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Association of Cadmium Ion or Lead Ion with Chloride or Bromide in Molten Mixtures of Lithium Nitrate and Potassium Nitrate[1]

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Association constants for the formation of $CdCl^+$, $CdCl_2$, $PbCl^+$, $PbCl_2$, $CdBr^+$, $CdBr_2$, $PbBr^+$, and $PbBr_2$ in molten mixtures of lithium nitrate and potassium nitrate were evaluated from electromotive force measurements at several temperatures. The results were compared with the quasi-lattice model of molten salt solutions and with previous results in other alkali nitrates. The solvent effect on the formation of $CdBr^+$ in mixtures of $LiNO_3$ and KNO_3 is discussed in terms of the reciprocal coulomb effect.

Introduction

Association equilibria of cadmium ion with bromide or iodide ion and of lead ion with bromide ion in molten equimolar sodium nitrate–potassium nitrate have been described in previous papers.[2] In this paper, we describe association equilibria in the molten salt solvent equimolar lithium nitrate–potassium nitrate and in several other molten mixtures of lithium nitrate and potassium nitrate. Association constants for $PbCl^+$, $PbCl_2$, $PbBr^+$, $PbBr_2$, $CdCl^+$, $CdCl_2$, $CdBr^+$, and $CdBr_2$ are evaluated from electromotive force measurements and compared with association constants in other molten salt solvents. The applicability of the quasi-lattice model of molten salt solutions[3] to the temperature dependence of the equilibrium constants is further tested and the effect of the solvent cation on the association equilibria is discussed.

Experimental

The measurement of the electromotive force of molten salt concentration cells with (saturated) silver–silver halide electrodes has been described previously.[2] Reagent grade salts from Mallinckrodt or J. T. Baker were used without further purification. Lithium nitrate was dried *in vacuo* at 120° before use, but results obtained with lithium nitrate which had not been predried did not differ from those obtained with the predried salt. Anhydrous cadmium nitrate was prepared and analyzed as described previously.[2b] The halides were added as the potassium salts to avoid drying the hygroscopic lithium halides.

Results

The electromotive force was measured of the concentration cells

$$\begin{array}{c|l||l|c} & \mathrm{AgX(s)} & \mathrm{AgX(s)} & \\ \mathrm{Ag} & \mathrm{(Li,K)X} & \mathrm{M(NO_3)_2} & \mathrm{Ag} \\ & \mathrm{(Li,K)NO_3} & \mathrm{(Li,K)X} & \\ & & \mathrm{(Li,K)NO_3} & \end{array}$$

where X is chloride or bromide, M is cadmium ion or lead ion, and the solvent is a molten mixture of lithium nitrate and potassium nitrate. In the absence of cations (M) which associate with X, the e.m.f. of the cell is given by the Nernst equation in the stoichiometric concentration of halide ion. The stoichiometric activity coefficient was calculated by means of the relation

$$1/\gamma_{\mathrm{(Li,K)X}} = \exp(F\Delta\mathrm{e.m.f.}/RT)$$

from the difference (Δe.m.f.) between the e.m.f. of the above cell and the e.m.f. of the cell in which M (Cd^{2+} or Pb^{2+}) was absent from the right-hand half cell.

Values of Δe.m.f. were obtained for additions of $Cd(NO_3)_2$ to: solutions of chloride in equimolar KNO_3–$LiNO_3$ at 160, 180, and 200°, in 0.6 (mole fraction) KNO_3–$0.4LiNO_3$, and in 0.4 (mole fraction) KNO_3–$0.6LiNO_3$ at 180°; solutions of bromide in equimolar $LiNO_3$–KNO_3 at 171° and in 0.2 (mole fraction) KNO_3–$0.8LiNO_3$, $0.35KNO_3$–$0.65LiNO_3$, equimolar KNO_3–$LiNO_3$, $0.6KNO_3$–$0.4LiNO_3$, and $0.74KNO_3$–$0.26LiNO_3$ at 240°. Δe.m.f. was obtained also for additions of $Pb(NO_3)_2$ to: solutions of chloride in equimolar KNO_3–$LiNO_3$ at 160, 180, and 200°; solutions of bromide in equimolar KNO_3–$LiNO_3$ at 160 and 200°.[4] The additions of $Cd(NO_3)_2$ to solutions of chloride in $0.4KNO_3$–$0.6LiNO_3$ and in $0.6KNO_3$–$0.4LiNO_3$ at 180° were made to clarify discrepancies in the literature which have been described previously.[5] The concentration units are the stoichiometric mole ratios, R (moles of solute per mole of nitrate solvent).

