diction not significantly different from that for compounds used in the original regression analysis.

For the pure (supercooled) liquid to aqueous solution step, a very simple model involving the total surface area (TSA) of the molecule can be used to estimate $\Delta G_1°$ for alkyl, aromatic, and alkyl aromatic hydrocarbons. The apparent success of this simple model for $\Delta G_1°$ is due to considerable free energy compensation since it is much less satisfactory for $\Delta G_2°$ and $\Delta G_3°$. The failure of the simple TSA model for $\Delta G_2°$ and $\Delta G_3°$ appears to be due to a need to treat aromatic carbon and hydrogen atoms as distinct units. The results for $\delta\Delta G_3°$, for example, suggest that the aromatic carbon is considerably more hydrophylic and the aromatic hydrogen considerably more hydrophobic than aliphatic methylene units on a per unit area basis.

The group surface area approach has the advantage of providing all group area terms in one calculation. It is not necessary to account directly for group proximity effects since these are included implicitly in the area calculation. Consequently it can be used to estimate $\Delta G_1°$, $\Delta G_2°$, and $\Delta G_3°$ for compounds for which data are unavailable or difficult to obtain.

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**Supplementary Material Available:** Solubility and free energy of solution (aqueous), heats of fusion, melting points, and vapor pressures of alkyl aromatic compounds (15 pages). Ordering information is given on any current masthead page.

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# Isopiestic Determination of the Osmotic Coefficients of Aqueous $Na_2SO_4$, $MgSO_4$, and $Na_2SO_4$–$MgSO_4$ at 25 °C

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**The osmotic coefficients of aqueous $Na_2SO_4$, $MgSO_4$, and an equimolal mixture of these salts have been measured by the isopiestic method at 25 °C. The solubilities of KCl, $Na_2SO_4\cdot10H_2O$, and $MgSO_4\cdot7H_2O$ have also been determined. The results are compared to other available activity and solubility data for these salts. Least-squares equations were used to represent these data and to calculate activity coefficients of $Na_2SO_4$ and $MgSO_4$. Discrepancies between isopiestic and freezing-point-depression measurements for most 2–2 electrolytes may be due to the neglect of the temperature dependence of the heat capacities.**

## Introduction

Solutions of $Na_2SO_4$ and $MgSO_4$ are of geochemical interest because of their presence in seawater and certain other natural brines. In addition, $Na_2SO_4$, $Na_2SO_4\cdot10H_2O$, $MgSO_4$, $MgSO_4\cdot7H_2O$, $Na_2SO_4\cdot MgSO_4\cdot4H_2O$, and $Na_2SO_4\cdot MgSO_4\cdot2.5H_2O$ all form natural minerals, so data for their solutions are of interest in interpreting their dissolution behavior.

The mutual diffusion coefficients of aqueous $Na_2SO_4$ and $MgSO_4$ have recently been reported (*1*). To convert these values to thermodynamic diffusion coefficients requires activity-coefficient or osmotic-coefficient derivatives. Examination of the available activity data for these salts at 25 °C indicated discrepancies of up to several percent between the various studies. In addition, osmotic coefficients from the freezing-point-depression and isopiestic methods are not in very good agreement for $MgSO_4$ (*2*, *3*). Since differentiation yields even larger uncertainties, it was clear that additional accurate activity measurements are required for these salts. In this report isopiestic data are presented for aqueous $Na_2SO_4$, $MgSO_4$, and their equimolal mixture.

## Experimental Section

The isopiestic apparatus is the same as previously described (*4*). The measurements were performed at 25.00 ± 0.005 °C (IPTS-68). The molecular weights used were 18.0154 g/mol for $H_2O$, 142.037 g/mol for $Na_2SO_4$, 120.363 g/mol for $MgSO_4$, 95.211 g/mol for $MgCl_2$, 74.551 g/mol for KCl, and 98.074 g/mol for $H_2SO_4$.

The preparation and analyses of the KCl and $H_2SO_4$ isopiestic standards have been described elsewhere (*4*, *5*). The $Na_2SO_4$ and $MgSO_4$ were from the same high-purity samples used for the diffusion coefficient study (*1*). Mallinckrodt analytical reagent $MgSO_4$ and Baker Analyzed $Na_2SO_4$ were recrystallized and filtered. A sample of the $MgSO_4$ stock solution was evaporated to dryness and then analyzed for impurities by using direct current arc optical emission spectroscopy. The impurities found were ca. 0.003% Ca, 0.001% B, 0.0008% Si, and less than 0.00002% Na by weight. Other alkali and alkaline earths were below their detection limits. The stock solutions' concentrations were obtained with a precision of ~0.01% by dehydration of weighed samples at 500 °C.

