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ENTHALPIES OF SOLUTION OF RbCl IN WATER AT 298.15 K AND LOW MOLALITIES

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ABSTRACT

The enthalpies of solution of RbCl in water have been measured at 298.15 K in the molality range 0.003–0.095 mol kg^{-1}. The molality range was extended to lower concentrations with respect to previous works in the literature to obtain a better extrapolation to infinite dilution. After treating all the data, a new value for the enthalpy of solution at infinite dilution, $\Delta_{sol}H_m^\infty$ has been obtained.

INTRODUCTION

There have been a great number of experimental determinations of the enthalpies of solution of RbCl in water at 298.15 K [1–5]. However, no systematic analysis of the entire data set exists to date in order to obtain an accurate value for $\Delta_{sol}H_m^\infty$, the enthalpy of solution at infinite dilution. The data obtained by different authors show a wide scattering and the number of experimental points is in general rather low, i.e. 3 or fewer [2,3]. The standard reference, ref. 1, gives a $\Delta_{sol}H_m^\infty$ value of 4130 ± 75 cal mol^{-1} ** at 298.15 K. To obtain this value, Parker employed the data available at that time [1,4], which consisted of six references giving $\Delta_{sol}H_m^\infty$ values ranging from 4000 to 4151 cal mol^{-1} and, with one exception, at temperatures different from 298.15 K. The extrapolation was accomplished using interpolated L_ϕ data for RbCl which increased the uncertainties in the finally proposed $\Delta_{sol}H_m^\infty$ value even more. By using more recent data for $\Delta_{sol}H_m$ [2–9] and L_ϕ [10], it is possible to obtain a value for $\Delta_{sol}H_m^\infty$ which is more reliable at 298.15 K. The resulting value is significantly lower than Parker's estimate [4]. Results obtained more recently [3,5] confirm this trend.

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** 1 cal = 4.184 J throughout this paper.

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There is another problem associated with the determination of $\Delta_{sol}H_m^\infty$. All the experimental measurements quoted above [2–7,9] are restricted to the molality range 0.028–0.14 mol kg^{-1}. For a better extrapolation to zero molality, it would be interesting to extend the determinations of $\Delta_{sol}H_m$ at lower concentrations. These measurements should confirm the lowering of $\Delta_{sol}H_m^\infty$ obtained by using the more recent $\Delta_{sol}H_m$ data [5].

This work presents measurements for the enthalpy of solution of RbCl in water at 298.15 K. The molality range covered was from 0.003 to 0.095 mol kg^{-1}. We have extended the range to lower molalities for a more reliable extrapolation to infinite dilution. Using our data together with the data reported in the literature, a new value for $\Delta_{sol}H_m^\infty$ has been obtained by means of two different methods of extrapolation.

EXPERIMENTAL

The enthalpy of solution was measured with a Tian–Calvet-type calorimeter described in detail in previous works [11,12]. For each measurement the temperature was determined within ±0.02 K, an electrical calibration was carried out before and after each solution process and the initial mechanical effect was corrected as explained earlier. The calorimetric resolution is 0.02 J and the reproducibility of the measurements is about 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. The molalities are better than 0.01% and the solute weighings are accurate to 0.003%.

RESULTS

The results obtained for the enthalpies of solution of RbCl in water at 298.15 K are shown in Table 1. The molar mass of RbCl used was 120.9208 g mol^{-1}. In Table 1, m_s is the solute mass, m is the molality and T is the temperature for each solution. $\Delta_{sol}H_m(T)$ is the molar enthalpy of solution at T and $\Delta_{sol}H_m$(298.15 K) is the molar enthalpy adjusted to 298.15 K. ϵ is the experimental error. The adjustments were found as follows

$$\Delta_{sol}H_m(298.15\ \mathrm{K}) = \Delta_{sol}H_m(T) + C_{p,m}(298.15\ \mathrm{K} - T) \qquad (1)$$

where $C_{p,m} = C_{\phi,m} - C_{p,m}^\star$. $C_{\phi,m}$ is the apparent molar heat capacity of the dissolved salt at the given molality and $C_{p,m}^\star$ is the molar capacity of the salt before solution. Literature values [13,14] of $C_{p,m}^\star$ and $C_{\phi,m}$ were employed. The error due to condensation of solvent is given approximately by

$$\delta_{sol}H_m = -(2xp^\star v_m^g/R\,T)\Delta_l^g H_m^\star \qquad (2)$$

where x denotes the mole fraction of the solute after dissolution, $p^\star$ the

TABLE 1

The enthalpies of solution of RbCl in water at 298.15 K

Solute mass m_s (g)	Molality m (mol kg^{-1})	T (K)	$\Delta_{sol}H_m(T)$ (cal mol^{-1})	$\Delta_{sol}H_m$ (298.15 K (cal mol^{-1})	Errors ϵ (cal mol^{-1})
0.01274	0.00354	298.27	3991	3996	80
0.03544	0.00986	297.95	4014	4005	38
0.07050	0.01944	298.01	4042	4036	21
0.10128	0.02804	298.33	4039	4047	14
0.11969	0.03323	298.59	4079	4098	8
0.15149	0.04177	298.01	4060	4054	1
0.17063	0.04723	298.59	4056	4075	11
0.19865	0.05480	297.95	4117	4108	3
0.20715	0.05760	298.27	4068	4073	27
0.23100	0.06395	298.33	4038	4046	10
0.25667	0.07104	298.91	4058	4091	18
0.31375	0.08712	298.53	4076	4092	8
0.34119	0.09470	298.56	4022	4039	12

