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Surface Tension and Density of the Molten KCl–LiCl and $PbCl_2$–KCl–LiCl Systems

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The maximum bubble pressure method was used to determine the surface tension and density of melts within the binary KCl–LiCl and the ternary $PbCl_2$–KCl–LiCl systems. The temperature range of this study was from 723 to 1173 K. In all cases, the surface tension was found to decrease with increasing temperature. In the ternary system at constant molar ratios of KCl to LiCl, a minimum in the surface tension was observed at approximately 45 mol % $PbCl_2$. The ternary surface tension values were found to obey this simple additivity expression of the binary surface tensions of KCl–LiCl and KCl–$PbCl_2$. Based on these findings, constant surface tension contours have been evaluated. The density obtained in the present study agree well with the previously determined densities obtained by using a bottom-balance Archimedean technique reported by this laboratory.

Introduction

The present process for the extraction of lead from lead sulfide concentrates gives rise to problems with respect to environmental concerns. In anticipation of strict legislation controlling the emissions of heavy metals as well as sulfur dioxide, new processes have been proposed. One such process is the conversion of lead sulfide to a chloride followed by fused-salt electrolysis to produce metallic lead and chlorine (*1-3*). The chlorine produced is recycled directly or indirectly for the production of lead chloride.

Lead chloride alone is not a good electrolyte because it has a high vapor pressure and exhibits poor current efficiency with respect to lead production. Both the $PbCl_2$–KCl–LiCl and $PbCl_2$–KCl–NaCl ternary systems have been suggested as possible electrolytes due to their suitable physical properties. The $PbCl_2$–KCl–LiCl system has a higher molar conductivity, but due to the hygroscopic nature of LiCl, the $PbCl_2$–KCl–NaCl ternary system has been suggested as an alternative electrolyte.

Recently, the surface tensions of melts in the $PbCl_2$–KCl–NaCl ternary system were determined in this laboratory (*4*). As a continuation of this work, the surface tension of the molten salt system $PbCl_2$–KCl–LiCl as a function of composition and temperature in the range of interest for the electrolytic process of lead recovery was studied. For the determination of the ternary system, reliable data on the binary KCl–LiCl were not available. Consequently, the surface tension of the binary KCl–LiCl was also measured.

Experimental Section

The experimental apparatus and procedure adopted for the present study have been described in detail previously (*4*) and thus only a brief description is given here. The well established maximum bubble pressure technique was selected for the determination of the surface tension and density. It involves the slow formation of a gas bubble at the tip of a capillary immersed in the molten salt. Simultaneously, the pressure of the gas used to form the bubble is measured in order to determine the maximum pressure developed inside the bubble at the very instant it bursts. Schrödinger (*5*) developed the following relationship between the surface tension and the maximum bubble pressure.

$$\gamma = \frac{rP_\gamma}{2}\left[1 - \tfrac{2}{3}\left(\frac{r\rho g}{P_\gamma}\right) - \tfrac{1}{6}\left(\frac{r\rho g}{P_\gamma}\right)^2\right] \qquad (1)$$

γ is the surface tension, r is the radius of the capillary, P_γ is the maximum pressure difference inside and outside the bubble at the capillary tip, ρ is the density difference between the liquid salt and the gas, and g is the acceleration of gravity.

Apparatus. The overall apparatus used in this investigation is shown in Figure 1. The furnace had a uniform temperature (2.5 K) region of 5 cm. The salt mixtures were contained in graphite crucibles with an inner diameter of 26 mm and a height of 47 mm under a purified argon atmosphere. The quartz capillary tubes were 5 cm long, with an outer diameter of about 2.1 mm and with an inner diameter of about 1.03 mm.

Procedure. The potassium chloride (Fisher A.C.S. grade), the lithium chloride (CERAC, 99.8%), and the lead chloride (Baker Analysed reagent grade) were stored and handled in a drybox filled with a dry argon atmosphere. The salts were predried in a vacuum oven at 423 K before mixing. A graphite crucible with the salt mixture was positioned inside the furnace which was flushed with argon and heated to the desired temperature. Excess pressure was applied to the capillary while it was lowered toward the melt surface. The capillary was then lowered very slowly until a sudden pressure jump was registered by the pressure transducer, indicating that the capillary had touched the melt surface and the surface position was recorded.

