous to a nonaqueous solvent reflects the difference between the transfer activity coefficients of the metal ion and the hydrogen ion, according to the following equation:

$$\log {}_m\gamma_{M^+} - \log {}_m\gamma_{H^+} = \frac{{}_sE^o - {}_wE^o}{0.05916} \qquad (29)$$

From equation (29), the transfer activity coefficient differences can be calculated for M = Li, Na, or K using the standard potentials listed in Tables XIX - XXI. Tables XXIX - XXXI list these values and Figure VIII shows them graphically.

The significance of these values is two-fold. The most obvious use of these data is to compare directly the transfer activity coefficients of these cations and gain insight into the relative solvating properties of various solvents. The second purpose is the calculation of single-ion transfer activity coefficients. While this subject is beyond the scope of this work, it is obvious from equation (29) that knowledge of the transfer activity coefficient of the hydrogen ion would allow the calculation of the transfer activity coefficients of the alkli-metal ions in the same solvent. (In fact, knowledge of

the transfer act. coef. of any single ion would allow the calculation of that of all other ions through the thermodynamically accessible transfer activity coefficients of neutral combinations of ions.)

Table XXIX

Cation Transfer Activity Coefficients: Li vs. H

Wt % EtOH	$\log_m \gamma_{Li} - \log_m \gamma_H$	Wt % MeOH	$\log_m \gamma_{Li} - \log_m \gamma_H$
10.0	0.24	10.0	0.10
20.1	0.42	20.0	0.20
30.4	0.63	30.0	0.32
40.3	0.81	40.0	0.44
49.9	0.95	50.3	0.64
60.3	1.08	60.0	0.68
70.3	1.32	69.9	0.76
80.4	1.47	80.0	0.69
90.4	1.64	90.0	0.56
		99.0	-1.00
100.0	0.39	100.0	-0.95

Table XXX

Cation Transfer Activity Coefficients: Na vs. H

Wt % EtOH	$\log {}_m\gamma_{Na} - \log {}_m\gamma_H$	Wt % MeOH	$\log {}_m\gamma_{Na} - \log {}_m\gamma_H$
10.1	0.20	10.0	0.19
20.4	0.42	20.0	0.39
30.8	0.69	30.0	0.61
40.6	0.96	40.0	0.81
50.5	1.25	50.0	1.06
60.6	1.47	60.0	1.25
69.9	1.79	69.8	1.45
80.0	1.96	80.0	1.52
90.5	2.64	90.0	1.35
		95.0	0.88
		99.0	-0.08
100.0	1.18	100.0	-0.22

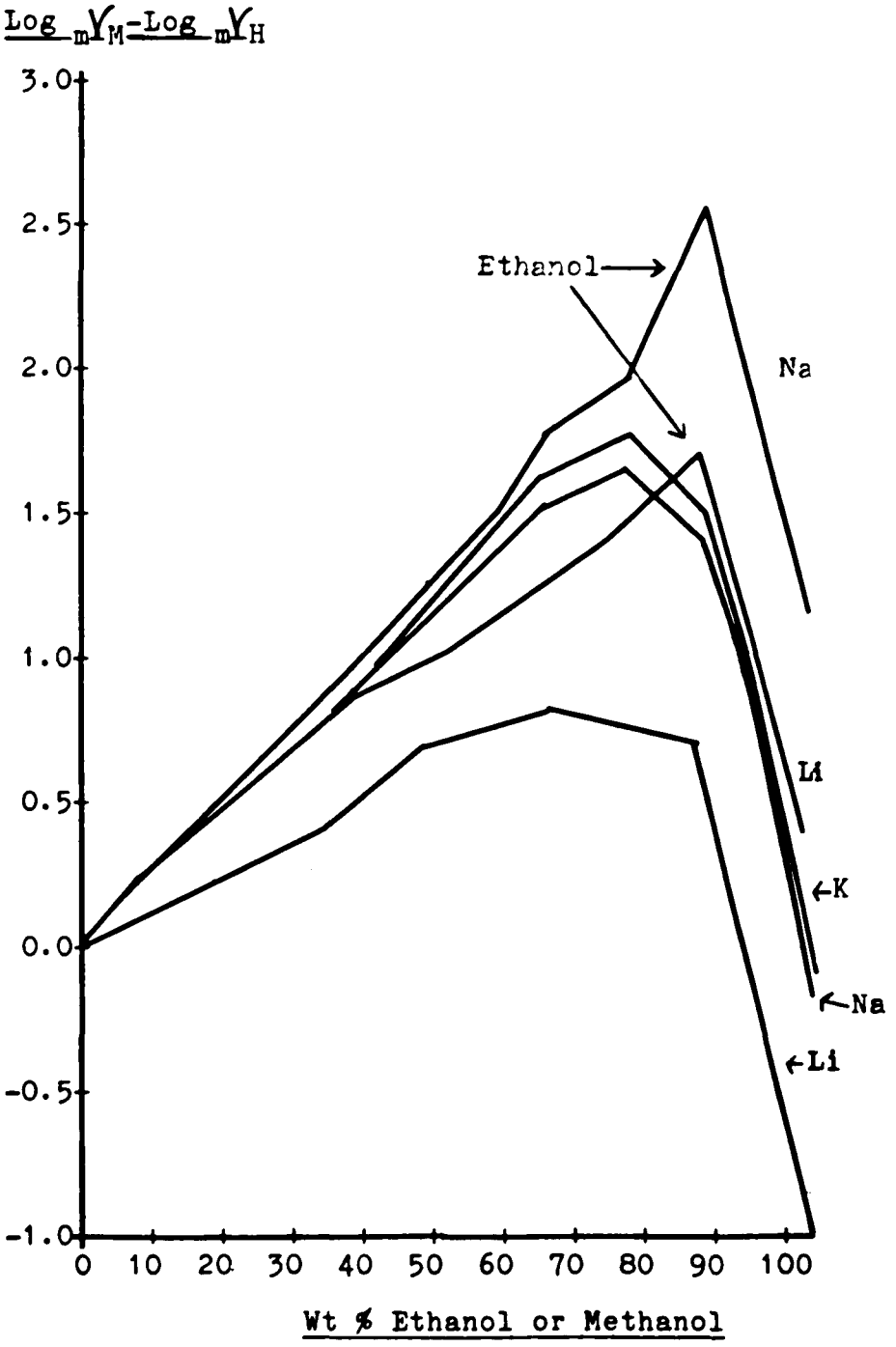
Table XXXI

Cation Transfer Activity Coefficients: K vs. H

Wt % Methanol	$\log {}_m\gamma_K - \log {}_m\gamma_H$
10.0	0.19
20.0	0.39
28.9	0.59
40.0	0.83
49.7	1.05
60.0	1.32
70.1	1.52
80.0	1.67
90.6	1.47
99.0	0.14
100.0	-0.08

Figure VIII

Transfer Activity Coefficient Differences



H. The Born Model

In 1920, Born(46) introduced a simple model to represent ion solvation. In this model, every ion is treated as a charged sphere of radius r. The solvation energy, G^{o}(Born), is calculated as the net electrostatic free energy required to discharge the sphere in vacuum and then recharge it in a medium with dielectric constant D. This quantity is calculated from equation (30); G^{o}(Born) is in kcal/mole when r is expressed in Angstroms.

$$G^{o}(\text{Born}) = \frac{-166}{r}\left(1-\frac{1}{D}\right) \qquad (30)$$

Free energies of transfer for an ion can be calculated by subtracting the G^{o}(Born) for the aqueous solution from those of nonaqueous solutions. The free energy of transfer for each alkali-metal chloride in a given solvent can be calculated by summing the free energies of transfer of the chloride ion with that of each cation, respectively. The results of these calculations are shown in Table XXXII. Figures IX - XIII compare graphically these values and the experimental results displayed in Figures II - VI. The dielectric constants(20,47) and ionic radii(48) used in the calculations were taken from the literature.

