model also gives moderately good agreement.

Recently Pesuit (*30*) has discussed the estimation of K_{12} values for various types of binary systems and has concluded that the Hiza–Duncan relation (eq 14) is a useful relation for predictions of K_{12} interaction constants.

Extraction of the Second Virial Interaction Coefficient B_{12} from Gas–Liquid and Gas–Solid Phase Equilibrium Data

Reuss and Benakker (*28*), Rowlinson and Richardson (*17*), Mullins (*2*), and Chui and Canfield (*29*) among others have discussed the calculation of the second virial interaction coefficient B_{12} from experimental gas–liquid and gas–solid phase equilibrium data.

If the virial equation of state in the Leiden form (eq 3) through the third coefficient is used to describe the gas-phase mixture of a gas–liquid equilibrium, then eq 6 may be rearranged and solved for B_{12} to give

$$B_{12} = \frac{V_m}{2y_2}\left[\left(\frac{2B_{11}}{V_{01}} + \frac{3C_{111}}{2V_{01}^2} \right) - \ln Z_{01} - \right.$$

$$\frac{3}{2V_m^2}(y_1^2 C_{111} + 2y_1 y_2 C_{112} + y_2^2 C_{122}) + \frac{1}{RT}\int_{P_{01}}^{P} V_1^c \, dP -$$

$$\left. 2y_1\frac{B_{11}}{V_m} + \ln Z_m + \ln x_1 - \ln \frac{Py_1}{P_{01}} \right] \quad (15)$$

along a given experimental isotherm eq 15 is solved for B_{12} for each pressure by making use of experimental values for y_i, x_i, V_{01}, and V_1^c and P_{01} for the saturated phase and B_{11} and B_{22} and by assuming a model from which the third virial interaction coefficient C_{112} and C_{122} as well as C_{111} and C_{222} may be calculated. The volume V_m is also calculated by using these third virial coefficients together with an estimated value of B_{12}. The values of B_{12} so found from eq 15 are then plotted vs. the quantity $(P - P_{01})$ and the curve is extrapolated to $(P - P_{01}) = 0$ to obtain B_{12}. The values of B_{12} so obtained for each temperature were then plotted as a function of T (K) and a smooth curve was drawn through the data. Smoothed values were then read from this curve. Smoothed values of B_{12} for the two systems are shown in Table VIII. The uncertainty listed

for each value is based primarily upon the effects on B_{12} of the uncertainty in the experimental values of y_i and x_i on the calculation of B_{12} from eq 15.

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Solubility of Some Alkali and Alkaline Earth Chlorides in Water at Moderate Temperatures

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Solubilities for the binary systems, salt–H_2O, of the chlorides of lithium, rubidium, cesium, magnesium, calcium, strontium, and barium from near 0 °C to the saturated boiling point are reported. The experimental data and coefficients of an equation for a smoothed curve describing each system are listed in the tables. The data are improvements on those previously reported in the literature, having a precision on the average of ±0.09%.

Introduction

The solubilities of simple salts in pure water and aqueous solutions at moderate temperatures have a wide variety of

applications. Geothermal energy, solution mining, radioactive waste disposal, and desalinization technologies all have need for accurate data on salt solubility. In addition, recently developed empirical models for the solubility of salts in complex brines require as input reliable binary and ternary solubility data (*1*). However, much of the older, available data lack the desired level of internal consistency (*1, 2*). To improve the existing data base as well as to better understand the physical chemistry of concentrated electrolyte solutions, we have undertaken the measurement of the solubility of highly soluble salts. Previously we reported solubility data for NaCl, KCl, $CaCl_2$, Na_2SO_4, and K_2SO_4 (*3*). This paper reports on the solubilities of additional highly soluble salts in pure water from near 0 °C to the saturated

