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Association Constants of Cadmium Ion with Chloride in Molten $LiNO_3$ and in Mixtures of $LiNO_3$ with KNO_3 from Measurements of the Solubility of Silver Chloride*

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Received July 29,1967

The solvent effect on association of cadium ion with halide in molten alkali nitrates has been investigated extensively by emf methods, using silver-silver halide electrodes.[1,2,3,4] *It has not been possible to measure the association constants directly in lithium nitrate or in mixtures containing more than about 75%* $LiNO_3$ *because of the failure to obtain reliable Nernst slopes with the silver-silver halide electrodes in these melts. In order, therefore, to determine the association constants as a function of solvent composition, a solubility method was developed for the evaluation of the association constant of cadmium ion with chloride in* $LiNO_3$ *and in some* $LiNO_3$*-*KNO_3 *mixtures, including the equimolar mixture for which emf results are available as a test of the new method.*

Experimental Section

The liquidus temperatures of silver chloride in a fused $LiNO_3$ solvent with potassium chloride, silver nitrate, and cadmium nitrate as solutes were determined at different cadmium nitrate and potassium chloride concentrations.

Chemicals. Reagent grade KNO_3, $AgNO_3$, $LiNO_3$ and KCl from the Mallinckrodt Chemical Works were used without further purification. Mallinckrodt reagent grade $Cd(NO_3)_2 \cdot 4H_2O$ was dried and analyzed. The moisture content of the dried material was found to be less than 0.3% and was used without further purification.

Temperature Control and Measurement. Four moles of $LiNO_3$-KNO_3 mixture were melted in a 300 ml Pyrex tall form beaker and heated to the desired temperature in a resistance furnace equipped with a Variac for manual control of the temperature. A chromel-alumel thermocouple calibrated against the melting points of bismuth, cadmium and zinc metals was used to measure the temperature. The thermocouple was contained in a Pyrex cell and was immersed in the center of the melt. The emf of the thermocouple was bucked by a Leeds-Northrup type K-3 potentiometer and the excess potential was recorded on a Sargent Model SR recorder. The potentiometer was equipped with an Eppley standard cell and a Leeds-Northrup galvanometer with a sensitivity of 0.003 microamperes per millimeter. The recorder had a one millivolt range on a ten inch scale, or approximately 3/8 of an inch per degree.

Experimental Procedure. Four moles of $LiNO_3$-KNO_3 mixture, with five milliliters of a standardized aqueous silver nitrate solution added to the mixture to provide a mole ratio of $AgNO_3$ in the melt of $R_{AgNO_3} = 1.75\ 10^{-4}$, were heated to the desired temperature in a 300 ml Pyrex tall-form beaker and stirred vigorously with a Pyrex propeller.

The solution was purged with helium for two to three hours, which was found to be sufficient time to remove water and gases from the solution. At the end of this period the flow of helium was discontinued.

A weighed amount of potassium chloride that would saturate the solution with silver chloride a few degrees below the temperature of interest was added. The melt was cooled to within five degrees of the expected liquidus temperature and the furnace was set such that there was no further cooling. The solution was now cooled by increments of two to three tenths of one degree by immersing in it a cold glass rod. The glass rod served a dual purpose; it cooled the solution and prevented supercooling by shocking the system. The temperature at which the first faint cloudiness appeared was taken as the saturation temperature. Cooling an additional 0.5 degree yielded a pronounced precipitate. If this precipitate had not coagulated, it would redissolve within 0.5° of the liquidus temperature. This temperature was reproducible to ±0.2° in all cases.

A second increment of potassium chloride was added to make a total chloride concentration that would precipitate silver chloride at a temperature slightly above the temperature of interest and its liquidus temperature determined. The potassium chloride concentration at the desired temperature was found by interpolation.

Addition of cadmium nitrate decreased the liquidus

(*) Research supported under USAEC contract AT(30-1)-2873. Report number NYO 2873-21.

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temperature below the temperature of interest and a new liquidus temperature was determined by repeating the above procedure, i.e. adding increments of KCl.

Potassium chloride and cadmium nitrate were added alternately as above until equilibrium chloride concentrations at five or six cadmium concentrations could be determined at temperatures near the desired temperature.

