Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Bi-Univalent Compounds of Zinc, Cadmium, and Ethylene Bis(Trimethylammonium) Chloride and Iodide

R. N. Goldberg

National Measurement Laboratory, National Bureau of Standards, Washington, D.C., 20234

A critical evaluation of the mean activity and osmotic coefficients in aqueous solutions of eleven bi-univalent compounds of zinc and cadmium and ethylene bis(trimethylammonium) chloride and iodide at 298.15 K is presented. Osmotic coefficients were calculated from direct vapor pressure measurements, from isopiestic measurements and from freezing point depression measurements. Activity coefficients were calculated from electromotive force measurements on galvanic cells with and without transference. Given are empirical coefficients for three different correlating equations, obtained by a weighted least squares fit of the experimental data, and tables consisting of the activity coefficients of the compounds, the osmotic coefficients and activity of water, and the excess Gibbs energy of the solution as functions of the molality for each electrolyte system. The literature coverage is through the computerized version of Chemical Abstracts of September 1979.

Key words: Activity coefficient; cadmium; critical evaluation; electrolyte; ethylene bis(trimethylammonium) chloride; ethylene bis(trimethylammonium) iodide; excess Gibbs energy; osmotic coefficient; solutions; thermodynamic properties; zinc.

Contents

1. Introduction

This paper presents a continuation of work at the National Bureau of Standards towards the evaluation of activity and osmotic coefficients in aqueous solutions. Previously, evaluations have been made for the uni-univalent electrolytes [1],[1] calcium chloride [2], the alkaline earth metal halides [3], sulfuric acid [4], $FeCl_2$ and the bi-univalent compounds of iron, nickel, and cobalt [5], the bi-univalent compounds of lead, copper, manganese, and uranium [6], and the alkali metal nitrites [7]. The evaluation procedures have been described [2,3,8] in substantial detail and a biliography [9] giving the results of a search of the scientific literature for relevant sources of experimental data has been published. The evaluations presented here complete the systematic coverage of the data for the bi-univalent electrolytes with the exception of the non-halide compounds of magnesium, calcium, strontium, and barium (i.e., the nitrites, nitrates, perchlorates, acetates, etc.) and the cadmium halides.

[1] Figures in brackets indicate literature references.

© 1981 by the U.S. Secretary of Commerce on behalf of the United States. This copyright is assigned to the American Institute of Physics and the American Chemical Society.

We present our evaluations in detail so that any potential users of the data, as well as future data evaluators, can have a better view of the status of the measurements on these systems. We also give coefficients, obtained by a weighted least-squares fit of the experimental data, for as many as three different correlating equations and tables consisting of the mean activity coefficients of the electrolyte, the osmotic coefficient and activity of water, and the excess Gibbs energy of the solution as functions of the molality for each electrolyte system at 298.15 K. The literature coverage is through the computerized version of Chemical Abstracts of September 1979.

The reader is referred to the glossary of symbols at the end of this paper for the definitions of the various symbols used throughout the paper. In general, we have attempted to adhere to the recommendations of the IUPAC [10] with regard to nomenclature and units.

2. Evaluated Activity and Osmotic Coefficients

2.1. Presentation of Data

We have arranged the presentation of data according to compound. For each compound that has been evaluated we present:

1. The recommended values of the activity and osmotic coefficients, the activity of water, and the excess Gibbs energy per kilogram of solvent at selected molalities, which extend up to the highest molality for which data of non-zero weight exist, including, where possible, values at saturation. The latter molalities, indicated by (sat) in the tables, were, unless indicated otherwise, calculated from the data given in the compilation of Linke and Seidell [11]. Estimates of the standard deviations of the calculated values of the osmotic coefficient [$\sigma(\phi)$], the activity coefficient [$\sigma(\gamma)$], and the natural logarithm of the activity coefficient [$\sigma(\ln\gamma)$], all at selected molalities, are given at the bottom of each table.

2. The coefficients, standard deviations of the coefficients [σ(coeff)], and standard deviation for observations of unit weights [σ(eq)] for as many as three different correlating equations. The correlating equations we have used are:

$$\ln\gamma = -\frac{A_1 I^{1/2}}{1+BI^{1/2}} + Cm + Dm^2 + Em^3 + \ldots, \quad (1a)$$

$$\ln\gamma = -A_1 I^{1/2} - A_2 I \ln I + \sum_{i=1}^{N} B_i m^{(i+1)/2}, \quad (2a)$$

$$\ln\gamma = -A_1 I^{1/2} + \sum_{i=1}^{N} B_i m^{(i+1)/2} \quad (3a)$$

The corresponding equations for the osmotic coefficient become:

$$\phi = 1 + \frac{A_1}{B^3 I}\{-(1+BI^{1/2}) + 2\ln(1+BI^{1/2}) + 1/(1+BI^{1/2})\} + 1/2Cm + 2/3Dm^2 + 3/4Em^3 + \ldots, \quad (1b)$$

$$\phi = 1 - \frac{A_1}{3} I^{1/2} - \frac{A_2}{2} I[\ln I + 1/2] + \sum_{i=1}^{N} B_i \frac{(i+1)}{(i+3)} m^{(i+1)/2} \quad (2b)$$

and

$$\phi = 1 - \frac{A_1}{3} I^{1/2} + \sum_{i=1}^{N} B_i \frac{(i+1)}{(i+3)} m^{(i+1)/2} \quad (3b)$$

For 2-1 electrolytes in water at 25 °C, $A_1 = 2A$ and $A_2 = \frac{2}{3}A^2$, where A is the constant in the Debye-Hückel equation and is equal to 0.51084 $\log_{10}$ kg$^{1/2}$ · mol$^{-1/2}$ at 25 °C. Using this value of A and ten significant figures, A_1 = 2.352505138 mol$^{-1/2}$ · kg$^{1/2}$ and A_2 = 0.9223800706 mol^{-1} · kg. The user should note that in our tables, where we have given the coefficients of these correlating equations for the various systems that have been evaluated, we have used a shorthand notation to designate the various parameters, i.e., parameter 1 corresponds to either B in eqs 1, or B_1 in eqs 2 or 3, parameter 2 corresponds to either C in eqs 1 or B_2 in eqs 2 or 3, parameter 3 corresponds to either D in eqs 1 or B_3 in eqs 2 or 3, etc. Also, powers of ten are implied in the representation of a number, e.g., .499-02 is .499 × 10^{-2}. We have retained at least ten digits for the coefficients in order to avoid a loss of potentially useful information which might be of value for some applications in which the derivative of the activity coefficient with respect to the molality is of interest. The digits in excess of those required to ensure a precision of 0.001 or better in the calculation of ϕ or $\ln\gamma$ have not been underlined. Unless indicated otherwise, eqs (1a) and (1b) were used to produce the activity and osmotic coefficients given in the tables of recommended values.

3. The calculated values of ϕ and/or γ/γ_{ref} obtained from the experimental measurements reported by the various authors and the weights assigned to the various data sets. It should be noted that, in most cases, these are not original data, but rather the result of an intermediate calculation. The results of these intermediate calculations are of an additional utility in that if one wishes to employ a different correlating equation(s) or model(s) than the ones we have used, these intermediate results represent the essential experimental data which, if the experiments are deemed to be reliable, must be accommodated. Individual data points designated by an asterisk (*) were given zero weight.

and

4. A deviation plot in $\Delta\phi$ and/or $\Delta\gamma$ as a function of the molality. In these plots the symbol Δ means "observed minus calculated" values.

The excess Gibbs energy ΔG^{ex}, is given by $\Delta G^{ex} = G_{real} - G_{ideal} = \nu mRT(1-\phi+\ln\gamma)$.

2.2. Evaluated Systems

$C_8H_{22}N_2Cl_2$

Recommended Values for the mean activity and osmotic coefficient of ethylene bis(trimethylammonium) chloride, $C_8H_{22}N_2Cl_2$, in H_2O at 298.15 K

m/mol·kg^{-1}	γ	ϕ	a_w	ΔG^{ex}/J·kg^{-1}
.001	.8840	.9598	.999948	-1.
.002	.8426	.9447	.999898	-2.
.003	.8130	.9336	.999849	-3.
.004	.7895	.9246	.999800	-5.
.005	.7697	.9169	.999752	-7.
.006	.7526	.9102	.999705	-9.
.007	.7375	.9041	.999658	-11.
.008	.7238	.8986	.999612	-13.
.009	.7114	.8936	.999565	-16.
.010	.7001	.8889	.999520	-18.
.020	.6199	.8545	.999077	-50.
.030	.5677	.8315	.998653	-89.
.040	.5302	.8141	.998242	-133.
.050	.5008	.8002	.997840	-183.
.060	.4768	.7886	.997446	-236.
.070	.4566	.7786	.997059	-293.
.080	.4393	.7700	.996676	-353.
.090	.4241	.7624	.996298	-415.
.100	.4107	.7557	.995924	-480.
.200	.3275	.7135	.992317	-1234.
.300	.2844	.6931	.988825	-2120.
.400	.2572	.6822	.985359	-3095.
.500	.2381	.6769	.981875	-4134.
.600	.2241	.6752	.978342	-5225.
.700	.2134	.6763	.974740	-6356.
.800	.2050	.6794	.971051	-7520.
.900	.1985	.6843	.967262	-8711.
1.000	.1932	.6906	.963364	-9924.
1.250	.1845	.7113	.953084	-13027.
1.500	.1801	.7373	.941980	-16195.
1.750	.1785	.7671	.930015	-19393.
2.000	.1792	.7996	.917199	-22595.
2.250	.1814	.8339	.903571	-25781.
2.500	.1850	.8692	.889196	-28937.
2.750	.1897	.9049	.874155	-32052.
3.000	.1953	.9407	.858538	-35116.
3.250	.2017	.9761	.842440	-38123.
3.500	.2087	1.0109	.825949	-41068.
3.750	.2163	1.0449	.809148	-43948.
4.000	.2245	1.0781	.792103	-46760.
4.250	.2332	1.1104	.774865	-49502.
4.400	.2387	1.1295	.764443	-51113.

m/mol·kg^{-1}	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0001	.0001	.0001
.010	.0004	.0009	.0006
.100	.0015	.0041	.0017
1.000	.0013	.0051	.0019
2.000	.0017	.0056	.0019
4.400	.0032	.0064	.0015

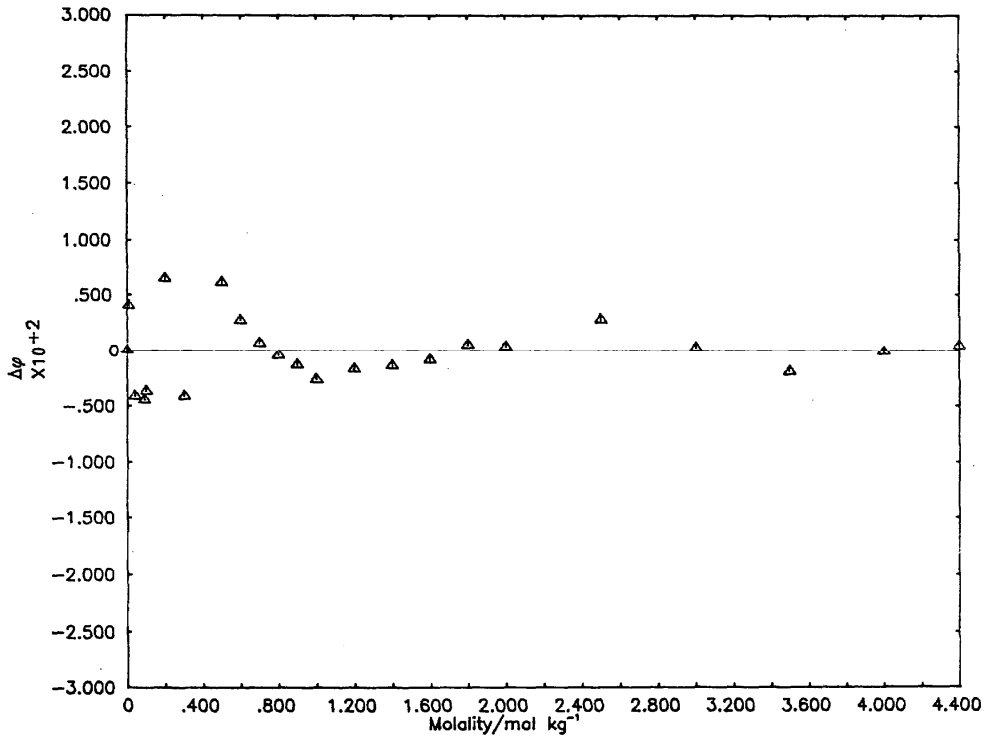
Coefficients of Correlating Equations

	Eqs 1		Eqs 2		Eqs 3	
Par	coefficient	σ(coeff)	coefficient	σ(coeff)	coefficient	σ(coeff)
1	.8383414949+00	.234-01	-.60401163?9+01	.490+00	.5237133667+01	.766-01
2	-.8041026855-01	.410-01	.3331002842+02	.302+01	-.5174941970+01	.201+00
3	.1169278318+00	.231-01	-.5185829843+02	.800+01	.3322422357+01	.206+00
4	-.1987824495-01	.638-02	.5443432116+02	.115+02	-.1105872136+01	.933-01
5	.1236462194-02	.637-03	-.3568257799+02	.955+01	.1457539432+00	.156-01
6			.1412027397+02	.461+01		
7			-.3091370753+01	.120+01		
8			.2878232862+00	.130+00		
	σ(eqs 1) = .341-02		σ(eqs 2) = .292-02		σ(eqs 3) = .290-02	

Experimental Data Employed in Generation of Correlating Equations

Bonner and Kim [11a]. Vapor pressure osmometry and isopiestic measurements, reference electrolyte was NaCl [11b]. The authors do not report the isopiestic molalities. Assigned weight is 1.0.

m/mol·kg^{-1}	$\phi_{298.15}$
.010000	.8930
.040000	.8100
.090000	.7580
.100000	.7520
.200000	.7200
.300000	.6990
.500000	.6830
.600000	.6780
.700000	.6770
.800000	.6790
.900000	.6830
1.000000	.6880
1.200000	.7050
1.400000	.7250
1.600000	.7480
1.800000	.7740
2.000000	.8000
2.500000	.8720
3.000000	.9410
3.500000	1.0090
4.000000	1.0780
4.400000	1.1300



Deviation Plot For $C_8H_{22}N_2Cl_2$: $\Delta\phi$ vs molality

△ Bonner and Kim [11a]- vapor pressure osmometry and isopiestic vs NaCl

$C_8H_{22}N_2I_2$

Recommended Values for the mean activity and osmotic coefficient of ethylene bis(trimethylammonium) iodide, $C_8H_{22}N_2I_2$, in H_2O at 298.15 K

m/mol·kg^{-1}	γ	ϕ	a_w	ΔG^{ex}/J·kg^{-1}
.001	.8828	.9591	.999948	-1.
.002	.8403	.9433	.999898	-2.
.003	.8098	.9316	.999849	-3.
.004	.7853	.9220	.999801	-5.
.005	.7647	.9137	.999753	-7.
.006	.7468	.9064	.999706	-9.
.007	.7308	.8997	.999660	-11.
.008	.7165	.8937	.999614	-14.
.009	.7034	.8881	.999568	-16.
.010	.6913	.8828	.999523	-19.
.020	.6045	.8431	.999089	-52.
.030	.5486	.8152	.998679	-93.
.040	.5073	.7932	.998287	-140.
.050	.4746	.7749	.997908	-193.
.060	.4478	.7590	.997542	-251.
.070	.4250	.7451	.997185	-313.
.080	.4053	.7325	.996838	-378.
.090	.3880	.7211	.996499	-447.
.100	.3726	.7106	.996167	-519.
.200	.2756	.6352	.993158	-1374.
.300	.2241	.5861	.990542	-2413.
.400	.1909	.5497	.988187	-3587.
.500	.1672	.5211	.986018	-4870.
.600	.1494	.4979	.983983	-6243.
.700	.1355	.4790	.982043	-7694.
.800	.1243	.4633	.980167	-9213.
.900	.1151	.4504	.978329	-10793.
1.000	.1074	.4398	.976510	-12427.
1.250	.0928	.4212	.971948	-16716.
1.500	.0826	.4107	.967255	-21248.
1.750	.0750	.4056	.962366	-25977.
2.000	.0691	.4039	.957285	-30870.
2.250	.0645	.4040	.952055	-35904.
2.500	.0606	.4051	.946732	-41060.
2.750	.0574	.4066	.941365	-46324.
3.000	.0546	.4081	.935970	-51686.
3.250	.0521	.4100	.930513	-57136.
3.500	.0500	.4128	.924884	-62667.
3.750	.0483	.4174	.916884	-68269.
4.000	.0469	.4251	.912200	-73932.

m/mol·kg^{-1}	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0000	.0001	.0001
.010	.0002	.0005	.0004
.100	.0010	.0026	.0019
1.000	.0008	.0031	.0003
2.000	.0011	.0035	.0002
4.000	.0022	.0040	.0002

Coefficients of Correlating Equations

	Eqs 1		Eqs 2		Eqs 3	
Par	coefficient	σ(coeff)	coefficient	σ(coeff)	coefficient	σ(coeff)
1	.7014955383+00	.156-01	-.6197029197+01	.214+00	.4101816790+01	.707-01
2	-.5868515919+00	.350-01	.2870723899+02	.140+01	-.4455516414+01	.196+00
3	.2443951427+00	.200-01	-.3991307386+02	.391+01	.3225201035+01	.210+00
4	-.5380099008-01	.589-02	.3990551878+02	.593+01	-.1209473698+01	.100+00
5	.4671638602-02	.636-03	-.2581158583+02	.521+01	.1784897683+00	.176-01
6			.1030872539+02	.266+01		
7			-.2318178593+01	.728+00		
8			.2251123930+00	.829-01		

σ(eqs 1) = .221-02
σ(eqs 2) = .111-02
σ(eqs 3) = .247-02

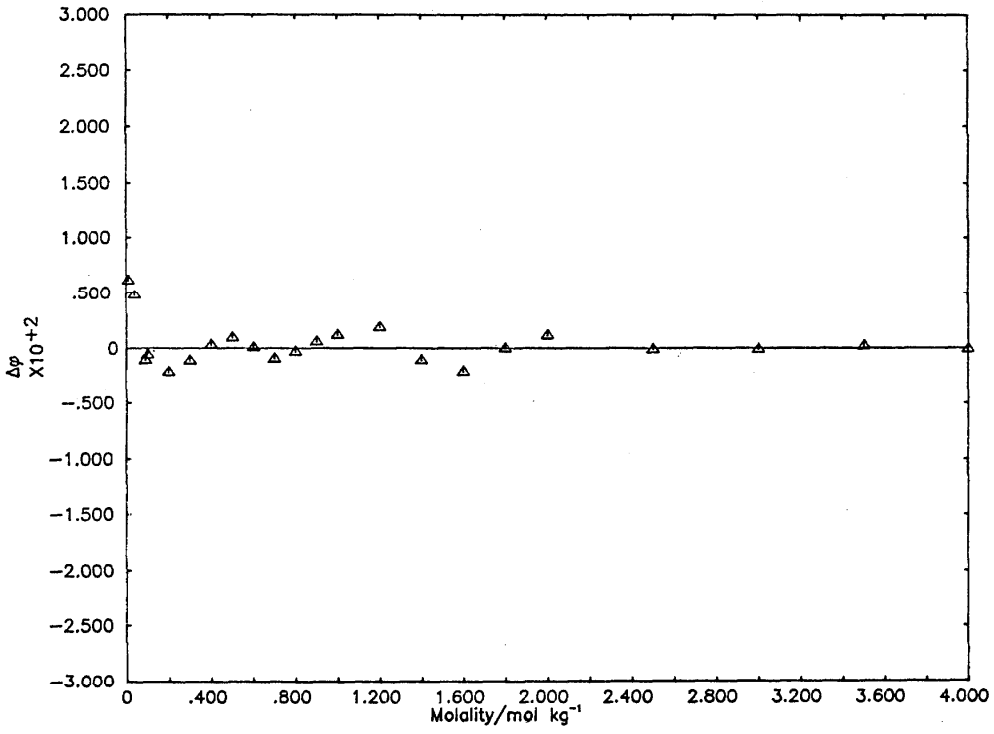
Experimental Data Employed in Generation of Correlating Equations

Bonner and Kim [11a]. Vapor pressure osmometry and isopiestic measurements, reference electrolyte was NaCl[11b]. The authors do not report the isopiestic molalities. Assigned weight is 1.0.

m/mol·kg^{-1}	$\phi_{298.15}$
.010000	.8890
.040000	.7980
.090000	.7200
.100000	.7100
.200000	.6330
.300000	.5850
.400000	.5500
.500000	.5220
.600000	.4980
.700000	.4780
.800000	.4630
.900000	.4510
1.000000	.4410
1.200000	.4260
1.400000	.4130
1.600000	.4060
1.800000	.4050
2.000000	.4050
2.500000	.4050
3.000000	.4080
3.500000	.4130
4.000000	.4250

Comments

The data for this compound are indicative of a substantial degree of ion-pairing.



