retical analysis by modified (*13*) or unmodified regular solution (*10*) or scaled particle theories (*14*). We therefore conclude that the solubility of each steroid is best predicted from the reported best-fit equations.

Registry No. Cholesterol, 57-88-5; sitosterol, 83-46-5; cholesteryl acetate, 604-35-3; methanol, 67-56-1; ethanol, 64-17-5; acetone, 67-64-1; acetonitrile, 75-05-8; 2-propanol, 67-63-0.

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Isopiestic Determination of the Osmotic and Activity Coefficients of Aqueous $MnCl_2$, $MnSO_4$, and RbCl at 25 °C

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The osmotic coefficients of aqueous $MnCl_2$, $MnSO_4$, and RbCl have been measured to high concentrations at 25 °C by the isopiestic method. Data for RbCl solutions extend to saturation; data for $MnCl_2$ and $MnSO_4$ extend to supersaturated concentrations. Solubilities were determined for solid $MnCl_2 \cdot nH_2O$ and for RbCl. Results are compared to other activity and solubility data for these salts and, in most cases, the agreement is good. Oxidation of these Mn^{2+} salts was shown to have a negligible effect when care was taken to exclude air, but even without precautions it probably would have been insignificant. Two samples of commercial "99.9%" RbCl were found upon analysis to contain 0.69 and 3.4 mol % impurities, with 64–88% of that amount being potassium. The presence of 1% KCl in RbCl was shown to have a negligible effect on osmotic coefficients below 2.3 mol kg^{-1}, but it lowers them by 0.3% at saturation. Its presence can be accurately corrected for.

Introduction

Activity coefficient data for aqueous electrolyte solutions have numerous applications including solubility, speciation, and other chemical equilibrium calculations. Isopiestic measurements yield accurate solvent activities as a function of concentration, and an integration of these data via the Gibbs–Duhem equation yields solute activity coefficients.

Two sets of isopiestic data have been reported for aqueous $MnSO_4$ at high concentrations (*1*, *2*), but their osmotic coefficients differ by 1.4% at 4.2 mol kg^{-1}. This is a factor of 7–10 times the reproducibility of the isopiestic method (*3*) under favorable conditions. Robinson and Sinclair (*4*) reported isopiestic data for aqueous RbCl from 0.42 to 4.96 mol kg^{-1}, but their data are fairly scattered especially below 1.5 mol kg^{-1}. Robinson later reinvestigated RbCl (*5*) with "purer" material and reported smoothed isopiestic data that are up to 1% higher than his earlier study (*4*). However, Makarov et al.'s high-concentration results (*6*) agree better with the earlier study. Additional isopiestic data for $MnSO_4$ and RbCl are necessary to resolve these significant discrepancies.

Activity data for aqueous $MnCl_2$ are in closer agreement. Three sets of isopiestic data are available, and they agree to 0.5% or better in their overlapping concentration regions (*7*–*9*). However, from 3.59 to 7.70 mol kg^{-1} there are only the 11 points of Robinson (cited in Stokes' Appendix (*8*)), and his point at 4.203 mol kg^{-1} is considerably in error and probably contains a misprint. In addition, they contain three concentration gaps of 0.6 mol kg^{-1} and one of 1.0 mol kg^{-1} in this region. Consequently, additional data are needed to better characterize this salt at high concentrations.

In view of the above considerations, we have made isopiestic measurements at 25 °C for aqueous RbCl to saturation, and for $MnCl_2$ and $MnSO_4$ to supersaturated concentrations.

Experimental Section

The experimental details are nearly identical with those described elsewhere (*3*, *10*). Isopiestic equilibrations were made at 25.00 ± 0.005 °C (IPTS-68), with aqueous NaCl and $CaCl_2$ solutions as reference solutions. Four-day or longer equilibrations were used at the higher concentrations, but this was gradually increased to four weeks by the lowest concentrations. Triplicate samples of $CaCl_2$ solutions were used, and duplicate samples for the other electrolytes. Molalities of each electrolyte at isopiestic equilibrium agreed to better than ±0.1%. All weights were corrected to vacuum.

All isopiestic equilibrations were made in inert cups of tantalum metal. A corrosion test indicated that no significant reaction occurred between $MnCl_2$ and Ta when air was excluded (as occurs during isopiestic equilibrations).

Solutions of NaCl and $CaCl_2$, used as isopiestic standards, have been described elsewhere (*3*). The NaCl stock was analyzed both by dehydration and by AgCl precipitation; $CaCl_2$ was analyzed both by conversion to the anhydrous sulfate and by dehydration (*3*). Molecular masses were 110.986 g mol^{-1} for $CaCl_2$, 136.14 g mol^{-1} for $CaSO_4$, 58.443 g mol^{-1} for NaCl, 125.844 g mol^{-1} for $MnCl_2$, and 150.996 g mol^{-1} for $MnSO_4$.

The $MnCl_2$ stock solution was prepared from filtered Mallinckrodt AR $MnCl_2 \cdot nH_2O$. Direct current arc optical emission spectroscopic analysis (DCAOES) of an evaporated sample detected the presence of only 30 ppm Ca, <20 ppm Si, 3 ppm Mg, and 3 ppm Na by weight. The stock concentration was

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determined to be 3.2746 ± 0.0026 mol kg^{-1} by mass titration with $AgNO_3$ solutions, and 3.2719 ± 0.0013 mol kg^{-1} by conversion to the anhydrous sulfate. The average was used for calculations. Samples from this same stock solution were also used for density measurements (*11*).

The natural pH values of $MnCl_2$ solutions are acidic, and a published potential-pH diagram for Mn^{2+}–H_2O indicates they ought to be stable in air (*12*). A 4.12 mol kg^{-1} test solution in contact with air showed a nearly linear pH decrease with time, pH 2.57–1.81, over a 13.5-month period. Precipitation of $Mn(OH)_2$, or oxidation to form MnO(OH) or Mn_3O_4, generates two H^+ ions per Mn^{2+} involved. Approximating concentrations by activities indicates that if oxidation is involved, it occurs at about 0.1% per year. Since the isopiestic measurements took about 1 year, the stock solution was protected by deaeration with nitrogen to eliminate this source of error.

