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A Method for Determining the Degree of Dissociation of Symmetrical Associated Electrolytes from the Conductivity and Activity Data

Reita TAMAMUSHI

The Institute of Physical and Chemical Research, 2-1 Hirosawa, Wako, Saitama 351

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Synopsis. A method is presented for determining the degree of dissociation of symmetrical associated electrolytes from a set of conductivity and activity data. The method was applied to the determination of the dissociation constants of several metal sulfates in aqueous solutions.

In a previous paper,[1] individual ionic activity coefficients were estimated on the basis of the conductivity data by using the correlation between the activity and conductivity equations, in which the effect of the Debye-Hückel interaction is assumed to be represented by a common parameter, χ, on both the activity and the conductivity. A similar consideration provides a new method for determining the degree of dissociation of symmetrical associated electrolytes from a set of conductivity and activity coefficient data. This method does not require an *a priori* assumption of the ion-size parameter.

Let us consider the following dissociation equilibrium of a symmetrical electrolyte, MA, in solution;

$$\mathrm{MA} \rightleftharpoons \mathrm{M} + \mathrm{A} \tag{1}$$

with

$$K_c = \frac{\alpha^2 c}{1-\alpha} = K(\gamma_M \gamma_A)^{-1} \tag{2}$$

where α is the degree of dissociation; c, the stoichiometric concentration of MA; γ, the individual ionic activity coefficient; K_c, the conditional dissociation constant, and K, the thermodynamic dissociation constant; the charge of each ionic species is omitted for the sake of simplicity. In Eq. (2) the activity coefficient of the associated electrolyte is assumed to be unity.

The stoichiometric mean activity coefficient, $\gamma_\pm$, of the electrolyte, which can be determined directly from measurements, is given by,[2]

$$\log \gamma_\pm = \log \gamma_\pm{}^{\mathrm{DH}} + \log \alpha \tag{3}$$

where $\gamma_\pm{}^{\mathrm{DH}}$ is the activity coefficient due to the Debye-Hückel ionic interaction. In dilute solutions, $\gamma_\pm{}^{\mathrm{DH}}$ can be represented by the Debye-Hückel equation:

$$\log \gamma_\pm{}^{\mathrm{DH}} = -A\chi^{-1} \tag{4}$$

where A is the Debye-Hückel limiting slope and where χ is the length which is related to the thickness of the ionic atmosphere (see Eq. (8)). By rearranging the relation obtained by introducing Eq. (4) into Eq. (3), we obtain χ as a function of α and $\gamma_\pm$;

$$\chi^{-1} = (\log \alpha - \log \gamma_\pm)/A \tag{5}$$

On the other hand, the Onsager-Robinson-Stokes

TABLE 1. DEGREE OF DISSOCIATION α, CONDITIONAL DISSOCIATION CONSTANT K_c, AND ION-SIZE PARAMETER a OF SEVERAL METAL SULFATES IN AQUEOUS SOLUTIONS, AS DERIVED BY THE PRESENT METHOD FROM THE CONDUCTIVITY AND ACTIVITY DATA.[4—9]

(Parentheses are used to present the a-values which very much exceed Bjerrum's parameter)

Metal sulfate		Concentration/mM							
		0.5	1	2	3	5	10	20	50
$MgSO_4$ (0 °C)[a]	α	0.951	0.912	0.879	0.855	—	—	—	—
	$-\log(K_c/\mathrm{mol\ dm^{-3}})$	2.04	2.02	1.89	1.82	—	—	—	—
	a/Å	6.7	12.5	8.8	7.9	—	—	—	—
$NiSO_4$ (0 °C)[a]	α	0.920	0.877	0.828	0.795	—	—	—	—
	$-\log(K_c/\mathrm{mol\ dm^{-3}})$	2.28	2.20	2.10	2.03	—	—	—	—
	a/Å	(30.8)	(26.3)	18.4	16.1	—	—	—	—
$CuSO_4$ (25 °C)[b]	α	—	0.828	—	—	0.645	0.593	0.556	0.503
	$-\log(K_c/\mathrm{mol\ dm^{-3}})$	—	2.40	—	—	2.23	2.06	1.86	1.59
	a/Å	—	(74.5)	—	—	(94.2)	(27.5)	11.1	7.5
$ZnSO_4$ (25 °C)[b]	α	—	0.863	0.808	—	0.732	0.665	0.616	0.571
	$-\log(K_c/\mathrm{mol\ dm^{-3}})$	—	2.26	2.17	—	2.00	1.88	1.70	1.42
	a/Å	—	16.7	12.5	—	8.3	7.8	6.0	4.8
$CdSO_4$ (25 °C)[c]	α	—	0.826	0.761	—	0.660	0.596	—	0.496
	$-\log(K_c/\mathrm{mol\ dm^{-3}})$	—	2.41	2.31	—	2.19	2.06	—	1.61
	a/Å	—	(58.1)	(43.0)	—	(24.1)	15.5	—	6.9

a) The conductivity data were taken from Ref. 4, and the activity data from Ref. 5. b) The conductivity data were taken from Ref. 6, and the activity data from Ref. 7. c) The conductivity data were taken from Ref. 8 and 9, and the activity data from Ref. 7.

theory[3] gives the conductivity equation for a symmetrical associated electrolyte;

$$\Lambda = \alpha(\Lambda^{\infty} - S\chi^{-1}) \tag{6}$$

where Λ is the equivalent conductivity; Λ^{∞}, the Λ-value at an infinite dilution, and S, the Onsager limiting slope.