Results and Discussion

The solubility of silver chloride in a fused $LiNO_3$-KNO_3 solvent containing $AgNO_3$ increases with increasing $Cd(NO_3)_2$ concentration. This increased solubility can be interpreted on the basis of complex formation.

In a solution saturated with AgCl at a known $Cd(NO_3)_2$ concentration in which association of the type AgCl, $AgCl_2^-$, $CdCl^+$, $CdCl_2$, etc. may occur, the total stoichiometric concentrations of $AgNO_3$, KCl, and $Cd(NO_3)_2$ are:

$$R_{Cd(NO_3)_2} = R'_{Cd} + R'_{CdCl} + R'_{CdCl_2} + 2R'_{Cd_2Cl} + \ldots . \tag{1}$$

$$R_{AgNO_3} = R'_{Ag} + R'_{AgCl} + R'_{AgCl_2} + 2R'_{Ag_2Cl} + \ldots . \tag{2}$$

$$\begin{aligned} R_{KCl} = {} & R'_{Cl} + R'_{AgCl} + 2R'_{AgCl_2} + R'_{Ag_2Cl} + \ldots . \\ & + R'_{CdCl} + 2R'_{CdCl_2} + R'_{Cd_2Cl} + \ldots . \end{aligned} \tag{3}$$

where the concentrations are expressed in mole ratios $\left(R = \dfrac{\text{moles solute}}{\text{moles solvent}}\right)$. The prime denotes the free species considered and the unprimed values the stoichiometric concentrations.

Dependence of R_{KCl} on $R_{Cd(NO_3)_2}$. Assuming that the deviation from ideality in the system is a result of complex ion formation, we may write the association quotients of the silver and cadmium complexes and the solubility product of silver chloride in the usual manner as

$$S = R'_{Cl}R'_{Ag} \qquad \alpha_1 = \frac{R'_{AgCl}}{R'_{Ag}R'_{Cl}} \qquad \alpha_2 = \frac{R'_{AgCl_2}}{R'_{AgCl}R'_{Cl}}$$

$$\alpha_{1\,2} = \frac{R'_{Ag_2Cl}}{R'_{AgCl}R'_{Cl}} \qquad K_1 = \frac{R'_{CdCl}}{R'_{Cd}R'_{Cl}} \qquad K_2 = \frac{R'_{CdCl_2}}{R'_{CdCl}R'_{Cl}}$$

$$K_{1\,2} = \frac{R'_{Cd_2Cl}}{R'_{CdCl}R'_{Cl}} \qquad \text{etc.}$$

With the above quotients, equations (1) and (3) can be written

$$R_{Cd(NO_3)_2} = R'_{Cd}(1 + K_1R'_{Cl} + K_1K_2R'^2_{Cl} + \ldots .) \tag{4}$$

$$\begin{aligned} R_{KCl} = {} & R'_{Cl}(1 + \alpha_1R'_{Ag} + 2\alpha_1\alpha_2R'_{Cl}R'_{Ag} + \ldots .) + \\ & K_1R'_{Cd}R'_{Cl}(1 + 2K_2R'_{Cl} + \ldots .) \end{aligned} \tag{5}$$

Combining (4) and (5) gives

$$\begin{aligned} R_{KCl} = {} & R'_{Cl}(1 + \alpha_1R_{Ag} + 2\alpha_1\alpha_2R'_{Cl}R'_{Ag} + \ldots .) + \\ & K_1R_{Cl}R_{Cd(NO_3)_2}\left[\frac{1 + 2K_2R'_{Cl} + \ldots .}{1 + K_1R'_{Cl} + K_1K_2R'^2_{Cl} + \ldots .}\right] \end{aligned} \tag{6}$$

Differentiation of equation (6) with respect to $R_{Cd(NO_3)_2}$ yields

$$\frac{dR_{KCl}}{dR_{Cd(NO_3)_2}} = K_1R'_{Cl}\left[\frac{1 + 2K_2R'_{Cl} + \ldots .}{1 + K_1R'_{Cl} + K_1K_2R'^2_{Cl} + \ldots .}\right] \tag{7}$$

