Evaluation of Pitzer Ion Interaction Parameters of Aqueous Electrolytes at 25 °C. 1. Single Salt Parameters

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Ion interaction parameters for 304 single salts in aqueous solution have been obtained for Pitzer's equations. For most of the cases we evaluated, the range of molality extended up to saturation when data were available. The calculated activity coefficients of HCl, LiBr, $CaBr_2$, $Pr(NO_3)_3$, and $MgSO_4$ from our results and Pitzer's were compared to available smoothed experimental data. The comparisons show better agreement with experimental data when we use values of our parameters which were evaluated at higher concentrations than those used by Pitzer.

Introduction

The principal thermodynamic properties of interest for predicting solubilities are activity and osmotic coefficients. The lack of accurate activity coefficients can result in large errors when predicting the solubility in aqueous multicomponent ionic solutions of high ionic strength even when few chemical species are present.

Ionic interaction models provide the simplest and most coherent procedures for calculating the properties of electrolyte compponents. They use a single set of equations to describe the osmotic and activity coefficients of the components of single salts and mixtures with common ions. An ion interaction model for electrolyte activity coefficients 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 model is applicable to solutions of high ionic strength. Moreover, these equations can be used in iterative calculations since the ion interaction parameters are expressed as explicit functions of ionic strength and need very few parameters to estimate properties of both single and mixed electrolytes. Many publications (*5-11*) have shown that the Pitzer model results in excellent solubility predictions.

The purpose of this work is to obtain Pitzer ion interaction parameters from osmotic coefficient data on single electrolytes at high concentration, up to nearly saturation. We used a form of the Pitzer ionic interaction model which was developed by Harvie and Weare (*5*) to predict the solubility of minerals in concentrated mixed salt solutions. The ionic interaction model was fit to published osmotic coefficient data at 25 °C to obtain ion interaction parameters for solution of single salts. The ion interaction parameters from our results are stored on file in a computer as a database, and activity and osmotic coefficients can be calculated simply by identifying the salt and defining the appropriate ionic strength.

General Equations

Recently, Harvie and Weare (*5*) developed a chemical equilibrium model for calculating mineral solubilities in the Na-K-Mg-Ca-Cl-SO_4-H_2O system at 25 °C. This model was based on the Pitzer equations (*1*, *2*) for aqueous electrolyte solutions. Their equations for calculating the osmotic and mean ionic activity coefficients for single electrolyte solutions can be written as follows:

$$\phi = 1 + \frac{2}{(m_M + m_X)}\left\{\frac{-A^\phi I^{3/2}}{1 + bI^{1/2}} + m_M m_X(B^\phi_{MX} + ZC_{MX})\right\} \quad (1)$$

$$\ln \gamma_{MX} = -|z_M z_X| A^\phi \left[\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b}\ln(1 + bI^{1/2})\right] + 4m\left(\frac{\nu_M \nu_X}{\nu}\right)\left(B_{MX} + \frac{I}{2}B'_{MX}\right) + 6m^2\left(\frac{\nu_M \nu_X}{\nu}\right)\nu_M z_M C_{MX} \quad (2)$$

In eq 1 and 2, m_M is the molality (mol/kg of solvent) of a cation with charge z_M corresponding to stoichiometric coefficient ν_M. Similarly, the subscript X refers to an anion. Also $\nu = \nu_M + \nu_X$ and $I = {}^1/_2\sum_i m_i z_i^2$ is the ionic strength. 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 A^ϕ is the Debye-Hückel coefficient for the osmotic coefficient and is given by

$$A^\phi = \frac{1}{3}\left(\frac{2\pi N_0 d_w}{1000}\right)^{1/2}\left(\frac{e^2}{DkT}\right)^{3/2} \quad (3)$$

where N_0 is Avogadro's number, d_w is the density of water, and D is the static dielectric constant of water at temperature T. Also, k is Boltzmann's constant and e is the electronic charge. The value of A^ϕ at 25 °C is 0.392 and the term b in eq 1 and 2 is an empirical parameter equal to 1.2 at 25 °C (*2*). 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

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

$$f'(x) = -2[1 - (1 + x + 0.5x^2)e^{-x}]/x^2 \quad (8)$$

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 where $\alpha_1 = 2$ (*2*). For higher valence type electrolytes, 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. They are independent of ionic strength. The parameters C_{MX} and C^ϕ_{MX}, the corresponding coefficients for calculating the osmotic coefficient, are related by (*2*)

$$C_{MX} = C^\phi_{MX}/(2|z_M z_X|^{1/2}) \quad (9)$$

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Table I. Ion Interaction Parameters for 1-1 Electrolytes at 25 °C