The association constants, defined as

$$K_1 = \frac{R_{\mathrm{MX}}}{R_{\mathrm{M}}R_{\mathrm{X}}}$$

$$K_2 = \frac{R_{\mathrm{MX_2}}}{R_{\mathrm{MX}}R_{\mathrm{X}}}$$

$$K_{12} = \frac{R_{\mathrm{M_2X}}}{R_{\mathrm{M}}R_{\mathrm{MX}}}$$

in which R represents the mole ratios of the associated and unassociated species, were obtained graphically[2,5] from the relations

$$K_1 = \lim_{R_{\mathrm{KX}}\to 0} \left\} \lim_{R_{\mathrm{M(NO_3)_2}}\to 0} \left(\frac{\partial\, 1/\gamma_{\mathrm{(Li,K)X}}}{\partial R_{\mathrm{M(NO_3)_2}}}\right)_{R_{\mathrm{(Li,K)X}}} \right\{$$

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[1] Supported by the U. S. Atomic Energy Commission under Contract No. AT(30-1)-2873 with the University of Maine.

[2] (a) D. L. Manning, M. Blander, and J. Braunstein, *Inorg. Chem.*, **2**, 345 (1963); (b) J. Braunstein and R. M. Lindgren, *J. Am. Chem. Soc.*, **84**, 1534 (1962).

[3] M. Blander and J. Braunstein, *Ann. N.Y. Acad. Sci.*, **79**, 838 (1960).

[4] The data have been deposited with the ADI Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C. Document Number 7732.

[5] J. Braunstein, M. Blander, and R. M. Lindgren, *J. Am. Chem. Soc.*, **84**, 1529 (1962).