Deviation Plot for $C_8H_{22}N_2I_2$: $\Delta\phi$ vs molality

△ Bonner and Kim [11a] - vapor pressure osmometry and isopiestic vs NaCl

ZnF_2

Recommended Values for the mean activity and osmotic coefficient of ZnF_2 in H_2O at 298.15 K

m/mol·kg^{-1}	γ	ϕ	a_w	ΔG^{ex}/J·kg^{-1}
.001	.8831	.9593	.999948	-1.
.002	.8409	.9437	.999898	-2.
.003	.8107	.9322	.999849	-3.
.004	.7866	.9228	.999801	-5.
.005	.7663	.9148	.999753	-7.
.006	.7486	.9077	.999706	-9.
.007	.7330	.9013	.999659	-11.
.008	.7190	.8955	.999613	-13.
.009	.7062	.8902	.999567	-16.
.010	.6944	.8852	.999522	-19.
.020	.6105	.8483	.999083	-51.
.030	.5571	.8234	.998666	-91.
.040	.5181	.8043	.998263	-137.
.050	.4876	.7889	.997871	-189.
.060	.4625	.7758	.997487	-244.
.070	.4413	.7644	.997112	-303.
.080	.4231	.7543	.996744	-366.
.090	.4070	.7451	.996382	-431.
.100	.3928	.7367	.996026	-499.
.142	.3459	.7067	.994598	-810.

m/mol·kg^{-1}	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0001	.0003	.0003
.010	.0011	.0023	.0016
.100	.0035	.0058	.0023
.142	.0089	.0098	.0034

Coefficients of Correlating Equations

	Eqs 2		Eqs 3	
Par	coefficient	σ(coeff)	coefficient	σ(coeff)
1	-.3709000087+01	.293+00	.4617689871+01	.323+00
2	.1308751917+02	.865+00	-.3408696087+01	.953+00

σ(eqs 2) = .118-01
σ(eqs 3) = .130-01

Experimental Data Employed in Generation of Correlating Equations

Cook, Davies, and Staveley [12]. Emf measurements. Zn-Hg (two phase); $ZnF_2(m)$; $PbF_2(s)$, Pb-Hg (two phase). m_{ref} = 0.141808 mol kg^{-1}. Assigned weight is 1.0, except for three points at the lowest molalities which were weighted zero.

m/mol·kg^{-1}	γ/γ_{ref}
.141808	1.0000
.129609	1.0361
.088033	1.1768
.069706	1.2555
.045486	1.4501
.034746	1.5384
.028407	1.6188
.017112	1.8591
.012544	1.9667
.009663	2.0266
.006102	2.2433*
.004847	2.2476*
.003766	2.1801*

Comments

The cell studied by Cook, Davies, and Staveley [12] is complicated by the solubility of the $PbF_2(s)$ in the ZnF_2 solution. We have calculated the amount of $PbF_2(s)$ soluble in the ZnF_2 solutions using the formula

$$K_{s0} = 4\ (m_{Pb^{2+}})(m + m_{Pb^{2+}})^2\ \gamma^3_{PbF_2} \qquad (A)$$

where K_{s0} is the solubility product of the $PbF_2(s)$ and which we have taken as 2.69×10^{-8} $mol^3 \cdot kg^{-3}$ [13]; $m_{Pb^{2+}}$ is the molality of Pb^{2+} in the equilibrium solution; m is the experimentally known molalty of ZnF_2; and γ_{PbF_2} is the activity coefficient of the PbF_2 in the ZnF_2 solution. Since we do not know γ_{PbF_2} under such conditions, we have estimated it by assuming that it is equal to γ for ZnF_2 evaluated at the experimentally known molality of ZnF_2. The above equation was solved for $m_{Pb^{2+}}$ by successive approximations using the experimentally known values of m, the value of K_{s0} and, for the first approximation, taking γ equal to unity at all molalities. Solution of this equation for each data point yielded a value of $m_{Pb^{2+}}$ which was used to calculate the total amount of fluoride ion, m_{F^-}, in the equilibrium solution, i.e. $m_{F^-} = 2\ (m + m_{Pb^{2+}})$.

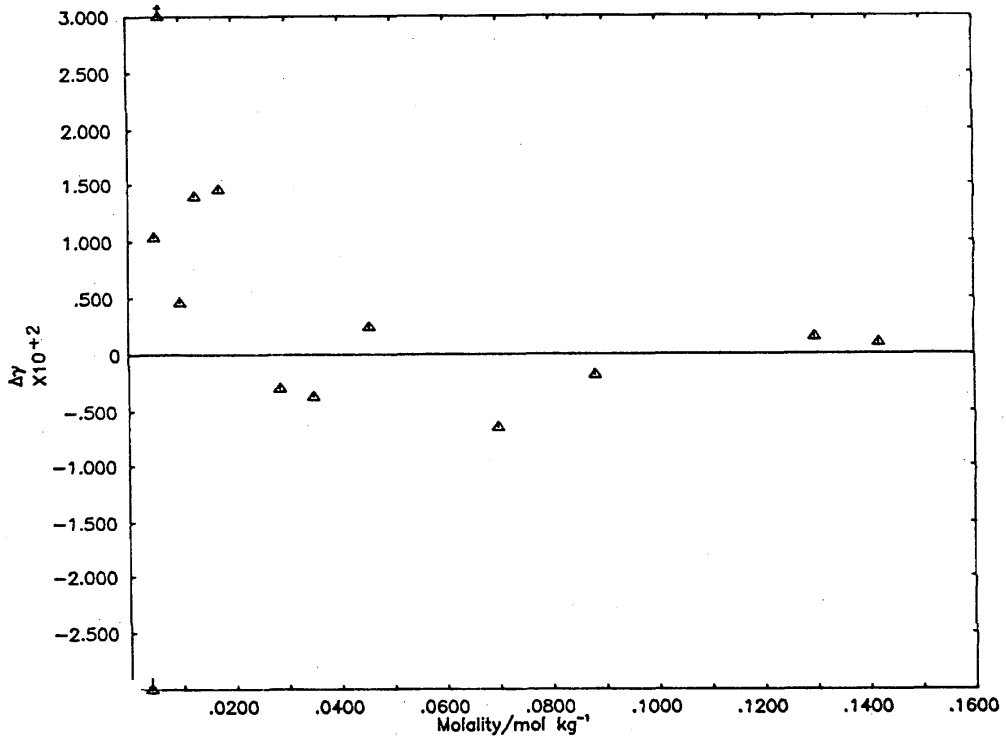
The measured cell emf, E, is given by

$$E = E^\circ - \frac{RT}{2F} \ln\ (m_{Zn^{2+}}\ m^2_{F^-}\ \gamma^3) \qquad (B)$$

where $m_{Zn^{2+}}$ is the molality of the zinc in solution and γ is the activity coefficient of ZnF_2. This equation was then combined with a similar equation which refers to a reference molality to yield values of (γ/γ_{ref}) at the various molalities. These values of (γ/γ_{ref}) were then used to calculate, using previously described techniques [2], values of the coefficients of the correlating equations and thence values of the activity coefficients. These new activity coefficients were then used for an improved calculation of values of $m_{Pb^{2+}}$ for equation (A) above, which, in turn, were used for an improved calculation of the activity coefficients, etc. It was found that this iterative approach yielded values of the activity coefficient which converged to within 0.4 percent after two iterations. In these iterative calculations, the values of γ/γ_{ref} were taken to refer to the molalities given by $(m + m_{Pb^{2+}})$.

It should be noted that we have given zero weight to the three measurements at the lowest molalties, since for these three point, the percent solubility correction $[(m_{Pb^{2+}}/m_{Zn^{2+}}) \times 100\%]$ varied from 7 to 33 percent. We have also chosen our reference molality as the molality (0.1418 $mol \cdot kg^{-1}$) where the solubility correction was the smallest (0.006 percent). Equations 1 could not be used since attempts to apply it yielded values of the B coefficient which were too negative. The numbers in our table of recommended values are based on equations 3.

Our final tabulated values of the activity coefficient are slightly higher (3 to 6 percent) than the values calculated by Cook, Davies, and Staveley [12]. These workers used the Debye-Hückel limiting law to calculate values of γ_{PbF_2} and used extrapolation procedures to obtain a value of $E^\circ = -.4163$ V in equation (B) and thence values of the activity coefficients at various molalties. The observed differences are undoubtably attributable to these different calculational procedures.



Deviation Plot for ZnF_2: $\Delta\gamma$ vs molality

△ Cook, Davies, and Staveley [12], emf measurements

$ZnCl_2$

Recommended Values for the mean activity and osmotic coefficient of $ZnCl_2$ in H_2O at 298.15 K

m/mol·kg^{-1}	γ	ϕ	a_w	ΔG^{ex}/J·kg^{-1}
.001	.8867	.9613	.999948	-1.
.002	.8475	.9476	.999898	-2.
.003	.8201	.9379	.999848	-3.
.004	.7986	.9302	.999799	-5.
.005	.7807	.9239	.999750	-6.
.006	.7654	.9184	.999702	-8.
.007	.7520	.9137	.999654	-10.
.008	.7400	.9094	.999607	-13.
.009	.7292	.9056	.999560	-15.
.010	.7194	.9022	.999513	-17.
.020	.6516	.8791	.999050	-46.
.030	.6109	.8663	.998596	-80.
.040	.5825	.8582	.998146	-119.
.050	.5609	.8528	.997698	-160.
.060	.5438	.8490	.997251	-204.
.070	.5298	.8464	.996803	-251.
.080	.5180	.8445	.996355	-299.
.090	.5079	.8432	.995907	-348.
.100	.4991	.8423	.995458	-400.
.200	.4467	.8415	.990945	-963.
.300	.4193	.8421	.986439	-1587.
.400	.3998	.8403	.981998	-2252.
.500	.3842	.8363	.977653	-2949.
.600	.3707	.8310	.973411	-3674.
.700	.3589	.8250	.969269	-4424.
.800	.3483	.8188	.965216	-5197.
.900	.3388	.8126	.961237	-5992.
1.000	.3302	.8071	.957316	-6807.
1.250	.3124	.7960	.947647	-8920.
1.500	.2989	.7859	.937969	-11126.
1.750	.2892	.7893	.928064	-13404.
2.000	.2826	.7939	.917762	-15733.
2.250	.2785	.8033	.906940	-18098.
2.500	.2767	.8168	.895512	-20482.
2.750	.2768	.8339	.883427	-22871.
3.000	.2787	.8542	.870658	-25254.
3.250	.2821	.8772	.857202	-27619.
3.500	.2870	.9024	.843068	-29956.
3.750	.2931	.9296	.828280	-32258.
4.000	.3006	.9584	.812871	-34517.
4.250	.3093	.9885	.796862	-36725.
4.500	.3192	1.0197	.780358	-38878.
4.750	.3302	1.0519	.763347	-40970.
5.000	.3425	1.0848	.745903	-42997.
5.250	.3560	1.1184	.728079	-44953.
5.500	.3706	1.1525	.709931	-46836.
5.750	.3865	1.1870	.691514	-48643.
6.000	.4037	1.2217	.672886	-50370.
6.250	.4221	1.2567	.654102	-52015.
6.500	.4419	1.2917	.635218	-53576.
6.750	.4631	1.3268	.616287	-55051.
7.000	.4856	1.3619	.597364	-56438.
7.250	.5096	1.3968	.578501	-57736.
7.500	.5351	1.4315	.559746	-58944.
7.750	.5621	1.4660	.541148	-60061.
8.000	.5906	1.5002	.522753	-61086.
8.250	.6208	1.5340	.504601	-62019.
8.500	.6524	1.5674	.486734	-62859.
8.750	.6857	1.6002	.469188	-63607.
9.000	.7207	1.6325	.451996	-64262.
9.250	.7572	1.6642	.435187	-64825.
9.500	.7953	1.6952	.418789	-65296.
9.750	.8350	1.7255	.402823	-65677.
10.000	.8763	1.7550	.387310	-65967.
10.250	.9192	1.7837	.372265	-66168.
10.500	.9635	1.8116	.357701	-66281.
10.750	1.0092	1.8386	.343627	-66307.

Recommended Values for the mean activity and osmotic coefficient of $ZnCl_2$ in H_2O at 298.15 K - continued

m/mol·kg^{-1}	γ	ϕ	a_w	ΔG^{ex}/J·kg^{-1}
11.000	1.0563	1.8646	.330049	-66247.
11.250	1.1047	1.8897	.316970	-66103.
11.500	1.1543	1.9137	.304390	-65877.
11.750	1.2049	1.9368	.292306	-65571.
12.000	1.2566	1.9588	.280715	-65185.
12.250	1.3092	1.9798	.269610	-64722.
12.500	1.3625	1.9998	.258980	-64184.
12.750	1.4165	2.0187	.248816	-63572.
13.000	1.4711	2.0365	.239106	-62890.
13.250	1.5261	2.0533	.229837	-62138.
13.500	1.5814	2.0690	.220993	-61319.
13.750	1.6368	2.0838	.212560	-60434.
14.000	1.6924	2.0975	.204522	-59487.
14.250	1.7480	2.1103	.196863	-58479.
14.500	1.8034	2.1221	.189564	-57411.
14.750	1.8587	2.1330	.182610	-56286.
15.000	1.9137	2.1431	.175984	-55107.
15.250	1.9685	2.1523	.169667	-53874.
15.500	2.0228	2.1607	.163644	-52589.
15.750	2.0768	2.1684	.157898	-51255.
16.000	2.1304	2.1754	.152412	-49872.
16.250	2.1835	2.1818	.147170	-48443.
16.500	2.2363	2.1876	.142157	-46969.
16.750	2.2888	2.1929	.137358	-45451.
17.000	2.3409	2.1977	.132760	-43890.
17.250	2.3928	2.2021	.128348	-42288.
17.500	2.4445	2.2061	.124110	-40646.
17.750	2.4960	2.2099	.120033	-38965.
18.000	2.5476	2.2134	.116108	-37245.
18.250	2.5991	2.2167	.112322	-35488.
18.500	2.6508	2.2198	.108668	-33694.
18.750	2.7028	2.2228	.105137	-31863.
19.000	2.7550	2.2257	.101722	-29997.
19.250	2.8075	2.2286	.098415	-28095.
19.500	2.8605	2.2314	.095212	-26158.
19.750	2.9139	2.2342	.092108	-24187.
20.000	2.9678	2.2370	.089100	-22182.
20.250	3.0222	2.2397	.086186	-20142.
20.500	3.0770	2.2425	.083364	-18069.
20.750	3.1320	2.2451	.080635	-15963.
21.000	3.1873	2.2477	.077999	-13824.
21.250	3.2425	2.2501	.075457	-11653.
21.500	3.2975	2.2523	.073013	-9450.
21.750	3.3518	2.2541	.070670	-7217.
22.000	3.4051	2.2556	.068433	-4953.
22.250	3.4569	2.2565	.066307	-2661.
22.500	3.5066	2.2567	.064299	-341.
22.750	3.5534	2.2560	.062416	2004.
23.000	3.5965	2.2544	.060667	4372.
23.193	3.6267	2.2523	.059414	6216.

m/mol·kg^{-1}	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0000	.0000	.0000
.010	.0001	.0003	.0002
.100	.0004	.0012	.0006
1.000	.0012	.0018	.0006
2.000	.0016	.0024	.0007
5.000	.0021	.0031	.0010
10.000	.0033	.0046	.0040
20.000	.0052	.0065	.0193
23.193	.0065	.0072	.0263

Coefficient of Correlating Equations

Par	Eqs 2 coefficient	σ(coeff)	Eqs 3 coefficient	σ(coeff)
1	-.485782186002+01	.212+00	.891992914434+01	.409-01
2	.444068610803+02	.158+01	-.120120602552+02	.145+00
3	-.101526598719+03	.484+01	.943485259095+01	.204+00
4	.149818916689+03	.812+01	-.449243619154+01	.147+00
5	-.145402981822+03	.844+01	.133508324971+01	.597-01
6	.969926254657+02	.581+01	-.242300612813+00	.138-01
7	-.455868111267+02	.275+01	.245086458799-01	.168-02
8	.152297964409+02	.919+00	-.105593130612-02	.839-04
9	-.359576095773+01	.218+00		
10	.586270037436+00	.365-01		
11	-.627860601780-01	.414-02		
12	.397347017274-02	.287-03		
13	-.112595366991-03	.916-05		

σ(eqs 2) = .747-02
σ(eqs 3) = .684-02

Experimental Data Employed in Generation of Correlating Equations

Fricke and Havestadt [14]. Vapor pressure measurements at 15°C. Φ_L data for $Zn(NO_3)_2$ were used to adjust the data to 25°C, since the thermal data for $ZnCl_2$ do not extend to high enough molalities. Assigned weight is zero.

m/mol·kg^{-1}	$\phi_{298.15}$
7.760000	1.2100
6.401000	1.2300
5.653000	1.1390
4.357000	.9900

Ishikawa and Takai [15]. Vapor pressure measurements. Assigned weight is zero.

m/mol·kg^{-1}	$\phi_{298.15}$
.518800	.6304
1.036000	.7151
1.832000	.6850
2.330000	.6751
3.147000	.6840

Jones [16]. Freezing point depression measurements. Φ_L and Φ_C data for $ZnCl_2$ were used in treating these and the other freezing point depression data for this system. Assigned weight is zero.

m/mol·kg^{-1}	$\phi_{298.15}$
.001000	.9840
.002990	.9617
.004960	.9408
.006910	.9312
.008840	.9229
.020010	.9186
.038030	.8879
.054250	.8444
.068870	.8367
.082020	.8223

Jones and Getman [17]. Freezing point depression measurements. Assigned weight is zero.

m/mol·kg^{-1}	$\phi_{298.15}$
.049350	.9408
.098770	.9012
.197700	.8879
.297600	.8791
.397000	.8842

Pan [18]. Isopiestic measurements, reference salt is $CaCl_2$. Assigned weight is 0.50.

m/mol·kg^{-1}	$\phi_{298.15}$
.161600	.8459
.270300	.8431
.415300	.8429
.617200	.8328
.844100	.8156
.843900	.8165
.970500	.8050
1.059000	.8013
1.184300	.7972
1.328100	.7924
1.331200	.7923
1.477100	.7906
1.535500	.7891
1.868900	.7939
1.952900	.7961
2.020600	.7976
2.205200	.8062
2.294200	.8099
2.421400	.8181

Stokes [19]. Isopiestic measurements, reference electrolyte is H_2SO_4. Assigned weight is 1.0.

m/mol·kg^{-1}	$\phi_{298.15}$
11.814000	1.9494
13.552000	2.0768
14.044000	2.0985
15.130000	2.1457
17.333000	2.2006
19.853000	2.2341
22.073000	2.2609
23.193000	2.2495

Stokes [19]. Isopiestic measurements, reference electrolyte is $CaCl_2$. Assigned weight is 1.0.

m/mol·kg^{-1}	$\phi_{298.15}$
3.347000	.8888
3.394000	.8934
3.894000	.9442
3.932000	.9515
4.724000	1.0474
5.100000	1.0948
5.837000	1.2021
7.119000	1.3846
7.950000	1.4963
9.013000	1.6364
9.991000	1.7512

Brüll [20]. Emf measurements. Zn-Hg (two phase); $ZnCl_2(m)$; $Hg_2Cl_2(s)$, Hg(l). m_{ref} = 0.001697 mol·kg^{-1}. Assigned weight is 0.20.

m/mol·kg^{-1}	γ/γ_{ref}
.865450	.4101
.427410	.4626
.283970	.4946
.212710	.5180
.170060	.5366
.141600	.5527
.084910	.5989
.028290	.7114
.016970	.7706
.005010	.9083

Egan and Partington [21]. Emf measurements. Zn(s); $ZnCl_2(m_{ref})$; $Hg_2Cl_2(s)$, Hg(l) - Hg(l), Hg_2Cl_2 (s); $ZnCl_2(m)$; Zn(s). m_{ref} = 0.4984 mol·kg^{-1}. Assigned weight is 0.20.

m/mol·kg^{-1}	γ/γ_{ref}
.415300	1.0164
.298800	1.0841
.212400	1.1582
.100300	1.2986
.052900	1.3982
.018200	1.6555
.013800	1.7374
.012200	1.7993
.008100	1.8697
.004700	2.0726

Egan and Partington [21]. Emf measurements. Same cell as above. m_{ref} = 0.4942 mol·kg^{-1}. Assigned weight is 0.20.

m/mol·kg^{-1}	γ/γ_{ref}
.431700	1.0125
.288600	1.0918
.199200	1.1794
.116200	1.2671
.080000	1.3525
.050000	1.4642
.020000	1.6723
.011600	1.8307
.009200	1.8828
.008300	1.9037
.007000	1.9438
.005800	1.9792
.005000	2.0190
.004700	2.0208
.003500	2.0743
.002300	2.1665
.001200	2.2858

Egan and Partington [21]. Emf measurements. Same cell as above. m_{ref} = 0.3606 mol·kg^{-1}. Assigned weight is 0.20.

m/mol·kg^{-1}	γ/γ_{ref}
.288600	1.0392
.199200	1.1147
.116200	1.2063
.080000	1.2830
.050000	1.3962
.020000	1.5984
.011600	1.7439
.008300	1.8139
.007000	1.8477
.005800	1.8804
.005000	1.9237
.002300	2.0637
.001200	2.1836

Harris and Parton [22]. Emf measurements. $Zn(Hg)_x$(l); $ZnCl_2(m)$; AgCl(s), Ag(s). m_{ref} = 0.50 mol·kg^{-1}. Assigned weight is 0.50.

m/mol·kg^{-1}	γ/γ_{ref}
.700000	.9578
.900000	.8933
1.000000	.8691
2.000000	.7418
3.000000	.7356
4.000000	.7914
5.000000	.9035
6.000000	1.0634
7.000000	1.2381
8.000000	1.5024
9.000000	1.7954 *
10.000000	2.1166 *
11.000000	2.4622 *
12.000000	2.8362 *

Horsch [23]. Emf measurements. Zn(s); $ZnCl_2(m)$; AgCl(s), Ag(s). m_{ref} = 0.0003478 mol·kg^{-1}. Assigned weight is zero.

m/mol·kg^{-1}	γ/γ_{ref}
.010210	.6619
.006022	.6961
.003112	.7789
.001453	.8364
.001253	.8068
.000772	.8100
.000649	.9100
.000400	.8751

Ishikawa and Takai [15]. Emf measurements. Hg(10%Zn)(l); $ZnCl_2(m)$; $Hg_2Cl_2(s)$, Hg(l). m_{ref} = 0.11 mol·kg^{-1}. Assigned weight is zero.

m/mol·kg^{-1}	γ/γ_{ref}
.398000	.8198
.733200	.7216
1.021800	.6691
1.553100	.6064
2.118300	.5761
2.707000	.5696
3.324300	.5859

Jahn [24]. Emf measurements. Zn(s); $ZnCl_2(m)$; AgCl(s), Ag(s). m_{ref} = 0.566 mol·kg^{-1}. Assigned weight is zero.

m/mol·kg^{-1}	γ/γ_{ref}
1.112000	.7226
2.220000	1.1079

Lutfullah et al. [25]. Emf measurements. Zn-Hg (two phase); $ZnCl_2(m)$; AgCl(s), Ag(s). m_{ref} = 0.00043035 mol·kg^{-1}. Assigned weight is 0.60.

m/mol·kg^{-1}	γ/γ_{ref}
.000611	.9757
.000634	.9820
.000832	.9643
.000981	.9585
.003663	.8606
.004420	.8464
.008051	.7955
.008272	.7882
.008857	.7845
.011150	.7618
.012040	.7539
.015490	.7259
.018120	.7102
.020190	.7007
.030180	.6594
.035710	.6427
.039110	.6327
.040860	.6219
.047750	.6135
.058220	.5925
.061540	.5813
.072810	.5711
.081890	.5611
.086600	.5524
.101800	.5406
.102990	.5388
.158070	.5045
.162520	.5017
.164310	.5020
.193000	.4841
.222530	.4793
.231140	.4748
.296030	.4539
.327920	.4510
.339600	.4493
.485160	.4184
.513300	.4192
.524900	.4094
.649800	.3956
.665000	.3972
.663900	.3943
.682800	.3914
.860700	.3707
.860500	.3746
.876600	.3701

Robinson and Stokes [26]. Emf measurements. Zn-Hg (two phase); $ZnCl_2(m)$; AgCl(s), Ag(s). m_{ref} = 0.003151 mol·kg^{-1}. Assigned weight is 1.0.

m/mol·kg^{-1}	γ/γ_{ref}
.005082	.9429
.007354	.8971
.010400	.8658
.017530	.8012
.018540	.7984
.022010	.7769
.026710	.7561
.046020	.6938
.064390	.6553
.104200	.6016
.130600	.5853
.185600	.5477
.301300	.5197
.322300	.5021
.432000	.4808
.712100	.4318
1.031000	.3951
1.490000	.3619
2.830000	.3331

Scatchard and Tefft [27]. Emf measurements. Zn-Hg (two phase); $ZnCl_2(m)$; AgCl(s), Ag(s). m_{ref} = 0.002941 mol·kg^{-1}. Assigned weight is 1.0.

