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Isopiestic Determination of the Osmotic and Relative Activity Coefficients in $BaCl_2$–$ZnCl_2$–H_2O at 25 °C

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The three-component system $BaCl_2$–$ZnCl_2$–H_2O has been studied at 25 °C by the isopiestic method with calcium chloride as reference. Measurements were made over a total concentration range from approximately 0.1 to 1.8 *m* for mixtures of eleven different values of the molality fraction of zinc chloride (y). Values of the osmotic coefficients at constant total molality interpolated from the experimental data were represented by a polynomial function of the fourth degree in y. The relative values of activity coefficients of barium chloride and zinc chloride were obtained from new forms of the McKay–Perring equation. The variation of these values becomes increasingly complicated at higher concentrations. Zinc chloride shows a greater influence on the activity coefficient of barium chloride than vice versa. The anomalous variations in the experimental results may be qualitatively accounted for by ion association and hydration.

The thermodynamic properties of aqueous electrolyte solutions may be described in terms of activity and osmotic coefficients in the solutions. These coefficients may be determined experimentally by a number of methods, principally measurements of the colligative properties of the solutions and of the electromotive forces of suitable galvanic cells containing the solution. However, many ternary systems have been studied by isopiestic vapor pressure measurements (*1–8*). The osmotic coefficients of solutions are obtained directly from the measurements and the activity coefficients of the electrolytes can be calculated from the Gibbs–Duhem relationship by means of some forms of the McKay–Perring equation (*5*, *9–11*). In the present investigation (*5*), measurements of the system $BaCl_2$–$ZnCl_2$–H_2O were carried out over a total concentration range from approximately 0.1 to 1.8 *m* for mixtures of eleven different values of the molality fraction of zinc chloride.

Experimental Section

Apparatus and Experimental Procedure**.** Since no isopiestic apparatus is commercially available, the apparatus for this work was designed and constructed following the conventional type first employed by Sinclair with some modifications (*5*). The main parts of the apparatus are a constant temperature bath including heating and cooling systems, rocking mechanism, evacuating and drying system, desiccators containing copper blocks designed to accommodate seven equally spaced gold dishes, stirrers for solutions, and a vapor stirrer.

Gold dishes containing weighed quantities of carefully prepared aqueous test or reference solutions are placed in a large copper blcok in the desiccator which is then evacuated. The desiccator is gently rocked in a thermostat until equilibrium is attained, and the dishes are reweighed. Experiments are repeated to cover, at reasonable intervals, the entire range of all independent composition variables. The temperature was constant to within approximately to ±0.01 °C.

Table I. Composition Range of Mixed Solutions

y	m_{min}	m_{max}.	y	m_{min}	m_{max}.
0.0000	0.1300	1.8167	0.5856	0.1469	2.6047
0.1003	0.1397	1.8764	0.7077	0.2008	2.6800
0.1987	0.1180	1.8648	0.7996	0.1198	2.5572
0.3039	0.1549	2.3848	0.9004	0.3209	2.3783
0.3849	0.1284	2.2865	1.0000	0.1616	2.4214
0.4888	0.2023	2.6773			

Isopiestic Measurements**.** The basic quantity measured in the experiment is the isopiestic ratio *R*, the ratio of molalities of reference and test solutions in isopiestic equilibrium. Calcium chloride solutions were used as the reference (*8*, *12*). The osmotic coefficients of the calcium chloride solution at round values of molality were taken from Robinson and Stokes (*8*). The values of ϕ_{CaCl_2} at any concentration can be interpolated from the plot of ϕ_{CaCl_2} against m_{CaCl_2}. The measurements were made over the concentration range shown in Table I.

Because of the relatively lower solubility of barium chloride in water, 1.8 *m* is the upper limit of the concentration of the mixtures of interest. Each equilibrium concentration was taken from the mean measured concentration of triplicate dishes. No results were reported unless the deviations in molality from the mean concentration were less than 0.3%. The equilibrium time was generally from 2 to 10 days for each experiment. The more dilute solutions needed longer times to attain equilibrium. The values of *R* are not reported here for reasons of space, but were incorporated in the data treatment leading to the final values of osmotic and relative activity coefficients given in the Results and Discussion section. The plots of *R* vs. *m* are shown in Figures 1 and 2.

Materials and Method**.** Stock solutions of the solute components and the reference electrolyte were prepared on a weight basis from the purified electrolytes and conductivity water. The water was first distilled, then passed through a mixed-bed ion exchange deionizer, and finally boiled to remove dissolved gases and inhibit bacterial growth. The solutes were purified as follows.

Calcium Chloride. Mallinckrodt Analytical Reagent grade $CaCl_2 \cdot 2H_2O$ was recrystallized twice from conductivity water and dried for 24 h in a vacuum oven. The salt was then fused in a tubular combustion furnace at its melting point under 1 atm of HCl gas in order to get a completely dehydrated and neutral salt.

Stock solutions of calcium chloride were analyzed gravimetrically for chloride content by precipitation as AgCl. A check of their isopiestic ratios against NaCl solution was made; the ratios were consistent with Stokes' data (*13*) within experimental error. The purified solid was stored in a vacuum desiccator over $Mg(ClO_4)_2$.