The terms containing $\dfrac{dR'_{Cl}}{dR_{Cd(NO_3)_2}}$ and $\dfrac{dR'_{Ag}}{dR_{Cd(NO_3)_2}}$ are zero at saturation with silver chloride at a fixed stoichiometric mole ratio of silver nitrate and fixed temperature, if the reasonable assumption is made that mixed species such as $(Cd\text{-}Cl\text{-}Ag)^{2+}$ are not formed at these concentrations. For, under these conditions, R'_{Ag} depends only on R'_{Cl}. Hence the solubility product depends only on R'_{Cl},

$$S = R'_{Ag}R'_{Cl} = f(R'_{Cl})R'_{Cl} = F(R'_{Cl})$$

Since S is constant, R'_{Cl} (and also, therefore, R'_{Ag}) is independent of $R_{Cd(NO_3)_2}$ under the above conditions.

With the condition of low silver chloride solubility ($R_{AgCl} \cong 3 \times 10^{-4}$) the term in brackets in equation (7) is equal to unity within a few tenths of one percent for any reasonable choice of K_1 and K_2 values. This is equivalent to the condition that a silver-silver chloride electrode follow the Nernst equation in chloride concentration, a situation which has been verified in equimolar $LiNO_3$-KNO_3. With this condition, equation (7) reduces to

$$\frac{dR_{KCl}}{dR_{Cd(NO_3)_2}} \cong K_1R'_{Cl} \tag{8}$$

The species chloride (R'_{Cl}) and the stoichiometric chloride (R_{KCl}) concentrations can be related through equations (2) and (3) by introducing the association quotients of the silver chloride complexes. In the absence of $Cd(NO_3)_2$, equation (3) reduces to

$$\left.\frac{R_{KCl}}{R'_{Cl}}\right|_{(R_{Cd(NO_3)_2}=0)} = 1 + \alpha_1R'_{Ag}(1 + 2\alpha_2R'_{Cl} + \ldots .) \tag{9}$$

and equation (2) becomes

$$\frac{R_{AgNO_3}}{R'_{Ag}} = (1 + \alpha_1R'_{Cl} + \alpha_1\alpha_2R'^2_{Cl} + \ldots .) \tag{10}$$

Combination of (9) and (10) gives

$$\left.\frac{R_{KCl}}{R'_{Cl}}\right|_{(R_{Cd(NO_3)_2}=0)} =$$

$$= 1+\alpha_1 R_{AgNO_3}\left[\frac{1+2\alpha_2 R'_{Cl}}{1+\alpha_1 R'_{Cl}+\alpha_1\alpha_2 R'^{2}_{Cl}+\ldots}\right] \qquad (11)$$

As in equation (7) the term in brackets is virtually equal to unity. (In cases where this may not be so, the calculated K must be corrected for the solubility of AgCl.) Combining equations (8) and (11) yields

$$\frac{dR_{KCl}}{dR_{Cd(NO_3)_2}} = K_1 \frac{R_{KCl}\Big|_{(R_{Cd(NO_3)_2}=0)}}{1+\alpha_1 R_{AgNO_3}} \qquad (12)$$

The association constant for the complex $CdCl^+$ can be calculated from equation (12) if the increased solubility of potassium chloride upon additions of cadmium nitrate is determined and the AgCl association constant can be estimated.

To calculate the association quotient for the reaction $Cd^{2+}+Cl^- = CdCl^+$ by equation (12), the potassium chloride concentrations in a saturated solution of silver chloride at several cadmium nitrate concentrations at constant temperature is needed. In this work potassium chloride concentrations in saturated silver chloride solutions were determined at temperatures slightly above and below the temperature under investigation, at constant cadmium nitrate concentration, for several cadmium nitrate concentrations. In order to use this data in equation (12), the potassium chloride concentration at the temperature of interest was interpolated from large scale plots of log R_{KCl} vs. 1000/T at each cadmium concentration.

Figure 1 is a plot of log R_{KCl} vs. 1000/T over a 70°C temperature range. Over this temperature range the curves are all linear, as this plot shows. In the bulk of the data the temperature range was approximately 10°, and in this range any curvature is negligible.

Plots of $R_{Cd(NO_3)_2}$ vs. R_{KCl} are presented in Figures 2 through 7. The linearity of these plots is in agreement with equation (12) and justifies neglect of the terms which were dropped from equation (7).