Table I. Experimentally Determined Solubilities Compared to Those Calculated from Regression Equations[a]

temp, °C	exptl solu- tion, wt %	calcd solu- tion, wt %	difference	temp, °C	exptl solu- tion, wt %	calcd solu- tion, wt %	difference
BaCl₂·2H₂O				15.40	44.10	44.14	−0.04
				18.96	45.10	45.08	0.02
6.20	24.25	24.30	−0.05	24.80	45.69	45.72	0.03
18.02	26.11	26.05	0.06	27.35	46.05	45.95	−0.10
21.05	26.49	26.48	0.01	33.29	46.48	46.52	0.04
24.61	27.03	26.97	0.06	43.88	47.61	47.69	0.08
33.29	28.10	28.13	−0.03	44.20	47.67	47.72	0.05
48.73	30.00	30.11	−0.11	54.25	49.04	48.98	−0.06
58.95	31.48	31.40	0.08	55.30	49.22	49.13	−0.09
61.73	31.65	31.75	−0.10	67.95	50.98	50.97	−0.01
71.75	33.17	33.04	0.13	78.43	52.61	52.68	0.07
81.57	34.37	34.36	0.01	91.95	55.15	55.13	−0.02
93.55	35.99	36.07	−0.08	**LiCl**			
99.29	36.98	36.95	0.03				
CaCl₂·2H₂O				100.83	55.98	55.98	0.00
				112.50	56.30	56.31	−0.01
49.37	56.03	56.00	0.03	124.97	56.72	56.71	0.01
61.81	56.85	56.85	0.00	144.05	57.46	57.46	0.00
68.63	57.28	57.34	−0.06	155.45	57.98	57.98	0.00
85.85	58.69	58.69	0.00	**MgCl₂·6H₂O**			
97.65	59.75	59.72	0.03				
108.40	60.82	60.77	0.05	15.29	35.30	35.25	0.05
127.71	62.88	62.93	−0.05	29.95	36.12	36.20	−0.08
149.21	65.84	65.86	−0.02	45.68	37.10	37.10	0.00
160.25	67.64	67.62	0.02	53.11	37.49	37.54	−0.05
CsCl				70.49	38.91	38.77	0.14
				82.62	39.99	39.92	0.07
15.83	64.46	64.51	−0.05	93.18	41.16	41.20	−0.04
30.58	66.44	66.30	0.14	101.50	42.32	42.44	−0.08
47.56	68.22	68.30	−0.08	108.80	43.62	43.71	−0.09
60.26	69.64	69.70	−0.06	114.32	44.96	44.82	0.16
77.83	71.48	71.43	0.05	**SrCl₂·6H₂O**			
95.31	72.87	72.84	0.03				
114.95	73.92	73.94	−0.02	18.15	34.06	34.12	−0.06
RbCl				30.65	36.71	36.58	0.14
				43.47	39.86	39.92	−0.08
14.23	46.28	46.29	−0.01	55.45	43.66	43.78	−0.10
31.29	49.59	49.57	0.02	61.17	45.98	45.88	0.09
46.40	52.03	51.98	0.05				
62.26	54.03	54.13	−0.10	**SrCl₂·2H₂O**			
80.26	56.28	56.25	0.03				
92.43	57.62	57.58	0.04	62.40	46.21	46.19	0.02
104.99	59.25	59.27	−0.02	69.53	46.76	46.79	−0.03
LiCl·2H₂O				75.05	47.27	47.27	0.00
				89.27	48.69	48.66	0.03
4.30	41.68	41.69	−0.01	98.28	49.73	49.70	0.03
9.43	42.76	42.73	0.03	100.30	49.91	49.96	−0.05
11.66	43.24	43.23	0.01	114.25	52.02	52.01	0.01

[a] All solubilities are in g/100 g.

boiling point of the individual salt solutions.

