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THE INFLUENCE OF THE EXTRAPOLATION METHOD ON ENTHALPIES OF SOLUTION AT INFINITE DILUTION

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ABSTRACT

Analyses have been performed on solution enthalpy data for KCl and NaCl in water at 298.15 K in the molality range below 1 mol kg^{-1}. In order to calculate the enthalpy of solution at infinite dilution, ΔH_s^∞, the available data have been extrapolated using five different methods. The influence of the extrapolation method on ΔH_s^∞ has been discussed taking into account the discrepancies between the different data sets.

INTRODUCTION

Experimental data for the enthalpy of solution of electrolytes are, generally, corrected to infinite dilution using known values for the relative apparent molar enthalpy, $L_\phi(m)$. In spite of the fact that information on $L_\phi(m)$ is nearly complete for aqueous 1 : 1 electrolytes at 298.15 K [1–3], the $L_\phi(m)$ data are practically nonexistent at different temperatures. The situation becomes worse for more complex electrolytes and non-aqueous solutions.

In previous work [4–7], the enthalpies of solution of KCl and NaCl in water at 298.15, 303.15, 308.15 and 313.15 K were measured. To extrapolate our experimental values at zero molality we had to use interpolated $L_\phi(m)$ data [6]. This possibility has also been employed by other authors [8,9] but, in general, is not feasible for complex electrolytes in aqueous or non-aqueous solvents.

In this work five different methods for extrapolating the experimental enthalpies of solution have been considered. The results obtained for aqueous enthalpies of solution of KCl and NaCl at 298.15 K in the molality range below 1 mol kg^{-1} using the different methods have been analysed. Finally, the influence on the enthalpy of solution at infinite dilution, ΔH_s^∞, due to the extrapolation method has been evaluated. The present analysis has not been extended to other electrolytes due to the lack of extensive heat of solution data.

Thermodynamics gives the following expression for the enthalpy of solution as a function of molality

$$\Delta H_s = \Delta H_s^\infty + L_\phi(m) \tag{1}$$

In obtaining the molality dependence of L_ϕ, two alternatives can be considered.

(1) To employ L_ϕ experimental data obtained by measuring enthalpies of dilution. The extrapolated value, ΔH_s^∞, is obtained as

$$\Delta H_s^\infty = \langle \Delta H_s(m_i) - L_\phi(m_i) \rangle \tag{2}$$

where m_i are the experimental molalities at which the heat of solution has been measured.

(2) To express L_ϕ by an analytical expression in m. In this case five alternatives have been considered.

(A) The Debye–Hückel limiting law plus a linear term [10,11]

$$\Delta H_s = \Delta H_s^\infty + A_H m^{1/2} + B_1 m \tag{3}$$

Where A_H is the limiting slope for the enthalpy [12] and B_1 is an adjustable parameter which takes into account all deviations from the limiting law. Equation (3) can be employed satisfactorily to 1 mol kg^{-1}.

(B) An extended form of the Debye–Hückel limiting law plus a linear term, generally referred to as the Criss and Cobble method [10,13]

$$\Delta H_s = \Delta H_s^\infty + A'_H m^{1/2}\{1/(1+m^{1/2}) - [\sigma(m)/3]\} + B_2 m \tag{4}$$

where

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

and $A'_H = (3/2)A_H$. B_2 is an adjustable parameter. Equation (4) covers the same molality range as eqn. (3).

(C) In the molality range below 1 mol kg^{-1}, the Pitzer equation [14] takes the following form

$$\Delta H_s = \Delta H_s^\infty + \nu\,|Z_M Z_X|\,(A_H/2b)\ln(1 + bI^{1/2}) - 2\nu_M\nu_X RT^2 B'_{MX} \tag{5}$$

where

$$B'_{MX} = 2(\partial\beta^{(0)}/\partial T) + (2/\alpha^2 I)(\partial\beta^{(1)}/\partial T)\{1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})\}$$

and where $I = \frac{1}{2}\Sigma_i m_i z_i^2$ is the ionic strength, Z_M and Z_X are the charge numbers of the cation and anion, ν_M and ν_X are the numbers of cations and anions per molecule of solute, respectively, $\nu = \nu_M + \nu_X$, b and α are given for each electrolyte [14]. The difference between eqn. (5) and the usual one [14] is in the term $m^2 C_{MX}$. This term is not significant below 1 mol kg^{-1}. $\partial\beta^{(0)}/\partial T$ and $\partial\beta^{(1)}/\partial T$ are adjustable parameters.

(D) An expression based on Bahe's lattice model [15] which reads (for

1 : 1 electrolytes) [16]

$$\Delta H_s = \Delta H_s^\infty + \sum_{j=0}^{3} A_j m^{j+(1/3)} - 2RT^2(\partial B/\partial T)F_1(m) - 2RT^2 BF_2(m) \quad (6)$$

with

$$F_1(m) = (\rho_0/2)m + (B'/3)m^2 + (C'/4)m^3$$

$$F_2(m) = [\partial F_1(m)/\partial T]_{P,m}$$

The coefficients A_j are related to coulombic interactions and B is due to the coulombic–dielectric gradient interactions [16,17]. The parameters ρ_0, B', C' and their temperature derivatives appear in the conversion from molarity to molality and were determined for each solution [16,17]. $\partial B/\partial T$ is an adjustable parameter. The validity range of eqn. (6) is greater than 1 mol kg^{-1}.

