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The Freezing Points of Aqueous Solutions. IX. Mixtures of the Reciprocal Salt Pair: Potassium Nitrate–Lithium Chloride[1]

BY GEORGE SCATCHARD AND S. S. PRENTISS

In the study of mixtures of electrolytes there are advantages in treating together all possible mixtures of a reciprocal salt pair. The system potassium nitrate–lithium chloride was selected because of the great difference in behavior of the simple salts. The osmotic coefficient of potassium nitrate differs little from the Debye–Hückel limiting law, and that of lithium nitrate passes through a minimum and becomes positive at about one molal. The coefficient of lithium chloride is almost the same as that of lithium nitrate, and that of potassium chloride is about the average of those of the two nitrates.

Solutions of a reciprocal salt pair may be regarded as a three-solute system by omitting one salt and permitting negative concentrations of the salt having no ion in common with the omitted one. The results are symmetrical, however, if it is treated as a four-solute system with one equation of condition. If the ions are taken as the solute components, the condition is the law of electrical neutrality

$$(K^+) + (Li^+) = (NO_3^-) + (Cl^-)$$

where the symbols in parentheses represent concentrations. The method of analysis developed in our earlier papers is simpler if the four salts are regarded as the solute components. The corresponding condition is the chemical equation (identity)

$$\underset{1}{KNO_3} + \underset{3}{LiCl} = \underset{2}{KCl} + \underset{4}{LiNO_3}$$

The numbers under the formulas indicate the subscripts which will be used in this paper. They are so chosen that the two odd salts (or the two even salts) have no ion in common.

The above condition relates the ten B (or C) coefficients by four equations of the type

$$B_{1j} + B_{3j} = B_{2j} + B_{4j} \qquad (1)$$

and the twenty D (or E) coefficients by ten equations of the type

$$D_{1jk} + D_{3jk} = D_{2jk} + D_{4jk} \qquad (2)$$

These equations permit covering the whole field (up to the five-halves power of the concentration) with measurements only on the single salts and on mixtures with a common ion. If two mixtures are measured for each of two such pairs, one mixture each is sufficient for each of the other two. The mixture of equal parts of all four ions was also studied as a check. The measurements on the single salts have already been reported. The mixtures studied are: $KNO_3(0.75) - KCl(0.25)$; $KNO_3(0.5) - KCl(0.5)$; $KNO_3(0.7316) - LiNO_3(0.2684)$; $KNO_3(0.5150) - LiNO_3(0.4850)$; $KCl(0.5) - LiCl(0.5)$; $LiNO_3(0.5) - LiCl(0.5)$; $KNO_3(0.5) - LiCl(0.5)$. The last mixture is also $KCl(0.5) - LiNO_3(0.5)$.

TABLE I

EQUATIONS FOR CONDUCTANCES AT 10°

KNO_3	$\Lambda = 105.000 - 45.2135\,M^{1/2} + 1.7860\,M + 31.9477\,M^{3/2} - 26.5585\,M^2 + 6.4726\,M^{5/2}$
KCl	$\Lambda = 107.377 - 45.5871\,M^{1/2} + 37.6022\,M - 18.0042\,M^{3/2} + 3.6623\,M^2 - 0.1586\,M^{5/2}$
$LiNO_3$	$\Lambda = 78.257 - 41.0097\,M^{1/2} + 38.3162\,M - 30.3563\,M^{3/2} + 12.8752\,M^2 - 2.2836\,M^{5/2}$
$LiCl$	$\Lambda = 80.634 - 41.3834\,M^{1/2} + 36.4632\,M - 27.1076\,M^{3/2} + 10.2546\,M^2 - 1.5638\,M^{5/2}$

DEVIATIONS FROM ADDITIVITY

$KNO_3(0.75) - KCl(0.25)$	$\Delta\Lambda = +0.0421\,M^2 - 0.0613\,M^{5/2}$
$KNO_3(0.5) - KCl(0.5)$	$\Delta\Lambda = -\ .1592\,M^2 + .0666\,M^{5/2}$
$KNO_3(0.732) - LiNO_3(0.268)$	$\Delta\Lambda = -\ .4871\,M^2 + .2340\,M^{5/2}$
$KNO_3(0.515) - LiNO_3(0.485)$	$\Delta\Lambda = -\ .9066\,M^2 + .4882\,M^{5/2}$
$KCl(0.5) - LiCl(0.5)$	$\Delta\Lambda = -\ .6998\,M^2 + .3540\,M^{5/2}$
$LiNO_3(0.5) - LiCl(0.5)$	$\Delta\Lambda = +\ .0322\,M^2 + .0270\,M^{5/2}$
$KNO_3(0.5) - LiCl(0.5)$	$\Delta\Lambda = -1.1512\,M^2 + .6148\,M^{5/2}$

The experimental procedure was the same as that described in the earlier papers, and the salts used were materials purified for the measurements on the single salts except that, for the mixture with potassium nitrate, new lithium nitrate was prepared by essentially the same method as before.