Figure IX - XIII indicate a similarity between the experimental results and the values calculated using equation (30). However, the differences are quite significant. Agreement is fairly good for the NaCl systems. The

Born calculations agree with the experimental results for the LiCl systems up to 20 wt % alcohol, but rise sharply higher for the more alcoholic media. The Born calculations for the KCl systems yield transfer free energies significantly lower than the experimental results.

While the Born free energy may be a useful approximation, it does not account for all the important interactions in the solvation process. By assuming that the solvent surrounding the ion has the same dielectric properties as the bulk solvent, the Born model disregards the effect of the ion's electric field on nearby solvent molecules. This is a very significant omission for ions with radii of less than 4-5 Angstroms(49).

When an ion is solvated by water it is surrounded by a "solvation shell" of water molecules. These molecules are oriented by the ion's electric field. The strongest electrostatic interaction between the ion and the water is an ion-dipole attraction. Ion-quadrupole and ion-induced dipole forces are also significant. In addition, nonelectrostatic components must be included in the solvation energy, especially for large ions. These would be similar to the forces acting on an uncharged species of the same size. Furthermore, specific chemical interactions may also be important for certain ions.

These ion-solvent interactions are also present in ethanol-water and methanol-water solvents. Accurate cal-

culation of free energies of transfer must include the change in each of these interactions from aqueous to nonaqueous solutions. At present, not enough information exists regarding the solvation shell of the nonaqueous solutions to allow accurate theoretical calculation of free energies of transfer(50).

The failure of the Born equation to predict transfer free energies for certain ions may be quite severe. It is clear from the transfer free energies of the alkali-metal chlorides reported in this work that the transfer free energy of the lithium ion in ethanol-water and methanol-water solvents is less than those of the sodium and potassium ions, in contradiction to the Born equation. This means that other interactions may be of equal or greater importance than the Born charging energy in determining tranfer free energies for these systems.

It has been suggested(51) that there are three main factors which determine these transfer free energies. Firstly, the ion interacts with nearby electron pairs on the solvent molecules in the first solvation shell. Secondly, there are ion-dipole attractions between the ion and the solvent molecules just beyond the primary shell which may be strong enough to cause dielectric saturation. Thirdly, solvent molecules further from the ion experience a very weak electric field and interact with the ion according to the Born equation.

We already know that the third(Born) factor will lead to a positive transfer free energy for ions in ethanol-water and methanol-water solvents because of the decrease in the dielectric constant. The second(ion-dipole) interaction also leads to positive transfer free energies since water has a higher dipole moment than the alcohols. It is only the first factor which distinguishes markedly between cations and anions. Since the alchol molecules contain alkyl groups, which tend to be electron-donors, the electrons on the oxygen atoms interact more strongly with cations than do the oxygen atoms on water molecules. This leads to a negative contribution to the transfer free energy of cations. Anions, however, interact more strongly with water molecles which can more easily accept electron pairs. For anions, then, all three factors contribute positively to the transfer free energy in these solvents.

The smaller lithium ion has a higher charge density than the sodium or potassium ion. This increases the strength of the interaction in the first shell to a greater extent than the other interactions and accounts for the lower medium effect for LiCl in ethanol-water and methanol-water solvents. The Born theory predicts a greater transfer free energy for the small lithium ion and a lesser one for the larger potassium ion. This explains why the Born values are far too high for LiCl and low for

KCl.

Table XXXII

Free Energies of Transfer(kcal/mole) from Born Calculations

Wt % Methanol	LiCl	NaCl	KCl
10	0.3	0.2	0.2
20	0.6	0.4	0.4
30	1.0	0.7	0.6
40	1.4	1.0	0.8
50	1.8	1.3	1.1
60	2.4	1.8	1.5
70	3.1	2.3	1.8
80	3.9	2.9	2.3
90	5.0	3.6	3.0
100	6.6	4.8	3.9
Wt % Ethanol			
10	0.4	0.3	
20	0.8	0.6	
30	1.4	1.0	
40	2.0	1.4	
50	2.8	2.1	
60	3.8	2.8	
70	5.0	3.6	
80	6.5	4.7	
90	8.4	6.1	
100	10.5	7.6	

Figure IX

Transfer Free Energies of LiCl in Ethanol-Water Solvents from Experiment and from Born Calculations (kcal/mole)