The bubbling rate was adjusted to about 1 bubble/min which was in the region where the transducer output was independent of the gas flow rate. The pressure was increased linearly with the immersion depth until a bubble was released at the capillary tip followed by a sudden decrease in the pressure. The capillary immersion depth was changed several times while the maxi-

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Table I. Surface Tension for the KCl-LiCl System in mN/m

compostn, mol %		temp, K							$\gamma = A + BT$(K)		
KCl	LiCl	873	923	973	1023	1073	1123	1173	A	$B \times 10^2$	std error of estimn
0	100		130.3	127.2	123.7	120.8	117.8		188.2	−6.28	0.18
25	75	122.6	118.5	115.0	111.5	108.1	105.0		183.4	−7.01	0.31
50	50	117.7	112.8	108.1	105.1	101.8	97.9		184.2	−7.71	0.73
75	25		111.3	106.0	102.0	97.8	94.1		189.4	−8.52	0.51
100	0					97.4	93.7	90.0	178.9	−7.58	0.07

Table II. Density for the KCl-LiCl System in kg/m^3

compostn, mol %		density, $\rho \times 10^3$							$\rho = C + DT$(K)		
KCl	LiCl	873 K	923 K	973 K	1023 K	1073 K	1123 K	1173 K	$C \times 10^3$	$D \times 10^7$	std error of estimn
0	100		1.48	1.46	1.44	1.42	1.40		1.85	−4.00	
25	75	1.54	1.51	1.48	1.46	1.44	1.41		1.98	−5.03	4.2×10^{-6}
50	50	1.58	1.56	1.53	1.50	1.48	1.45		2.04	−5.26	3.2×10^{-6}
75	25		1.57	1.54	1.52	1.49	1.47		2.03	−5.00	3.2×10^{-6}
100	0					1.51	1.48	1.45	2.11	−5.62	3.2×10^{-6}

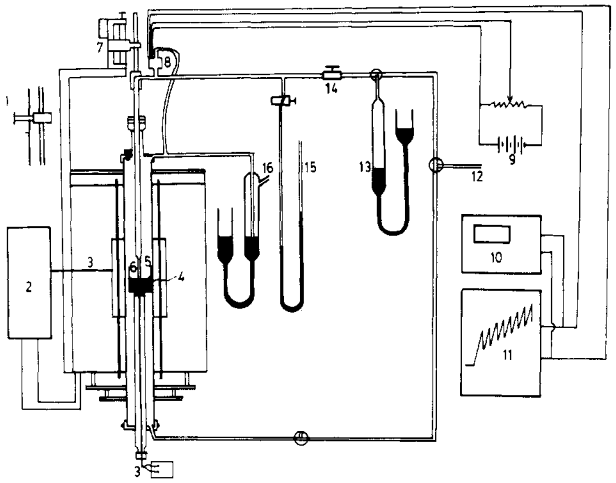

Figure 1. Experimental apparatus: 1, cathetometer; 2, temperature controller; 3, thermocouple; 4, sample; 5, graphite crucible; 6, capillary; 7, capillary drive; 8, pressure transducer; 9, dry cell; 10, digital multimeter; 11, recorder; 12, purified argon inlet; 13, gas reservoir; 14, needle valve; 15, manometer; 16, gas outlet.

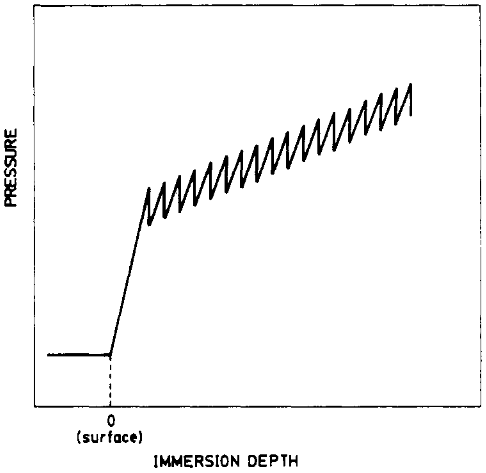

Figure 2. Relation between maximum pressure and immersion depth.

