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Conductimetric Study of the Ion Pair Formation in Mixtures of Bivalent Metal Nitrates and Sodium Sulfate in Aqueous Solutions

Shunzo KATAYAMA,* Kazuko TANAKA, and Reita TAMAMUSHI

Inorganic Chemistry Laboratory, The Institute of Physical and Chemical Research, Wako, Saitama 351

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The conductance behavior of electrolyte mixtures was investigated for the systems of bivalent metal nitrates and sodium sulfate in aqueous solutions of high ionic strengths ($I \geq 0.3$ mol dm^{-3}) at 25 °C. Significant deviations of the measured conductivities from the additivity were observed in all the systems, which can be attributed to the ion pair formation of the bivalent metal ion with sulfate ion. The conditional formation constants, K_c, were determined by means of computer analysis of the deviation; K_c-values at each ionic strength were found to decrease in the sequence Cd>Mn≃Ni≃Co≃Zn>Mg.

The measurement of electrolytic conductivity of mixtures of two electrolytes provides a valuable method of studying the ionic interaction. The conductance behavior of binary mixtures of 1-1, 2-1, and 2-2 type electrolytes was studied by Rysselberghe *et al.*[1,2] and by Davies.[3,4] Recently, Fisher[5] reported about the ion association in mixtures of 0.005 mol dm^{-3} $MgCl_2$ and 0.005 mol dm^{-3} Na_2SO_4 solutions as a function of pressure.

In our previous works,[6,7] the continuous variation method was applied to the determination of the ion pair formation constants of $[Co(NH_3)_6]^{3+}\cdot SO_4{}^{2-}$, $[Co(en)_3]^{3+}\cdot SO_4{}^{2-}$, $[Co(en)_3]^{3+}\cdot$(Maleate)$^{2-}$, and $[Co(en)_3]^{3+}\cdot$(Fumarate)$^{2-}$ from the conductivity measurement of mixtures. Good agreement of the results obtained for $[Co(NH_3)_6]^{3+}\cdot SO_4{}^{2-}$ with those of Jenkins and Monk[8] suggests that the conductivity measurement of mixtures is a useful method for determining formation constants.

The application of the conductimetric continuous variation method to the determination of formation constants appears to have the advantage that the measured quantities can be analysed, in principle, without relying on the quantitative validity of the theoretical equation of conductivity; this advantage is particularly important when the method is applied to systems of higher ionic strengths.[9]

This paper deals with the determination of ion pair formation constants of bivalent metal ions (Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+}) with sulfate ion at 25 °C in aqueous solutions of apparent ionic strengths 0.3—6 mol dm^{-3} from the conductivity measurements of electrolytic solution mixtures.

Experimental

Materials and Preparation of Solutions. $Mg(NO_3)_2\cdot 6H_2O$, $Mn(NO_3)_2\cdot 6H_2O$, $Co(NO_3)_2\cdot 6H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, $Zn(NO_3)_2\cdot 6H_2O$, $Cd(NO_3)_2\cdot 4H_2O$, and Na_2SO_4 of analytical reagent grade were used without further purification. The purity of the samples was determined by chemical analysis of the components. The analysis gave results which were in good agreement with the theoretical values.

Solutions of different concentrations were prepared by using conductivity water (conductivity$<2.0\times 10^{-7}$ Ω^{-1} cm^{-1} at 25 °C).

Conductivity Measurements. Electrolytic conductivities of mixtures were measured by mixing the solutions of the same ionic strength at various volume fractions. A conductance-linear-bridge, operated at 1000 Hz, was used for conductivity measurements as described in previous papers.[10,11] The resistance readings of the bridge were calibrated by the substitution method with a precision decade resistance box (Dekastat RS-624, Electro Scientific Industries; accuracy ±0.005%). Three conductivity cells designed for solutions of moderate and high conductivities were used. The cell constants were determined to be 11.093 cm^{-1}, 35.422 cm^{-1}, and 97.349 cm^{-1} by using standard potassium chloride solutions. The reproducibility of the conductivity measurements was better than 0.05%. All measurements were carried out in a water–ethylene glycol mixture bath of 25.000±0.003 °C, which was electrically grounded.