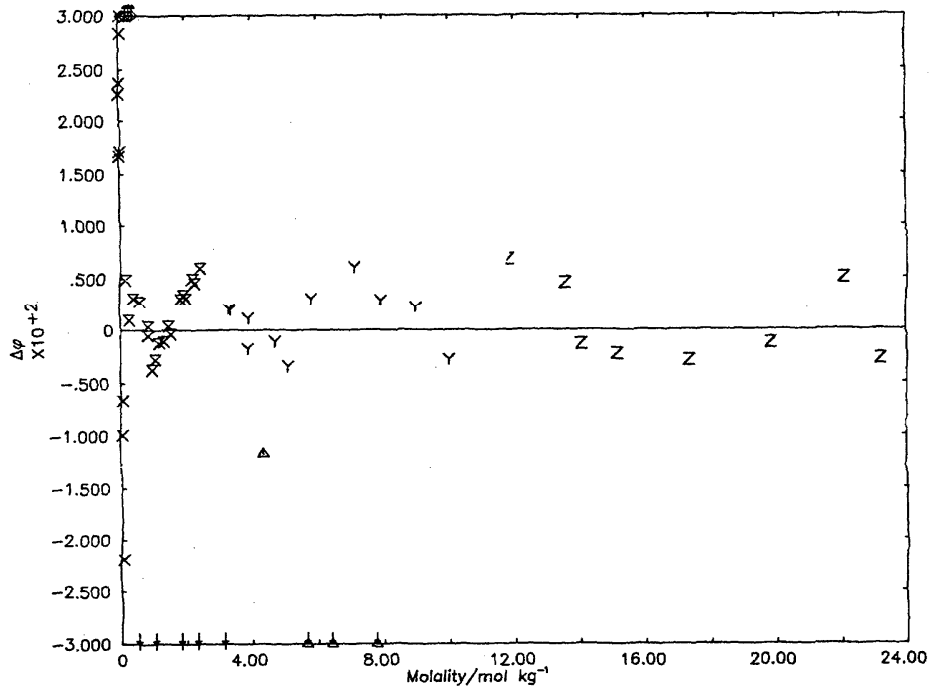
m/mol·kg^{-1}	γ/γ_{ref}
.007814	.8928
.012360	.8443
.021440	.7867
.042420	.7046
.090480	.6259
.221100	.5403
.449900	.4799
.640400	.4454
1.480200	.3613

Comments

The experimental data for $ZnCl_2$ is in remarkably good agreement as is evident from an examination of the deviation plots. Particularly noteworthy is the fact that the results obtained from four different types of electrochemical cells are in excellent agreement with each other and with the results of three different isopiestic investigations. (Note that we have preferred the results of the isopiestic measurements over the measurements of Harris and Parton [22] in the range 9 to 12 mol·kg^{-1}.)

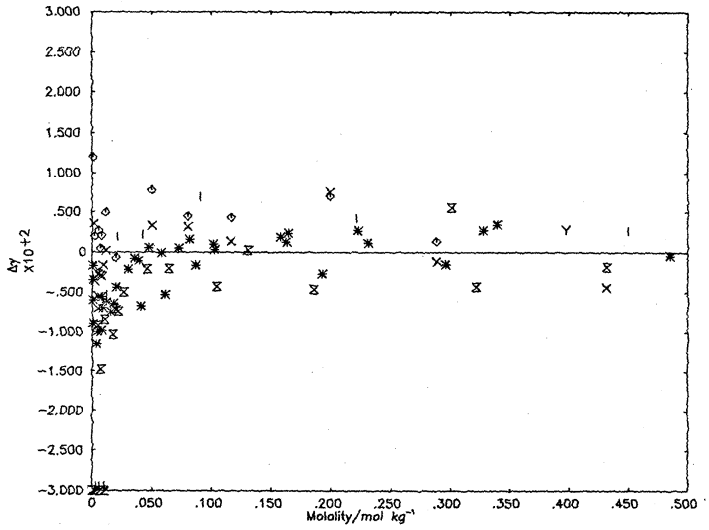
The freezing point depression measurements of Biltz [28] yield unreasonable results and are not given above. Data involving concentration cells with transference have been reported by Masaki [29], Lehfeldt [30], and Foxton and Shutt [31]. We have used the transference numbers of Kaimakov and Sharkov [32] in treating the data of Masaki and find that the calculated values of γ/γ_{ref} are unreasonable and we have not included these data in the above material. The data of Lehfeldt could not be treated since it is not clear what the reference molality is for his measurements. Foxton and Shutt performed their measurements at 60.5 and 80.5°C. In view of the absence of transference numbers at that temperature and the uncertainties inherent in correcting to 25°C, we have not treated their data. We suggest that, in view of the apparent reliability of the activity coefficients for $ZnCl_2$, careful measurements on a concentration cell with transference should yield reliable values for the transference number.

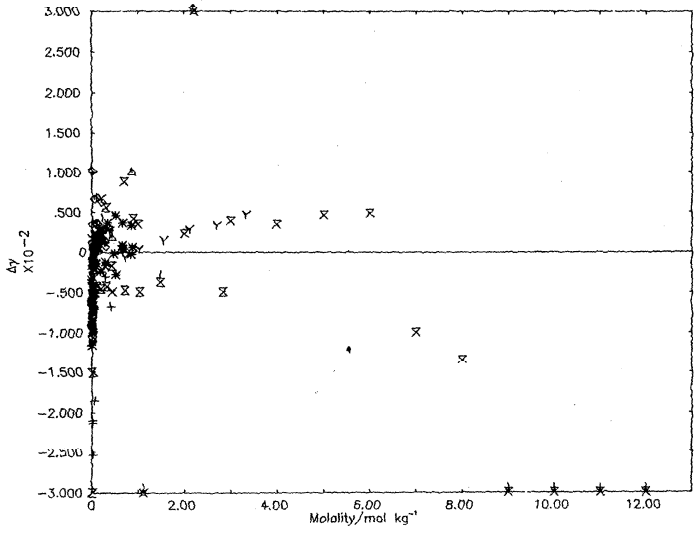
We have described the behavior of this system from zero to 25 mol·kg^{-1} by means of nine empirical coefficients using eqs 3 and by means of twelve empirical coefficients using eqs 2. It was not possible to describe the experimental data using eqs 1. The table of recommended values is based on eqs 3.



Deviation Plot for $ZnCl_2$: $\Delta\phi$ vs molality

- Fricke and Havestadt [14], vapor pressure
- Ishikawa and Takai [15], vapor pressure
- Jones [16], freezing point depression
- Jones and Getman [17], freezing point depression
- Pan [18], isopiestic vs $CaCl_2$
- Stokes [19], isopiestic vs H_2SO_4
- Stokes [19], isopiestic vs $CaCl_2$


3.000
2.500
2.000
1.500
1.000
.500
0
-.500
-1.000
-1.500
-2.000
-2.500
-3.000
Δγ X10+2
0
.050
.100
.150
.200
.250
.300
.350
.400
.450
.500
Molality/mol kg⁻¹


3.000
2.500
2.000
1.500
1.000
.500
0
-.500
-1.000
-1.500
-2.000
-2.500
-3.000
Δγ X10-2
0
2.00
4.00
6.00
8.00
10.00
12.00
Molality/mol kg⁻¹

Deviation Plots for $ZnCl_2$: $\Delta\gamma$ vs molality

△ Brüll [20], emf - Zn-Hg amalgam vs Hg_2Cl_2, Hg

\+ Egan and Partington [21], emf - Zn vs Hg_2Cl_2, Hg, m_{ref} = .4984 mol·kg^{-1}

× Egan and Partington [21], emf - Zn vs Hg_2Cl_2, Hg, m_{ref} = .4942 mol·kg^{-1}

◇ Egan and Partington [21], emf - Zn vs Hg_2Cl_2, m_{ref} = .3606 mol·kg^{-1}

⋈ Harris and Parton [22], emf - Zn-Hg amalgam vs Ag, AgCl

Z Horsch [23], emf - Zn vs Ag, AgCl

Y Ishikawa and Takai [15], emf - Zn-Hg amalgam vs Hg_2Cl_2, Hg

⊠ Jahn [24], emf - Zn - Hg amalgam vs Hg_2Cl_2, Hg

✱ Lutfullah et al. [25], emf - Zn-Hg amalgam vs Ag,AgCl

⧖ Robinson and Stokes [26], emf - Zn-Hg amalgam vs Ag,AgCl

| Scatchard and Tefft [27], emf - Zn-Hg amalgam vs Ag,AgCl

$Zn(ClO_4)_2$

Recommended Values for the mean activity and osmotic coefficient of $Zn(ClO_4)_2$ in H_2O at 298.15 K

m/mol·kg^{-1}	γ	ϕ	a_w	ΔG^{ex}/J·kg^{-1}
.001	.8901	.9631	.999948	-1.
.002	.8536	.9509	.999897	-2.
.003	.8285	.9426	.999847	-3.
.004	.8090	.9362	.999798	-4.
.005	.7929	.9310	.999748	-6.
.006	.7793	.9266	.999700	-8.
.007	.7674	.9228	.999651	-10.
.008	.7568	.9195	.999603	-12.
.009	.7474	.9166	.999554	-14.
.010	.7388	.9140	.999506	-16.
.020	.6809	.8977	.999030	-42.
.030	.6471	.8899	.998558	-73.
.040	.6241	.8860	.998086	-106.
.050	.6071	.8841	.997614	-142.
.060	.5941	.8837	.997139	-180.
.070	.5839	.8841	.996661	-220.
.080	.5756	.8853	.996180	-260.
.090	.5689	.8870	.995695	-302.
.100	.5633	.8890	.995207	-344.
.200	.5433	.9208	.990096	-790.
.300	.5522	.9615	.984531	-1239.
.400	.5746	1.0064	.978478	-1667.
.500	.6067	1.0542	.971914	-2060.
.600	.6472	1.1045	.964818	-2408.
.700	.6958	1.1570	.957173	-2705.
.800	.7531	1.2115	.948965	-2946.
.900	.8196	1.2680	.940185	-3126.
1.000	.8964	1.3264	.930823	-3240.
1.250	1.1424	1.4798	.904865	-3222.
1.500	1.4887	1.6428	.875308	-2732.
1.750	1.9761	1.8141	.842331	-1731.
2.000	2.6638	1.9925	.806242	-189.
2.250	3.6371	2.1765	.767463	1920.
2.500	5.0183	2.3647	.726507	4618.
2.750	6.9815	2.5558	.683953	7923.
3.000	9.7722	2.7485	.640416	11848.
3.250	13.7344	2.9413	.596524	16402.
3.500	19.3425	3.1328	.552885	21591.
3.750	27.2423	3.3217	.510068	27417.
4.000	38.2953	3.5065	.468583	33878.
4.250	53.6255	3.6858	.428866	40970.
4.300(sat)	57.3246	3.7209	.421167	42463.
4.311	58.1702	3.7286	.419485	42794.

m/mol·kg	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0000	.0001	.0001
.010	.0002	.0004	.0003
.100	.0005	.0016	.0009
1.000	.0009	.0015	.0013
2.000	.0010	.0016	.0044
4.311	.0026	.0031	.1811

Coefficients of Correlating Equations

	Eqs 1		Eqs 2		Eqs 3	
Par	coefficient	σ(coeff)	coefficient	σ(coeff)	coefficient	σ(coeff)
1	.1826491001+01	.128-01	.3083326019+01	.987-02	.8708630442+01	.745-01
2	.6821360413+00	.797-02	.4587372726+01	.121-01	-.9259132049+01	.228+00
3	.2072748265+00	.371-02	-.6042988336+00	.368-02	.6183650458+01	.256+00
4	-.2011571951-01	.529-03			-.1992352632+01	.124+00
5					.2463951692+00	.217-01

σ(eqs 1) = .494-02
σ(eqs 2) = .615-02
σ(eqs 3) = .764-02

Experimental Data Employed in Generation of Correlating Equations

Libus and Sadowska [33]. Isopiestic measurements. Authors do not specify the reference electrolyte. Assigned weight is 0.10.

m/mol·kg^{-1}	$\phi_{298.15}$
.837300	1.2594
1.483200	1.6615
2.617600	2.4910
3.221100	2.9785

Stokes and Levien [34]. Isopiestic measurements, reference electrolyte is KCl. Assigned weight is 1.0.

m/mol·kg^{-1}	$\phi_{298.15}$
.091730	.8935
.114300	.8985
.121900	.8999
.233300	.9405
.302200	.9690
.381100	1.0021
.447200	1.0330
.471300	1.0447
.577000	1.0921
.606290	1.1063
.618400	1.1178
.640000	1.1265
.654900	1.1353
.811500	1.2201
.877200	1.2569
.927000	1.2832
.934000	1.2872
1.001000	1.3278
1.018000	1.3366
1.069000	1.3678
1.153000	1.4206
1.202000	1.4474
1.268000	1.4884
1.301000	1.5130
1.318000	1.5226
1.369000	1.5567
1.374000	1.5566
1.446000	1.6005
1.528000	1.6597
1.660000	1.7492
1.668000	1.7477

Stokes and Levien [34]. Isopiestic measurements, reference electrolyte is H_2SO_4. Assigned weight is 1.0.

m/mol·kg^{-1}	$\phi_{298.15}$
1.754000	1.8097
1.837000	1.8707
1.881000	1.9023
2.044000	2.0223
2.051000	2.0296
2.126000	2.0861
2.618000	2.4618
2.815000	2.6099
2.935000	2.7030
3.042000	2.7870
3.173000	2.8804
3.284000	2.9661
3.461000	3.1001
3.789000	3.3416
3.886000	3.4185
4.015000	3.5106
4.268000	3.7042
4.282000	3.7095
4.311000	3.7313

Stokes and Levien [34]. Emf measurements. Zn-Hg (two phase amalgam); $Zn(ClO_4)_2(m_1)$, $Zn(ClO_4)_2(m_2)$; Zn-Hg (two phase amalgam). m_{ref} = 0.100 mol·kg^{-1}. The transference number and density data for $Zn(ClO_4)_2$ given in the table of auxiliary data were used in treating these measurements.

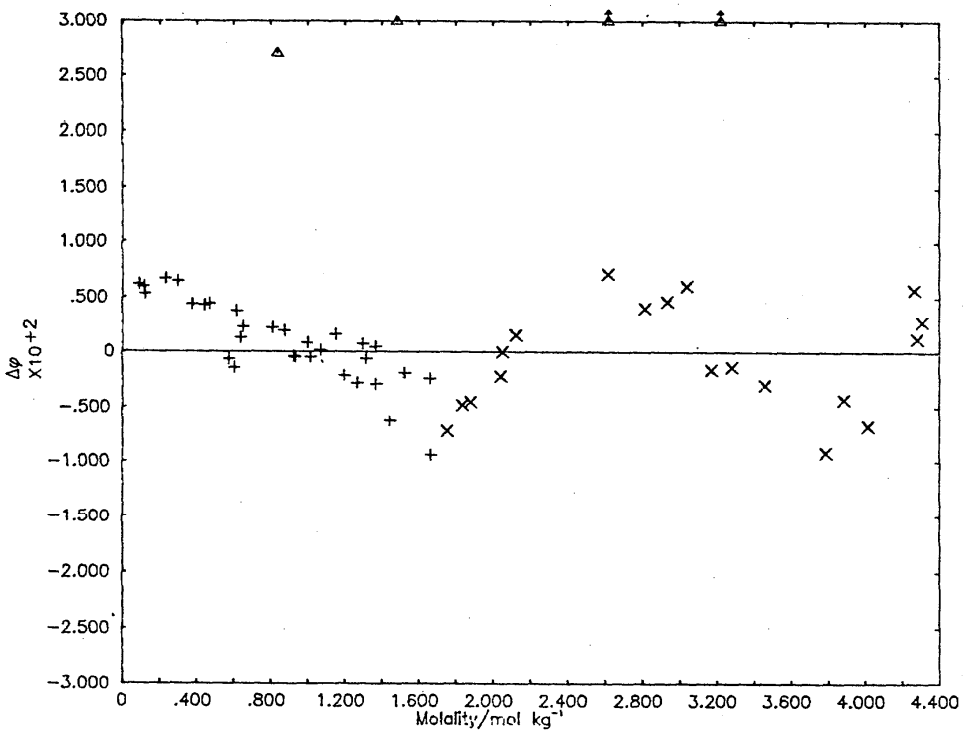
m/mol·kg^{-1}	γ/γ_{ref}
.150000	.9663
.200000	.9532
.300000	.9744
.400000	1.0152
.500000	1.0687
.600000	1.1377
.700000	1.2328
.800000	1.3348
.900000	1.4567
1.000000	1.5916
1.100000	1.7434
1.200000	1.9264
1.300000	2.1362
1.400000	2.3750
1.500000	2.6484
1.600000	2.9491
1.700000	3.2991
1.800000	3.7100
2.000000	4.7281
2.500000	8.9163

Comments

Lilich et al. [35] report isopiestic measurements at 0 and 50°C using H_2SO_4 as the reference electrolyte. We have chosen not to treat these measurements since: (1) the molalities of the H_2SO_4 and the $Zn(ClO_4)_2$ are given to only two significant figures and (2) the uncertainties inherent in adjusting the measurements to 25°C are not negligible.

Sircar and Prasad [36] report measurements on the cell Zn-Hg (2 phase amalgam); $Zn(ClO_4)_2(m_1)$; agar salt bridge; $Zn(ClO_4)_2(m_2)$; Zn-Hg (2 phase amalgam). The interpretation of this cell involves unknown liquid junction potentials and we have chosen no to treat these measurements.

There is good agreement between the isopiestic data and the emf measurements of Stokes and Levien [34].

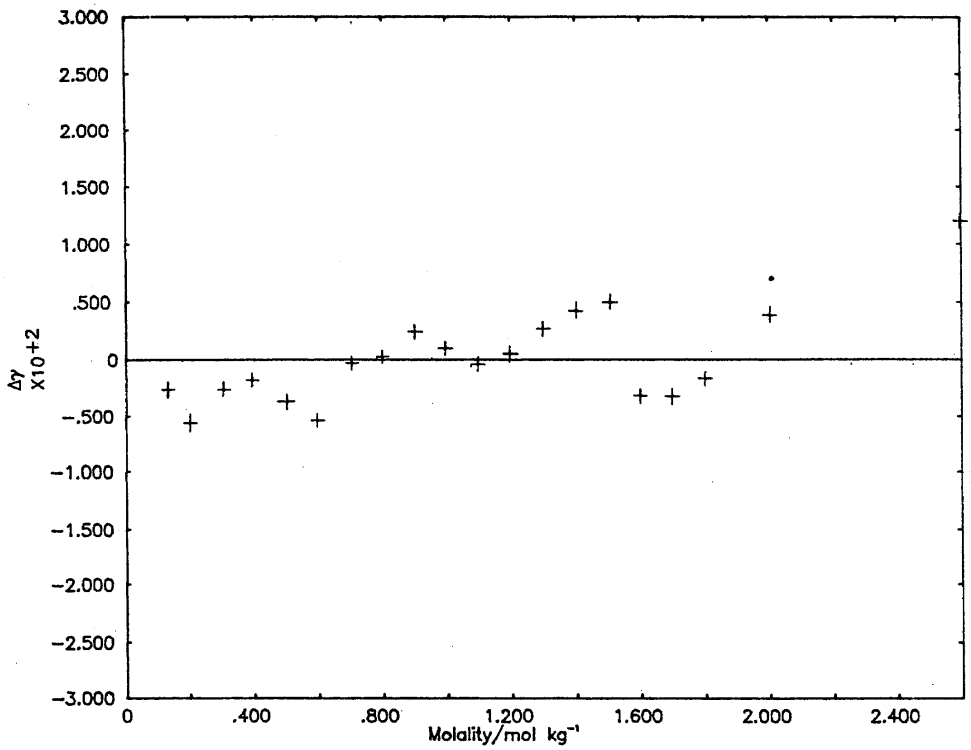


Deviation Plot for $Zn(ClO_4)_2$: $\Delta\phi$ vs molality

△ Libus and Sadowska [33], isopiestic vs ?