mum bubble pressure was recorded. By measuring the maximum bubble pressure at different immersion depths, we can calculate the density of the salt from the slope of the experimental data when the maximum pressure is plotted as a function of immersion depth as shown in Figure 2. From the same plot, the pressure drop caused by the formation of the bubble can be found as the maximum pressure for zero immersion depth. From this pressure value the surface tension of the salt mixture can be calculated by using Schrödingers equation. The temperature effect on the surface tension and the density were determined during both heating and cooling cycles. Since the salt wetted the capillary tip, the inner radius of the capillary tip was used for the surface tension calculation. All measurements were corrected for thermal expansion of the capillary orifice.

Results and Discussion

The maximum bubble pressure apparatus was tested by measuring the surface tension of pure $PbCl_2$ and the LiCl-KCl binary system over a temperature range of 793–973 and 873–1173 K, respectively. The surface tension data for pure $PbCl_2$ were in excellent agreement with those of Dahl and Duke (*6*). The surface tension of LiCl-KCl mixtures are summarized in Table I and the results for 1073 K are shown in Figure 3 together with those of Nissen et al. (*7*) and Smirnov and Stepanov (*8*). Fairly good agreement is observed between the three investigations for KCl-rich melts while more scatter is observed for the LiCl-rich melts. The literature values of the surface tension of pure LiCl show a large scatter from 107.9 to 125.9 mN/m at 1073 K (*7*–*13*). The value obtained in the present study was 120.8 mN/m at 1073 K. The density data,

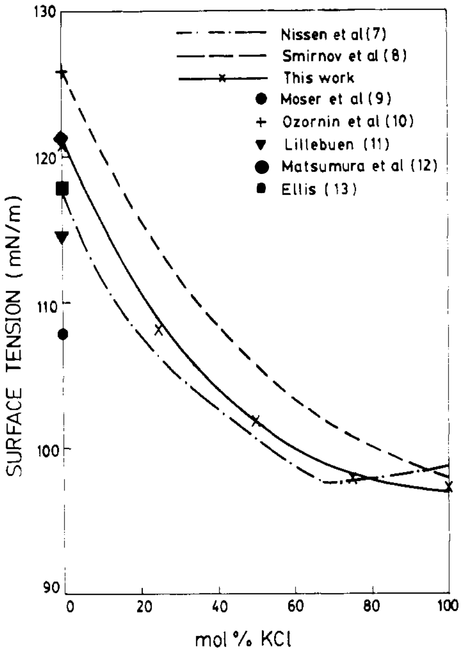

Figure 3. Surface tension of LiCl-KCl binary mixtures at 1073 K.

Table III. Surface Tension for the $PbCl_2$-KCl-LiCl Ternary System in mN/m

compostn, mol %			temp, K							$\gamma = A + BT(K)$		
$PbCl_2$	KCl	LiCl	723	773	823	873	923	973	1073	A	$B \times 10^2$	std error of estimn
100	0	0		136.0[a]	132.6	126.2	121.3	114.8		228.5	−11.67	0.40
80	5	15	136.3	130.5	127.2	121.0	115.9	111.7	101.5	207.6	−9.90	0.60
80	10	10	134.0	128.8	122.8	118.2	114.3	108.7	98.3	206.4	−10.06	0.56
80	15	5	132.0	127.0	120.7	116.4	111.0	106.4	95.8	206.2	−10.29	0.44
60	10	30	135.4	131.4	124.0	121.0	115.2	109.3	99.8	210.1	−10.30	0.87
60	20	20	129.8	124.9	120.6	113.8	109.6	105.6	94.3	202.9	−10.09	0.71
60	30	10	126.2	121.5	115.9	110.3	107.0	100.2	91.2	199.0	−10.08	0.69
40	15	45	129.8	127.0	122.8	119.1	114.3	111.6	101.2	189.6	−8.14	0.89
40	30	30	129.2	125.2	120.1	115.3	109.6	105.6	97.0	197.3	−9.40	0.57
40	45	15	122.9	118.6	114.2	108.5	105.6	101.4	91.7	186.7	−8.83	0.62
20	20	60		126.5	123.5	119.9	117.1	112.6	104.9	182.9	−7.22	0.58
20	60	20			115.0	112.3	108.4	104.8	98.6	170.3	−6.69	0.36

[a] 793 K.