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[1] Paper VIII in this series appeared in THIS JOURNAL, **56**, 2314 (1934).

As in paper VIII we express the conductance of the simple salts by equations of the type

$$L/M = (L/M)_0 + \alpha M^{1/2} + \beta M + \gamma M^{3/2} + \delta M^2 + \epsilon M^{5/2} \qquad (3)$$

The coefficients were determined by least squares, relating $(L/M)_0$ and α by the Onsager equation. The original results were adjusted slightly to make the limiting conductances additive functions of the ions. For the mixtures the first four coefficients were taken as additive, and the deviations of the last two from additivity, expressed as $\Delta\Lambda$, determined by least squares. For the equimolal mixture of all four ions, the additive value is the mean of those of the four single salts. Table I contains these values of the coefficients, and the deviations of the individual measurements from the equations are shown in Fig. 1.

The very small β and positive γ of potassium nitrate are worthy of notice. This behavior corresponds to that noted by Shedlovsky[2] for this salt at 25°. In spite of this irregularity, mixtures with other salts show only slight deviations from additivity. Our solutions were handled in the air since the solutions to be analyzed must be so handled. The conductances could be measured with greater accuracy in investigations planned for that alone, and our conductance results may be looked upon as exploratory.

Figure 2 shows the osmotic coefficients of potassium nitrate, of lithium nitrate and of their equimolar mixtures. The broken line is the mean of those for the two single salts. Figure 3 shows the corresponding quantities for the chlorides. Figure 4 shows equimolal mixtures of potassium nitrate and chloride, and of the lithium salts. The means of the osmotic coefficients of the component salts are not shown as they never differ from the measured values of the mixtures by the width of the lines as drawn. Figure 5 shows the osmotic coefficient of the equimolar mixture of potassium nitrate and lithium chloride, or of potassium chloride and lithium nitrate. The lower broken curve is the mean of the coefficients of the first pair, the upper one the mean of the coefficients of the second pair. The middle broken line is the mean of all four salts.

The curves show the most important characteristics of the osmotic coefficients for these mixtures: that they are additive up to fairly high concentrations, and that the deviations are never great even at the limit of our measurements.

In determining the coefficients by least squares it was found in fact that the B coefficients were linear for mixtures with a common ion as closely as the calculated coefficients fitted the condition equations (1). When this slight adjustment was made to make the B's linear, the same relation was found for the C coefficients. When these were adjusted to linearity, the D's and then the