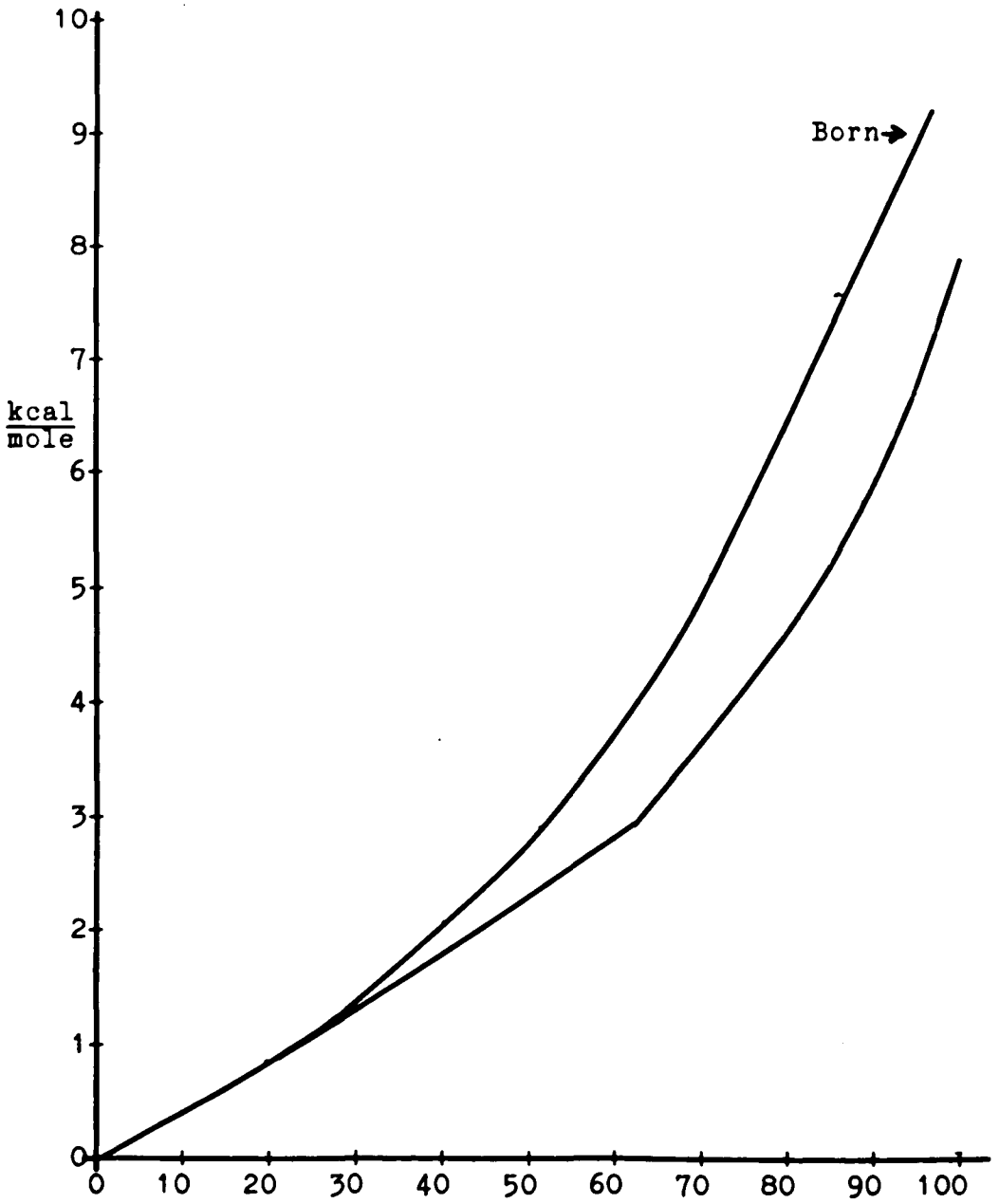


Figure X

Transfer Free Energies of LiCl in Methanol-Water Solvents from Experiment and from Born Calculations (kcal/mole)

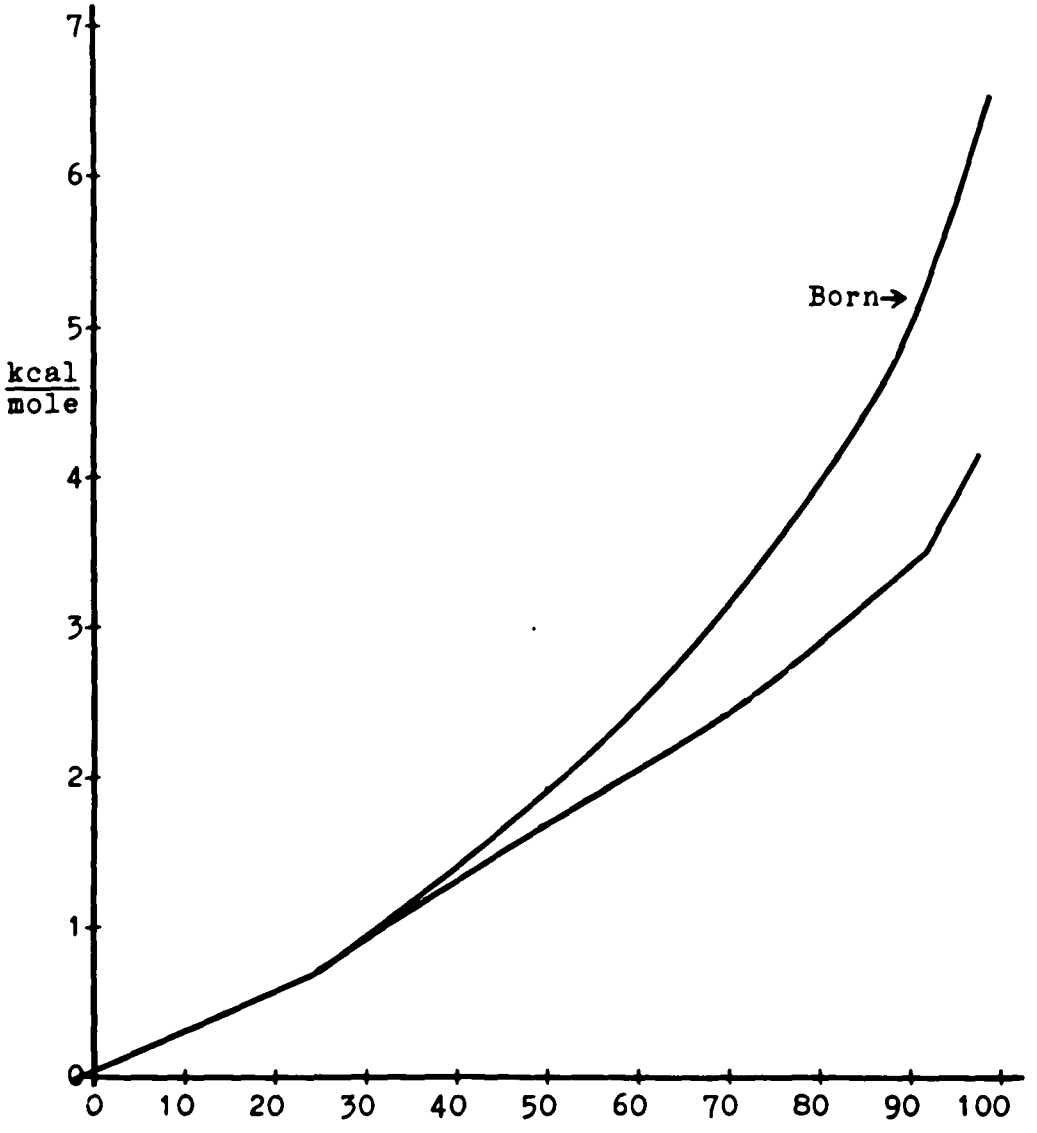


Figure XI

Transfer Free Energies of NaCl in Ethanol-Water Solvents from Experiment and from Born Calculations (kcal/mole)