compd	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	max m	SD	R	ref
HF	0.022 12	0.401 56	−0.000 18	20.000	0.003 05	0.9996	*12*
HCl	0.203 32	−0.016 68	−0.003 72	16.000	0.014 43	0.9999	*12*
HBr	0.241 53	−0.161 19	−0.001 01	11.000	0.029 20	0.9994	*12*
HI	0.239 93	0.283 51	0.001 38	10.000	0.015 93	0.9998	*12*
$HClO_4$	0.216 17	−0.227 69	0.001 92	16.000	0.036 18	0.9996	*12*
HNO_3	0.088 30	0.483 38	−0.002 33	28.000	0.027 64	0.9960	*12*
LiCl	0.209 72	−0.343 80	−0.004 33	19.219	0.053 39	0.9982	*12*
LiBr	0.245 54	−0.442 44	−0.002 93	20.000	0.093 91	0.9974	*12*
LiI	0.146 61	0.753 94	0.021 26	3.000	0.001 55	0.9999	*12*
LiOH	0.050 85	−0.072 47	−0.003 37	5.000	0.004 94	0.9959	*12*
$LiClO_4$	0.204 00	0.322 51	−0.001 18	4.500	0.001 57	1.0000	*12*
$LiNO_3$	0.130 08	0.049 57	−0.003 82	20.000	0.006 39	0.9999	*12*
$LiNO_2$	0.121 47	0.457 34	−0.003 83	19.900	0.010 91	0.9997	*25*
$LiClO_3$	0.170 49	0.229 44	−0.005 24	4.200	0.001 85	0.999	*26*
$LiBrO_3$	0.089 28	0.215 73	−0.000 05	5.000	0.000 96	1.0000	*26*
LiAc[a]	0.112 15	0.202 43	−0.005 19	4.000	0.001 17	0.9999	*12*
NaF	0.031 83	0.186 97	−0.008 40	1.000	0.000 29	0.9999	*12*
NaCl	0.077 22	0.251 83	0.001 06	6.144	0.000 64	1.0000	*12*
NaBr	0.110 77	0.137 60	−0.001 53	9.000	0.004 48	0.9999	*12*
NaI	0.134 63	0.194 79	−0.001 17	12.000	0.009 24	0.9998	*12*
NaOH	0.170 67	−0.084 11	−0.003 42	29.000	0.085 91	0.9950	*12*
$NaClO_3$	0.019 08	0.279 32	0.001 81	3.000	0.000 32	0.9999	*12*
$NaClO_4$	0.254 46	0.275 69	−0.001 02	6.000	0.001 01	0.9999	*12*
$NaBrO_3$	−0.021 54	0.182 07	0.006 33	2.167	0.000 85	0.9973	*12*
$NaNO_3$	0.003 88	0.211 51	−0.000 06	10.830	0.000 73	0.9985	*41*
$NaNO_2$	0.047 93	0.224 65	−0.002 26	12.340	0.006 39	0.9980	*25*
NaH_2PO_4	−0.047 46	−0.075 86	0.006 59	6.500	0.004 07	0.9910	*12*
NaH_2AsO_4	−0.079 97	0.358 66	0.022 67	1.300	0.000 29	0.9998	*12*
NaCNS	0.123 73	0.083 85	−0.003 82	18.000	0.028 57	0.9973	*12*
$NaBO_2$	−0.052 89	−0.108 88	0.014 97	4.000	0.002 18	0.9998	*27*
$NaBF_4$	−0.026 03	−0.100 84	0.001 71	9.000	0.003 55	0.9948	*27*
NaAc[a]	0.137 23	0.341 95	−0.004 74	3.500	0.000 96	1.0000	*12*
KF	0.100 13	−0.021 75	−0.001 59	17.500	0.020 93	0.9989	*12*
KCl	0.046 61	0.223 41	−0.000 44	4.803	0.000 36	1.0000	*12*
KBr	0.055 92	0.220 94	−0.001 62	5.500	0.000 36	1.0000	*12*
KI	0.072 53	0.277 10	−0.003 81	4.500	0.000 60	0.9999	*12*
KOH	0.175 01	−0.016 34	−0.002 67	20.000	0.026 50	0.9995	*12*
$KClO_3$	−0.091 93	0.233 43		0.700	0.000 23	0.9999	*12*
$KBrO_3$	−0.114 26	0.204 14		0.500	0.000 21	0.9999	*12*
KNO_3	−0.085 11	0.105 18	0.007 73	3.500	0.000 42	1.0000	*12*
KNO_2	0.003 49	0.157 08	−0.000 25	34.120	0.011 96	0.9776	*25*
KH_2PO_4	−0.114 11	0.068 98	0.020 69	1.800	0.000 24	1.0000	*12*
KH_2AsO_4	−0.126 14	0.254 57	0.040 02	1.300	0.000 27	0.9999	*12*
KCNS	0.038 91	0.253 61	−0.001 92	5.000	0.000 62	0.9999	*12*
KPF_6	−0.137 10	−0.427 85		0.500	0.001 43	0.9996	*12*
KAc[a]	0.152 83	0.355 13	−0.004 32	3.500	0.000 87	1.0000	*12*
RbF	0.108 72	0.398 04	−0.008 74	3.500	0.001 91	0.9998	*12*
RbCl	0.046 60	0.129 83	−0.001 63	7.800	0.001 29	0.9999	*12*
RbBr	0.038 68	0.167 23	−0.001 23	5.000	0.000 48	0.9999	*12*
RbI	0.039 02	0.152 24	−0.000 95	5.000	0.000 35	1.0000	*12*
$RbNO_3$	−0.081 74	−0.031 75	0.006 24	4.500	0.002 26	0.9996	*12*
$RbNO_2$	−0.003 03	0.051 30	−0.000 14	62.300	0.019 44	0.9736	*25*
RbAc[a]	0.162 96	0.329 18	−0.005 61	3.500	0.000 62	1.0000	*12*
CsF	0.136 44	0.141 66	−0.006 74	3.500	0.001 69	0.9999	*12*
CsCl	0.036 43	−0.011 69	−0.000 96	11.000	0.003 65	0.9993	*12*
CsBr	0.023 11	0.045 87	0.000 92	5.000	0.001 41	0.9995	*12*
CsI	0.021 21	0.073 07	−0.003 07	3.000	0.000 38	0.9997	*12*
$CsNO_3$	−0.130 04	0.081 69	0.030 18	1.500	0.000 57	0.9999	*12*
$CsNO_2$	0.009 26	0.320 52	−0.000 36	36.000	0.017 96	0.9330	*25*
CsOH	0.147 68	0.345 72	−0.008 19	1.200	0.000 37	1.0000	*12*
CsAc[a]	0.171 44	0.328 96	−0.007 93	3.500	0.000 63	1.0000	*12*
$AgNO_3$	−0.071 02	−0.167 93	0.003 22	13.000	0.008 23	0.9984	*12*
TlCl	−3.164 06	−2.438 21		0.010	0.000 24	0.9996	*12*
$TlClO_4$	−0.111 11	0.075 53		0.500	0.000 39	0.9999	*12*
$TlNO_3$	−0.125 18	−0.301 45		0.400	0.000 37	0.9999	*12*
$TlNO_2$	−0.650 41	−0.110 38	0.377 82	1.400	0.000 26	1.0000	*12*
TlAc[a]	0.008 78	−0.041 05	−0.001 53	6.000	0.002 15	0.8848	*12*
NH_4Cl	0.051 91	0.179 37	−0.003 01	7.405	0.000 93	0.9999	*12*
NH_4I	0.057 01	0.315 66	−0.003 08	7.500	0.001 74	0.9998	*28*
NH_4ClO_4	−0.006 97	−0.056 18	−0.000 71	2.100	0.000 24	0.9995	*12*
NH_4NO_3	−0.014 76	0.138 26	0.000 29	25.954	0.005 38	0.9977	*12*
NH_4SCN	0.005 28	−0.340 80	−0.000 36	23.431	0.004 90	0.9822	*29*
Et_4NNO_3	−0.040 22	−0.871 08	0.005 65	8.000	0.007 58	0.9893	*28*
Me_4NNO_3	0.012 24	−0.329 33	0.000 90	7.000	0.002 12	0.9991	*28*
$MeNH_3ClO_4$	−0.033 71	0.005 73	0.003 45	4.000	0.001 68	0.9980	*30*
$Me_2NH_2ClO_4$	−0.043 95	−0.171 91	0.002 40	7.500	0.001 12	0.9999	*30*
Me_3NHClO_4	−0.114 47	−0.171 29	0.013 48	1.800	0.002 35	0.9992	*30*

Table I (Continued)

compd	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	max m	SD	R	ref
GuCl	−0.028 55	−0.109 97	0.001 77	12.000	0.006 77	0.9845	*31*
Li *p*-tol[b]	0.012 23	0.466 53	0.006 33	4.500	0.003 02	0.9986	*12*
Na *p*-tol[b]	−0.039 58	0.478 46	0.005 71	4.000	0.002 52	0.9951	*12*
Na form[c]	0.071 87	0.322 47	−0.002 36	3.500	0.000 59	0.9999	*12*
Na propion[d]	0.188 13	0.267 72	−0.012 88	3.000	0.000 46	1.0000	*12*
Na butyr[e]	0.260 81	0.163 68	−0.033 58	3.500	0.003 73	0.9998	*12*
Na valer[f]	0.334 73	−0.113 24	−0.073 94	2.000	0.002 95	0.9998	*12*
Na capryl[g]	−0.451 20	−7.736 38	0.059 02	3.000	0.016 95	0.9963	*12*
Na pelargon[h]	0.037 28	−10.3798	−0.071 64	2.500	0.016 85	0.9933	*12*
Na capr[i]	0.079 92	−7.401 38	−0.060 28	1.800	0.003 30	0.9987	*12*
NaH malon[j]	0.021 66	0.176 11	−0.000 89	5.000	0.000 53	0.9998	*12*
NaH succ[k]	0.034 63	0.140 36	0.000 61	5.000	0.002 04	0.9994	*12*
NaH adip[l]	0.043 25	0.339 88		0.700	0.000 30	0.9999	*12*
K *p*-tol[b]	−0.098 42	0.471 88	0.011 82	3.500	0.002 04	0.9995	*12*
KH malon	−0.004 74	0.061 28	0.000 48	5.000	0.002 74	0.8707	*12*
KH succ	0.013 09	0.109 78	0.002 15	4.500	0.002 35	0.9972	*12*
KH adip	−0.039 98	0.475 95	0.055 23	1.000	0.000 70	0.9997	*12*

[a] Acetate. [b] *p*-Toluenesulfonate. [c] Formate. [d] Propionate. [e] Butyrate. [f] Valerate. [g] Caprylate. [h] Pelargonate. [i] Caprate. [j] Malonate. [k] Succinate. [l] Adipate.