\+ Stokes and Levien [34], isopiestic vs KCl

× Stokes and Levien [34], isopiestic vs H_2SO_4



Deviation Plot for $Zn(ClO_4)_2$: Δγ vs molality

+ Stokes and Levien [34], emf

$ZnBr_2$

Recommended Values for the mean activity and osmotic coefficient of $ZnBr_2$ in H_2O at 298.15 K

$m/mol \cdot kg^{-1}$	γ	ϕ	a_w	$\Delta G^{ex}/J \cdot kg^{-1}$
.001	.8905	.9634	.999948	-1.
.002	.8543	.9513	.999897	-2.
.003	.8294	.9432	.999847	-3.
.004	.8102	.9369	.999797	-4.
.005	.7943	.9318	.999748	-6.
.006	.7808	.9275	.999699	-8.
.007	.7691	.9238	.999651	-10.
.008	.7587	.9205	.999602	-12.
.009	.7493	.9177	.999554	-14.
.010	.7408	.9151	.999506	-16.
.020	.6830	.8984	.999029	-42.
.030	.6484	.8896	.998559	-72.
.040	.6242	.8841	.998091	-106.
.050	.6058	.8804	.997624	-142.
.060	.5911	.8780	.997157	-180.
.070	.5791	.8764	.996690	-220.
.080	.5690	.8754	.996222	-261.
.090	.5605	.8749	.995753	-304.
.100	.5531	.8749	.995283	-347.
.200	.5152	.8877	.990450	-819.
.300	.5064	.9117	.985326	-1321.
.400	.5088	.9383	.979920	-1826.
.500	.5162	.9636	.974296	-2324.
.600	.5254	.9859	.968535	-2809.
.700	.5348	1.0044	.962713	-3281.
.800	.5436	1.0192	.956892	-3740.
.900	.5513	1.0303	.951120	-4188.
1.000	.5578	1.0383	.945430	-4626.
1.250	.5686	1.0478	.931662	-5692.
1.500	.5738	1.0480	.918546	-6732.
1.750	.5762	1.0449	.905897	-7760.
2.000	.5780	1.0423	.893449	-8782.
2.250	.5810	1.0425	.880939	-9797.
2.500	.5860	1.0465	.868149	-10799.
2.750	.5937	1.0546	.854920	-11782.
3.000	.6041	1.0668	.841157	-12736.
3.250	.6174	1.0827	.826813	-13653.
3.500	.6336	1.1017	.811881	-14526.
3.750	.6525	1.1234	.796378	-15348.
4.000	.6741	1.1473	.780341	-16112.
4.250	.6984	1.1730	.763811	-16812.
4.500	.7254	1.2003	.746833	-17445.
4.750	.7551	1.2288	.729450	-18005.
5.000	.7877	1.2585	.711704	-18488.
5.250	.8232	1.2892	.693634	-18891.
5.500	.8617	1.3209	.675278	-19210.
5.750	.9036	1.3533	.656672	-19443.
6.000	.9490	1.3866	.637855	-19586.
6.250	.9981	1.4206	.618868	-19637.
6.500	1.0512	1.4553	.599754	-19592.
6.750	1.1085	1.4905	.580562	-19450.
7.000	1.1703	1.5263	.561342	-19209.
7.250	1.2368	1.5624	.542150	-18865.
7.500	1.3082	1.5989	.523043	-18418.
7.750	1.3847	1.6355	.504079	-17865.
8.000	1.4664	1.6721	.485319	-17207.
8.250	1.5536	1.7086	.466819	-16442.
8.500	1.6462	1.7448	.448636	-15569.
8.750	1.7444	1.7806	.430822	-14588.
9.000	1.8482	1.8159	.413424	-13500.
9.250	1.9574	1.8505	.396484	-12304.
9.500	2.0721	1.8843	.380038	-11003.
9.750	2.1922	1.9172	.364117	-9596.
10.000	2.3173	1.9491	.348743	-8085.
10.250	2.4474	1.9799	.333933	-6471.
10.500	2.5821	2.0095	.319699	-4757.
10.750	2.7212	2.0379	.306046	-2945.

Recommended Values for the mean activity and osmotic coefficient of $ZnBr_2$ in H_2O at 298.15 K - Continued

m/mol·kg^{-1}	γ	ϕ	a_w	ΔG^{ex}/J·kg^{-1}
11.000	2.8644	2.0650	.292974	-1036.
11.250	3.0113	2.0908	.280479	968.
11.500	3.1616	2.1153	.268554	3063.
11.750	3.3149	2.1384	.257186	5247.
12.000	3.4707	2.1601	.246364	7518.
12.250	3.6287	2.1805	.236070	9873.
12.500	3.7884	2.1995	.226288	12310.
12.750	3.9494	2.2172	.217001	14825.
13.000	4.1112	2.2336	.208189	17416.
13.250	4.2734	2.2486	.199833	20081.
13.500	4.4356	2.2624	.191915	22816.
13.750	4.5972	2.2749	.184416	25619.
14.000	4.7578	2.2862	.177316	28487.
14.250	4.9169	2.2962	.170599	31418.
14.500	5.0741	2.3051	.164244	34409.
14.750	5.2289	2.3127	.158235	37457.
15.000	5.3811	2.3193	.152553	40559.
15.250	5.5302	2.3248	.147180	43713.
15.500	5.6760	2.3292	.142099	46917.
15.750	5.8184	2.3327	.137290	50169.
16.000	5.9572	2.3353	.132735	53465.
16.250	6.0925	2.3370	.128415	56804.
16.500	6.2245	2.3380	.124312	60184.
16.750	6.3534	2.3384	.120404	63602.
17.000	6.4798	2.3383	.116674	67058.
17.250	6.6041	2.3377	.113102	70550.
17.500	6.7270	2.3369	.109668	74077.
17.750	6.8493	2.3360	.106356	77638.
18.000	6.9717	2.3350	.103148	81232.
18.250	7.0949	2.3341	.100033	84859.
18.500	7.2194	2.3334	.096999	88518.
18.750	7.3456	2.3328	.094043	92209.
19.000	7.4732	2.3324	.091165	95932.
19.250	7.6014	2.3320	.088375	99688.
19.500	7.7283	2.3314	.085690	103474.
19.750	7.8510	2.3302	.083139	107291.
20.000	7.9647	2.3278	.080767	111136.
20.100	8.0062	2.3264	.079880	112681.

m/mol·kg^{-1}	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0001	.0001	.0001
.010	.0003	.0007	.0005
.100	.0006	.0012	.0006
1.000	.0011	.0018	.0010
2.000	.0015	.0026	.0015
5.000	.0017	.0029	.0023
10.000	.0026	.0036	.0084
20.000	.0045	.0053	.0422
20.100	.0049	.0055	.0442

Coefficients of Correlating Equations

Par	Eqs 1 coefficient	Eqs 1 σ(coeff)	Eqs 2 coefficient	Eqs 2 σ(coeff)	Eqs 3 coefficient	Eqs 3 σ(coeff)
1	.176073113615+01	.252-01	.183450603194+01	.120+00	.140170270083+02	.150+00
2	.682797034713+00	.248-01	.505103744932+01	.790+00	-.399940382693+02	.117+01
3	-.356463857827+00	.190-01	.687764115080+01	.215+01	.834587602259+02	.378+01
4	.102429959187+00	.702-02	-.183715716044+02	.321+01	-.113845069181+03	.670+01
5	-.155298973223-01	.137-02	.193183310799+02	.292+01	.101830114673+03	.733+01
6	.136914643033-02	.148-03	-.116768309032+02	.171+01	-.613646151843+02	.526+01
7	-.705503289954-04	.896-05	.443175346754+01	.659+00	.253900671477+02	.255+01
8	.196481418164-05	.284-06	-.107640610230+01	.166+00	-.723674484168+01	.837+00
9	-.227893788490-07	.366-08	.162838325048+00	.263-01	.139791084737+01	.185+00
10			-.139983093014-01	.237-02	-.174924840792+00	.261-01
11			.522899998894-03	.933-04	.128017254910-01	.214-02
12					-.416223359926-03	.773-04

σ(eqs 1) = .128-01
σ(eqs 2) = .555-02
σ(eqs 3) = .480-02

Experimental Data Employed in Generation of Correlating Equations

Ishikawa et al. [37]. Vapor pressure measurements. Assigned weight is zero.

m/mol·kg^{-1}	$\phi_{298.15}$
10.172000	2.0226
8.831000	1.8121
6.637000	1.5917
5.796000	1.5147
4.761000	1.4634
2.516000	1.3030
2.377000	1.2592
1.036000	1.2458

Stokes, Stokes and Robinson [38]. Isopiestic measurements, reference salt is KCl. The $ZnBr_2$ was prepared from Analar ZnO and Analar HBr. Assigned weight is 1.0.

m/mol·kg^{-1}	$\phi_{298.15}$
.091460	.8685
.102300	.8681
.158100	.8780
.158600	.8768
.164600	.8806
.179500	.8825
.244500	.8996
.296000	.9077
.320100	.9163
.345300	.9232
.353900	.9258
.492800	.9629
.582000	.9822
.615000	.9912
.633700	.9905
.710500	1.0079
.817900	1.0218
.898000	1.0342
.975500	1.0405
1.175000	1.0453
1.237000	1.0481
1.325000	1.0483
1.453000	1.0476
1.702000	1.0427
2.136000	1.0429
2.404000	1.0447
2.868000	1.0627
2.886000	1.0692

Acheson [39]. Vapor pressure measurement over the saturated solution. Assigned weight is zero.

m/mol·kg^{-1}	$\phi_{298.15}$
20.88(sat)[39]	2.2381

Stokes, Stokes, and Robinson [38]. Isopiestic measurements, reference electrolyte is H_2SO_4. The $ZnBr_2$ solution is that used by Parton and Mitchell in their investigation [40]. Assigned weight is 1.0.

m/mol·kg^{-1}	$\phi_{298.15}$
2.832000	1.0579
2.838000	1.0573
2.870000	1.0594
2.887000	1.0604
3.430000	1.1384 *
3.608000	1.1102
3.933000	1.1403
3.980000	1.1438
4.420000	1.1867
4.718000	1.2272
5.266000	1.2911
5.563000	1.3319
5.695000	1.3443
5.824000	1.3637
6.014000	1.3799
6.185000	1.4156
6.810000	1.5004
7.040000	1.5350
7.288000	1.5689
7.326000	1.5738
7.902000	1.6596
7.946000	1.6645
8.828000	1.7888
8.847000	1.7939
10.065000	1.9536
11.760000	2.1410
11.790000	2.1451
13.010000	2.2287
13.530000	2.2730
13.840000	2.2763
14.910000	2.3111
15.370000	2.3277
15.650000	2.3334
17.020000	2.3396
18.440000	2.3328
20.100000	2.3265

Stokes, Stokes, and Robinson [38]. Reference salt is KCl. Assigned weight is 1.0.

m/mol·kg^{-1}	$\phi_{298.15}$
.102900	.8729
.174300	.8777
.192000	.8873
.265700	.9004
.293400	.8730 *
.435100	.9445
.449500	.9469
.563600	.9112 *
.659100	.9955
.745990	1.0110
.847500	1.0246
.969600	1.0378
1.048000	1.0389
1.104000	1.0420
1.195000	1.0449
1.356000	1.0463
1.796000	1.0410
1.954000	1.0418
2.437000	1.0451

Egan and Partington [21]. Emf measurements. Zn(s); $ZnBr_2(m_{ref})$; $Hg_2Br_2(s)$, Hg(l)-Hg(l), $Hg_2Br_2(s)$; $ZnBr_2(m)$; Zn(s). m_{ref} = 0.3782 mol·kg^{-1}. Assigned weight is 0.50.

m/mol·kg^{-1}	γ/γ_{ref}
.311800	1.0062
.199900	1.0200
.138800	1.0593
.095900	1.1141
.080400	1.1313
.047400	1.2184
.022400	1.3129
.012500	1.4072
.009000	1.4690
.007100	1.5012
.005000	1.5572
.003100	1.6409
.001700	1.6904
.001000	1.7595

Egan and Partington [21]. Emf measurements. Same cell as above. m_{ref} = 0.3819 mol·kg^{-1}. Assigned weight is 0.50.

m/mol·kg^{-1}	γ/γ_{ref}
.311200	1.0064
.280600	.7541*
.140100	1.0526
.100000	1.1038
.078800	1.1440
.062600	1.1770
.050000	1.2092
.032500	1.2712
.020900	1.3282
.018700	1.3516
.009800	1.4431
.008800	1.4573
.007800	1.4824
.007100	1.5014
.006300	1.5193
.005000	1.5521
.004100	1.5899
.003100	1.6313
.001900	1.6908
.001000	1.7583

Iskihawa et al. [37]. Emf measurements. Zn(Hg) (1); $ZnBr_2(m)$; $Hg_2Br_2(s)$; Hg(l). m_{ref} = 0.011 mol·kg^{-1}. Assigned weight is zero.

m/mol·kg^{-1}	γ/γ_{ref}
11.486000	4.0658
10.824000	3.8209
5.285000	1.1375
2.455000	.8060
1.838000	.7944
.812200	.7390
.360600	.6822
.160000	.7159
.079200	.7731
.040800	.8452
.023200	.9079

Parton and Mitchell [40]. Emf measurements. Ag(s), AgBr(s); $ZnBr_2(m_{ref})|ZnBr_2(m)$; AgBr(s), Ag(s). m_{ref} = 0.507 mol·kg^{-1}. The transference number and density data for $ZnBr_2$ given in the table of auxiliary data were used in treating these measurements. Assigned weight is zero.

m/mol·kg^{-1}	γ/γ_{ref}
.030000	.8864
.040000	.8769
.050000	.8412
.060000	.8040
.070000	.7706
.080000	.7445
.090000	.7215
.100000	.6948

Parton and Mitchell [40]. Emf measurements. Zn-Hg (two phase); $ZnBr_2(m)$; AgBr(s), Ag(s). m_{ref} = 0.02 mol·kg^{-1}. Assigned weight is 0.60 up to 0.3 mol·kg^{-1} and zero from 0.40 to 16.0 mol·kg^{-1}.

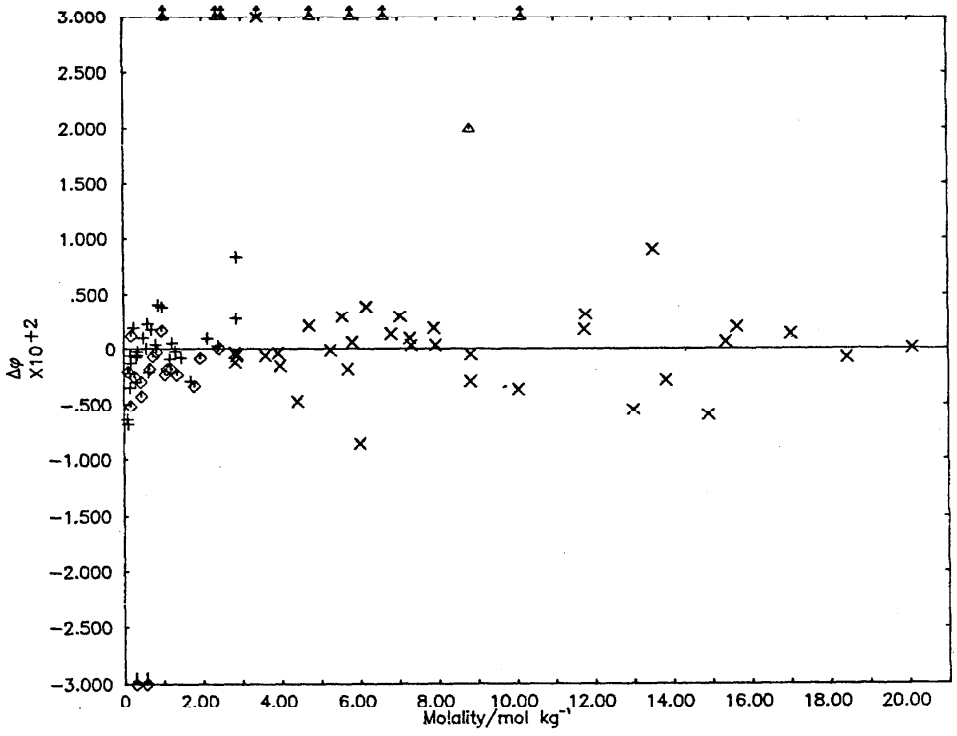
m/mol·kg^{-1}	γ/γ_{ref}
.030000	.9440
.040000	.9083
.050000	.8828
.060000	.8619
.070000	.8455
.080000	.8337
.090000	.8200
.100000	.8103
.200000	.7553
.300000	.7337
.400000	.7245*
.500000	.7153*
.600000	.7074*
.700000	.7086*
.800000	.7133*
.900000	.7163*
1.000000	.7189*
1.200000	.7203*
1.400000	.7252*
1.600000	.7358*
1.800000	.7446*
2.000000	.7532*
2.500000	.7955*
3.000000	.8461*
3.500000	.9232*
4.000000	.9968*
4.500000	1.0934*
5.000000	1.1955*
6.000000	1.4254*
7.000000	1.7618*
8.000000	2.1324*
9.000000	2.5614*
10.000000	3.0512*
11.000000	3.6334*
12.000000	4.3402*
13.000000	5.1802*
14.000000	6.0132*
15.000000	6.9255*
16.000000	7.7863*

Stokes and Stokes [41]. Emf measurements. Zn-Hg (two phase); $ZnBr_2(m)$; AgBr(s), Ag(s). m_{ref} = 0.002026 mol·kg^{-1}. Assigned weight is 1.0.

m/mol·kg^{-1}	γ/γ_{ref}
.003250	.9661
.004245	.9458
.007622	.8938
.008216	.8880
.012810	.8476
.018870	.8055
.032100	.7474
.057050	.6915
.072890	.6680
.100000	.6408
.202800	.5974
.381000	.5940
.455400	.5973
.698600	.6287
.708200	.6296
.990000	.6532

Comments

The isopiestic investigation of Stokes et al. [38], in which two different preparations of $ZnBr_2$ and two different reference electrolytes were used, is internally consistent and in good agreement with the careful emf measurements of Stokes and Stokes [41]. We have relied largely upon these two investigations in obtaining a "best" fit to the data for $ZnBr_2$. We note that the agreement with the emf measurements of Egan and Partington [21] is very good, but that the data of Parton and Mitchell [40], for the most part, must be considered inaccurate. We have chosen not to use the vapor pressure measurement of Acheson [39] for the saturated solution since the result does not correlate well with the isopiestic measurements. As was the case for $ZnCl_2$, the data cover a broad range of molalities, and we have had to use between nine and twelve empirical coefficients to describe this system. The table of recommended values and the deviation plots are based on eqs. 5.