The isopiestic molalities are the average of two samples, and are known to at least ±0.1% (in most cases to ±0.05% or better). All weights were converted to mass. The molalities of the solutions at isopiestic equilibrium are listed in Tables I and II. Also included in Table II are four $MgCl_2$ points; up to 8 weeks were allowed for these low-concentration equilibrations. The osmotic coefficients of the KCl and $H_2SO_4$ isopiestic standards were calculated from available equations (*6*, *7*). The

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Table I. Isopiestic Molalities of $Na_2SO_4$, $MgSO_4$, $Na_2SO_4$–$MgSO_4$, and KCl at 25 °C

| *m*, $Na_2SO_4$ | *m*, $MgSO_4$ | *m*, $Na_2SO_4$–$MgSO_4$ | *m*, KCl | Φ, KCl |
|---|---|---|---|---|
| | | 2.0230 | 4.8088[a] | 0.9897 |
| | | 2.0184 | 4.7912 | 0.9892 |
| | | 1.9619 | 4.5726 | 0.9821 |
| | | 1.9111 | 4.3869 | 0.9762 |
| | 3.6176 | 1.8766 | 4.2583 | 0.9721 |
| | | 1.8701 | 4.2382 | 0.9715 |
| 3.7000 | 3.5685 | 1.8445 | 4.1452 | 0.9686 |
| | | 1.8186 | 4.0480 | 0.9655 |
| 3.6189 | 3.5185 | 1.8122 | 4.0321 | 0.9651 |
| 3.5379 | 3.4679 | 1.7788 | 3.9180 | 0.9615 |
| 3.4607 | 3.4209 | 1.7474 | 3.8115 | 0.9583 |
| 3.3853 | 3.3728 | 1.7157 | 3.7035 | 0.9551 |
| 3.3096 | 3.3240 | 1.6839 | 3.6018 | 0.9520 |
| 3.2463 | 3.2832 | 1.6574 | 3.5151 | 0.9495 |
| 3.1766 | 3.2397 | 1.6284 | 3.4185 | 0.9467 |
| 3.1101 | 3.1965 | 1.6008 | 3.3352 | 0.9443 |
| 3.0458 | 3.1569 | 1.5737 | 3.2508 | 0.9419 |
| 2.9776 | 3.1095 | 1.5445 | 3.1679 | 0.9396 |
| 2.9210 | 3.0734 | 1.5213 | 3.0966 | 0.9377 |
| 2.8694 | 3.0394 | 1.4993 | 3.0332 | 0.9359 |
| | 3.0211[b] | | 2.9866 | 0.9347 |
| | 3.0116 | | 2.9654 | 0.9341 |
| 2.8124 | 3.0037 | 1.4753 | 2.9613 | 0.9340 |
| 2.7572 | 2.9675 | 1.4519 | 2.8961 | 0.9323 |
| 2.7200 | 2.9455 | 1.4369 | 2.8512 | 0.9311 |
| 2.7030 | 2.9321 | 1.4294 | 2.8309 | 0.9306 |
| 2.6507 | 2.8993 | 1.4074 | 2.7699 | 0.9290 |
| 2.6122 | 2.8752 | 1.3914 | 2.7251 | 0.9279 |
| 2.5957 | 2.8643 | 1.3845 | 2.7051 | 0.9274 |
| 2.5367 | 2.8244 | 1.3594 | 2.6370 | 0.9257 |
| 2.4753 | 2.7833 | 1.3339 | 2.5673 | 0.9240 |
| 2.4237 | 2.7474 | 1.3099 | 2.5109 | 0.9226 |
| 2.3784 | 2.7181 | 1.2909 | 2.4590 | 0.9214 |
| 2.3733 | 2.7123 | 1.2877 | 2.4505 | 0.9212 |
| 2.3338 | 2.6883 | 1.2717 | 2.4111 | 0.9202 |
| 2.3179 | 2.6780 | 1.2648 | 2.3948 | 0.9199 |
| 2.2923 | 2.6606 | 1.2541 | 2.3648 | 0.9192 |
| 2.2495 | 2.6322 | 1.2352 | 2.3183 | 0.9181 |
| 2.2153 | 2.6067 | 1.2198 | 2.2822 | 0.9173 |
| 2.1719 | 2.5772 | 1.2009 | 2.2346 | 0.9163 |
| 2.0094 | 2.4649 | 1.1288 | 2.0662 | 0.9127 |
| 1.9611 | | 1.1063 | 2.0164 | 0.9117 |
| 1.9526[c] | | 1.1027 | 2.0079 | 0.9115 |
| 1.9221 | 2.4022 | 1.0881 | 1.9716 | 0.9108 |
| 1.8608 | 2.3565 | 1.0616 | 1.9171 | 0.9097 |
| 1.7505 | 2.2727 | 1.0101 | 1.8021 | 0.9076 |
| 1.7364 | 2.2640 | 1.0027 | 1.7850 | 0.9073 |
| 1.6411 | 2.1885 | 0.95871 | 1.6926 | 0.9056 |
| 1.5775 | 2.1407 | 0.92839 | 1.6284 | 0.9046 |
| 1.4528 | 2.0397 | 0.86706 | 1.5073 | 0.9027 |
| 1.3562 | 1.9577 | 0.81888 | 1.4160 | 0.9014 |
| 1.2387 | 1.8522 | 0.75892 | 1.3036 | 0.9000 |
| 1.1144 | 1.7354 | 0.69364 | 1.1852 | 0.8988 |
| 0.99140 | 1.6102 | 0.62706 | 1.0677 | 0.8978 |
| 0.89427 | 1.5037 | 0.57228 | 0.97256 | 0.8972 |
| 0.81402 | 1.4114 | 0.52613 | 0.89475 | 0.8969 |
| 0.74958 | 1.3319 | 0.48841 | 0.83157 | 0.8968 |
| 0.68175 | 1.2446 | 0.44776 | 0.76398 | 0.8968 |
| 0.62760 | 1.1702 | 0.41468 | 0.70999 | 0.8970 |
| 0.56843 | 1.0860 | 0.37818 | 0.64945 | 0.8974 |
| 0.51239 | 0.99917 | 0.34262 | 0.59078 | 0.8979 |
| 0.46554 | 0.92538 | 0.31281 | 0.54253 | 0.8985 |