(E) A polynomial expression in $m^{1/2}$ [18–20]

$$\Delta H_s = \Delta H_s^\infty + Cm^{1/2} + Dm \quad (7)$$

where C and D are adjustable parameters.

If necessary, when covering an extended molality range ($>$ 1mol kg^{-1}), more terms can be taken. This method can be useful in the absence of precise values for A_H or A_j.

RESULTS AND DISCUSSION

The experimental data from the references considered in this work were extrapolated using Parker values [1] for $L_\phi(m)$ in a previous paper [4]. The averaged values were (4113 ± 6) and (924 ± 6) cal$_{th}$ mol^{-1}* for KCl and NaCl, respectively (see Table 6 from ref. 4). The low standard deviations obtained (±6 cal$_{th}$ mol^{-1}) show the good agreement between different authors.

The results obtained from the same references using eqns. (3)–(7) are sumarized in Tables 1–3.

The results of the fit using eqn. (3) are exhibited in Table 1. N denotes the number of experimental points, m_{min} and m_{max} are the least and greatest molality, respectively, ΔH_s^∞ is the enthalpy of solution at infinite dilution, B_1 the adjustable parameter and σ the standard deviation of the fit. ΔH_s^∞ and B_1 have been calculated using the least-squares method. The averaged values of ΔH_s^∞ are also given with the corresponding standard deviation of the mean. Table 2 includes the results obtained by means of eqns. (4) and (6). Table 3 shows the results according to eqns. (5) and (7).

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* 1 cal$_{th}$ = 4.184 J throughout this paper.

TABLE 1

Results of ΔH_s treatment using eqn. (3)

	Ref.	N	m_{min} (mol kg^{-1})	m_{max} (mol kg^{-1})	ΔH_s^∞ (cal$_{\text{th}}$ mol^{-1})	B_1	σ (cal$_{\text{th}}$ mol^{-1})
KCl	4	19	0.010	0.065	4119	−1226.4	17
	21	13	0.021	0.063	4088	−233.7	6
	22	6	0.035	1.11	4099	−452.5	15
	23	6	0.067	0.111	4082	−395.0	11
	24	6	0.008	0.080	4115	−699.1	7
	25	8	0.017	0.022	4051	2487.2	7
	26	7	0.004	0.07	4117	−740.3	0.7
	27	10	0.033	0.056	4110	−611.7	10
					$\overline{4098 \pm 22}$		
NaCl	4	16	0.012	0.12	947	−1131.6	17
	28	16	0.05	1.3	893	−456.8	12
	29	11	0.03	1.1	905	−485.8	13
	30	23	0.019	0.72	914	−523.3	6
	24	6	0.035	1.11	917	−476.6	19
	13	8	0.001	0.02	918	−1489.2	13
					$\overline{916 \pm 16}$		

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[a] Smoothed data.

TABLE 2

Results of ΔH_s data treatment with eqns. (4) and (6)

	Ref.	ΔH_s^∞ (cal$_{\text{th}}$ mol^{-1})	B_2	σ (cal$_{\text{th}}$ mol^{-1})	ΔH_s^∞ (cal$_{\text{th}}$ mol^{-1})	$\partial B/\partial T$	σ (cal$_{\text{th}}$ mol^{-1})
KCl	4	4120	−940.2	17	4119	-6.8×10^{-3}	23
	21	4089	49.8	6	4090	4.2×10^{-3}	6
	22	4109	−263.9	9	4132	-2.5×10^{-3}	5
	23	4085	−163.2	11	4093	6.2×10^{-4}	11
	24	4116	−415.6	7	4114	-9.8×10^{-4}	8
	25	4051	2790.7	7	4048	0.037	7
	26	4117	−450.3	0.6	4113	-6.5×10^{-4}	2
	27	4111	−332.0	10	4112	-4.0×10^{-4}	10
		$\overline{4100 \pm 22}$			$\overline{4103 \pm 24}$		
NaCl	4	948	−859.1	17	949	-6.8×10^{-3}	24
	28	910	−276.1	6	942	-2.8×10^{-3}	4
	29	917	−295.1	7	942	−2.9	3
	30	918	−304.4	4	930	-2.4×10^{-3}	7
	24	928	−287.9	12	951	−2.8	4
	13	918	−1179.5	13	913	-6.7×10^{-3}	13
		$\overline{923 \pm 12}$			$\overline{938 \pm 13}$		

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[a] Smoothed data.