Table II. Ion Interaction Parameters for 1-2 Electrolytes at 25 °C

compd	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	max m	SD	R	ref
H_2SO_4	0.140 98	−0.568 43	−0.002 37	27.500	0.048 74	0.9984	*32*
Li_2SO_4	0.144 73	1.299 52	−0.006 16	3.000	0.004 48	0.9996	*13*
$Li_2C_6H_4S_2O_6$	0.408 62	1.924 82	−0.032 40	2.500	0.003 11	0.9999	*13*
$Li_2C_{14}H_{12}S_2O_6$	0.121 89	1.487 71	0.034 15	1.000	0.003 95	0.9992	*13*
Na_2SO_4	0.046 04	0.933 50	−0.004 83	1.750	0.001 12	0.9996	*13*
Na_2SO_3	0.080 15	1.185 00	−0.004 36	2.000	0.001 87	0.9996	*13*
Na_2CO_3	0.053 06	1.292 62	0.000 94	2.750	0.002 57	0.9993	*13*
Na_HPO_4	−0.021 69	1.244 72	0.007 26	2.000	0.000 52	0.9997	*13*
Na_2CrO_4	0.065 26	1.632 56	0.008 84	4.250	0.005 12	0.9997	*13*
$Na_2S_2O_3$	0.063 47	1.321 15	0.004 75	4.000	0.003 35	0.9997	*13*
$Na_2S_2O_6$	0.085 26	1.189 61		0.800	0.002 71	0.9986	*13*
$Na_2S_2O_8$	0.280 75	1.017 50		0.090	0.000 45	0.9999	*13*
$Na_2C_2H_4S_2O_6$	0.287 82	1.314 51	−0.048 35	1.750	0.005 18	0.9994	*13*
$Na_2C_6H_4S_2O_6$	0.252 77	2.022 65	−0.021 32	3.000	0.002 40	0.9999	*13*
$Na_2C_{14}H_{12}S_2O_6$	0.008 08	1.601 99		0.400	0.004 27	0.9926	*13*
$Na_2C_{14}H_{12}S_2O_8$	−0.368 38	0.169 58		0.400	0.009 83	0.9817	*13*
$Na_2B_{12}H_{12}$	0.516 66	1.765 89	−0.018 34	1.500	0.000 91	1.0000	*13*
Na_2WO_4	0.203 18	0.876 16	−0.019 41	2.500	0.002 83	0.9999	*13*
Na_2HAsO_4	0.136 07	1.701 25	0.012 02	1.000	0.000 58	0.9999	*13*
$Na_2C_4H_2O_4$[a]	0.235 06	0.873 29	−0.021 55	2.000	0.003 90	0.9997	*13*
$Na_2C_4H_2O_4$[b]	0.140 05	0.452 88	−0.009 11	2.750	0.002 54	0.9998	*13*
K_2SO_4	0.075 48	0.443 71		0.692	0.001 36	0.9990	*13*
K_2HPO_4	0.053 07	1.102 71		0.800	0.000 49	0.9999	*13*
$K_2H_2P_2O_7$	−0.005 85	1.251 98	0.005 24	3.000	0.000 84	0.9995	*13*
K_2HAsO_4	0.106 70	1.717 14		0.800	0.001 43	0.9998	*13*
K_2CrO_4	0.077 02	1.226 81	−0.000 95	3.250	0.002 74	0.9997	*13*
$K_2Cr_2O_7$	−0.011 11	2.333 06		0.507	0.015 52	0.9144	*13*
$K_2Pt(CN)_4$	0.059 55	2.255 39		0.948	0.004 20	0.9984	*13*
Rb_2SO_4	0.091 23	0.778 63	−0.012 82	1.500	0.000 97	0.9999	*13*
$Rb_2S_2O_8$	0.204 64	−0.263 40		0.070	0.000 05	0.9999	*13*
Cs_2SO_4	0.141 74	0.694 56	−0.026 86	1.831	0.001 13	0.9999	*13*
$Cs_2S_2O_8$	0.132 83	−0.764 29		0.109	0.000 06	0.9999	*13*
$(NH_4)_2SO_4$	0.048 41	1.132 40	−0.001 55	5.500	0.001 85	0.9996	*22*
$(NH_4)_2HPO_4$	−0.042 5.	−0.698 71	0.005 27	3.000	0.001 55	0.9990	*13*
$(NH_4)_2B_{10}H_{10}$	0.158 24	1.462 02	−0.017 10	3.750	0.006 75	0.9988	*13*
$(CN_3H_6)_2CO_3$	−0.074 20	0.228 09	0.013 80	2.500	0.002 11	0.9983	*13*
$C_2H_6S_2O_6$	0.428 97	2.006 94	−0.019 84	5.500	0.007 82	0.9999	*13*
$C_6H_6S_2O_6$	0.413 81	2.018 36	−0.020 71	1.750	0.002 08	0.9999	*13*

[a] Sodium fumarate. [b] Sodium maleate.

Evaluation of Ion Interaction Parameters

The ion interaction parameters for single electrolytes were evaluated from recently published osmotic coefficient data by using multiple regression analysis to fit eq 1 to the data at 25 °C. We used the computer program SIPS (Statistical Interactive Programming System), which was developed at Oregon State University, for this purpose. The best values of these fitting parameters are given in Tables I–VI. Tables I–VI also contain the maximum molality for which data are available, frequently up to saturation. Thus the maximum molalities for most cases in our evaluation go beyond that of Pitzer's evaluation (*2*).

The standard deviation of fit (SD) for the osmotic coefficient data and the multiple correlation coefficient, R, which is a measure of the closeness of fit to a linear relationship, are also listed in Tables I–VI. The source of the osmotic coefficient data is listed in the last column in the tables.