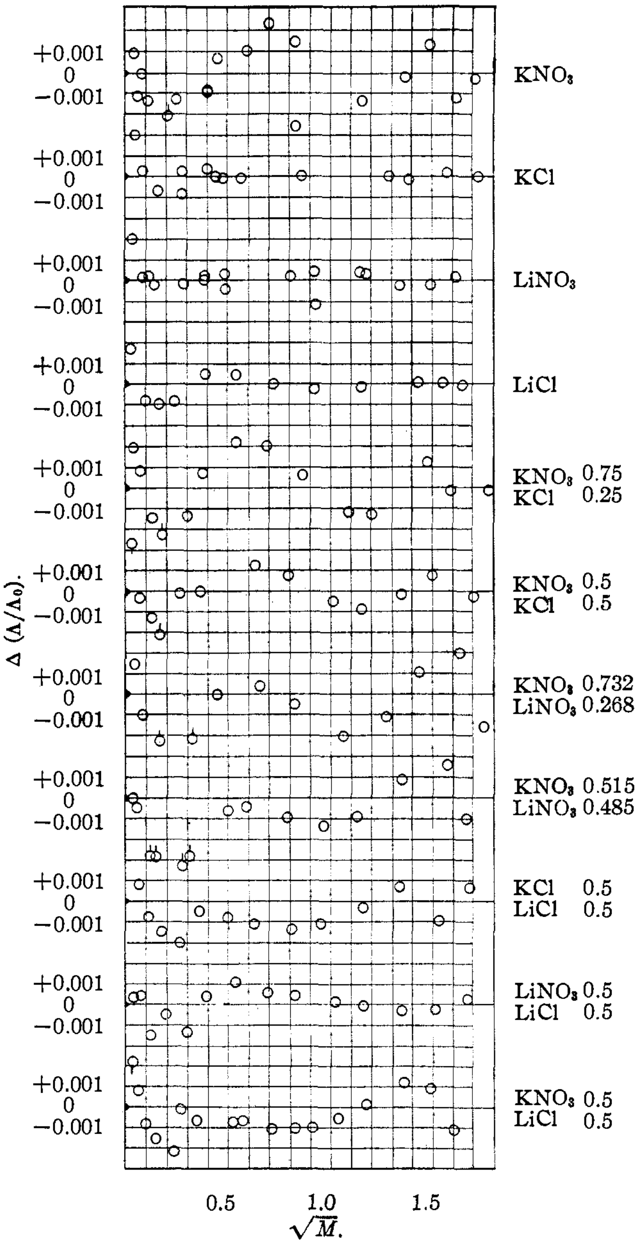

Fig. 1.—Deviations of conductance ratios.

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[2] T. Shedlovsky, THIS JOURNAL, **54**, 1411 (1932).

E's were found to reduce to quadratics instead of cubics. The coefficients so determined gave a maximum error of 0.15% for the mixture without a common ion. The final coefficients were determined to spread this error among the eleven measurements. From the reduction in the number of terms necessary to express our measurements it follows that there were many more determinations than necessary to specify the system. The *B* and *C* coefficients are determined by the measurements on the single salts alone, and three measurements on mixtures would have been sufficient to determine the *D* and *E* coefficients. The coefficients so determined are given in Table II, and the deviations of the individual measurements from the osmotic coefficients calculated from these constants are given in Fig. 6.

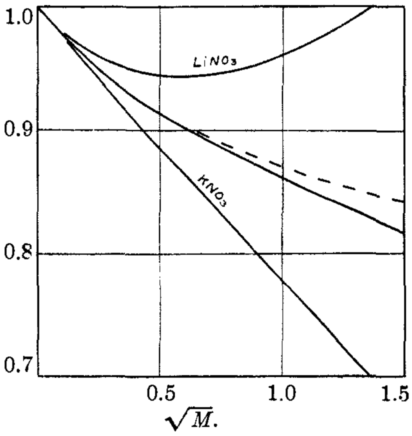

Fig. 2.—Osmotic coefficients of nitrates.

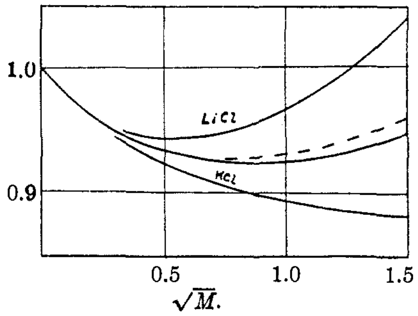

Fig. 3.—Osmotic coefficients of chlorides.

TABLE II

COEFFICIENTS IN TERMS OF SALT COMPONENTS

A_1'	−0.52864	D_{111}'	0.02690	E_{111}'	−0.00387
A_2'	− .52864	D_{222}'	.06935	E_{222}'	− .01144
A_3'	− .52864	D_{333}'	.04950	E_{333}'	− .00557
A_4'	− .52864	D_{444}'	.13880	E_{444}'	− .02652
		D_{112}'	.04189	E_{112}'	− .00699
B_{11}'	.11596	D_{122}'	.05604	E_{122}'	− .00951
B_{22}'	.32640	D_{113}'	.07079	E_{113}'	− .01176
B_{33}'	.40156	D_{133}'	.08202	E_{133}'	− .01305
B_{44}'	.47478	D_{114}'	.05580	E_{114}'	− .00865
B_{12}'	.22118	D_{144}'	.09310	E_{144}'	− .01620
B_{13}'	.40059	D_{223}'	.05644	E_{223}'	− .00695
B_{14}'	.29538	D_{233}'	.04983	E_{233}'	− .00499
B_{23}'	.36398	D_{224}'	.04312	E_{224}'	− .00502
B_{24}'	.25876	D_{244}'	.06576	E_{244}'	− .01029
B_{34}'	.43818	D_{334}'	.08170	E_{334}'	− .01363
		D_{344}'	.11146	E_{344}'	− .02061
C_{11}'	− .07744	D_{123}'	.06483	E_{123}'	− .00990
C_{22}'	− .18650	D_{124}'	.05068	E_{124}'	− .00737
C_{33}'	− .17019	D_{134}'	.08798	E_{134}'	− .01492
C_{44}'	− .30763	D_{234}'	.05822	E_{234}'	− .00794
C_{12}'	− .13197				
C_{13}'	− .24707				
C_{14}'	− .19259				
C_{23}'	− .17834				
C_{24}'	− .12381				
C_{34}'	− .23891				

