in the electrostriction partial molal volume $\bar{V}^0$ (elect) at higher temperature. Estimation of $\phi_V{}^0$ values from eq 4 shows that $\phi_V{}^0$ of LiCl in system I goes through a minimum around 60 °C which shows that $\bar{V}^0$ (elect) decreases at temperatures above 60 °C. In other words, $\bar{V}^0$ (int), the intrinsic partial molal volume, is more dominant than $\bar{V}^0$ (elect). The apparent molal expansibilities, $\phi_E{}^0 = (\delta\phi_V{}^0/\delta t)$ calculated from eq 4 between 0 and 100 °C, indicate increases with increase in temperature and this is contrary to the behavior of most common electrolytes in that $\phi_E{}^0$ decreases with increasing temperature. This may be attributed to (*i*) the presence of strong ion–ion interaction, (*ii*) the increase in association of ions by the addition of one electrolyte to a solution, and (iii) the decrease of overall solvation of ions in a multicomponent electrolyte solution. Using the reasoning of Hepler (*6*) one can attribute this behavior to the ability of lithium chloride to act as a structure maker.

The, $\phi_V{}^0$, values for lithium chloride in system I decrease with increasing content of dioxane at 40 °C. In aqueous dioxane (*1*), inorganic ions are preferentially solvated by dioxane, and dioxane–water mixtures form an associated complex in the liquid state by the attachment of two water molecules to the oxygen atoms of dioxane through hydrogen bonding. Since lithium salts are more solvated (*5*), the decrease with increasing content of dioxane indicates the encagement of the lithium chloride ions in the vacant space of the associated complex of water–dioxane. Since it behaves as a structure maker, there is no possibility of its breaking the structure of aqueous dioxane and, therefore, it may not be interacting with the associated solvent molecules. Lithium ions have the tendency of interacting with the water molecules and this interaction goes on decreasing due to decrease in water molecules with the increase in the dioxane content and more and more of the ions start getting into the void space of the structure of the solvent and there is a gradual decrease in the $\phi_V{}^0$ values of lithium chloride in system I.

The effect of temperature on $\phi_V{}^0$ for sodium chloride in system II with increasing temperature can be attributed to the same reasoning as applied to system I and the minimum is again obtained at 60 °C. According to Hepler (*6*), the positive value of $(\delta^2\phi_V{}^0/\delta t^2)$ for a salt shows the structure-making character of the salt. On comparing the magnitudes of LiCl in system I and of NaCl in system II, we find that lithium chloride is more of a structure maker than sodium chloride in their respective systems.

The apparent molal expansibilities, $\phi_E{}^0 =' \delta\phi_V{}^0/\delta t$ calculated from eq 5 between 0 and 100 °C, show that it increases with increase in temperature and it may be attributed to the nonelectrolytic behavior as this behavior is very much common for nonelectrolytes or tetraalkylammonium salts. In the case of system II, we find that $\phi_V{}^0$ increases with increase in the dioxane content. This has been attributed to the greater ionic size of the sodium ion and the vacant site in the solvent containing the molecules of the associated complex is not of sufficient dimensions for the salt to be trapped in and the electrolyte remains outside the void space. This void space goes on increasing with the increase in the content of the dioxane and, therefore, it is expected the $\phi_V{}^0$ will increase with increasing content of dioxane because sodium chloride ions go on occupying space outside the solvent matrix.

The effect of temperature on the $\phi_V{}^0$ of KCl in system III can be explained similar to that of system I and II. The evaluation of $\phi_V{}^0$ from eq 6 in the temperature range suggests that the minimum in this approaches at 60 °C. Helper's reasoning suggests (*6*) that potassium chloride in system III behaves like a structure maker. The effect of dioxane on the $\phi_V{}^0$ values in the case of system III suggests that a minimum is observed around 50% dioxane mixture at 40 °C and this may be attributed to the increasing dominance of the intrinsic partial molal volume over the electrostriction partial molal volume.

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Isopiestic Determination of the Osmotic Coefficients of Aqueous $CaCl_2$ Solutions at 25 °C

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The isopiestic molalities of $CaCl_2$ and H_2SO_4 solutions have been determined at 25 °C for $CaCl_2$ concentrations between 2.6 and 8.8 mol kg^{-1}. The osmotic coefficients of the $CaCl_2$ solutions were calculated using available osmotic coefficients for H_2SO_4. These results can be combined with other published data to give accurate osmotic and activity coefficients for $CaCl_2$ solutions.