Experimental Method

The experimental technique used in this study is a modification of the commonly applied visual or synthetic method and has been discussed in detail in an earlier report (3). To summarize: the method involves loading a Pyrex glass test tube with salt and water at a precisely known bulk composition. A stirring mechanism is inserted into the tube and a layer of silicone oil added to prevent water gain or loss. The tube is then placed in a bath containing either water (2–85 °C) or ethylene glycol (85–170 °C) as a heating medium. The tube is thermally equilibrated and the solution plus salt crystal assemblage vigorously stirred until dissolution of salt ceases. The bath is heated incrementally and the above procedure repeated. Heating increments are made progressively smaller as the amount of salt decreases. The temperature at which the last salt crystal dissolves is taken as the saturation point of the particular bulk composition of the tube. The temperature limits of this method are the freezing and boiling points of the saturated salt–water systems.

Experimental Results

The measured solubilities for the phases studied, $BaCl_2·2H_2O$, $CaCl_2·2H_2O$, $CsCl$, $RbCl$, $LiCl·2H_2O$, $LiCl·H_2O$, $LiCl$, $MgCl_2·6H_2O$, $SrCl_2·6H_2O$, and $SrCl_2·2H_2O$, are listed in Table I along with smoothed values and the deviation of the measured values from the smoothed results. The smooth values were obtained from a least-squares regression of the experimental values to an equation of the form

$$S = \sum_0^i a_i t^i \tag{1}$$

where t is the temperature in degrees Celsius and S is the solubility in grams of the anhydrous salt per 100 g of saturated solution (g/100 g). The coefficients for the regression equation are listed in Table II along with the mean deviations in g/100 g and percent deviation.

$$\frac{S_{exptl} - S_{calcd}}{S_{exptl}} \times 10^2 \tag{2}$$

Table II. Regression Coefficients and Mean Deviation for Solubility Equations

compd	coefficients				mean dev	
	a_0	a_1	a_2	a_3	g/100 g	%
$BaCl_2 \cdot 2H_2O$	23.304	0.164 16	-7.259×10^{-4}	4.595×10^{-6}	±0.071	±0.205
$CaCl_2 \cdot 2H_2O$	52.805	0.068 20	-1.666×10^{-4}	1.984×10^{-6}	±0.030	±0.048
CsCl	62.609	0.118 50	-1.621×10^{-4}	2.922×10^{-6}	±0.064	±0.090
RbCl	42.996	0.251 99	$-0.001 50$	5.90×10^{-6}	±0.038	±0.071
$LiCl \cdot 2H_2O$	40.394	0.162 74	0.002 95		±0.021	±0.051
$LiCl \cdot H_2O$	44.014	0.049 66	-7.749×10^{-4}		±0.054	±0.114
LiCl	55.434	$-0.014 86$	2.010×10^{-4}		±0.004	±0.010
$MgCl_2 \cdot 6H_2O$	33.960	0.098 82	$-0.001 08$	9.111×10^{-6}	±0.078	±0.188
$SrCl_2 \cdot 6H_2O$	31.937	0.074 47	0.002 51		±0.093	±0.237
$SrCl_2 \cdot 2H_2O$	39.121	0.180 31	$-0.001 66$	9.322×10^{-6}	±0.023	±0.046

The experimental precision obtained by the modified visual method is quite good and in addition avoids many of the problems encountered by other methods (3).

Discussion of the Results

Much of the available solubility data for salts as well as other compounds have been summarized and partially evaluated (2). These data have a wide range of quality. Often, the smoothed values (2) show a high degree of scatter.

The experimental solubility data for $BaCl_2 \cdot 2H_2O$ agree moderately well with previous studies (2), although above 50 °C the values measured in this study are systematically lower than the older data by as much as 0.3 g/100 g.