Results and Discussion

Analysis of Conductivity of Electrolyte Mixtures.[6] Let us consider the conductivity of a solution prepared by mixing volume ϕV of a solution of molar concentration, c_1, of MA_2 (M: bivalent metal, A: NO_3) and volume $(1-\phi)V$ of a solution of molar concentration, c_2, of N_2B (N: Na, B: SO_4) to give the solution of total volume V; the concentrations, c_1 and c_2, are adjusted so that the apparent ionic strength of the mixtures is independent of volume fraction, ϕ (in the present study $c_1=c_2=c$).

The conductivity, κ_{calcd}, of the mixture calculated by using the additivity rule is given by

$$\begin{aligned}10^3\kappa_{\text{calcd}} &= z_M\lambda_M c\phi + z_A\lambda_A 2c\phi + z_N\lambda_N 2c(1-\phi)\\ &\quad + z_B\lambda_B c(1-\phi),\end{aligned} \tag{1}$$

where z is the charge number of ionic species, and λ the ionic equivalent conductivity at the ionic strength of the mixture. If the following ion pair formation is assumed in the mixture:

$$M^{2+} + B^{2-} \rightleftharpoons M^{2+}\cdot B^{2-},$$

the observed conductivity, κ_{obsd}, of the mixture is given by

$$\begin{aligned}10^3\kappa_{\text{obsd}} &= z_M\lambda_M(c\phi - [M^{2+}\cdot B^{2-}])\\ &\quad + z_A\lambda_A 2c\phi + z_N\lambda_N 2c(1-\phi)\\ &\quad + z_B\lambda_B(c(1-\phi) - [M^{2+}\cdot B^{2-}]),\end{aligned} \tag{2}$$

where $[M^{2+}\cdot B^{2-}]$ is the concentration of ion pairs $M^{2+}\cdot B^{2-}$. The deviation, $\Delta\kappa$, of the observed conductivity from additivity is given by

$$\begin{aligned}10^3\Delta\kappa &= 10^3\kappa_{\text{obsd}} - 10^3\kappa_{\text{calcd}}\\ &= -(z_M\lambda_M + z_B\lambda_B)[M^{2+}\cdot B^{2-}].\end{aligned} \tag{3}$$

The deviation $\Delta\kappa$ is then represented by the equation:[6]

$$10^3\Delta\kappa = \Delta\lambda[c+K_c^{-1} - \sqrt{(c+K_c^{-1})^2-4c^2\phi(1-\phi)}]/2, \tag{4}$$

where

$$\Delta\lambda = -(z_M\lambda_M+z_B\lambda_B), \tag{5}$$

and where K_c is the conditional formation constant of $M^{2+}\cdot B^{2-}$ as given by

$$K_c = \frac{[M^{2+}\cdot B^{2-}]}{[M^{2+}][B^{2-}]}. \tag{6}$$

A set of K_c and $\Delta\lambda$ values giving the best fit between the observed and calculated $\Delta\kappa$ values can be determined by computer calculation.

Conductivities of Mixtures in the Absence of Specific Ionic Interactions. The difficulty involved in the conductimetric continuous variation method consists in the fact that the deviation of the observed conductivity from additivity may be caused not only by specific ionic interactions but also by the non-specific effect of the added ions on the mobility of the ions.[12,13] In the present study, the deviation due to the non-specific effect was examined with mixtures of simple electrolytes, in which no specific individual effects is expected.

The conductivities of ($KCl+KNO_3$) and ($KCl+NaCl$) mixtures at apparent ionic strengths $I_{app}=2$ mol dm^{-3} gave slightly smaller values than those expected from additivity; the deviation reached the maximum value of about 0.7% at the volume fraction $\phi=0.5$, as shown in Fig. 1 (curves (1) and (2)). The conductivity of ($Mg(NO_3)_2+Na_2SO_4$) mixtures of $I_{app}=3$ mol dm^{-3}, however, showed a large deviation from additivity of about 12% at $\phi=0.5$ on account of the ion pair formation between Mg^{2+} and SO_4^{2-} (Fig. 1, curve (3)).