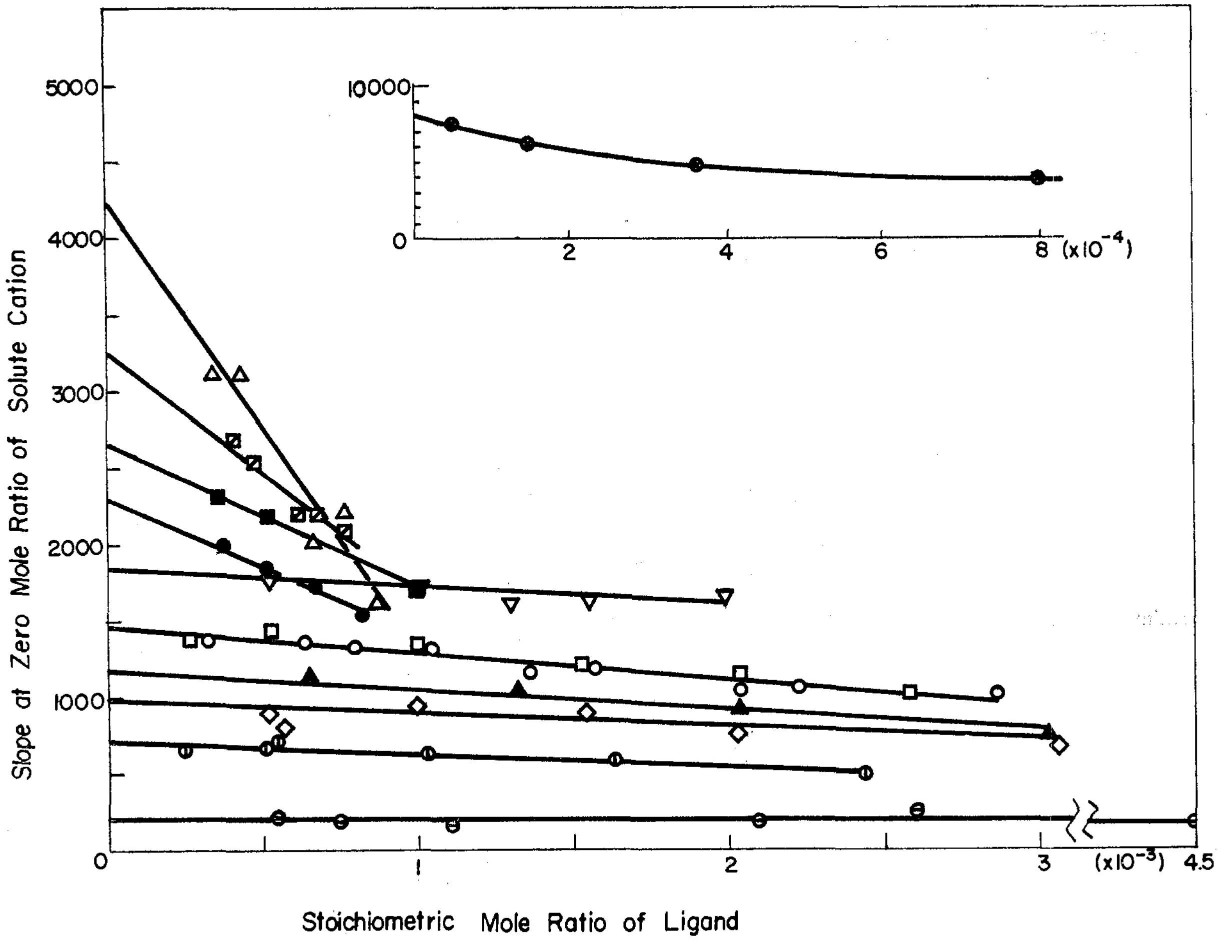

Fig. 1.—Extrapolation of

$$\lim_{R_{M(NO_3)_2}\to 0}\left(\frac{\partial 1/\gamma_{(Li,K)X}}{\partial R_{M(NO_3)_2}}\right)_{R_{(Li,K)X}}$$

to zero concentration of bromide to obtain K_1 and K_2 in mixtures of $LiNO_3$ and KNO_3: △ Cd, Br, 240°, $0.2KNO_3$; ☒ Cd, Br, 240°, $0.5KNO_3$; ■ Cd, Br, 240°, $0.6KNO_3$; ● Cd, Br, 240°, $0.74KNO_3$; ▼ Cd, Cl, 160°, $0.5KNO_3$; O Cd, Cl, 180°, $0.5KNO_3$; □ Cd, Cl, 180°, $0.6KNO_3$; ▲ Cd, Cl, 200°, $0.5KNO_3$; ◇ Pb, Br, 160°, $0.5KNO_3$; ⦶ Pb, Br, 200°, $0.5KNO_3$; ⊖ Pb, Cl, 200°, $0.5KNO_3$. Insert: ⊗ Cd, Br, 171°, $0.5KNO_3$.

and

$$K_1(2K_2 - K_1) = \lim_{R_{KX}\to 0}\left\{\frac{\partial}{\partial R_{KX}}\left[\lim_{R_{M(NO_3)_2}\to 0}\left(\frac{\partial 1/\gamma_{(Li,K)X}}{\partial R_{M(NO_3)_2}}\right)_{R_{(Li,K)X}}\right]\right\}$$

The extrapolations used to obtain the association constants of Cd^{2+} and Pb^{2+} with Cl^- and Br^- in equimolar $LiNO_3$–KNO_3 are shown in Fig. 1. These are thermodynamic constants since they are obtained by extrapolation to a fixed reference state (infinite dilution).

The constant K_{12} for the formation of binuclear species M_2X is given by the relation

$$2K_1K_{12} = \lim_{\substack{R_{(Li,K)X}\to 0\\ R_{M(NO_3)_2}\to 0}}\left\{\left(\frac{\partial^2 1/\gamma_{(Li,K)X}}{\partial R^2_{M(NO_3)_2}}\right)_{R_{(Li,K)X}}\right\}$$

and is negligibly small relative to K_1, as seen by the absence of positive curvature in plots of $1/\gamma_{(Li,K)X}$ vs. $R_{M(NO_3)_2}$.

The constants which were obtained from these measurements are collected in Table I, along with the constants for the association of lead or cadmium with bromide ion in equimolar $NaNO_3$–KNO_3 from previous work.[2] In addition to the association constants, specific Helmholtz free energies of association were calculated from the equation derived from the quasi-lattice model[3,6]

$$K_1 = Z(\exp(-\Delta A/RT) - 1)$$

in which ΔA is the specific Helmholtz free energy and Z is the quasi-lattice coordination number, here taken as $Z = 6$.

Discussion

In Fig. 2 some of the values of $(1/\gamma_{(Li,K)Br}) - 1$ at fixed bromide concentrations are plotted as functions of the concentration of added cadmium nitrate to illustrate the dependence of $1/\gamma$ on the concentration of bromide, temperature, and solvent. (The data in $(Na,K)NO_3$ are from ref. 2b.) The concentration dependence of the slopes of $(1/\gamma_{(Li,K)Br}) - 1$ at 240° indicates the need to extrapolate to zero concentration,

(6) M. Blander, *J. Chem. Phys.*, **34**, 342 (1961).