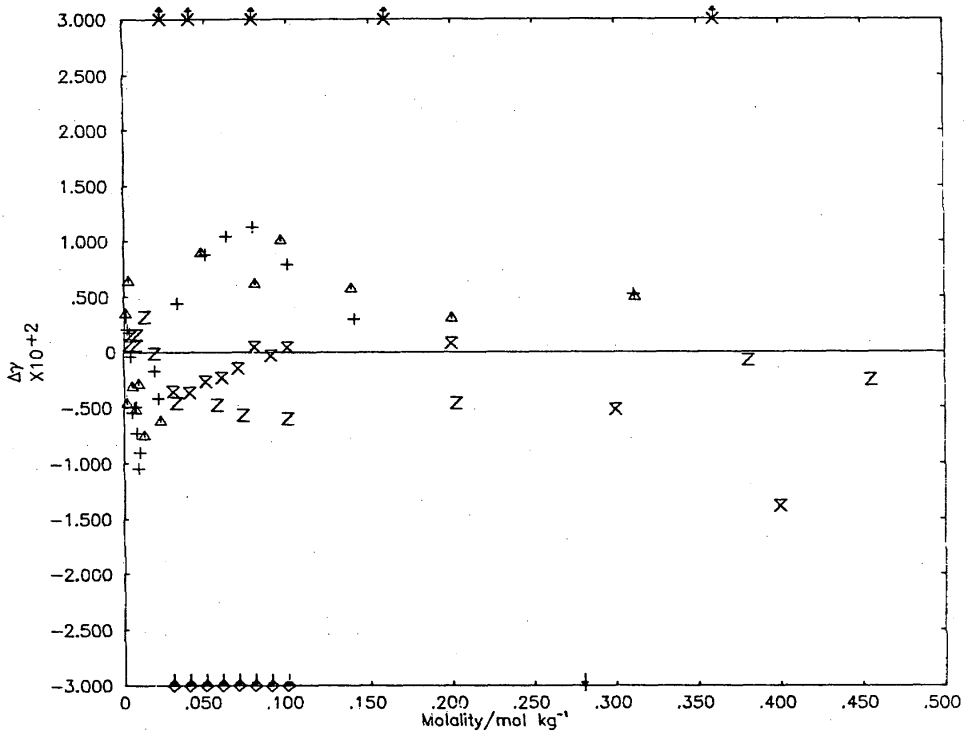
Deviation Plot for $ZnBr_2$: $\Delta\phi$ vs molality

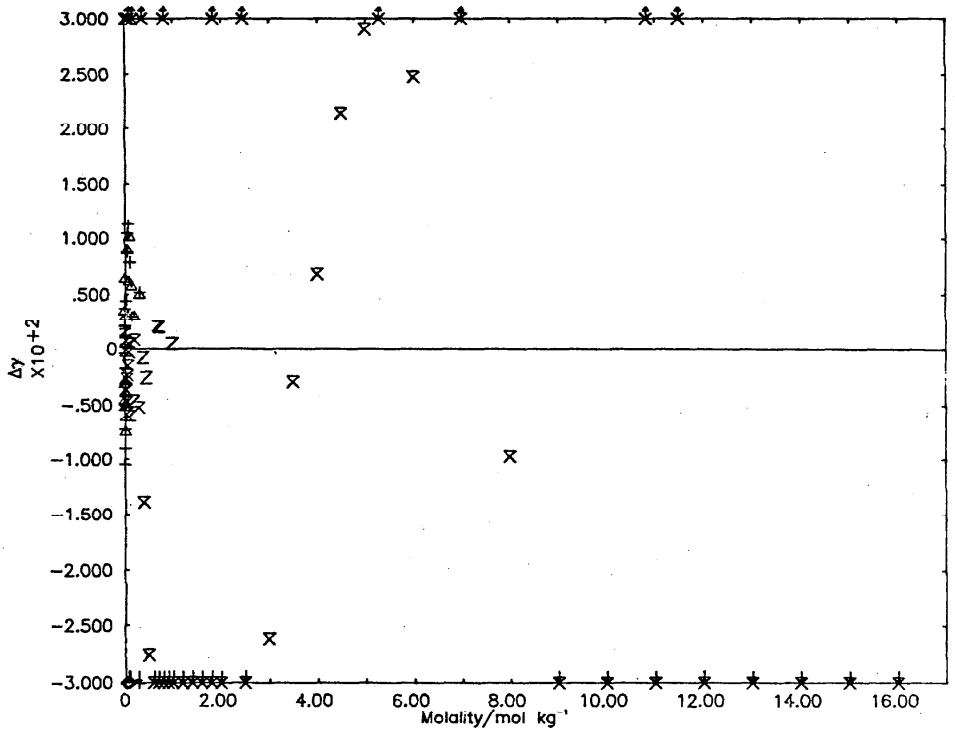
△ Ishikawa et al. [37], vapor pressure

◇ Stokes et al. [38], isopiestic vs KCl (solution B of $ZnBr_2$)

\+ Stokes et al. [38], isopiestic vs KCl (solution A of $ZnBr_2$)

× Stokes et al. [38], isopiestic vs H_2SO_4


3.000
2.500
2.000
1.500
1.000
.500
0
−.500
−1.000
−1.500
−2.000
−2.500
−3.000
Δγ X10+2
0
.050
.100
.150
.200
.250
.300
.350
.400
.450
.500
Molality/mol kg⁻¹


3.000
2.500
2.000
1.500
1.000
.500
0
−.500
−1.000
−1.500
−2.000
−2.500
−3.000
Δγ X10+2
0
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
Molality/mol kg⁻¹

Deviation Plots for $ZnBr_2$: $\Delta\gamma$ vs molality

△ Egan and Partington [21], emf - Zn vs Hg_2Br_2, Hg. $m_{ref} = 0.3782$ mol·kg^{-1}

+ Egan and Partington [21], emf - Zn vs Hg_2Br_2, Hg. $m_{ref} = 0.3819$ mol·kg^{-1}

× Ishikawa et al. [39], emf - Zn-Hg amalgam vs Hg_2Br_2,Hg

◇ Parton and Mitchell [40], emf - concentration cell with transference (Ag, AgBr electrode)

⧖ Parton and Mitchell [40], emf - Zn-Hg amalgam vs Ag, AgBr

Z Stokes and Stokes [41], emf - Zn-Hg amalgam vs Ag, AgBr

ZnI_2

Recommended Values for the mean activity and osmotic coefficient of ZnI_2 in H_2O at 298.15 K

m/mol·kg^{-1}	γ	ϕ	a_w	ΔG^{ex}/J·kg^{-1}
.001	.8931	.9648	.999948	-1.
.002	.8592	.9541	.999897	-2.
.003	.8362	.9470	.999846	-3.
.004	.8187	.9418	.999796	-4.
.005	.8044	.9376	.999747	-6.
.006	.7924	.9343	.999697	-7.
.007	.7820	.9314	.999648	-9.
.008	.7728	.9290	.999598	-11.
.009	.7647	.9268	.999549	-13.
.010	.7573	.9250	.999500	-15.
.020	.7082	.9139	.999013	-39.
.030	.6796	.9087	.998528	-66.
.040	.6596	.9056	.998044	-96.
.050	.6445	.9037	.997561	-128.
.060	.6325	.9025	.997078	-161.
.070	.6225	.9018	.996594	-196.
.080	.6142	.9015	.996110	-231.
.090	.6072	.9015	.995624	-268.
.100	.6011	.9019	.995137	-306.
.200	.5741	.9198	.990107	-706.
.300	.5798	.9668	.984622	-1117.
.400	.6025	1.0008	.978596	-1510.
.500	.6351	1.0482	.972071	-1868.
.600	.6734	1.0939	.965148	-2184.
.700	.7145	1.1355	.957950	-2455.
.800	.7563	1.1718	.950597	-2684.
.900	.7971	1.2023	.943195	-2872.
1.000	.8358	1.2272	.935829	-3023.
1.250	.9197	1.2672	.917950	-3262.
1.500	.9830	1.2834	.901189	-3352.
1.750	1.0287	1.2848	.885572	-3339.
2.000	1.0623	1.2793	.870855	-3255.
2.250	1.0893	1.2720	.856694	-3119.
2.500	1.1142	1.2662	.842751	-2938.
2.750	1.1399	1.2638	.828754	-2716.
3.000	1.1683	1.2654	.814511	-2450.
3.250	1.2004	1.2710	.799912	-2136.
3.500	1.2366	1.2803	.784909	-1770.
3.750	1.2771	1.2928	.769498	-1345.
4.000	1.3219	1.3080	.753701	-859.
4.250	1.3711	1.3253	.737551	-306.
4.500	1.4248	1.3446	.721078	316.
4.750	1.4831	1.3655	.704301	1011.
5.000	1.5464	1.3880	.687233	1783.
5.250	1.6153	1.4121	.669874	2633.
5.500	1.6903	1.4377	.652222	3567.
5.750	1.7723	1.4650	.634274	4586.
6.000	1.8619	1.4939	.616034	5696.
6.250	1.9600	1.5245	.597517	6899.
6.500	2.0675	1.5567	.578755	8199.
6.750	2.1850	1.5904	.559795	9601.
7.000	2.3132	1.6253	.540702	11107.
7.250	2.4526	1.6612	.521559	12720.
7.500	2.6035	1.6979	.502458	14444.
7.750	2.7661	1.7350	.483498	16279.
8.000	2.9401	1.7721	.464781	18227.
8.250	3.1254	1.8089	.446402	20289.
8.500	3.3214	1.8450	.428447	22464.
8.750	3.5278	1.8803	.410985	24752.
9.000	3.7439	1.9145	.394071	27152.
9.250	3.9692	1.9474	.377736	29660.
9.500	4.2035	1.9791	.361996	32277.
9.750	4.4464	2.0094	.346849	34999.
10.000	4.6982	2.0386	.332283	37825.
10.250	4.9588	2.0666	.318281	40751.
10.500	5.2283	2.0935	.304829	43778.
10.750	5.5060	2.1192	.291931	46901.

Recommended Values for the mean activity and osmotic coefficient of ZnI_2 in H_2O at 298.15 K - Continued

m/mol·kg^{-1}	γ	ϕ	a_w	ΔG^{ex}/J·kg^{-1}
11.000	5.7902	2.1435	.279618	50120.
11.250	6.0770	2.1659	.267965	53430.
11.500	6.3588	2.1854	.257105	56828.
11.750	6.6230	2.2004	.247249	60306.
11.892	6.7582	2.2062	.242213	62313.

m/mol·kg^{-1}	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0001	.0003	.0003
.010	.0007	.0017	.0013
.100	.0015	.0034	.0020
1.000	.0034	.0063	.0052
2.000	.0035	.0065	.0069
5.000	.0044	.0077	.0119
10.000	.0074	.0100	.0472
11.892	.0110	.0130	.0878

Coefficients of Correlating Equations

	Eqs 2		Eqs 3	
Par	coefficient	σ(coeff)	coefficient	σ(coeff)
1	.547742963214+01	.305+00	.174986783353+02	.364+00
2	-.126715350978+02	.218+01	-.556400497896+02	.260+01
3	.469434585059+02	.633+01	.114573582166+03	.756+01
4	-.670175952462+02	.992+01	-.142922075597+03	.119+02
5	.542451308758+02	.934+01	.111382863967+03	.112+02
6	-.270682199344+02	.552+01	-.557380144366+02	.659+01
7	.850601619923+01	.207+01	.179545185412+02	.247+01
8	-.164292311573+01	.477+00	-.360464908084+01	.569+00
9	.178329426597+00	.616-01	.410810960688+00	.736-01
10	-.833021069833-02	.342-02	-.203130361402-01	.409-02

σ(eqs 2) = .927-02
σ(eqs 3) = .111-01

Experimental Data Employed in Generation of Correlating Equations

Stokes and Levien [42]. Isopiestic measurements, reference salt is NaCl. Assigned weight is 1.0.

m/mol·kg^{-1}	$\phi_{298.15}$
1.167000	1.2558
1.253000	1.2669
1.335000	1.2759
1.350000	1.2785
2.234000	1.2678
2.554000	1.2631
3.113000	1.2623

Stokes and Levien [42]. Isopiestic measurements, reference electrolyte is H_2SO_4. Assigned weight is 1.0.

m/mol·kg^{-1}	$\phi_{298.15}$
2.204000	1.2696
2.737000	1.2712
3.682000	1.2918
3.814000	1.2971
3.825000	1.2968
4.033000	1.3062
4.595000	1.3490
4.950000	1.3883
5.192000	1.4084
5.593000	1.4437
5.848000	1.4771
5.956000	1.4899
6.392000	1.5434
6.542000	1.5636
6.848000	1.6035
7.963000	1.7632
8.454000	1.8385
9.464000	1.9758
9.994000	2.0396
10.960000	2.1379
11.892000	2.2066

Stokes [43]. Isopiestic measurements, reference electrolyte is KCl. Assigned weight is 1.0.

m/mol·kg^{-1}	$\phi_{298.15}$
.105200	.8960
.124400	.9001
.145800	.9059
.305500	.9582
.366000	.9824
.496800	1.0378
.518100	1.0473
.713800	1.1331
.857000	1.1800
.943500	1.2092
1.124000	1.2467
1.228000	1.2620
1.343000	1.2785
1.520000	1.2860
1.709000	1.2874
1.833000	1.2877
2.050000	1.2824
2.099000	1.2783
2.513000	1.2640

Bates [44]. Emf measurements. Zn-Hg (two phase); $ZnI_2(m)$; AgI(s), Ag(s). Reference molality is 0.001182 mol·kg^{-1}. Assigned weight is 0.90.

m/mol·kg^{-1}	γ/γ_{ref}
.002026	.9933
.004140	.9546
.004692	.9434
.005683	.9221
.008455	.8830
.009650	.8736
.012770	.8490
.018010	.8249
.026750	.7795
.042940	.7343
.056190	.7212
.060680	.7154
.074410	.6944
.122400	.6708
.177100	.6605
.328900	.6654
.417600	.6965
.800800	.8636

Egan and Partington [21]. Emf measurements. Zn(s); $ZnI_2(m_{ref})$; Hg_2I_2(s), Hg(l)-Hg(l), Hg_2I_2(s); $ZnI_2(m)$; Zn(s). m_{ref} = 0.2499 mol·kg^{-1}. Assigned weight is zero.

m/mol·kg^{-1}	γ/γ_{ref}
.193800	.7247
.131800	.5715
.121000	.5525
.098600	.4889
.076500	.4117
.047000	.3099
.024900	.3374
.016600	.3510
.011400	.3724
.008100	.3940
.005100	.4046

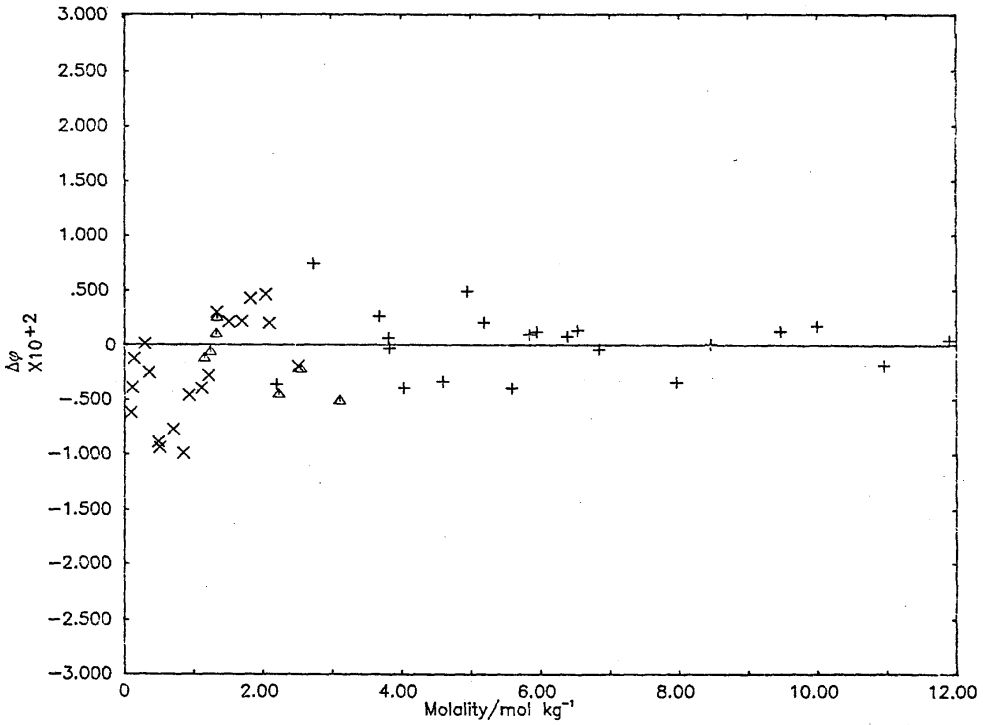
Partington and Torto [45]. Emf measurements. Zn-Hg (two phase); $ZnI_2(m)$; AgI(s), Ag(s). m_{ref} = 0.00695 mol·kg^{-1}. Assigned weight is 0.60.

m/mol·kg^{-1}	γ/γ_{ref}
.007500	.9939
.008000	.9891
.008500	.9831
.009010	.9769
.012220	.9509
.017380	.9105
.024330	.8676
.034420	.8352
.046200	.8130
.069440	.7759
.090210	.7486
.114750	.7433
.163400	.7392
.219930	.7212
.390600	.7630

Comments

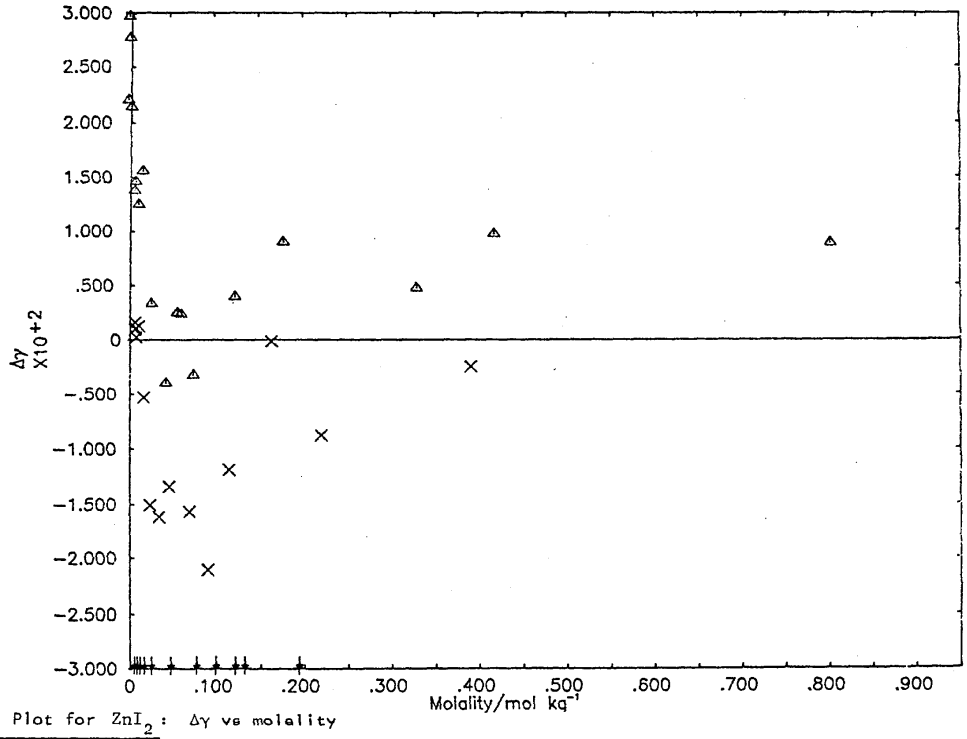
The isopiestic measurements [42,43] are in reasonable agreement with the emf measurements of Bates [44] and of Partington and Torto [45]. The measurements of Egan and Partington [21], which utilized a cell different than the other electrochemical investigations, are not in agreement with either them or the isopiestic measurements. Unfortunately, Partington [45] did not attempt to reconcile his separate results. We also note that, for the lowest molalities, the emf measurements of Partington and Torto [45] are not in complete agreement with the results of Bates [44]. While we have given a slightly higher weight to the results of Bates [44], both the nature of the correlating equations and the preponderant weight of the data in the region 0.01 to 0.20 mol·kg^{-1} make it difficult to make a completely satisfactory accomodation of the lowest four data points of Bates [44] in the molality range 0.002 to 0.0057 mol·kg^{-1}.

Eqs 1 could not be used to correlate the data for this system. The table of recommended values and the deviation plots are based on eqs 3.



Deviation Plot for ZnI_2: $\Delta\phi$ vs molality

▲ Stokes and Levien [42], + Stokes and Levien [42], × Stokes [43]



Deviation Plot for ZnI_2: $\Delta\gamma$ vs molality

▲ Bates [44], emf - Zn-Hg amalgam vs Ag,AgI

× Partington and Torto [45], emf - Zn-Hg amalgam vs Ag, AgI

+ Egan and Partington [21], emf - Zn vs Hg_2I_2, Hg

$Zn(NO_3)_2$

Recommended Values for the mean activity and osmotic coefficient of $Zn(NO_3)_2$ in H_2O at 298.15 K

m/mol·kg^{-1}	γ	ϕ	a_w	ΔG^{ex}/J·kg^{-1}
.001	.8893	.9627	.999948	-1.
.002	.8522	.9501	.999897	-2.
.003	.8264	.9414	.999847	-3.
.004	.8064	.9346	.999798	-4.
.005	.7898	.9291	.999749	-6.
.006	.7757	.9244	.999700	-8.
.007	.7633	.9203	.999652	-10.
.008	.7523	.9167	.999604	-12.
.009	.7424	.9134	.999556	-14.
.010	.7334	.9105	.999508	-16.
.020	.6718	.8914	.999037	-43.
.030	.6349	.8811	.998572	-75.
.040	.6090	.8746	.998111	-110.
.050	.5894	.8704	.997651	-148.
.060	.5739	.8677	.997190	-189.
.070	.5612	.8659	.996730	-231.
.080	.5506	.8648	.996268	-275.
.090	.5416	.8642	.995805	-320.
.100	.5338	.8640	.995341	-366.
.200	.4916	.8738	.990600	-868.
.300	.4771	.8917	.985646	-1409.
.400	.4736	.9127	.980463	-1964.
.500	.4762	.9353	.975041	-2518.
.600	.4830	.9591	.969376	-3065.
.700	.4929	.9839	.963461	-3599.
.800	.5054	1.0095	.957293	-4116.
.900	.5202	1.0357	.950870	-4613.
1.000	.5372	1.0626	.944189	-5087.
1.250	.5883	1.1322	.926364	-6160.
1.500	.6521	1.2047	.906957	-7052.
1.750	.7292	1.2793	.886035	-7744.
2.000	.8210	1.3556	.863702	-8222.
2.250	.9291	1.4329	.840092	-8474.
2.500	1.0554	1.5107	.815362	-8493.
2.750	1.2022	1.5887	.789688	-8272.
3.000	1.3721	1.6663	.763255	-7807.
3.250	1.5677	1.7431	.736251	-7095.
3.500	1.7920	1.8190	.708864	-6135.
3.750	2.0483	1.8936	.681273	-4926.
4.000	2.3400	1.9668	.653647	-3470.
4.250	2.6709	2.0383	.626139	-1766.
4.500	3.0449	2.1080	.598886	183.
4.750	3.4665	2.1760	.572004	2374.
5.000	3.9405	2.2421	.545591	4804.
5.250	4.4722	2.3065	.519724	7472.
5.500	5.0678	2.3693	.494463	10373.
5.750	5.7342	2.4306	.469845	13505.
6.000	6.4797	2.4907	.445895	16866.
6.250	7.3142	2.5498	.422618	20453.
6.500	8.2498	2.6082	.400008	24265.
6.750(sat)	9.3013	2.6664	.378047	28300.
7.000	10.4873	2.7248	.356708	32557.
7.103	11.0203	2.7490	.348089	34377.

m/mol·kg^{-1}	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0001	.0001	.0001
.010	.0003	.0008	.0006
.100	.0010	.0030	.0016
1.000	.0007	.0036	.0019
2.000	.0007	.0035	.0029
5.000	.0016	.0040	.0157
7.103	.0074	.0093	.1029

Coefficients of Correlating Equations

	Eqs 1		Eqs 2		Eqs 3	
Par	coefficient	σ(coeff)	coefficient	σ(coeff)	coefficient	σ(coeff)
1	.1737838301+01	.209-01	.1602902387+01	.749-01	.9005722093+01	.108+00
2	.3152128814+00	.105-01	.7459717601+01	.226+00	-.1153452275+02	.326+00
3	.9323196573-01	.531-02	-.3790437090+01	.281+00	.9188895864+01	.407+00
4	-.1451102764-01	.113-02	.1623731669+01	.174+00	-.4117908187+01	.251+00
5	.7310567456-03	.823-04	-.4147301741+00	.527-01	.9661726148+00	.762-01
6			.4435811596-01	.624-02	-.9273541114-01	.902-02

