S_1	solubility of CO at atmospheric pressure and room temperature, m^3/m^3
S	solubility of CO, $kmol/m^3$
H	Henry's coefficient of solubility, $kmol/(m^3\ kPa)$
P	barometric pressures, kPa
P_w	vapor pressure of water at temperature T_w, kPa
P_{vap}	vapor pressure of solvent in eq 3, kPa
P_{CO}	partial pressure of CO in the autoclave, kPa
T	temperature in the autoclave, K
T_w	temperature in the gas buret, K
V	volume of water displaced by the desorbed CO gas, m^3
V_1	volume of the liquid sample withdrawn from autoclave, m^3
X	mole fraction of the organic component in water

Registry No. CO, 630-08-0; allyl alcohol, 107-18-6; diethylamine, 109-89-7; triethylamine, 121-44-8.

Literature Cited

(1) Halligudi, S. B.; Chaudhari, R. V.; Doraiswamy, L. K. *Ind. Eng. Chem. Process Des. Dev.* **1984**, *23*, 794.
(2) Taqui Khan, M. M.; Halligudi, S. B.; Abdi, S. H. R. *J. Mol. Catal.* **1988**, *44*, 179.
(3) Wender, I. *Catal. Rev.—Sci. Eng.* **1976**, *14*(1), 97.
(4) Costa, L. C. *Catal. Rev.—Sci. Eng.* **1983**, *25*(3), 325.
(5) Taqui Khan, M. M.; Halligudi, S. B.; Abdi, S. H. R. *J. Mol. Catal.*, in press.
(6) Radhakrishnan, K.; Ramachandran, P. A.; Brahme, P. H.; Chaudhari, R. V. *J. Chem. Eng. Data* **1983**, *28*, 1.
(7) Chaudhary, V. R.; Parande, M. G.; Brahme, P. H. *Ind. Eng. Chem. Fundam.* **1982**, *21*, 472.
(8) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977; p 629.
(9) Battino, R.; Clever, H. L. *Chem. Rev.* **1966**, *60*, 395.
(10) Dake, S. B.; Chaudhari, R. V. *J. Chem. Eng. Data* **1985**, *30*, 400.

Received for review May 27, 1987. Revised December 14, 1987. Accepted March 9, 1988.

Evaluation of Pitzer Ion Interaction Parameters of Aqueous Mixed Electrolyte Solutions at 25 °C. 2. Ternary Mixing Parameters

Hee-Taik Kim and William J. Frederick, Jr.*

Department of Chemical Engineering, Oregon State University, Corvallis, Oregon 97331

The Pitzer mixing parameters θ_{ij} and ψ_{ijk} were evaluated for 49 ternary mixtures with common ions at 25 °C. The Harvie and Weare model, which is based on Pitzer equations for aqueous mixed electrolyte solutions, was used for these evaluations. Evaluation of these parameters for mixed electrolyte solutions required only the single-salt parameters and experimental values of ln $\gamma_\pm$ or ϕ for ternary mixtures with common ions. The effects of the higher order electrostatic terms were considered for all asymmetrical mixtures of electrolytes. The mean standard deviation for the calculated ln $\gamma_\pm$ or ϕ values is 0.0070 when compared with the experimental values used to obtain the ternary mixing parameters.

Introduction

In recent years there has been increasing interest in the thermodynamic properties of aqueous mixed electrolyte solutions, especially at high concentrations. In fields such as sea water desalination, geothermal energy recovery, chemical oceanography, hydrometallurgy, and pulp and paper chemistry, it is essential to have accurate data on the thermodynamic properties of mixed electrolyte solutions.

The nonideality of a single electrolyte solution is conventionally represented in terms of the mean activity coefficient, $\gamma_\pm$.

Activity coefficients are of primary importance in describing accurately the thermodynamic behavior of aqueous mixed electrolyte solutions. The lack of accurate activity coefficient predictions can result in large errors when calculating the solubility of inorganic species in aqueous multicomponent ionic solutions of high ionic strength even when only a few chemical species are present.

Among recently developed models of electrolyte solutions, ionic interaction models provide the simplest and most coherent procedures for calculating the thermodynamic properties of electrolyte components. They use a single set of equations to describe the activity and osmotic coefficients of the components of aqueous single and mixed electrolyte solutions. An ion interaction model for predicting activity coefficients of mixed electrolyte solutions was developed by Pitzer and co-workers (*1–4*) in the early 1970s. The Pitzer model extended the Debye–Hückel method, using a virial expansion to account for the ionic strength dependence of the short-range forces in binary and ternary ion interactions. The virial expansion approach accurately represents the compositional dependence of the thermodynamic properties in most multicomponent electrolyte solutions to high ionic strengths. Also, these equations can be used in iterative calculations since the ion interaction parameters are expressed as explicit functions of ionic strength, and only a few parameters are needed to evaluate properties of both single and mixed electrolyte solutions. Many publications (*5–11*) have shown that the Pitzer model results in excellent solubility prediction.

The purpose of this work is to obtain Pitzer mixing ion interaction parameters, θ_{ij} and ψ_{ijk}, from experimental data on aqueous mixed electrolyte solutions with common ions. The θ-terms summarize interaction between ions of like charged sign that are independent of the common ion in a ternary mixture and the ψ-terms account for the modifying influence of the common ion on these interactions. The mixing ion interaction parameters from our results are stored in a computer as a database with single-salt parameters, and activity or osmotic coefficients for mixed electrolyte solutions can be calculated simply by identifying the salt and defining the appropriate ionic strength.

General Equation for Mixed-Electrolyte Solutions

Recently Harvie and Weare (*5*) have developed a chemical equilibrium model for calculating mineral solubilities in brines from zero to high ionic strengths at 25 °C. This model was based on the semiempirical equations of Pitzer and co-workers

0021-9568/88/1733-0278$01.50/0

(*1–4*) for the thermodynamics of aqueous electrolyte solutions.