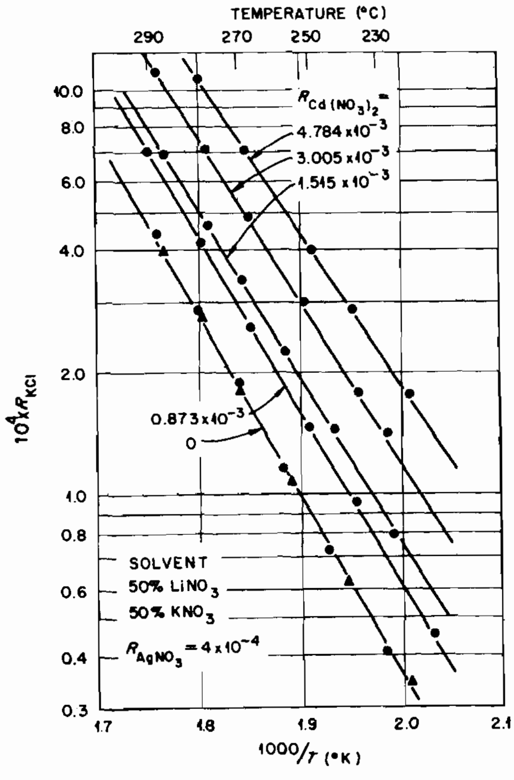


Figure 1.

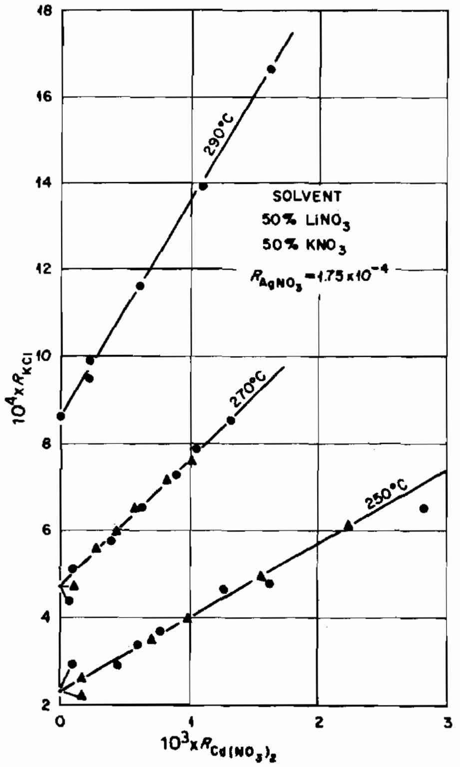
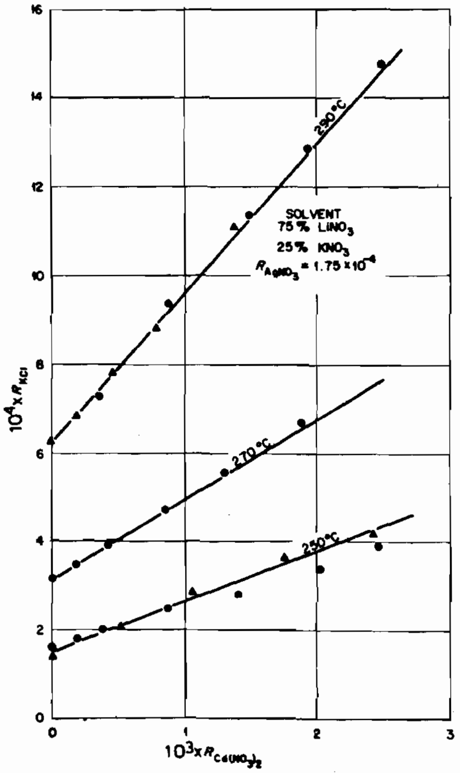


Figure 2.