Zinc Chloride. *Sample I*. Fisher Certified Reagent grade $ZnCl_2$ was recrystallized twice from conductivity water. The recrystallization was followed by drying and fusion by the same procedure as for the calcium chloride.

Sample II. Another source of zinc chloride was obtained by dissolving high purity zinc metal in hydrochloric acid. (The zinc metal, containing less than 2 parts per million of total impurities, was obtained from the Consolidated Mining and Smelting Co. of Canada Ltd, Trail, British Columbia.) The zinc

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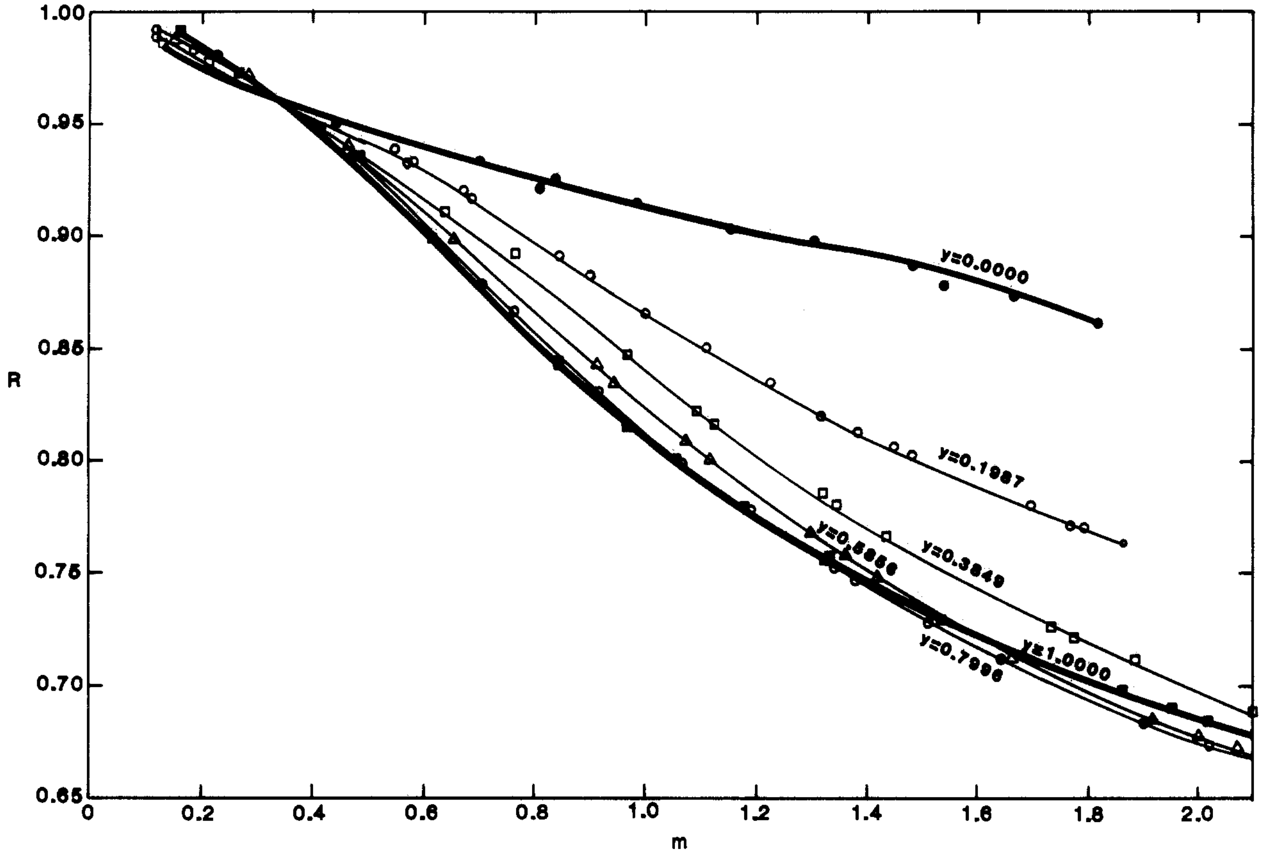

Figure 1. Isopiestic ratios for barium chloride-zinc chloride solutions with calcium chloride as the reference.