The following set of equations for mixed electrolytes are identical with the form used by Harvie and Weare (*5*) for modeling the osmotic coefficient and the activity coefficient of a neutral electrolyte.

$$\phi - 1 = \frac{2}{\sum m_i}\left\{\frac{-A^{\phi}I^{3/2}}{1 + bI^{1/2}} + \sum_{c}\sum_{a} m_c m_a (B^{\phi}_{ca} + ZC_{ca}) + \sum_{c<}\sum_{c'} m_c m_{c'}(\Phi^{\phi}_{cc'} + \sum_{a} m_a \psi_{cc'a}) + \sum_{a<}\sum_{a'} m_a m_{a'}(\Phi^{\phi}_{aa'} + \sum_{c} m_c \psi_{aa'c})\right\} \quad (1)$$

$$\ln \gamma_{MX} = |Z_M Z_X|\,F + \left(\frac{2\nu_M}{\nu}\right)\sum_{a} m_a\left[B_{Ma} + \frac{Z}{2}C_{Ma} + \left(\frac{\nu_X}{\nu_M}\right)\Phi_{Ma}\right] + \left(\frac{2\nu_X}{\nu}\right)\sum_{c} m_c\left[B_{cX} + \frac{Z}{2}C_{cX} + \left(\frac{\nu_M}{\nu_X}\right)\Phi_{cX}\right] + \nu^{-1}\sum_{c}\sum_{a} m_c m_a[2\nu_M Z_M C_{ca} + \nu_M\psi_{Mca} + \nu_X\psi_{Xac}] + \sum_{c<}\sum_{c'} m_c m_{c'}\left(\frac{\nu_X}{\nu}\right)\psi_{cc'X} + \sum_{a<}\sum_{a'} m_a m_{a'}\left(\frac{\nu_M}{\nu}\right)\psi_{aa'M} \quad (2)$$

The term F in eq 2 depends only on ionic strength and temperature. The defining equation of F is given by

$$F = -A^{\phi}\left[\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b}\ln(1 + bI^{1/2})\right] + \sum_{c}\sum_{a} m_c m_a B'_{ca} + \sum_{c<}\sum_{c'} m_c m_{c'}\Phi'_{cc'} + \sum_{a<}\sum_{a'} m_a m_{a'}\Phi'_{aa'} \quad (3)$$

where $A^{\phi} = {}^1/_3(2\pi N_0 d_w/1000)^{1/2}(e^2/DkT)^{3/2}$.

A^{ϕ} is the Debye–Hückel coefficient for the osmotic coefficient and equals 0.392 for water at 25 °C (*2*). N_0 is Avogadro's number. d_w and D are the density and static dielectric constant of the solvent (water in this case) at temperature T. Also k is Boltzmann's constant and e is the electronic charge. The empirical parameter b in eq 1 and 3 is taken as 1.2 at 25 °C (*2*).

In eq 1, 2, and 3, the subscripts M, c, and c′ represent cations. Similarly, the subscripts X, a, and a′ refer to anions. The designations

$$\sum_{c<}\sum_{c'} \text{ and } \sum_{a<}\sum_{a'}$$

in eq 1, 2, and 3 mean the sum over all distinguishable pairs of dissimilar anions or cations (*5*). m_M is the molality (mol/kg of solvent) of a cation with charge z_M corresponding to stoichiometric coefficient ν_M, and $\nu = \nu_M + \nu_X$. The function Z is defined by

$$Z = \sum_{i} m_i|z_i| = 2(\sum_{M} m_M z_M) = 2(\sum_{X} m_X|z_X|)$$

and

$$I = {}^1\!/_2\sum_{i} m_i z_i^2$$

is the total ionic strength of given system.

The parameters B^{ϕ}_{MX}, B_{MX}, and B'_{MX} which describe the interaction of pairs of oppositely charged ions represent measurable combinations of the second virial coefficients. They are defined as explicit functions of ionic strength by using the following equations.

$$B^{\phi}_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX}e^{-\alpha_1 I^{1/2}} + \beta^{(2)}_{MX}e^{-\alpha_2 I^{1/2}} \quad (4)$$

$$B_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX}f(\alpha_1 I^{1/2}) + \beta^{(2)}_{MX}f(\alpha_2 I^{1/2}) \quad (5)$$

$$B'_{MX} = \beta^{(1)}_{MX}f'(\alpha_1 I^{1/2})/I + \beta^{(2)}_{MX}f'(\alpha_2 I^{1/2})/I \quad (6)$$

where

$$f(\chi) = 2[1 - (1 + \chi)e^{-\chi}]/\chi^2 \quad (7)$$

$$f'(\chi) = -2[1 - (1 + \chi + 1/2\chi^2)e^{-\chi}]/\chi^2 \quad (8)$$

For one or both ions in univalent type electrolytes, the first two terms of eq 4 and 5, and only the first term of eq 6, are considered, and $\alpha_1 = 2$ (*2*). For higher valence type, such as 2-2 electrolytes, the full eq 4, 5, and 6 are used, and $\alpha_1 = 1.4$ and $\alpha_2 = 12$ (*3*).

The single-electrolyte third virial coefficients, C_{MX}, account for short-range interaction of ion triplets and are important only at high concentration. These terms are independent of ionic strength. The parameters C_{MX} and C^{ϕ}_{MX}, the corresponding coefficients for calculating the osmotic coefficient, are related by the following the equation (*2*)

$$C_{MX} = C^{\phi}_{MX}/2[|Z_M Z_X|]^{1/2} \quad (9)$$

The mixed electrolyte second virial coefficients, Φ_{ij}, account for interactions between ions of the same signs, and are defined by eq 10–12. θ_{ij} is a adjustable parameter for each pair of

$$\Phi^{\phi}_{ij} = \theta_{ij} + {}^{E}\theta_{ij}(I) + I\,{}^{E}\theta'_{ij}(I) \quad (10)$$

$$\Phi_{ij} = \theta_{ij} + {}^{E}\theta_{ij}(I) \quad (11)$$

$$\Phi'_{ij} = {}^{E}\theta'_{ij}(I) \quad (12)$$

anions or cations. The third virial coefficients, ψ_{ijk}, in eq 1 and 2 are mixed electrolyte parameters for each cation–cation–anion and anion–anion–cation triplet in mixed electrolyte solutions. These parameters are also assumed to be independent of ionic strength.