Table I

Association Constants (Moles of Solvent/Mole) and Specific Helmholtz Free Energies of Association (Kcal./Mole) in Mixtures of $LiNO_3$ and KNO_3

			Solvent					
Cation	Anion	T, °C.	$LiNO_3$	KNO_3	K_1	$-\Delta A_1$	K_2	$-\Delta A_2$
Cd^{2+}	Cl^-	160	0.5	0.5	1850	4.94	890	5.05
		180	0.5	0.5	1450	4.94	665	5.02
		180	0.4	0.6	1500	4.96	714	5.08
		180	0.6	0.4	[1300][a]	[4.85][a]	[600][a]	[4.93][a]
		200	0.5	0.5	1200	4.97	537	5.04
Pb^{2+}	Cl^-	160	0.5	0.5	250	3.20	110	3.20
		180	0.5	0.5	230	3.28	93	3.24
		200	0.5	0.5	205	3.34	90	3.39
Cd^{2+}	Br^-	171	0.5	0.5	8000	6.33	3300	6.3
		240	0.8	0.2	[4200][a]	6.67	1700	6.7
		240	0.65	0.35	3600	6.58	1600	6.6
		240	0.50	0.50	3200	6.38	1300	6.4
		240	0.4	0.6	2650	6.20	1100	6.2
		240	0.26	0.74	2300	6.06	1000	6.1
		240	[(0.5$NaNO_3$-0.5KNO_3)		1520	5.67	680	[5.73][b]
Pb^{2+}	Br^-	160	0.5	0.5	990	4.40	400	4.36
		200	0.5	0.5	730	4.52	300	4.53
		240	[(0.5$NaNO_3$-0.5KNO_3)		250	3.83	125	[4.0][c]

[a] Uncertainty in K_1 20%; other uncertainties in K_1 are 5%. [b] Reference 2b. [c] Reference 2a.

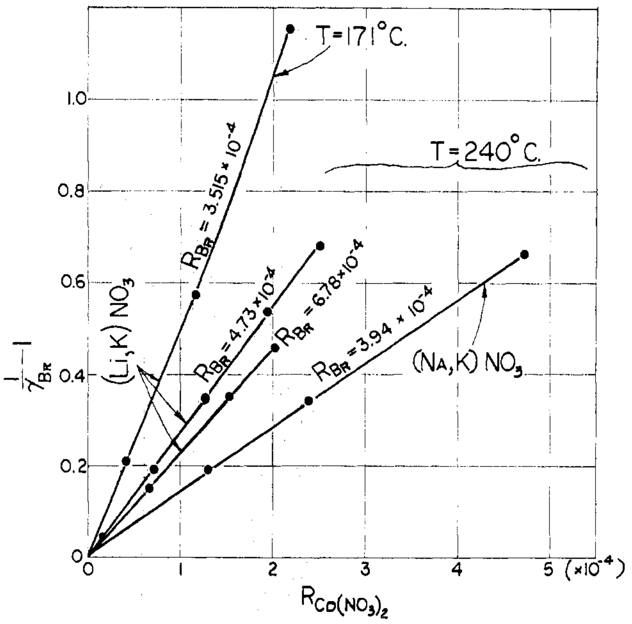

Fig. 2.—Activity coefficients of (Li,K)Br in the presence of cadmium ion. $(1/\gamma_{Br}) - 1$ is the ratio of "associated" to "unassociated" bromide ion. The lowest curve (in (Na,K)NO_3) is from data in ref. 2b.

as in Fig. 1, to obtain the thermodynamic association constants.

When these extrapolations are carried out, giving the association constants listed in Table I, the calculated specific Helmholtz free energies of association for $CdBr^+$ in equimolar $LiNO_3$-KNO_3 at 171 and 240° are -6.33 and -6.38 kcal./mole, respectively, which agree within the experimental error. The variation of ΔA with temperature for $PbCl^+$ and $PbBr^+$ is barely outside the experimental error, while the constancy of ΔA for $CdCl^+$ is striking. Thus, the quasi-lattice model, although derived for monovalent ions, predicts the temperature coefficient of the association constant for divalent ions also.