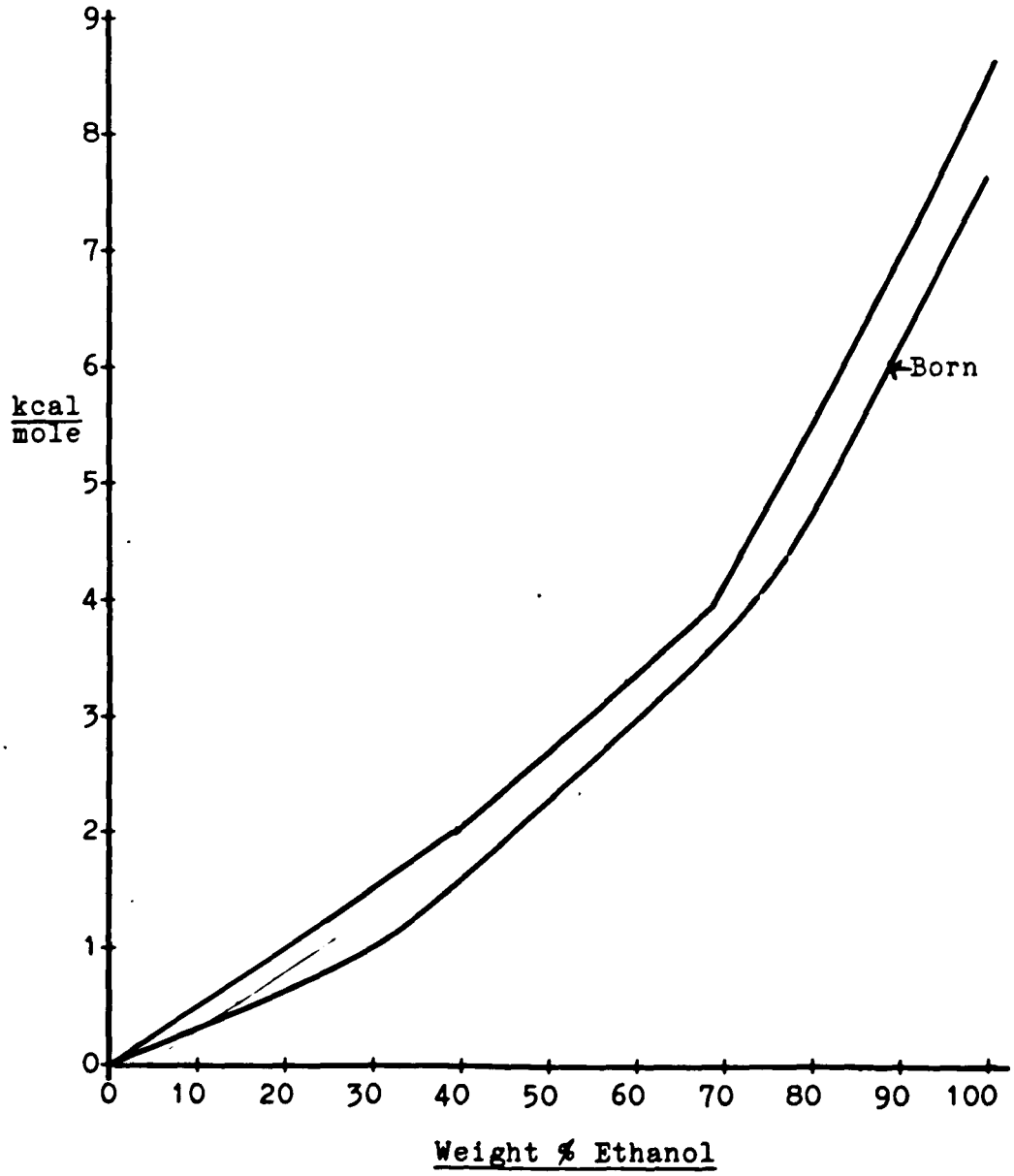


Figure XII

Transfer Free Energies of NaCl in Methanol-Water Solvents from Experiment and from Born Calculations (kcal/mole)

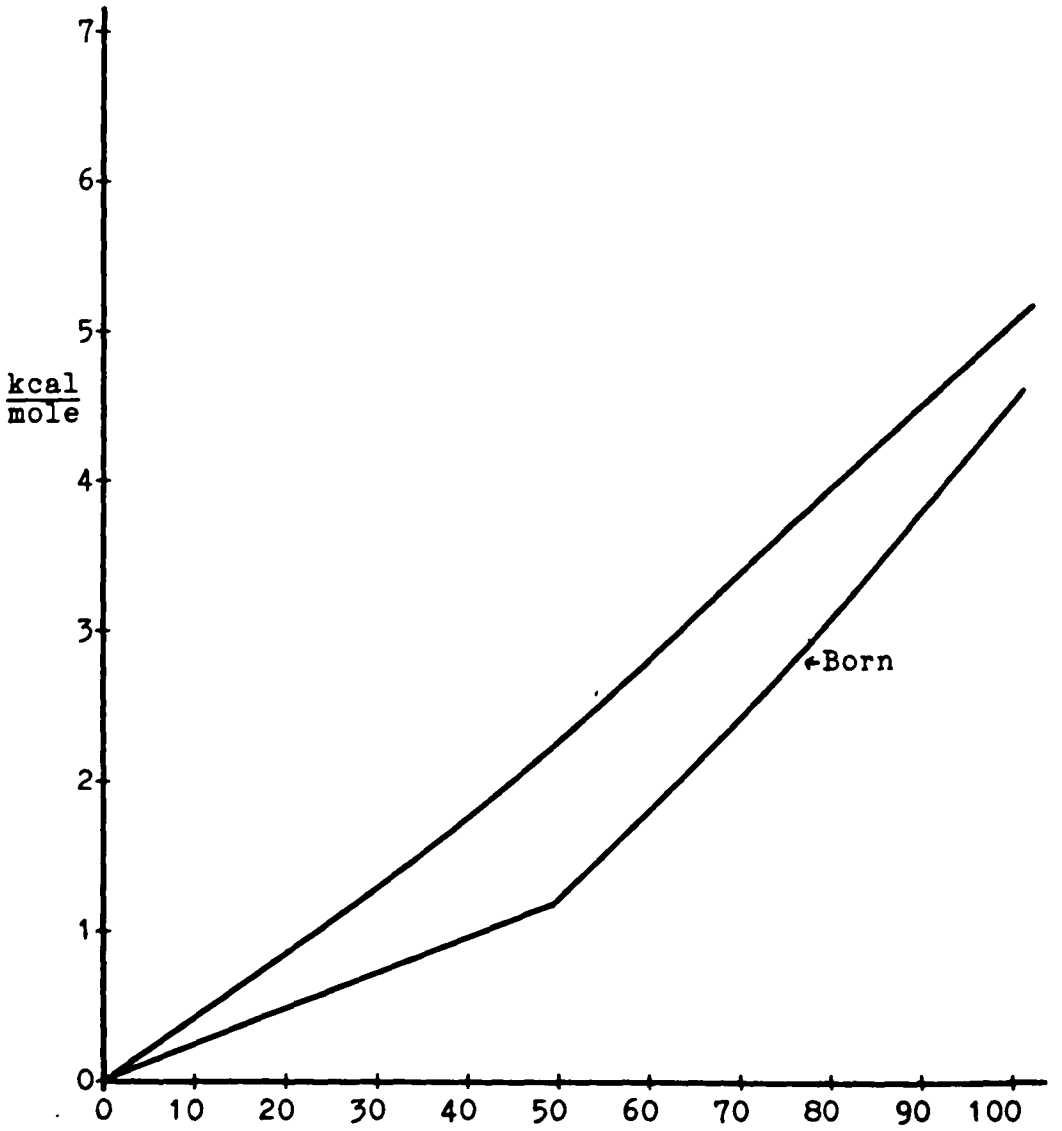
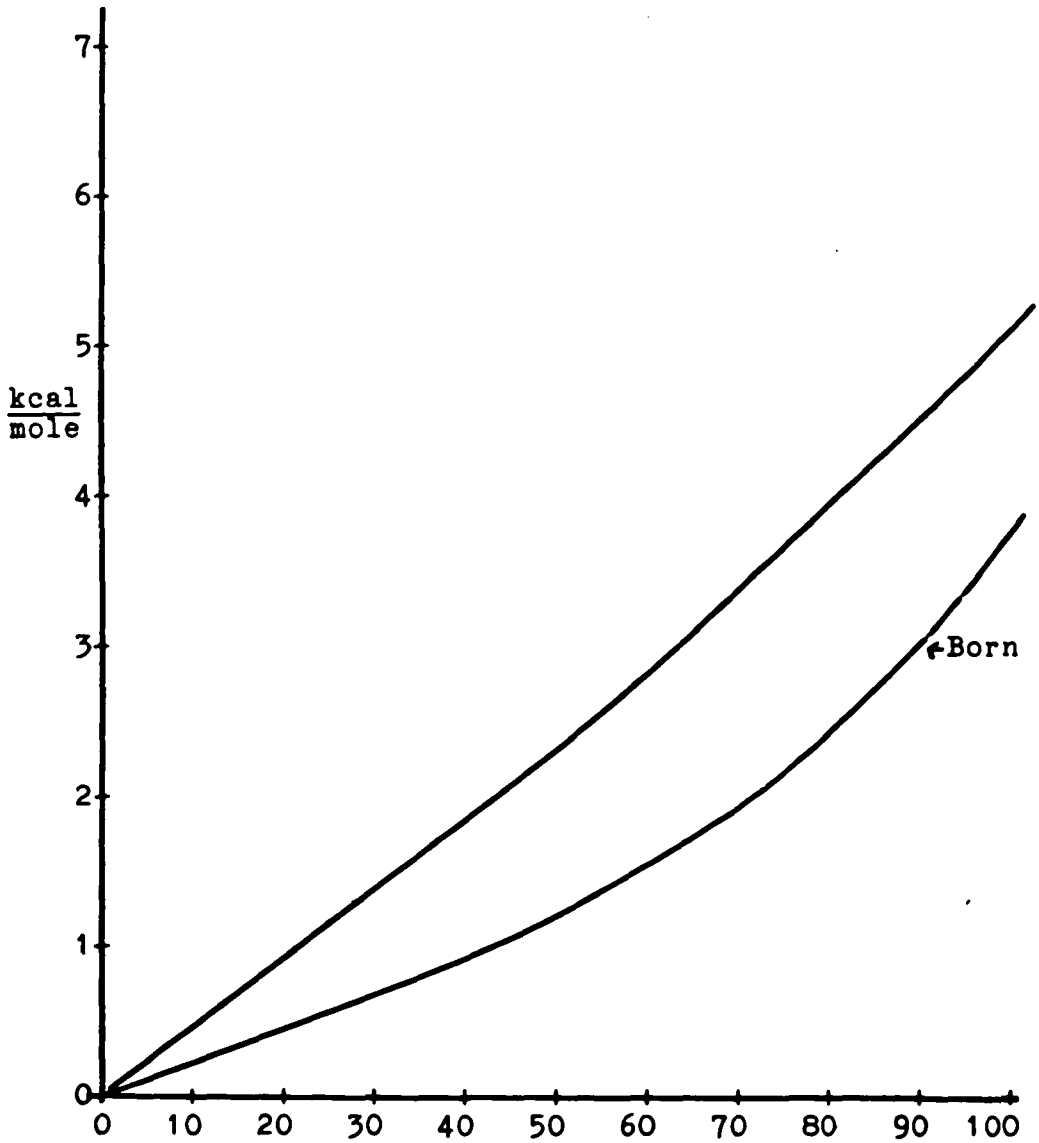