[a] Saturated solution in equilibrium with solid KCl. [b] Saturated solution in equilibrium with $MgSO_4 \cdot 7H_2O$. [c] Saturated solution in equilibrium with $Na_2SO_4 \cdot 10H_2O$.

ratio of molalities of $Na_2SO_4$ to $MgSO_4$ in the mixed salt solution is 1/0.999998.

Each saturated-solution concentration was determined by equilibrating two samples of stock solution with another isopiestic cup containing saturated solution and crystals. The reported solubilities in Table I are the average of three different equilibration times.

Table II. Isopiestic Molalities of $MgSO_4$, $MgCl_2$, KCl, and $H_2SO_4$ at 25 °C

| *m*, $MgSO_4$ | *m*, $MgCl_2$ | *m*, KCl | *m*, $H_2SO_4$ | Φ, $MgSO_4$ | Φ, $MgCl_2$ |
|---|---|---|---|---|---|
| 0.314 80 | 0.131 02 | 0.185 74 | 0.169 53 | 0.5390 | 0.8634 |
| 0.292 82 | 0.122 67 | 0.173 48 | 0.158 62 | 0.5425 | 0.8633 |
| 0.272 53 | 0.114 86 | 0.161 82 | 0.148 17 | 0.5450 | 0.8621 |
| 0.257 41 | 0.109 00 | 0.153 37 | 0.140 53 | 0.5478 | 0.8625 |

For KCl, 12–14-day equilibrations were used, and 4.8088 ± 0.0020 mol kg$^{-1}$ was obtained for the solubility; this value is in agreement to within 0.1% with solubilities obtained with shorter equilibration periods (*8*, *9*). The solubility of $Na_2SO_4 \cdot 10H_2O$ was determined to be 1.9526 ± 0.0013 mol kg$^{-1}$ by using 12–14-day equilibrations, and it is in good agreement with Platford's value (*10*) of 1.9503 ± 0.0020 mol kg$^{-1}$. A solubility of 3.0211 ± 0.0022 mol kg$^{-1}$ was obtained with 6–15-day equilibrations for $MgSO_4 \cdot 7H_2O$. This value is in good agreement with reported values of 3.026 and 3.015 mol kg$^{-1}$ (*11*, *12*). No variation of solubility with time was observed for these long equilibration periods, but shorter times between weighings gave erratic results for the hydrated sulfates.

Isopiestic measurements for $Na_2SO_4$ and $MgSO_4$ were made into the supersaturated region of concentration and were terminated when attempts to reach higher concentrations resulted in spontaneous crystallization. The measurements for $Na_2SO_4$–$MgSO_4$ were terminated at the solubility limit of the KCl isopiestic standard. The phase diagram given by Platford (*13*) indicates that the highest concentration in Table I is close to the solubility limit of this mixed salt.

## Calculations and Discussion

The osmotic coefficients were calculated by using the equation for isopiestic equilibrium, eq 1, where *m* is the molality

$$\Phi = \nu^* m^* \Phi^* / (\nu m) \qquad (1)$$

of the solution, Φ the molal osmotic coefficient, and ν the number of ions formed by the complete dissociation of one molecule of solute ($\nu = 5$ for the mixed salt $Na_2SO_4$–$MgSO_4$). The asterisked symbols refer to the isopiestic reference solution.

In addition to the present results, other isopiestic data are available for these solutions at 25 °C (*2*, *10*, *13–17*). These data were recalculated to conform to the same isopiestic standards used here. Isopiestic data are also available for $Na_2SO_4$ and $MgSO_4$ at other temperatures (*18*), but the available thermal data are not accurate enough to convert the higher-concentration data to 25 °C (*19–21*).

Direct vapor-pressure data for $Na_2SO_4$ and $MgSO_4$ solutions (*22–24*) were converted to osmotic coefficients at 25 °C with corrections made for the nonideal behavior of water vapor. Only Gibson and Adams' vapor-pressure data (*22*) for $Na_2SO_4$ at 27.5 °C were accurate enough to use in subsequent calculations, and their results are given in Table III. The correction to 25 °C was made by using available thermal data (*19–21*). The heat capacities of Desnoyers et al. were corrected for heat losses in the flow calorimeter (*25*).