σ(eqs 1) = .318-02
σ(eqs 2) = .318-02
σ(eqs 3) = .460-02

Experimental Data Employed in Generation of Correlating Equations

Dieterici [46]. Vapor pressure measurements at 0°C. The Φ_L and Φ_c data for $Zn(NO_3)_2$ given in the table of auxiliary data were used to adjust this and the other data obtained for this system at temperatures other than 25°C to that temperature. Assigned weight is zero.

m/mol·kg^{-1}	$\phi_{298.15}$
.498000	.8070
.994000	.8990
1.469000	1.0350
1.875000	1.1460
2.487000	1.3270
2.997000	1.4860
3.718000	1.6720

Ewing and Fisher [47]. Vapor pressure measurements at 20°C. Assigned weight is zero.

m/mol·kg^{-1}	$\phi_{298.15}$
.601000	1.3610
1.196000	1.4270
1.815000	1.1920
1.897000	1.4460
2.525000	1.5200
2.796000	1.6700
2.853000	1.7560
4.156000	2.0390
6.011000	2.3670
7.103000	2.5940

Ewing and Fisher [47]. Vapor pressure measurements at 30°C. Assigned weight is zero.

m/mol·kg^{-1}	$\phi_{298.15}$
.601000	1.4140
1.196000	1.3220
1.815000	1.2020
1.897000	1.5020
2.525000	1.6880
2.796000	1.5630
2.853000	2.0250
4.156000	2.0970
6.011000	2.3870
7.103000	2.7410

Jones et al. [48]. Freezing point depression measurements. Assigned weight is 0.10.

m/mol·kg^{-1}	$\phi_{298.15}$
.065170	.8863
.129700	.8815

Motornaya et al. [49]. Isopiestic measurements, reference salt is $CaCl_2$. Assigned weight is 0.60.

m/mol·kg^{-1}	$\phi_{298.15}$
.610000	.9663
.680000	.9708
.747000	.9902
.789000	1.0091
.825000	1.0166
.911000	1.0422
1.028000	1.0687
1.278000	1.1386
1.487000	1.1978
1.559000	1.2192

Stokes and Levien [34]. Isopiestic measurements, reference salt is KCl. Assigned weight is 1.0.

m/mol·kg^{-1}	$\phi_{298.15}$
.111300	.8663
.116100	.8671
.142100	.8640
.182300	.8702
.203700	.8713
.236400	.8777
.355900	.9029
.368000	.9065
.369300	.9044
.452000	.9230
.511600	.9370
.630400	.9670
.730700	.9925
.898400	1.0358
.902700	1.0384
.930200	1.0440
1.028000	1.0725
1.113000	1.0961
1.148000	1.1071
1.208000	1.1210
1.296000	1.1473
1.546000	1.2186
1.730000	1.2718
1.774000	1.2846
1.805000	1.2935
1.888000	1.3215
2.043000	1.3692
2.063000	1.3757
2.219000	1.4229
2.230000	1.4234

Stokes and Levien [34]. Isopiestic measurements, reference electrolyte is H_2SO_4. Assigned weight is 1.0.

m/mol·kg^{-1}	$\phi_{298.15}$
2.064000	1.3745
2.240000	1.4315
2.278000	1.4427
2.392000	1.4765
2.871000	1.6307
3.369000	1.7839
4.075000	1.9907
4.191000	2.0224
4.211000	2.0267
5.199000	2.2922
5.383000	2.3367
5.834000	2.4542
6.310000	2.5649
6.439000	2.5927

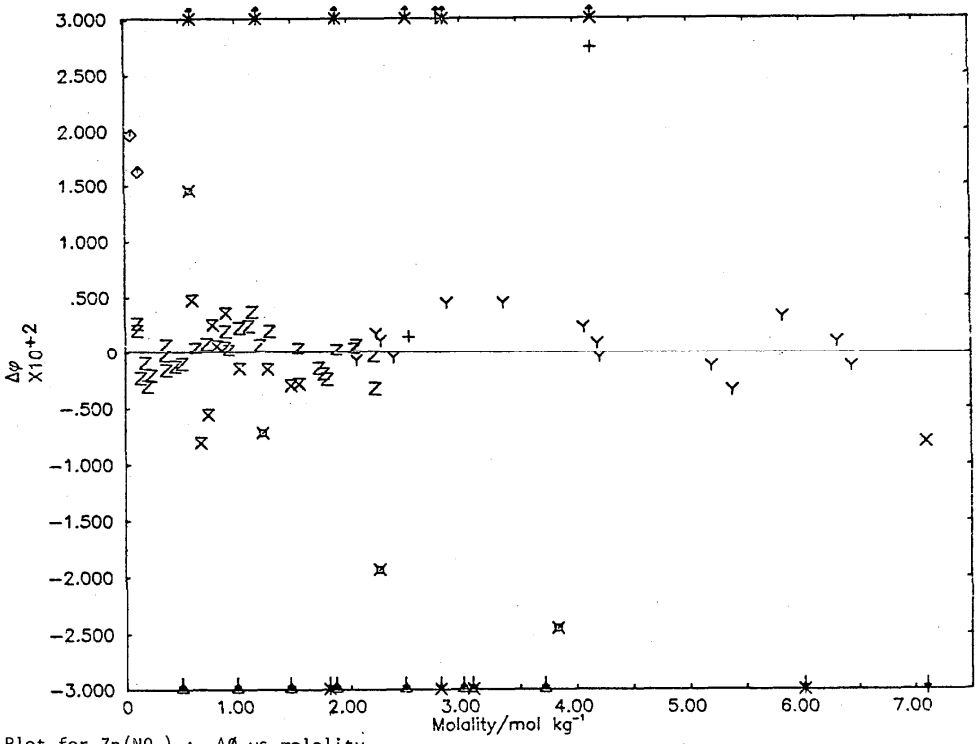
Yakimov and Guzhavina [50]. Vapor pressure measurements. Assigned weight is 0.10.

m/mol·kg^{-1}	$\phi_{298.15}$
3.833000	1.8936
3.082000	1.6589
2.265000	1.4182
1.231000	1.1196
.589000	.9710

Comments

The recent work of Motornaya et al. [49] is in excellent agreement with the results of the careful experiments of Stokes and Levien [34]. The rest of the data is largely scattered.

Stokes and Levien [34] have performed measurements on the cell Zn-Hg (2 phase amalgam); $Zn(NO_3)_2$ (m_1), $Zn(NO_3)_2$(m_2); Zn-Hg (2 phase amalgam) from which, in combination with activity coefficients, they have calculated transference numbers for $Zn(NO_3)_2$. The absence of independent transference numbers prevents us from using these measurements to calculate activity coefficients for this system.



Deviation Plot for $Zn(NO_3)_2$: $\Delta\phi$ vs molality

- Dieterici [46], vapor pressure
- Ewing and Fisher [47], vapor pressure measurements at 20°C
- Ewing and Fisher [47], vapor pressure measurements at 30°C
- Jones et al. [48], freezing point depression
- Motornaya et al. [49], isopiestic vs $CaCl_2$
- Stokes and Levien [34], isopiestic vs KCl
- Stokes and Levien [34], isopiestic vs H_2SO_4
- Yakimov and Guzhavina [50], vapor pressure

$Zn(C_7H_7O_3S)_2$

Recommended Values for the mean activity and osmotic coefficient of zinc p-toluene sulfonate, $Zn(C_7H_7O_3S)_2$, in H_2O at 298.15 K

m/mol·kg^{-1}	γ	ϕ	a_w	ΔG^{ex}/J·kg^{-1}
.001	.8884	.9622	.999948	-1.
.002	.8505	.9492	.999897	-2.
.003	.8241	.9400	.999848	-3.
.004	.8034	.9328	.999798	-5.
.005	.7862	.9269	.999750	-6.
.006	.7715	.9218	.999701	-8.
.007	.7586	.9173	.999653	-10.
.008	.7470	.9133	.999605	-12.
.009	.7366	.9097	.999558	-14.
.010	.7271	.9064	.999510	-17.
.020	.6610	.8837	.999045	-44.
.030	.6203	.8701	.998590	-78.
.040	.5911	.8605	.998141	-115.
.050	.5683	.8532	.997697	-156.
.060	.5498	.8474	.997256	-199.
.070	.5343	.8426	.996817	-244.
.080	.5209	.8385	.996381	-292.
.090	.5092	.8350	.995947	-341.
.100	.4988	.8319	.995514	-392.
.200	.4325	.8126	.991255	-968.
.300	.3953	.8011	.987096	-1627.

m/mol·kg^{-1}	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0002	.0004	.0003
.010	.0010	.0024	.0017
.100	.0024	.0080	.0040
.300	.0036	.0080	.0032

Coefficients of Correlating Equations

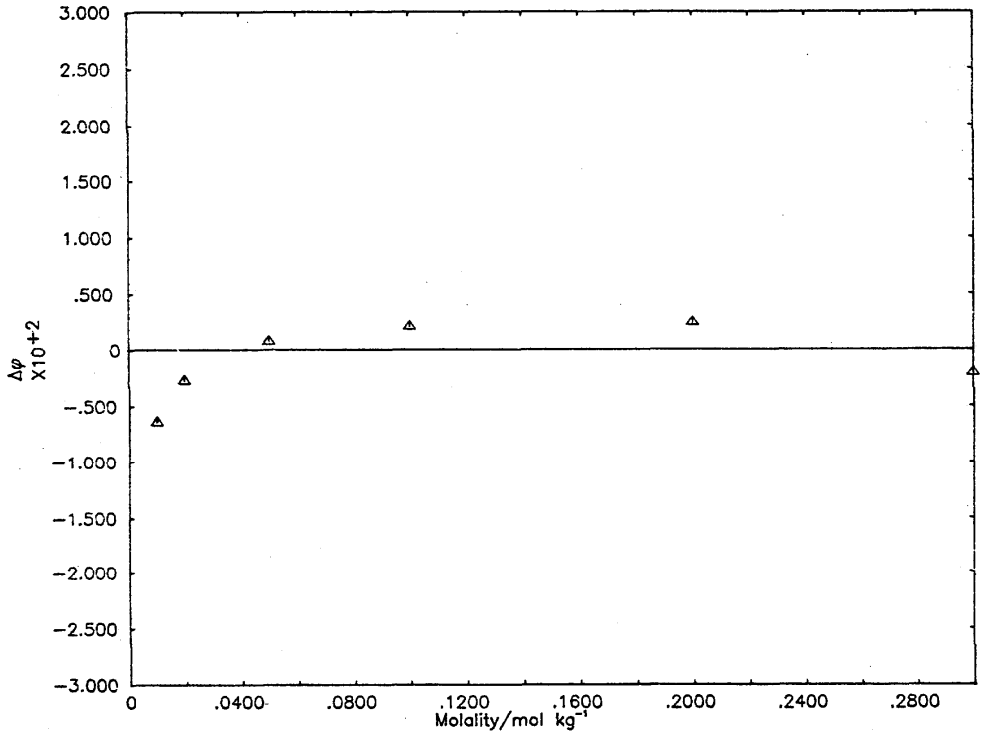
	Eqs 1		Eqs 2		Eqs 3	
Par	coefficient	σ(coeff)	coefficient	σ(coeff)	coefficient	σ(coeff)
1	.1656450715+01	.695-01	-.3667255232+01	.131+01	.9209325677+01	.233+00
2	-.2005284867+00	.618-01	.3473024298+02	.912+01	-.1281003438+02	.928+00
3			-.5966828227+02	.218+02	.7075251500+01	.969+00
4			.4012995258+02	.172+02		

σ(eqs 1) = .399-02
σ(eqs 2) = .438-02
σ(eqs 3) = .213-02

Experimental Data Employed in Generation of Correlating Equations

Bonner et al. [51]. Vapor pressure osmometry and isopiestic measurements performed at 37°C, reference electrolyte was NaCl [11b]. The authors do not report the measured isopiestic molalities. The data were adjusted to 25°C using the measured temperature dependency of the osmotic coefficient of copper p-toluene sulfonate [52]. Assigned weight is 1.0.

m/mol·kg^{-1}	$\phi_{298.15}$
.010000	.9000
.020000	.8810
.050000	.8540
.100000	.8340
.200000	.8150
.300000	.7990



Deviation Plot for $Zn(C_7H_7O_3S)_2$: $\Delta\phi$ vs molality

△ Bonner et al. [51], isopiestic vs NaCl and vapor pressure osmometry

$Cd(ClO_4)_2$

Recommended Values for the mean activity and osmotic coefficient of $Cd(ClO_4)_2$ in H_2O at 298.15 K

m/mol·kg^{-1}	γ	ϕ	a_w	ΔG^{ex}/J·kg^{-1}
.001	.8904	.9633	.999948	-1.
.002	.8541	.9512	.999897	-2.
.003	.8291	.9430	.999847	-3.
.004	.8098	.9366	.999798	-4.
.005	.7938	.9315	.999748	-6.
.006	.7803	.9271	.999699	-8.
.007	.7685	.9234	.999651	-10.
.008	.7580	.9201	.999602	-12.
.009	.7486	.9172	.999554	-14.
.010	.7400	.9146	.999506	-16.
.020	.6822	.8982	.999030	-42.
.030	.6481	.8900	.998558	-72.
.040	.6246	.8854	.998088	-106.
.050	.6072	.8829	.997617	-142.
.060	.5935	.8816	.997145	-180.
.070	.5825	.8813	.996672	-219.
.080	.5735	.8815	.996196	-260.
.090	.5660	.8822	.995718	-302.
.100	.5597	.8833	.995237	-345.
.200	.5300	.9042	.990274	-802.
.300	.5273	.9327	.984991	-1277.
.400	.5364	.9647	.979361	-1748.
.500	.5528	.9992	.973360	-2201.
.600	.5752	1.0358	.966968	-2627.
.700	.6030	1.0745	.960163	-3021.
.800	.6360	1.1153	.952923	-3378.
.900	.6745	1.1580	.945230	-3693.
1.000	.7188	1.2027	.937065	-3963.
1.250	.8593	1.3233	.914482	-4414.
1.500	1.0535	1.4564	.888631	-4511.
1.750	1.3220	1.6023	.859374	-4206.
1.928	1.5753	1.7140	.836438	-3722.

m/mol·kg^{-1}	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0005	.0010	.0009
.010	.0029	.0066	.0049
.100	.0074	.0233	.0131
1.000	.0098	.0228	.0164
1.928	.0087	.0258	.0406

Coefficients of Correlating Equations

Par	Eqs 1 coefficient	Eqs 1 σ(coeff)	Eqs 2 coefficient	Eqs 2 σ(coeff)	Eqs 3 coefficient	Eqs 3 σ(coeff)
1	.1925282146+01	.186+00	.2758501643+01	.160+00	.9827333339+01	.626+00
2	.4514899862+00	.874-01	.4728567850+01	.269+00	-.1236301718+02	.169+01
3	.1584100571+00	.297-01	-.6630687962+00	.115+00	.8275912476+01	.156+01
4					-.2043632974+01	.477+00

σ(eqs 1) = .157-01
σ(eqs 2) = .146-01
σ(eqs 3) = .161-01

Experimental Data Employed in Generation of Correlating Equations

Pan and Ni [53]. Isopiestic measurements, reference salt is KCl. Assigned weight is 1.0.

m/mol·kg^{-1}	$\phi_{298.15}$
.135000	.8975
.252000	.9173
.273000	.9315
.312000	.9388
.376000	.9576
.425000	.9719
.435000	.9769
.507000	.9855
.726000	1.0770
1.104000	1.2488
1.512000	1.5030
1.748000	1.5770
1.845000	1.6459
1.904000	1.7009
1.928000	1.7241

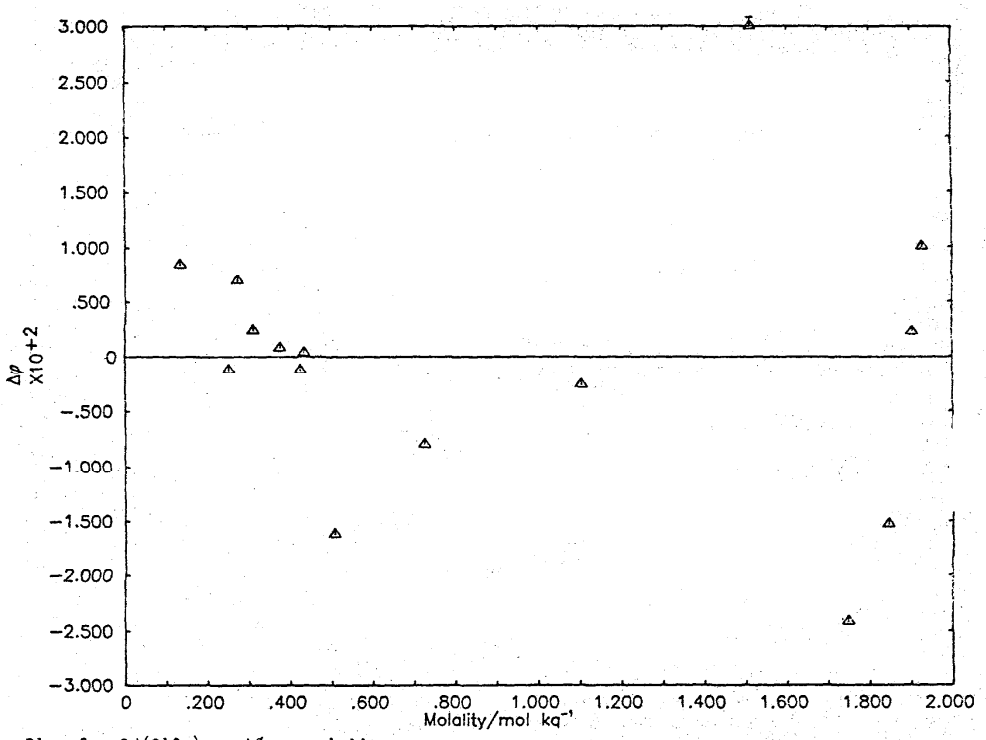
Kalman et al. [54]. Isopiestic measurements. Authors do not give the essential experimental data for this system. They report only their calculated activity coefficients. Assigned weight is zero. The results of Kalman et al. differ significantly from our final values and we do not present a deviation plot.

m/mol·kg^{-1}	$\gamma_{298.15}$
0.3	0.656
0.4	0.688
0.5	0.728
0.6	0.774
0.7	0.828
0.8	0.872
0.9	0.973
1.0	1.088
1.2	1.297
1.4	1.563
1.6	1.915
1.8	2.392
2.0	3.006
2.5	5.368
3.0	9.62
3.5	17.2
4.0	31.0
4.5	54.5
4.666 (sat)	65.3

Comments

We have selected the results of the isopiestic measurements of Pan and Ni [53] rather than the results of Kalman et al. [54], who did not report their essential experimental data. An additional, carefully done, set of measurements would be of value.

Jena and Prasad [55] report measurements on concentration cells with transference, both with and without the presence of a salt bridge. The results involving a salt bridge involve unknown liquid junction potentials and we have chosen not to treat those measurements. The results obtained without the use of a salt bridge could not be treated in the absence of reliable transference numbers. The diffusion measurements of Reilly and Stokes [63] cover the range 0.05 to 1.0 mol·l^{-1}. Since the method of obtaining activity coefficients from diffusion measurements is valid only for very dilute solutions, we have not utilized their data.