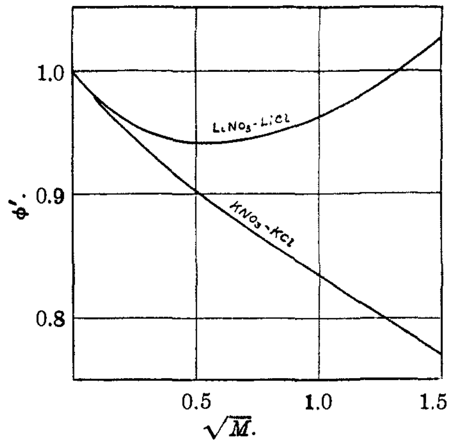

Fig. 4.—Osmotic coefficients of mixtures with common cation.

From the hypothesis that two ions of like charge repel each other so strongly that the interaction of their short range forces is negligible, Brönsted[3] derived the relations that the term proportional to the concentration in the osmotic coefficients of mixtures of salts with a common ion is linear, and that the corresponding term in ln γ of either salt changes just as much as the osmotic coefficient, so that this term for either salt in the other is the mean of the values for the two salts each in their own solution. Brönsted has given much experimental evidence supporting this theory, but the most extensive confirmation comes from the results reported here. Guggenheim[4] simplified the

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[3] J. N. Brönsted, THIS JOURNAL, **44**, 877 (1922); **45**, 2898 (1923).

[4] E. A. Guggenheim, Det 18 Skandinaviske Naturforskermøde (1929).

derivation and found also that the corresponding relation for equimolar mixtures without a common ion is that the linear term in the osmotic coefficient is the mean of the values for the salts concerned and for the reciprocal salt pair, and that the linear term in ln γ of either salt in the other is the mean of the values for the reciprocal salt pair. This is also confirmed by our measurements.

These relations follow simply and directly from the method of analysis we have developed and the hypothesis that ions of the same sign have a negligible interaction. It is necessary to develop the coefficients for the single ions as components. Let the subscripts $_{\text{K, L, N, C}}$ refer to K^+, Li^+, NO_3^- and Cl^-, respectively. In a solution of KNO_3 $x_K = x_N = 1/2$ and

$$\begin{aligned} B_{11} &= B_{KK}\,x_K^2 + 2B_{KN}\,x_K\,x_N + B_{NN}\,x_N^2 \\ &= (B_{KK} + 2B_{KN} + B_{NN})/4 \end{aligned}$$

If the interaction between ions of the same sign is negligible.

$$\begin{aligned} B_{KK} &= B_{NN} = 0, \text{ and} \\ B_{11} &= B_{KN}/2 \end{aligned}$$

In a mixture of KNO_3 and KCl $x_K = 1/2$, $x_N = x_1/2$, $x_C = x_2/2$. So, if $B_{KK} = B_{NN} = B_{CC} = 0$

$$\begin{aligned} B_x &= 2B_{KN}\,x_Kx_N + 2B_{KC}\,x_Kx_C = B_{KN}x_1/2 + B_{KC}x_2/2 \\ &= B_{11}x_1 + B_{22}x_2 \end{aligned}$$

In a mixture of KNO_3 and LiCl $x_K = x_N = x_1/2$, and $x_L = x_C = x_3/2$.

$$\begin{aligned} B_x &= 2(B_{KN}x_Kx_N + B_{KC}x_Kx_C + B_{LN}x_Lx_N + B_{LC}x_Lx_C) \\ &= (B_{KN}x_1^2 + B_{KC}x_1x_3 + B_{LN}x_1x_3 + B_{LC}x_3^2)/2 \\ &= [(B_{KN}x_1 + B_{LC}x_3) + (B_{KC} + B_{LN} - B_{KN} - B_{LC})x_1x_3]/2 \end{aligned}$$

since $x_3 = 1 - x_1$. When $x_1 = x_3 = 1/2$

$$\begin{aligned} B_x &= (B_{KN} + B_{KC} + B_{LN} + B_{LC})/8 \\ &= (B_{11} + B_{22} + B_{44} + B_{33})/4 \end{aligned}$$

The relations between the osmotic coefficients and the activity coefficients follow directly from the equations for these quantities.