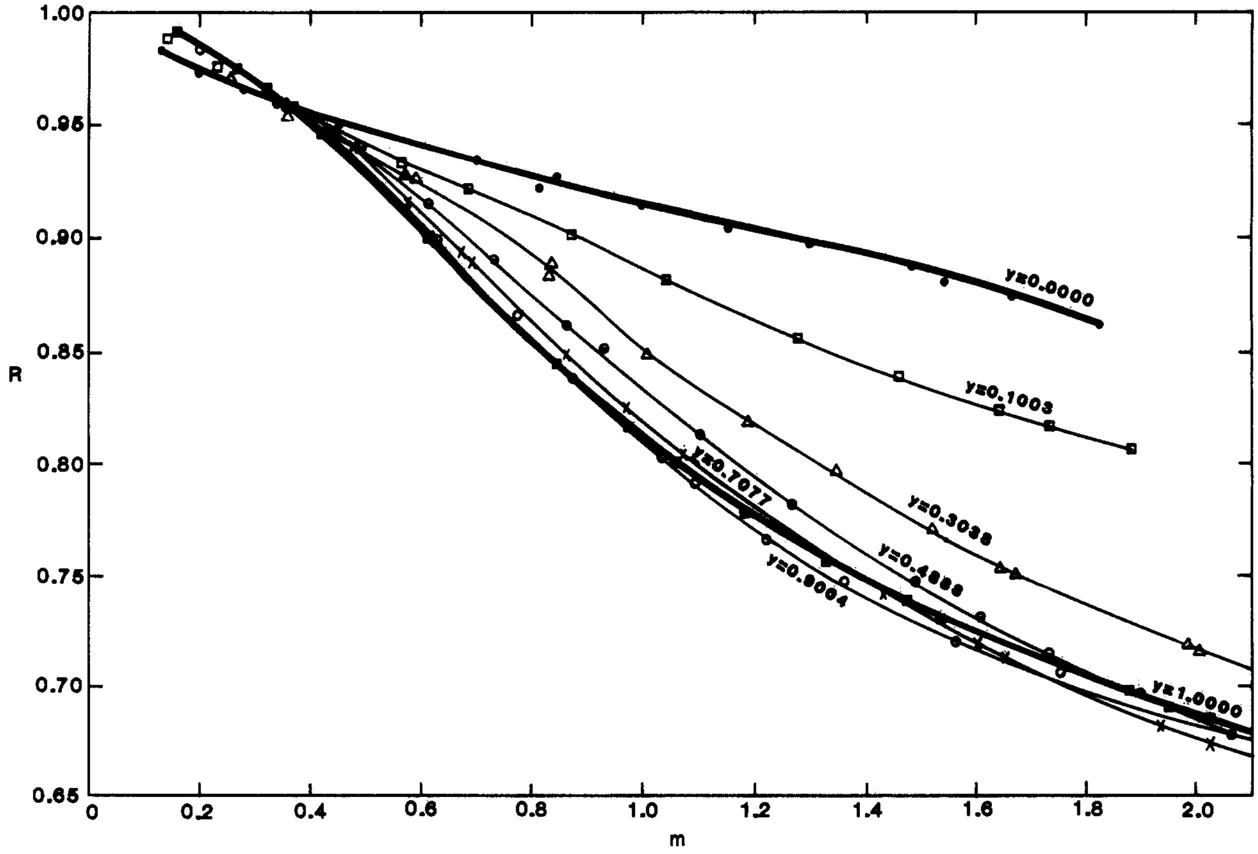

Figure 2. Isopiestic ratios for barium chloride-zinc chloride solutions with calcium chloride as the reference.

Table II. Osmotic Coefficients at Round Value of Molality Interpolated from Curves ϕ vs. m

	y										
m	0.0000	0.1003	0.1987	0.3039	0.3849	0.4888	0.5856	0.7077	0.7996	0.9004	1.000
0.2	0.839	0.845	0.846	0.846	0.844	0.848	0.847	0.838	0.850	0.850	0.851
0.3	0.843	0.847	0.847	0.845	0.848	0.847	0.847	0.848	0.849	0.849	0.847
0.4	0.851	0.851	0.850	0.847	0.848	0.846	0.848	0.852	0.847	0.847	0.846
0.5	0.863	0.858	0.859	0.853	0.849	0.853	0.847	0.851	0.847	0.844	0.842
0.6	0.876	0.865	0.866	0.860	0.853	0.849	0.844	0.838	0.839	0.838	0.837
0.7	0.890	0.874	0.870	0.858	0.856	0.847	0.840	0.836	0.832	0.831	0.829
0.8	0.898	0.882	0.871	0.857	0.855	0.842	0.834	0.828	0.826	0.823	0.821
0.9	0.919	0.890	0.872	0.857	0.849	0.839	0.828	0.820	0.816	0.810	0.812
1.0	0.937	0.898	0.871	0.853	0.843	0.833	0.820	0.812	0.809	0.804	0.804
1.2	0.967	0.913	0.879	0.851	0.835	0.819	0.809	0.801	0.798	0.798	0.798
1.4	1.001	0.940	0.883	0.850	0.827	0.810	0.799	0.792	0.790	0.786	0.793
1.6	1.028	0.952	0.892	0.846	0.826	0.804	0.792	0.788	0.785	0.783	0.792
1.8	1.055	0.966	0.899	0.848	0.820	0.799	0.787	0.783	0.783	0.791	0.795

content was confirmed by analysis by the gravimetric sulfate method.

In order to ensure the stoichiometric content of chloride, the stock solutions of samples I and II were analyzed for chloride by precipitation with $AgNO_3$ solutions. The two samples gave the correct stoichiometric content of chloride and were isopiestically identical.