TABLE 3

Results of ΔH_s data treatment using eqns. (5) and (7)

	Ref.	ΔH_s^∞ (cal$_{th}$ mol^{-1})	$\partial\beta^{(0)}/\partial T$	$\partial\beta^{(1)}/\partial T$	σ (cal$_{th}$ mol^{-1})	ΔH_s^∞ (cal$_{th}$ mol^{-1})	C	D	σ (cal$_{th}$ mol^{-1})
KCl	4	4130	-1.6×10^{-8}	4.4×10^{-3}	16	4168	-14.7	0.01	16
	21	4079	4.8×10^{-3}	-7.2×10^{-3}	6	4073	628.6	-631.6	6
	22	4121	6.1×10^{-4}	8.9×10^{-4}	5	4146	273.6	-299.0	7
	23 [a]	4490	-0.06	0.103	8	5121	-6578.1	11495.8	11
	24	4106	8.1×10^{-3}	-0.01	7	4086	830.2	-1646.9	10
	25 [a]	5060	-1.45	1.91	6	6629	-36261.3	13311.2	6
	26 [b]	4118	7.3×10^{-4}	9.9×10^{-4}	0.5	4118	444.7	-652.8	3
	27 [a]	3830	0.115	-0.17	9	3387	7358.0	-16924.2	11
		4242 ± 351				4466 ± 928			
		4111 ± 18 [c]				4118 ± 36 [c]			
NaCl	4	958	1.1×10^{-9}	4.2×10^{-3}	17	1000	-36.8	-0.003	19
	28	929	6.6×10^{-4}	9.5×10^{-4}	2	961	249.8	-303.2	4
	29	933	6.4×10^{-4}	1.1×10^{-3}	2	960	255.0	-315.9	4
	30	920	8.3×10^{-4}	1.4×10^{-3}	4	930	377.5	-420.4	4
	24	948	5.5×10^{-4}	1.4×10^{-3}	4	980	210.6	-274.0	5
	13	938	-0.10	0.13	11	968	-746.9	5030.9	11
		938 ± 12				967 ± 21			

[a] These references were not considered in the second evaluation of an averaged ΔH_s^∞.

[b] Smoothed data.

[c] Mean obtained without the references marked [a].

As we can see from Tables 1–3, the parameters which give the molality dependence of ΔH_s (B_1, B_2, $\partial\beta^{(0)}/\partial T$, $\partial\beta^{(1)}/\partial T$, $\partial B/\partial T$) are strongly dependent on the data set considered. The reason for this erratic behaviour can be understood if we remember that $L_\phi(m) \ll \Delta H_s^\infty$ in the molality range covered. Therefore, the discussion has been limited to the ΔH_s^∞ values.

If we compare the averaged ΔH_s^∞ values given in Tables 1–3, the following remarks can be noted.

(1) Equations (3), (4) and (6) provide equivalent averaged values of ΔH_s^∞ for KCl. The largest difference (5 cal_th mol^{-1}) is smaller than the disagreement among the results (± 22 cal_th mol^{-1}) arising from the different authors.

The same data sets show a different behaviour when they are fitted using eqns. (5) and (7). The discrepancies between the authors are higher (± 351 and ± 928 cal_th mol^{-1} for eqns. (5) and (7), respectively) and the averaged values of ΔH_s^∞ are remarkably different from those obtained through eqns. (3), (4) and (6). However, a close analysis of the data shows that in refs. 23, 25 and 27 only a narrow molality range is covered and the ΔH_s^∞ values differ markedly from the mean. It seems that eqns. (5) and (7) are more sensitive than eqns. (3), (4) and (6) in fitting experimental data with a short-interval molality range. If these references are deleted, the discrepancies among the authors are lowered (± 18 and ± 36 cal_th mol^{-1}) and the averaged values now match those obtained using eqns. (3), (4) and (6). As a consequence, the influence on the enthalpy of solution of KCl at infinite dilution due to the extrapolation method (0.2%) seems not to be significant.

(2) The influence of the extrapolation method on ΔH_s^∞ determinations is more evident for NaCl. Whereas the disagreement among the results (± 15 cal_th mol^{-1}) arising from the different authors is low, the averaged values obtained from the different methods can differ by as much as 51 cal_th mol^{-1}. Therefore, the influence of the extrapolation method can be as high as 6%.

CONCLUSIONS

From the analysis presented above, the following conclusions can be inferred.

(1) When an analytical expression for L_ϕ is employed the disagreement among the results of ΔH_s^∞ arising from different authors is higher than those obtained using L_ϕ data.

(2) In extrapolating experimental heats of solution using an analytical expression a sufficiently wide molality range must be considered, especially when eqns. (5) and (7) are employed.

(3) The influence on ΔH_s^∞ values due to different extrapolation methods is not negligible when ΔH_s^∞ decreases.

(4) If precise values for A_H or A_J are available, the fit through eqn. (7) seems to be less suitable compared to the other possibilities.

We think that it is necessary to analyse the data carefully, using different extrapolation methods, before a value for ΔH_s can be proposed, especially when a comparison with other authors is not possible.

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