The solubilities of $CaCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 4H_2O$, and $CaCl_2 \cdot 2H_2O$ up to 85 °C were recently measured (3). This study extends the measured solubility of $CaCl_2 \cdot 2H_2O$ up to 160 °C; the data were regressed with the earlier results. The solubilities of $CaCl_2 \cdot 2H_2O$ obtained here are consistently lower than the older, more frequently cited data (4) by as much as 1.5 g/100 g. However, more recent data (5) agree with ours by ±0.2 g/100 g. Utilizing our solubility data for $CaCl_2 \cdot 2H_2O$, the lower temperature solubility data for $CaCl_2 \cdot 2H_2O$ (3), and the solubility data for $CaCl_2 \cdot 4H_2O$ (3), we found the transition temperature and composition for $CaCl_2 \cdot 4H_2O \rightleftharpoons CaCl_2 \cdot 2H_2O + 2H_2O$ to be 45.19 ± 0.07 °C and 55.73 ± 0.03 g/100 g, which agrees well with the values of 45.1 °C and 55.9 g/100 g determined by (5) but not with the older values of 45 °C and 56.6 g/100 g (4).

Of the evaluated data sets for CsCl, the data of the Earl of Berkeley (6) are considered to be the most precise and reliable (2). These data show a mean deviation from ours of ±0.14 g/100 g with a strong tendency for the solubilities to be higher than ours at temperatures greater than 60 °C.

On the basis of an evaluation (2) of the existing data, the most reliable and internally consistent values for the solubility of RbCl are those of Berkeley (6) and Rimbach (7). Their data show a mean deviation from ours of ±0.17 g/100 g.

LiCl exhibits three hydration states over the temperature range investigated. Our solubility data for $LiCl \cdot 2H_2O$ and $LiCl \cdot H_2O$ agree moderately well with older work (8, 9). The deviations of the previous studies from ours are ±0.12 g/100 g for $LiCl \cdot 2H_2O$ (9). The data for LiCl (10) show a systematic and increasing deviation from ours with increasing temperature. For example, at 100 °C the reported solubility is higher than ours by 0.3 g/100 g and at 160 °C the reported value is 0.9 g/100 g higher. The dehydration of $LiCl \cdot 2H_2O$ to $LiCl \cdot H_2O$ occurs at 19.73 ± 0.13 °C and 45.29 g/100 g. Previous studies have put this transition temperature between 12.5 and 19.1 °C (2). The dehydration of $LiCl \cdot H_2O$ to LiCl occurs at 95.6 ± 0.3 °C and 55.85 g/100 g, a value lying in the middle of the reported temperature range of 93–100.5 °C (2).

$MgCl_2 \cdot 6H_2O$ proved to be the most difficult salt to work with due to its strongly hygroscopic behavior. Previous studies (11–14) show a scatter of ±0.13 g/100 g around our values which is well within the stated precision of the previous studies.

Below the boiling point of the salt-saturated solution, two hydrates of $SrCl_2$ exist, $SrCl_2 \cdot 6H_2O$ and $SrCl_2 \cdot 2H_2O$. The most consistent solubility data set (2) over the temperature range of interest is that of Menzies (15), whose values are slightly higher than ours by 0.1 to 0.4 g/100 g. These values, however, lie within the stated accuracy of his method, ±1%. Solubility measurements employing Menzie's method are frequently found to be high by as much as 1% (3, 16). The dehydration of the hexahydrate occurs at 61.45 ± 0.1 °C and 46.09 g/100 g. The transition temperature agrees well with the literature values of 61.4 ± 0.2 °C (15) and 61.36 °C (17).

Conclusions

The data presented here represent a more internally consistent and precise set of solubility measurements than currently available for $BaCl_2 \cdot 2H_2O$, $CaCl_2 \cdot 2H_2O$, CsCl, RbCl, $LiCl \cdot 2H_2O$, $LiCl \cdot H_2O$, LiCl, $MgCl_2 \cdot 6H_2O$, $SrCl_2 \cdot 6H_2O$, and $SrCl_2 \cdot 2H_2O$. The range of the deviations of the measured solubilities from the smooth curves is 0.01–0.24% and is approximately equal to the precision of the measurements. The data sets taken from the literature have precisions ranging from 0.2 to 1.0% and accuracies are usually not defined. Analyses of the possible sources of error for the method employed in this study yield accuracies of 0.1–0.2% (3).

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