Barium Chloride. Baker Analyzed Reagent grade $BaCl_2{\cdot}2H_2O$ was purified, dried, and stored in the same manner as for $CaCl_2$. The stock solution of $BaCl_2$ was analyzed for barium by gravimetric determination as the sulfate and for chloride by precipitation with $AgNO_3$ solution.

The concentrated stock solutions were weighed into the dishes to prepare the desired mixed electrolyte solutions and reference solutions. The covered dishes were placed in the copper block and desiccator, the covers were removed, the vapor stirrer was mounted, and the desiccator was sealed, evacuated, and placed on the rocking shelf in the thermostat. When equilibrium was attained, dry air was carefully admitted and the dishes covered, removed, and weighed.

When one set of solutions had been weighed after equilibration, small amounts of water were added to all and the equilibration process was repeated to give a second set of data for more dilute solutions of the same solute composition. After several equilibrations, portions of the diluted, well-mixed solutions were removed and the process further continued to the limit of reliability of the method, usually at molalities in the neighborhood of 0.1–0.2 m. Then a whole new set of equilibrations was started with a different solute composition.

Method of Calculation

The isopiestic ratio R of mixtures containing electrolytes B and C is defined as

$$R = \frac{\nu_R m_R}{\nu_B m_B + \nu_C m_C} \qquad (1)$$

in which ν_i is the number of ions per "molecule" of electrolyte i, m_i is the molality of solute i, and the subscript R represents the reference electrolyte. For the system under investigation, $\nu_B = \nu_C = \nu_R = 3$, and $R = m_R/m$, where $m = m_B + m_C$. The osmotic coefficient of the mixture can thus be obtained from the concentration of two isopiestic solutions; they are equal in water activities, i.e.

$$\phi = R\phi_R \qquad (2)$$

where ϕ is the osmotic coefficient of the test solution and ϕ_R that of the reference solution when they are in isopiestic equilibrium.

For the special case where both electrolytes are of the same charge type, the Mckay–Perring equation (*9*) may be expressed in convenient forms (*10*), i.e.

$$\ln \gamma_B = (\phi - 1) + \int_{m=0}^{m} (\phi - 1)\, \mathrm{d} \ln m + (1 - y) \int_{m=0}^{m} \left(\frac{\partial \phi}{\partial y}\right)_m \mathrm{d} \ln m$$

$$\ln \gamma_C = (\phi - 1) + \int_{m=0}^{m} (\phi - 1)\, \mathrm{d} \ln m - y \int_{m=0}^{m} \left(\frac{\partial \phi}{\partial y}\right)_m \mathrm{d} \ln m \qquad (3)$$

or

$$\ln \frac{\gamma_B}{\gamma_B^{0}} = (\phi - \phi^0) + \int_{m=m^0}^{m} (\phi - 1)\, \mathrm{d} \ln m + (1 - y) \int_{m=m^0}^{m} \left(\frac{\partial \phi}{\partial y}\right)_m \mathrm{d} \ln m$$

$$\ln \frac{\gamma_C}{\gamma_C^{0}} = (\phi - \phi^0) + \int_{m=m^0}^{m} (\phi - 1)\, \mathrm{d} \ln m - y \int_{m=m^0}^{m} \left(\frac{\partial \phi}{\partial y}\right)_m \mathrm{d} \ln m \qquad (4)$$

in which γ_B and γ_C are the activity coefficients of electrolytes B and C, respectively, y is the molality fraction of electrolyte B, and γ_B^0, γ_C^0 and ϕ^0 are the corresponding activity and osmotic coefficients in the solution of molality m^0 and the same solute molality fraction y. The integrations at constant y may be performed by graphical methods.

Equations 3 and 4 can be applied to calculate the mean activity coefficients of two electrolyte solutes of the same charge type in mixed solutions if sufficient information about the osmotic coefficient of the mixture is available. At fixed total molality, the osmotic coefficient of the mixture may be expressed as a polynomial function of the stoichiometric molaltiy fraction of an electrolyte, from which the integrands in the equations can easily be evaluated. In this article eq 4 was used to calculate the relative activity coefficients, since osmotic data for solutions in dilute regions could not be obtained, and extrapolation of the osmotic ratios to infinite dilution was not possible, even in the pure $BaCl_2$ solution.

Results and Discussion

The experimental values of R against m at fixed values of y are plotted in Figures 1 and 2, where y is the molality fraction of $ZnCl_2$ in mixtures. The values of ϕ, obtained from eq 2 at different concentrations, were interpolated at round values of

Table III. Osmotic Coefficients as Polynomial Functions of the Molality Fraction of Zinc Chloride[a]

m	a_0	a_1	a_2	a_3	a_4	$10^3 \times \delta$[b]
0.2	0.8390	0.07808	−0.2604	0.3128	−0.1183	3
0.3	0.8436	0.03394	−0.1278	0.1919	−0.09440	1
0.4	0.8516	−0.005404	−0.05381	0.1388	−0.08599	1
0.5	0.8624	−0.02740	−0.03800	0.1272	−0.08332	2
0.6	0.8747	−0.05516	−0.0005264	−0.0008873	0.01940	2
0.7	0.8886	−0.1272	0.1372	−0.1390	0.07016	2
0.8	0.8973	−0.1557	0.1118	−0.06062	0.02850	2
0.9	0.9189	−0.3382	0.6256	−0.7100	0.3153	1
1.0	0.9365	−0.4621	0.8475	−0.8775	0.3596	1
1.2	0.9655	−0.5819	0.8405	−0.6393	0.2135	1
1.4	1.001	−0.8151	1.324	−1.117	0.3994	3
1.6	1.028	−0.9248	1.361	−0.9734	0.3004	2
1.8	1.056	−1.020	1.287	−0.6138	0.08671	1