Higher Order Electrostatic Terms

The terms ${}^{E}\theta_{ij}(I)$ and ${}^{E}\theta'_{ij}(I)$ from eq 10, 11, and 12 account for electrostatic unsymmetric mixing effects. Friedman (*12*) predicted the existence of these significant effects for unsymmetrical mixtures when ions of the same sign, but different charges, are mixed. Pitzer (*13*) derived equations for calculating these effects, and Harvie and Weare (*5*) summarized Pitzer's equations in a convenient form as follows:

$${}^{E}\theta_{MN}(I) = \frac{Z_M Z_N}{4I}\left[J0(X_{MN}) - \frac{1}{2}J0(X_{MM}) - \frac{1}{2}J0(X_{NN})\right] \quad (13)$$

$${}^{E}\theta'_{MN}(I) = \frac{Z_M Z_N}{8I^2}[J1(X_{MN}) - {}^1\!/_2 J1(X_{MM}) - {}^1\!/_2 J1(X_{NN})] - \frac{{}^{E}\theta_{MN}}{I} \quad (14)$$

where $X_{MN} = 6z_M z_N A^{\phi} I^{1/2}$, for cations M and N. ${}^{E}\theta_{MN}(I)$ and ${}^{E}\theta'_{MN}(I)$ are zero when $z_M = z_N$ and are functions of ionic strength, the electrolyte pair type, and temperature. For anion pairs, equations similar to eq 13 and 14 are defined. The terms $J0(X)$ and $J1(X)$ are given by following integrals.

$$J0(X) = \frac{1}{4}X - 1 + \frac{1}{X}\int_0^{\infty}[1 - e^{[-(X/Y)e^{-Y}]}]Y^2\,dY \quad (15)$$

$$J1(X) = \frac{1}{4}X - \frac{1}{X}\int_0^{\infty}\left[1 - \left(1 + \frac{X}{Y}e^{-Y}\right)e^{[-(X/Y)e^{-Y}]}\right]Y^2\,dY \quad (16)$$

These terms $J0(X)$ and $J1(X)$ are equal to $J(X)$ and $XJ'(X)$, respectively, which are given by Pitzer (*13*). Pitzer has given convenient forms (*13*) for evaluating approximate values of his expressions, $J(X)$ and $J'(X)$. However, we chose to evaluate the integrals $J0(X)$ and $J1(X)$ directly using the IMSL library

Table I. Values of the Integrals $J0(X)$ and $J1(X)$

X	$J0(X)$	$J1(X)$
0.01	0.000 051 78	0.000 136 27
0.05	0.001 139 41	0.001 928 58
0.10	0.003 600 30	0.005 862 02
0.20	0.010 880 57	0.016 991 79
0.30	0.020 320 05	0.030 864 22
0.40	0.031 311 83	0.046 557 32
0.50	0.043 507 65	0.063 575 38
0.60	0.056 679 30	0.081 610 27
0.70	0.070 665 33	0.100 453 79
0.80	0.085 345 49	0.119 957 32
0.90	0.100 627 10	0.140 010 19
1.00	0.116 437	0.160 528
2.00	0.294 158	0.381 213
3.00	0.492 823	0.615 992
4.00	0.702 924	0.856 962
5.00	0.920 340	1.101 259
6.00	1.142 862	1.347 551
7.00	1.369 157	1.595 127
8.00	1.598 356	1.843 571
9.00	1.829 861	2.092 624
10.00	2.063 238	2.342 115
20.00	4.454 392	4.846 403
30.00	6.893 411	7.354 296
40.00	9.352 336	9.861 749
50.00	11.822 009	12.368 340
60.00	14.298 329	14.874 126
70.00	16.779 125	17.379 234
80.00	19.263 116	19.883 775
90.00	21.749 488	22.387 845
100.00	24.237 693	24.891 520
200.00	49.195 521	49.915 589
400.00	99.117 123	99.937 508
600.00	149.093 071	149.948 642
800.00	199.078 617	199.955 682
1000.00	249.068 759	249.960 644
5000.00	1249.024 371	1249.984 829
10000.00	2499.015 087	2499.990 364

subroutine DMLIN (*14*). We have included values of $J0(X)$ and $J1(X)$, calculated by our method for various X values, in Table I. Also, the values of $J0(X_{\mathrm{MN}})$, $J1(X_{\mathrm{MN}})$, $J0(X_{\mathrm{MM}})$, $J1(X_{\mathrm{MM}})$, $J0(X_{\mathrm{NN}})$, $J1(X_{\mathrm{NN}})$, ${}^{E}\theta_{\mathrm{MN}}$, and ${}^{E}\theta'_{\mathrm{MN}}$ for $MX-NX_2-H_2O$ systems where M and N denote the different anions and X denotes an anion as a common ion at constant total ionic strength at 25 °C are shown in Table II.

Evaluation of Mixing Ion Interaction Parameters

The set of parameters defining the model for calculating the thermodynamic properties of mixed electrolyte solutions is $\beta^{(0)}_{\mathrm{MX}}$, $\beta^{(1)}_{\mathrm{MX}}$, $\beta^{(2)}_{\mathrm{MX})}$, C^{ϕ}_{MX}, θ_{ij}, and ψ_{ijk}. Among these parameters, the parameters $\beta^{(0)}_{\mathrm{MX}}$, $\beta^{(1)}_{\mathrm{MX}}$, $\beta^{(2)}_{\mathrm{MX}}$, and C^{ϕ}_{MX} are readily obtained from single-salt data as shown in our earlier tabulation (*15*). However, for many salts, experimental data for mixtures with common ions are not available at high concentrations. For example, in the system $HCl-NCl_2-H_2O$, where N = Ba, Ca, Co, Mg, Mn, or Ni, the maximum molality of HCl for which data is reported in the literature is 5.0 *m*. The maximum molality in our evaluation of single salt parameters for HCl was 16.0 *m*. Use of the single-salt parameters evaluated at a higher concentration range may result in inaccurate values of mixing parameters. In order to avoid this problem, we reevaluated the single-salt parameters for pure electrolyte solutions at a reduced maximum molality which corresponded to the maximum molality for the ternary mixture data. The results for single salts are shown in Table III.