Theoretically, the conductivity of electrolyte mixtures is never strictly additive, because of the effect of added ions on the time of relaxation[13]; in our present systems, however, this effect is shown to be negligibly small in comparison with the specific individual effect as seen from Fig. 1. In the following discussion, therefore, the deviation of the observed conductivities from additivity was attributed entirely to the ion pair formation of bivalent metal ion with sulfate ion, the ion association between the bivalent metal ion and nitrate ion and that between sodium ion and sulfate ion being neglected for the sake of simplicity.

Ion Pair Formation Constants of Bivalent Metal Ions with Sulfate Ion. In mixtures of bivalent metal nitrate and sodium sulfate, a large deviation of the measured conductivity from additivity was observed at each ionic strength, as shown by curve (3) in Fig. 1. The conductivities of the mixtures were always smaller than those expected from additivity and showed an extreme at $\phi=0.5$ in each system. Conductivities, κ, of mixtures and the deviation, $\Delta\kappa$, of the observed conductivities from calculated values are shown in Tables 1—6 as a function of the volume fraction, ϕ, of the bivalent metal nitrate. In our present systems, the volume changes of mixing were smaller than about 0.1% and were neglected in the calculation of $\Delta\kappa$.

The conditional formation constants of ion pair, K_c, were determined by analysing the $\Delta\kappa$ values according to Eq. 4. Table 7 summarizes the values of K_c thus determined for $M^{2+}\cdot SO_4^{2-}$ at various ionic strengths. For the six mixtures studied, the K_c values at 25 °C decrease in the sequence: Cd>Mn≃Ni≃Co≃Zn>Mg.

The conditional formation constants at sufficiently low ionic strengths can be estimated from the knowledge of the thermodynamic association constant K_A[10,14,15] and the activity coefficient $y_\pm$ according to the following equations:

$$K_c = K_A y_\pm, \tag{7}$$

$$\log y_\pm = -A|z_M z_B|I^{1/2}/(1+BaI^{1/2}), \tag{8}$$

where A and B are the Debye-Hückel constants and a is the ion-size parameter. Under the assumption that Eqs. 7 and 8 could be satisfied in solutions of

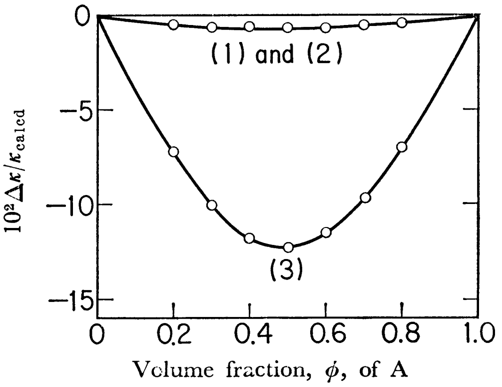

Fig. 1. Deviations, $\Delta\kappa$, of the observed conductivities of mixtures from additivity (25 °C).
(1): $KCl(A)+KNO_3(B)$ mixtures, $I_{app}=2$ mol dm^{-3};
(2): $KCl(A)+NaCl(B)$ mixtures, $I_{app}=2$ mol dm^{-3};
(3): $Mg(NO_3)_2(A)+Na_2SO_4(B)$ mixtures, $I_{app}=3$ mol dm^{-3}.

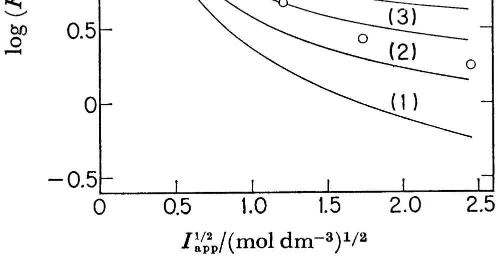

Fig. 2. Experimental (open circle ○) and calculated (solid line —) formation constants for ion pair $Mg^{2+}\cdot SO_4^{2-}$ as a function of apparent ionic strength: a/nm= 0.4 (1), 0.5 (2), 0.6 (3), and 0.7 (4); $K_A=135$ dm^3 mol^{-1}.[10]