Figure XIII

Transfer Free Energies of KCl in Methanol-Water Solvents from Experiment and from Born Calculations (kcal/mole)



I. Recommended Future Research

Section E indicates that more data are needed for the standard reduction potentials of the alkali metals in 100% methanol and ethanol. This is particularly true for lithium, where discrepancies of tens of millivolts exist among the reported values.

The disagreement among the data for the standard free energy of transfer of potassium chloride in 100% methanol is not satisfactory; this problem should be resolved through additional studies.

It would be useful if other workers would make measurements of the medium effects and standard potentials for alkali metal chlorides in ethanol-water solvents so that a comparison with this study would be possible. The wide use of these solvents would certainly justify further study.

The free energies of transfer reported here for the alkali-metal chlorides would be useful in estimating single-ion transfer activity coefficients. Indeed, the study of single-ion properties in our laboratory was an important impetus for this work. Future calculations in this area will make use of the results reported in this study.

Appendix I

Table XXXIII

Data from Lithium Chloride in Aqueous Solutions

M	m	$I^{\frac{1}{2}}$	E	E+2k log m
0.02035	0.02041	0.1429	2.4266	2.2267
0.02422	0.02429	0.1559	2.4193	2.2283
0.02819	0.02827	0.1681	2.4123	2.2291
0.03138	0.03147	0.1774	2.4071	2.2294
0.03366	0.03376	0.1837	2.4037	2.2296
0.03628	0.03639	0.1908	2.3998	2.2296
0.03756	0.03767	0.1941	2.3986	2.2301
0.04100	0.04112	0.2028	2.3945	2.2305
0.04508	0.04521	0.2126	2.3901	2.2310
0.05247	0.05262	0.2294	2.3835	2.2322
0.02170	0.02176	0.1475	2.4243	2.2276
0.02734	0.02742	0.1656	2.4139	2.2291
0.02859	0.02867	0.1693	2.4112	2.2294
0.03147	0.03156	0.1777	2.4070	2.2294
0.03487	0.03497	0.1870	2.4027	2.2304
0.03961	0.03973	0.1993	2.3969	2.2312
0.04371	0.04384	0.2094	2.3923	2.2316
0.04645	0.04659	0.2158	2.3892	2.2317

Table XXXIII (continued)

M	m	$I^{\frac{1}{4}}$	E	E+2k log m
0.02118	0.02124	0.1457	2.4376	2.2397
0.02833	0.02841	0.1686	2.4241	2.2411
0.03109	0.03118	0.1766	2.4197	2.2415
0.03645	0.03656	0.1912	2.4125	2.2425
0.03961	0.03973	0.1993	2.4087	2.2430
0.04242	0.04254	0.2063	2.4055	2.2433
0.04584	0.04597	0.2144	2.4017	2.2435
0.02614	0.02622	0.1619	2.4279	2.2408
0.02857	0.02865	0.1693	2.4236	2.2411
0.03088	0.03097	0.1760	2.4203	2.2418
0.03322	0.03332	0.1825	2.4168	2.2420
0.03791	0.03802	0.1950	2.4108	2.2428
0.04065	0.04077	0.2019	2.4075	2.2431
0.04565	0.04578	0.2140	2.4024	2.2440
0.05044	0.05059	0.2249	2.3975	2.2442
0.05678	0.05695	0.2386	2.3922	2.2450

Table XXXIV

Data from Solutions of LiCl in 10.0% Ethanol

M	m	I^{μ}	E	E+2k log m	log $\gamma_{\pm}$
0.01977	0.02016	0.1420	2.4065	2.2059	-.135
0.02257	0.02302	0.1517	2.4016	2.2078	-.151
0.02449	0.02498	0.1580	2.3975	2.2079	-.152
0.02812	0.02868	0.1693	2.3921	2.2096	-.166
0.03053	0.03114	0.1765	2.3883	2.2101	-.170
0.04003	0.04083	0.2021	2.3775	2.2132	-.196
0.04381	0.04468	0.2114	2.3736	2.2139	-.202
0.04551	0.04642	0.2154	2.3720	2.2143	-.205
0.04954	0.05053	0.2248	2.3695	2.2161	-.221

