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Isopiestic Determination of the Osmotic and Activity Coefficients of Aqueous $MgCl_2$ Solutions at 25 °C

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The osmotic coefficients of aqueous $MgCl_2$ solutions have been measured at 25 °C by the isopiestic method. These and other available accurate data were represented by a least-squares equation, and this equation was used to calculate water activities and mean molal activity coefficients. Osmotic coefficients from some previous studies are lower than the present results, while other data are in agreement. Some lower osmotic coefficients reported by other workers may be due to alkali contamination of their $MgCl_2$ solutions. The isopiestic standards NaCl, KCl, $CaCl_2$, and H_2SO_4 have been intercompared in this study, and these data can be used to refine the standards' osmotic coefficients. Several different $MgCl_2$, $CaCl_2$, and NaCl solutions were used to determine the reproducibility of isopiestic measurements. It is concluded that independent isopiestic measurements should agree to 0.1–0.2% in most cases, relative to the same isopiestic standard. The solubilities of NaCl and $MgCl_2 \cdot 6H_2O$ have also been determined at 25 °C.

Introduction

The mutual diffusion coefficients of aqueous $MgCl_2$ solutions have been measured in this laboratory (*1*) at 25 °C. To convert these data to thermodynamic diffusion coefficients requires accurate activity-coefficient or osmotic-coefficient derivatives. Examination of the available activity data for this salt (*2–14*) indicated uncertainties of ±0.4–0.5% in the osmotic coefficients, even after obviously unreliable data (*5, 6, 8*) were rejected. Differentiation of experimental data produces larger errors, so more accurate data are required for this purpose.

At high concentrations there are three isopiestic studies (*4, 7, 9*) at 25 °C; two of these are in reasonably good agreement (*4, 7*) while the third study (*9*) gives higher osmotic coefficients. As a check, several isopiestic measurements were performed in this laboratory, and they agreed well with Platford's results (*9*), but not with the other two investigations (*4, 7*). Since Platford's data only extend to 2.76 mol kg^{-1}, new measurements are desirable at high concentrations (the solubility of $MgCl_2 \cdot 6H_2O$ is 5.81 mol kg^{-1}).

In this report isopiestic data are presented for $MgCl_2$ from 1.41 mol kg^{-1} to slightly supersaturated concentrations at 25 °C. The lower-concentration data were measured with several different isopiestic standards to allow a comparison of the internal consistency of the available standard data for NaCl, $CaCl_2$, and H_2SO_4. These new data can also be used to refine the osmotic coefficients of these isopiestic standards.

Experimental Section

The isopiestic measurements were performed at 25.00 ± 0.005 °C (IPTS-68) in the isopiestic apparatus described previously (*15*). All weights were converted to mass. The molecular weights used were 95.211 g mol^{-1} for $MgCl_2$, 120.363 g mol^{-1} for $MgSO_4$, 110.986 g mol^{-1} for $CaCl_2$, 136.138 g mol^{-1} for $CaSO_4$, 58.443 g mol^{-1} for NaCl, 74.551 g mol^{-1} for KCl, and 98.074 g mol^{-1} for H_2SO_4.

Since there are significant discrepancies between the present results and some of the available literature data, a number of different solutions were used in the isopiestic equilibrations. The $MgCl_2$ stock no. 1 was from a mixed batch of recrystallized "Baker analyzed" and Mallinckrodt analytical reagent, while $MgCl_2$ stock no. 2 was prepared from recrystallized Mallinckrodt analytical reagent (separate lot). The $MgCl_2$ stock no. 3 was prepared by R. H. Stokes from "Univar" material.

Two $CaCl_2$ stock solutions were prepared by the method of Stokes (*16*) from HCl (stock no. 1 Dupont reagent grade; stock no. 2 Mallinckrodt analytical reagent) and separate lots of Mallinckrodt primary standard $CaCO_3$. The $CaCl_2$ stock no. 2 was adjusted to its equivalence pH, which was obtained by titration of samples with dilute HCl. $CaCl_2$ stock no. 1 was not adjusted to its equivalence pH, but this $CaCl_2$ was purified by recrystallization. Stock no. 2 was also used for most of the diffusion-coefficient measurements (*17*).

Two NaCl solutions were prepared by mass from separate lots of Mallinckrodt analytical reagent NaCl. The preparation of the KCl and H_2SO_4 standards has been described earlier (*15, 18*). All water used in this study was first deionized and then distilled.

