the best correlations.

It has happened that in some cases, Eq. (1) and Eq. (2) give values of X_A much larger than $1 - X_G$ and give an abnormal concavity in plotting X_A against X_G on a triangular graph in a system whose maximum value of X_A is relatively high, even if σ is the lowest. So the conditions of the best correlation require that the correlation does not give X_A much larger than $1 - X_G$ and that it does not give an abnormal concavity.

From Table 1, it is clear that cases 2-a and 2-b give most of the best correlations.

Correlation 2-a gave the best correlation for systems whose maximum value of X_A was smaller than 0.56, and correlation 2-b represented well the data of systems whose maximum value of X_A was between 0.41 and 0.87.

Figures 1 and 2 show examples of the best correlations. These figures and Table 1 show that the correlations of this work are useful.

Nomenclature

d_1	= weight fraction of water in solvent phase at $X_A=0$	[—]
d_2	= weight fraction of water in water phase at $X_A=0$	[—]
i	= integer	[—]
m	= constant	[—]
n	= constant	[—]
p	= constant	[—]
s	= number of data	[—]

X_A	= weight fraction of solute in solution	[—]
$X_{A,cal,i}$	= calculated weight fraction of solute in solution	[—]
$X_{A,exp,i}$	= experimental weight fraction of solute in solution	[—]
X_B	= weight fraction of solvent in solution	[—]
X_G	= weight fraction of diluent(=water) in solution	[—]
α	= constant	[—]
σ	= root mean square deviation defined by Eq. (5)	[—]
σ_{min}	= minimum value of σ	[—]

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CORRELATION FOR ACTIVITIES OF WATER IN AQUEOUS ELECTROLYTE SOLUTIONS USING ASOG MODEL

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The ASOG (Analytical Solutions of Groups) model^{1,7,12)} has successfully been applied to predict phase equilibria^{5,9-11)} using group Wilson parameters. In the present study, the ASOG model is extended to correlate activities of water in aqueous electrolyte solutions.

The activity coefficient of component i in liquid solution is usually given by the ASOG model⁵⁾ as follows.

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$$\ln \gamma_i = \ln \gamma_i^{FH} + \ln \gamma_i^G \quad (1)$$

where

$$\ln \gamma_i^{FH} = \ln (\nu_i^{FH} / \sum_j x_j \nu_j^{FH}) + 1 - \nu_i^{FH} / \sum_j x_j \nu_j^{FH} \quad (2)$$

$$\ln \gamma_i^G = \sum_k \nu_{ki} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \quad (3)$$

The activity coefficient for group k , Γ_k , is given by

$$\ln \Gamma_k = -\ln \sum_l X_l a_{l/k} + 1 - \sum_l (X_l a_{l/k} / \sum_m X_m a_{l/m}) \quad (4)$$

where

$$X_k = \sum_i x_i \nu_{ki} / \sum_i x_i \sum_k \nu_{ki} \quad (5)$$

To calculate γ_i at given mole fraction, the group

Fig. 1 Schematic model for aqueous electrolyte solution

Wilson parameters $a_{k/l}$ and $a_{l/k}$ are needed. Tochigi and Kojima^{8,9)} have determined the values of the parameters for various groups.

In the present study, we consider an electrolyte solution consisting of a single electrolyte and water. The structure of the solution is assumed to be represented by Fig. 1. As qualitatively shown in this figure, it is assumed that electrolytes in the solution completely decompose to produce cations and anions, and that water molecules are bound to them. The hydration numbers for cation and anion are respectively denoted by n_+ and n_- which are assumed to be constant. A hydration water is distinguished from a free water because the hydration water is so tightly bound that its motion and intramolecular states are different from those of the free water.

According to the above-mentioned concept, an aqueous electrolyte solution can be regarded as a solution consisting of free water, hydrated cations, and hydrated anions. Where a hydrated cation (n_+ water molecules and a cation) and a hydrated anion (n_- water molecules and an anion) are treated as components. The sizes of free water, hydration water, and ions are assumed to be same. Then the values of ν_i^{FH} for a free water, a hydrated cation, and a hydrated anion are 1, (n_++1) , and (n_-+1) respectively. Therefore, the $\ln \gamma_i^{\text{FH}}$ term can easily be obtained from Eq. (2). The remaining term, $\ln \gamma_i^{\text{G}}$, can be calculated from Eq. (3) when the group Wilson parameters $a_{\text{OH}/\text{OH}^*}$ and $a_{\text{OH}^*/\text{OH}}$ are known, where OH denotes a free water and OH* a hydration water. The interaction between water molecules and ions is not taken into account except for hydration. The electrostatic contribution to the activity coefficient of the solvent, i.e., water can be given by the theory of Fowler and Guggenheim²⁾ as follows⁶⁾.