The functions B^{ϕ}_{MX}, B_{MX}, $B'_{\mathrm{M}}X$, and C_{MX} may be calculated from their defining eq 4, 5, 6, and 9 by using single-salt-parameter values which are given in Table III and our earlier paper (*15*). Mixed electrolyte terms Φ^{ϕ}_{ij}, Φ_{ij}, and Φ'_{ij} were obtained from ${}^{E}\theta_{ij}$ and ${}^{E}\theta'_{ij}$ values, calculated from eq 13 and 14. The remaining terms in eq 1, 2, and 3 contain θ_{ij} and ψ_{ijk} which are the adjustable parameters in our evaluation for mixed electrolyte solutions with common ions.

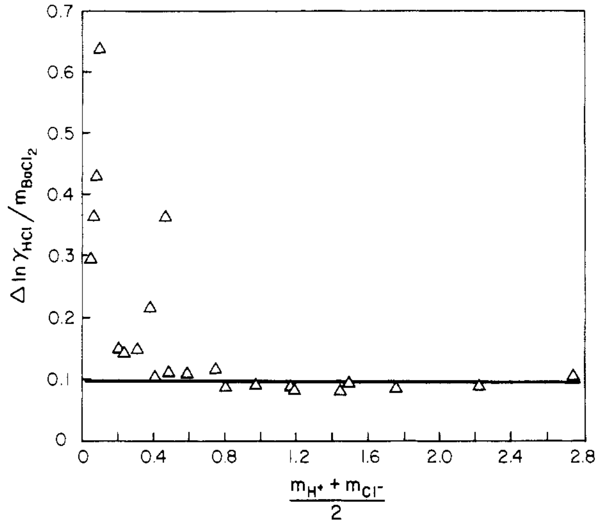

Figure 1. Fits of eq 19 for $HCl-BaCl_2-H_2O$ system at 25 °C.

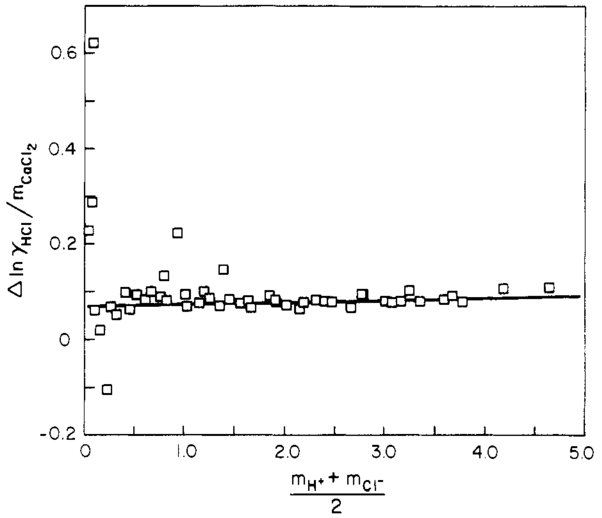

Figure 2. Fits of eq 19 for $HCl-CaCl_2-H_2O$ system at 25 °C.

Pitzer (*4*) suggested simplified equations and a simple graphical procedure for evaluation of θ_{ij} and ψ_{ijk}. For the activity and osmotic coefficients of an MX–NX mixture, he obtained

$$\Delta\phi\left(\frac{\sum_i m_i}{2m_{\mathrm{M}}m_{\mathrm{N}}}\right) = \theta_{\mathrm{MN}} + m_{\mathrm{X}}\psi_{\mathrm{MNX}} \qquad (17)$$

and

$$\Delta \ln \gamma_{\mathrm{MX}}\left(\frac{\nu}{2\nu_{\mathrm{M}}n_{\mathrm{N}}}\right) = \theta_{\mathrm{MN}} + \frac{1}{2}\left(m_{\mathrm{X}} + m_{\mathrm{M}}\left|\frac{Z_{\mathrm{M}}}{Z_{\mathrm{X}}}\right|\right)\psi_{\mathrm{MNX}} \qquad (18)$$

The terms $\Delta\phi$ and $\Delta \ln \gamma_{\mathrm{MX}}$ are the difference between the experimental values of ϕ or $\ln \gamma_{\mathrm{MX}}$ and the calculated values of ϕ or $\ln \gamma_{\mathrm{MX}}$ with the appropriate single-salt parameters values for the pure single-electrolyte terms, but with $\theta_{\mathrm{MN}} = \psi_{\mathrm{MNX}} = 0$ in eq 1 and 2.

The quantity on the left-hand side of eq 17 or 18 is plotted against the coefficients of on the right-hand side. The values of θ_{MN} and ψ_{MNX} are obtained from the linear plot as the intercept, θ_{MN} and the slope ψ_{MNX}, respectively. However, Khoo (*53*) pointed out the disadvantage of this procedure. According to Khoo, eq 18 and 19 represent a nonlinear plot particularly at low molality of the solute NX. That is, the uncertainties in $\Delta\phi$

Table II. High-Order Electrostatic Functions at Constant Total Ionic Strength for $MX-NX_2-H_2O$ Systems at 25 °C

I	$J0(X_{MN})$	$J1(X_{MN})$	$J0(X_{MM})$	$J1(X_{MM})$	$J0(X_{NN})$	$J1(X_{NN})$	${}^{E}\theta_{MN}$	${}^{E}\theta'_{MN}$
0.10	0.199 40	0.265 39	0.077 01	0.108 92	0.487 77	0.610 05	−0.414 77	1.795 42
0.50	0.560 37	0.694 11	0.231 15	0.304 58	1.290 14	1.508 97	−0.200 28	0.187 91
1.00	0.855 38	1.028 70	0.362 38	0.462 84	1.924 87	2.194 37	−0.144 13	0.069 15
1.50	1.089 34	1.288 60	0.468 39	0.587 55	2.421 42	2.722 53	−0.118 52	0.038 30
2.00	1.290 14	1.508 97	0.560 37	0.694 11	2.844 31	3.168 55	−0.103 05	0.025 13
2.50	1.469 15	1.703 78	0.642 98	0.788 79	3.219 34	3.561 85	−0.092 40	0.018 10
3.00	1.632 39	1.880 29	0.718 75	0.874 90	3.559 99	3.917 60	−0.084 50	0.013 83
3.50	1.783 49	2.042 87	0.789 20	0.954 42	3.874 37	4.244 86	−0.078 33	0.011 02
4.00	1.924 87	2.194 37	0.855 38	1.028 70	4.167 81	4.549 53	−0.073 34	0.009 04
4.50	2.058 25	2.336 79	0.917 99	1.098 64	4.444 07	4.835 72	−0.069 20	0.007 60
5.00	2.184 86	2.471 60	0.977 60	1.164 95	4.705 86	5.106 43	−0.065 69	0.006 50