Table 1. Conductivities, $\kappa/\Omega^{-1}\,\mathrm{cm}^{-1}$, of ($Mg(NO_3)_2+Na_2SO_4$) mixtures and deviations, $\Delta\kappa/\Omega^{-1}\,\mathrm{cm}^{-1}$, of the observed conductivities from calculated values as a function of the volume fraction, ϕ, of $Mg(NO_3)_2$ at various apparent ionic strengths, $I_{\mathrm{app}}/\mathrm{mol\,dm^{-3}}$

ϕ	$10^3\kappa$	$10^3\Delta\kappa$	$10^3\kappa$	$10^3\Delta\kappa$	$10^3\kappa$	$10^3\Delta\kappa$	$10^3\kappa$	$10^3\Delta\kappa$
	($I_{\mathrm{app}}=0.3$)		($I_{\mathrm{app}}=1.5$)		($I_{\mathrm{app}}=3$)		($I_{\mathrm{app}}=6$)	
0	16.325	—	59.25	—	93.77	—	125.62	—
0.2	15.538	−1.017	56.95	−4.25	90.14	−7.33	119.33	−10.76
0.3	15.285	−1.385	56.39	−5.78	89.31	−10.01	117.36	−14.97
0.4	15.165	−1.621	56.36	−6.78	89.32	−11.85	116.69	−17.87
0.5	15.189	−1.712	56.97	−7.14	90.47	−12.55	117.73	−19.07
0.6	15.384	−1.632	58.26	−6.82	92.83	−12.05	120.66	−18.38
0.7	15.722	−1.409	60.19	−5.86	96.35	−10.38	125.46	−15.81
0.8	16.204	−1.043	62.70	−4.33	100.86	−7.72	131.87	−11.64
1.0	17.477	—	68.97	—	112.28	—	147.98	—

Table 2. Conductivities, $\kappa/\Omega^{-1}\,\mathrm{cm}^{-1}$, of ($Mn(NO_3)_2+Na_2SO_4$) mixtures and deviations, $\Delta\kappa/\Omega^{-1}\,\mathrm{cm}^{-1}$, of the observed conductivities from calculated values as a function of the volume fraction, ϕ, of $Mn(NO_3)_2$ at various apparent ionic strengths, $I_{\mathrm{app}}/\mathrm{mol\,dm^{-3}}$

ϕ	$10^3\kappa$	$10^3\Delta\kappa$	$10^3\kappa$	$10^3\Delta\kappa$	$10^3\kappa$	$10^3\Delta\kappa$	$10^3\kappa$	$10^3\Delta\kappa$
	($I_{\mathrm{app}}=0.3$)		($I_{\mathrm{app}}=1.5$)		($I_{\mathrm{app}}=3$)		($I_{\mathrm{app}}=6$)	
0	16.325	—	59.25	—	93.77	—	125.62	—
0.2	15.327	−1.251	55.91	−5.18	88.40	−8.55	117.10	−11.19
0.3	14.998	−1.707	54.94	−7.07	86.82	−11.72	114.19	−15.43
0.4	14.830	−2.002	54.64	−8.29	86.33	−13.80	112.63	−18.32
0.5	14.850	−2.109	55.17	−8.69	87.25	−14.47	113.03	−19.26
0.6	15.076	−2.009	56.55	−8.23	89.63	−13.68	115.56	−18.06
0.7	15.497	−1.715	58.73	−6.97	93.33	−11.56	119.94	−15.01
0.8	16.078	−1.261	61.54	−5.08	98.08	−8.40	125.59	−10.69
1.0	17.592	—	68.46	—	109.66	—	138.95	—

Table 3. Conductivities, $\kappa/\Omega^{-1}\,\mathrm{cm}^{-1}$, of ($Co(NO_3)_2+Na_2SO_4$) mixtures and deviations, $\Delta\kappa/\Omega^{-1}\,\mathrm{cm}^{-1}$, of the observed conductivities from calculated values as a function of the volume fraction, ϕ, of $Co(NO_3)_2$ at various apparent ionic strengths, $I_{\mathrm{app}}/\mathrm{mol\,dm^{-3}}$