Table III. Ion Interaction Parameters for 2-1 Electrolytes at 25 °C

compd	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	max m	SD	R	ref
$MgCl_2$	0.355 73	1.617 38	0.004 74	5.750	0.003 60	1.0000	*14*
$MgBr_2$	0.434 6	1.731 84	0.002 75	5.610	0.005 85	1.0000	*14*
MgI_2	0.491 61	1.782 73	0.007 80	5.000	0.004 21	1.0000	*14*
$Mg(ClO_4)_2$	0.497 53	1.794 92	0.008 75	4.000	0.006 61	0.9999	*22*
$Mg(NO_3)_2$	0.342 84	2.682 44	−0.007 23	5.000	0.007 60	0.9999	*22*
$Mg(Ac)_2$	0.229 30	2.041 67	−0.014 60	4.000	0.003 70	0.9999	*22*
$CaCl_2$	0.325 79	1.384 12	−0.001 74	6.000	0.015 82	0.9998	*14*
$CaBr_2$	0.338 99	2.045 51	0.010 67	6.000	0.007 15	1.0000	*14*
CaI_2	0.432 25	1.848 79	0.000 85	1.915	0.001 62	1.0000	*14*
$Ca(ClO_4)_2$	0.479 24	2.162 87	−0.008 37	6.000	0.017 30	0.9999	*22*
$Ca(NO_3)_2$	0.170 30	2.021 06	−0.006 90	6.000	0.013 46	0.9987	*22*
$SrCl_2$	0.281 70	1.616 66	−0.000 71	3.500	0.003 92	0.9999	*14*
$SrBr_2$	0.324 10	1.782 23	0.003 44	2.100	0.000 86	1.0000	*14*
SrI_2	0.393 94	1.925 36	0.004 74	1.970	0.000 89	1.0000	*14*
$Sr(ClO_4)_2$	0.441 38	2.002 36	−0.014 54	6.000	0.006 41	0.9999	*22*
$Sr(NO_3)_2$	0.118 32	2.415 03	−0.008 52	4.000	0.005 94	0.9970	*22*
$BaCl_2$	0.290 73	1.249 98	−0.030 46	1.785	0.001 47	0.9999	*14*
$BaBr_2$	0.315 52	1.570 56	−0.016 10	2.300	0.002 69	0.9999	*14*
BaI_2	0.402 27	1.908 62	−0.009 36	1.998	0.001 75	1.0000	*14*
$Ba(ClO_4)_2$	0.326 73	2.538 59	−0.015 76	5.500	0.010 15	0.9998	*22*
$Ba(NO_3)_2$	−0.043 71	1.117 78		0.400	0.001 38	0.9815	*22*
$Ba(Ac)_2$	0.287 25	2.875 07	−0.045 39	3.500	0.006 63	0.9994	*22*
$MnCl_2$	0.294 86	2.012 51	−0.015 28	7.500	0.024 34	0.9990	*16*
$MnBr_2$	0.446 55	1.344 77	−0.022 69	5.640	0.005 46	0.9999	*16*
$Mn(ClO_4)_2$	0.509 57	2.162 09	0.011 44	3.456	0.003 24	1.0000	*16*
$NiCl_2$	0.393 04	0.997 73	−0.016 58	5.500	0.013 86	0.9998	*15*
$NiBr_2$	0.443 05	1.483 23	−0.005 90	4.500	0.008 66	0.9999	*15*
$Ni(ClO_4)_2$	0.492 85	1.985 17	0.016 79	3.500	0.002 37	1.0000	*15*
$Ni(NO_3)_2$	0.309 78	2.106 44	−0.003 94	4.500	0.010 24	0.9999	*15*
$CoCl_2$	0.373 51	1.259 99	−0.018 03	4.000	0.007 11	0.9999	*15*
$CoBr_2$	0.471 72	0.984 25	−0.017 16	5.750	0.021 59	0.9997	*15*
CoI_2	0.519 53	1.712 66	−0.001 01	4.000	0.015 70	0.9999	*15*
$Co(NO_3)_2$	0.306 54	1.801 97	−0.006 49	5.500	0.004 91	0.9999	*15*
$Co(ClO_4)_2$	0.504 09	1.966 64	0.013 49	3.500	0.003 25	1.0000	*15*
$CuCl_2$	0.230 52	2.208 97	−0.016 39	5.750	0.006 64	0.9976	*16*
$CuBr_2$	0.412 47	1.662 70	−0.042 62	3.606	0.005 86	0.9999	*16*
$Cu(ClO_4)_2$	0.489 84	1.903 61	0.008 39	3.500	0.001 73	1.0000	*16*
$Cu(NO_3)_2$	0.281 24	1.729 06	−0.008 42	7.840	0.003 07	1.0000	*16*
$Cu(C_7H_7O_3S)_2$	0.084 73	1.795 23		0.800	0.002 07	0.9995	*16*
$FeCl_2$	0.350 11	1.400 92	−0.014 12	2.000	0.001 82	1.0000	*15*
ZnF_2	0.001 44	−0.087 46		0.142	0.000 57	0.9327	*17*
$ZnCl_2$	0.088 87	2.948 69	0.000 95	10.000	0.014 42	0.9995	*17*
$ZnBr_2$	0.187 28	4.346 74	−0.009 11	6.000	0.045 79	0.9888	*17*
ZnI_2	0.285 96	5.080 37	−0.020 04	6.000	0.072 65	0.9813	*17*
$Zn(ClO_4)_2$	0.523 65	1.465 69	0.007 48	4.300	0.010 12	0.9999	*17*
$Zn(NO_3)_2$	0.325 87	1.907 81	−0.008 42	6.750	0.002 83	1.0000	*17*
$Zn(C_7H_7O_3S)_2$	0.118 40	1.671 38		0.300	0.000 37	0.9999	*17*
$CdCl_2$	0.016 24	0.439 45	0.001 09	6.000	0.001 08	0.9998	*22*
$CdBr_2$	0.020 87	−0.863 02	0.002 84	4.000	0.003 70	0.9989	*22*
CdI_2	0.149 16	0.559 35	−0.011 17	2.500	0.003 41	0.9995	*22*
$Cd(ClO_4)_2$	0.389 86	1.996 10	0.020 75	1.750	0.001 17	1.0000	*17*
$Cd(NO_2)_2$	0.002 65	−2.158 54	0.003 02	7.840	0.019 03	0.9917	*17*
$Cd(NO_3)_2$	0.287 64	1.684 68	−0.025 87	2.500	0.003 18	0.9999	*17*
$Cd(C_7H_7O_3S)_2$	0.071 61	1.758 17		0.600	0.002 86	0.9999	*17*
$PbCl_2$	0.080 10	−2.571 26		0.039	0.003 75	0.9833	*16*
$Pb(ClO_4)_2$	0.335 00	1.618 13	−0.009 04	10.830	0.004 61	1.0000	*16*
$Pb(NO_3)_2$	0.015 06	−0.270 95	−0.013 30	1.830	0.004 79	0.9410	*16*
UO_2Cl_2	0.040 951	1.749 13	−0.029 49	3.174	0.005 38	0.9999	*16*
$UO_2(ClO_4)_2$	0.665 63	1.428 53	0.006 99	4.000	0.013 02	0.9999	*16*
$UO_2(NO_3)_2$	0.478 03	1.595 30	−0.039 71	5.500	0.014 44	0.9997	*16*
$C_8H_{22}N_2Cl_2$	0.103 90	−0.105 68	0.001 65	4.400	0.004 52	0.9998	*17*
$C_8H_{22}N_2I_2$	−0.071 60	−0.857 78	0.011 56	4.000	0.009 41	0.9792	*17*
$[Co(NH_3)_5NO_2]Cl_2$	−2.711 03	6.039 02		0.100	0.003 24	0.9958	*15*
$[Co(NH_3)_5Cl]Cl_2$	1.444 07	0.630 74		0.008	0.000 31	0.9991	*15*
$[Co(NH_3)_5F]Cl_2$	0.039 45	0.649 84	−0.009 76	1.000	0.000 37	0.9999	*15*
$[Co(NH_3)_5Cl](ClO_4)_2$	0.035 50	0.611 67		0.100	0.001 55	0.9914	*15*
$[Co(NH_3)_5CH_3CH_2COO](NO_3)_2$	−0.012 98	0.467 47		0.400	0.000 84	0.9950	*15*
$[Co(NH_3)_5CH_3CH_2COO]I_2$	0.023 42	0.555 20		0.500	0.002 97	0.9833	*15*
$[Co(NH_3)_5CH_3CH_2COO]Br_2$	0.052 40	0.487 11	−0.005 39	1.200	0.000 62	0.9998	*15*
$[Co(NH_3)_5CH_3CH_2COO]Cl_2$	0.111 94	0.344 89	−0.013 39	2.400	0.001 87	0.9997	*15*
$[Co(NH_3)_5CH_3COO](NO_3)_2$	0.389 56	−0.411 44		0.050	0.000 09	0.9998	*15*
$[Co(NH_3)_5CH_3COO]I_2$	0.407 28	−0.311 06		0.100	0.000 42	0.9996	*15*
$[Co(NH_3)_5CH_3COO]Br_2$	0.046 21	0.524 15		0.600	0.001 15	0.9986	*15*
$[Co(NH_3)_5CH_3COO]Cl_2$	0.071 97	0.399 10		0.600	0.004 22	0.9857	*15*
$[Co(NH_3)_5(CH_3)_2CHCOO](NO_3)_2$	−0.018 31	0.352 51	0.002 79	2.500	0.002 01	0.9844	*15*
$[Co(NH_3)_5(CH_3)_2CHCOO]I_2$	0.002 03	0.585 39		0.800	0.002 52	0.9832	*15*
$[Co(NH_3)_5(CH_3)_2CHCOO]Br_2$	0.051 08	0.367 26		0.800	0.003 69	0.9880	*15*