Samples of each $MgCl_2$ stock solution and $CaCl_2$ stock no. 1 were evaporated to dryness and then analyzed for impurities by using direct current arc optical emission spectroscopy. The approximate amounts of impurities found are given in percent by weight. $MgCl_2$ stocks no. 1 and 2 had 0.0003% or less of Ca, Fe, Sr, Ni, and B. Na was below its detection limit of 0.002%, and less than 0.0001% Sr was present. $MgCl_2$ stock no. 3 (Univar) contained ~0.2% Na, 0.02% Ca, 0.02% Fe, and 0.005% Cr, with other impurities in lesser amounts. The $CaCl_2$ stock no. 1 contained ~0.1% Sr, 0.003% Ba, 0.01% Si, and less than 0.005% Na and Fe.

Some of the $CaCl_2$ stock no. 2 was converted to $CaSO_4$ and then analyzed by X-ray fluorescence spectroscopy. This $CaCl_2$ contained ~0.01% Sr. Both K and Ba were present in

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Table I. Summary of Concentrations of Stock Solutions

electrolyte	stock no.	method	concn, *m*
$MgCl_2$	1	sulfate	5.6720 ± 0.0013
	1	sulfate	5.6736 ± 0.0021
	1	chloride	5.6702 ± 0.0040
	1	chloride	5.6755^a
$MgCl_2$	2	sulfate	5.2448 ± 0.0019
	2	chloride	5.2469 ± 0.0011
$MgCl_2$^{b}	3	chloride	4.3058 ± 0.0013
$CaCl_2$	1	sulfate	6.6262 ± 0.0004
	1	sulfate	6.6263 ± 0.0019
	1	dehydration	6.6267 ± 0.0018
$CaCl_2$^{c}	2	sulfate	6.8540 ± 0.0011
H_2SO_4		KOH titration	15.398 ± 0.012
		NaOH titration	15.390^a
NaCl	1	direct weighing	5.9054
	1	chloride	5.9068 ± 0.0011
	1	chloride	5.9055 ± 0.0010
	1	dehydration	5.9021 ± 0.0007
NaCl	2	direct weighing	4.9601
	2	chloride	4.9613 ± 0.0026
	2	dehydration	4.9608 ± 0.0010
KCl		direct weighing	0.76929
		chloride	0.76952 ± 0.00009

[a] Back-calculated from analysis of a dilution of this stock solution. [b] This $MgCl_2$ solution contains 0.2% Na, 0.02% Ca, and 0.02% Fe. [c] This $CaCl_2$ solution was adjusted to its equivalent pH.

Table II. Isopiestic Molalities of $MgCl_2$ Stock No. 1 from Measurements with $CaCl_2$ Reference Solution No. 1

$[MgCl_2]$, *m*	$[CaCl_2]$, *m*	$[MgCl_2]$, *m*	$[CaCl_2]$, *m*
5.9188	6.9627	4.6574	5.1329
5.8344	6.8107	4.5580	5.0134
5.8260	6.7974	4.4428	4.8769
5.8101^a	6.7671	4.3288	4.7454
5.8096	6.7651	4.2522	4.6550
5.7513	6.6651	4.1878	4.5814
5.6737	6.5373	4.1040	4.4850
5.5757	6.3791	4.0251	4.3962
5.5220	6.2934	4.0106	4.3785
5.4398	6.1720	3.9102	4.2659
5.3898	6.0959	3.8325	4.1781
5.3651	6.0617	3.7551	4.0898
5.3511	6.0398	3.6776	4.0036
5.1237	5.7257	3.6028	3.9192
5.1167	5.7175	3.5359	3.8442
5.0708	5.6540	3.4802	3.7823
4.9698	5.5224	3.4329	3.7293
4.9018	5.4353	3.3261	3.6108
4.7739	5.2742		

[a] Saturated solution in equilibrium with $MgCl_2\cdot 6H_2O$.

Table III. Isopiestic Molalities of $MgCl_2$ Stock No. 1 from Measurements with $CaCl_2$ No. 1, H_2SO_4, and NaCl No. 1 Reference Solutions

$[MgCl_2]$, *m*	$[CaCl_2]$, *m*	$[H_2SO_4]$, *m*	[NaCl], *m*
3.6424	3.9625	5.9623	
2.9636	3.2041	4.7155	
2.9633	3.2047	4.7191	
2.7596	2.9771	4.3563	
	2.9772	4.3555	6.1580^a
2.7383	2.9520	4.3181	6.0967
2.7033	2.9157	4.2611	
2.6111	2.8137	4.0952	5.7368
2.5063	2.6974	3.9153	5.4439
2.5033	2.6944	3.9124	
2.4935	2.6841	3.8980	
2.4081	2.5884	3.7477	5.1732
2.3108	2.4802	3.5780	4.9051
2.2291	2.3927	3.4443	4.6912
2.1421	2.2957	3.2965	4.4588
1.9846	2.1234	3.0323	4.0481
1.8279	1.9513	2.7721	3.6499
1.6793	1.7872	2.5275	3.2754
1.5414	1.6371	2.3034	2.9413
1.5387	1.6344	2.2993	2.9359
1.4338	1.5194	2.1296	2.6863
1.4217	1.5069	2.1114	2.6591
1.4099	1.4934	2.0910	2.6304

[a] Saturated solution in equilibrium with solid NaCl.