Table XXXV

Data from Solutions of LiCl in 20.1% Ethanol

M	m	$I^{\frac{1}{2}}$	E	E+2k log m	log $\gamma_{\pm}$
0.02336	0.02417	0.1555	2.3872	2.1959	-.164
0.02621	0.02712	0.1647	2.3824	2.1971	-.174
0.02793	0.02890	0.1700	2.3799	2.1978	-.180
0.03199	0.03311	0.1819	2.3741	2.1990	-.190
0.03470	0.03591	0.1895	2.3716	2.2007	-.204
0.04017	0.04157	0.2039	2.3654	2.2020	-.216
0.04506	0.04663	0.2159	2.3609	2.2034	-.227

Table XXXVI

Data from Solutions of LiCl in 30.4% Ethanol

M	m	I^k	E	E +2k log m	log $\gamma_\pm$
0.02161	0.02275	0.1508	2.3836	2.1892	-.156
0.02659	0.02799	0.1673	2.3756	2.1919	-.178
0.02779	0.02926	0.1710	2.3742	2.1928	-.186
0.03013	0.03172	0.1781	2.3705	2.1932	-.189
0.03277	0.03450	0.1857	2.3677	2.1947	-.202
0.03602	0.03792	0.1947	2.3635	2.1954	-.208
0.03911	0.04117	0.2029	2.3604	2.1965	-.217
0.04501	0.04738	0.2177	2.3544	2.1977	-.228

Table XXXVII

Data from Solutions of LiCl in 40.3% Ethanol

M	m	$I^{1/2}$	E	E+2k log m	log $\gamma_{\pm}$
0.02347	0.02521	0.1588	2.3446	2.1555	-.173
0.02779	0.02986	0.1728	2.3383	2.1579	-.194
0.03397	0.03650	0.1910	2.3302	2.1601	-.212
0.03565	0.03830	0.1957	2.3283	2.1601	-.217
0.03791	0.04073	0.2018	2.3259	2.1615	-.224
0.04003	0.04301	0.2074	2.3238	2.1622	-.230
0.04303	0.04623	0.2151	2.3208	2.1629	-.236

Table XXXVIII

Data from Solutions of LiCl in 49.9% Ethanol

M	m	α	$I^{1/2}$	E	E+2klog(cm)	log $\gamma_{\pm}$
.02173	.02388	.970	.1522	2.3414	2.1480	-.168
.02315	.02544	.968	.1569	2.3387	2.1484	-.172
.02661	.02924	.965	.1680	2.3330	2.1497	-.184
.02864	.03147	.963	.1741	2.3303	2.1507	-.194
.03053	.03355	.962	.1797	2.3274	2.1510	-.197
.03234	.03553	.960	.1847	2.3255	2.1519	-.206
.03619	.03976	.957	.1951	2.3212	2.1533	-.218
.03862	.04243	.956	.2014	2.3183	2.1536	-.222

Table XXXIX

Data from Solutions of LiCl in 60.3% Ethanol

M	m	α	$I^{1/2}$	E	E+2klogγm	log $\gamma_{\pm}$
.02663	.03005	.957	.1695	2.2856	2.1033	-.159
.02857	.03223	.956	.1755	2.2827	2.1039	-.164
.03100	.03498	.953	.1825	2.2789	2.1042	-.166
.03241	.03657	.952	.1866	2.2778	2.1053	-.175
.03562	.04019	.949	.1953	2.2733	2.1055	-.178
.03817	.04307	.947	.2019	2.2710	2.1066	-.187
.04433	.05002	.943	.2171	2.2655	2.1086	-.204
.04968	.05605	.939	.2295	2.2610	2.1097	-.213

Table XL

Data from Solutions of LiCl in 70.3% Ethanol

M	m	α	$I^{1/2}$	E	E+2klogγm	log $\gamma_{\pm}$
.02600	.03014	.952	.1694	2.2881	2.1057	-.249
.02814	.03262	.950	.1760	2.2861	2.1076	-.266
.02944	.03413	.949	.1799	2.2843	2.1081	-.269
.03208	.03719	.946	.1875	2.2812	2.1092	-.279
.03458	.04009	.944	.1945	2.2790	2.1108	-.292
.03715	.04307	.942	.2014	2.2766	2.1120	-.297
.03958	.04588	.940	.2077	2.2741	2.1126	-.308
.04206	.04876	.939	.2140	2.2723	2.1139	-.318

Table XLI

Data from Solutions of LiCl in 80.4% Ethanol

M	m	α	$I^{\frac{1}{2}}$	E	E+2klog(m)	log $\gamma_{\pm}$
.02611	.03115	.940	.1711	2.2501	2.0687	-.197
.02883	.03440	.937	.1796	2.2453	2.0688	-.198
.03050	.03639	.936	.1846	2.2450	2.0714	-.219
.03314	.03954	.933	.1920	2.2408	2.0713	-.219
.03555	.04241	.931	.1987	2.2382	2.0722	-.226
.03871	.04618	.928	.2070	2.2354	2.0736	-.238
.04360	.05202	.924	.2193	2.2312	2.0753	-.252
.04303	.05730	.921	.2297	2.2277	2.0766	-.263
.05103	.06088	.919	.2365	2.2253	2.0772	-.269

Table XLII

Data from Solutions of LiCl in 90.4% Ethanol

M	m	α	$I^{1/2}$	E	E+2klogαm	log $\gamma_{\pm}$
.02201	.02709	.928	.1586	2.0124	2.0086	-.282
.02517	.03097	.924	.1692	2.0156	2.0115	-.307
.02817	.03467	.920	.1786	2.0178	2.0135	-.324
.03149	.03875	.916	.1884	2.0278	2.0152	-.338
.03265	.04018	.915	.1916	2.0209	2.0163	-.347
.03572	.04396	.912	.2003	2.0220	2.0172	-.355
.03833	.04717	.910	.2072	2.0242	2.0193	-.373
.04355	.05359	.905	.2202	2.0277	2.0225	-.400
.04569	.05623	.904	.2254	2.0281	2.0229	-.403

Table XLIII

Data from Solutions of LiCl in 100.0% Ethanol

M	m	α	$I^{1/2}$	E	E+2klog$\gamma_{\pm}$m	log $\gamma_{\pm}$
.01371	.01746	.915	.1265	2.1724	1.9599	-.420
.01493	.01902	.912	.1317	2.1699	1.9616	-.434
.01960	.02497	.902	.1501	2.1649	1.9700	-.505
.02189	.02789	.897	.1582	2.1623	1.9728	-.529
.02527	.03219	.891	.1693	2.1602	1.9777	-.571
.02869	.03655	.886	.1800	2.1572	1.9810	-.598
.03465	.04414	.878	.1969	2.1544	1.9874	-.653

Table XLIV

Data from Solutions of LiCl in 30.0% Methanol

M	m	$I^{1/2}$	E	E+2klog m	log $\gamma_{\pm}$
.02404	.02536	.1592	2.3746	2.1858	-.093
.02760	.02911	.1706	2.3684	2.1867	-.101
.03265	.03444	.1856	2.3606	2.1875	-.107
.03598	.03795	.1948	2.3566	2.1885	-.116
.03987	.04205	.2051	2.3516	2.1888	-.118
.04218	.04449	.2109	2.3496	2.1897	-.126
.04506	.04753	.2180	2.3465	2.1900	-.128
.04900	.05168	.2273	2.3427	2.1905	-.133
.05237	.05524	.2350	2.3398	2.1910	-.137