Although the $MnCl_2$ isopiestic samples come in contact with air when they are removed from the chambers for weighing, such contact is only for a few hours per week so no significant oxidation should occur. Two checks were made to verify this. The first check involved making several equilibrations using the same samples with the solutions' concentrations initially being decreased by addition of H_2O; later solvent was removed to return these samples to the higher concentrations. These reequilibrations confirmed the earlier results within experimental scatter. The second check involved equilibrating fresh $MnCl_2$ stock solution samples with other samples that had been used for a number of previous equilibrations. Isopiestic equilibrium molalities were (3.8554 ± 0.0018, 3.8574 ± 0.0031) and (3.6247 ± 0.0015, 3.6255 ± 0.0031), where the first concentration in each pair is the fresh $MnCl_2$ sample. Equilibration results agree within their uncertainties, which indicates the effects of oxidation are much less than experimental scatter.

The solubility of solid $MnCl_2{\cdot}nH_2O$ was determined to be 6.0869 ± 0.0041 mol kg^{-1} by using two 5-day isopiestic equilibrations. This value is lower than Linke's (*13*) average of 6.130 mol kg^{-1} from available literature data for $MnCl_2{\cdot}4H_2O$. The solid phase was not identified in our study and probably was not pure $MnCl_2{\cdot}4H_2O$. $MnCl_2$ solutions readily supersaturate, and no crystallization occurred in the concentration region investigated.

The $MnSO_4$ stock solution was prepared from filtered Mallinckrodt AR $MnSO_4{\cdot}H_2O$. Its concentration of 0.674 10 ± 0.000 37 mol kg^{-1} was obtained by dehydration. DCAOES of the original material indicated the presence of about 300 ppm Na, ≤30 ppm Si, 30 ppm Ti, and 10 ppm Ni by weight. Both Si and Ti should be nearly insoluble at the stock solution pH, so they should have been removed by filtering. Atomic absorption analyses (AA) of the stock solution detected 502 ppm Na relative to 10^6 ppm $MnSO_4$ by weight. The average impurity analysis of 401 ± 100 ppm Na was accepted. Our stock is thus a mixture of 99.868 mol % $MnSO_4$ and 0.132 mol % Na_2SO_4. The presence of this Na^+ was not acknowledged by the original supplier.

This Na_2SO_4 in the $MnSO_4$ stock solution will affect the osmotic coefficients in two ways. First, it will affect the number of moles of salt calculated from the dehydration analysis; this was compensated for by using the molecular weight of $0.99868MnSO_4{\cdot}0.00132Na_2SO_4$ in calculating concentrations. Second, the osmotic coefficient of pure $MnSO_4$ will be replaced by that for the mixture

$$\Phi = \frac{\nu_A m_A}{\sum \nu_i m_i}\Phi_A{}^\circ + \frac{\nu_B m_B}{\sum \nu_i m_i}\Phi_B{}^\circ + \delta\Phi_{mix} \qquad (1)$$

Here $\Phi_A{}^\circ$ and $\Phi_B{}^\circ$ are the osmotic coefficients of pure $MnSO_4$ and Na_2SO_4, respectively, at the total ionic strength of the mixture, $\delta\Phi_{mix}$ is the difference due to nonideal mixing, and $\nu_A = 2$ and $\nu_B = 3$ are the number of ions produced by complete dissociation of $MnSO_4$ and Na_2SO_4, respectively. Values of $\delta\Phi_{mix}$ are not available for $MnSO_4$–Na_2SO_4 mixtures. However, as shown below, published data for $CuSO_4$–Na_2SO_4 and $MgSO_4$–Na_2SO_4 mixtures indicate that this term is small and nearly independent of the divalent cation.

Downes and Pitzer have analyzed $CuSO_4$–Na_2SO_4 data by using the Pitzer formulation (*14*), and Rush has analyzed $MgSO_4$–Na_2SO_4 by using Scatchard's neutral electrolyte formulation (*15*). These two model systems yield very similar values for $\delta\Phi_{mix}$. They indicate that Φ is higher than $\Phi_A{}^\circ$ by 0.06% or less below 2.0 mol kg^{-1}; it is lower by 0.08% or less up to 4 mol kg^{-1}; and it is low by about 0.13% at the highest experimental concentration of 4.966 mol kg^{-1} (for 0.132 mol % Na_2SO_4). Since the precision of the osmotic coefficient measurements is around 0.1–0.2%, contamination of our $MnSO_4$ with small amounts of Na_2SO_4 has little effect on the overall accuracy.

A 1.03 mol kg^{-1} $MnSO_4$ solution had an initial pH of 3.17; after $8^1/_2$ months of contact with air this had decreased to 3.03. This indicates that oxidation occurs at about 0.02% per year, and it is thus a negligible source of error. This slower pH change for $MnSO_4$ relative to $MnCl_2$ implies that complex formation inhibits oxidation, which seems reasonable. However, the same precautions to exclude air were made as for $MnCl_2$.

An attempt was made to determine the solubility of $MnSO_4$ by using the isopiestic method. Pink crystals of $MnSO_4{\cdot}nH_2O$ were grown from a supersaturated solution. The molality of a solution "equilibrated" with these crystals increased continuously; after 1 month this solubility determination attempt was abandoned. Clearly a metastable hydrate was obtained, which was very slowly being transformed into thermodynamically stable $MnSO_4{\cdot}H_2O$ (*13*). Linke gives the solubility of $MnSO_4{\cdot}H_2O$ as 4.27 mol kg^{-1} at 25 °C (*13*).

Samples of $MnSO_4$ near and above saturation were examined for crystals at the end of equilibrations; only those results without crystallization are reported here. Below 4.8 mol kg^{-1} no problems with crystallization were encountered, but at higher concentrations experiments were more difficult and were sometimes unsuccessful.

Two samples of "99.9%" RbCl were purchased and then spectroscopically analyzed for impurities. Alfa "99.9%" was actually found to contain (AA analysis) 0.577 mol % KCl, 0.053 mol % NaCl, and (DCAOES analysis) 0.059% CsCl impurities. The original sample also contained small amounts of Cr, Ni, and Fe, but they precipitated out from the stock solution and were quantitatively removed by filtration. The other brand of "99.9%" RbCl (4 times as expensive) was rejected since it contained about 3 mol % KCl and 0.4 mol % NaCl. Since there was no way of knowing which other sources of commercial RbCl were any purer, we decided to use the Alfa material and correct for the presence of the alkali-metal impurities.

The RbCl stock concentration was determined both by dehydration and by mass titration with $AgNO_3$. The calculated molalities were very sensitive functions of the assumed impurity content (and each impurity concentration is uncertain by at least 5–10% of its value). By using the total number of moles of salt from $AgNO_3$ titrations and the water content from dehydration, we obtained a total stock molality that is independent of any assumptions about impurity content (since all salts were of the same valence type). This amounts to using an effective molecular weight.