One of the most widely used methods for the determination of water activities of aqueous solutions is the isopiestic method. This method consists of allowing solutions of various electrolytes to reach thermodynamic equilibrium, through the vapor phase, with standard solutions whose water activities should be accurately known as a function of concentration.

$CaCl_2$ has become one of the most important isopiestic standards since this use was suggested by Stokes (*4*). Below 3 mol kg^{-1} (water activities between 0.75 and 1.00) this salt has been extensively studied by isopiestic comparison to NaCl and KCl solutions, by freezing point depression measurements, and by use of electromotive force and diffusion coefficient measurements. Most of these data are in good agreement. Above 3 mol kg^{-1}, the $CaCl_2$ osmotic coefficients are based mainly on Stokes' isopiestic comparison to H_2SO_4 (*4*). Very few reliable vapor pressure measurements are available for $CaCl_2$ solutions. The available isopiestic data above 3 mol kg^{-1} do not connect up smoothly with lower concentration data. Spedding et al. (*3*) and others have noted that discrepancies occur when KCl and $CaCl_2$ are both used as isopiestic standards. Consequently, we decided to supplement existing osmotic coefficient data by redetermining the osmotic coefficients of $CaCl_2$ solutions from 2.6 to 8.8 mol kg^{-1} at 25 °C.

Experimental Section

The isopiestic determinations were made with the same stainless steel isopiestic chambers that were used for the rare earth chloride study (*3*). Chemically inert cups of tantalum metal were used, and tight fitting plastic caps were added when these cups were removed from the chambers for weighing. Duplicate or triplicate samples of $CaCl_2$ and H_2SO_4 were equilibrated at 25.00 ± 0.01 °C for 4 days or longer. Water was added to the cups in such a manner that equilibrium was approached from above and below at each concentration. The individual $CaCl_2$ and H_2SO_4 isopiestic equilibrium molalities agreed to within at least ±0.08% of the average for each electrolyte. For many of the equilibrations the agreement was much better than this. Conductivity water was used for all solution preparations and dilutions. All weights were converted to mass using the densities listed in the International Critical Tables. The IUPAC-1969 molecular weights of 98.074 g mol^{-1} for H_2SO_4 and 110.986 g mol^{-1} for $CaCl_2$ were used in the calculations.

The $CaCl_2$ stock solution was prepared by the method of Stokes (*4*) from Mallinckrodt primary standard $CaCO_3$ and Dupont reagent grade HCl. The resulting $CaCl_2$ crystals were recrystallized several times before being used to prepare the stock solution. Redistilled reagent grade sulfuric acid was used in preparing the other stock solution.

The $CaCl_2$ stock solution was analyzed in triplicate by a gravimetric method and a concentration of 6.6262 ± 0.0004 mol kg^{-1} obtained. The H_2SO_4 stock solution was analyzed by titration with a KOH solution, using phenolphthalein as the indicator. The KOH solution had been standardized with oven-dried "Baker analyzed" primary standard potassium biphthalate. All of these titrations were performed within a 2-h period to minimize carbon dioxide absorption problems. The titrations were performed using weight burettes for greater accuracy. The concentration of the H_2SO_4 stock solution was determined to be 15.398 ± 0.012 mol kg^{-1} (five samples titrated).

Discussion

The osmotic coefficients of the $CaCl_2$ solutions were calculated from the experimental isopiestic molalities and the sulfuric acid osmotic coefficients of Rard, Habenschuss, and Spedding (*1*). The molal osmotic coefficient of a $CaCl_2$ solution in equilibrium with a H_2SO_4 solution is given by

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

where ϕ^{*} is the osmotic coefficient of H_2SO_4, m is the molality of the $CaCl_2$ solution, and m^{*} is the molality of the H_2SO_4 solution. The data and results are given in Table I. These osmotic coefficients will be compared to other available data for $CaCl_2$ in a forthcoming paper (*2*). In that paper a semiempirical equation for ϕ will be given and activity coefficients will be calculated.