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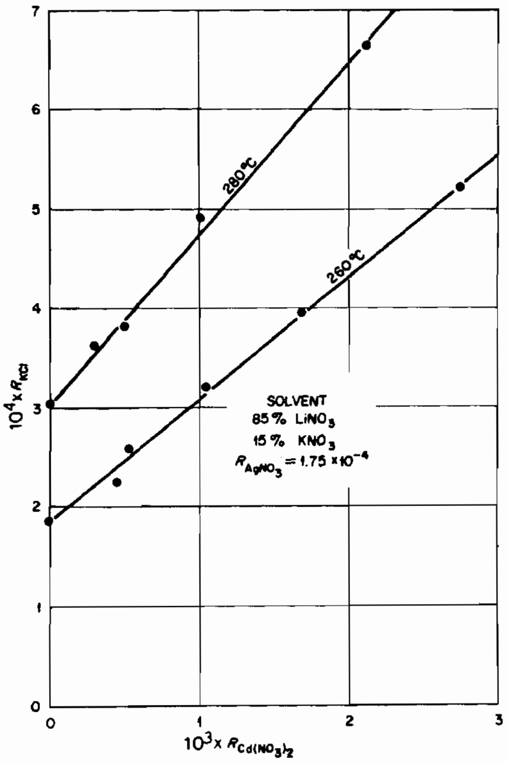

Figure 4

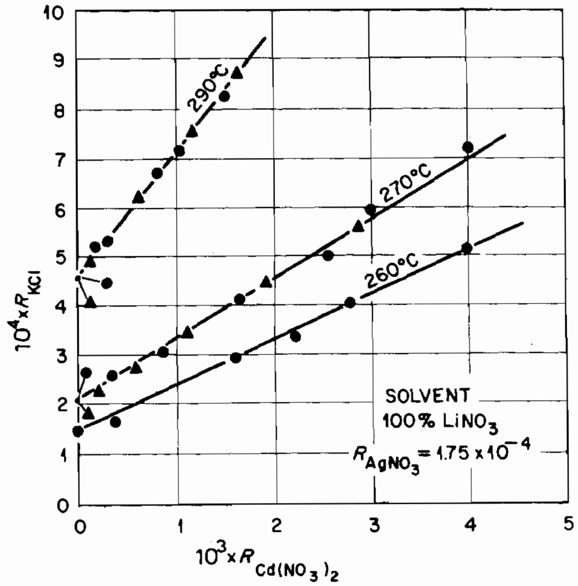

Figure 6

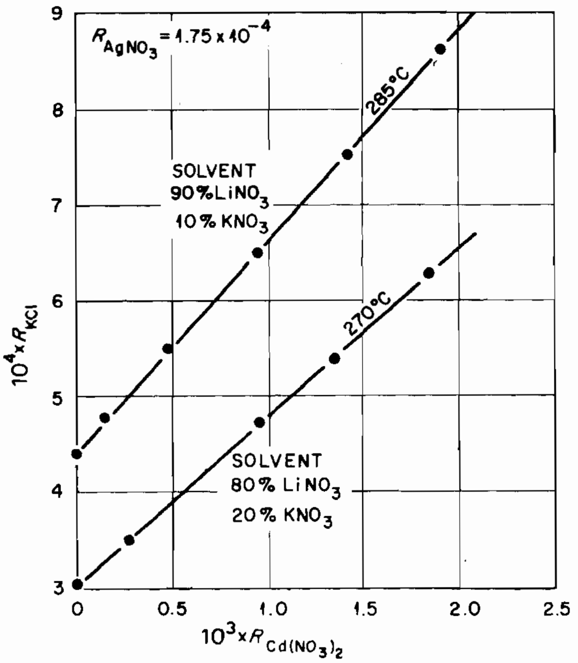

Figure 5.

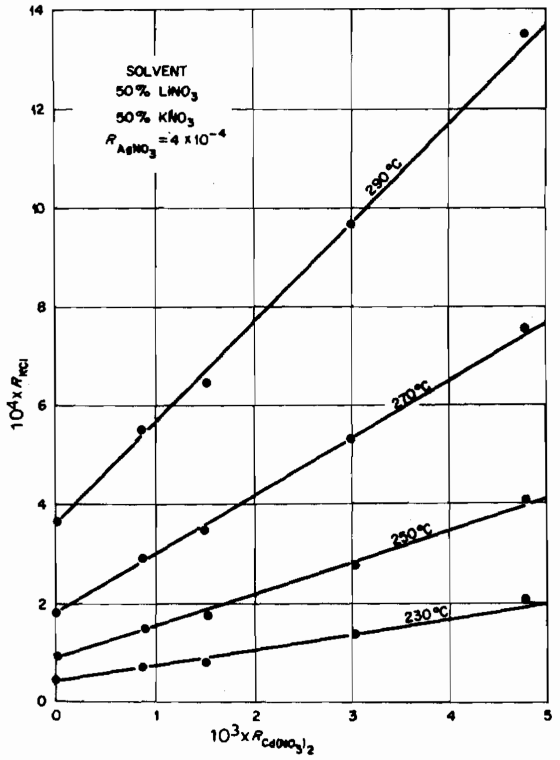

Figure 7.