More important than the simpler derivations of the conclusions of Brönsted and Guggenheim about the linear term is the extension to the coefficients of the higher powers. If the number of pairs of ions with the same charge is negligible, their interaction with their ion atmospheres must also be negligible, so that terms such as C_{KK} and C_{NN} are also zero, and the equations given above for the B's also hold for the C's. It follows that for salts with a common ion the term in the osmotic coefficient proportional to the three-halves power of concentration is also linear. The corresponding term in ln γ is not linear, however, because the added salt also changes I. Physically this corresponds to its contribution to the ion atmospheres. This term in ln γ for a salt in the solution of another salt with a common ion is 1/10 the difference between the corresponding values for the single salts nearer the value for the solvent salt than the mean of the two.

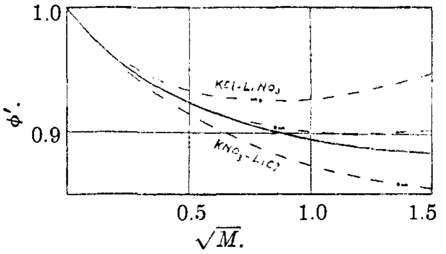

Fig. 5.—Osmotic coefficients of mixtures of four ions.

If the interaction of pairs of ions of the same charge is negligible, that of three ions of the same charge must certainly be. Then for a solution of KNO_3

$$\begin{aligned} D_{111} &= 3D_{KKN}x_K^2x_N + 3D_{KNN}x_Kx_N^2 \\ &= 3(D_{KKN} + D_{KNN})/8 \end{aligned}$$

For a mixture of KNO_3 and KCl

$$\begin{aligned} D_x &= 3(D_{KKN}x_K^2x_N + D_{KNN}x_Kx_N^2 + 2D_{KNC}x_Kx_Nx_C + D_{KKC}x_K^2x_C + D_{KCC}x_Kx_C^2) \\ &= 3(D_{KKN}x_1 + D_{KNN}x_1^2 + 2D_{KNC}x_1x_2 + D_{KKC}x_2 + D_{KCC}x_2^2)/8 \\ &= 3[(D_{KKN} + D_{KNN})x_1 + (D_{KKC} + D_{KCC})x_2 + (2D_{KNC} - D_{KNN} - D_{KCC})x_1x_2]/8 \end{aligned}$$

The cubic expression degenerates to a quadratic, and the deviation from linearity is only twice the difference between the interaction of a group of three molecules in which the two ions of the same sign are different and the average of those of the two possible groups in which the two are the same. In most cases it may be expected to be small compared to the linear term. These conclusions may be extended to the E coefficients by the same argument that the conclusions derived for the B's were extended to the C's. It follows that these terms in the osmotic coefficient must be quadratic functions of the composition for mixtures with a common ion, and that the deviations from linearity should be small.

These conclusions are all confirmed by our measurements. The generalization of these results to other cases should be reasonably safe, for solutions of uni-univalent electrolytes in water are relatively unfavorable for the electrostatic forces to prevent the formation of groups of ions all of the same sign. For two ions this repulsion is proportional to the product of the valences of the ions and to the reciprocal of the dielectric constant. and the generalization to ions of higher valence or to solvents of smaller dielectric constant should be particularly safe. We must, of course, expect some exceptions, such as the mercurous ion where very strong specific forces appear to overcome the electrostatic repulsion.