Deviation Plot for $Cd(ClO_4)_2$: ΔØ vs molality

▲ Pan and Ni [53], isopiestic vs KCl

$Cd(NO_2)_2$

Recommended Values for the mean activity and osmotic coefficient of $Cd(NO_2)_2$ in H_2O at 298.15 K

m/mol·kg^{-1}	γ	ϕ	a_w	ΔG^{ex}/J·kg^{-1}
.001	.8813	.9583	.999948	-1.
.002	.8375	.9417	.999898	-2.
.003	.8058	.9293	.999849	-3.
.004	.7804	.9189	.999801	-5.
.005	.7588	.9100	.999754	-7.
.006	.7400	.9020	.999708	-9.
.007	.7232	.8948	.999662	-11.
.008	.7081	.8881	.999616	-14.
.009	.6943	.8819	.999571	-17.
.010	.6815	.8761	.999527	-19.
.020	.5892	.8313	.999102	-54.
.030	.5296	.7993	.998705	-97.
.040	.4856	.7739	.998328	-148.
.050	.4509	.7527	.997968	-204.
.060	.4225	.7344	.997621	-266.
.070	.3986	.7182	.997287	-332.
.080	.3780	.7038	.996962	-403.
.090	.3600	.6907	.996646	-477.
.100	.3442	.6789	.996338	-554.
.200	.2469	.5974	.993563	-1482.
.300	.1982	.5506	.991113	-2608.
.400	.1682	.5199	.988823	-3875.
.500	.1476	.4989	.986610	-5251.
.600	.1325	.4840	.984427	-6715.
.700	.1210	.4735	.982244	-8253.
.800	.1119	.4662	.980043	-9853.
.900	.1046	.4614	.977809	-11508.
1.000	.0985	.4583	.975533	-13210.
1.250	.0871	.4566	.969623	-17639.
1.500	.0792	.4605	.963357	-22269.
1.750	.0735	.4679	.956710	-27056.
2.000	.0691	.4777	.949678	-31969.
2.250	.0658	.4890	.942264	-36983.
2.500	.0632	.5016	.934478	-42082.
2.750	.0611	.5149	.926330	-47249.
3.000	.0594	.5288	.917835	-52473.
3.250	.0581	.5431	.909008	-57743.
3.500	.0570	.5578	.899865	-63052.
3.750	.0561	.5726	.890424	-68393.
4.000	.0555	.5876	.880703	-73759.
4.250	.0549	.6027	.870724	-79144.
4.500	.0546	.6177	.860506	-84546.
4.750	.0543	.6327	.850073	-89959.
5.000	.0541	.6476	.839449	-95380.
5.250	.0540	.6624	.828658	-100806.
5.500	.0539	.6770	.817726	-106235.
5.750	.0539	.6913	.806681	-111664.
6.000	.0540	.7053	.795551	-117092.
6.250	.0541	.7190	.784366	-122517.
6.500	.0542	.7324	.773154	-127938.
6.750	.0544	.7453	.761949	-133353.
7.000	.0546	.7577	.750780	-138763.
7.250	.0548	.7696	.739679	-144166.
7.500	.0550	.7809	.728681	-149552.
7.750	.0552	.7915	.717817	-154952.
7.840	.0553	.7952	.713945	-156890.

m/mol·kg^{-1}	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0000	.0000	.0000
.010	.0001	.0003	.0002
.100	.0008	.0019	.0006
1.000	.0017	.0059	.0006
2.000	.0016	.0056	.0004
5.000	.0019	.0056	.0003
7.840	.0031	.0058	.0003

Coefficients of Correlating Equations

	Eqs 2		Eqs 3	
Par	coefficient	σ(coeff)	coefficient	σ(coeff)
1	-.3182647978+01	.238+00	.2489247431+01	.288-01
2	.1337688119+02	.609+00	-.9190705467+00	.381-01
3	-.7503383808+01	.642+00	.2072450729+00	.175-01
4	.2769933726+01	.336+00	-.2071611108-01	.267-02
5	-.5640974025+00	.867-01		
6	.4802008727-01	.878-02		

σ(eqs 2) = .345-02
σ(eqs 3) = .336-02

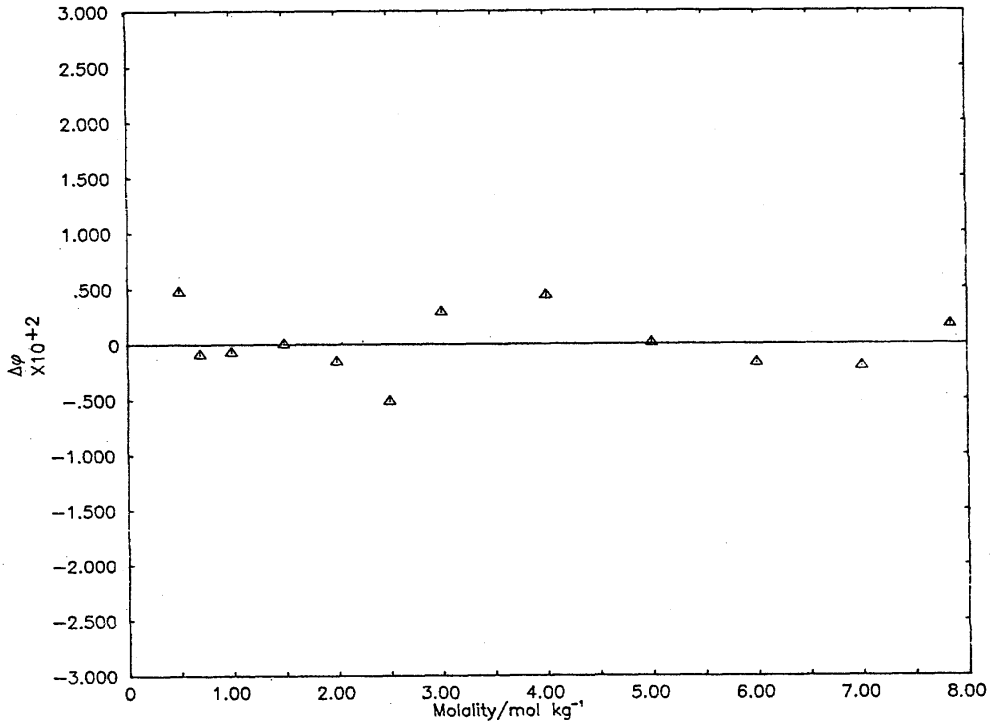
Experimental Data Employed in Generation of Correlating Equations

Chekhunova et al. [56]. Vapor pressure measurements. Assigned weight is 1.0.

m/mol·kg^{-1}	$\phi_{298.15}$
.500000	.5036
.700000	.4726
1.000000	.4576
1.500000	.4605
2.000000	.4761
2.500000	.4964
3.000000	.5317
4.000000	.5920
5.000000	.6477
6.000000	.7036
7.000000	.7556
7.840000	.7969

Comments

The activity coefficients of $Cd(NO_2)_2$ drop to rather low values, a phenomena which is interpretable in terms of a subtantial amount of ion-pairing. While the nitrites of charge type 1-1 show [7] a moderate degree of this type of behavior, the extent demonstrated by $Cd(NO_2)_2$ seems rather large and while we have based our table of recommended values upon the only existing set of measurements, we would feel more comfortable if there were confirmatory data. Eqs 1 could not be used for this data set and the table of recommended values is based on eqs 3.



Deviation Plot for $Cd(NO_2)_2$: ΔØ vs molality

▲ Chekhunova et al. [56], vapor pressure

$Cd(NO_3)_2$

Recommended Values for the mean activity and osmotic coefficient of $Cd(NO_3)_2$ in H_2O at 298.15 K

m/mol·kg^{-1}	$\gamma_\pm$	ϕ	a_w	ΔG^{ex}/J·kg^{-1}
.001	.8884	.9622	.999948	-1.
.002	.8506	.9493	.999897	-2.
.003	.8243	.9402	.999848	-3.
.004	.8037	.9331	.999798	-5.
.005	.7866	.9272	.999749	-6.
.006	.7720	.9222	.999701	-8.
.007	.7593	.9178	.999653	-10.
.008	.7479	.9140	.999605	-12.
.009	.7376	.9105	.999557	-14.
.010	.7283	.9073	.999510	-17.
.020	.6637	.8861	.999043	-44.
.030	.6247	.8741	.998584	-77.
.040	.5971	.8663	.998129	-114.
.050	.5761	.8609	.997676	-153.
.060	.5592	.8570	.997225	-196.
.070	.5454	.8542	.996774	-240.
.080	.5337	.8521	.996323	-286.
.090	.5237	.8506	.995871	-333.
.100	.5149	.8496	.995419	-382.
.200	.4649	.8518	.990834	-919.
.300	.4434	.8626	.986111	-1508.
.400	.4327	.8760	.981241	-2123.
.500	.4276	.8903	.976228	-2751.
.600	.4260	.9051	.971076	-3385.
.700	.4266	.9201	.965789	-4019.
.800	.4289	.9351	.960374	-4651.
.900	.4324	.9502	.954834	-5278.
1.000	.4370	.9652	.949174	-5897.
1.250	.4519	1.0024	.934522	-7407.
1.500	.4706	1.0392	.919201	-8847.
1.750	.4923	1.0757	.903265	-10207.
2.000	.5168	1.1118	.886765	-11479.
2.250	.5439	1.1476	.869749	-12659.
2.500	.5735	1.1831	.852264	-13743.
2.638	.5909	1.2026	.842429	-14298.

m/mol·kg^{-1}	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0000	.0001	.0000
.010	.0002	.0004	.0003
.100	.0006	.0017	.0009
1.000	.0006	.0033	.0015
2.000	.0008	.0031	.0016
2.638	.0012	.0029	.0017

Coefficients of Correlating Equations

	Eqs 1		Eqs 2		Eqs 3	
Par	coefficient	σ(coeff)	coefficient	σ(coeff)	coefficient	σ(coeff)
1	.1585019220+01	.924-02	.1178436006+01	.125+00	.9086181054+01	.125+00
2	.2601065525+00	.160-02	.8130502368+01	.415+00	-.1234869965+02	.419+00
3			-.4356174299+01	.541+00	.9992863487+01	.545+00
4			.1645689513+01	.313+00	-.4216167554+01	.315+00
5			-.2723912106+00	.667-01	.7153523847+00	.673-01

σ(eqs 1) = .306-02
σ(eqs 2) = .311-02
σ(eqs 3) = .314-02

Experimental Data Employed in Generation of Correlating Equations

Dieterici [46]. Vapor pressure measurements performed at 0°C. The Φ_L and Φ_c data for $Cd(NO_3)_2$ given in the table of auxiliary data were used to adjust these and the other data obtained at temperatures other than 25°C to that temperature. Assigned weight is zero.

m/mol·kg^{-1}	$\phi_{298.15}$
.501000	.7720
.998000	.8700
1.496000	.9610
1.994000	1.0450
2.500000	1.1100

Ewing and Guyer [57]. Vapor pressure measurements at 20°C. Assigned weight is zero.

m/mol·kg^{-1}	$\phi_{298.15}$
.517000	.9910
1.289000	1.0660
1.720000	1.1540

Ewing and Guyer [57]. Vapor pressure measurements at 30°C. Assigned weight is zero.

m/mol·kg^{-1}	$\phi_{298.15}$
.517000	.9050
1.289000	1.0430
1.720000	1.1220

Ewing and Guyer [57]. Vapor pressure measurements at 40°C. Assigned weight is zero.

m/mol·kg^{-1}	$\phi_{298.15}$
.517000	.8730
1.289000	1.0230
1.720000	1.1030

Jones [58]. Freezing point depression measurements. Assigned weight is zero.

m/mol·kg^{-1}	$\phi_{298.15}$
.001000	.9745
.002980	.9560
.004920	.9530
.006910	.9373
.008760	.9324
.020000	.9269
.036020	.9234
.048850	.9230

Jones et al. [48]. Freezing point depression measurements. Assigned weight is zero.

m/mol·kg^{-1}	$\phi_{298.15}$
.084800	.9399
.170300	.9114
.343200	.9436

Kovyrzina et al. [59]. Vapor pressure measurements. Assigned weight is zero.

m/mol·kg^{-1}	$\phi_{298.15}$
.250000	1.5273
.500000	2.2492
1.000000	1.8349
1.500000	1.5942
2.500000	1.1012

Motornaya et al. [49]. Isopiestic measurements, reference salt is $CaCl_2$. Assigned weight is 0.50.

m/mol·kg^{-1}	$\phi_{298.15}$
.640000	.9210
.704000	.9197
.819000	.9305
.840000	.9428
.889000	.9457
.990000	.9534

Motornaya and Ben'yash [60]. Isopiestic measurements. Authors did not give the isopiestic molalities nor did they state which reference electrolyte was used. Assigned weight is 0.50.

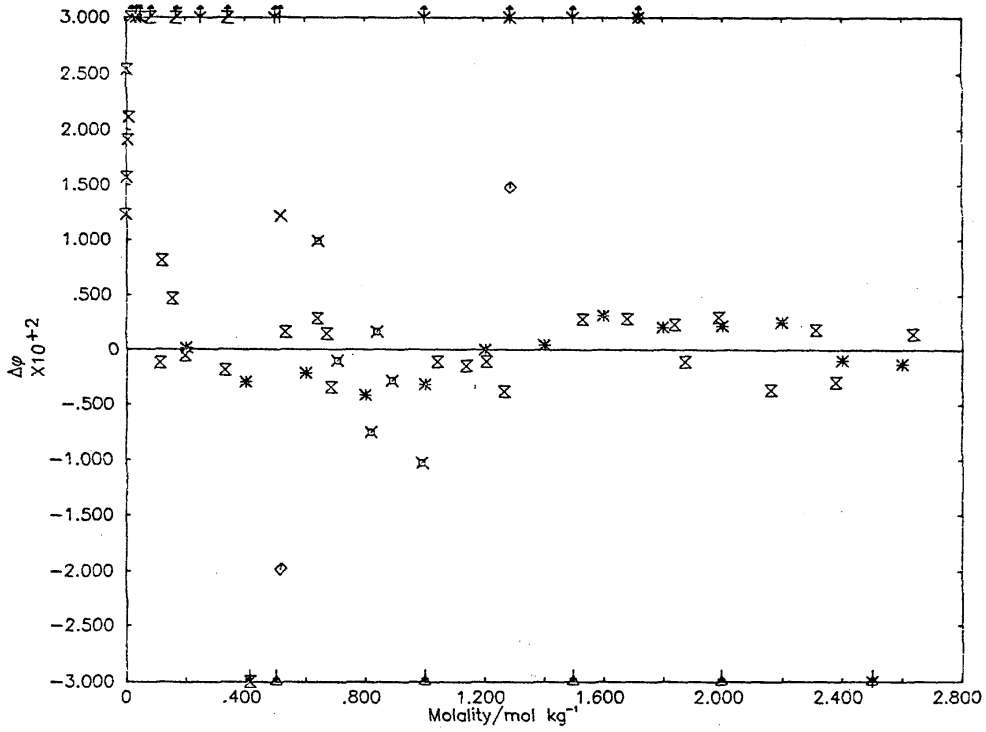
m/mol·kg^{-1}	$\phi_{298.15}$
.200000	.8520
.400000	.8730
.600000	.9030
.800000	.9310
1.000000	.9620
1.200000	.9950
1.400000	1.0250
1.600000	1.0570
1.800000	1.0850
2.000000	1.1140
2.200000	1.1430
2.400000	1.1680
2.600000	1.1960

Robinson, Wilson, and Ayling [61]. Isopiestic measurements, reference electrolyte is KCl. Assigned weight is 1.0.

m/mol·kg^{-1}	$\phi_{298.15}$
.113400	.8476
.121700	.8567
.155900	.8537
.197500	.8511
.330900	.8647
.414100	.7333*
.534500	.8970
.640900	.9141
.673000	.9175
.686300	.9146
1.041000	.9702
1.138000	.9843
1.206000	.9948
1.267000	1.0011
1.531000	1.0466
1.681000	1.0685
1.841000	1.0912
1.873000	1.0924
1.989000	1.1132
2.162000	1.1314
2.315000	1.1587
2.381000	1.1633
2.638000	1.2041

Comments

The recent work of Motornaya et al. [49,60] is in excellent agreement with the results of the careful measurements of Robinson, Wilson, and Ayling [61]. The rest of the data is largely scattered.



Deviation Plot for $Cd(NO_3)_2$: $\Delta\phi$ vs molality

- Dieterici [46], vapor pressure
- Ewing and Guyer [57], vapor pressure measurements at 20°C
- Ewing and Guyer [57], vapor pressure measurements at 30°C
- Ewing and Guyer [57], vapor pressure measurements at 40°C
- Jones [58], freezing point depression
- Jones et al. [48], freezing point depression
- Kovyrzina et al. [59], vapor pressure
- Motornaya et al. [49], isopiestic vs $CaCl_2$
- Motornaya and Ben'yash [60], isopiestic vs ?
- Robinson, Wilson, and Ayling [61], isopiestic vs KCl

$Cd(C_7H_7O_3S)_2$

Recommended Values for the mean activity and osmotic coefficient of cadmium p-toluene sulfonate, $Cd(C_7H_7O_3S)_2$, in H_2O at 298.15 K

m/mol·kg^{-1}	γ	ϕ	a_w	ΔG^{ex}/J·kg^{-1}
.001	.8884	.9622	.999948	-1.
.002	.8506	.9492	.999897	-2.
.003	.8242	.9401	.999848	-3.
.004	.8034	.9329	.999798	-5.
.005	.7863	.9269	.999750	-6.
.006	.7715	.9218	.999701	-8.
.007	.7586	.9173	.999653	-10.
.008	.7471	.9133	.999605	-12.
.009	.7367	.9097	.999558	-14.
.010	.7272	.9064	.999510	-17.
.020	.6609	.8835	.999045	-44.
.030	.6199	.8696	.998591	-78.
.040	.5903	.8596	.998143	-115.
.050	.5673	.8520	.997700	-156.
.060	.5485	.8458	.997261	-199.
.070	.5326	.8406	.996825	-245.
.080	.5189	.8361	.996391	-293.
.090	.5068	.8322	.995960	-343.
.100	.4961	.8287	.995531	-394.
.200	.4268	.8049	.991337	-976.
.300	.3867	.7887	.987293	-1648.
.400	.3582	.7748	.983390	-2384.
.500	.3357	.7617	.979628	-3172.
.600	.3170	.7489	.976009	-4006.

m/mol·kg^{-1}	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0002	.0003	.0003
.010	.0009	.0022	.0016
.100	.0018	.0066	.0033
.600	.0029	.0071	.0022

Coefficients of Correlating Equations

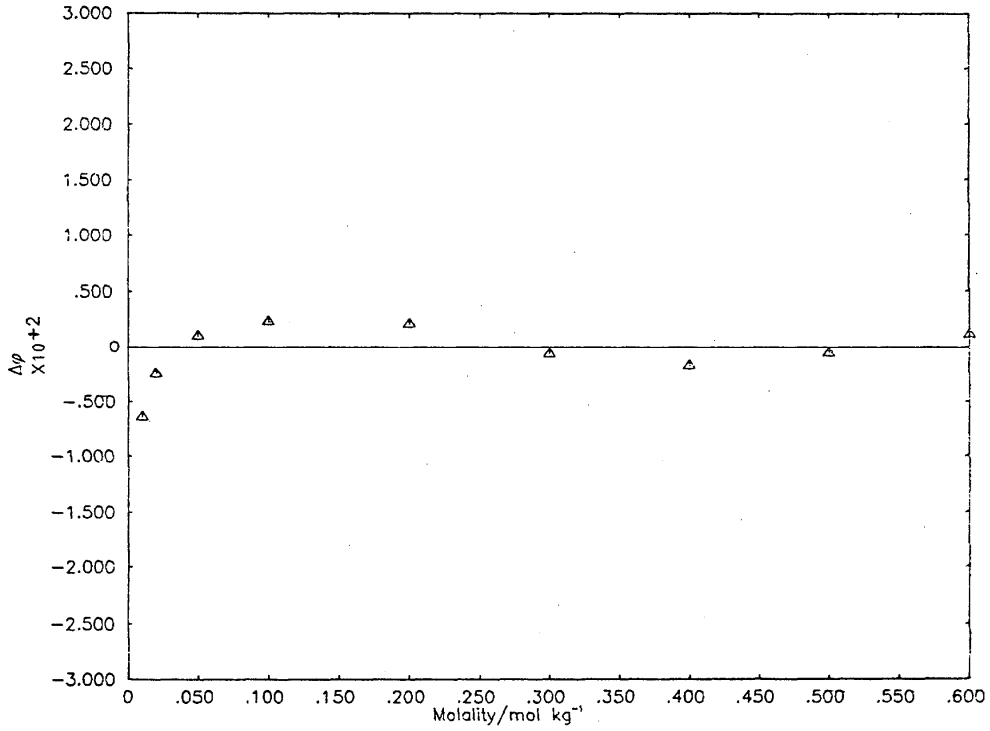
	Eqs 1		Eqs 2		Eqs 3	
Par	coefficient	σ(coeff)	coefficient	σ(coeff)	coefficient	σ(coeff)
1	.1680063040+01	.697-01	-.3488542177+01	.933+00	.8671712572+01	.192+00
2	-.2989528189+00	.834-01	.3521417670+02	.680+01	-.1098276536+02	.527+00
3	.1252038044-02	.808-01	-.7181067190+02	.190+02	.5274732280+01	.384+00
4			.7604224814+02	.232+02		
5			-.3074143207+02	.104+02		

σ(eqs 1) = .324-02
σ(eqs 2) = .338-02
σ(eqs 3) = .386-02

Experimental Data Employed in Generation of Correlating Equations

Bonner, Breazeale, and Rushing [52]. Vapor pressure osmometry and isopiestic measurements performed at 37°C, reference electrolyte was NaCl [11b]. The authors do not report the measured isopiestic molalities. The data were adjusted to 25°C using the measured temperature dependency of the osmotic coefficient of copper p-toluene sulfonate [52]. Assigned weight is 1.0.

m/mol·kg^{-1}	$\phi_{298.15}$
.010000	.9000
.020000	.8810
.050000	.8530
.100000	.8310
.200000	.8070
.300000	.7880
.400000	.7730
.500000	.7610
.600000	.7500



Deviation Plot for $Cd(C_7H_7O_3S)_2$: $\Delta\phi$ vs molality

△ Bonner, Breazeale, and Rushing [52], vapor pressure osmometry and isopiestic vs NaCl

2.3. Systems Not Treated

Kertèsz [62] reports measurements on the cell Cd(2 phase amalgam); $CdR_2(m)$; KCl(sat); $Hg_2Cl_2(s)$, $Hg(\ell)$ where R is trichloroacetate (CCl_3COO), sulfosalicylate ($C_6H_3OHCOOHSO_3$), or sulfanilate ($C_6H_4NH_2SO_3$). The use of these data to obtain activity coefficients involves the interpretation of unknown liquid junction potentials and we have chosen not to treat these data.

The cadmium halides present a particularly difficult problem in data analysis. In attempting to apply the correlating equations which we have used previously, we find that these equations do not represent the experimental data adequately. The reason for this is that the activity coefficients drop rapidly to very low values, i.e., γ for $CdCl_2$ is 0.22 at $m = 0.10$ mol·kg^{-1} [64]. This type of behavior, which is typical of highly associated electrolytes, makes it a very difficult task for polynomial representations to reconcile both the Debye-Hückel limiting law and the experimental data, hence eqs 2 and 3 (see section 2.1) cannot be used. Eqs 1 are also inappropriate since too negative a value of the B coefficient is required which, in turn, causes the osmotic coefficient to become an imaginary number. While the experimental data themselves can be represented by discarding the Debye-Hückel limiting law, the author is not completely satisfied by that type of treatment and attempts are currently underway to devise a more satisfactory method of analysis. We note that Reilly and Stokes [63] in treating the data for $CdCl_2$ used an association model and assumptions about single-ion activities. The activity coefficients they [63] calculate for $CdCl_2$ and the ones tabulated by Robinson and Stokes [64] for $CdBr_2$ and CdI_2 probably represent the best numbers presently available for these systems.

We note that, for the bi-univalent compounds of mercury, there exist only the old boiling point elevation measurements of Kahlenburg [65] and the freezing point depression measurements of Biltz [28] for $HgCl_2$ and the freezing point depression measurements of Jones and Caldwell [66] for $Hg(CN)_2$. None of these data sets is sufficiently precise to warrant the generation of a set of recommended activity and osmotic coefficients. This is unfortunate in view of the environmental and general chemical importance of mercury compounds.