Table IV. Isopiestic Molalities of $MgCl_2$ Stock No. 2 from Measurements with both $CaCl_2$ Reference Solutions

$[MgCl_2]$, *m*	$[CaCl_2]$,^{a} *m*	$[CaCl_2]$,^{b} *m*
5.3737	6.0663	6.0694
5.3695	6.0607	6.0644
5.2453	5.8852	5.8888
4.8912	5.4182	5.4205
4.5148	4.9589	4.9603
4.2484	4.6455	4.6489
3.9684	4.3281	4.3305
3.6284	3.9456	3.9474
3.3552	3.6413	3.6427
3.1825	3.4486	3.4497
3.0015	3.2472	3.2483

[a] Stock no. 1, normal isopiestic preparation. [b] Stock no. 2, pH-adjusted solution.

Table V. Isopiestic Molalities of $CaCl_2$ Stock No. 1, NaCl Stock No. 2, and KCl Solutions

$[CaCl_2]$, *m*	[NaCl], *m*	[KCl], *m*
2.9758	6.1589^a	
2.8372	5.7991	
2.2491	4.3472	4.9873^b
2.0201	3.8090	4.3043

[a] Saturated solution in equilibrium with solid NaCl. [b] Supersaturated solution.

amounts below their 0.01% detection limits.

A variety of chemical analyses was used to determine the concentrations of the stock solutions. Samples of the $MgCl_2$ and $CaCl_2$ solutions were slowly evaporated to dryness on a hot plate, in the presence of an excess of H_2SO_4. When evolution of H_2O, HCl, and SO_3 ceased, the samples were placed in a muffle furnace and then ignited to the anhydrous sulfates at 500 °C.

Dehydration analyses were performed for NaCl and $CaCl_2$ by acidifying weighed samples with HCl and then drying at 200 °C. Although this method was successful for $CaCl_2$, it is not to be recommended since $CaCl_2$ tends to splatter while being dried. Dehydration could not be used for the $MgCl_2$ solutions since much of the Cl^- is lost during the drying process.

Concentrations of the $MgCl_2$, NaCl, and KCl solutions were also determined by mass titration with $AgNO_3$ (dichlorofluorescein end-point indicator, dextrin colloid stabilizer). The H_2SO_4 standard solution was mass titrated with KOH and NaOH by using phenolphthalein as the end-point indicator. These alkali solutions were standardized against oven-dried "Baker analyzed" potassium biphthalate (different lots).

All concentration-analysis results are listed in Table I. The errors quoted are average deviations from the mean. The sulfate and dehydration analyses were performed in triplicate; $AgNO_3$ analyses were quadruplicate; and four or five samples were used for the alkali titrations.

Duplicate samples of each electrolyte were used in the isopiestic experiments, and the molalities of each electrolyte were within 0.1% of the average at equilibrium. In most cases the agreement was to better than 0.05%. Isopiestic equilibration times varied from 4 to 14 days except for the saturated $MgCl_2$ solutions. The experimental molality results are reported in Tables II–VI. Attempts to reach higher $MgCl_2$ concentrations resulted in spontaneous crystallization.

Table VI. Isopiestic Molalities of $MgCl_2$ Stock No. 3 with 0.2% Na from Measurements with $CaCl_2$ No. 1 Reference Solution

$[MgCl_2]$,[a] m	$[CaCl_2]$, m	$[MgCl_2]$, m	$[CaCl_2]$, m
4.6615	5.1190	3.8797	4.2175
4.4106	4.8205	3.7044	4.0229
4.1300	4.5014	3.3640	3.6446

[a] The $MgCl_2$ concentrations were calculated as if the solution were pure $MgCl_2$.

The solubility of $MgCl_2 \cdot 6H_2O$ at 25 °C was obtained by equilibration of two samples of stock no. 1 with another cup containing saturated solution and crystals. Results for 4- and 22-day equilibrations were within 0.01% of each other. The observed solubility was 5.8101 ± 0.0013 mol kg^{-1} (equilibration uncertainty only). This value is in excellent agreement with Berecz and Båder's (*19*) value of 5.811 mol kg^{-1}, which is an average of available literature data. Individual determinations of the solubility in the literature, however, show considerable variation for this salt.