Freezing-point-depression measurements for $Na_2SO_4$ and $MgSO_4$ (*26–30*) were converted to osmotic coefficients at 25 °C by using standard methods (*31*) and available thermal data (*19–21*, *25*). These values are reported in Tables III and IV. Vapor-phase-osmometry results for $MgSO_4$ (*32*) are in reasonably good agreement with the freezing-point-depression values but were not included in the calculations since the reliability of the experimental method is less well established. Emf values for both salts (*33–36*) are too widely spaced to allow an accurate Gibbs–Duhem extrapolation to obtain osmotic coefficients. Also, with the exception of Harned and Hecker's

Table III. Freezing-Point-Depression and Vapor-Pressure Data for $Na_2SO_4$

| $m$ | $\Phi_f{}^a$ | $\Phi$ | $m$ | $\Phi_f{}^a$ | $\Phi$ |
|---|---|---|---|---|---|
| Randall and Scott (*27*), Freezing Point Depression | | | | | |
| 0.000 875 | 0.9825 | 0.9813[b] | 0.016 155 | 0.8806 | 0.8796 |
| 0.001 797 | 0.9528 | 0.9514 | 0.032 064 | 0.8475 | 0.8483 |
| 0.003 527 | 0.9341 | 0.9324 | 0.060 975 | 0.8143 | 0.8188 |
| 0.005 766 | 0.9205 | 0.9188 | 0.103 38 | 0.7821 | 0.7919 |
| 0.008 603 | 0.9075 | 0.9059 | | | |
| Indelli (*28*), Freezing Point Depression | | | | | |
| 0.006 678 | 0.9179 | 0.9162 | 0.059 37 | 0.8098 | 0.8141 |
| 0.012 612 | 0.8906 | 0.8893 | 0.063 65 | 0.8063 | 0.8111 |
| 0.018 072 | 0.8724 | 0.8716 | 0.073 02 | 0.7976 | 0.8036 |
| 0.019 288 | 0.8662 | 0.8655 | 0.088 97 | 0.7876 | 0.7956 |
| 0.022 833 | 0.8610 | 0.8607 | 0.090 47 | 0.7845 | 0.7927 |
| 0.027 169 | 0.8526 | 0.8529 | 0.099 58 | 0.7793 | 0.7887 |
| 0.035 862 | 0.8400 | 0.8413 | 0.118 75 | 0.7663 | 0.7780 |
| 0.037 395 | 0.8341 | 0.8356 | 0.123 70 | 0.7636 | 0.7760 |
| 0.043 52 | 0.8271 | 0.8294 | 0.160 47 | 0.7448 | 0.7616 |
| 0.054 24 | 0.8142 | 0.8178 | 0.222 09 | 0.7113 | 0.7354[b] |
| Gibson and Adams (*22*), Vapor Pressure at 27.5 °C | | | | | |
| 0.960 1 | 0.6504 | 0.6466 | 1.760 | 0.6258 | 0.6216 |
| 1.338 | 0.6335 | 0.6294 | 1.985 | 0.6279 | 0.6238 |
| 1.544 | 0.6272 | 0.6230 | 2.222 | 0.6353 | 0.6312 |

[a] The osmotic coefficient at the experimental temperature (freezing temperature for freezing-point-depression data). Next entry to right is osmotic coefficient at 25 °C. [b] This point given zero weight in the least-squares calculations.

Table IV. Freezing-Point-Depression Data for $MgSO_4$

| $m$ | $\Phi_f{}^a$ | $\Phi$ | $m$ | $\Phi_f{}^a$ | $\Phi$ |
|---|---|---|---|---|---|
| Hall and Harkins (*26*) | | | | | |
| 0.003 21 | 0.8375 | 0.8277 | 0.026 76 | 0.6762 | 0.6689 |
| 0.005 37 | 0.7985 | 0.7885 | 0.048 92 | 0.6496 | 0.6416 |
| 0.007 48 | 0.7782 | 0.7684 | 0.095 94 | 0.6062 | 0.5959 |
| 0.013 14 | 0.7396 | 0.7310 | 0.221 7 | 0.5538 | 0.5460 |
| Brown and Prue (*29*) | | | | | |
| 0.006 10 | 0.7757 | 0.7657[b] | 0.056 10 | 0.6365 | 0.6280 |
| 0.009 67 | 0.7562 | 0.7469 | 0.065 20 | 0.6276 | 0.6186 |
| 0.015 23 | 0.7167 | 0.7084 | 0.066 70 | 0.6264 | 0.6172 |
| 0.019 35 | 0.7017 | 0.6939 | 0.068 60 | 0.6244 | 0.6151 |
| 0.026 50 | 0.6818 | 0.6745 | 0.079 00 | 0.6153 | 0.6055 |
| 0.028 30 | 0.6793 | 0.6720 | 0.079 16 | 0.6148 | 0.6050 |
| 0.032 10 | 0.6726 | 0.6653 | 0.088 25 | 0.6087 | 0.5986 |
| 0.036 38 | 0.6659 | 0.6585 | 0.089 45 | 0.6075 | 0.5973 |
| 0.039 15 | 0.6634 | 0.6560 | 0.093 00 | 0.6042 | 0.5940 |
| 0.041 68 | 0.6586 | 0.6510 | 0.099 05 | 0.5999 | 0.5896 |
| 0.049 28 | 0.6471 | 0.6390 | 0.102 15 | 0.5986 | 0.5882 |
| 0.052 45 | 0.6418 | 0.6336 | 0.102 78 | 0.5978 | 0.5874 |
| Isono (*30*) | | | | | |
| 0.002 00 | 0.9006 | 0.8916[b] | 0.037 4 | 0.6678 | 0.6605 |
| 0.003 14 | 0.8476 | 0.8378 | 0.046 2 | 0.6553 | 0.6475 |
| 0.003 84 | 0.8191 | 0.8091 | 0.067 6 | 0.6340 | 0.6248 |
| 0.005 80 | 0.7973 | 0.7872 | 0.086 4 | 0.6131 | 0.6030 |
| 0.007 96 | 0.7802 | 0.7705 | 0.120 8 | 0.5945 | 0.5844 |
| 0.009 84 | 0.7541 | 0.7448 | 0.127 2 | 0.5862 | 0.5763 |
| 0.013 6 | 0.7295 | 0.7209 | 0.156 4 | 0.5747 | 0.5661 |
| 0.020 6 | 0.6943 | 0.6867 | 0.175 2 | 0.5732 | 0.5654 |