Table III (Continued)

compd	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	max m	SD	R	ref
$[Co(NH_3)_5(CH_3)_2CHCOO]Cl_2$	0.109 66	0.351 57	−0.012 93	2.500	0.002 01	0.9997	*15*
cis-$[Co(C_2H_8N_2)NH_3NO_2](NO_3)_2$	−0.075 13	0.395 44		0.600	0.000 70	0.9983	*15*
cis-$[Co(C_2H_8N_2)NH_3NO_2]I_2$	−0.138 44	0.645 45		0.600	0.002 49	0.9941	*15*
cis-$[Co(C_2H_8N_2)NH_3NO_2]Br_2$	−0.114 89	0.368 41	0.034 49	1.000	0.002 11	0.9970	*15*
cis-$[Co(C_2H_8N_2)NH_3NO_2]Cl_2$	−0.012 70	0.571 58	0.007 24	2.800	0.001 57	0.9957	*15*
trans-$[Co(C_2H_8N_2)NH_3NO_2](NO_3)_2$	−0.064 65	0.317 15		0.800	0.001 12	0.9978	*15*
trans-$[Co(C_2H_8N_2)NH_3NO_2]I_2$	−0.176 04	1.096 89		0.300	0.001 77	0.9852	*15*
trans-$[Co(C_2H_8N_2)NH_3NO_2]Br_2$	−0.058 42	0.393 91	0.013 33	2.400	0.000 83	0.9993	*15*
trans-$[Co(C_2H_8N_2)NH_3NO_2]Cl_2$	0.014 21	0.590 51	0.004 82	2.400	0.000 84	0.9997	*15*