The solubility of NaCl was determined twice. Three equilibrations were performed for samples from stock no. 1 and 6.1580 ± 0.0050 mol kg^{-1} obtained with 4–7-day equilibrations. A solubility of 6.1589 ± 0.0041 was obtained for 5- and 6-day equilibrations of stock no. 2 samples. Solubilities from other isopiestic studies range from 6.144 to 6.147 mol kg^{-1} (*20*, *21*). However, Åkerlöf and Turck (*22*) obtained 6.163 by direct chemical analysis. These authors made an "extensive survey of the literature" and obtained 6.162 ± 0.001 as the average molality from 30 separate determinations. Our solubilities are ~0.06% below their mean. Lower solubilities from earlier isopiestic studies noted above may be due to using times too short to reach thermodynamic equilibrium.

Calculations and Discussion for $MgCl_2$. The osmotic coefficients of $MgCl_2$ solutions were calculated from eq 1,

$$\phi = \nu^* m^* \phi^* / (\nu m) \tag{1}$$

where m is the molality of $MgCl_2$, $\nu = 3$ is the number of ions formed by the complete dissociation of one molecule of $MgCl_2$, and ϕ is the molal osmotic coefficient of $MgCl_2$. The asterisk indicates corresponding quantities for the NaCl, $CaCl_2$, and H_2SO_4 reference solutions.

Osmotic coefficients for the reference solutions were calculated by using available equations (*23*, *24*). Other isopiestic data at 25 °C (*3*, *4*, *7–11*, *13*, *14*) were recalculated to conform to the same isopiestic reference-solution values. Isopiestic and vapor-pressure data are available at other temperatures (*25*, *26*), but the available thermal data (*27–29*) are not sufficiently accurate to convert the higher-concentration data to 25 °C. Vapor-pressure data at 25 °C (*5*, *6*) are too inaccurate and too scattered to use in subsequent calculations.

Several sets of freezing-point-depression data are available (*30*); the more accurate results (*2*, *12*) were converted to osmotic coefficients at 25 °C and are reported in Table VII. Gibbard and Gossmann's data (*12*) above 1.016 mol kg^{-1} were not included because the temperature conversions to 25 °C are too large to make accurately. The heat-capacity measurements of Perron et al. (*29*) were corrected as recommended by Desnoyers et al. (*31*).

The osmotic coefficients in Tables II–IV and VII, and other accurate data at 25 °C, were fitted to eq 2, where $A = 4.0744$

$$\phi = 1 - (A/3)m^{1/2} + \sum_i A_i m^{r_i} \tag{2}$$

is the Debye–Hückel limiting slope. The mean molal activity coefficients are then given by eq 3, which is the Debye–Hückel limiting law plus a series in the molality to represent higher-concentration data. The weights for the various sets of data were assigned on the basis of internal consistency and upon agreement with other studies.

$$\ln \gamma_\pm = -Am^{1/2} + \sum_i A_i \left(\frac{r_i + 1}{r_i}\right) m^{r_i} \tag{3}$$

Table VII. Osmotic Coefficients of $MgCl_2$ from Freezing-Point-Depression Measurements

m	ϕ_f[a]	ϕ	m	ϕ_f[a]	ϕ
		Menzel (*2*)			
0.6724	1.0183	0.9988	0.1330	0.8738	0.8674
0.5388	0.9716	0.9558	0.0797	0.8639	0.8583
0.3956	0.9364	0.9243	0.0640	0.8674	0.8620
0.2759	0.8996	0.8904			
		Gibbard and Gossmann (*12*)			
1.0161[b]	1.1482	1.1187	0.2500	0.8928	0.8842
0.90805	1.1057	1.0796	0.1746	0.8739	0.8669
0.90415	1.1056	1.0795	0.1671	0.8739	0.8669
0.7255	1.0387	1.0178	0.1492	0.8700	0.8634
0.6118	0.9979	0.9801	0.1218	0.8686	0.8624
0.5348	0.9733	0.9576	0.11835	0.8683	0.8621
0.53415	0.9695	0.9538	0.07865	0.8691	0.8634
0.47585	0.9532	0.9391	0.05675	0.8699	0.8645
0.40445	0.9324	0.9201	0.054575	0.8714	0.8661
0.3325	0.9106	0.9001	0.031965	0.8854	0.8805
0.25645	0.8905	0.8818	0.02805	0.8863	0.8815

[a] The osmotic coefficient of the solution at its freezing temperature. The number to the right is the corresponding osmotic coefficient converted to 25 °C. [b] Data were measured at higher concentrations, but the available thermal data are not accurate enough to allow an accurate conversion of these data to 25 °C.