Table III. Ion Interaction Parameters for Single Salts at 25 °C

compd	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	max m	SD[a]	R[b]	ref
HCl	0.180 24	0.271 54	0.000 06	6.00	0.0013	1.000	*16*
HBr	0.196 22	0.345 29	0.007 62	4.00	0.006	1.000	*16*
$HClO_4$	0.172 38	0.317 08	0.008 55	6.00	0.0019	1.000	*16*
LiCl	0.146 67	0.337 03	0.003 93	6.00	0.0020	1.000	*16*
LiBr	0.173 62	0.259 76	0.005 56	4.50	0.0016	1.000	*16*
$LiNO_3$	0.140 60	0.288 94	−0.005 47	6.00	0.0012	1.000	*16*
NaBr	0.099 34	0.262 02	0.000 97	5.00	0.0010	1.000	*16*
$NaNO_3$	0.004 79	0.202 41	−0.000 27	6.00	0.0005	0.999	*17*
NaH_2PO_4	−0.06509	0.09100	0.01138	4.00	0.0023	0.998	*16*
$NaClo_4$	0.056 21	0.271 77	−0.001 43	5.00	0.0005	1.000	*16*
$Na2CO_3$	0.071 85	1.156 45	−0.008 35	1.50	0.0007	0.999	*18*
$NaHCO_3$[c]	0.028 00	0.044 00					*19*
KCl	0.046 80	0.220 96	−0.000 50	4.00	0.0003	1.000	*16*
KH_2PO_4	−0.112 80	0.060 58	0.020 12	1.80	0.0003	1.000	*16*
CsCl	0.029 95	0.063 67	0.000 27	6.00	0.0007	0.999	*16*
$CaCl_2$	0.306 54	1.642 78	0.002 22	3.50	0.0028	1.000	*20*
$CaBr_2$	0.362 72	1.815 85	0.003 49	2.50	0.0016	1.000	*20*
$Ca(NO_3)_2$	0.184 72	1.645 00	−0.010 69	4.00	0.0074	0.999	*21*
$CoCl_2$	0.356 23	1.540 19	−0.012 51	3.00	0.0039	0.999	*22*
$CuCl_2$	0.313 73	1.246 07	−0.042 22	2.00	0.0021	0.999	*23*
$MgCl_2$	0.353 72	1.700 54	0.005 24	5.00	0.0029	1.000	*20*
$Mg(NO_3)_2$	0.365 16	1.595 63	−0.019 71	2.00	0.0023	1.000	*21*
$NiCl_2$	0.346 57	1.589 40	−0.003 26	2.50	0.0020	1.000	*22*
$MnCl_2$	0.335 47	1.460 33	−0.023 24	3.50	0.0012	1.000	*23*
$UO_2(ClO_4)_2$	0.623 46	1.973 57	0.020 84	2.50	0.0030	1.000	*23*
$La(ClO_4)_3$	0.764 85	6.533 33	0.002 75	3.00	0.0007	0.999	*24*

[a] SD, standard deviation of fit for the osmotic coefficient data. [b] R, multiple correlation coefficient which is a measure of the closeness of linear relationship. [c] Used the values of Peiper and Pitzer (see ref *19*).

and $\Delta \ln \gamma_{MX}$ are greatly magnified at low values of the coefficients of ψ_{MNX} in eq 17 and 18, so that one must observe the least-squares fitting carefully. The validity of Khoo's indication was clearly represented in Figures 1 and 2, which show plots of $\Delta \ln \gamma_A/m_B$ versus $^1/_2 (m_{H^+} + m_{Cl^-})$ from eq 18 for the $HCl(A)-BaCl_2(B)-H_2O$ system (*35*) and the $HCl(A)-CaCl_2(B)-H_2O$ system (*37*), respectively.

Our method of obtaining θ_{ij} and ψ_{ijk} considers all experimental points in a fitting to eq 1 or 2 using multiple regression. We used the regression package in Number Cruncher Statistical System (NCSS) (*54*). The resulting values of mixing parameters, θ_{ij} and ψ_{ijk}, for 49 ternary mixtures with common ions at 25 °C are listed in Table IV.

It was suggested that the same pair of cations or anions should have the same value of θ_{ij} but different values of ψ_{ijk} in ternary or multicomponent mixtures. For example, the value of $\theta_{HNa} = 0.0368$ in the present study was selected by considering all systems ($HCl-NaCl-H_2O$, $HBr-NaBr-H_2O$, and $HClO_4-NaClO_4-H_2O$) which contain both of H^+ and Na^+.

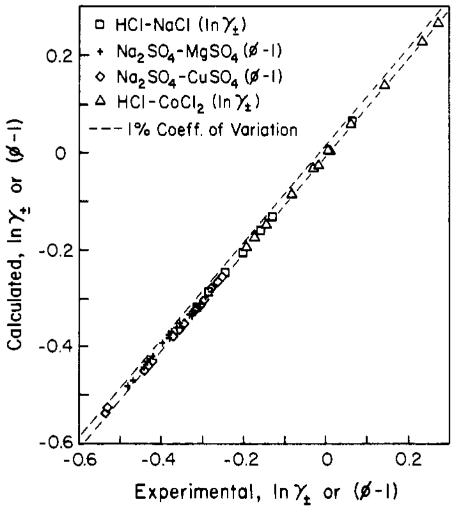

Figure 3. Comparison of experimental and calculated $\ln \gamma_\pm$ or $(\phi - 1)$ for various systems at 25 °C.