The slopes of the lines in Figures 2-7 were determined from large scale plots and are equal to $\dfrac{R_{KCl}\Big|_{(R_{Cd}=0)}}{1+\alpha_1 R_{AgNO_3}}$; $R_{KCl}\Big|_{(R_{Cd(NO_3)_2}=0)}$ can be read from the plots and R_{AgNO_3} was known experimentally. The association constant for the silver chloride complex, α_1, can be calculated from the Helmholtz free energy of formation of this complex with the assumptions that the equation of the quasi-lattice model holds and that there is little solvent effect on the free energy.

The specific Helmholtz free energy of AgCl has been determined to be −5.1 kcal/mole at 240° in 70% KNO_3, 30% $LiNO_3$.[5] It has been shown that over small temperature ranges, the equation from the quasi-lattice model, $\alpha_1 = Z[\exp(-\Delta A_1/RT) - 1]$, is valid.[6] The assumption of small solvent effect is demonstrated by the reported free energy value of −5.2 kcal/mole in lithium nitrate.[7]

The factor $(1+\alpha_1 R_{AgNO_3})$ is approximately 1.15. Therefore, an error of 20% in α_1 would cause less than 3% error in K_1.

Values of K_1 for CdCl calculated in this way are listed in Table I.

Table I.

Solvent $LiNO_3$	KNO_3	T°C	K_1 (mole ratio units)	$-\Delta A$ (kcal/mole)
0.50	0.50	250	837	5.15
		270	710	5.15
		290	652	5.26
0.75	0.25	250	845	5.15
		270	659	5.09
		290	589	5.15
0.80	0.20	270	660	5.09
0.85	0.15	260	759	5.14
		280	662	5.17
0.90	0.10	285	552	5.02
1.00	0	260	675	5.01
		270	657	5.09
		290	572	5.11

The solubility of potassium chloride as a function of cadmium nitrate concentration in the presence of silver nitrate is plotted in Figures 2-7 at several temperatures in mixtures of lithium nitrate and potassium nitrate. The calculated association constants of $CdCl^+$ and the specific Helmholtz free energies of association are summarized in Table I.

The equation of the quasi-lattice model, $K_1 = Z[\exp(-\Delta A/RT) - 1]$, in which Z is the quasi-lattice coordination number, here taken as 6, and ΔA is the specific Helmholtz free energy, was used to find ΔA. These values together with the values of the stability constants are tabulated in Table I. A weighted least squares fit of these values (weighted by number of runs made at each set of conditions) gives the result $-\Delta A = 5.08 + 0.18\ N_{KNO_3}$; N_{KNO_3} is the mole fraction of KNO_3 in the solvent. With N_{KNO_3} equal to 0.5, $-\Delta A$ is 5.17 as compared to 4.95 from emf measurements.[2]

This difference amounts to a 20% difference in K_1 at 250°C, which is slightly beyond the experimental limits of the two methods, 10% for the method used in this work, and 5% for the emf method. Although this would seem to indicate an inherent error in one of the two methods, a thorough examination of the technique and method indicated none. In past work,[7] the stability was found to increase slightly with increasing temperature. This trend might be large enough to place the results within the experimental accuracy. It is difficult to determine accurately the association constant of AgCl in mixtures containing $LiNO_3$ because of the very low solubility of AgCl at low temperatures, and the poor behaviour of silver electrodes in lithium containing melts at high temperatures. The absolute values of the association constants determined from the solubility measurements may therefore be in error by about 15%, but the relative values are probably more precise. Even a 15% error constitutes much better agreement between different methods for evaluating association constants in nitrate melts than has been demonstrated previously. The method therefore gives probably the most reliable estimates to date for values of the association constant in $LiNO_3$ and in other (mixed) systems where emf methods could not be applied. The observed small solvent effect is consistent with the small solvent effect observed over a more limited range of solvent compositions with an emf method.

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