ϕ	$10^3\kappa$	$10^3\Delta\kappa$	$10^3\kappa$	$10^3\Delta\kappa$	$10^3\kappa$	$10^3\Delta\kappa$	$10^3\kappa$	$10^3\Delta\kappa$
	($I_{\mathrm{app}}=0.3$)		($I_{\mathrm{app}}=1.5$)		($I_{\mathrm{app}}=3$)		($I_{\mathrm{app}}=6$)	
0	16.325	—	59.25	—	93.77	—	125.62	—
0.2	15.356	−1.224	56.12	−4.96	88.69	−8.22	117.74	−10.50
0.3	15.038	−1.670	55.23	−6.77	87.20	−11.28	115.09	−14.46
0.4	14.874	−1.962	55.01	−7.91	87.09	−12.96	113.83	−17.03
0.5	14.899	−2.065	55.58	−8.26	88.01	−13.61	114.38	−17.79
0.6	15.126	−1.965	56.96	−7.79	90.39	−12.79	116.81	−16.67
0.7	15.542	−1.677	59.09	−6.58	94.03	−10.72	120.89	−13.90
0.8	16.116	−1.231	61.80	−4.79	98.57	−7.75	126.13	−9.97
1.0	17.602	—	68.42	—	109.46	—	138.72	—

Table 4. Conductivities, $\kappa/\Omega^{-1}\,\mathrm{cm}^{-1}$, of ($Ni(NO_3)_2+Na_2SO_4$) mixtures and deviations, $\Delta\kappa/\Omega^{-1}\,\mathrm{cm}^{-1}$, of the observed conductivities from calculated values as a function of the volume fraction, ϕ, of $Ni(NO_3)_2$ at various apparent ionic strengths, $I_{\mathrm{app}}/\mathrm{mol\,dm^{-3}}$

ϕ	$10^3\kappa$	$10^3\Delta\kappa$	$10^3\kappa$	$10^3\Delta\kappa$	$10^3\kappa$	$10^3\Delta\kappa$	$10^3\kappa$	$10^3\Delta\kappa$
	($I_{\mathrm{app}}=0.3$)		($I_{\mathrm{app}}=1.5$)		($I_{\mathrm{app}}=3$)		($I_{\mathrm{app}}=6$)	
0	16.325	—	59.25	—	93.77	—	125.62	—
0.2	15.307	−1.236	55.91	−5.03	88.45	−8.10	117.34	−10.38
0.3	14.959	−1.693	54.96	−6.83	86.89	−11.06	114.49	−14.28
0.4	14.772	−1.989	54.66	−7.97	86.45	−12.89	113.06	−16.76
0.5	14.779	−2.091	55.17	−8.31	87.33	−13.40	113.41	−17.47
0.6	14.988	−1.991	56.48	−7.84	89.56	−12.56	115.63	−16.30
0.7	15.392	−1.696	58.57	−6.60	93.00	−10.51	119.45	−13.53
0.8	15.955	−1.242	61.22	−4.79	97.31	−7.60	124.38	−9.65
1.0	17.415	—	67.70	—	107.69	—	136.13	—

Table 5. Conductivities, $\kappa/\Omega^{-1}\,\mathrm{cm}^{-1}$, of $(\mathrm{Zn(NO_3)_2}+\mathrm{Na_2SO_4})$ mixtures and deviations, $\Delta\kappa/\Omega^{-1}\,\mathrm{cm}^{-1}$, of the observed conductivities from calculated values as a function of the volume fraction, ϕ, of $\mathrm{Zn(NO_3)_2}$ at various apparent ionic strengths, $I_{\mathrm{app}}/\mathrm{mol\,dm^{-3}}$