Discussion

Although Pitzer (*13*) has pointed out that the higher order electrostatic effects may be ignored for several M^+-N^{2+} systems, we included these effects for all ternary mixtures of asymmetrical electrolytes with common ions. Table IV shows that the standard deviations in $\ln \gamma_\pm$ or ϕ are less than 0.01 in 38 systems among the total 49 sets of ternary mixtures which were considered in the present work. The mean standard deviation for the 49 data sets is 0.0070. Only for two systems, however, the standard deviations in ϕ are above 0.02. These latter results are due to the relatively large values of ionic strengths (maximum I = 18.25 mol/kg for $CaCl_2-Ca(NO_3)_2-H_2O$ and 14.25 mol/kg for $NaClO_4-UO_2(ClO_4)_2-H_2O$) in these two

Table IV. Pitzer's Mixing Parameters for Mixtures with Common Ion

system	exptl	θ	ψ	SD (θ and ψ)	SD (θ=ψ=0)	max I	ref
HCl–KCl	ln γ	0.0067	–0.0081	0.0128	0.0177	3.51	*25*
HBr–KBr	ln γ	0.0067	–0.0215	0.0065	0.0257	3.01	*25*
HCl–NaCl	ln γ	0.0368	–0.0033	0.0014	0.0439	3.01	*25*
HBr–NBr	ln γ	0.0368	–0.0107	0.0032	0.0323	3.01	*25*
$HClO_4$–$NaClO_4$	ϕ	0.0368	–0.0162	0.0017	0.0163	5.35	*26*
HCl–LiCl	ln γ	0.0151	–0.0022	0.0052	0.0215	4.01	*25*
$HClO_4$–$LiClO_4$	ϕ	0.0151	0.0000	0.0028	0.0109	4.45	*26*
HBr–LiBr	ln γ	0.0151	0.0101	0.0141	0.0351	3.01	*25*
HCl–CsCl	ln γ	–0.0459	0.0040	0.0100	0.0371	3.00	*27*
NaCl–KCl	ln γ	0.0070	–0.0098	0.0112	0.0274	4.30	*28*
NaH_2PO_4–KH_2PO_4	ϕ	0.0070	–0.0162	0.0072	0.0302	6.04	*29*
NaCl–LiCl	ϕ	0.0120	–0.0022	0.0020	0.0027	5.84	*30*
$NaNO_3$–$LiNO_3$	ϕ	0.0120	–0.0065	0.0028	0.0216	5.92	*30*
NaOAc–LiOAc	ϕ	0.0120	–0.0065	0.0064	0.0185	6.05	*30*
$NaClO_4$–$LiClO_4$	ϕ	0.0120	–0.0061	0.0028	0.0094	5.82	*26*
KCl–KH_2PO_4	ϕ	0.1071	–0.0160	0.0026	0.0243	2.07	*29*
NaCl–NaH_2PO_4	ϕ	0.1071	–0.0147	0.0048	0.0335	2.37	*29*
NaCl–NaF	ln γ	–0.0028	0.0076	0.0019	0.0021	1.05	*10, 31*
NaCl–$NaHCO_3$	ln γ	0.0735	0.0989	0.0135	0.0200	1.10	*32*
HCl–$CoCl_2$	ln γ	0.0829	0.0075	0.0039	0.0310	3.00	*33*
HCl–$NiCl_2$	ln γ	0.0895	0.0044	0.0039	0.0316	3.00	*34*
HCl–$BaCl_2$	ln γ	0.0991	–0.0081	0.0050	0.0300	3.00	*35*
HBr–$BaBr_2$	ln γ	0.0991	0.0035	0.0060	0.0268	2.00	*36*
HCl–$CaCl_2$	ln γ	0.0682	0.0043	0.0046	0.0120	5.00	*37*
HBr–$CaBr_2$	ln γ	0.0682	0.0285	0.0060	0.0284	2.00	*38*
HCl–$MnCl_2$	ln γ	0.0899	–0.0092	0.0050	0.0372	5.00	*39*
HCl–$MgCl_2$	ln γ	0.0891	–0.0006	0.0065	0.0483	5.00	*40*
HCl–$SrCl_2$	ln γ	0.0728	0.0050	0.0016	0.0286	3.00	*41*
HBr–$SrBr_2$	ln γ	0.0728	0.0310	0.0055	0.0197	2.00	*42*
$HClO_4$–$UO_2(ClO_4)_2$	ϕ	0.1377	–0.0319	0.0131	0.0603	10.88	*43*
KCl–$SrCl_2$	ϕ	0.0149	–0.0201	0.0018	0.0214	4.80	*44*
LiCl–$BaCl_2$	ϕ	0.0243	0.0208	0.0057	0.0188	4.32	*45*
CsCl–$BaCl_2$	ϕ	–0.0441	–0.0229	0.0026	0.0167	4.08	*45*
NaCl–$MnCl_2$	ϕ	0.0907	–0.0190	0.0019	0.0130	9.30	*46*
NaCl–$CoCl_2$	ϕ	0.0382	–0.0056	0.0036	0.0063	7.29	*47*
$NaClO_4$–$UO_2(ClO_4)_2$	ϕ	0.0231	–0.0437	0.0257	0.2993	14.25	*43*
$MgCl_2$–$Mg(NO_3)_2$	ϕ	0.0002	0.0073	0.0163	0.0353	13.70	*48*
$CaCl_2$–$Ca(NO_3)_2$	ϕ	0.0002	–0.0116	0.0268	0.1180	18.25	*48*
$Mg(NO_3)_2$–$Ca(NO_3)_2$	ϕ	–0.1844	0.0252	0.0125	0.0219	14.42	*48*
Na_2SO_4–$MgSO_4$	ϕ	0.0970	–0.0352	0.0051	0.0126	8.83	*49*
NaCl–$MgCl_2$	ϕ	0.0970	–0.0517	0.0149	0.0528	7.14	*49*
$CuCl_2$–$CuSO_4$	ϕ	0.0380	0.0234	0.0022	0.0253	6.90	*50*
$MgCl_2$–$MgSO_4$	ϕ	0.0380	–0.0062	0.0052	0.0100	7.71	*49*
NaCl–Na_2SO_4	ϕ	0.0380	0.0081	0.0100	0.0249	6.00	*49*
NaCl–$CuCl_2$	ϕ	0.0370	–0.0129	0.0044	0.0070	7.30	*50*
Na_2SO_4–$CuSO_4$	ϕ	0.0370	–0.0235	0.0031	0.0041	5.47	*50*
NaCl–Na_2CO_3	ϕ	–0.0630	0.0025	0.0076	0.0163	5.70	*51*
$NaClO_4$–$La(ClO_4)_3$	ϕ	0.2174	–0.0202	0.0049	0.0158	4.90	*52*
$CaCl_2$–$CoCl_2$	ϕ	0.1722	–0.0332	0.0114	0.0300	13.08	*47*

systems. A comparison between the calculated values using our results and experimental values of ln $\gamma_\pm$ or (ϕ – 1) for several systems is shown in Figure 3. It is clear that ln $\gamma_\pm$ or ϕ for mixed electrolyte solutions with common ions can be predicted accurately by using our evaluated values of ternary mixing parameters.