[a] $\phi = \phi(y) = \sum_{n=0}^{4} a_n y^n$. [b] δ = root mean square deviation.

m and compiled in Table II. The figures in this and Tables IV, VI, and VII are given to three decimal places to reflect the reproducibility of experiments (0.3%), although the average of triplicate determinations is probably somewhat better. These values for mixtures were expressed as polynomial functions of solute composition at constant total molality, the polynomials of fourth degree being obtained by the method of least squares with the aid of an IBM-7040 computer; the coefficients are presented in Table III.

The variation of $\phi = \phi(y)$ at different fixed molalities is shown in Figures 3 and 4. The experimental values of ϕ are shown as points, the smoothed polynomial functions as solid curves.

The values of ϕ at round values of y are calculated directly from the polynomials, and those of $(\partial\phi/\partial y)_m$ from the derivatives of the polynomials. They are compiled in Tables IV and V.

Neither reliable extrapolation methods nor theories or empirical rules were found to be useful to evaluate the absolute

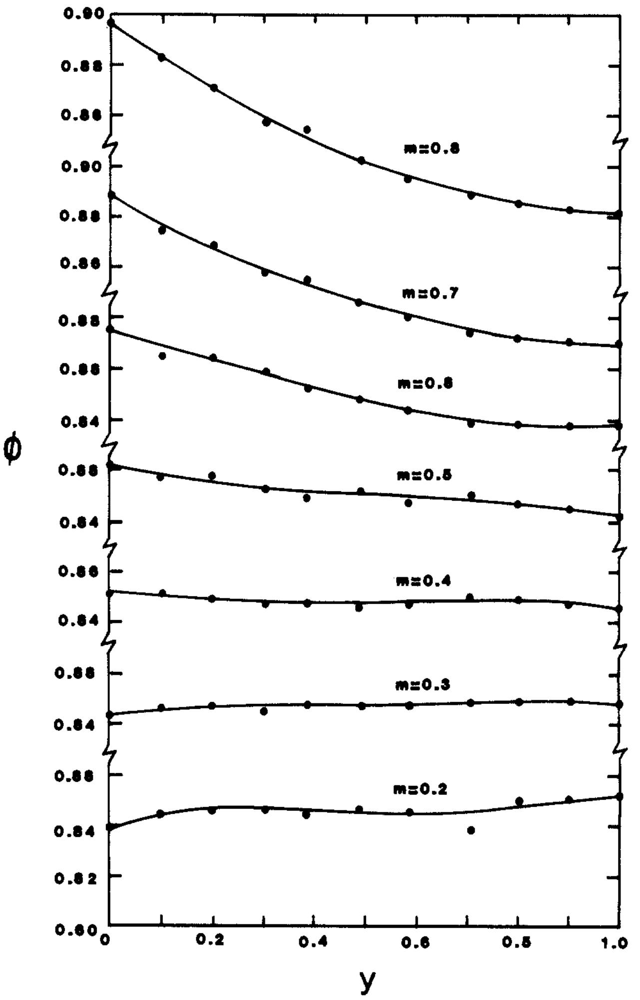

Figure 3. Osmotic coefficients of aqueous barium chloride–zinc chloride solutions as a function of the molality fraction of zinc chloride.

Table IV. Osmotic Coefficients Calculated from the Polynomials in y

m	y 0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0.2	0.839	0.845	0.847	0.847	0.846	0.845	0.844	0.845	0.847	0.849	0.851
0.3	0.844	0.846	0.847	0.847	0.847	0.847	0.847	0.848	0.849	0.849	0.847
0.4	0.852	0.851	0.849	0.848	0.848	0.847	0.848	0.848	0.849	0.848	0.845
0.5	0.862	0.860	0.856	0.854	0.851	0.850	0.849	0.848	0.847	0.845	0.841
0.6	0.875	0.869	0.864	0.858	0.853	0.848	0.844	0.840	0.838	0.837	0.838
0.7	0.889	0.877	0.868	0.860	0.853	0.846	0.841	0.836	0.832	0.830	0.830
0.8	0.897	0.883	0.870	0.859	0.850	0.842	0.835	0.829	0.825	0.822	0.821
0.9	0.919	0.891	0.871	0.857	0.846	0.837	0.829	0.821	0.815	0.811	0.812
1.0	0.937	0.898	0.872	0.853	0.840	0.830	0.821	0.814	0.807	0.805	0.804
1.2	0.966	0.915	0.878	0.851	0.832	0.818	0.809	0.802	0.798	0.797	0.798
1.4	1.001	0.932	0.883	0.849	0.826	0.810	0.799	0.792	0.788	0.788	0.792
1.6	1.028	0.948	0.890	0.849	0.821	0.803	0.792	0.786	0.784	0.786	0.791
1.8	1.056	0.966	0.899	0.850	0.817	0.796	0.786	0.783	0.785	0.790	0.796