Osmotic coefficients for these RbCl solutions will be given by

$$\Phi = y_A\Phi_A{}^\circ + y_B\Phi_B{}^\circ + y_C\Phi_C{}^\circ + y_D\Phi_D{}^\circ + \delta\Phi_{mix} \qquad (2)$$

where A denotes RbCl, B denotes KCl, C denotes CsCl, D denotes NaCl, and y_i is the ionic strength fraction of salt i. Since all these salts are of the same valence type, νm ratios and ionic strength ratios are equivalent. The binary contribution (first four terms) is within 0.01% of $\Phi_A{}^\circ$ at 2 mol kg^{-1}, and

Table I. Isopiestic Molalities of RbCl, $MnSO_4$, $MnCl_2$, and NaCl Solutions at 25 °C

[RbCl], *m*	[$MnSO_4$], *m*	[$MnCl_2$], *m*	[NaCl], *m*	Φ*(NaCl)
0.36364	0.67798	0.25207	0.35437	0.9194
0.46080	0.85391	0.31430	0.44676	0.9197
0.56635	1.0328	0.37949	0.54609	0.9212
0.60648	1.0976	0.40390	0.58413	0.9219
0.67129	1.1963	0.44235	0.64384	0.9233
0.78200	1.3558	0.50695	0.74651	0.9261
0.88830	1.5003	0.56725	0.84474	0.9292
0.96314	1.5942	0.60849	0.91424	0.9316
1.0441	1.6921	0.65296	0.98751	0.9343
1.1254	1.7843	0.69703	1.0612	0.9371
1.2258	1.8910	0.74910	1.1520	0.9408
1.2796	1.9497	0.77816	1.2015	0.9429
1.3056	1.9765	0.79077	1.2236	0.9439
1.3729	2.0427	0.82542	1.2840	0.9465
1.4600	2.1250	0.86984	1.3611	0.9500
1.5610	2.2174	0.91995	1.4517	0.9543
1.6079			1.4937	0.9563
1.6590	2.3029	0.96681	1.5378	0.9585
1.6910	2.3276		1.5653	0.9598
1.7035	2.3394	0.98695	1.5779	0.9604
1.8416	2.4529		1.7009	0.9667
1.8809	2.4828		1.7324	0.9683
1.9116	2.5053	1.0872	1.7581	0.9697
1.9319	2.5234		1.7760	0.9706
1.9720	2.5531	1.1156	1.8112	0.9725
2.0479	2.6084	1.1519	1.8758	0.9760
2.0912	2.6402	1.1712	1.9139	0.9780
2.1364	2.6727	1.1914	1.9527	0.9802
2.1796	2.7040	1.2120	1.9899	0.9822
2.2506	2.7529	1.2445	2.0488	0.9855
2.3053	2.7930	1.2691	2.0955	0.9882
2.4077	2.8657	1.3138	2.1839	0.9933
2.4646	2.8974	1.3385	2.2299	0.9960
2.5191	2.9344	1.3638	2.2785	0.9988
2.5778	2.9723	1.3900	2.3277	1.0018
2.6420	3.0119	1.4172	2.3801	1.0049
2.6925	3.0405	1.4407	2.4232	1.0075
2.7111	3.0558	1.4463	2.4368	1.0084
2.7722	3.0926	1.4748	2.4918	1.0117
2.8458	3.1302	1.5070	2.5502	1.0154
2.8515	3.1351	1.5059	2.5523	1.0155
2.9938	3.2199	1.5704	2.6723	1.0230
3.1510	3.3065	1.6369	2.7998	1.0312
3.2390	3.3551	1.6743	2.8722	1.0359
3.2795	3.3806		2.9059	1.0381
3.3564	3.4203		2.9688	1.0423
3.4012		1.7418	3.0032	1.0445
3.4354		1.7584	3.0291	1.0463
3.4759	3.4877		3.0615	1.0484
3.6007	3.5523		3.1565	1.0548
3.6296	3.5652	1.8369	3.1851	1.0568
3.7611	3.6303	1.8911	3.2889	1.0639
3.9104	3.7041	1.9518	3.4055	1.0720
4.0732	3.7884	2.0185	3.5327	1.0809
4.2246	3.8632	2.0796	3.6498	1.0892
4.2426	3.8721		3.6592	1.0899
4.4022	3.9468	2.1518	3.7868	1.0991
4.5857	4.0317	2.2248	3.9260	1.1092
4.6054	4.0391	2.2335	3.9409	1.1103
4.6450	4.0526	2.2490	3.9713	1.1125
4.7153	4.0922	2.2790	4.0244	1.1164
4.8181	4.1345	2.3195	4.1034	1.1223
4.9273	4.1863	2.3632	4.1833	1.1282
4.9892	4.2210	2.3879	4.2302	1.1317
5.0721	4.2568	2.4201	4.2900	1.1362
5.1507	4.2896	2.4510	4.3511	1.1408
5.2245	4.3294	2.4824	4.4043	1.1448
5.3078	4.3596	2.5124	4.4612	1.1491
5.3912	4.3959	2.5460	4.5239	1.1539
5.5463	4.4689	2.6094	4.6390	1.1627
5.6447	4.5100	2.6473	4.7068	1.1679
5.7482	4.5578	2.6894	4.7843	1.1738
5.8327	4.5911	2.7229	4.8436	1.1784
5.9161	4.6245	2.7559	4.9037	1.1831
		2.7822	4.9561	1.1871
6.0056	4.6675	2.7898	4.9664	1.1879
6.1077	4.7114	2.8304	5.0371	1.1934
6.2043	4.7545	2.8675	5.1049	1.1987
6.3022	4.7936	2.9060	5.1757	1.2042
6.3764	4.8263	2.9362	5.2291	1.2084
6.4483		2.9640	5.2746	1.2119
		2.9878	5.3222	1.2157
6.5170		2.9934	5.3226	1.2157
6.6356	4.9352		5.4085	1.2224
6.6569			5.4227	1.2235
6.7207	4.9664	3.0715	5.4667	1.2270
6.7904		3.0997	5.5145	1.2308
6.8708		3.1296	5.5704	1.2352
7.0015			5.6553	1.2418
7.1467		3.2398	5.7549	1.2497
7.2585		3.2815	5.8295	1.2555
7.4311		3.3493	5.9469	1.2648
		3.4323	6.0863	1.2758
7.6824		3.4465	6.1119	1.2778
7.7603			6.1655	1.2820
7.7832[a]			6.1789	1.2831