By introducing Eq. (5) into Eq. (6), the relationship among Λ, α, and $\gamma_{\pm}$ is derived;

$$\frac{\Lambda}{\Lambda^{\infty}} = \alpha\left[\left(1+\frac{S}{A\Lambda^{\infty}}\log\gamma_{\pm}\right) - \frac{S}{A\Lambda^{\infty}}\log\alpha\right] \tag{7}$$

This relationship can be used for the determination of α from the conductivity and activity data. It must be noted that, in the derivation of Eq. (7), it is not necessary to know the exact expression of the χ parameter.

Only a small number of experimental data are available in the literature[4–9] for use in estimating the applicability of the present method. Table 1 shows the results obtained with several sulfate salts of divalent metal ions in aqueous solutions.

The thermodynamic dissociation constants, which were determined by the extrapolation of the plot of log K_c as a function of the square root of the ionic strength, I, as is shown in Fig. 1, are compared in Table 2 with the values reported in the literature.

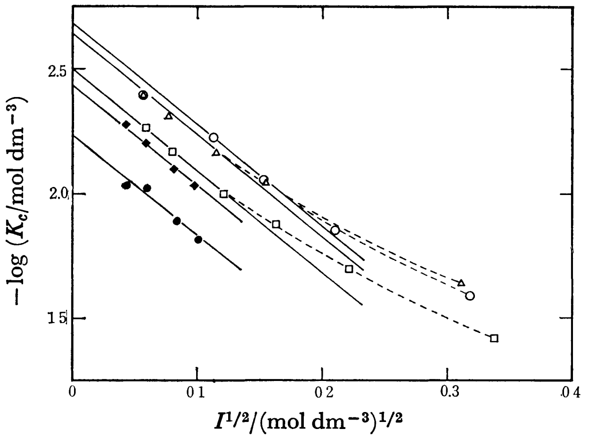

Fig. 1. Plot of $-\log K_c$ as a function of $I^{1/2}$ ($I=4\alpha c$): ● $MgSO_4$ (0°C), ■ $NiSO_4$ (0°C), ○ $CuSO_4$ (25°C), □ $ZnSO_4$ (25 °C), △ $CdSO_4$ (25 °C). The solid lines represent the theoretical slope by the Debye-Hückel limiting equation.

TABLE 2. THERMODYNAMIC DISSOCIATION CONSTANTS OF SEVERAL METAL SULFATES IN AQUEOUS SOLUTIONS, AS COMPUTED BY DIFFERENT METHODS

Metal sulfate	$-\log(K/\text{mol dm}^{-3})$			
	Present method	Cond.[4]	Activ.[5]	Lit.[10]
$MgSO_4$ (0 °C)	2.2_3	2.01[a]	1.66—2.35[c]	1.96—2.39
$NiSO_4$ (0 °C)	2.4_3	2.19[b]	1.80—2.40[c]	2.06—2.39
$CuSO_4$ (25 °C)	2.6_7	—	—	2.10—2.46
$ZnSO_4$ (25 °C)	2.5_0	—	—	2.27—2.38
$CdSO_4$ (25 °C)	2.6_5	—	—	2.29

a) Ion-size parameter a=5.59Å. b) Ion-size parameter a=5.86Å. c) Depending on the ion-size parameter (a=3—4 Å).

In Table 2, the third column gives the log K-values[4] determined by the analysis of the conductivity data according to the Fuoss-Onsager equation, in which a set of log K and the ion-size parameter, a, is obtained in such a way that the theoretical equation gives the best fit to the experimental conductivity data. The fourth column of Table 2 gives the log K-values[5] calculated from the activity data by assuming different values of the ion-size parameter. The present method seems to result in slightly larger values of pK than the values reported in the literature.

It is the advantage of the present method that an *a priori* assumption of ion-size parameter is not required in the determination of the dissociation constant. However, if we assume the Debye-Hückel expression for χ;

$$\chi = a + \kappa^{-1} \tag{8}$$

where κ^{-1} is the Debye-Hückel length of the ionic atmosphere, we can calculate the ion-size parameter, a, by means of Eqs. (5) and (8). The -*a*values derived in this way at each concentration are shown in Table 1. The present method gives concentration-dependent values for the ion-size parameter; the a-values at lower concentrations are larger than those commonly accepted, and in some cases they exceed Bjerrum's parameter (14 Å for 2 : 2 electrolytes in aqueous solutions). The relatively large pK values obtained by the present method may be correlated with the large ion-size parameters, as has been mentioned above.

Further discussions on the validity of the present method will become possible only when more accurate experimental data have been obtained with various electrolytes.

References

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