Table V. Values of $(\partial\phi/\partial y)_m$ Calculated from the Polynomials in y

m	y 0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0.2	0.0781	0.0349	0.0077	−0.0065	−0.0104	−0.0069	0.0012	0.0110	0.0197	0.0245	0.0225
0.3	0.0339	0.0138	0.0028	−0.0011	−0.0004	0.0029	0.0063	0.0076	0.0046	−0.0051	−0.0236
0.4	−0.0054	−0.0123	−0.0130	−0.0095	−0.0038	0.0019	0.0056	0.0053	−0.0011	−0.0157	−0.0406
0.5	−0.0274	−0.0315	−0.0300	−0.0249	−0.0181	−0.0117	−0.0076	−0.0079	−0.0146	−0.0297	−0.0551
0.6	−0.0552	−0.0552	−0.0549	−0.0536	−0.0510	−0.0467	−0.0400	−0.0306	−0.0180	−0.0017	0.0187
0.7	−0.1272	−0.1037	−0.0868	−0.0748	−0.0662	−0.0592	−0.0521	−0.0432	−0.0309	−0.0135	0.0108
0.8	−0.1557	−0.1351	−0.1174	−0.1019	−0.0881	−0.0751	−0.0624	−0.0492	−0.0349	−0.0187	0.0000
0.9	−0.3382	−0.2140	−0.1631	−0.1206	−0.0979	−0.0876	−0.0820	−0.0737	−0.0550	−0.0183	0.0438
1.0	−0.4621	−0.3175	−0.2169	−0.1517	−0.1134	−0.0931	−0.0824	−0.0725	−0.0550	−0.0210	0.0379
1.2	−0.5819	−0.4321	−0.3156	−0.2272	−0.1617	−0.1142	−0.0793	−0.0521	−0.0274	0.0000	0.0351
1.4	−0.8151	−0.5822	−0.4068	−0.2791	−0.1898	−0.1291	−0.0875	−0.0554	−0.0232	0.0187	0.0799
1.6	−0.9248	−0.6806	−0.4876	−0.3386	−0.2263	−0.1436	−0.0832	−0.0379	−0.0006	0.0361	0.0792
1.8	−1.0200	−0.7807	−0.5761	−0.4041	−0.2628	−0.1499	−0.0635	−0.0013	0.0386	0.0582	0.0598

Table VI. Relative Activity Coefficients[a] of Zinc Chloride in Aqueous $BaCl_2$-$ZnCl_2$ Solutions

	y										
m	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0.2	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.3	0.964	0.950	0.942	0.939	0.940	0.941	0.944	0.944	0.943	0.941	0.937
0.4	0.933	0.913	0.903	0.900	0.900	0.902	0.904	0.904	0.903	0.899	0.895
0.5	0.910	0.888	0.877	0.873	0.873	0.874	0.875	0.874	0.872	0.866	0.860
0.6	0.893	0.869	0.856	0.851	0.848	0.843	0.845	0.842	0.839	0.834	0.832
0.7	0.877	0.850	0.834	0.828	0.824	0.819	0.820	0.817	0.813	0.807	0.805
0.8	0.855	0.830	0.813	0.806	0.800	0.795	0.795	0.791	0.788	0.783	0.780
0.9	0.842	0.811	0.791	0.783	0.778	0.773	0.772	0.767	0.763	0.757	0.756
1.0	0.814	0.788	0.768	0.761	0.755	0.750	0.750	0.745	0.741	0.738	0.735
1.2	0.755	0.740	0.727	0.721	0.716	0.711	0.711	0.709	0.707	0.705	0.705
1.4	0.702	0.693	0.686	0.684	0.682	0.679	0.680	0.678	0.677	0.677	0.679
1.6	0.643	0.648	0.649	0.652	0.652	0.651	0.653	0.654	0.655	0.656	0.659
1.8	0.592	0.608	0.615	0.622	0.625	0.626	0.631	0.635	0.639	0.642	0.646

[a] $\gamma_{ZnCl_2}(m)/\gamma^0_{ZnCl_2}(0.2)$.