$$\ln \gamma_w^{\text{el}} = -\frac{\bar{v}_w}{24\pi N_A a^3} (\kappa a)^3 \sigma(\kappa a) \quad (6)$$

where

$$\sigma(y) = \frac{3}{y^3} \left\{ 1 + y - \frac{1}{1+y} - 2 \ln(1+y) \right\} \quad (7)$$

$$\kappa = (4\pi e^2 \sum_n N_n z_n^2 / DkT)^{1/2} \quad (8)$$

This term, $\ln \gamma_w^{\text{el}}$ should be added to the right-hand side of Eq. (1) to obtain the activity coefficient of water when ion-ion interactions exist^{3,8)} in the aqueous solution. An aqueous electrolyte solution containing 1000 g water and m moles of single electrolyte is considered here. The molality of the solution is given by m . Then the mole fractions of water, cation, and anion can ordinarily be calculated as

$$x_w^0 = 55.51 / (m\bar{v} + 55.51) \quad (9)$$

$$x_c^0 = m\bar{v}_+ / (m\bar{v} + 55.51) \quad (10)$$

$$x_a^0 = m\bar{v}_- / (m\bar{v} + 55.51) \quad (11)$$

where

$$\bar{v} = \bar{v}_+ + \bar{v}_- \quad (12)$$

However, hydrated ions exist in the solution so that the mole fractions of free water, hydrated cation, and hydrated anion become

$$x_w = \frac{x_w^0 - (n_+ x_c^0 + n_- x_a^0)}{x_w^0 - x_c^0(n_++1) - x_a^0(n_-+1)} \quad (13)$$

$$x_c = x_c^0 / \{x_w^0 - x_c^0(n_++1) - x_a^0(n_-+1)\} \quad (14)$$

$$x_a = x_a^0 / \{x_w^0 - x_c^0(n_++1) - x_a^0(n_-+1)\} \quad (15)$$

By use of the mole fractions given by Eqs. (13) to (15), the activity coefficient of free water, γ_w , can be calculated from Eqs. (1) to (8). In the present calculation, the value of ν_{ki} for water is taken as 1.6 according to Kojima *et al.*⁵⁾. To calculate Γ_k , the values of $a_{\text{OH}/\text{OH}^*}$ and $a_{\text{OH}^*/\text{OH}}$ appearing in Eq. (4) are required. These values and hydration numbers n_+ and n_- were determined by using a non-linear least squares method minimizing the deviation $|a_w^{\text{calc}} - a_w^{\text{exp}}| / a_w^{\text{exp}}$, where calculated water activities are given by $\gamma_w x_w$. The experimental values for a_w at 25°C were cited from the literature⁶⁾. The partial molar volume for water, $\bar{v}_w$, was determined at each molality by use of the density data⁴⁾ of the aqueous electrolyte solution. The value of the ion size parameter, a , was fixed as 4×10^{-8} cm for each ion according to Stokes and Robinson⁸⁾. The dielectric constant of the solution, D , was approximated by that of pure water as usual^{3,8)}.

The optimum values obtained for $a_{\text{OH}/\text{OH}^*}$ and $a_{\text{OH}^*/\text{OH}}$ are as follows.

$$a_{\text{OH}/\text{OH}^*} = 1.82, \quad a_{\text{OH}^*/\text{OH}} = 1.78$$

The values of n_+ and n_- for common ions are presented in Table 1. These values for the Group Wilson parameters and the hydration numbers were determined on the basis of the experimental activities⁶⁾ for water in 14 electrolyte solutions presented in Table 2. When the hydration number for cations are plotted against the Pauling ionic radius, a straight line is obtained as illustrated in Fig. 2. The value of n_+ decreases with the increase of ionic radius. This tendency qualitatively coincides with the literature³⁾.