Two sets of vapor-pressure data (*5*, *6*) and one set of isopiestic data (*8*) are badly scattered, or discrepant from other available results, and were given zero weights in the least-squares calculations. Because of scatter, the data of Frolov et al. (*11*), Saad et al. (*13*), and Padova and Saad (*14*) were given weights of 0.5; Robinson and Stokes' data (*3*) were given this weight above 0.43 mol kg^{-1}, and zero weight below. Platford's data (*9*) were given zero weight below 0.985 mol kg^{-1}, also because of scatter, and unit weights at higher concentrations. A few outlying points from the above studies were also given zero weight. The data of Wu et al. (*10*), and Gibbard and Gossmann (*12*) up to 1.016 mol kg^{-1}, are of higher precision and were assigned unit weights. Menzel's freezing-point-depression data (*2*) were given zero weight because of large scatter, but their results are consistent with Gibbard and Gossmann's (*12*).

At high concentrations, the osmotic coefficients from Tables II–IV agree with Platford's study (*9*). The data of Wu et al. (*10*) and Gibbard and Gossmann (*12*) connect up fairly smoothly with these higher-concentration results (this may be partly fortuitous for Gibbard and Gossmann's data since the temperature corrections to freezing-point-depression data (*12*) are quite large at higher concentrations). The data of Stokes (*4*) and Robinson and Bower (*7*) yield lower osmotic coefficients, while the remaining sets of data (*2*, *11*, *13*, *14*) are too scattered to group with either trend.

R. H. Stokes furnished us with a $MgCl_2$ stock solution containing 0.2% Na, and several isopiestic measurements were performed with this solution. These results are listed in Table VI. The osmotic coefficients of this solution are ~0.2% above Stokes' (*4*) and Robinson and Bower's (*7*) values, and ~0.6% below the values from Tables II–IV. This indicates that small amounts of alkali contamination could possibly be the orgin of the lower osmotic coefficients found in these two studies (*4*, *7*). Potassium is a more likely contaminant in the earlier studies since the $MgCl_2$ was probably prepared from carnallite, $KMgCl_3 \cdot 6H_2O$ (*32*).

The osmotic coefficients of Stokes and of Robinson and Bower are also low at lower concentrations, and this is concordant with the above supposition. Recrystallization is not very

Table VIII. Powers and Coefficients for the Osmotic Coefficient Polynomial

i	r_i[a]	A_i[a]	r_i[b]	A_i[b]
1	1.0	5.315 953	0.75	−6.954 804
2	1.5	−11.803 27	1.00	66.107 82
3	2.0	17.483 81	1.25	−212.957 0
4	2.5	−16.412 564	1.50	375.762 5
5	3.0	9.784 278	1.75	−394.045 4
6	3.5	−3.550 148	2.00	244.681 7
7	4.0	0.709 023 4	2.25	−82.936 271
8	4.5	−0.059 380 28	2.50	11.809 57
SD[c]		0.002 15		0.002 11

[a] Powers and parameters for eq 2 and 3 including estimated dilute solution data (based on $CaCl_2$). These parameters were used in computing results for Table IX. [b] Powers and parameters for eq 2 and 3 using only freezing-point-depression data in the dilute region. [c] Standard deviation.

satisfactory for purifying alkaline earth chlorides from alkali chlorides (*16*).

Alkali contamination is suggested as a possible explanation for low osmotic-coefficient values (*4*, *7*). It is not our intention to single out these two studies for criticism, since none of the other studies reported an analysis for impurities. Alkali contamination of alkaline earth salts may be more common than is usually supposed, and future workers should take the precaution of having their solutions analyzed for impurities.

Because of the above considerations, the higher-concentration data of Stokes (*4*) were weighted zero, while his lower-concentration data with a KCl reference were weighted 0.5. Similarly, Robinson and Bower (*7*) were weighted 0.5 up to 1.748 mol kg^{-1} and zero at higher concentrations. The data of Tables II–IV were given unit weight. If more than one reference solution was used, each reference was calculated separately and each was given unit weight. The four low-concentration points reported elsewhere (*33*), with KCl and H_2SO_4 standards, were also given unit weights.

The above osmotic coefficients were accurately represented by several different sets of powers and coefficients for eq 2, but calculated activity coefficients differed by several percent. This results because too few accurate freezing-point-depression values are available for $MgCl_2$ below 0.1 mol kg^{-1} to adequately constrain eq 2. There is also a lack of accurate emf data for this salt at low concentrations. In order to better constrain the least-squares fits at low concentrations and to obtain more reliable activity coefficients, we estimated additional osmotic coefficients for $MgCl_2$ by using the following modification of the Åkerlöf–Thomas approach (*34*) and available accurate data for $CaCl_2$ (*24*) at low concentrations.