Table IV. Density for the $PbCl_2$-KCl-LiCl Ternary System in kg/m^3

compostn, mol %			density, $\rho \times 10^3$							$\rho = C + DT(K)$		
$PbCl_2$	KCl	LiCl	723 K	773 K	823 K	873 K	923 K	973 K	1073 K	$C \times 10^3$	$D \times 10^6$	std error of estimn
100	0	0		4.93[a]	4.87	4.80	4.74	4.66		6.07	−1.45	8×10^{-6}
80	5	15	4.55	4.50	4.43	4.37	4.29	4.21	4.08	5.56	−1.38	10×10^{-6}
80	10	10	4.50	4.44	4.40	4.31	4.28	4.22	4.10	5.32	−1.14	11×10^{-6}
80	15	5	4.47	4.41	4.33	4.27	4.18	4.12	3.98	5.50	−1.42	7×10^{-6}
60	10	30	4.03	3.99	3.94	3.88	3.83	3.77	3.64	4.85	−1.12	11×10^{-6}
60	20	20	3.97	3.91	3.84	3.79	3.73	3.67	3.51	4.90	−1.28	12×10^{-6}
60	30	10	3.90	3.84	3.77	3.71	3.66	3.60	3.48	4.76	−1.19	5×10^{-6}
40	15	45	3.44	3.39	3.34	3.28	3.25	3.18	3.06	4.22	−1.07	10×10^{-6}
40	30	30	3.36	3.32	3.28	3.22	3.17	3.11	3.03	4.07	−0.98	8×10^{-6}
40	45	15	3.29	3.25	3.19	3.16	3.08	3.05	2.92	4.06	−1.05	13×10^{-6}
20	20	60		2.62	2.57	2.51	2.47	2.41	2.32	3.39	−1.01	6×10^{-6}
20	60	20			2.44	2.40	2.37	2.31	2.22	3.18	−0.89	9×10^{-6}

[a] 793 K.

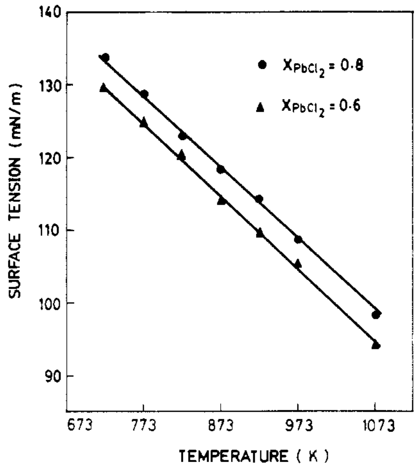

Figure 4. Temperature dependency of surface tension in the $PbCl_2$-KCl-LiCl system at a molar ratio of KCl/LiCl = 1.

summarized in Table II, for the corresponding systems are also in good agreement with published data (*14*–*16*).

The compositions of the ternary system can be expressed by the parameters y and t, where

$$y = 1 - x_{KCl}; \quad t = x_{LiCl}/(x_{LiCl} + x_{PbCl_2}) \qquad (2)$$

The results of the surface tension and density for the $PbCl_2$-KCl-LiCl ternary mixtures are listed in Tables III and IV, respectively. Both the surface tension data and the density data have been subjected to a least-squares analysis. The surface tension data were fitted to a linear equation of the form