In order to compare our results with previously published mixing parameter values, we chose HX–CaX systems with X = Cl and Br. The activity coefficients of these systems have been measured and interpreted, based on the Pitzer equations, by various methods. Khoo et al. (*38*, *55*) obtained the values of θ_{HCa} = 0.0739 and ψ_{HCaCl} = 0.003 for HCl–$CaCl_2$–H_2O and θ_{HCa} = 0.0600 and ψ_{HCaBr} = 0.0009 for HBr–$CaBr_2$–H_2O, respectively. Also, θ_{HCa} = 0.0612 and ψ_{HCaBr} = 0.0008 were obtained for HCl–$CaCl_2$–H_2O by Roy et al. (*37*). These values are close to, but not identical with, our result in Table IV. This is due to the following reasons:

1. Roy et al. (*37*) used a linear plot of eq 18, as suggested by Pitzer (*4*), to obtain θ_{HCa} and ψ_{HCaCl}, while Khoo et al. (*38*, *55*) utilized a nonlinear regression method in eq 2. We used multiple linear regression with eq 2 to obtain θ_{HCa} and ψ_{HCaX} for both systems, HCl–$CaCl_2$–H_2O and HBr–$CaBr_2$–H_2O simultaneously.

2. Khoo et al. (*38*, *55*) covered ionic strengths only up to 3.0 mol/kg for HCl–$CaCl_2$–H_2O, but Roy et al. (*37*) and our work included data up to I = 5.0 mol/kg for HCl–$CaCl_2$–H_2O.

It can be seen from Table IV that θ_{MN} values for the HX–NX_2–H_2O systems, where X = Cl and Br, and N = Co, Ni, Ba, Ca, Mn, Mg, and Sr, are close to each other. This could be expected to define an average value for θ_{HN} and to characterize H^+ and N^{2+} interactions which are not specific to the N^{2+} ion. The average value of θ_{HN} is 0.0838 in the present work, whereas θ_{HN} = 0.078 obtained by Khoo et al. (*33*) for six HCl–NCl_2–H_2O systems where N = Mg, Ca, Sr, Ba, Mn, and Co.

Literature Cited

(1) Pitzer, K. S. *J. Phys. Chem.* **1973**, *77*, 268.
(2) Pitzer, K. S.; Mayorga, G. *J. Phys. Chem.* **1973**, *77*, 2300.
(3) Pitzer, K. S.; Mayorga, G. *J. Solution Chem.* **1974**, *3*, 539.
(4) Pitzer, K. S.; Kim, J. J. *J. Am. Chem. Soc.* **1974**, *96*, 5701.
(5) Harvie, C. E.; Weare, J. H. *Geochim. Cosmochim. Acta* **1980**, *44*, 981.
(6) Harvie, C. E.; Eugster, H. P.; Weare, J. H. *Geochim. Cosmochim. Acta* **1982**, *46*, 1603.
(7) Harvie, C. E.; Moller, N.; Weare, J. H. *Geochim. Cosmochim. Acta* **1984**, *48*, 723.
(8) Chen, C. C.; Britt, H. I.; Boston, J. F.; Evans, L. B. *AIChE J.* **1979**, *25*, 820.
(9) Whitfield, M. *Mar. Chem.* **1975**, *3*, 197.