[a] The osmotic coefficient at the freezing temperature. Next entry to right is osmotic coefficient at 25 °C. [b] This point given a weight of zero in the least-squares fit.

$Na_2SO_4$ data (*36*), these emf data are of low accuracy.

The available osmotic coefficients were fitted to least-squares equations of the type

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

where $A$ is the Debye–Hückel limiting slope (4.0744 for $Na_2SO_4$; 9.4097 for $MgSO_4$). The value of $A$ was allowed to vary for the mixed salt $Na_2SO_4$–$MgSO_4$ since data were not available at low enough concentrations to allow a meaningful extrapolation. The least-squares coefficients and standard deviations for the best fits are given in Table V.

Table V. Coefficients and Powers for the Osmotic Coefficient Polynomial for 25 °C

| $i$ | $r_i$ | $A_i$ | $r_i$ | $A_i$ | $r_i$ | $A_i$ |
|---|---|---|---|---|---|---|
| | | $Na_2SO_4$ | | $Na_2SO_4$–$MgSO_4$ | | $MgSO_4$ |
| 1 | 1.00 | 4.861 114 | 0.50 | 3.8069[a] | 0.75 | −49.9893 |
| 2 | 1.25 | −3.910 475 | 0.75 | 8.7138 | 0.875 | 193.5199 |
| 3 | 1.50 | −5.964 58 | 1.00 | −8.3851 | 1.00 | −206.6263 |
| 4 | 1.75 | 10.995 11 | 1.25 | 3.1242 | 1.25 | 94.81615 |
| 5 | 2.00 | −6.208 11 | | | 1.50 | −34.98183 |
| 6 | 2.25 | 1.228 528 | | | 1.75 | 5.927029 |
| SD | | 0.001 3 | | 0.0005 | | 0.0032 |

[a] This is actually $A/3$ in the notation of eq 2 and 3.

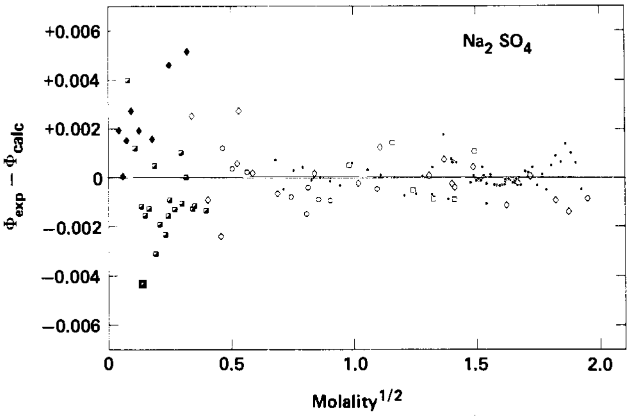

**Figure 1.** Differences between experimental and calculated osmotic coefficients of $Na_2SO_4$ at 25 °C: (⊙) this research; (◇) Platford (*10*); (○) Downes and Pitzer (*17*); (◆) Randall and Scott (*27*); (◪) Indelli (*28*); (□) Gibson and Adams (*22*).

