(16) Boardman, N. F.; Dorman, F. H.; Heymann, E. *J. Phys. Chem.* **1949**, *53*, 375-382.
(17) Gutierrez, A.; Toguri, J. M. *J. Chem. Eng. Data* **1982**, *27*, 109-113.
(18) Sternberg, S.; Terzi, M.; Kucharski, M. *Arch. Hutn.* **1977**, *22*, 169-179.
(19) Tanaka, M.; Balasubramanyam, K.; Bockris, J.O.'M. *Electrochim. Acta*. **1963**, *8*, 621-629.
(20) Bloom, H. *The Chemistry of Molten Salts*; Benjamin: New York, 1967.
(21) Bertozzi, G.; Soldani, G. *J. Phys. Chem.* **1968**, *72*, 353-356.

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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) = (22179 ± 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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Table II. Analysis of the Available ΔH_s Data for the RbBr Using the Two Methods Explained in the Text

method	ref	ΔH_s^∞/ (J mol^{-1})	B/ (J kg mol^{-2})	s/ (J mol^{-1})
L_ϕ data	*4*	22 185 ± 34		
	this work	22 207 ± 61		
eq 3	*4*	22 182 ± 72	−3384 ± 1197	39
	this work	22 166 ± 35	−2394 ± 994	65

of L_ϕ(m), the relative apparent molar enthalpy, is necessary. The only available experimental values of L_ϕ(m) for RbBr aqueous solutions at 298.15 K are from Fortier et al. (*9*). On the other hand, the experimental values of ΔH_s could be analyzed in terms of an equation in m and the value at infinite dilution found as the intercept at zero molality. In a previous work (*10*) it was shown that the following expression can be used satisfactorily (for 1-1 electrolytes) in the molality range covered in this work

$$\Delta H_s = \Delta H_s^\infty + A_H m^{1/2}\{(1/(1 + m^{1/2})) - [\sigma(m)/3]\} + Bm \quad (3)$$

where

$$\sigma(m) = (3/m^{1/2})\{1 + m^{1/2} - [1/(1 + m^{1/2})] - 2\ln(1 + m^{1/2})\}$$

A_H is the Debye–Hückel limiting slope (*11*), ΔH_s^∞ and B are adjustable parameters.

In the first possibility the enthalpy of solution at infinite dilution, ΔH_s^∞, is obtained as the mean of the extrapolated values. The uncertainty is the standard deviation of the mean. By use of eq 3 the values of ΔH_s^∞ and B are obtained by the least-squares method. The uncertainty in the estimation of the adjustable parameters P (B and ΔH_s^∞) has been calculated as (*12*)

$$\sigma^2(P) = s^2 \sum_i \left(\frac{\partial P}{\partial y_i}\right)^2 \quad (4)$$

where y_i represent the experimental values of ΔH_s and s the standard deviation of the fit

$$s = \left[\frac{\sum_i (\Delta H_{s(\mathrm{calcd})} - \Delta H_{s(\mathrm{exptl})})^2}{n - q}\right]^{1/2} \quad (5)$$

In eq 5, n is the number of experimental data and q is the number of parameters.

The experimental data presented in Table I and those reported by Weintraub et al. (*4*) have been analyzed by using the two methods explained above. The results are summarised in Table II. One can see that no appraisable differences exist, within the error, between the two data sets and the two extrapolation methods employed. The agreement is not only restricted to ΔH_s^∞ values. The molality dependence of ΔH_s, reflected on the parameter B, is the same in the common molality range. This behavior can be seen clearly in Figure 1. For this reason, we think that a reliable value of ΔH_s^∞ could be obtained using our ΔH_s data combined with those of Weintraub et al. (*4*). The proposed value of ΔH_s^∞ for RbBr in water at 298.15 K is

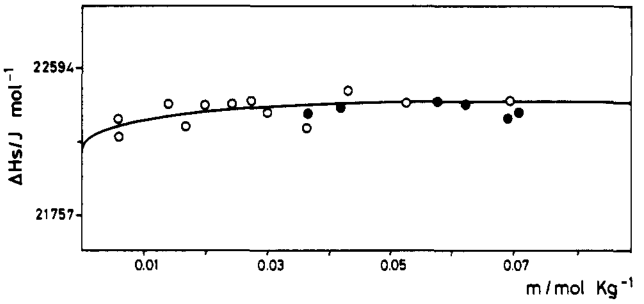

Figure 1. Plot of ΔH_s against molality. Reference *4* (●); present work (○); fit of the experimental values presented in this work by means of eq 3 (—).

$$\Delta H_s^\infty(298.15\ \mathrm{K}) = (22179 \pm 28)\ \mathrm{J\ mol^{-1}}$$

The value has been obtained after extrapolating the combined data by means of eq 3.

Registry No. RbBr, 7789-39-1.

Literature Cited

(1) Parker, V. B. "Thermal Properties of Aqueous Uni-univalent Electrolytes"; *Natl. Bur. Stand.* (*U.S.*) 1965; p 31-32.
(2) Lange, E.; Martin, W. *Z. Phys. Chem.* **1937**, *A180*, 233-245.
(3) Thourey, J.; Perachon, G. *Thermochim. Acta* **1980**, *39*, 243-252.
(4) Weintraub, R.; Apelblat, A.; Tamir, A. *J. Chem. Thermodyn.* **1982**, *14*, 887-892.
(5) Sanahuja, A.; Cesari, E. *J. Chem. Thermodyn.* **1984**, *16*, 1195-1202.
(6) Landolt-Börnstein. *Kalorische Zustandsgrössen*; Springer Verlag: West Berlin, 1961; II Band, 4 Teil; p 487.
(7) Desnoyers, J. E.; de Visser, C.; Perron, G.; Picker, P. *J. Solution Chem.* **1976**, *5*, 605-616.
(8) McGlashan, M. L. *Chemical Thermodynamics*; Academic: London, 1979; p 68-69.
(9) Fortier, J. L.; Leduc, P. A.; Desnoyers, J. E. *J. Solution Chem.* **1974**, *3*, 323-349.
(10) Sanahuja, A.; Gómez-Estévez, J. L. *Thermochim. Acta* **1985**, *94*, 223-229.
(11) Clarke, E. C. W.; Glew, D. N. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1911-1916.
(12) Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969; p 113.

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Densities of Aqueous Strontium Chloride Solutions up to 200 °C and at 20 bar

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Densities of aqueous $SrCl_2$ are reported from 50 to 200 °C at 20.27 bar pressure up to a concentration of 2.7 mol kg^{-1}. Apparent molal volumes calculated from densities can be fitted with Pitzer's equations with a standard deviation of 0.09 cm^3 mol^{-1}.

Introduction

Aqueous solutions of alkali and alkaline earth metal chlorides are important components of natural brines and are used in industrial processes. A literature survey reveals that density data on these solutions especially at high temperatures and

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