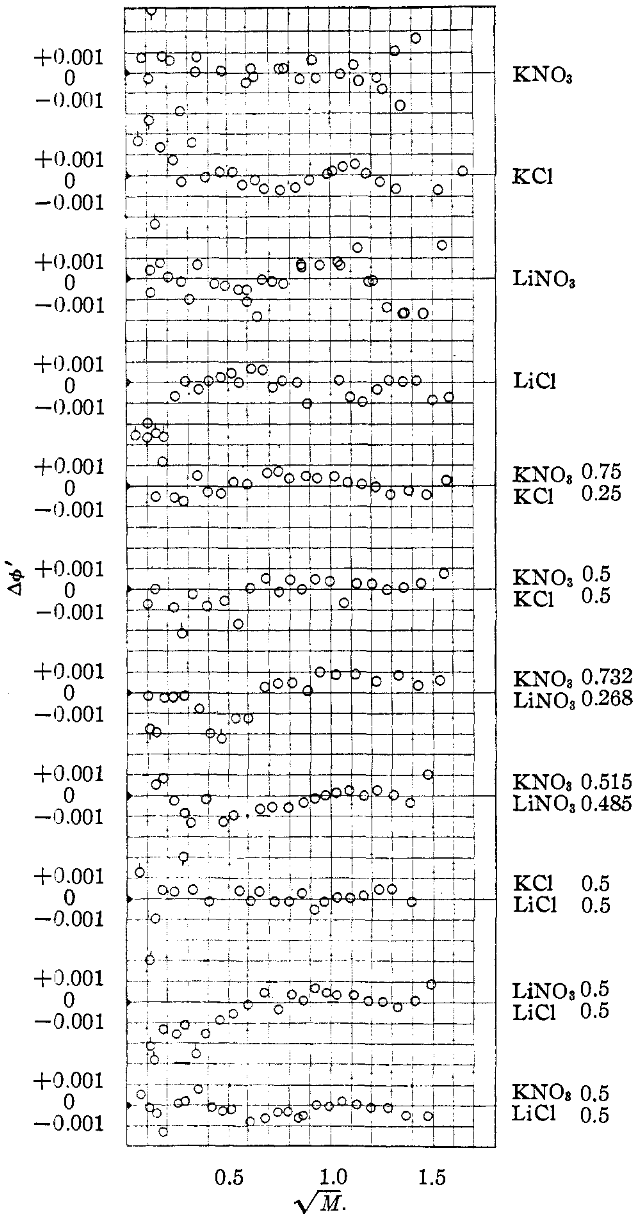

Fig. 6.—Deviations of osmotic coefficients. A few large deviations in very dilute solutions are not shown.

The regularities are brought out most sharply if we adopt another method of expression. Letting C represent the fraction of chloride and L the fraction of lithium salt, $(1 - C)$ is the fraction of nitrate and $(1 - L)$ the fraction of potassium salt. Any possible mixture of the reciprocal salt pair can be represented by giving C and L appropriate values between zero and unity, including the limits. We shall express our results as φ_μ, $\ln \gamma_1$, $\ln (\gamma_2/\gamma_1)$ and $\ln (\gamma_4/\gamma_1)$; $\ln (\gamma_3/\gamma_1) = \ln (\gamma_2/\gamma_1) + \ln (\gamma_4/\gamma_1)$. Table III gives the general coefficients, neglecting groups of ions all of the same charge, and Table IV gives the special values for φ_μ' for the mixtures we have studied.

The relations derived by Brönsted and by Guggenheim for the linear terms in the activity coefficients, which appear to hold accurately for these terms, may be expected to apply approximately to the higher terms as well even though they cannot hold exactly. Our results permit a test for eight solutions of a salt in another with a common ion, and for four in another without a common ion. The presentation of a complete test would take too much space. We have therefore averaged the absolute values of the deviation of $\ln \gamma$ for each salt in each of the others. In Fig. 7 curve O represents $\ln \gamma$ itself (absolute value); curve A is the difference from the Debye–Hückel limiting law, and curve B is corrected also for the term linear in the concentration in accordance with Brönsted's theory. For these three the mixtures with and without a common ion are practically identical, for the other curves the two groups are separated. Curve C gives the deviations from the mean of the values for the two salts for those with a common ion. Curve D is the same for those without a common ion, and curve E is the deviation from the mean for the reciprocal salt pair for mixtures without a common ion. The O curve is half the error of the classical law of the solubility product in the limit of zero concentration of the saturating salt; A shows half the error of correcting by the Debye–Hückel limiting law, and B that of correcting by the original Brönsted theory. C and E show half the error of correcting by the approximate extension of the Brönsted theory to the higher coefficients. D gives half the error of correcting mixtures without a common ion by the method which works so well for those with a com-