Table XLV

Data for Solutions of LiCl in 50.3% Methanol

M	m	$I^{1/2}$	E	E+2klog m	log $\gamma_{\pm}$
.02086	.02289	.1513	2.3360	2.1419	-.100
.02392	.02625	.1620	2.3296	2.1426	-.106
.02621	.02876	.1696	2.3250	2.1427	-.107
.02736	.03002	.1733	2.3241	2.1440	-.117
.04180	.04586	.2142	2.3052	2.1468	-.141
.05150	.05651	.2377	2.2960	2.1484	-.155

Table XLVI

Data for Solutions of LiCl in 69.9% Methanol

M	m	$I^{1/2}$	E	E+2klog m	log $\gamma_{\pm}$
.02157	.02488	.1577	2.3105	2.1207	-.107
.02269	.02617	.1618	2.3083	2.1211	-.110
.02854	.03292	.1814	2.2982	2.1228	-.124
.03925	.04528	.2128	2.2842	2.1252	-.145
.04260	.04914	.2217	2.2806	2.1258	-.150
.04881	.05630	.2373	2.2750	2.1272	-.161

Table XLVII

Data for Solutions of LiCl in 90.0% Methanol

M	m	$I^{1/2}$	E	E+2klog m	log $\gamma_{\pm}$
.02030	.02491	.1578	2.2885	2.0988	-.232
.02306	.02830	.1682	2.2842	2.1010	-.251
.02713	.03329	.1825	2.2784	2.1036	-.273
.03003	.03685	.1920	2.2746	2.1050	-.285
.03163	.03881	.1970	2.2727	2.1058	-.292
.03470	.04236	.2058	2.2698	2.1074	-.305

Table XLVIII

Data for Solutions of LiCl in 100.0% Methanol

M	m	$I^{1/2}$	E	E+2klog m	log $\gamma_{\pm}$
.02113	.02687	.1639	2.2730	2.0872	-.246
.02654	.03374	.1837	2.2648	2.0907	-.276
.02965	.03770	.1942	2.2620	2.0936	-.300
.03425	.04355	.2087	2.2570	2.0960	-.320
.03772	.04796	.2190	2.2543	2.0982	-.339
.04093	.05204	.2281	2.2510	2.0991	-.347
.04522	.05750	.2398	2.2483	2.1016	-.368
.04921	.06257	.2501	2.2446	2.1022	-.373

Table XLIX

Data for Solutions of NaCl in 10.1% Ethanol

M	m	$I^{1/2}$	E	E+2klog m	log $\gamma_{\pm}$
.01680	.01714	.1309	2.2093	2.0004	-.065
.01882	.01920	.1386	2.2038	2.0007	-.068
.02171	.02215	.1488	2.1972	2.0015	-.074
.02279	.02325	.1525	2.1949	2.0016	-.075
.02598	.02656	.1628	2.1886	2.0021	-.080
.02781	.02837	.1684	2.1855	2.0025	-.083
.03061	.03123	.1767	2.1812	2.0031	-.088
.03465	.03535	.1880	2.1754	2.0037	-.093
.04002	.04082	.2021	2.1688	2.0045	.100

Table L

Data for Solutions of NaCl in 20.4% Ethanol

M	m	$I^{1/2}$	E	E+2klog m	log $\gamma_{\pm}$
.02276	.02357	.1535	2.1631	1.9706	-.067
.02396	.02481	.1575	2.1609	1.9710	-.070
.02668	.02762	.1662	2.1559	1.9715	-.074
.03042	.03150	.1775	2.1498	1.9722	-.080
.03315	.03432	.1853	2.1457	1.9725	-.083
.04175	.04323	.2079	2.1350	1.9736	-.092
.04678	.04844	.2201	2.1297	1.9742	-.097

Table LI

Data for Solutions of NaCl in 30.8% Ethanol

M	m	$I^{1/2}$	E	E+2klog m	log $\gamma_{\pm}$
.01790	.01886	.1373	2.1523	2.9483	-.072
.02269	.02390	.1546	2.1416	1.9498	-.085
.02957	.03115	.1765	2.1292	1.9510	-.095
.03937	.04148	.2037	2.1162	1.9527	-.109
.04499	.04740	.2177	2.1102	1.9535	-.116
.05255	.05536	.2353	2.1034	1.9547	-.126

Table LII

Data for Solutions of NaCl in 40.6% Ethanol

M	m	$I^{1/2}$	E	E+2klog m	log $Y_{\pm}$
.01872	.02013	.1419	2.1315	1.9308	-.090
.02225	.02392	.1547	2.1241	1.9323	-.102
.03077	.03308	.1819	2.1091	1.9340	-.117
.03575	.03844	.1961	2.1027	1.9353	-.128
.04129	.04439	.2107	2.0965	1.9365	-.138
.05082	.05464	.2338	2.0873	1.9379	-.150

Table LIII

Data for Solutions of NaCl in 50.5% Ethanol

M	m	$I^{1/2}$	E	E+2klog m	log $\gamma_{\pm}$
.02057	.02264	.1505	2.1020	1.9074	-.117
.02288	.02518	.1587	2.0979	1.9087	-.128
.02935	.03230	.1797	2.0866	1.9102	-.141
.03273	.03602	.1898	2.0824	1.9116	-.153
.03581	.03941	.1985	2.0780	1.9119	-.156
.03898	.04290	.2071	2.0749	1.9131	-.166
.04312	.04745	.2178	2.0709	1.9143	-.176
.04807	.05290	.2300	2.0660	1.9150	-.182
.05175	.05695	.2386	2.0630	1.9158	-.186

Table LIV

Data for Solutions of NaCl in 60.6% Ethanol

M	m	$I^{1/2}$	E	E+2klog m	log $\gamma_{\pm}$
.02281	.02576	.1605	2.0743	1.8863	-.133
.02764	.03121	.1767	2.0661	1.8880	-.147
.02928	.03307	.1818	2.0638	1.8886	-.152
.03402	.03842	.1960	2.0573	1.8899	-.163
.03698	.04176	.2044	2.0538	1.8906	-.169
.05404	.06143	.2479	2.0383	1.8950	-.206

Table LV

Data for Solutions of NaCl in 69.9% Ethanol

M	m	$I^{1/2}$	E	E+2klog m	log $\gamma_{\pm}$
.02010	.02357	.1526	2.0496	1.8564	-.144
.02365	.02739	.1655	2.0427	1.8579	-.156
.02803	.03246	.1802	2.0354	1.8593	-.168
.03499	.04052	.2013	2.0265	1.8618	-.189
.04798	.05556	.2357	2.0141	1.8656	-.221
.05192	.06012	.2452	2.0111	1.8667	-.231

Table LVI

Data for Solutions of NaCl in 80.0% Ethanol

M	m	$I^{1/2}$	E	E+2klog m	log $\gamma_{\pm}$
.02974	.03545	.1883	1.9823	1.8107	-.178
.03172	.03781	.1944	1.9794	1.8111	-.182
.04020	.04791	.2189	1.9702	1.8141	-.207
.04405	.05250	.2291	1.9669	1.8155	-.219
.05111	.06092	.2468	1.9609	1.8171	-.232
.05638	.06720	.2592	1.9571	1.8184	-.243
.06778	.08079	.2842	1.9507	1.8214	-.269