At low concentrations a series expansion of the expression for the osmotic coefficient, using the ion size approximation, indicates the ϕ should equal a limiting-law value plus a series in $m^{1/2}$ starting with m. Taking the difference between osmotic coefficients for two salts of the same valence results in cancellation of the limiting-law term. The difference between the osmotic coefficients of $MgCl_2$ and $CaCl_2$ is then found to be

$$\Delta\phi = 0.0365m + 0.033m^{3/2} \qquad (4)$$

where the constants were obtained by using smoothed $MgCl_2$ (second set of constants in Table VIII) and $CaCl_2$ (*24*) osmotic coefficients from 0.3 to 0.8 mol kg^{-1}. This is the concentration region for which the data follow this two-parameter equation. Equation 4 was then used to generate 10 points for $MgCl_2$ from 0.01 to 0.10 mol kg^{-1} at equal intervals. These estimated values were included in the data base, and the least-squares calculations were repeated.

The least-squares parameters for the best fits to eq 2, both with and without the estimated data from $CaCl_2$, are given in Table VIII. Activity coefficients for the best fit including the estimated data were judged to be more reliable, so this fit was used in subsequent calculations. However, the osmotic coefficients for $MgCl_2$ below 0.1 mol kg^{-1} and, therefore, absolute activity-coefficient values are still somewhat uncertain. Additional freezing-point-depression or emf measurements would be quite desirable at low concentrations to reduce the remaining uncertainty.

Table IX. Osmotic Coefficients, Water Activities, and Activity Coefficients at Round Molalities

m	ϕ	a_1	$\gamma_\pm$
0.1	0.8605	0.995360	0.5241
0.2	0.8725	0.990613	0.4829
0.3	0.8931	0.98562	0.4699
0.4	0.9177	0.98036	0.4685
0.5	0.9451	0.97479	0.4741
0.6	0.9747	0.96889	0.4848
0.7	1.0062	0.96265	0.4995
0.8	1.0393	0.95606	0.5178
0.9	1.0738	0.94911	0.5396
1.0	1.1096	0.94180	0.5646
1.2	1.1848	0.92604	0.6252
1.4	1.2646	0.90875	0.7008
1.6	1.3485	0.8899	0.7939
1.8	1.4364	0.8696	0.9077
2.0	1.5279	0.8478	1.046
2.2	1.6226	0.8245	1.215
2.4	1.7199	0.8000	1.420
2.6	1.8195	0.7744	1.668
2.8	1.9208	0.7478	1.968
3.0	2.0232	0.7203	2.332
3.2	2.1265	0.6923	2.771
3.4	2.2302	0.6638	3.302
3.6	2.3342	0.6350	3.942
3.8	2.4382	0.6061	4.714
4.0	2.5424	0.5772	5.648
4.2	2.6469	0.5484	6.777
4.4	2.7519	0.5197	8.146
4.6	2.8579	0.4914	9.813
4.8	2.9653	0.4634	11.85
5.0	3.0747	0.4357	14.36
5.2	3.1868	0.4084	17.46
5.4	3.3021	0.3815	21.33
5.6	3.4213	0.3551	26.18
5.8	3.5451	0.3291	32.33
5.8101[a]	3.5515	0.3278	32.68
5.9188	3.6210	0.3140	36.75

[a] Saturated solution in equilibrium with $MgCl_2 \cdot 6H_2O$.

Table X. Parameters for Pitzer's Equation

parameter	value
$(^4/_3)\beta^{(0)}$	0.46791
$(^4/_3)\beta^{(1)}$	2.2010
$(2^{5/2}/3)C^{\phi}$	0.01227
α_1	2.0
SD[a]	0.0029

[a] Standard deviation.

The differences between the experimental osmotic coefficients and eq 2 (best fit) are shown in Figure 1. The osmotic coefficients of $MgCl_2$ are now known to ~0.2% over most of the concentration range, with a slightly larger uncertainty at lower concentrations. Values of ϕ, a_1 (water activity), and $\gamma_\pm$ at round concentrations are given in Table IX. Differences between the present results and previous evaluations (*35*, *36*) are due to the inclusion of the present measurements on more completely characterized samples.

The osmotic coefficients up to 4.0 mol kg^{-1} were also fitted to Pitzer's equation (*37*) by using the weights listed above. The parameters to this equation are given in Table X. Pitzer's equation does not represent the data as well as eq 2 since it contains fewer parameters.