TABLE III

GENERAL COEFFICIENTS IN TERMS OF ION COMPOSITIONS

		1	C	L	CL	C^2	L^2	C^2L	CL^2
A	φ_μ	a							
	$\ln \gamma_1$	$3a$							
	$\ln (\gamma_2/\gamma_1)$								
	$\ln (\gamma_4/\gamma_1)$								
B	φ_μ	$2b$	$2c$	$2d$	$2e$				
	$\ln \gamma_1$	$4b$	$2c$	$2d$					
	$\ln (\gamma_2/\gamma_1)$	$2c$		$2e$					
	$\ln (\gamma_4/\gamma_1)$	$2d$	$2e$						
C	φ_μ	$3f$	$3g$	$3h$	$3i$				
	$\ln \gamma_1$	$5f$	$3g$	$3h$	i				
	$\ln (\gamma_2/\gamma_1)$	$2g$		$2i$					
	$\ln (\gamma_4/\gamma_1)$	$2h$	$2i$						
D	φ_μ	$4j$	$4k$	$4l$	$4m$	$4n$	$4o$	$4p$	$4q$
	$\ln \gamma_1$	$6j$	$4k$	$4l$	$2m$	$2n$	$2o$		
	$\ln (\gamma_2/\gamma_1)$	$2k$	$4n$	$2m$	$4p$		$2q$		
	$\ln (\gamma_4/\gamma_1)$	$2l$	$2m$	$4o$	$4q$	$2p$			
E	φ_μ	$5r$	$5s$	$5t$	$5u$	$5v$	$5w$	$5x$	$5y$
	$\ln \gamma_1$	$7r$	$5s$	$5t$	$3u$	$3v$	$3w$	x	y
	$\ln (\gamma_2/\gamma_1)$	$2s$	$4v$	$2u$	$4x$		$2y$		
	$\ln (\gamma_4/\gamma_1)$	$2t$	$2u$	$4w$	$4y$	$2x$			

TABLE IV

COEFFICIENTS OF φ'_μ FOR RECIPROCAL SALT PAIR: KNO_3–LiCl

	A	B	C	D	E
1	−0.26432	0.11596	−0.10616	0.05379	−0.00968
C		.21043	− .16359	.08996	− .02337
L		.35882	− .34529	.17340	− .03581
CL		− .28365	.36976	− .24134	.06589
C^2				− .00506	.00443
L^2				.05041	− .02079
C^2L				− .00950	.00362
CL^2				− .01267	.00178

mon ion, but which is erroneous for those without. The extended Brönsted theory gives accurate results to moderately high concentrations and no serious error up to one molal salt solutions.

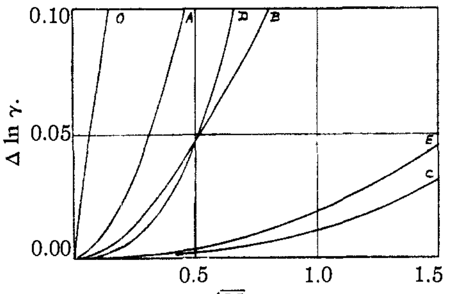

Fig. 7.—Average errors in activity coefficients.

If these results can be generalized they give a very useful approximation. The effect of any salt with a common ion on the solubility of a slightly soluble salt can be determined approximately from the activity coefficients of the solvent salts dissolved in themselves and the measurement of the effect of the addition of one salt on the solubility. The logarithm of the solubility product in any two salts differs by minus the difference in the logarithms of the mean activity coefficients of the solvent salts, whether they share the same ion with the solute or not.

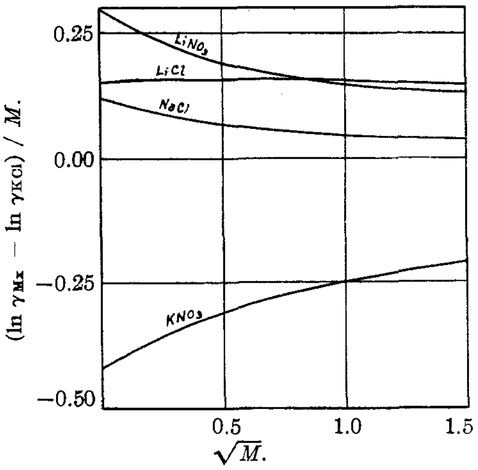

Fig. 8.—Test of Åkerlöf–Thomas hypothesis.

The effect of the addition of a salt without a common ion may be determined without making any measurements on mixtures. The logarithm of the solubility product changes from its value at zero concentration by minus the sum of the logarithms of the mean activity coefficients of the reciprocal salt pair. For example, the effect of potassium nitrate on the solubility of silver chloride may be determined from the mean activity coefficients of silver nitrate and of potassium chloride.

The approximations of ln γ in mixed solutions do not lend themselves to a brief quantitative summary. We shall content ourselves with stating that the logarithms of the activity coefficients are nearly linear functions of the solute composition so that the errors expressed in curves C and E of Fig. 7 are approximately proportional to the fraction of the added salt.