ϕ	$10^3\kappa$	$10^3\Delta\kappa$	$10^3\kappa$	$10^3\Delta\kappa$	$10^3\kappa$	$10^3\Delta\kappa$	$10^3\kappa$	$10^3\Delta\kappa$
	($I_{\mathrm{app}}=0.3$)		($I_{\mathrm{app}}=1.5$)		($I_{\mathrm{app}}=3$)		($I_{\mathrm{app}}=6$)	
0	16.325	—	59.25	—	93.77	—	125.62	—
0.2	15.326	−1.230	56.08	−5.01	88.79	−8.20	118.09	−10.87
0.3	14.992	−1.680	55.18	−6.83	87.36	−11.24	115.71	−14.93
0.4	14.812	−1.975	54.93	−8.00	87.05	−13.16	114.69	−17.62
0.5	14.823	−2.080	55.48	−8.38	88.05	−13.77	115.49	−18.49
0.6	15.038	−1.981	56.87	−7.91	90.46	−12.97	118.29	−17.36
0.7	15.441	−1.693	59.03	−6.67	94.09	−10.95	122.75	−14.57
0.8	16.008	−1.242	61.75	−4.87	98.69	−7.96	128.60	−10.40
1.0	17.481	—	68.46	—	109.87	—	142.34	—

Table 6. Conductivities, $\kappa/\Omega^{-1}\,\mathrm{cm}^{-1}$, of $(\mathrm{Cd(NO_3)_2}+\mathrm{Na_2SO_4})$ mixtures and deviations, $\Delta\kappa/\Omega^{-1}\,\mathrm{cm}^{-1}$, of the observed conductivities from calculated values as a function of the volume fraction, ϕ, of $\mathrm{Cd(NO_3)_2}$ at various apparent ionic strengths, $I_{\mathrm{app}}/\mathrm{mol\,dm^{-3}}$

ϕ	$10^3\kappa$	$10^3\Delta\kappa$	$10^3\kappa$	$10^3\Delta\kappa$	$10^3\kappa$	$10^3\Delta\kappa$	$10^3\kappa$	$10^3\Delta\kappa$
	($I_{\mathrm{app}}=0.3$)		($I_{\mathrm{app}}=1.5$)		($I_{\mathrm{app}}=3$)		($I_{\mathrm{app}}=6$)	
0	16.325	—	59.25	—	93.77	—	125.62	—
0.2	15.133	−1.317	55.21	−4.66	87.32	−6.58	116.55	−5.95
0.3	14.710	−1.803	53.84	−6.34	85.09	−8.88	112.90	−8.06
0.4	14.454	−2.122	53.13	−7.36	83.85	−10.19	110.13	−9.28
0.5	14.418	−2.221	53.21	−7.59	83.69	−10.42	108.55	−9.31
0.6	14.593	−2.108	54.07	−7.04	84.63	−9.54	107.99	−8.32
0.7	14.984	−1.780	55.57	−5.85	86.43	−7.81	108.16	−6.60
0.8	15.532	−1.295	57.55	−4.18	88.81	−5.50	108.73	−4.47
1.0	16.952	—	62.35	—	94.44	—	110.10	—

Table 7. Conditional formation constants, $K_c/\mathrm{dm^3\,mol^{-1}}$, of $\mathrm{M^{2+}\cdot SO_4^{2-}}$ at 25 °C in aqueous solutions of various apparent ionic strengths, I_{app}

Ion pair	$I_{\mathrm{app}}/\mathrm{mol\,dm^{-3}}$			
	0.3	1.5	3.0	6.0
$\mathrm{Mg^{2+}\cdot SO_4^{2-}}$	20.6	4.6	2.6	1.7
$\mathrm{Mn^{2+}\cdot SO_4^{2-}}$	26.3	6.1	3.5	2.7
$\mathrm{Co^{2+}\cdot SO_4^{2-}}$	28.8	6.1	3.2	2.2
$\mathrm{Ni^{2+}\cdot SO_4^{2-}}$	28.8	6.1	3.4	2.3
$\mathrm{Zn^{2+}\cdot SO_4^{2-}}$	28.1	6.2	3.4	2.2
$\mathrm{Cd^{2+}\cdot SO_4^{2-}}$	31.7	7.4	3.8	3.1

higher ionic strengths, the conditional formation constants for ion pair $\mathrm{Mg^{2+}\cdot SO_4^{2-}}$ were calculated and are shown in Fig. 2 as a function of ionic strength. The calculation was made at different a-values, the most probable value of a being considered to be about 0.5—0.6 nm.[10] Similar results were obtained for the other systems investigated. It is rather surprising that the experimental values are not very much different from the values estimated by using Eqs. 7 and 8, even at the highest apparent ionic strength (6 mol dm^{-3}).

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