Table 1 Hydration number

$$a_{\text{OH}/\text{OH}^*}=1.82, a_{\text{OH}^*}/\text{OH}=1.78$$

Ion	Hydration number
Li^+	1.8
Na^+	1.0
K^+	0.4
Mg^{2+}	3.6
Ba^{2+}	1.9
Ca^{2+}	3.1
Ni^{2+}	3.2
Fe^{2+}	3.1
I^-	1.0
Br^-	0.8
Cl^-	0.5

Table 2 Comparison between calculated and experimental activities for water

Electrolyte	max.dev.* [%]	mean dev.** [%]	max.molality
MgI_2	4.88	0.98	5.0
MgBr_2	2.08	0.84	5.0
MgCl_2	3.68	0.85	5.0
BaI_2	1.69	0.32	2.0
BaCl_2	0.60	0.18	1.8
NaBr	1.46	0.36	4.0
NaCl	0.93	0.36	6.0
CaCl_2	5.52	0.92	7.2
CaBr_2	13.90	2.04	6.0
NiCl_2	7.18	1.09	5.0
FeCl_2	1.32	0.45	2.0
LiCl	10.36	1.09	14.0
LiBr	2.57	0.99	14.0
KCl	0.34	0.13	4.5

$$* \text{ dev.} = (|a_W^{\text{calc}} - a_W^{\text{exp}}| / a_W^{\text{exp}}) \times 100$$

$$** \text{ mean dev.} = \sum_N \text{dev.} / N, N = \text{number of data}$$

The comparison between calculated and experimental activities of water is presented in Table 2 and graphical representations for typical 1:1 and 2:1 electrolytes are shown in Figs. 3 and 4, respectively. As shown in Table 2, activities of water in electrolyte solutions can be correlated up to concentrated regions. It is found from Figs. 3 and 4 that the extent of contribution from the electrostatic term, Eq. (6), is relatively small.

As shown above, the ASOG model in conjunction with the hydration model may be useful in estimating activities of water in aqueous electrolyte solutions. Applications of the present model to other temperatures and to aqueous multi-electrolyte solutions still remain to be investigated.

Nomenclature

a	= ion-size parameter (mean distance of closest approach of ions)	[cm]
a_W	= activity of water	[—]
$a_{k/l}, a_{l/k}$	= group Wilson parameters	[—]
$a_{\text{OH}/\text{OH}^*}, a_{\text{OH}^*}/\text{OH}$	= group Wilson parameters between free and hydration water molecules	[—]
D	= dielectric constant	$[\text{C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1}]$
e	= protonic charge (opposite in sign to that of an electron)	[C]

Fig. 2 Relation between hydration number of cation and ionic radius **Fig. 3 Activity of water in aqueous NaCl solution at 25°C** **Fig. 4 Activity of water in aqueous CaCl_2 solution at 25°C**

k	= Boltzmann constant	[J·K ⁻¹]
m	= molality (moles of electrolyte per kg of solvent)	[mol·kg ⁻¹]
N	= number of ions per unit volume of solution	[cm ⁻³]
N_A	= Avogadro number	[mol ⁻¹]
n_+	= number of water molecules bound to a cation	[—]
n_-	= number of water molecules bound to an anion	[—]
r	= ionic radius	[cm]
T	= absolute temperature	[K]
$\bar{v}$	= partial molar volume	[cm ³ ·mol ⁻¹]
X	= group fraction	[—]
x	= mole fraction	[—]
z	= algebraic valence	[—]
γ	= activity coefficient	[—]
Γ	= group activity coefficient	[—]
κ	= reciprocal of average radius of ionic atmosphere (the Debye reciprocal length)	[cm ⁻¹]
ν	= number of groups	[—]
$\tilde{\nu}$	= $\tilde{\nu}_+ + \tilde{\nu}_-$	[—]
$\tilde{\nu}_+, \tilde{\nu}_-$	= numbers of cations and anions produced by dissociation of one molecule of electrolyte	[—]
<Subscripts>		
A	= anion	
C	= cation	
i, j	= molecule i and j	
k, l, m	= group k, l , and m	
ki	= group k in molecule i	
n	= ion n	
W	= water	
<Superscripts>		
el	= electrostatic contribution	

FH	= size contribution given by the Flory-Huggins equation
G	= group contribution
(i)	= standard state
o	= absence of hydration

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EFFECT OF PERFORATED PLATE BAFFLES ON PARTICLE SEGREGATION IN GAS FLUIDISED BEDS OF SOLID MIXTURES

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Although solid mixing is very rapid and effective in a gas fluidised bed of uniform particles¹⁾, segregation may occur when mixtures of particles differing in size and/or particularly in density are fluidised, even vigor-

ously⁴⁾. In some solid treatment processes such as the fluidised bed coal char gasifier²⁾, solid segregation is preferable because it enables us to divide the bed into two series zones in each of which different reactions proceed selectively. As in the gasifier fewer char particles become distributed in the lower part of

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