The association constant for $CdCl^+$ at 180° was obtained in the solvent mixtures 0.6$LiNO_3$–0.4KNO_3, 0.5$LiNO_3$–0.5KNO_3, and 0.4$LiNO_3$–0.6KNO_3. The results for the latter two mixtures were the same within experimental error and the difference observed for 0.6$LiNO_3$–0.4KNO_3 may be due to decreased stability of the e.m.f. in melts containing more than 50% lithium nitrate. In a previous paper,[5] the association constant for $CdCl^+$ in the eutectic mixture of $LiNO_3$ and KNO_3 at 180° was recalculated from other workers' polarographic data,[7] and the value 900 ± 200 (moles of solvent/mole) was obtained. It was pointed out that this apparent association constant was a minimum value since it was based on a finite concentration of $Cd(NO_3)_2$. Our new value for this association constant, based on more precise and complete data, is 1500 ± 50. Our new value for the association constant for $PbCl^+$ at 180° is 230 ± 20. Our estimated value of the association constant based on our recalculation of polarographic data[5,7] was 270 ± 80. Thus the need for data at low concentrations and an extrapolation to zero concentration is demonstrated.

A striking solvent effect is observed for the association of cadmium or lead with bromide ions in mixtures of $LiNO_3$ and KNO_3 (Table I) in which the association constants are larger than in $NaNO_3$–KNO_3 and increase with increasing proportions of lithium nitrate in the melt, as shown in Fig. 3. At first sight, the direction of the solvent effect appears to be anomalous when compared with the effect of solvent cation on the association of Ag^+ with Cl^-, Br^-, or I^- in $NaNO_3$ and KNO_3[8] and of Pb^{2+} with Br^- in mixtures of $NaNO_3$ and KNO_3.[2a] In the solvents $NaNO_3$ and KNO_3, the direction of the solvent cation effect was predicted

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[7] J. H. Christie and R. A. Osteryoung, *J. Am. Chem. Soc.*, **82**, 1841 (1960).

[8] (a) A. Alvarez-Funes, J. Braunstein, and M. Blander, *ibid.*, **84**, 1538 (1962); (b) D. L. Manning, R. C. Bansal, J. Braunstein, and M. Blander, *ibid.*, **84**, 2028 (1962); (c) J. Braunstein and R. Hagman, *J. Phys. Chem.*, **67**, 2281 (1963).

correctly by the "reciprocal coulomb effect." If one considers the change of coulombic energy in the exchange of nearest neighbors taking place in an association reaction in the two solvents BD and B′D

$$\mathrm{MD} + \mathrm{BX} = \mathrm{MX} \times \mathrm{BD};\quad \Delta U$$
$$\mathrm{MD} + \mathrm{B'X} = \mathrm{MX} + \mathrm{B'D};\quad \Delta U'$$

where M and X are the associating cation and anion, respectively, B and B′ are the solvent cations in the two solvents, and D is the solvent anion (nitrate ion), the difference is

$$\Delta U' - \Delta U = -Ne^2\left[\frac{1}{r_{\mathrm{B'}} + r_{\mathrm{D}}} + \frac{1}{r_{\mathrm{B'}} + r_{\mathrm{X}}} - \frac{1}{r_{\mathrm{B'}} + r_{\mathrm{X}}} - \frac{1}{r_{\mathrm{B}} + r_{\mathrm{D}}}\right] \quad (1)$$

where the r are the ionic radii, N is Avogadro's number, and e is the electronic charge.[8b] If the separation of the cation and anion of the solvent BD ($r_{\mathrm{B}} + r_{\mathrm{D}}$) is called d and the fractional differences of size of B′ and X are defined as $\beta = (r_{\mathrm{B'}} - r_{\mathrm{B}})/d$ and $\alpha = (r_{\mathrm{X}} - r_{\mathrm{D}})/d$, eq. 1 becomes

$$\Delta U' - \Delta U = \frac{Ne^2}{d}\,\frac{2\beta\alpha[1 + {}^1/_2(\beta + \alpha)]}{(1 + \beta)(1 + \alpha)(1 + \beta + \alpha)} \quad (2)$$

If β and α have the same sign (*e.g.*, B′ (Li^+) smaller than B (K^+) and X (Cl^-) smaller than D ($\mathrm{NO_3}^-$)), the energy difference is positive, predicting lower stability (smaller association constants) for MX in the solvent B′D than in BD. In this calculation, only the coulombic energy of nearest neighbor ions has been considered, neglecting energy differences due to more distant ions. Calculations for a linear infinite chain indicate that the magnitude of the energy difference is smaller when all interionic distances are considered.[8b]