If eq 2 is substituted into the Gibbs–Duhem equation and integrated, then eq 3 is obtained, where $\gamma\pm$ is the mean molal activity coefficient of the solute. The water activity can be calculated from eq 4, where $M_1$ is the molecular weight of water.

$$\ln \gamma\pm = -Am^{1/2} + \sum_i A_i \frac{(r_i + 1)}{r_i} m^{r_i} \qquad (3)$$

$$\ln a_1 = -\nu m M_1 \Phi / 1000 \qquad (4)$$

Smoothed values of $\Phi$, $a_1$, and $\gamma\pm$ are given in Table VI and were computed from the above equations. Parameters for Pitzer's equation (*37*) are given in Table VII for $Na_2SO_4$ and $MgSO_4$. Pitzer's papers should be consulted for the meaning of these parameters (*37*, *38*). For $MgSO_4$ $\alpha_1 = 1.4$ and $\alpha_2 = 12.0$, while for $Na_2SO_4$ $\alpha_1 = 2.0$ and $\alpha_2 = \beta^{(2)} = 0$, as recommended by Pitzer. Equation 2 gives a slightly better fit to the experimental data than Pitzer's equation since it contains more parameters and, consequently, is recommended for activity calculations. The present Pitzer parameters should be more reliable than those in Pitzer's tabulations since they depend on a larger and more accurate data base. Mixing parameters were not calculated for $Na_2SO_4$–$MgSO_4$ since data were measured only for the 50–50 mixture.

In the least-squares calculations for $Na_2SO_4$, unit weights were given to the present results, the isopiestic data of Platford (*10*) and Downes and Pitzer (*17*), the vapor-pressure data of Gibson and Adams (*22*), and the freezing-point-depression results of Randall and Scott (*27*) and Indelli (*28*). Figure 1 illustrates the difference between the experimental data and eq 2. The osmotic coefficients of $Na_2SO_4$ from the various studies are in excellent agreement and are known to ca. 0.001 above 0.3 mol kg$^{-1}$ and 0.003 at lower concentrations. The emf data of Harned and Hecker (*36*) are in excellent agreement with the present correlation and seem to be the most reliable set for this

Table VI. Osmotic Coefficients, Water Activities, and Activity Coefficients at Even Molalities at 25 °C

| $m$ | $\Phi$ | $a_1$ | $\gamma\pm$ |
|---|---|---|---|
| | | $Na_2SO_4$ | |
| 0.1 | 0.7885 | 0.995 748 | 0.4483 |
| 0.2 | 0.7505 | 0.991 920 | 0.3679 |
| 0.3 | 0.7263 | 0.988 29 | 0.3230 |
| 0.4 | 0.7077 | 0.984 82 | 0.2923 |
| 0.5 | 0.6924 | 0.981 46 | 0.2692 |
| 0.6 | 0.6793 | 0.978 21 | 0.2509 |
| 0.7 | 0.6682 | 0.975 04 | 0.2360 |
| 0.8 | 0.6586 | 0.971 93 | 0.2235 |
| 0.9 | 0.6504 | 0.968 86 | 0.2128 |
| 1.0 | 0.6435 | 0.965 82 | 0.2036 |
| 1.2 | 0.6329 | 0.959 78 | 0.1886 |
| 1.4 | 0.6263 | 0.953 72 | 0.1769 |
| 1.6 | 0.6230 | 0.947 55 | 0.1677 |
| 1.8 | 0.6226 | 0.941 23 | 0.1604 |
| 2.0 | 0.6249 | 0.934 69 | 0.1545 |
| 2.2 | 0.6295 | 0.927 89 | 0.1498 |
| 2.4 | 0.6361 | 0.920 80 | 0.1460 |
| 2.6 | 0.6448 | 0.913 38 | 0.1431 |
| 2.8 | 0.6553 | 0.905 60 | 0.1409 |
| 3.0 | 0.6675 | 0.897 4 | 0.1394 |
| 3.2 | 0.6815 | 0.888 8 | 0.1384 |
| 3.4 | 0.6971 | 0.879 8 | 0.1380 |
| 3.6 | 0.7145 | 0.870 2 | 0.1380 |
| 3.8 | 0.7337 | 0.860 1 | 0.1386 |
| 3.8140 | 0.7351 | 0.859 4 | 0.1387 |
| | | $MgSO_4$ | |
| 0.1 | 0.5934 | 0.997 864 | 0.1613 |
| 0.2 | 0.5578 | 0.995 988 | 0.1160 |
| 0.3 | 0.5396 | 0.994 184 | 0.0948 |
| 0.4 | 0.5286 | 0.992 410 | 0.0820 |
| 0.5 | 0.5221 | 0.990 639 | 0.0733 |
| 0.6 | 0.5188 | 0.988 85 | 0.0669 |
| 0.7 | 0.5183 | 0.987 01 | 0.0621 |
| 0.8 | 0.5199 | 0.985 13 | 0.0583 |
| 0.9 | 0.5236 | 0.983 16 | 0.0553 |
| 1.0 | 0.5291 | 0.981 12 | 0.0529 |
| 1.2 | 0.5448 | 0.976 72 | 0.0494 |
| 1.4 | 0.5663 | 0.971 84 | 0.0471 |
| 1.6 | 0.5931 | 0.966 38 | 0.0458 |
| 1.8 | 0.6249 | 0.960 28 | 0.0451 |
| 2.0 | 0.6616 | 0.953 44 | 0.0451 |
| 2.2 | 0.7032 | 0.945 79 | 0.0456 |
| 2.4 | 0.7496 | 0.937 24 | 0.0466 |
| 2.6 | 0.8010 | 0.927 71 | 0.0482 |
| 2.8 | 0.8575 | 0.917 12 | 0.0504 |
| 3.0 | 0.9193 | 0.905 40 | 0.0532 |
| 3.2 | 0.9866 | 0.892 5 | 0.0567 |
| 3.4 | 1.0596 | 0.878 3 | 0.0611 |
| 3.6 | 1.1384 | 0.862 7 | 0.0664 |
| 3.6176 | 1.1456 | 0.861 3 | 0.0670 |
| | | $Na_2SO_4$-$MgSO_4$ | |
| 0.1 | 0.6829 | 0.993 868 | |
| 0.2 | 0.6444 | 0.988 46 | |
| 0.3 | 0.6252 | 0.983 25 | |
| 0.4 | 0.6149 | 0.978 09 | |
| 0.5 | 0.6104 | 0.972 88 | |
| 0.6 | 0.6104 | 0.967 55 | |
| 0.7 | 0.6143 | 0.962 01 | |
| 0.8 | 0.6217 | 0.956 19 | |
| 0.9 | 0.6323 | 0.950 03 | |
| 1.0 | 0.6460 | 0.943 47 | |
| 1.2 | 0.6822 | 0.928 92 | |
| 1.4 | 0.7293 | 0.912 13 | |
| 1.6 | 0.7869 | 0.892 8 | |
| 1.8 | 0.8544 | 0.870 6 | |
| 2.0 | 0.9315 | 0.845 5 | |
| 2.0230 | 0.9409 | 0.842 4 | |