Table I. $CaCl_2$ Osmotic Coefficients from Isopiestic Measurements with H_2SO_4 Reference Solutions

m^{*}, H_2SO_4 (mol kg^{-1})	ϕ^{*}, H_2SO_4	m, $CaCl_2$ (mol kg^{-1})	ϕ, $CaCl_2$
13.288	2.1086	8.8254	3.1748
13.052	2.0961	8.6225	3.1728
12.992	2.0928	8.5626	3.1754
12.880	2.0866	8.4736	3.1717
12.740	2.0788	8.3557	3.1695
12.567	2.0688	8.2107	3.1665
12.450	2.0620	8.1196	3.1617
12.376	2.0576	8.0596	3.1595
12.206	2.0473	7.9234	3.1538
12.185	2.0460	7.9019	3.1549
12.111	2.0414	7.8496	3.1496
12.036	2.0367	7.7902	3.1467
11.939	2.0305	7.7117	3.1436
11.844	2.0244	7.6387	3.1389
11.763	2.0191	7.5779	3.1343
11.638	2.0109	7.4876	3.1255
11.556	2.0054	7.4258	3.1207
11.480	2.0002	7.3631	3.1185
11.348	1.9911	7.2720	3.1071
11.349	1.9911	7.2701	3.1083
11.301	1.9878	7.2344	3.1051
11.237	1.9833	7.1874	3.1007
11.192	1.9801	7.1606	3.0948
11.074	1.9716	7.0717	3.0874
11.056	1.9703	7.0570	3.0867
10.923	1.9605	6.9692	3.0727
10.819	1.9527	6.8956	3.0637
10.714	1.9447	6.8246	3.0530
10.588	1.9350	6.7375	3.0408
10.482	1.9267	6.6662	3.0295
10.369	1.9176	6.5926	3.0161
10.203	1.9041	6.4828	2.9968
10.030	1.8897	6.3690	2.9759
9.8271	1.8723	6.2426	2.9474
9.6885	1.8602	6.1563	2.9274
9.5049	1.8437	6.0416	2.9006
9.3449	1.8290	5.9438	2.8756
9.1765	1.8132	5.8422	2.8480
9.0406	1.8001	5.7609	2.8250
8.8855	1.7850	5.6677	2.7984
8.7390	1.7704	5.5826	2.7713
8.7166	1.7681	5.5703	2.7668
8.7043	1.7669	5.5630	2.7646
8.7002	1.7665	5.5592	2.7645
8.3817	1.7335	5.3739	2.7038
8.1238	1.7059	5.2225	2.6536
7.7500	1.6642	5.0084	2.5752
7.4182	1.6256	4.8164	2.5038
7.1360	1.5916	4.6554	2.4397
6.7945	1.5490	4.4573	2.3613
6.4495	1.5044	4.2558	2.2799
6.1892	1.4697	4.1022	2.2175
5.8672	1.4256	3.9105	2.1390
5.5427	1.3799	3.7152	2.0587
5.2915	1.3437	3.5613	1.9965
4.9087	1.2873	3.3263	1.8996
4.6645	1.2505	3.1746	1.8374
4.3210	1.1981	2.9581	1.7501
4.0329	1.1535	2.7748	1.6766
3.8135	1.1194	2.6341	1.6206

The $CaCl_2$ osmotic coefficients measured in this research agree with Stokes' data (*4*) to 0.0–0.3% above 3.9 mol kg^{-1}. This is within the combined experimental errors for these two independent studies. If both sets of H_2SO_4–$CaCl_2$ isopiestic data are plotted as the isopiestic molality ratio vs. m, and a smooth curve drawn through the two sets of data above 3.9 mol kg^{-1}, extrapolation of this curve below 3.9 mol kg^{-1} appears to agree with our data but disagrees with Stokes' four lowest concentrations by about 0.4–0.5%. Since the agreement between these two sets of osmotic coefficients is so good in most of the overlap region, Stokes' data at higher concentrations can be used with confidence. These two sets of $CaCl_2$ osmotic coefficients will be compared in more detail elsewhere (*2*).

The osmotic coefficients of sulfuric acid solutions appear to be known to about ±0.3% at the high concentrations studied here (*1*). The results reported here, together with Stokes' data, can therefore yield the osmotic coefficients of $CaCl_2$ to 0.4–

0.5% above 3 mol kg^{-1}. If more reliable standard data become available for H_2SO_4 at high concentrations, a corresponding improvement will occur in the $CaCl_2$ osmotic coefficients. It should be noted that the data reported here exhibit less scatter than Stokes' results, especially below 7.0 mol kg^{-1}. This presumably occurs because of the longer equilibration times used by us. The osmotic coefficients from this research also agree reasonably well with those from other sources below 3 mol kg^{-1}.