Table IV. Ion Interaction Parameters for 3-1, 1-3 Electrolytes at 25 °C

compd	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	max m	SD	R	ref
$LaCl_3$	0.596 02	5.6000	−0.024 64	3.800	0.0083	0.9999	*18*
$La(ClO_4)_3$	0.838 15	6.5333	−0.012 88	4.500	0.0269	0.9998	*33*
$La(NO_3)_3$	0.305 07	5.1333	−0.017 50	4.000	0.0314	0.9963	*21*
$La(C_2H_5SO_4)_3$	0.805 06	5.2315	−0.103 89	1.100	0.0003	1.0000	*34*
$PrCl_3$	0.588 04	5.6000	−0.020 60	3.800	0.0108	0.9999	*18*
$Pr(ClO_4)_3$	0.824 54	6.5333	−0.009 14	4.500	0.0240	0.9999	*33*
$Pr(NO_3)_3$	0.326 15	5.1333	−0.018 51	4.000	0.0290	0.9973	*21*
$Pr(C_2H_5SO_4)_3$	0.809 96	5.3111	−0.099 72	0.800	0.0003	1.0000	*34*
$NdCl_3$	0.586 74	5.6000	−0.018 82	3.800	0.0102	0.9999	*18*
$Nd(ClO_4)_3$	0.814 68	6.5333	−0.006 77	4.500	0.0209	0.9999	*33*
$Nd(NO_3)_3$	0.339 27	5.1333	−0.019 45	4.000	0.0277	0.9977	*21*
$Nd(C_2H_5SO_4)_3$	0.791 01	5.4928	−0.091 35	1.100	0.0003	1.0000	*34*
$SmCl_3$	0.593 61	5.6000	−0.019 14	3.600	0.0095	0.9999	*18*
$Sm(ClO_4)_3$	0.826 73	6.5333	−0.004 87	4.500	0.0211	0.9999	*33*
$Sm(NO_3)_3$	0.358 02	5.1333	−0.018 84	4.200	0.0235	0.9987	*20*
$Sm(C_2H_5SO_4)_3$	0.844 86	5.8016	−0.100 39	0.800	0.0002	1.0000	*34*
$EuCl_3$	0.601 35	5.6000	−0.019 26	3.400	0.0089	0.9999	*18*
$Eu(C_2H_5SO_4)_3$	0.801 48	5.6723	−0.086 13	1.100	0.0003	1.0000	*34*
$Ga(ClO_4)_3$	0.785 35	5.2055	0.042 02	2.000	0.0072	0.9999	*22*
$GdCl_3$	0.611 42	5.6000	−0.019 24	3.400	0.0084	0.9999	*18*
$Gd(ClO_4)_3$	0.848 32	6.5333	−0.007 92	4.500	0.0197	0.9999	*33*
$Gd(NO_3)_3$	0.378 41	5.1333	−0.019 60	4.200	0.0283	0.9986	*20*
$Gd(C_2H_5SO_4)_3$	0.851 52	5.4619	−0.102 24	0.800	0.0004	1.0000	*34*
$TbCl_3$	0.622 31	5.6000	−0.019 23	3.400	0.0088	0.9999	*18*
$Tb(ClO_4)_3$	0.883 29	6.5333	−0.011 12	4.600	0.0290	0.9998	*19*
$Tb(NO_3)_3$	0.368 50	5.1333	−0.017 94	4.400	0.0291	0.9983	*20*
$Tb(C_2H_5SO_4)_3$	0.849 99	5.6688	−0.096 76	1.100	0.0004	1.0000	*34*
$DyCl_3$	0.628 26	5.6000	−0.018 95	3.600	0.0108	0.9999	*18*
$Dy(ClO_4)_3$	0.880 21	6.5333	−0.009 47	4.500	0.0297	0.9998	*33*
$Dy(C_2H_5SO_4)_3$	0.851 38	5.9023	−0.092 48	1.100	0.0003	1.0000	*34*
$HoCl_3$	0.623 46	5.6000	−0.016 75	3.600	0.0111	0.9999	*18*
$Ho(ClO_4)_3$	0.871 29	6.5333	−0.006 99	4.500	0.0346	0.9998	*33*
$Ho(C_2H_5SO_4)_3$	0.843 17	5.4972	−0.093 96	1.100	0.0003	1.0000	*34*
$ErCl_3$	0.621 58	5.6000	−0.015 24	3.600	0.0109	0.9999	*18*
$Er(ClO_4)_3$	0.875 06	6.5333	−0.006 71	4.500	0.0348	0.9998	*33*
$Er(NO_3)_3$	0.431 14	5.1333	−0.025 87	4.000	0.0289	0.9983	*20*
$Er(C_2H_5SO_4)_3$	0.853 45	5.6291	−0.093 71	1.100	0.0004	1.0000	*34*
$TmCl_3$	0.626 40	5.6000	−0.015 13	3.800	0.0120	0.9999	*18*
$Tm(ClO_4)_3$	0.875 13	6.5333	−0.006 17	4.500	0.0342	0.9998	*33*
$Tm(NO_3)_3$	0.453 94	5.1333	−0.027 76	4.000	0.0277	0.9986	*20*
$Tm(C_2H_5SO_4)_3$	0.845 89	5.6167	−0.092 79	1.100	0.0003	1.0000	*oj*
$YbCl_3$	0.625 80	5.6000	−0.014 53	4.000	0.0120	0.9999	*18*
$Yb(ClO_4)_3$	0.881 16	6.5333	−0.006 64	4.500	0.0315	0.9998	*33*
$Yb(NO_3)_3$	0.467 44	5.1333	−0.028 12	4.000	0.0242	0.9990	*20*
$Yb(C_2H_5SO_4)_3$	0.859 15	5.6640	−0.090 78	1.200	0.0002	1.0000	*34*
$LuCl_3$	0.621 06	5.6000	−0.013 56	4.000	0.0113	0.9999	*18*
$Lu(ClO_4)_3$	0.868 83	6.5333	−0.001 88	4.000	0.0291	0.9998	*33*
$Lu(C_2H_5SO_4)_3$	0.862 56	5.7210	−0.091 67	1.200	0.0003	1.0000	*34*
$AlCl_3$	0.686 27	6.0203	0.008 10	1.800	0.0088	0.9999	*22*
$ScCl_3$	0.720 87	6.5317	0.033 67	1.800	0.0044	0.9999	*22*
$CrCl_3$	0.690 81	2.7849	−0.043 90	1.200	0.0033	0.9999	*22*
$Cr(NO_3)_3$	0.724 90	6.3169	−0.059 93	1.400	0.0035	0.9999	*22*
YCl_3	0.625 70	5.6000	−0.015 71	3.800	0.0117	0.9999	*18*
$Y(C_2H_5SO_4)_3$	0.851 87	5.6577	−0.093 22	1.200	0.0003	1.0000	*34*
$CeCl_3$	0.635 09	7.4991	−0.030 01	2.000	0.0127	0.9996	*22*
$FeCl_3$	0.236 17	−5.3975	−0.007 96	10.000	0.0087	0.9999	*35*
Na_3PO_4	0.135 14	5.4136		0.700	0.0063	0.9401	*22*
Na_3AsO_4	0.201 93	5.5366		0.700	0.0048	0.9932	*22*
K_3PO_4	0.316 68	7.4659		0.700	0.0079	0.9942	*22*
K_3AsO_4	0.422 91	9.9809		0.011	0.0111	0.9934	*22*
$K_3Fe(cn)_6$	0.349 15	5.5849	−0.045 08	1.400	0.0034	0.9995	*22*
$K_3Co(cn)_6$	0.365 92	1.6190	−0.069 46	1.311	0.0247	0.9890	*36*
$Co(en)_3Cl_3$	0.185 92	3.8000	−0.027 83	1.000	0.0009	0.9997	*22*
$Co(en)_3(NO_3)_3$	0.103 40	3.5513		0.275	0.0013	0.9997	*36*
$Co(pn)_3(ClO_4)_3$	0.148 54	2.9504		0.261	0.0036	0.9973	*36*

Table V. Ion Interaction Parameters for 4-1, 1-4 Electrolytes at 25 °C

compd	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	max m	SD	R	ref
$K_4Mo(CN)_8$	0.00575	-7.4744	0.01015	1.400	0.0132	0.9878	*22*
$K_4Fe(CN)_6$	-0.00638	-10.6019		0.900	0.0155	0.9799	*22*
$K_4P_2O_7$	0.05939	-9.2939	0.01591	2.300	0.0099	0.9989	*37*
$K_4W(CN)_8$	0.38299	6.1624	-0.05810	1.500	0.0192	0.9948	*38*
K_4ATP^a	0.08619	-4.8045	0.01494	2.400	0.0080	0.9994	*39*
Na_4ATP^a	-0.04154	-6.0631	0.03044	2.000	0.0093	0.9974	*39*
$Na_4P_2O_7$	0.06250	-11.1364		0.230	0.0038	0.9929	*37*
$ThCl_4$	0.47146	-9.4843	-0.00078	1.800	0.0179	0.9994	*22*
$Th(NO_3)_4$	0.35392	-7.6453	-0.01869	5.000	0.0126	0.9997	*22*
$Pt(pn)_3Cl_4$	0.28756	10.7131		0.100	0.0063	0.9983	*38*
$[N(Me)_4]_4Mo(CN)_8$	0.53495	9.6607	0.08620	1.440	0.0120	0.9988	*38*

[a] ATP = adenosine 5'-triphosphate.