[a] Saturated solution in equilibrium with solid RbCl.

within 0.05% by saturation. Mixture data are unavailable for most salts with RbCl. However, published data for mixtures of NaCl or KCl with other alkali-metal chlorides (*16–18*) indicates mixing a given alkali-metal chloride with a lighter one gives $\delta\Phi_{mix}$ opposite in sign to when mixtures are made with a heavier one. The concentrations of NaCl and CsCl impurities are nearly equal, so their $\delta\Phi_{mix}$ values with RbCl should nearly cancel. If $\delta\Phi_{mix}$ for RbCl–KCl mixtures is similar to CsCl–KCl (*16*), then our 0.577% KCl will raise the osmotic coefficients of RbCl by 0.01%, which is negligible. If RbCl–KCl behaves more like CsCl–NaCl (*17*), then Φ will be too low by up to 0.12% by saturation. Thus, Φ and $\Phi_A{}^\circ$ should be within about 0.1% compared to a usual experimental error of 0.1–0.2%. We decided to check these calculations by doing additional equilibrations with samples of our RbCl stock solution doped with 1.064 mol % added KCl.

Tables I and II contain the isopiestic equilibrium molalities of RbCl, $MnSO_4$, and $MnCl_2$, and their NaCl and $CaCl_2$ reference solutions. Table III gives the isopiestic molalities of the doped RbCl solutions and their NaCl reference solutions. Osmotic coefficients were calculated with eq 3

$$\Phi = \nu^* m^* \Phi^* / \nu m \tag{3}$$

Table II. Isopiestic Molalities of $MnCl_2$ and $CaCl_2$ Solutions at 25 °C

[$MnCl_2$], *m*	[$CaCl_2$], *m*	Φ*($CaCl_2$)
3.3940	2.9366	1.7419
3.5351	3.0294	1.7798
3.6574	3.1083	1.8121
3.7976	3.1968	1.8485
3.8863	3.2521	1.8713
3.9821	3.3110	1.8956
4.0672	3.3617	1.9165
4.2290	3.4590	1.9568
4.2525	3.4728	1.9625
4.3500	3.5307	1.9865
4.4526	3.5898	2.0110
4.5785	3.6609	2.0405
4.7272	3.7445	2.0752
4.8470	3.8129	2.1035
4.9965	3.8949	2.1374
5.1612	3.9855	2.1747
5.2970	4.0585	2.2047
5.5259	4.1792	2.2540
5.6538	4.2461	2.2812
5.8192	4.3344	2.3169
6.0427	4.4507	2.3634
6.0795	4.4693	2.3708
6.0869[a]	4.4725	2.3721
6.2841	4.5748	2.4124
6.5108	4.6892	2.4570
6.7755	4.8266	2.5094
7.0576	4.9712	2.5634
7.3219	5.1067	2.6125
7.5646	5.2281	2.6551

[a] Saturated solution in equilibrium with a hydrate of uncertain composition.

where *m* represents the molality and ν the number of ions formed by the dissociation of one molecule of solute. Reference solution values are denoted with asterisks; their osmotic

Table III. Isopiestic Molalities of RbCl with Added KCl (98.936 mol % RbCl Stock and 1.064% Added KCl) Relative to NaCl Standards

[RbCl], m	[NaCl], m	Φ*(NaCl)	$\delta\Phi$(RbCl)[a]
1.3153	1.2336	0.9443	0.0000
1.3516	1.2654	0.9457	0.0000
1.4370	1.3417	0.9491	0.0000
1.6197	1.5024	0.9567	0.0000
1.9132	1.7590	0.9697	0.0000
2.2955	2.0867	0.9877	0.0000
3.1041	2.7590	1.0286	0.0009
3.1602	2.8044	1.0315	0.0009
3.7530	3.2780	1.0631	0.0005
4.8509	4.1188	1.1234	0.0012
6.0030	4.9561	1.1871	0.0011
6.5234	5.3222	1.2157	0.0008
7.3067	5.8537	1.2575	0.0013
7.6656	6.0863	1.2758	0.0018

[a] Lowering of the osmotic coefficient of RbCl due to the presence of KCl. This has been converted to the actual amount present in our original stock solution, 0.5771 mol %.

coefficients were taken from Hamer and Wu (*19*) and Rard et al. (*20*). $\delta\Phi_{mix}$ values are reported in Table III and were converted to the actual amount of KCl present in our original RbCl stock solution. They were applied as corrections to the data in Table I, and they indicate that our 0.577% KCl contamination lowered the osmotic coefficients of RbCl by 0.00% at low concentrations to 0.18% at high concentrations.

The solubility of RbCl in H_2O was determined to be 7.7832 ± 0.0071 mol kg^{-1} by using 7- and 10-day isopiestic equilibrations. Makarov et al. also reported a solubility of 7.78 mol kg^{-1} (*6*), and Linke cited literature values of 7.671–7.810 mol kg^{-1} (*13*). While these results are in reasonable agreement, our solubility is probably slightly low due to the presence of the KCl impurity. However, this same criticism probably applies to most of the earlier studies also.

Calculations and Discussion

To provide "best values" for the osmotic and activity coefficients of each salt, our data and published literature data were critically compared. Osmotic coefficients for $MnCl_2$, $MnSO_4$, and RbCl solutions were calculated (not tabulated) by using eq 3 and the reported isopiestic molalities and reference solution osmotic coefficients of Tables I and II. Osmotic coefficients for RbCl were then corrected for the presence of KCl impurities by using the correction factors reported in Table III. Published isopiestic data (*2*, *4*, *7–9*) were also recalculated to conform to the same isopiestic standards used here. Robinson and Sinclair's RbCl study (*4*) is the only one for which the impurity content was reported, and it was corrected for the presence of KCl. Robinson and Jones' isopiestic results for $MnSO_4$ (*1*) and Robinson's (*5*) and Makarov et al.'s for RbCl (*6*), were used as reported by them since they only tabulated smoothed values and provided no experimental details.

In addition, both reliable freezing point depression and emf results using Rb amalgam electrodes are available for RbCl solutions at lower concentrations (*21–23*), and they can be used to extrapolate isopiestic results to infinite dilution. These freezing point results (*21*) were converted to osmotic coefficients at 25 °C by using standard methods (*24*) and published enthalpy (*25*) and heat capacity data (*26*). Table IV contains the resulting values. The experimental freezing point depression results (*21*) extend to much higher concentrations, but there is a lack of reliable enthalpy and heat capacity data to calculate osmotic coefficients from them.