These results may also be used to test the hypothesis of Åkerlöf and Thomas[5] that the difference in the logarithms of the activity coefficients of any two electrolytes of the same valence type, or of the same electrolyte in different solvent salts, is proportional to the molality. In terms of Table III this hypothesis requires that the coefficients except a, b, c, d, e, f, j, r should be zero or negligibly small compared to those given above. Examination of Table IV will show that this

(5) G. Åkerlöf and H. C. Thomas, THIS JOURNAL, **56**, 593 (1934).

condition is far from fulfilled. There is, however, a compensation among the coefficients of the different powers of the concentration. In Fig. 8 is plotted $(\ln \gamma_{MX} - \ln \gamma_{KCl})/M$ for the other three salts and for sodium chloride.[1] The hypothesis of Åkerlöf and Thomas requires that each of these curves be horizontal. This condition is closely approximated for lithium chloride, but not for any of the other salts. The curves do, however, all become flatter with increasing concentration, and our measurements give no evidence against the usefulness of the hypothesis as an empirical approximation for higher concentrations.

Summary

Measurements are made of the freezing point depressions up to one molal of the five possible equimolal mixtures of the reciprocal salt pair: potassium nitrate–lithium chloride, and of two three to one mixtures.

The results of Brönsted's theory of the specific interaction of ions are derived more simply and are extended to the coefficients of the higher powers of the concentration.

The parameters necessary to determine the thermodynamic functions of any mixture of this reciprocal salt pair are determined and found to agree completely with the extended theory of Brönsted. Some of the consequences of this agreement are discussed.

CAMBRIDGE, MASS. RECEIVED AUGUST 2, 1934

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

The Effect of Electrolytes in Ionic Reactions

BY MARTIN KILPATRICK

In a recent paper La Mer and Greenspan[1] point out that the primary kinetic salt effects in the hydrolysis of acetylated hydroxyl acids are only in qualitative agreement with the Brönsted theory of reaction velocity. For reactions between ions Brönsted's equation is

$$\log k = \log k_0 + z_A z_B \sqrt{\mu} \qquad (1)$$

where k is the observed velocity constant, k_0 the velocity constant at zero ion concentration, z_A and z_B the valencies of the reacting ions and μ the ionic strength. This equation is based on the Debye limiting law

$$-\log f = 0.5\, z^2 \sqrt{\mu} \qquad (2)$$

Although La Mer and Greenspan recognize the fact that their results may have been obtained at too high ionic concentrations to give the theoretical slope, they favor another interpretation of the data.

Without going into this aspect of the problem, it is the purpose of the present paper to show that the failure to find agreement with equation (1) is due to the fact that the experimental results are not in the range of concentration where this equation applies. To do this we will use for the activity coefficients an equation applicable up to ionic strengths of 0.03–0.04. This equation

$$-\log f = 0.5\, z^2 \sqrt{\mu}/(1 + \sqrt{\mu}) \qquad (3)$$

is obtained from the equation of Debye

$$-\log f = 0.50\, z^2 \sqrt{\mu}/(1 + \kappa b)$$

on the assumption that b, the apparent average ionic diameter, is approximately 3.0×10^{-8} cm., κ being equal to $0.33 \times 10^8 \sqrt{\mu}$ cm.$^{-1}$ at 25°.[2] On this basis equation (1) becomes[3]

$$\log k = \log k_0 + z_A z_B \sqrt{\mu}/(1 + \sqrt{\mu}) \qquad (4)$$

A test of this equation can be made by plotting $\log k$ against $\sqrt{\mu}/(1 + \sqrt{\mu})$ and drawing the theoretical slope, just as La Mer and Greenspan tested equation (1) by plotting $\log k$ against $\sqrt{\mu}$ (see Fig. 1 of their paper). It is, however, more convincing to calculate k_0 from equation (4) and examine its constancy. The results of the computation are given in Table I.

With the exception of acetylbenzilic acid, and 1-acetylmalic acid (for which only two points are given, and at ionic strengths outside the range of applicability of equation (3)), the constancy of k_0 indicates agreement with equation (4). It should be emphasized that a few experimental points, with a relatively small change of ionic strength, are unsuitable for testing equation (1) or equation (4). It seems logical to conclude that, in so far as the accuracy of the experiments and our knowledge of activity coefficients from equilibrium measurements will permit us to judge, the results

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(1) La Mer and Greenspan, THIS JOURNAL, **56**, 1492 (1934).

(2) Guggenheim and Schindler, *J. Phys. Chem.*, **38**, 533 (1934).

(3) Scatchard, *Chem. Rev.*, **10**, 229 (1932).