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Heats of Dilution of Some Aqueous Rare Earth Electrolyte Solutions at 25 °C. 3. Rare Earth Chlorides

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The heats of dilution of aqueous $LaCl_3$, $PrCl_3$, $NdCl_3$, $SmCl_3$, $EuCl_3$, $GdCl_3$, $TbCl_3$, $DyCl_3$, $HoCl_3$, $ErCl_3$, $TmCl_3$, $YbCl_3$, and $LuCl_3$ solutions have been measured up to saturation at 25 °C. The integral heats of solution of $LaCl_3 \cdot 7H_2O$, $PrCl_3 \cdot 7H_2O$, $NdCl_3 \cdot 6H_2O$, $SmCl_3 \cdot 6H_2O$, $EuCl_3 \cdot 6H_2O$, $GdCl_3 \cdot 6H_2O$, $TbCl_3 \cdot 6H_2O$, $DyCl_3 \cdot 6H_2O$, $HoCl_3 \cdot 6H_2O$, $ErCl_3 \cdot 6H_2O$, $TmCl_3 \cdot 6H_2O$, $YbCl_3 \cdot 6H_2O$, and $LuCl_3 \cdot 6H_2O$ in water at 25 °C have also been measured. The heat of dilution data are represented by empirical equations, and relative partial molal heat contents are calculated. The heat content trends across the rare earth chloride series are similar to the trends found for the rare earth perchlorate heat data, and can be correlated with a change in the inner sphere cation water coordination across the rare earth cation series.

The heats of dilution of aqueous rare earth chloride solutions up to 0.2 *m* have been reported (*28, 32*). These dilute data for the chlorides were shown to conform to the Debye–Hückel limiting law, and the heat content trends across the rare earth chloride series showed the two series effect attributed to a change in the inner sphere water coordination of the rare earth cations between Nd and Tb (*28*).

Recently, we have extended many of the dilute thermodynamic and transport measurements to higher concentrations (*13, 23, 27, 36, 37*) where short range ion–ion interactions become important. The heats of dilution reported for the rare earth perchlorates (*31*) up to saturation show that the two-series effect across the rare earth perchlorate series persists to high concentrations virtually unchanged. In contrast, although the two-series effect is observable in very dilute nitrate solutions, the heats of dilution for the rare earth nitrates outside this region were found to be correlated with the available stability constants of the rare earth nitrate complexes (*30*). In this report we present the heats of dilution measurements for the rare earth chlorides up to saturation, and compare these to the results of the perchlorate and nitrate studies.

Experimental Section

The apparatus, an adiabatically jacketed differential calorimeter similar to that of Gucker, Pickard, and Planck (*12*), was the same one used for the rare earth perchlorate (*31*) and nitrate (*30*) experiments and has been previously described (*28, 32*). The calorimeter was operated at a sensitivity of about 4×10^{-4} cal/mm chart displacement. The accuracy of the calorimeter has been established and was monitored throughout the present experiments by measuring the heat of neutralization of HCl by NaOH. From a total of ten measurements at 25.00 ± 0.02° we obtained $\Delta H^{\circ} = -13.334 \pm 0.018$ kcal mol^{-1} for the heat of neutralization corrected to infinite dilution. This is in good agreement with -13.34 kcal mol^{-1} recommended by Hepler and Woolley (*14*).

The stock solutions were prepared from the rare earth oxides and C.P. grade HCl. The oxides were purified by ion exchange methods by the Rare Earth Separation Group of the Ames Laboratory. The pH of the stock solutions was adjusted to guarantee a 1:3 ratio of rare earth to chloride ions. All secondary solutions were prepared by weight from the stock solutions and conductivity water with a specific conductance of less than 1×10^{-6} mho cm^{-1}, all weights being converted to mass. The stock, saturated, and some of the secondary solutions were analyzed by gravimetric oxide (*33*), sulfate (*33*), and/or EDTA (*29*) for the rare earth content and by a potentiometric $AgNO_3$ (*33*) method for the chloride content. The agreement between the anion and cation analyses was within 0.1%, showing that the stoichiometry was 1:3 for the rare earth to chloride ratio. The analyses indicated that the concentrations were known to better than ±0.1% in terms of the molality.

Hydrated crystals of the rare earth chlorides were grown from saturated solutions at 25.00 °C and were dried over $BaCl_2$ or $CaCl_2$. The ratio of rare earth chloride to number of water molecules was determined by EDTA titrations. $LaCl_3$ and $PrCl_3$ crystallized as the heptahydrate, while the rest crystallized as the hexahydrates, all within ±0.1% of the theoretical water content.

The experimental procedure for the heats of dilution and heats of solution measurements was similar to that employed for the rare earth perchlorate (*31*) and rare earth nitrate (*30*) experiments and is fully described elsewhere (*28, 32*). One or two samples of rare earth chloride solution were diluted into about 900 g of water. Diluting the first sample of initial molality m_1, containing n' moles of rare earth chloride, into the water giving