Table LVII

Data for Solutions of NaCl in 90.5% Ethanol

M	m	$I^{1/2}$	E	E+2klog m	log $\gamma_{\pm}$
.01806	.02223	.1491	1.9451	1.7495	-.319
.01932	.02378	.1542	1.9422	1.7501	-.324
.02156	.02654	.1629	1.9399	1.7534	-.352
.02587	.03185	.1785	1.9348	1.7577	-.388
.02698	.03321	.1822	1.9332	1.7583	-.393
.03107	.03825	.1956	1.9292	1.7615	-.420
.03549	.04369	.2090	1.9249	1.7641	-.442

Table LVIII

Data for Solutions of NaCl in 100.0% Ethanol

M	m	α	$I^{1/2}$	E	E+2klog(km)	log $\gamma_{\pm}$
.00351	.00447	.979	.0662	1.9311	1.6520	-.187
.00390	.00497	.978	.0697	1.9272	1.6535	-.199
.00468	.00596	.975	.0762	1.9193	1.6548	-.210
.00546	.00696	.973	.0823	1.9144	1.6578	-.236
.00624	.00795	.971	.0879	1.9093	1.6594	-.249
.00702	.00894	.969	.0931	1.9046	1.6606	-.260
.00781	.00995	.967	.0980	1.9015	1.6629	-.279

Table LIX

Data for Solutions of NaCl in 69.8% Methanol

M	m	$I^{1/2}$	E	E+2k log m	log $\gamma_{\pm}$
.01184	.01365	.1168	2.0997	1.8790	-.095
.01389	.01602	.1266	2.0924	1.8799	-.102
.02007	.02315	.1521	2.0759	1.8823	-.123
.02521	.02908	.1705	2.0657	1.8838	-.135
.03181	.03669	.1915	2.0557	1.8858	-.152
.03957	.04563	.2136	2.0471	1.8884	-.174

Table LX

Data for Solutions of NaCl in 100.0% Methanol

M	m	$I^{1/2}$	E	E+2klog m	log $\gamma_{\pm}$
.01545	.01964	.1402	2.0158	1.8139	-.195
.01805	.02295	.1515	2.0104	1.8165	-.217
.02091	.02659	.1631	2.0032	1.8168	-.220
.02815	.03579	.1892	1.9924	1.8214	-.259
.03084	.03921	.1980	1.9893	1.8229	-.271
.03332	.04236	.2058	1.9874	1.8250	-.289
.03780	.04806	.2192	1.9830	1.8271	-.307
.04124	.05243	.2290	1.9800	1.8285	-.319

Table LXI

Data for Solutions of KCl in 28.9% Methanol

M	m	$I^{1/2}$	E	E+2klog m	log $\gamma_{\pm}$
.01218	.01282	.1132	2.2080	1.9842	-.068
.01402	.01476	.1215	2.2007	1.9841	-.068
.02851	.03002	.1732	2.1682	1.9880	-.101
.03480	.03664	.1914	2.1589	1.9890	-.109
.04084	.04300	.2074	2.1522	1.9905	-.122
.05078	.05346	.2312	2.1428	1.9923	-.137
.05822	.06130	.2476	2.1364	1.9929	-.142

Table LXII

Data for Solutions of KCl in 49.7% Methanol

M	m	$I^{1/2}$	E	E+2klog m	log $\gamma_{\pm}$
.01324	.01451	.1205	2.1590	1.9415	-.068
.01963	.02151	.1467	2.1410	1.9438	-.087
.02446	.02681	.1637	2.1298	1.9439	-.088
.02794	.03062	.1750	2.1240	1.9449	-.096
.02983	.03269	.1808	2.1206	1.9449	-.096
.03336	.03656	.1912	2.1155	1.9455	-.101
.03635	.03984	.1996	2.1118	1.9462	-.108
.09213	.10098	.3178	2.0722	1.9544	-.177

Table LXIII

Data for Solutions of KCl in 70.1% Methanol

M	m	$I^{1/2}$	E	E+2klog m	log $\gamma_{\pm}$
.02186	.02523	.1588	2.0830	1.8939	-.136
.02491	.02875	.1696	2.0777	1.8954	-.148
.02841	.03279	.1811	2.0722	1.8966	-.158
.03219	.03715	.1928	2.0668	1.8976	-.167
.03743	.04320	.2079	2.0605	1.8991	-.179
.04029	.04650	.2156	2.0575	1.8999	-.186
.04708	.05434	.2331	2.0514	1.9018	-.202
.05646	.06517	.2553	2.0443	1.9040	-.221
.06167	.07118	.2668	2.0410	1.9052	-.231

Table LXIV

Data for Solutions of KCl in 90.6% Methanol

M	m	$I^{1/2}$	E	E+2klog m	log $\gamma_{\pm}$
.01772	.02179	.1476	2.0567	1.8601	-.159
.01872	.02301	.1517	2.0542	1.8604	-.162
.02052	.02523	.1588	2.0509	1.8618	-.174
.02849	.03503	.1872	2.0376	1.8654	-.204
.03400	.04180	.2045	2.0308	1.8677	-.223
.03999	.04916	.2217	2.0241	1.8693	-.237

Table LXV

Data for Solutions of KCl in 100.0% Methanol

M	m	$I^{1/2}$	E	E+2klog m	log $\gamma_{\pm}$
.01420	.01805	.1344	2.0277	1.8214	-.171
.01663	.02114	.1454	2.0216	1.8235	-.188
.01923	.02445	.1564	2.0155	1.8248	-.200
.02079	.02643	.1626	2.0122	1.8255	-.207
.02263	.02877	.1696	2.0085	1.8262	-.211
.02432	.03092	.1758	2.0060	1.8274	-.221
.02607	.03315	.1821	2.0035	1.8285	-.231
.03490	.04437	.2107	1.9932	1.8332	-.270

Appendix II

Density(g./ml.) of Ethanol-Water and Methanol-Water Solvents at 25 °C

Weight %	Ethanol(22)	Methanol(20)
0.0	0.997077	0.99707
2.0	0.993359	
5.0	0.988166	
6.0	0.986563	
10.0	0.980434	0.9799
15.0	0.973345	
20.0	0.966392	0.9644
25.0	0.958946	
30.0	0.950672	
35.0	0.941459	
40.0	0.931483	0.9316
45.0	0.920850	
50.0	0.909852	0.9119
55.0	0.898502	
60.0	0.886990	0.8907
65.0	0.875269	
70.0	0.863399	
75.0	0.851336	
80.0	0.839114	0.8425
85.0	0.826596	
90.0	0.813622	0.8150
95.0	0.799912	
98.0	0.791170	
99.0	0.788135	
100.0	0.785058	0.7866

Appendix III

Dielectric Constants

Wt. % Ethanol-Water(47)	
0.0	78.5
10.0	72.8
20.0	67.0
30.0	61.1
40.0	55.0
50.0	49.0
60.0	43.4
70.0	38.0
80.0	32.8
90.0	28.1
100.0	24.3
Wt. % Methanol(20)	
10.0	74.16
20.0	69.95
40.0	60.93
50.0	56.30
60.0	51.61
80.0	42.58
90.0	37.92
100.0	32.64

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