$$\gamma = A + BT(K) \text{ (mN/m)} \qquad (3)$$

while the density data were fitted to

$$\rho = C + DT(K) \text{ (g/cm}^3) \qquad (4)$$

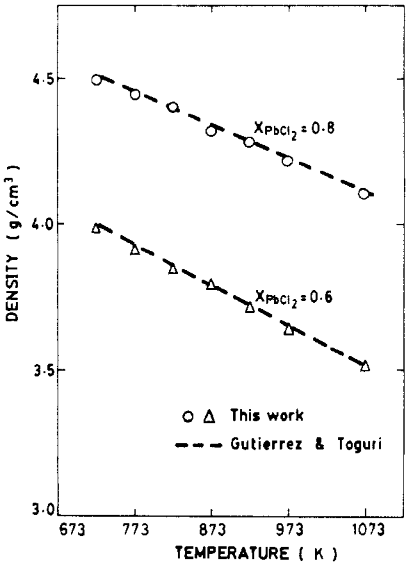

Figure 5. Temperature dependency of density in the $PbCl_2$-KCl-LiCl system at a molar ratio of KCl/LiCl = 1.

The surface tension of the ternary melts decreases linearly with increasing temperature for all compositions. Typical examples are shown in Figure 4 for two compositions, x_{PbCl_2} = 0.8 and 0.6 at $x_{KCl} = x_{LiCl}$. The corresponding density values, shown in Figure 5, display a similar linear decrease with increasing temperature and are in good agreement with the reported values of Gutierrez and Toguri (*17*) as shown by the dotted lines. Decreasing the concentration of $PbCl_2$ leads to a decrease in melt density. The surface tension of ternary melts with a given LiCl to KCl ratio exhibits a minimum at approximately 45 mol % $PbCl_2$. The results at 923 K shown in

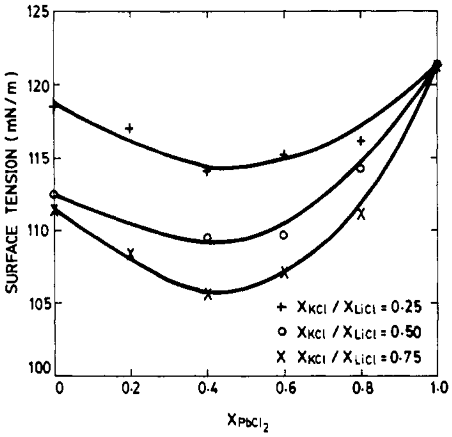

Figure 6. Effect of $PbCl_2$ on the surface tension of melts containing constant molar ratio of KCl/LiCl at 923 K.

Figure 6 are typical examples. This behavior corresponds with that observed by other researchers (*4*, *7*, *18*) and may be explained by the formation of surface active $PbCl_{2+n}{}^{n-}$ complexes, where the value of n may be 1, 2, or 4. Support for this suggestion comes from studies of Raman spectra (*19*), surface tension measurements (*7*), and density measurements (*20*). Similar complex formation has also been suggested in mixtures of $CdCl_2$ with alkali chlorides based on surface tension measurements (*21*).

In the $PbCl_2$–KCl–NaCl ternary system, the surface tension of the KCl–NaCl binary was almost a linear function of the composition and it has been shown (*4*) that the surface tension within the ternary system can be estimated from the $PbCl_2$–KCl and $PbCl_2$–NaCl binary systems by a simple additive rule. In the present ternary system, the surface tension in the KCl–LiCl binary system shows a negative deviation while the $PbCl_2$–LiCl shows an almost linear behavior. Thus, it was decided to test the additive rule within the ternary $PbCl_2$–KCl–LiCl system. For this purpose the following equation was used

$$\gamma(\text{ternary}) = t\gamma_{12} + (1 - t)\gamma_{13} \tag{5}$$

where γ_{12} and γ_{13} are the surface tension of the binaries LiCl–KCl and $PbCl_2$–KCl at constant KCl content, respectively. The surface tension values of the LiCl–KCl binary system as determined in this study can be described by the following equation:

LiCl–KCl:

$$\gamma_{12} = 176.55 + 0.98y + 0.82y^2 + 19.92y^3 - 0.073T(\text{K}) \tag{6}$$

By use of reported (*14*) binary surface tension values for the $PbCl_2$–KCl system and the surface tension of pure KCl obtained in this study, the following equation was found by a least-squares curve fitting:

$PbCl_2$–KCl:

$$\gamma_{13} = 176.29 + 13.65y + 16.14y^2 + 26.41y^3 - (0.073 + 0.05y)T(\text{K}) \tag{7}$$

To test the validity of this additive rule, the surface tension calculated by eq 5–7 were compared with all the experimental values at 773 K. The standard deviation was found to be 1.4 mN/m and the maximum deviation between the measured and calculated values was 2.8%. It is therefore concluded that the additive rule describes well the surface tension behavior within the ternary system and that the calculated values are within the experimental error. Figure 7 shows the liquidus lines and the constant surface tension lines for the $PbCl_2$–KCl–LiCl ternary system at 773 K as calculated by this procedure.

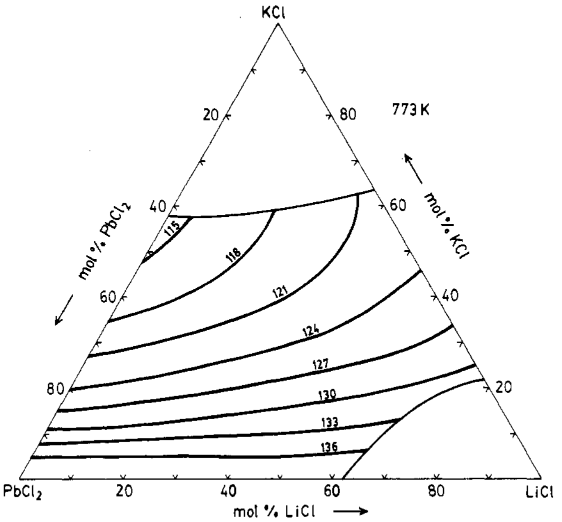

Figure 7. Calculated constant surface tension lines for the $PbCl_2$–KCl–LiCl ternary system at 773 K based on the binary systems.

The density values obtained in this work by using the maximum bubble pressure method are not expected to be of the same accuracy as those obtained by direct Archimedean methods. Nevertheless, the data obtained in the present study were in excellent agreement with those of Gutierrez and Toguri (*17*) who used a bottom-balance Archimedean technique.

Conclusions

(1) The surface tension and densities of the $PbCl_2$–KCl–LiCl ternary system have been determined over the temperature range of 723–1073 K by a maximum bubble pressure method.

(2) The surface tension of these melts were found to be approximately additive at constant values of y and this behavior could be described by the additivity rule with respect to t

$$\gamma_{\text{ternary}} = t\gamma_{12} + (1 - t)\gamma_{13}$$

where the binary systems, each containing a constant amount of KCl, are denoted by the subscripts 12 and 13.

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Registry No. $PbCl_2$, 7758-95-4; KCl, 7447-40-7; LiCl, 7447-41-8.

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Experimental Study at Low Molalities of the Enthalpies of Solution of RbBr in Water at 298.15 K

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Using the calorimeter and procedure described in a previous work, we measured the enthalpy of solution of RbBr in water at 298.15 K in the molality range from 0.006 to 0.072 mol kg^{-1}. Our results and the available data in the literature have been analyzed by two methods. As a result, the proposed value for the enthalpy of solution at infinite dilution is ΔH_s^∞(298.15 K) = (22 179 ± 28) J mol^{-1}.

Introduction

The available data for the enthalpy of solution of RbBr in water are practically nonexistent. In 1965, Parker (*1*) gave the value of (21 882 ± 418) J mol^{-1} for the enthalpy of solution at infinite dilution, ΔH_s^∞, at 298.15 K. This value was obtained by using only one experimental value at 0.11 mol kg^{-1} by Lange and Martin (*2*) and with the help of estimated L_ϕ data. More recently, Thourey and Perachon (*3*), gave the value 22 410 J mol^{-1}. The discrepancy between the two values is the 2.4%. In order to obtain more accurate values of ΔH_s, Weintraub et al. (*4*) measured the enthalpy of solution of RbBr in water at 298.15 K in the molality range from 0.038 to 0.073 mol kg^{-1}. The proposed value for ΔH_s^∞ was (22 184 ± 30) J mol^{-1}.