Table VI. Ion Interaction Parameters for 2-2 Electrolytes at 25 °C

compd	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	max m	SD	R	ref
$CuSO_4$	0.20458	2.7490	-42.038	0.01886	1.400	0.00175	0.9999	*22, 23*
$ZnSO_4$	0.18404	3.0310	-27.709	0.03286	3.500	0.00212	1.0000	*22, 23*
$CdSO_4$	0.20948	2.6474	-44.473	0.01021	3.500	0.00265	0.9999	*22, 23*
$NiSO_4$	0.15471	3.0769	-37.593	0.04301	2.500	0.00310	0.9999	*22, 23*
$MgSO_4$	0.22438	3.3067	-40.493	0.02512	3.000	0.00346	0.9999	*22, 23*
$MnSO_4$	0.20563	2.9362	-38.931	0.01650	4.000	0.00470	0.9999	*22, 23*
$BeSO_4$	0.31982	3.0540	-77.689	0.00598	4.000	0.00421	0.9999	*22, 23*
UO_2SO_4	0.33190	2.4208	98.958	-0.01789	6.000	0.00224	1.0000	*22*
$CaSO_4$	0.20000	3.7762	-58.388		0.020	0.00460	0.9863	*23*
$CoSO_4$	0.20000	2.9709	-28.752		0.100	0.00248	0.9992	*23*

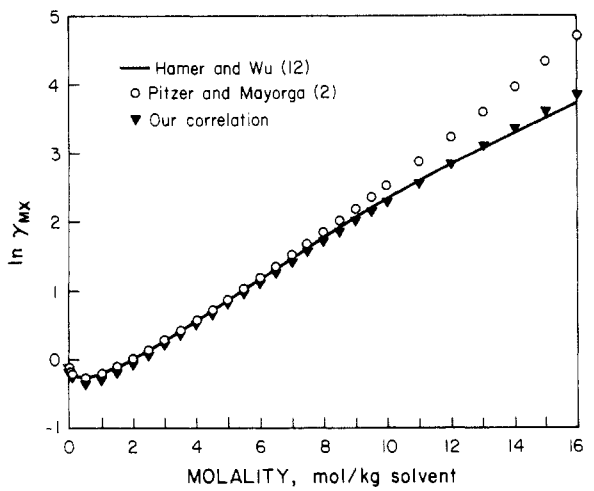

Figure 1. Comparison of experimental smoothed γ_{MX} with values calculated from Pitzer and present work for HCl at 25 °C.

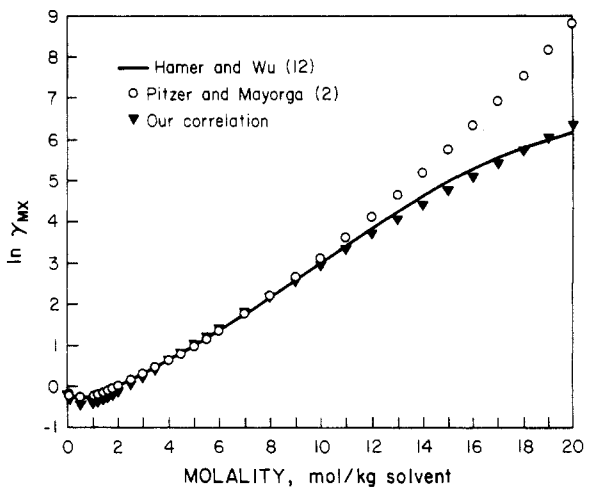

Figure 2. Comparison of experimental smoothed γ_{MX} with values calculated from Pitzer and present work for LiBr at 25 °C.

In most cases where one or both ions are univalent, we used the experimental osmotic coefficient data evaluated by Hamer and Wu (*12*) for 1-1 electrolytes, Goldberg (*13*) for 1-2 electrolytes, Goldberg and Nuttall (*14-17*) for 2-1 electrolytes, and Spedding et al. (*18-21*) for 3-1 electrolytes.

For 2-2 type electrolytes, we used osmotic coefficient data from Robinson and Stokes (*22*) and Pitzer (*23*) who provided the data below 0.1 m, except for UO_2SO_4. Data for UO_2SO_4 are available only over concentration range of 0.1-0.6 m.

The positive value of the coefficients B^{ϕ}_{MX} from eq 4 indicates the net predominance of repulsive short-range interaction forces according to Pitzer and Mayorga (*2*).

For pure electrolytes, the two ion interaction parameters, $\beta^{(0)}_{MX}$ and $\beta^{(1)}_{MX}$, define the second virial coefficients which describe the interaction of pairs of oppositely charged ions. However, for 2-2 and higher valence electrolytes, one additional term, $\beta^{(2)}_{MX}$, which reproduces the irregular behavior in the range below 0.1 m, is added (*3*). From eq 5 and 6, one finds that the $\beta^{(2)}_{MX}$ term is equal to 0.00005 $\beta^{(2)}_{MX}$ at 0.1 m and negligible above 0.1 m because of the large value of $\alpha_2 = 12.0$. For the case of UO_2SO_4, there are no osmotic coefficient data below 0.1 m; hence the $\beta^{(2)}_{MX}$ value does not affect the relative values of osmotic and activity coefficients in the given concentration range and has no meaningful value. In the cases of $CaSO_4$ and $CoSO_4$, where available data are limited to dilute solutions (below 0.1 m), we omitted the coefficients C^{ϕ}_{MX} and chose the value of $\beta^{(2)}_{MX} = 2.0$ which was proposed by Pitzer and Mayorga (*3*).

The third virial coefficients, C^{ϕ}_{MX}, which account for ion triplet interactions, are usually very small and sometimes negligible. Therefore C^{ϕ}_{MX} is omitted in cases where the experimental data exist only in the range below 1.0 m.

In some cases these coefficients, C^{ϕ}_{MX}, are negative, suggesting some tendency toward ion-pair formation (*2*). This trend appeared in most aqueous rare earth electrolyte solutions at 25 °C.

For the cases of aqueous solutions of rare earth chlorides, nitrates, and perchlorates, the importance of differences in the parameters $\beta^{(1)}_{MX}$ was already considered by Pitzer and colleagues (*24*). Thus, in this calculations, we used the values of

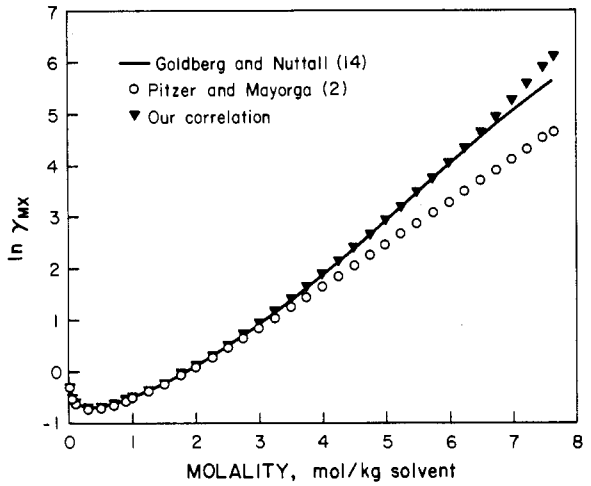

Figure 3. Comparison of experimental smoothed γ_{MX} with values calculated from Pitzer and present work for $CaBr_2$ at 25 °C.

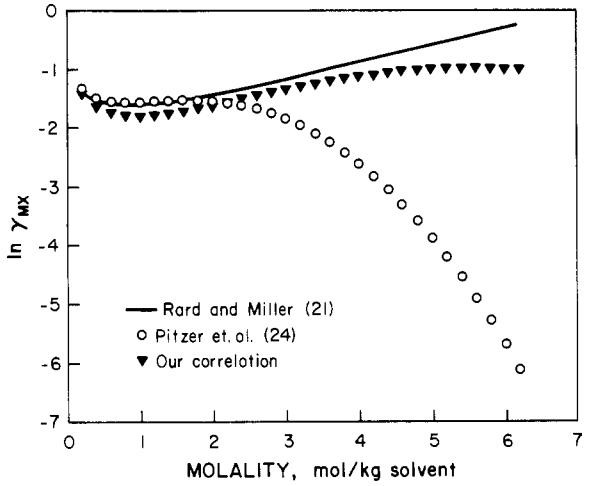

Figure 4. Comparison of experimental smoothed γ_{MX} with values calculated from Pitzer and present work for $Pr(NO_3)_3$ at 25 °C.