This simple calculation of the reciprocal coulomb effect leads to the wrong sign for the solvent effect on the association of cadmium ion with bromide in mixtures of $\mathrm{LiNO_3}$ and $\mathrm{KNO_3}$. The difficulty probably is due in part to the neglect of the polarization energy, which for nitrate ion may be appreciable. Another reason for the discrepancy may be the difficulty of assigning a single "effective ionic radius" to the nitrate ion, which is not spherical, in all molten alkali nitrates. If the distance of closest approach of a nitrate ion to a solvent cation were r_{BD} in the solvent BD (*e.g.*, $\mathrm{KNO_3}$) and $r_{\mathrm{B'D'}}$ in the solvent B′D′ (*e.g.*, $\mathrm{LiNO_3}$), and the fractional difference of "size" of D' were $\Delta = (r_{\mathrm{D'}} - r_{\mathrm{D}})/(r_{\mathrm{B}} + r_{\mathrm{D}})$, eq. 2 would be replaced by

$$\Delta U' - \Delta U = \frac{Ne^2}{d}\,\frac{\Delta[(1 + \alpha)^2 + \beta\alpha] + 2\beta\alpha[1 + {}^1/_2(\beta + \alpha)]}{(1 + \alpha)(1 + \beta + \alpha)(1 + \beta + \Delta)} \quad (3)$$

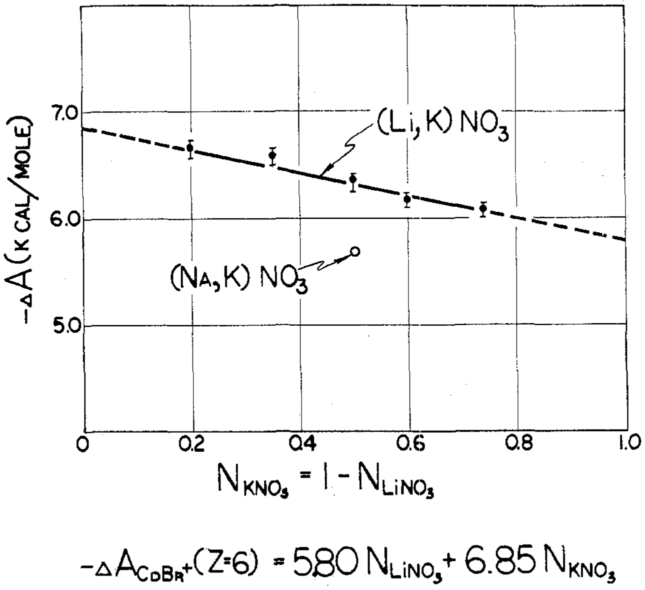

Fig. 3.—Variation of specific Helmholtz free energy (ΔA) of formation of $\mathrm{CdBr^+}$ (calculated for $Z = 6$) with solvent composition. $N_{\mathrm{KNO_3}}$ is the mole fraction of $\mathrm{KNO_3}$ in the solvent.

Taking the Pauling radii[9] of $\mathrm{Li^+}$, $\mathrm{K^+}$, $\mathrm{Br^-}$ (0.60, 1.33, 1.95 Å.) and the value 2.19 Å.[10] for the "radius" of nitrate ion, $\beta = -0.16$ and $\alpha = -0.053$. Since Δ appears in (3) as a first-order term, while β and α occur as products (second-order terms), a value of $\Delta = -0.018$, corresponding to a distance of closest approach 0.08 Å. smaller in $\mathrm{LiNO_3}$ than in $\mathrm{KNO_3}$, would change the sign of the "reciprocal coulomb effect." Since the nitrate ion is not spherical, and radii between 1.78 and 2.30 Å. have been used,[11] a difference of the above magnitude in the "distance of closest approach" or "effective radius" caused by an ion of high charge density such as $\mathrm{Li^+}$ may not be implausible. It should be recognized that, in the absence of an exact calculation of the coulombic energy and the polarization energy, the above rationalization of the anomalous solvent effect in $\mathrm{LiNO_3}$–$\mathrm{KNO_3}$ is not distinguishable from a statement that the increased polarization of $\mathrm{NO_3}^-$ by the small lithium ion may result in greater stability of an Li–$\mathrm{NO_3}$ "bond" and hence a greater stability of MX in $\mathrm{LiNO_3}$ than in $\mathrm{KNO_3}$.

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(9) Handbook of Chemistry, 9th Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1956, p. 108.

(10) O. J. Kleppa and L. S. Hersh, *J. Chem. Phys.*, **36**, 544 (1962).

(11) G. J. Janz and D. W. James, *Electrochim. Acta*, **7**, 427 (1962).