Goldberg et al. (*27*) list references to published freezing point depression data for $MnCl_2$ and $MnSO_4$ solutions. These data are from 1907 and earlier; they are of low quality; and consequently they are of little use in extrapolating isopiestic data to infinite dilution. Phang (*28*) reported emf data for $MnCl_2$ solutions from 0.1009 to 5.763 mol kg^{-1} using Ag/AgCl concentration cells with transport. However, since there are no reliable independent transference numbers for $MnCl_2$, these data cannot be used to obtain activities.

Table IV. Freezing Point Depression and Emf Data for Aqueous RbCl Solutions

m[a]	Φ_f[b]	Φ[c]
Momicchioli et al. (*21*), Freezing Point Depression		
0.012 86	0.9868	0.9860
0.021 45	0.9651	0.9644
0.026 50	0.9628	0.9622
0.040 55	0.9435	0.9431
0.055 22	0.9422	0.9421
0.061 60	0.9371	0.9372
0.078 26	0.9304	0.9308
0.121 77	0.9169	0.9183
0.162 32	0.9119	0.9142
0.199 74	0.9039	0.9071
0.242 22	0.8996	0.9038
0.303 23	0.8930	0.8986
0.353 72	0.8890	0.8957
0.430 05	0.8844	0.8928
0.608 27	0.8741	0.8867
0.849 10	0.8660	0.8846
Lebed' and Aleksandrov (*22*), Emf Measurements		
0.004 6		0.9766
0.018 2		0.9585
0.036 2		0.9465
0.072 5		0.9329
0.144 9		0.9189
Longhi et al. (*23*), Emf Measurements		
0.05		0.9383
0.10		0.9231
0.20		0.9078
0.30		0.8995
0.40		0.8942
0.45		0.8923
0.50		0.8906

[a] Molality of solution. [b] Osmotic coefficient at the freezing temperature. [c] Osmotic coefficient at 25 °C.

Yokoyama and Yamatera (*29*) have reported vapor-phase osmometry (VPO) measurements for $MnSO_4$ from 0.008 37 to 0.1264 mol kg^{-1}. These data are about 2.1% lower than isopiestic measurements in the overlap region. We have less confidence in VPO measurements since the reliability of that method is less well established. We decided to use osmotic coefficients from VPO to guide the extrapolation of isopiestic data to infinite dilution, but we normalized them to isopiestic values (*2*) by adding 0.0945 m to the VPO Φ values. Since this normalization function changes results only slightly, these adjusted Φ values should still yield activity coefficients reliable to a few percent.

We used an extension of the Åkerlöf–Thomas approach (*30*) to estimate Φ values for dilute $MnCl_2$ solutions. The difference between osmotic coefficients of two strong electrolytes of the same valence type up to moderate concentrations is given by

$$\Delta\Phi = Em + Fm^{3/2} \tag{4}$$

where E and F are empirical constants. $CaCl_2$ Φ values are well characterized up to high concentrations (*20*), so differences were calculated relative to them. Differences between $MnCl_2$ Φ values (present study up to 0.66 mol kg^{-1}) and $CaCl_2$ values (*20*) yield $E = -0.0327$ and $F = 0.0247$. Osmotic coefficients for $MnCl_2$ were then calculated from 0.01 to 0.10 mol kg^{-1}, at 0.01 intervals, by using these constants.

Both emf studies for RbCl at 25 °C used Rb amalgam and Ag–AgCl electrodes (*22*, *23*). Activity coefficients for each

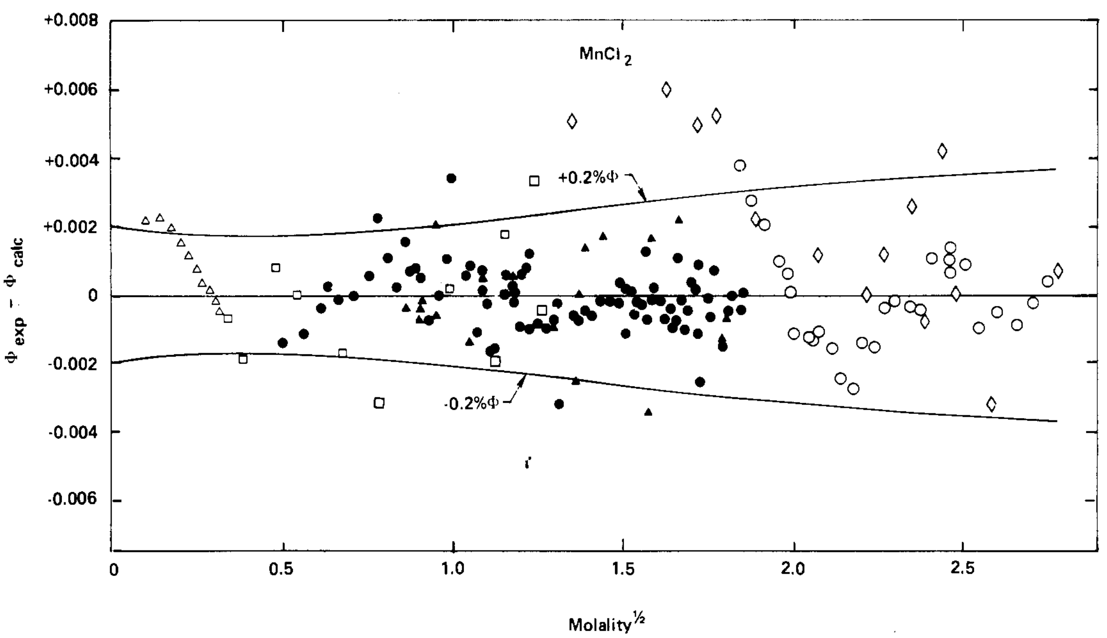

Figure 1. Differences between experimental and calculated osmotic coefficients of MnCl$_2$ at 25 °C: (□) Robinson and Stokes (*7*); (◊) Robinson (*8*); (▲) Downes (*9*); (●) this research, NaCl standard; (○) this research, CaCl$_2$ standard; (△) estimated dilute-solution data based on CaCl$_2$.