2.4. Previous Compilations and Evaluations

Previous evaluations and compilations of the activity and osmotic coefficients for six of the systems dealt with herein may be found in the book by Harned and Owen [67], the tables of Stokes [19] and Robinson and Stokes [64], and in the papers of Wu and Hamer [68] and Pitzer and Mayorga [69]. None of these previous reviews has presented data for ethylene bis(trimethylammonium) chloride and iodide, ZnF_2, zinc p-toluene sulfonate, $Cd(NO_2)_2$, or cadmium p-toluene sulfonate.

The tables of Robinson and Stokes [64] and Stokes [19] appear to be based largely upon their own isopiestic measurements; similarly, Harned and Owen [68] based their tables upon the calculations of Stokes [19]. For the compounds being examined in this paper, the coefficients of Pitzer and Mayorga [69] are based exclusively upon the smoothed osmotic coefficients given by Robinson and Stokes [64]. Wu and Hamer [68] utilized a larger data base than the others [19, 64, 67, 69] but, unfortunately, did not state how the various data sources were weighted to obtain their final tables of recommended values.

For the six systems of interest, there is summarized in table 1 the values of the activity coefficients at the maximum molality for which comparisons may be made between our evaluation and previous evaluations.

The evaluation of Wu and Hamer [68] for $ZnCl_2$ and $ZnBr_2$ shows unusually large differences between the numbers which we and Stokes [64] give for the values of the activity coefficients at the maximum possible molalities. We believe that the evaluations of Wu and Hamer [68] are in error at these extrema. For $ZnCl_2$ the numbers they [68] tabulate are in substantial agreement with our own up to 20 mol·kg^{-1}, while for $ZnBr_2$ the numbers they [68] give are systematically lower than the ones recommended in our own table.

The differences observed for ZnI_2 are undoubtedly due to the inclusion of additional data other than isopiestic in our evaluation procedure. The agreement for the other systems is satisfactory.

2.5. Relationship of Activity Coefficients to Solubility Data

Knowledge of the stoichiometric solubility (m_{sat}), the activity coefficient and activity of water at saturation, and a knowledge of the number (n) of waters of hydration to be associated with the solid phase in equilibrium with its saturated solution in pure water can be used to calculate the standard Gibbs energy of solution (ΔG°_{soln}). For an electrolyte $M_{\nu_+}X_{\nu_-}$,

$$\Delta G^\circ_{soln} = -RT\ell n\, a_w^n (\nu_+^{\nu_+}\nu_-^{\nu_-})\,(m\gamma)^\nu$$

where ΔG°_{soln} refers to the process

$$M_{\nu_+}X_{\nu_-}\cdot n H_2O(s) = \nu_+ M^{z+}(aq) + \nu_- X^{z-}(aq) + n H_2O(liq)$$

The solubility product (K_{s0}) is calculable using

$$K_{s0} = a_w^n (\nu_+^{\nu_+}\nu_-^{\nu_-})\,(m\gamma)^\nu$$

This sort of analysis can be useful in establishing the value of the solubility product or in the construction of a thermodynamic data network.

3. Auxiliary Data

Osmotic Coefficient Data

Evaluated data for several reference systems were needed in treating the isopiestic data. These systems and the sources of the evaluated data are: KCl[1], NaCl[1], $CaCl_2$[2], and H_2SO_4[4].

Relative Apparent Molal Enthalpy Data

The coefficients for the equation $\Phi_L/\mathrm{J\cdot mol^{-1}} = \sum_{i=1}^{N} \alpha_i m^{i/2}$ were obtained by a least squares fit to the values of Φ_L calculated from the enthalpies of formation as a function of the molality as given in NBS Technical Note 270-30 [70]. The coefficients are given in table 2.

Apparent Molal Heat Capacity Data

The coefficients for the equation $\Phi_c/\mathrm{J\cdot mol^{-1}\cdot K^{-1}} = \Phi_c^\circ + \sum_{i=1}^{N} \beta_i m^{i/2}$ are given in table 3.

Transference Number Data

The coefficients for the equation $t_+ = t_+^\circ + \sum_{i=1}^{N} \alpha_i C^{i/2}$, where C is the molarity in $\mathrm{mol\cdot dm^{-3}}$, are given in table 4. The transference numbers for $ZnBr_2$ are based on the measurements of Samis [73] performed at 40 °C with $\partial t_+^\circ/\partial T$ being estimated from the measurements of Keenan et al. [74] on $CaCl_2$ at several temperatures. The coefficients for $ZnCl_2$ and $Zn(ClO_4)_2$ are based on a fit to the Hittorf data of Agnew and Paterson [75, 76].

Density Data

Densities of $ZnCl_2$ and $Zn(ClO_4)_2$ solutions were calculated from the coefficients given in table 1 of the paper by Agnew and Paterson [75, 76]. The densities of $ZnBr_2$ solutions were calculated from the equation: $\rho/\mathrm{g\cdot cm^{-3}} = 0.997074 + 0.19744\ c - 0.0096776\ c^{3/2}$, where c is the molarity in $\mathrm{mol\cdot dm^{-3}}$. This latter equation was obtained using the apparent molal volume data tabulated by Millero [77].

4. Acknowledgments

The support of this research by the Division of Energy Storage Systems of the United States Department of Energy and by the Office of Standard Reference Data of the National Bureau of Standards is gratefully acknowledged.

Table 1. Comparison of Activity Coefficients from Different Sources

System	Maximum molality/mol·kg^{-1} for which data exist	γ[19,64]	γ[this evaluation]	molality/ mol·kg^{-1}	Δ(%)[a]	γ[68]	γ [this evaluation]	molality/ mol·kg^{-1}	Δ(%)	γ[69]	γ [this evaluation]	molality/ mol·kg^{-1}	Δ(%)
$ZnCl_2$	23.193	3.46	3.433	22.0	-0.8	4.44	3.433	22.0	-29.3	0.318	0.315	1.2	-1.0
$ZnBr_2$	20.100	7.86	7.965	20.0	+1.3	3.50	7.965	20.0	56.1	0.566	0.575	1.6	1.6
ZnI_2	11.892	6.41[b]	6.758	11.892	+5.1	3.59	3.744	9.0	4.1	0.706	0.756	0.8	6.6
$Zn(ClO_4)_2$	4.311	60.9[b]	59.3	4.311	-2.7	37.83	39.097	4.0	3.2	2.626	2.714	2.0	3.2
$Zn(NO_3)_2$	7.103	6.38	6.480	6.0	+1.1	6.80	6.480	6.0	-4.9	0.813	0.821	2.0	1.0
$Cd(NO_3)_2$	2.638	0.573	0.574	2.5	+0.2	0.568	0.574	2.5	1.0	0.570	0.574	2.5	0.7

[a] Δ(%) is defined to be [(this evaluation - previous evaluation) x 100%]/[this evaluation].

[b] Interpolated value.

Table 2. Coefficients Used to Calculate Relative Apparent Molal Enthalpies

System	Range of Validity molality/mol·kg^{-1}	α_1	α_2	α_3	α_4	α_5	α_6	α_7	α_8
$ZnCl_2$	0 to 1.39	10263.4	3105.56	4776.8	-2953.43	---------	-------	--------	-------
$Zn(NO_3)_2$	0 to 6.94	10263.4	-11248.1	-47636.7	129340.0	-129489.0	64295.4	-15827.2	1543.31

Table 3. Coefficients Used to Calculate Apparent Molal Heat Capacities

System	Range of Validity molality/mol·kg^{-1}	ϕ°_c	β_1	β_2	Reference
$ZnCl_2$	0.25 to 17.12	-169.4	147.63	-11.69	[71]
$Zn(NO_3)_2$	0.11 to 2.90	-186.6	146.44	-----	[72]

Table 4. Coefficients Used to Calculate Transference Numbers

System	Range of Validity C/mol·dm^{-3}	t°_+	α_1	α_2	α_3	α_4	α_5
$ZnCl_2$	0 to 3.37	0.419495	-0.431755	1.10289	-1.46948	0.691174	-0.111814
$Zn(ClO_4)_2$	0 to 2.43	0.414653	-0.0619701	-0.0166223	-	-	-
$ZnBr_2$	0 to 0.15	0.395403	0.0998432	-0.0426553	-	-	-

Additional auxiliary data follow:

ΔH°_{fus} = 6008 J·mol^{-1} [78]

Δb = -0.197 J·K^{-2}·mol^{-1} [78]

R = 8.31441 J·K^{-1}·mol^{-1} [79]

A = 0.51084 $\log_e 10$ kg$^{1/2}$·mol$^{-1/2}$ [2]

B_T = -992 cm^3·mol^{-1} at 25 °C [80]

ΔC°_{fus} = 38.1 J·mol^{-1}K^{-1} [73]

T_{fus} = 273.15 K for water [10]

F = 96484.56 C·mol^{-1} [74]

P° = 3168.6 Pa (23.7627 torr) for water at 25 °C [81]

5. REFERENCES

[1] Hamer, W. J., and Wu, Y. C., J. Phys. Chem. Ref. Data 1, 1047 (1972).

[2] Staples, B. R., and Nuttall, R. L., J. Phys. Chem. Ref. Data 6, 385 (1977).

[3] Goldberg, R. N., and Nuttall, R. L., J. Phys. Chem. Ref. Data 7, 263 (1978).

[4] Staples, B. R., "Activity and Osmotic Coefficients of Aqueous Sulfuric Acid," J. Phys. Chem. Ref. Data in press.

[5] Goldberg, R. N., Nuttall, R. L., and Staples, B. R., "Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Iron Chloride and the Bi-Univalent Compounds of Nickel and Cobalt," J. Phys. Chem. Ref. Data 8, 923 (1979).

[6] Goldberg, R. N., "Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Bi-Univalent Compounds of Lead, Copper, Manganese, and Uranium," J. Phys. Chem. Ref. Data 8, 1005 (1979).

[7] Staples, B. R., "Activity and Osmotic Coefficients of Aqueous Metal Nitrites," manuscript in review.

[8] Staples, B. R., and Nuttall, R. L., Computer Programs for the Evaluation of Activity and Osmotic Coefficients, Nat. Bur. Stand. (U.S.) Tech. Note 928. U.S. Gov't. Printing Office, Washington, D.C. (1976).

[9] Goldberg, R. N., Staples, B. R., Nuttall, R. L., and Arbuckle, R., A Bibliography of Sources of Experimental Data Leading to Activity or Osmotic Coefficients for Polyvalent Electrolytes in Aqueous Solution, Nat. Bur. Stand. Spec. Pub. 485, U.S. Gov't. Printing Office, Washington, D.C. (1977)

[10] McGlashan, M. L., Manual of Symbols and Terminology for Physicochemical Quantities and Units, Butterworths, London (1970).

[11] Linke, W. F., and Seidell, A., Solubilities: Inorganic and Metal-Organic Compounds -- A Compilation of Solubility Data from The Periodical Literature, Volume I: A-Ir and Volume II: K-Z, Volume I: D. Van Nostrand Co., Princeton, NJ (1958); Volume II: American Chemical Society, Washington, D.C. (1965).

[11a] Bonner, O. D., and Kim, S. J., J. Phys. Chem. 73, 1367 (1969).

[11b] Bonner, O. D., personal communication.

[12] Cook, R. O., Davies, A., and Staveley, L. A. K., J. Chem. Thermodyn. 3, 907 (1971).

[13] Ivett, R. W., and deVries, T., J. Am. Chem. Soc. 63, 2821 (1941).

[14] Fricke, R., and Havestadt, L., Z. Elektrochem. 33, 441 (1927).

[15] Ishikawa and Takai, Rikagaku Kenkyusho Iho 16, 1251 (1937).

[16] Jones, H. C., Z. Phys. Chem. (Leipzig) 11, 529 (1893).

[17] Jones, H. C., and Getman, F. H., Z. Phys. Chem. 46, 244 (1903).

[18] Pan, C. F., "Osmotic and Activity Coefficients in $BaCl_2$-$ZnCl_2$-H_2O at 25°C," Thesis, University of (1966).

[19] Stokes, R. H., Trans. Faraday Soc. 44, 295 (1948).

[20] Brüll, L., Gazz. Chim. Ital. 64, 261 (1934).

[21] Egan, D. M., and Partington, J. R., J. Chem. Soc. 157 (1943).

[22] Harris, A. C., and Parton, H. N., Trans. Faraday Soc. 36, 1139 (1940).

[23] Horsch, W. G., J. Am. Chem. Soc. 41, 1787 (1919).

[24] Jahn, H., Data given in paper by Horsch [23].

[25] Lutfullah, H. S. D., Dunsmore, H. S., and Paterson, R., J. Chem. Soc., Faraday Soc. I 72, 495 (1976).

[26] Robinson, R. A., and Stokes, R. H., Trans. Faraday Soc. 36, 740 (1940).

[27] Scatchard, G., and Tefft, R. F., J. Am. Chem. Soc. 52, 2272 (1930).

[28] Biltz, W., Z. Phys. Chem. (Leipzig) 40, 185 (1902).

[29] Masaki, K., Bull. Chem. Soc. Japan 7, 35 (1932).

[30] Lehfeldt, L., Z. Phys. Chem. (Leipzig) 35, 257 (1900).

[31] Foxton, F., and Shutt, W. J., Trans. Faraday Soc. 23, 480 (1927)

[32] Kaimakov, E. A., and Sharkov, V. I., Zh. Fiz. Khim. 38, 1645 (1964); Russ. J. Phys. Chem. 38, 893 (1964).

[33] Libus, Z., and Sadowska, T., J. Phys. Chem. 74, 3674 (1970).

[34] Stokes, R. H., and Levien, B. J., J. Am. Chem. Soc. 68, 333 (1946).

[35] Lilich, L. S., Chernykh, L. V., and Shelyapina, T. D., Russ. J. Phys. Chem. (Eng. Trans.) 49, 776 (1975); Zh. Fiz. Khim. 49, 1318 (1975).

[36] Sircar, S. C., and Prasad, B., J. Indian Chem. Soc. 31, 483 (1954).

[37] Ishikawa et al., Rikagaku Kenkyusho Iho 15, 339 (1936).

[38] Stokes, R. H., Stokes, J. M., and Robinson, R. A., Trans. Faraday Soc. 40, 533 (1944).

[39] Acheson, D. T., "Vapor Pressure of Saturated Aqueous Solutions of Selected Inorganic Salts," Master's Thesis, Univ. of Maryland (1965).

[40] Parton, H. N., and Mitchell, J. W., Trans. Faraday Soc. 35, 758 (1939).

[41] Stokes, R. H., and Stokes, J. M., Trans. Faraday Soc. 41, 688 (1945).

[42] Stokes, R. H., and Levien, B. J., J. Am. Chem. Soc. 68, 1852 (1946).

[43] Stokes, R. H., Trans. Faraday Soc. 41, 12 (1945).

[44] Bates, R. G., J. Am. Chem. Soc. 60, 2983 (1938).

[45] Partington, J. R., and Torto, F. G., J. Chem. Soc. 216 (1948).

[46] Dieterici, C., Ann. Phys. (Leipzig) 375, 617 (1923).

[47] Ewing, W. W., and Fisher, H. M., J. Am. Chem. Soc. 59, 1046 (1937).

[48] Jones, H. C., Getman, F. H., Bassett, H. P., McMaster, L., and Uhler, H. S., Carnegie Institution of Washington, Publication No. 60., Washington, DC (1907).

[49] Motornaya, G. A., Ben'yash, E. Ya., and Khristoforov, B. S., Izv. Sib. Otd. Akad. Nauk. SSSR. Ser. Khim. Nauk 5, 7 (1969); Chem. Abstr. 72, 136994 (1970).

[50] Yakimov, M. A., and Guzhavina, E. I., Russ. J. Inorg. Chem. (Eng. Trans.) 16, 934 (1971); Zh. Neorg. Khim. 16, 1758 (1971).

[51] Bonner, O. D., Rushing, C., and Torres, A. L., J. Phys. Chem. 72, 4290 (1965).

[52] Bonner, O. D., Breazeale, W. H., and Rushing, C., J. Phys. Chem. 69, 4345 (1965).

[53] Pan, K., and Ni, W. Y., J. Chin. Chem. Soc. Taipei 15, 69 (1968).

[54] Kalman, E., Horn, G., and Schwabe, K., Z. Phys. Chem. (Leipzig) 244, 106 (1970).

[55] Jena, P. K., and Prasad, B., J. Indian Chem. Soc. 31, 480 (1954).

[56] Chekhunova, N. P., Protsenko, P. I., and Venerovskaya, L. N., Russ. J. Phys. Chem. (Eng. Trans.) 43, 1158 (1969).

[57] Ewing, W. W., and Guyer, W. R. F., J. Am. Chem. Soc. 60, 2707 (1938).

[58] Jones, H. C., Z. Phys. Chem. (Leipzig) 11, 529 (1893).

[59] Kovyrzina, V. P., Sidorova, E. E., Zakharwa, T. N., and Berg, L. G., J. Phys. Chem. 40, 809 (1966).

[60] Motornaya, G. A., and Ben'yash, E. Ya., Russ. J. Phys. Chem. (Eng. Trans.); Zh. Fiz. Khim. 47, 2074 (1973).

[61] Robinson, R. A., Wilson, J. M., and Ayling, H. S., J. Am. Chem. Soc. 64, 1469 (1942).

[62] Kertèsz, F., J. Chim. Phys. Phys.-Chim. Biol. 35, 367 (1938).

[63] Reilly, P. J., and Stokes, R. H., Aust. J. Chem. 24, 1361 (1971).

[64] Robinson, R. A., and Stokes, R. H., Electrolyte Solutions, 3rd edition, Butterworth and Co., London, (1970).

[65] Kahlenburg, L., J. Phys. Chem. 5, 339 (1901).

[66] Jones, H. C., and Caldwell, B. P., Am. Chem. J. 25, 349 (1901).

[67] Harned, H. S., and Owen, B. B., The Physical Chemistry of Electrolytic Solutions, 3rd ed., Reinhold Pub. Corp., New York, (1958).

[68] Wu, Y. C., and Hamer, W. J., Electrochemical Data-Part XIV, Nat. Bur. Stand. (U.S.) Report 10052, U.S. Department of Commerce, Washington, DC (1969).

[69] Pitzer, K. S., and Mayorga, G., J. Phys. Chem. 77, 2300 (1973).

[70] Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., and Schumm, R. H., Selected Values of Chemical Thermodynamic Properties, Nat. Bur. Stand. (U.S.) Tech. Note 270-3, U.S. Gov't. Printing Office, Washington, DC (1968).

[71] Karapet'yants, M. Kh., Drakin, S. I., and Lantukhova, L. V., Zh. Fiz. Khim. 41, 2653 (1967); Russ. J. Phys. Chem. (Eng. Trans.) 41, 1436 (1967).

[72] Drakin, S. I., and Yu-min, C., Zh. Fiz. Khim. 38, 2800 (1964); J. Phys. Chem. (Eng. Trans.) 38, 1526 (1964)

[73] Samis, C. S., Trans. Faraday Soc. 33, 469 (1937).

[74] Keenan, A. G., McLeod, H. G., and Gordon, A. R., J. Chem. Phys. 13, 466 (1945).

[75] Agnew, A., and Paterson, R., J. Chem. Soc. Faraday Trans. 1 74, 2885 (1978).

[76] Agnew, A., and Paterson, R., J. Chem. Soc. Faraday Trans. 1 74, 2896 (1978).

[77] Millero, F. J. in "Wa - and Aqueous Solutions: Structure, Thermodynamics, and Transport Properties" (R. A. Horne, editor), Wiley-Interscience, New York, 1972, p. 533.

[78] Lewis, G. N., and Ranc l, M., Thermodynamics, revised by K. S. Pitzer and L. Brewer, 2nd edition, McGraw-Hill Book Co., New Yor (1961).

[79] Cohen, E. R., r, B. N., J. Phys. Chem. Ref. Data 2, 663 (1973).

[80] Keenan, J. ., Keyes, F. G., Hill, P. G., and Moore, J. G., Steam Tables, International Edition-Metric Units, Joh Wiley and Sons, Inc., New York, p. 148 (1969).

[81] Stimson, H ., J. Res. Nat. Bur. Stand. Sect. A 73, 493 (1969).

6. Glossary of Symbols

a_w	Activity of water
Δb	$(\partial \Delta \overline{C}_p / \partial T)_p$
c_B or c	concentration of solute substance B
m_B or m	molality of solute substance
t_i	transference number of ith ion
z_B	charge number of an ion B
A	constant in Debye-Hückel limiting law
A_1	$\lvert z_+ z_- \rvert A$
A_2	$\frac{(\sum_i \nu_i z_i^3)^2}{3\nu \sum_i (\nu_i z_i^2)}$
A_i	coefficients in a specified equation
$B, C, D, E \ldots$	coefficients in eqs (1)
B_i	coefficients in a specified equation
B_T	the second virial coefficient for water vapor
ΔC°_{fus}	the heat capacity change accompanying the fusion of the pure solvent at the freezing temperature of the pure solvent
$\Delta \overline{C}_p$	the difference between the partial molal heat capacity of the solvent in a solution and the molal heat capacity of the solid solvent at the freezing temperature of the solution
E	electromotive force
F	the Faraday Constant
ΔG^{ex}	the excess Gibbs energy of a solution containing one kilogram of solvent
ΔH°_{fus}	the enthalpy of fusion of the pure solvent at the freezing temperature of the pure solvent
I_m or I	ionic strength: $(I_m = \frac{1}{2}\sum_i m_i z_i^2)$
K_{s0}	solubility product
P	vapor pressure of a solution
P°	vapor pressure of pure solvent
R	molar gas constant
T	thermodynamic or absolute temperature

T_{fus}	absolute temperature of fusion of pure solvent	ν	total number of ions formed from one molecule of solute assuming complete dissociation: [$\nu = \sum_i \nu_i$]
α_i	coefficients in a specified equation		
β_i	coefficients in a specified equation	ρ	density
$\gamma_\pm$ or γ	activity coefficient, molality basis	σ	standard deviation
γ_{ref}	activity coefficient evaluated at a given reference molality (m_{ref})	ϕ or φ	osmotic coefficient
ν_i	number of ions of species i formed from one molecule of solute assuming complete dissociation	Φ_C	apparent molal heat capacity
		Φ_L	relative apparent molal enthalpy