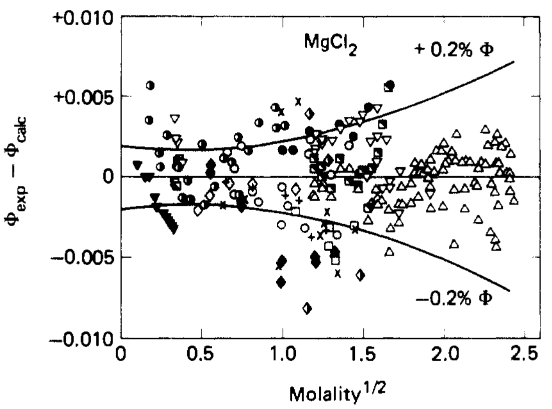

Figure 1. Differences between experimental and calculated osmotic coefficients of $MgCl_2$ at 25 °C: (◐) Gibbard and Gossmann (*12*); (○) Robinson and Stokes (*3*); (□) Stokes (*4*); (♦) Robinson and Bower (*7*); (●) Platford (*9*); (◊) Wu, Rush, and Scatchard (*10*); (♦) Frolov et al. (*11*); (×) Saad et al. (*13*); (+) Padova and Saad (*14*); (▽) H_2SO_4 standard (*33*) including present results; (■) Rard and Miller KCl standard (*33*); (△) present results $CaCl_2$ standard; (■) present results NaCl standard; (▼) estimated dilute solution data based on $CaCl_2$.

Isopiestic Accuracy and Standards. Isopiestic measurements were performed with two different pure $MgCl_2$, two different $CaCl_2$, and two different NaCl solutions, and one KCl and one H_2SO_4 solution. These data were measured in part to intercompare the isopiestic standards and to determine the reproducibility of the isopiestic method. Figure 1 allows a comparison using the $MgCl_2$ osmotic coefficients as a basis.

The two different preparations of $CaCl_2$ are compared in Table IV, and molality differences at isopiestic equilibrium are 0.03–0.07%. $CaCl_2$ stock no. 1 contained 0.1% Sr and was not adjusted to its equivalence pH (stock pH 4.33 at 6.6264 mol kg^{-1}), while stock no. 2 had only 0.01% Sr and was adjusted to its equivalence pH (a 6.645 mol kg^{-1} dilution had pH 1.62). The molality differences at isopiestic equilibrium are probably within the combined uncertainties of the stock solutions' analyses. This indicates that neither Sr contamination nor large pH differences have a significant effect on the osmotic coefficients of $CaCl_2$. This should also be true for other alkaline earth halides.

Several series of $MgCl_2$ equilibrations were made, with two different $MgCl_2$ solutions and two different $CaCl_2$ reference solutions (not including the Na-contaminated $MgCl_2$ solution). Osmotic coefficients from these data, in Tables II–IV, are within 0.05–0.2% of each other. Data for the osmotic coefficients of $CaCl_2$ relative to two different NaCl reference solutions can be obtained from the equilibrium molalities in Tables III and V. These two sets of osmotic coefficients of $CaCl_2$ agree within 0.05–0.1%. Data for $CaCl_2$ with H_2SO_4 as the reference (Table III) are ~0.22% higher, on the average, than reported earlier (*18*).

The above results indicate that the isopiestic method should yield osmotic coefficients reproducible to 0.1–0.2% in most cases if the same electrolyte is used as the reference solution. This is true provided pure chemicals are used, accurate chemical analyses are performed for stock-solution concentrations, and care is taken in the isopiestic measurements. At high temperatures isopiestic measurements become more difficult (*25*) so larger errors are to be expected. Also, associated electrolytes and salts of hydrolyzable ions may be very sensitive to slight pH variations.

Figure 1 indicates that some differences occur for the calculated $MgCl_2$ osmotic coefficients when different reference solutions are used. Over most of the concentration range, these differences are 0.2% or less, which is within the uncertainty of the isopiestic method. However, around 2.7 mol kg^{-1} $MgCl_2$, the differences are ~0.4%, with osmotic coefficients from the NaCl standard being higher than when $CaCl_2$ or H_2SO_4 standards were used. The osmotic coefficients of NaCl are accurately known and are probably not the cause of this discrepancy. The data obtained by using $CaCl_2$ and H_2SO_4 standards show similar trends in this region, and this suggests a common origin to the problem.

These discrepancies occur near the saturation concentration of NaCl. The H_2SO_4 standard osmotic coefficients are mainly based on KCl and NaCl isopiestic data at lower concentrations, and vapor-pressure data at higher concentrations. The $CaCl_2$ osmotic coefficients are based mainly on $CaCl_2$–H_2SO_4 isopiestic data at high concentrations and NaCl and KCl isopiestic data at lower concentrations (*24*, *35*). If the average of the H_2SO_4 vapor-pressure data is 0.2–0.4% higher from 4–6 mol kg^{-1}, the discrepancies noted above will vanish. Some additonal vapor-pressure measurements for 4–6 mol kg^{-1} H_2SO_4 solutions would help to clarify this situation.