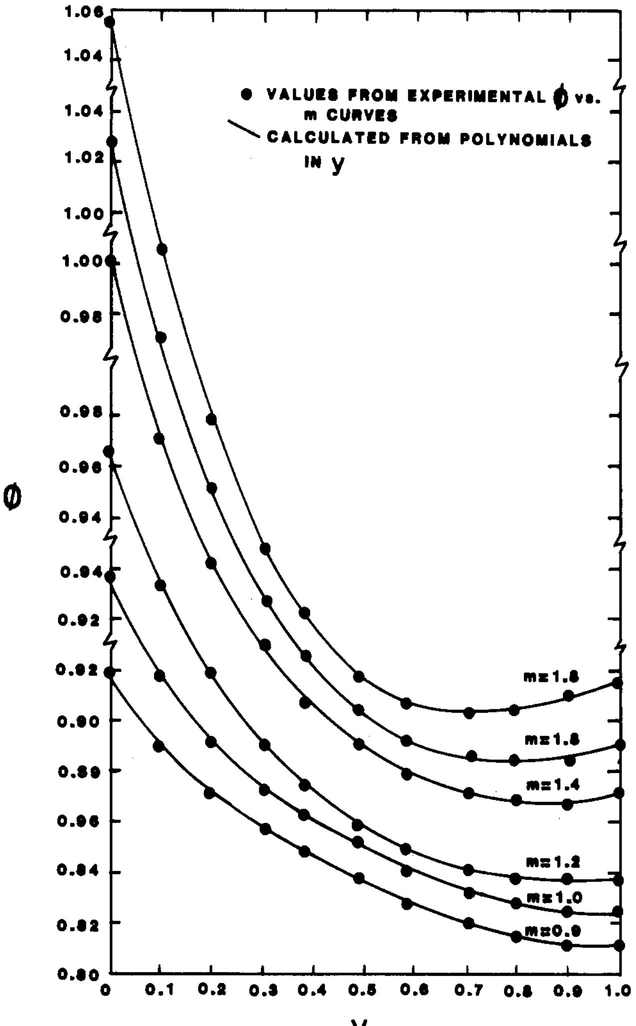

Figure 4. Osmotic coefficients of aqueous barium chloride-zinc chloride solutions as a function of the molality fraction of zinc chloride.

values of activity coefficients of each solute in the mixtures in the present system. The relative activity coefficients of each solute in the mixed solution were obtained from eq 4. All values of activity coefficients at different molality fraction refer to $m^0 = 0.2$. The values of the relative activity coefficients are collected in Tables VI and VII. The variation of the relative activity coefficients of barium chloride and zinc chloride with molality fraction y at fixed values of m is shown in Figures 5 and 6. The relative activity coefficients for pure $BaCl_2$ and pure $ZnCl_2$ solutions ($y = 0$ and $y = 1$, respectively) agree well with values computed from the values of Robinson and Stokes (*8*) over the entire range of molality studied.

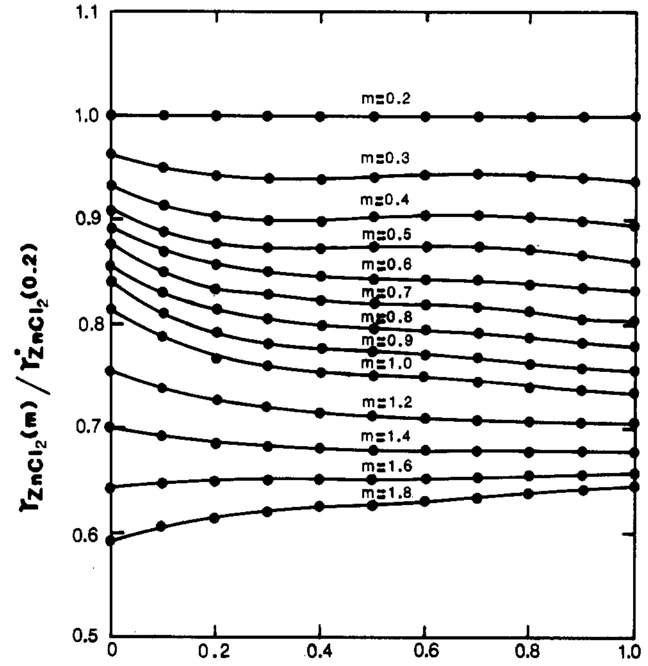

Figure 5. Relative activity coefficients of zinc chloride in aqueous barium chloride-zinc chloride solutions.

The new forms of the McKay-Perring equations contain the slope function of $(\partial\phi/\partial y)_m$. There is no certain way to obtain the exact slope at a particular point; polynomial functions will introduce some uncertainties. Apparent values of $(\partial\phi/\partial y)_m$ at fixed values of m and y depend on the degree of the polynomial. However, the uncertainties are believed to be minimized if the values of m are evenly and closely distributed and polynomials of the same degree are used for all values of m.

The osmotic coefficient of a mixture has often been expressed as a polynomial function of the solute composition at constant total molality. If Harned's rule holds for both electrolyte B and C, the osmotic coefficient of the mixture is a quadratic function of y. If a higher order term is necessary, the osmotic coefficient in the mixture is then at least a cubic function of y. The osmotic coefficients in aqueous mixtures of NaOH-NaCl (*14*) and NaCl-KCl (*15*), for example, have been expressed as cubic functions of y. Still higher order terms are required to show the deviations from Harned's rule when larger chemical interaction is to be expected. Interaction in the system under investigation is undoubtedly larger than that in the systems NaOH-NaCl and NaCl-KCl. The polynomials for ϕ for the system $BaCl_2$-$ZnCl_2$ should thus be a higher degree than cubic; i.e., at least quartic functions of y. In view of the ex-