(10) Whitfield, M. *Geochim. Cosmochim. Acta* **1975**, *39*, 1545.
(11) Kelly, B.; Frederick, W. J. Jr. *Application of Chemical Engineering Principles in the Forest Products and Related Industries*; Kayihan, F., Krieger-Brackett, B., Eds.; AIChE Forest Products Division: Seattle, WA, 1986.
(12) Friedman, H. L. *Ionic Solution Theory*; Interscience: New York, 1962.
(13) Pitzer, K. S. *J. Solution Chem.* **1975**, *4*, 249.
(14) *IMSL Library Subroutine DMLIN*, 9th ed.; IMSL: Houston, TX June, 1982.
(15) Kim, H. T.; Frederick, W. J. Jr. *J. Chem. Eng. Data*, **1988**, *33*, 177.
(16) Harmer, W. J.; Wu, Y. C. *J. Phys. Chem. Ref. Data* **1972**, *1*, 1047.
(17) Wu, Y. C.; Harmer, W. J. *J. Phys. Chem. Ref. Data* **1980**, *9*, 513.
(18) Goldberg, R. N.; *J. Phys. Chem. Ref. Data* **1981**, *10*, 671.
(19) Peiper, J. C.; Pitzer, K. S. *J. Chem. Thermodyn.* **1982**, *14*, 613.
(20) Goldberg, R. N.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1978**, *7*, 263.
(21) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworths: London, 1959.
(22) Goldberg, R. N.; Nuttall, R. L.; Staples, B. R. *J. Phys. Chem. Ref. Data* **1979**, *8*, 923.
(23) Goldberg, R. N. *J. Phys. Chem. Ref. Data* **1979**, *8*, 1005.
(24) Libus, Z.; Sadowaska, T. *J. Chem. Thermodyn.* **1979**, *11*, 1151.
(25) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolyte Solutions*, 3rd ed.; Reinhold: New York, 1958.
(26) Rush, R. M.; Johnson, J. S. *J. Phys. Chem.* **1968**, *72*, 767.
(27) Sankar, M.; Macaskill, J. B.; Bates, R. G. *J. Solution Chem.* **1981**, *10*, 169.
(28) Huston, R.; Butler, J. N. *Anal. Chem.* **1969**, *41*, 1695.
(29) Childs, C. W.; Downes, C. J.; Platford, R. F. *J. Solution Chem.* **1974**, *3*, 139.
(30) Robinson, R. A.; Wood, R. H.; Reilly, P. J. *J. Chem. Thermodyn.* **1971**, *3*, 461.
(31) Butler, J. N.; Huston, R. *Anal. Chem.* **1970**, *42*, 1308.
(32) Butler, J. N.; Huston, R. *J. Phys. Chem.* **1970**, *74*, 2976.
(33) Khoo, K. H.; Lim, T. K.; Chan, C. Y. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 2037.
(34) Khoo, K. H.; Lim, T. K.; Chan, C. Y. *J. Solution Chem.* **1978**, *7*, 291.
(35) Khoo, K. H.; Chan, C.Y.; Lim, T. K. *J. Chem Soc., Faraday Trans. 1* **1978**, *74*, 837.
(36) Khoo, K. H.; Lim, T. K.; Chan, C. Y. *J. Solution Chem.* **1979**, *8*, 227.
(37) Roy, R. N.; Gibbons, J. J.; Owens, L. K.; Bliss, G. A.; Hartley, J. J. *J. Chem. Soc., Faraday Trans. 1* **1981**, *78*, 1405.
(38) Khoo, K. H.; Lim, T. K.; Chan, C. Y. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 1067.
(39) Roy, R. N.; Gibbons, J. J.; Trower, J. K.; Lee, G. A. *J. Solution Chem.* **1980**, *9*, 535.
(40) Roy, R. N.; Gibbons, J. J.; Bliss, D. P. Jr.; Casebolt, R. G.; Baker, B. K. *J. Solution Chem.* **1980**, *9*, 911.
(41) Harned, H. S.; Paxton, T. R. *J. Phys. Chem.* **1953**, *57*, 531.
(42) Lim, T. K.; Khoo, K. H.; Chan, C. Y. *J. Solution Chem.* **1980**, *9*, 785.
(43) Rush, R. M.; Johnson, J. S. *J. Chem. Thermodyn.* **1971**, *3*, 779.
(44) Downes, C. J. *J. Chem Thermodyn.* **1974**, *6*, 317.
(45) Lindenbaum, S.; Rush, R. M.; Robinson, R. A. *J. Chem. Thermodyn.* **1972**, *4*, 381.
(46) Downes, C. J. *J. Chem. Eng. Data* **1975**, *18*, 412.
(47) Downes, C. J. *J Solution Chem.* **1975**, *4*, 191.
(48) Platford, R. F. *J. Chem Thermodyn.* **1971**, *3*, 319.
(49) Wu, Y. C.; Rush, R. M.; Scatchard, G. *J. Phys. Chem.* **1968**, *72*, 4048.
(50) Downes, C. J.; Pitzer, K. S. *J. Solution Chem.* **1976**, *5*, 389.
(51) White, D. R. Jr.; Bates, R. G. *Aust. J. Chem.* **1980**, *33*, 1903.
(52) Boyd, G. E. *J. Chem. Thermodyn.* **1978**, *10*, 415.
(53) Khoo, K. H. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 1.
(54) Hintze, J. L. *Number Cruncher Statistical System (4.21)*; Number Cruncher Statistical Systems: Kaysville, UT, 1986.
(55) Khoo, K. H.; Chan, C. Y.; Lim, T. K. *J. Solution Chem.* **1977**, *6*, 651.
(56) Robinson, R. A.; Roy, R. N.; Bates, R. G. *J. Solution Chem.* **1974**, *3*, 837.

Received for review May 26, 1987. Accepted January 27, 1988. We would like to thank the following companies for their advice and financial support: Associated Pulp and Paper Mills (Australia); Crown-Zellerbach Corp.; HPD, Inc.; Scott Paper Co.; International Paper Co.; Mead Corp.; Union Camp Corp.; Westfaco Corp.; and Weyerhaeuser Co.

Excess Molar Enthalpies for the Methanol–1-Butanol–Benzene System at 25 °C

Isamu Nagata* and Kazuhiro Tamura

Department of Chemical Engineering, Kanazawa University, Kanazawa 920, Japan

Excess molar enthalpies at 25 °C for methanol–1-butanol–benzene were measured with an isothermal dilution calorimeter. The experimental results agree well with those calculated from the UNIQUAC associated-solution model with two association constants for alcohols, three solvation constants for complex formation, and binary interaction parameters.

Introduction

Ternary excess molar enthalpies of 23 systems containing two aliphatic alcohols and one saturated hydrocarbon have been collected; however, those of systems of two alcohols with one unsaturated hydrocarbon are not filed in the compilation of Christensen et al. (*1*) and experimental results on only such two systems involving benzene at 25 °C have been reported from this laboratory: for ethanol–1-propanol–benzene (*2*) and for methanol–2-butanol–benzene (*3*). As part of a program to provide excess molar enthalpies on ternary systems formed by two alcohols and one unsaturated hydrocarbon, this paper reports the experimental results of the methanol–1-butanol–benzene system at 25 °C. The experimental results are compared with those calculated from the UNIQUAC associated-solution model (*2*). Excess molar enthalpies at 25 °C for the three binary systems forming the ternary system are available from the literature: methanol–1-butanol (*4*); methanol–benzene (*5*); 1-butanol–benzene (*5*).

Experimental Section

Analytical grade 1-butanol of specific purity 99.8 mol %, purchased from Wako Pure Chemical Industries Ltd., was directly used. C.P. methanol, treated with anhydrous copper sulfate, was distilled in a 1-m glass column packed with McMahon packing. C.P. benzene was purified by recrystallization three times. Densities of three chemicals at 25 °C, measured with an Anton Paar DMA40 densimeter, agreed excellently with the literature values (*6*). The isothermal dilution calorimeter as described by Nagata and Kazuma (*7*) was used to obtain ternary excess molar enthalpies. The experimental error involved in observed values was ±0.5% over the mole fraction range studied. Each experimental run was performed by adding benzene to a binary mixture of methanol and 1-butanol. A ternary mixture is regarded as a pseudobinary system made up of one binary mixture and benzene. One mole of the ternary mixture is prepared by mixing $(1 - x_3)$ of the initial binary mixture and x_3 of component 3. The ternary excess molar enthalpy H^E_{123} at x_1, x_2, and x_3 can be given as

$$H^E_{123} = \Delta H_m + (1 - x_3)H^E_{12} \qquad (1)$$

where ΔH_m is the observed molar excess enthalpy for the

0021-9568/88/1733-0283$01.50/0