study relative to their individual highest concentration were separately fitted to the extended Debye–Hückel equation

$$\ln \gamma_\pm = \ln (\gamma_\pm/\gamma_\pm') + \ln \gamma_\pm' = -Am^{1/2}/(1 + Bm^{1/2}) + Dm \quad (5)$$

where A is the Debye–Hückel limiting slope (1.1762 for 1–1 electrolytes), and $\gamma_\pm'$ is the activity coefficient of the highest experimental concentration. Values of $\gamma_\pm'$, B, and D were optimized by us using a nonlinear least-squares calculation. Lebed' and Aleksandrov's point at 0.0095 mol kg^{-1} was given zero weight; their other values give $B = 1.29$ and $D = -0.0010$ (*22*). Longhi et al.'s results (*23*) were averaged for the various amalgam concentrations (except for two discrepant points) and give least-squares values of $B = 1.16$ and $D = 0.0022$. A Gibbs–Duhem integration of eq 5 yields

$$\Phi = 1 - \left(\frac{A}{B^3 m}\right)\left[1 + Bm^{1/2} - \left(\frac{1}{1 + Bm^{1/2}}\right) - 2 \ln (1 + Bm^{1/2})\right] + D/2m \quad (6)$$

This equation was then used to calculate Φ values, and they are reported in Table IV.

The experimental and calculated osmotic coefficients for each salt over its concentration range were then represented by least-squares equations of the form

$$\Phi = 1 - (A/3)m^{1/2} + \sum_i A_i m^{r_i} \quad (7)$$

where A is the Debye–Hückel limiting slope (4.0744 for MnCl$_2$, 9.4097 for MnSO$_4$, and 1.1762 for RbCl). If a Gibbs–Duhem integration is performed on eq 7, then

$$\ln \gamma_\pm = -Am^{1/2} + \sum_i A_i \left(\frac{r_i + 1}{r_i}\right) m^{r_i} \quad (8)$$

where $\gamma_\pm$ is the mean molal activity coefficient of the solute. Water activities are given by

$$\ln a_1 = -\nu m M_1 \Phi/1000 \quad (9)$$

Table V. Coefficients and Powers for the Osmotic Coefficient Polynomial at 25 °C[a]

	MnCl$_2$		MnSO$_4$		RbCl	
i	r_i	A_i	r_i	A_i	r_i	A_i
1	1.0	4.989289	0.75	−21.39843	0.75	5.022568
2	1.5	−10.31340	1.00	159.7962	0.875	−24.14269
3	2.0	13.81392	1.25	−426.0224	1.00	47.00211
4	2.5	−11.51517	1.50	611.08135	1.125	−42.50403
5	3.0	6.010892	1.75	−513.9961	1.25	15.91482
6	3.5	−1.921719	2.00	252.5674	1.50	−1.016446
7	4.0	0.3441508	2.25	−66.58744		
8	4.5	−0.0263918	2.50	7.181363		
σ		0.00146		0.00149		0.00132

[a] These parameters apply up to 7.699 mol kg^{-1} for MnCl$_2$, to 4.9664 mol kg^{-1} for MnSO$_4$, and to 7.7832 mol kg^{-1} for RbCl.

where $M_1 = 18.0152$ g mol^{-1} is the molecular mass of H$_2$O. Least-squares parameters to eq 7 are given in Table V, and values of Φ, a_1, and $\gamma_\pm$ at various concentrations are in Table VI. Weights for the least-squares fits were based on internal consistency and upon agreement with other data sets.

For MnCl$_2$ Φ fits, unit weights were assigned to the present results, to Downes' results (*9*), and to the estimated low-concentration results. Unit weights were also given to Robinson and Stokes' points (*7*) except for their highest three concentrations which were weighted zero, and to Robinson's values (*8*) above 3.2 mol kg^{-1} except for 4.203 mol kg^{-1}. Robinson's results are up to 0.5% high between 1.838 and 3.163 mol kg^{-1} so they were given reduced weights of 0.5, but at least half of that difference is due to minor uncertainties in CaCl$_2$ Φ values (*3*). Figure 1 shows the differences between experimental Φ values and eq 7. Points given zero weight are not plotted.

Figure 2 shows the differences between experimental Φ data for MnSO$_4$ and eq 7. The present study, Libuš et al. (*2*), and the normalized VPO data (*29*) were given unit weights, except for rejecting Libuš et al.'s point at 1.9913 mol kg^{-1}. These two sets of isopiestic data are in excellent agreement. Robinson and Jones' discrepant results (*1*) were given zero weight. Their data are nearly correct around 2 mol kg^{-1}, but they are significantly low at most other concentrations. It is difficult to explain their problems since they reported no experimental details. However, if about 1.6 mol % Na$_2$SO$_4$ or some other alkali-metal sulfate were present in their solution, it could pro-

Table VI. Osmotic Coefficients, Water Activities, and Activity Coefficients at Rounded Molalities at 25 °C[a]