7.7, 8.4, and 9.8 for $(3/2)\beta^{(1)}_{MX}$ for nitrates, chlorides, and perchlorates, respectively, following Pitzer et al. (*24*).

Comparison with Previously Published Ion Interaction Parameters

The ion interaction parameters for various single electrolytes were evaluated by a multiple regression method. The maximum molality fitted by our evaluation was the saturation concentration when data for saturated solutions were available. The standard deviations in fitting the osmotic coefficient for many salts, for instance, HCl, LiBr, $CaBr_2$, and $Pr(NO_3)_3$, seem larger than Pitzer's result (*2*). It is important to recognize, however, that the maximum molalities for these salts are beyond those of Pitzer's evaluation.

The calculated mean activity coefficients for various single electrolytes from our results are shown in Figures 1–5 to give good agreement with available smoothed experimental data at high concentration. For example, the activity coefficient of HCl can be predicted with a standard deviation of 0.0285 in ln (γ_{HCl}) over the entire concentration range up to 16.0 m in the experimental smoothed data by using our evaluation parameters in Table I. However, using Pitzer's values (*2*) for this salt, we obtain a standard deviation of 0.220 when the maximum molality is 16.0. These results are given in Table VII. Also Figure 1 shows the comparison of experimental smoothed mean activity coefficients of HCl as ln (γ_{HCl}) with values calculated from

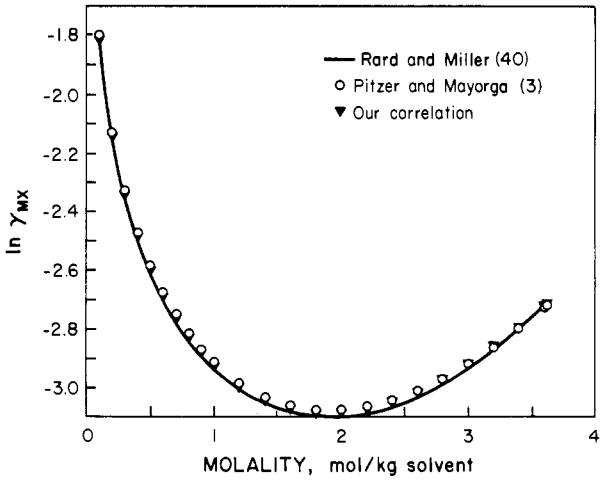

Figure 5. Comparison of experimental smoothed γ_{MX} with values calculated from Pitzer and present work for $MgSO_4$ at 25 °C.

Table VII. Comparison of Standard Deviations for Estimated versus Experimental Activity Coefficients in Figures 1–5

salt	max molality	stand dev[a]
HCl	16.00	0.02854
		(0.22031)
	6.00	0.02956
		(0.00311)
LiBr	20.00	0.07224
		(0.060991)
	2.50	0.06780
		(0.00286)
$CaBr_2$	7.66	0.08760
		(0.46557)
	2.00	0.00732
		(0.00773)
$Pr(NO_3)_3$	6.20	0.17827
		(1.78436)
	1.10	0.07117
		(0.00623)
$MgSO_4$	3.62	0.00574
		(0.00794)
	3.00	0.00385
		(0.00317)

[a] Standard deviations in parentheses are for salts using Pitzer's ion interaction parameter values (*2*) which were obtained from data up to the lower concentration given in the table for each compound. The other standard deviations are based on our evaluation of ion interaction parameters from data up to the higher concentrations reported here.

Pitzer and our work. It should be noted that the fit at lower concentrations is better using the ion interaction parameters reported by Pitzer. His parameters were obtained over a more limited range of concentration (0–6 *m*) than ours were.

Similar results are observed in all of the cases for which the maximum molalities go beyond that of Pitzer's evaluation. That is, Pitzer's fit gives accurate results at low concentration but poor agreements with experimental data at high concentration.

Figures 2–5 are the same kind of comparison plots of ln (γ_{MX}) as a function of the molality for LiBr, $CaBr_2$, $Pr(NO_3)_3$, and $MgSO_4$. In all of these comparisons, the parameters we evaluated using data at higher concentrations give us good or better fit to the experimental data over the entire concentration range than do Pitzer's parameters. Pitzer's parameters give a better fit over the more limited range of concentrations for which parameter values were obtained, however. Standard deviations for the estimated versus experimental activity coefficients in Figures 1–5 (as ln γ_{MX}) and the maximum concentrations corresponding to Pitzer's and our ion interaction parameter evaluations are given in Table VII.

Ternary ion interaction parameters for various mixture with common ion will be evaluated in a subsequent paper.

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Densities and Viscosities of Binary Liquid Mixtures Containing Bromoform at 45 °C

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Densities and viscosities of eight binary liquid mixtures of bromoform with carbon tetrachloride, dimethyl sulfoxide, cyclohexane, bromobenzene, dimethylformamide, methyl ethyl ketone, ethyl acetate, and methanol are presented at 45 °C as a function of composition of the mixtures. A theoretical correlation is attempted with McAllister, Heric, and Auslander viscosity models.

Introduction

In the course of our studies on the thermodynamic properties of binary mixtures, we have reported at 25 °C excess volumes (*1*) and viscosities (*2*) for binary mixtures of bromoform with carbon tetrachloride, dimethyl sulfoxide, cyclohexane, bromobenzene, dimethylformamide, methyl ethyl ketone, ethyl acetate, and methanol. As an extension of that work, we have now measured the densities and viscosities for the same eight systems at 45 °C.

Experimental Section

All the chemicals used were of reagent grade. They were distilled by fractionating through a 2-ft column. Only bromoform (Merck) was used directly without further purification since it was available in the highest commercial purity. Purity of the solvents was ascertained by the constancy of their boiling points during final distillations. Due to the nonavailability of direct experimental data at 45 °C for most of the solvents used here, the boiling points, viscosities, and refractive indices of the pure components at 25 °C were checked against the literature values (see Table I) to ascertain their purities (*4*).

Table I. Some Physical Properties of the Liquids Studied

component	boiling point, °C		viscosity, kg/(m/s)		refractive index[a]	
	measd	lit. (*4*)	measd	lit. (*4*)	measd	lit. (*4*)
bromoform	149.00	149.50	0.1873	0.1890	1.5950	1.5956
carbon tetrachloride	76.20	76.75	0.0892	0.0902	1.4571	1.4574
dimethyl sulfoxide	190.00	189.85	0.2024	0.2021	1.4777	1.4773
cyclohexane	80.10	80.74	0.0883	0.0886	1.4229	1.4235
bromobenzene	155.90	156.05	0.1081	0.1040	1.5580	1.5571
dimethylformamide	152.80	153.00	0.0805	0.0800	1.4278	1.4282
methyl ethyl ketone	79.00	79.60	0.0475	0.0480	1.3759	1.3764
ethyl acetate	77.10	77.26	0.0439	0.0424	1.3702	1.3698
methanol	64.20	65.15	0.0590	0.0547	1.3258	1.3265

[a] Refractive index was measured with a Abbe refractometer.

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