salt. Except for 0.025 mol kg$^{-1}$, their relative activity coefficients show a maximum difference of 0.003 from the present correlation.

Table VII. Parameters for Pitzer's Equation for 25 °C

| | $Na_2SO_4$ | | $MgSO_4$ |
|---|---|---|---|
| $(4/3)\beta^{(0)}$ | 0.02492 | $\beta^{(0)}$ | 0.21499 |
| $(4/3)\beta^{(1)}$ | 1.4659 | $\beta^{(1)}$ | 3.3646 |
| $(4/3)\beta^{(2)}$ | 0.0 | $\beta^{(2)}$ | −32.743 |
| $\alpha_1$ | 2.0 | $\alpha_1$ | 1.4 |
| $\alpha_2$ | 0.0 | $\alpha_2$ | 12.0 |
| $(2^{5/2}/3)C^{\Phi}$ | 0.010463 | $C^{\Phi}$ | 0.02797 |
| SD | 0.0028 | SD | 0.0047 |

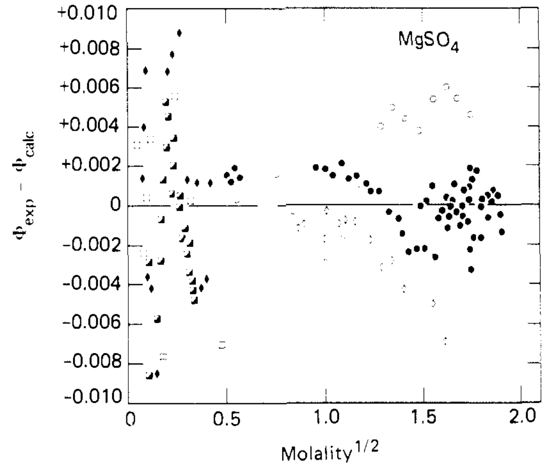

**Figure 2.** Differences between experimental and calculated osmotic coefficients of $MgSO_4$ at 25 °C: (●) this research; (○) Robinson and Jones smoothed data (*2*); (◇) Wu, Rush, and Scatchard (*16*); (□) Hall and Harkins (*26*); (♦) Isono (*30*); (▣) Brown and Prue (*29*).

Four sets of $Na_2SO_4$ data were not included in the least-squares fits because they appear to be of lower accuracy. The isopiestic data of Wu et al. (*16*) and the vapor-pressure data of Pearce and Eckstrom (*23*) are high, while the isopiestic data of Robinson et al. (*14*) and the vapor-pressure data of Kangro and Groeneveld (*24*) are low. The average of these four rejected sets of data, however, falls close to the more reliable data since there are approximately equal numbers of high and low points.

Figure 2 shows the difference between the experimental osmotic coefficients and eq 2 for $MgSO_4$. Unit weights were given to the present results, to two other isopiestic studies (*2*, *16*), and to freezing-point-depression data (*26*, *29*, *30*). Two points of Wu et al. (*16*) and one of Robinson and Jones (*2*) were given zero weight. Platford's $MgSO_4$ results (*15*) were given zero weight since the lower points are systematically low (the higher-concentration points are in better agreement); zero weight was also given to the very low results from vapor-pressure measurements (*24*).

Series in $m^{1/4}$ with consecutive terms worked well for eq 2 for both $Na_2SO_4$ (six terms required; standard deviation 0.0013) and $Na_2SO_4$–$MgSO_4$ (four terms required; standard deviation 0.0005). Starting the series at $m$ for $Na_2SO_4$ gave a slightly better fit than a leading term in $m^{3/4}$, and the better fit was used. However, powers below $m$ were necessary for $MgSO_4$, and nonsequential series also improved results.