m	Φ	a_1	$\gamma_\pm$	m	Φ	a_1	$\gamma_\pm$
		$MnCl_2$				RbCl	
0.1	0.8505	0.995 414	0.5114	0.01	0.9706	0.999 650	0.9143
0.2	0.8563	0.990 786	0.4642	0.02	0.9598	0.999 309	0.8832
0.3	0.8704	0.985 99	0.4452	0.03	0.9523	0.998 971	0.8611
0.4	0.8879	0.980 99	0.4376	0.05	0.9416	0.998 305	0.8292
0.5	0.9077	0.975 77	0.4362	0.07	0.9339	0.997 647	0.8058
0.6	0.9291	0.970 32	0.4390	0.1	0.9254	0.996 671	0.7791
0.7	0.9516	0.964 64	0.4449	0.2	0.9086	0.993 474	0.7233
0.8	0.9751	0.958 72	0.4532	0.3	0.8996	0.990 324	0.6894
0.9	0.9991	0.952 57	0.4635	0.4	0.8939	0.987 20	0.6655
1.0	1.0234	0.946 19	0.4754	0.5	0.8902	0.984 09	0.6472
1.2	1.0724	0.932 81	0.5036	0.6	0.8877	0.980 99	0.6326
1.4	1.1210	0.918 68	0.5366	0.7	0.8860	0.977 90	0.6207
1.5	1.1448	0.911 37	0.5546	0.8	0.8850	0.974 81	0.6106
1.6	1.1683	0.903 91	0.5735	0.9	0.8844	0.971 73	0.6020
1.8	1.2140	0.888 6	0.6140	1.0	0.8843	0.968 64	0.5947
2.0	1.2578	0.872 9	0.6576	1.2	0.8848	0.962 47	0.5826
2.5	1.3582	0.832 3	0.7786	1.4	0.8862	0.956 28	0.5732
3.0	1.4448	0.791 2	0.9135	1.5	0.8872	0.953 18	0.5693
3.5	1.5178	0.750 4	1.0584	1.6	0.8883	0.950 08	0.5658
4.0	1.5780	0.711 0	1.2095	1.8	0.8909	0.943 86	0.5599
4.5	1.6272	0.673 2	1.3641	2.0	0.8939	0.937 61	0.5553
5.0	1.6680	0.637 2	1.5211	2.5	0.9028	0.921 89	0.5477
5.5	1.7034	0.602 7	1.6825	3.0	0.9132	0.906 01	0.5441
6.0	1.7367	0.569 4	1.8518	3.5	0.9244	0.890 0	0.5434
6.5	1.7699	0.537 0	2.0333	4.0	0.9361	0.873 8	0.5447
7.0	1.8030	0.505 6	2.2277	4.5	0.9482	0.857 5	0.5476
7.5	1.8318	0.475 9	2.4259	5.0	0.9603	0.841 1	0.5515
7.699	1.8401	0.465 0	2.5004	5.5	0.9722	0.824 8	0.5564
				6.0	0.9837	0.808 4	0.5617
		$MnSO_4$		6.5	0.9948	0.792 2	0.5675
0.1	0.5832	0.997 901	0.1503	7.0	1.0052	0.776 1	0.5735
0.2	0.5398	0.996 117	0.1062	7.5	1.0149	0.760 1	0.5794
0.3	0.5140	0.994 460	0.0855	7.7832[b]	1.0199	0.751 2	0.5827
0.4	0.4975	0.992 856	0.0729				
0.5	0.4873	0.991 260	0.0644				
0.6	0.4815	0.989 64	0.0583				
0.7	0.4791	0.987 99	0.0537				
0.8	0.4793	0.986 28	0.0501				
0.9	0.4815	0.984 51	0.0472				
1.0	0.4854	0.982 66	0.0449				
1.2	0.4973	0.978 73	0.0414				
1.4	0.5139	0.974 41	0.0390				
1.5	0.5239	0.972 08	0.0381				
1.6	0.5348	0.969 64	0.0374				
1.8	0.5598	0.964 35	0.0363				
2.0	0.5888	0.958 46	0.0358				
2.5	0.6789	0.940 68	0.0360				
3.0	0.7926	0.917 89	0.0384				
3.5	0.9254	0.889 9	0.0429				
4.0	1.0701	0.857 1	0.0496				
4.5	1.2173	0.820 9	0.0584				
4.9664	1.3470	0.785 8	0.0684				

[a] Results for $MnCl_2$ below 0.252 07 mol kg^{-1}, for $MnSO_4$ below 0.677 98 mol kg^{-1}, and for RbCl below 0.363 64 mol kg^{-1} are based on an analysis of literature data. See text for details. [b] Saturated solution in equilibrium with solid RbCl.

duce deviations of the observed magnitude.

Differences between RbCl Φ data and eq 7 are shown in Figure 3. Unit weights were given to our data corrected for impurities, Makarov et al.'s (*6*) isopiestic data, emf results (*22*, *23*), and freezing point depression values (*21*). Momicchioli et al.'s lowest concentration point (*21*) was given zero weight, as was Robinson's later study (*5*) which is discrepant from all the other data sets. No experimental details were given in that study (*5*) which gave only smoothed data. Robinson and Sinclair's (*4*) rather scattered data were given weights of 0.5.

Our isopiestic equilibrium molalities for $MnSO_4$ had a precision comparable to the other salts, but several Φ points fell outside the ±0.2% uncertainty limits for these measurements. The other salts had no such problem, so it was specific to $MnSO_4$. However, since many data points were measured, smoothed results should be nearly as accurate as for the other two salts. Osmotic coefficients for these three salts are now known about as accurately as for most alkali-metal and alkaline-earth-metal chlorides.

Table VII. Parameters for Pitzer's Equations at 25 °C

	$MnCl_2$		$MnSO_4$[a]	RbCl
$(4/3)\beta^{(0)}$	0.44297	$\beta^{(0)}$	0.21300	0.04319
$(4/3)\beta^{(1)}$	2.0195	$\beta^{(1)}$	2.9380	0.15398
$(2^{5/2}/3)C^{\Phi}$	−0.04278	$\beta^{(2)}$	−41.906	
		α_1	1.4	
		α_2	12.0	
		C^{Φ}	0.01551	−0.001098
σ	0.0027	σ	0.0054	0.0026

[a] $\beta^{(2)}$, α_1, and α_2 are used only for divalent metal sulfates.

Osmotic coefficients for these three salts were also represented by Pitzer's equation (*18*) using $A^{\Phi} = 0.3920$. As recommended by Pitzer, $\alpha_1 = 1.4$ and $\alpha_2 = 12.0$ were fixed for $MnSO_4$ calculations. Table VII contains parameter values and standard deviations for these fits. The Pitzer equation fit for $MnCl_2$ was restricted to 4.0 mol kg^{-1} and lower, since including

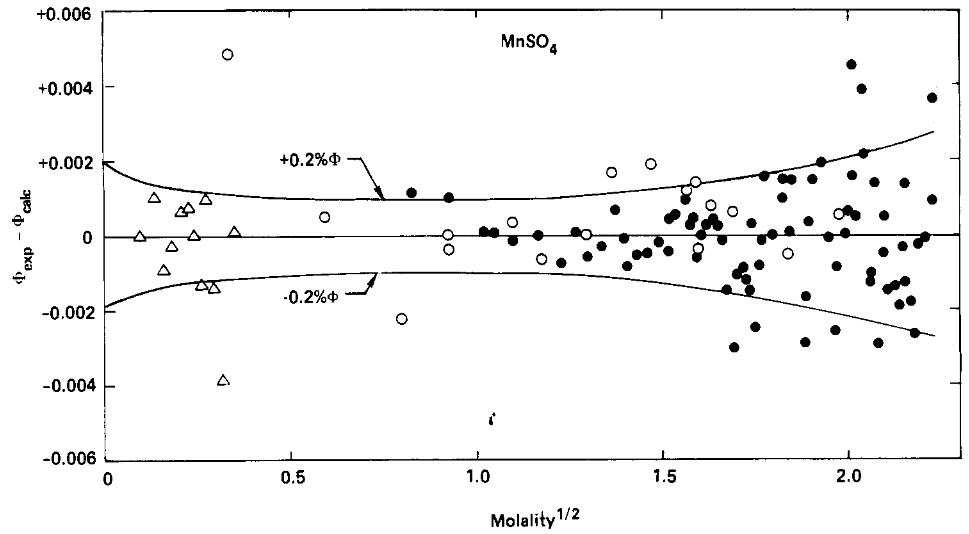

Figure 2. Differences between experimental and calculated osmotic coefficients of MnSO$_4$ at 25 °C: (○) Libuš et al. (*2*); (●) this research; (△) normalized VPO results (*29*).