The data in this present report include redeterminations of the NaCl–$CaCl_2$, NaCl–H_2SO_4, and H_2SO_4–$CaCl_2$ isopiestic ratios. A few points were likewise measured for the NaCl–KCl and KCl–$CaCl_2$ isopiestic ratios. All of these data can also be combined with other available data for these electrolytes to improve the values for the osmotic coefficients of the isopiestic standards.

The highest KCl concentration in Table V is a supersaturated solution. It was stable during the isopiestic measurements, but crystallization occurred when the solutions were cooled to the room temperature of 22 °C.

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Glossary

ϕ	molal osmotic coefficient
ν	number of ions formed by the dissociation of one molecule of solute
m	molal concentration, mol kg^{-1}, of the solute
$\gamma_\pm$	mean molal activity coefficient
a_1	water activity
A	Debye–Hückel constant
A_i	least-squares coefficients of eq 2 and 3
r_i	powers of eq 2 and 3
$\beta^{(0)}$, $\beta^{(1)}$, α_1, C^ϕ	parameters for Pitzer's equation

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Viscosity and Density of Aqueous Na_2SO_4 and K_2SO_4 Solutions in the Temperature Range 20–90 °C and the Pressure Range 0–30 MPa

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This paper presents experimental data of the viscosity of aqueous Na_2SO_4 and K_2SO_4 solutions. The viscosity was measured by the oscillating-disk method in the pressure range 0–30 MPa and the temperature range 20–90 °C. The measurements cover the concentration range 0–1.1 *m* for the first salt and 0–0.6 *m* for the second. The experimental results have an estimated uncertainty of ±1.0%. The effect of pressure on the density of these solutions has also been measured. These measurements constitute the first study of the viscosity and the density of Na_2SO_4 and K_2SO_4 solutions over an extended range of pressure, temperature, and concentration. The viscosity and density data have been correlated in terms of pressure, temperature, and concentration. The correlations reproduce the original data to within the quoted uncertainty. The paper includes comparisons between our correlations and the experimental results of other investigators.

Introduction

This paper is the seventh in a series (*1–3*, *6–8*) that is intended to provide data on the viscosity of the prevalent constituents in geothermal brines. The previous publications included measurements of the viscosity of distilled water (*8*) and aqueous solutions of NaCl (*6*, *7*), KCl (*3*), NaCl-KCl mixtures (*1*), and Na_2CO_3 and K_2CO_3 (*2*). In this paper we present measurements of the viscosity of aqueous Na_2SO_4 and K_2SO_4 solutions in the temperature range 20–90 °C and a pressure range of 0–30 MPa. The concentration range extends from 0 to 1.1 *m* for aqueous Na_2SO_4 solutions and from 0 to 0.6 *m* for aqueous K_2SO_4 solutions. These measurements are believed to be the only ones covering a range of pressure, temperature, and concentration corresponding to liquid-dominated geothermal reservoirs.

A careful search of the available literature (*16*) revealed the viscosity measurements on Na_2SO_4 solutions by Korosi and Fabuss (*13*) to be the only data available for comparison. Since it was also shown that only inadequate data on the density as a function of pressure exist for these solutions, it was decided to measure this effect as well. The viscosity and density are used to develop correlations valid over the entire range of temperature, pressure, and concentration covered by the measurements.

Experimental Procedure

The measurements of viscosity were performed in an oscillating-disk viscometer which has been described in detail in our previous publications (*4*, *8*, *10*). The theory of the instrument and the experimental procedure were also given there. The characteristics of the oscillating system are the same as those given in ref *1*.

The viscometer was calibrated with respect to distilled water in the manner described in ref *6* and *8*. The edge-correction factor *C* (*9*, *12*) for the viscometer is described as a function of the boundary-layer thickness, δ (*8*, *11*), defined as

$$\delta \equiv (\nu T_0/2\pi)^{1/2} \tag{1}$$

Here, ν is the kinematic viscosity of the fluid and T_0 is the period of oscillation in vacuo. Figure 1 depicts the results of the calibration where the solid line represents the least-squares fit of the experimental data given by eq 2. The original calibration

$$C(\delta) = 1.000 + 0.04085(\delta/\text{mm}) + 0.09365(\delta/\text{mm})^2 - 0.03767(\delta/\text{mm})^3 \tag{2}$$

points are shown as open symbols while the solid ones are check measurements which were taken after each cleaning and realignment of the oscillating system. It can be seen that the check points deviate from the line represented by eq 2 by less than ±0.2%.

The solutions were prepared by mixing reagent-purity salts with distilled, deaerated water. The K_2SO_4 solutions were prepared gravimetrically by means of a high-precision, high-