A considerable number of series in $m^{1/2}$, $m^{1/4}$, and $m^{1/8}$ with four to eight parameters in eq 2 were tried for the $MgSO_4$ data. The fit finally chosen to represent the $MgSO_4$ data had six parameters and a standard deviation of 0.003 17. Using seven or eight parameters only produced a marginal improvement (lowest standard deviation 0.003 155). Allowing the limiting slope to vary only improved things slightly.

The least-squares equations reliably fit the data for $MgSO_4$ above 0.8 mol kg$^{-1}$, whereas some cycling may be occurring at low concentrations. This is a common problem for associated electrolytes with negative deviations for the Debye–Hückel limiting law. However, inaccuracies in the conversion of freezing-point-depression data to 25 °C are probably the

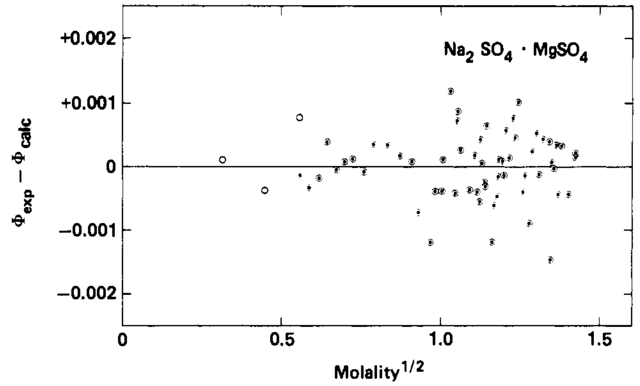

**Figure 3.** Differences between experimental and calculated osmotic coefficients of $Na_2SO_4$-$MgSO_4$ at 25 °C: (⊙) this research; (○) Platford's smoothed data (*13*).

main problem, since the least-squares equations must bridge the resulting discontinuity. These difficulties can arise in the enthalpy or heat-capacity corrections to freezing-point data.

An attempt was made to improve the enthalpy of dilution correction to $MgSO_4$ freezing-point-depression data by reextrapolation of Lange's data (*39–41*) using a speciation model. Experimental enthalpy-of-dilution data have to be extrapolated to infinite dilution; this extrapolation can be quite uncertain for 2–2 electrolytes. This approach was not entirely successful, so National Bureau of Standards enthalpy values (*19*) were used in our actual calculations.

The heat-capacity correction to the freezing-point-depression results of $MgSO_4$ is about one-half of the enthalpy correction, and is opposite in sign, at 0.1–0.2 mol kg$^{-1}$. The temperature dependence of the heat capacity was neglected, owing to a lack of experimental data, but is probably significant. The partial molal enthalpy of the solvent should be less at lower temperatures because of the dissociation of ion pairs (*3*). This neglect of the heat-capacity temperature dependence may be the reason that the freezing-point values are significantly lower than the isopiestic results for $MgSO_4$ and most other 2–2 sulfates. It is significant in this regard that $CuSO_4$, which exhibits good agreement between freezing-point and isopiestic data (*42*), has a near cancellation of enthalpy and heat-capacity terms at 0.1 mol kg$^{-1}$ (the corrections become ~4 times larger for $CuSO_4$ at lower concentrations).

The $MgSO_4$ isopiestic data from the various studies also show significant differences at high concentrations. The $MgSO_4$ used for the present study was analyzed for impurities (see the Experimental Section), and the pH values of the solutions have been reported (*1*). This information was not provided in the other studies, so it is not possible to explain all of the differences in the activity data. However, an associated electrolyte like $MgSO_4$ should be sensitive to contamination by bisulfate and alkali metals.

Because of the above problems, the activity coefficients of $MgSO_4$ are uncertain by ~2%. However, the present $\gamma\pm$ values are in reasonably good agreement with the detailed calculations of Glueckauf (*43*) and are in excellent agreement with Pitzer's values (*3*) from 0.1 to 3.0 mol kg$^{-1}$, with the maximum difference from Pitzer being 0.0005.

The differences between experimental and calculated $\Phi$ values of $Na_2SO_4$-$MgSO_4$ are shown in Figure 3. The smoothed data given by Platford (*13*) for 0.1-0.3 mol kg$^{-1}$ were also included to help constrain eq 2 at lower concentrations. Platford's values (*13*) are based on his four points and the data of Wu et al. (*16*), interpolated to the equimolal mixture. His smoothed results agree with the present results to within 0.003 up to 1.4 mol kg$^{-1}$.

The four $MgCl_2$ points in Table II are in good agreement with Robinson and Stokes' (*44*) data.

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## Glossary

| | |
|---|---|
| $\Phi$ | molal osmotic coefficient |
| $\nu$ | 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 |
| $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $\alpha_1$, $\alpha_2$, $C^{\Phi}$ | parameters for Pitzer's equation |
| * | symbols with asterisks refer to KCl and $H_2SO_4$ isopiestic standards |

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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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