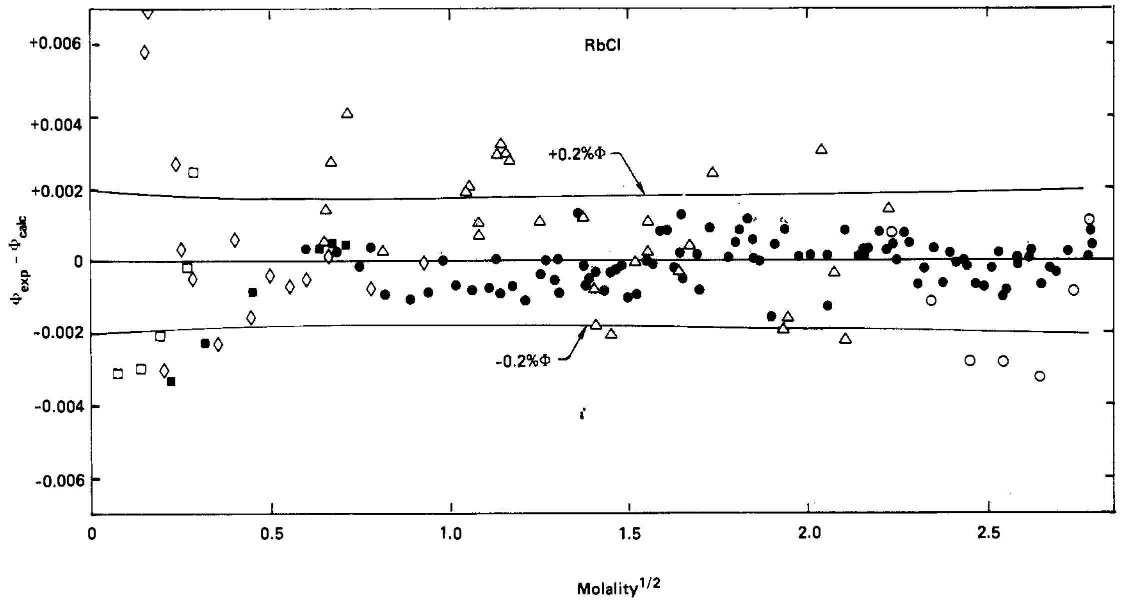

Figure 3. Differences between experimental and calculated osmotic coefficients of RbCl at 25 °C: (△) Robinson and Sinclair (*4*); (○) Markarov et al. (*6*); (●) this research; (◇) freezing point depression (*21*); (□) Lebed' and Aleksandrov emf (*22*); (■) Longhi et al. emf (*23*).

higher concentrations caused excessive cycling of the equation.

Values of Φ and $\gamma_\pm$ were computed, as usual, by treating all electrolytes formally as if they were completely dissociated. MnSO$_4$ solutions are extensively associated, which results in low values for these quantities for that salt.

Certain electrolyte properties show a $c^{1/3}$ dependence on concentration over fairly large concentration intervals, where c is the molar concentration of the electrolyte. This is usually interpreted as indicating a quasi-crystalline structure. Bahe (*31*) found that

$$\log \gamma_\pm + 0.28894c^{1/3} + \log(1 + 0.03603m) = a + B'c \qquad (10)$$

for 1-1 electrolytes assuming a rock salt structure for aqueous solutions at 25 °C. Data for RbCl in Table VI from 0.3 to 4.0 mol kg^{-1} can be accurately represented by this equation with $a = 0.0159$ and $B' = 0.0618$. Dr. Bahe kindly calculated these parameters.

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Glossary

Φ	molal osmotic coefficient
Φ_i°	molal osmotic coefficient of salt i of a mixture at the total ionic strength
y_i	ionic strength fraction of salt i in a mixture
$\delta\Phi_{mix}$	change in osmotic coefficient due to mixing different salts
ν	number of ions formed by complete dissociation of one molecule of solute
m	molality of solution, mol kg^{-1}
A	Debye–Hückel constant
B, D	parameters for eq 5 and 6

E, F	parameters for eq 4
A_i	least-squares coefficients of eq 7 and 8
r_i	powers of eq 7 and 8
$\gamma_\pm$	mean molal activity coefficient of solute
a_1	water activity
M_1	molecular mass of water
a, B'	parameters of Bahe's equation (eq 10)
$\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, α_1, α_2, C^Φ	parameters of Pitzer's equation
A^Φ	Pitzer's Φ equation Debye-Hückel constant for 1-1 electrolytes
σ	standard deviation of fitting equations

Registry No. $MnCl_2$, 7773-01-5; $MnSO_4$, 7785-87-7; RbCl, 7791-11-9.

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Vapor-Liquid Equilibrium in Aqueous Solutions of Various Glycols and Poly(ethylene glycols). 2. Tetraethylene Glycol and Estimation of UNIFAC Parameters

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The activity of water in tetraethylene glycol solutions has been measured at 298.1 K. Vapor-liquid equilibrium data in aqueous solutions of tri- and tetraethylene glycols are used to estimate the interaction parameters for the UNIFAC group contribution model. The activity of water in poly(ethylene glycol) 300 and poly(propylene glycol) 400 is calculated by the UNIFAC method. Good agreement with experimental data is obtained for the former and moderate agreement for the latter.

Introduction

The UNIFAC method for predicting activity coefficients in mixtures of nonelectrolyte solutions has been widely used in recent years (*1*). It is based on the group contribution concept which assumes that the liquid mixture consists of functional groups such as CH_2, CH_2O rather than molecules of various components. The activity coefficients are divided into a combinatorial part and a residual part.

$$\ln \gamma_i = \ln \gamma_i^{C} + \ln \gamma_i^{R} \qquad (1)$$

The combinatorial part is a function of the mole fractions and the reduced van der Waals parameters. The residual part depends on adjustable parameters called group interaction parameters. The equations of γ_i^{C} and γ_i^{R} and a list of parameters are given elsewhere (*1*, *2*).

The water activity in triethylene glycol solution was recently measured by an isopiestic method (*3*). These data together

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