Table VII. Relative Activity Coefficients[a] of Barium Chloride in Aqueous $BaCl_2$-$ZnCl_2$ Solutions

	y										
m	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0.2	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.3	0.942	0.940	0.940	0.941	0.942	0.942	0.942	0.940	0.939	0.937	0.938
0.4	0.909	0.904	0.903	0.903	0.902	0.902	0.901	0.899	0.899	0.899	0.904
0.5	0.890	0.884	0.880	0.879	0.877	0.875	0.872	0.869	0.870	0.870	0.879
0.6	0.879	0.871	0.865	0.863	0.857	0.849	0.846	0.840	0.839	0.840	0.852
0.7	0.876	0.862	0.853	0.848	0.840	0.831	0.826	0.819	0.816	0.814	0.821
0.8	0.871	0.855	0.842	0.834	0.825	0.814	0.808	0.799	0.795	0.791	0.795
0.9	0.880	0.852	0.833	0.822	0.811	0.799	0.791	0.781	0.773	0.767	0.768
1.0	0.889	0.851	0.826	0.810	0.797	0.783	0.775	0.764	0.756	0.750	0.744
1.2	0.907	0.858	0.820	0.795	0.775	0.757	0.747	0.735	0.727	0.718	0.710
1.4	0.937	0.869	0.818	0.784	0.758	0.736	0.723	0.710	0.699	0.690	0.678
1.6	0.965	0.884	0.822	0.778	0.746	0.719	0.704	0.689	0.677	0.672	0.652
1.8	0.997	0.904	0.828	0.775	0.735	0.703	0.686	0.671	0.662	0.661	0.634

[a] $\gamma_{BaCl_2}(m)/\gamma^0_{BaCl_2}(0.2)$.

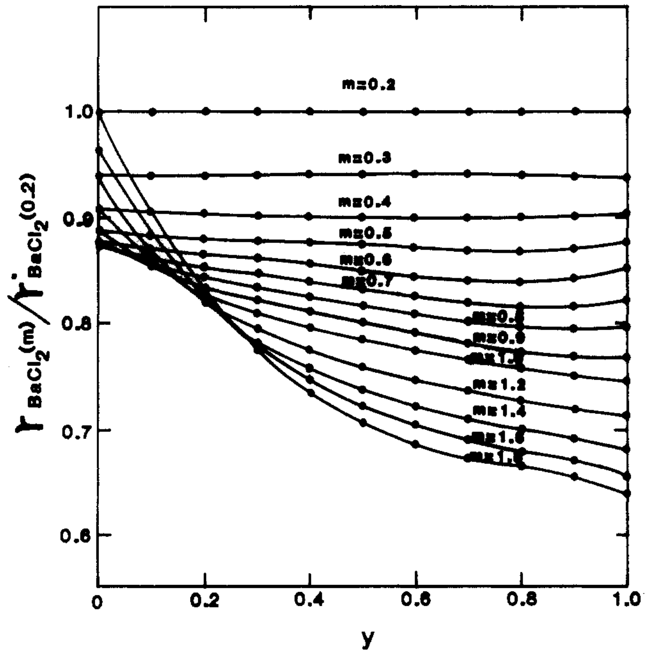

Figure 6. Relative activity coefficients of barium chloride in aqueous barium chloride-zinc chloride solutions.

perimental values of ϕ related to y at each fixed m (see Figures 3 and 4), it is believed that quartic functions are adequate to represent the experimental data.

The system $BaCl_2$-$ZnCl_2$ is probably the most complex one of the systems of bivalent metal chloride mixtures so far investigated. Figures 5 and 6 indicate that zinc chloride has a greater influence on the activity coefficient of barium chloride, especially when at higher concentrations, than vice versa.

The plot of R vs. m at each fixed value of y has been shown in Figures 1 and 2. The shape and location of these fundamental isopiestic experimental curves are principally determined by two factors: ion association and hydration of ions (*5*). Ion association may lead to significant concentrations of the species $ZnCl^+$, $ZnCl_2$, $ZnCl_3^-$, and $ZnCl_4^{2-}$ (*16*). In other methods of determination of solute activities in such solutions large departures from limiting law behavior have been attributed to this factor (*17*, *18*), and here also it tends to cause the isopiestic curves to be lowered relative to limiting law behavior (the same for the osmotic and activity coefficient curves). On the other hand, hydration of ions, particularly the small doubly charged Zn^{2+} ion, causes a reverse effect; i.e., it raises the curves of R vs. m, ϕ vs. m, or γ vs. m. Because these two opposing effects are superimposed, the experimental curves in Figures 1 and 2 show complex behavior; at fixed solute composition the relative effect of the two is, except at high $ZnCl_2$ fractions, not very sensitive to total molality, although one should expect in general the association effect to predominate as the total molality approaches high values, and the hydration effect to predominate as the total molality approaches zero. At fixed molality, the hydration effect becomes increasingly important as the $ZnCl_2$ fraction is increased, mainly because of the smaller size of Zn^{2+} ion than Ba^{2+} ion (*19*) and the more pronounced acceptor role of Zn^{2+} ion in complex formation, specifically, hydrated ion formation.

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