In order to avoid the significant scatter among the proposed values, in this work, measurements for the enthalpy of solution of RbBr in water at 298.15 K are presented. The molality range covered was from 0.006 to 0.071 mol kg^{-1}. We have extended the molality range to lower molalities for a more reliable extrapolation to infinite dilution.

Experimental Section

The enthalpy of solution was measured with the Tian-Calvet calorimeter type described in detail in a previous paper (*5*). The temperature controller used regulates to better than ±0.01 K over 24 h. An electrical calibration is carried out before and after each measurement. The calorimetric energy equivalent is about 43 mV/W and the values are accurate to 0.1%. The initial mechanical effect was also considered. The estimated uncertainty on the enthalpy of solution determinations is better than 1%.

The water used was doubly distilled and the solid sample was Merck Suprapur. It was heated for 5 h in a furnace at (774 ± 5) K. A test for the moisture of the salt in the calorimetric cell before the dissolution showed no significant change in mass over 24 h. An evaporation test showed that the solvent lost about 0.1% of its mass.

Table I. Calorimetric Molar Enthalpies of Solution of RbBr in Water at 298.15 K

w_s/g	w_w/g	m/(mol kg^{-1})	T/K	ΔH_s(298.165)/ (J mol^{-1})
0.034 693	34.312 13	0.006 11	298.32	22 334
0.035 115	34.299 00	0.006 19	298.22	22 231
0.082 538	34.312 13	0.014 55	298.32	22 416
0.099 218	34.297 00	0.017 49	298.24	22 294
0.118 010	34.573 38	0.020 64	298.29	22 414
0.144 658	34.667 83	0.025 23	298.50	22 418
0.163 170	34.616 58	0.028 50	298.45	22 437
0.179 265	34.699 96	0.031 24	298.52	22 368
0.214 033	34.297 00	0.037 74	298.24	22 281
0.255 435	34.573 38	0.044 68	298.52	22 491
0.311 833	34.616 58	0.054 47	298.45	22 423
0.412 288	34.667 83	0.071 91	298.43	22 439

Experimental Results

The obtained results for the enthalpies of solution of RbBr in water at 298.15 K are shown in Table I. The molar mass of RbBr used is 165.3718 g mol^{-1} (*4*). In Table I, w_s and w_w are the solute and solvent masses, respectively. All solute weighings were made on a single-pan balance with a sensitivity of 1 μg. All solvent weighings were made on a single-pan balance with a sensitivity of 10 μg; m is the molality and the values are accurate to 0.1% due to the evaporation of the solvent. T is the temperature for each solution and the values are accurate to ±0.03 K. ΔH_s(298.15 K) is the molar enthalpy of solution adjusted to 298.15 K. The adjustments were found as follows (*5*)

$$\Delta H_s(298.15\ \mathrm{K}) = \Delta H_s(T) + C_{p,\mathrm{m}}(298.15 - T) \qquad (1)$$

where $C_{p,\mathrm{m}} = C_{\phi,\mathrm{m}} - C^*_{p,\mathrm{m}}$; $C_{\phi,\mathrm{m}}$ is the apparent molar heat capacity of the dissolved salt at the given molality and $C^*_{p,\mathrm{m}}$ is the molar capacity of the salt before solution. Literature values of $C^*_{p,\mathrm{m}}$ (*6*) and $C_{\phi,\mathrm{m}}$ (*7*) were employed. The error due to condensation of solvent is given approximately by (*8*)

$$\delta H_s = -(2xp^* V_\mathrm{m}^\mathrm{g}/RT)\Delta_\mathrm{l}^\mathrm{g} H^*_\mathrm{m} \qquad (2)$$

where x denotes the mole fraction of the solute after dissolution, p^* the vapor pressure of the pure solvent, and $\Delta_\mathrm{l}^\mathrm{g} H^*_\mathrm{m}$ the molar enthalpy of evaporation of the pure solvent. The correction for the solvent-condensation effect is negligible.

Discussion

In order to analyze the experimental results and to calculate the enthalpy of solution at infinite dilution, ΔH_s^∞, a knowledge

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