vapour pressure of the pure solvent and $\Delta_l^g H_m^\star$ the molar enthalpy of evaporation of the pure solvent. The correction for the solvent condensation effect was negligible in all cases.

DISCUSSION

For treatment of the experimental $\Delta_{sol}H_m$ values, several methods are available [15]. Basically, two alternatives can be used. In the first possibility, the enthalpy of solution at infinite dilution $\Delta_{sol}H_m^\infty$ is obtained as the mean of the extrapolated values with the help of the relative apparent molar enthalpy L_ϕ(m). The uncertainty is the standard deviation of the mean. The second method consists of fitting the experimental data by means of an analytical equation in m. In this paper the following expression was used

$$\Delta_{sol}H_m = \Delta_{sol}H_m^\infty + A_H m^{1/2} + Bm \tag{3}$$

where A_H is the Debye–Hückel limiting slope [16] and $\Delta_{sol}H_m^\infty$ and B are the adjustable parameters. The uncertainty in the estimation of these adjustable parameters was calculated in the normal manner [17].

The experimental data presented in Table 1 were analysed by using the two methods explained above. The values found for $\Delta_{sol}H_m^\infty$ were 3986 ± 2 and 4001 ± 25 cal mol^{-1} respectively. They are lower than the recent values obtained by Johnson and Gayer [4], 4064 ± 6, and by Weintraub et al [5], 4034 ± 11 cal mol^{-1}. These discrepancies can be explained if the different range of molality covered by the experiments is taken into account. For

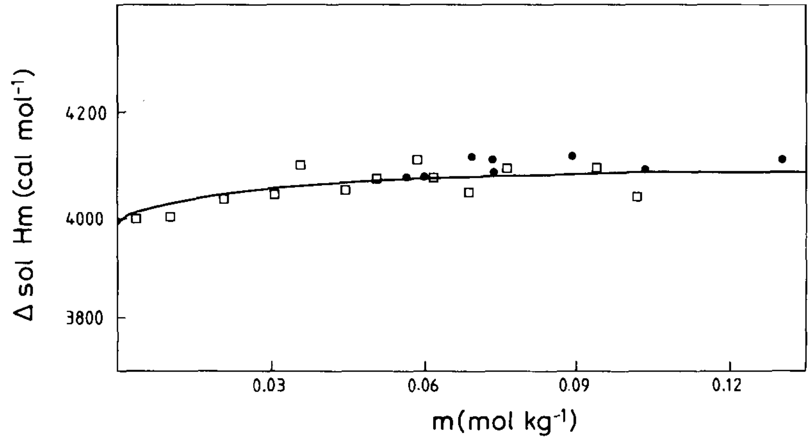

Fig. 1. Plot of the integral enthalpies of solution $\Delta_{sol}H_m$ vs. molality. Experimental values from ref. 5 (●) and the present work (□). ——— Fit of the experimental data using eqn. (3).

example, in reference 5 the molality range covered was 0.05–0.12 mol kg^{-1} whereas in our case the minimum molality was 0.003 mol kg^{-1}. If the first four measurements quoted in Table 1 are omitted in a second fit of the data, our experimental molality range matches well with that of Weintraub et al. The values of $\Delta_{sol}H_m^\infty$ obtained in this case were 4039 ± 3 and 4011 ± 24 cal mol^{-1} respectively. The agreement is now satisfactory, clearly showing the influence of the minimum molality attainable on the experimental determination of $\Delta_{sol}H_m$. A comparison with the Merck Suprapur data points obtained by Weintraub et al. [5] in the common molality range, see Fig. 1, shows good agreement within experimental uncertainties. For this reason, a reliable $\Delta_{sol}H_m^\infty$ value for RbCl in water at 298.15 K could be obtained by fitting our $\Delta_{sol}H_m$ data combined with those of Weintraub et al. [5] by means of eqn. (3). The value obtained for $\Delta_{sol}H_m^\infty$ is 3984 ± 2 cal mol^{-1}. This value agrees well ($\leqslant 0.7\%$) with that obtained as a mean after extrapolation to infinite dilution using L_ϕ data [10]. As a final test for our proposed value for $\Delta_{sol}H_m^\infty$, the entire data set of experimental $\Delta_{sol}H_m$ values available [1–4,6–9] was analysed using the two methods explained above. The agreement was better than 0.8%.

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