

Quantitative Treatment of the Variation of Partial Molal Entropy of Hydration of the Strong Electrolytes in Solution with their Hydration Number, their Viscosity *B*-Coefficient and with Rise of Temperature

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In previous publications, Jones and Dole's equation for the viscosity of solutions of the strong electrolytes had been modified and its modified *B*-coefficient has been identified with the Einstein expression $2.5\bar{V}$, where \bar{V} represents the volume fraction per unit concentration of the electrolyte. It has been shown that the modified *B*-coefficient varies linearly with $(h - \phi/18)$, where *h* is the hydration number, ϕ the apparent molal volume of the electrolyte and 18 the molecular volume of water at 25°. This relationship has been subjected to further test using fresh data collected from the literature and has been found satisfactory.

It has also been shown that the partial molal entropy of hydration of a strong electrolyte in solution varies linearly with the absolute temperature in the range 298.2–473.2 K.

In previous publications^{1,2} it has been shown that the partial molal entropy of hydration ($-\bar{S}_h^0$, cal mol⁻¹ K⁻¹) of a strong electrolyte in solution varies with its hydration number (*h*) and the viscosity *B*-coefficient according to equations,

$$(-\bar{S}_h^0) = m(h - \phi/18) + C \quad (1)$$

and

$$(-\bar{S}_h^0) = m_0(B) + C_0 \quad (2)$$

where, *C* and *C*₀ are constants, *h* the hydration number, ϕ the apparent molal volume of the electrolyte in solution and 18 the molecular mass of water at 25°. It may be pointed out that the *B*-coefficient in equation (2) is the same as that which occurs in the following modified equation†,

$$\eta/\eta_0 = 1 + AC^{1/3} + BC \quad (3)$$

It has been shown in the previous publication² that the viscosity equation of Jones and Dole³ should be modified and replaced by equation (3), where *A* and *B* are constants.

On the basis of the assumptions of Frank and Wen⁴, the following equation has been deduced previously,

$$B = 0.045[(h - \phi/18) - \phi_{KCl}/18] \quad (4)$$

In equation (4)† ϕ_{KCl} has been taken as the standard for reference. Since the *B*-coefficient of the KCl

solution is very small (0.008), it may be taken as zero. Henceforth ϕ_{KCl} in equation (4) will be replaced by ϕ_* of an imaginary electrolyte, the *B*-coefficient of which is zero and will be used as

$$B = 0.045[(h - \phi/18) - \phi_*/18] \quad (4a)$$

It may be noted that by eliminating $(-\bar{S}_h^0)$ from equations (1) and (2) and simplifying, the following equation can be obtained,

$$B = (m/m_0)[(h - \phi/18)] + [(C - C_0)]/m_0 \quad (5)$$

In the following section the aforesaid equations have been subjected to further test using some fresh data collected from the literature and have been found satisfactory.

Variation of $(-\bar{S}_h^0)$ with the absolute temperature :

According to equation (2), $(-\bar{S}_h^0)$ varies with *B* and it is known that *B* of the strong electrolyte solutions increases with the rise of temperature⁵. Hence the following linear relationship between $(-\bar{S}_h^0)$ and the absolute temperature has been investigated,

$$(-\bar{S}_h^0) = S_0 + bT \quad (6)$$

where, *S*₀ and *b* are constants. For the values of $(\bar{S}_h^0)_1$ and $(-\bar{S}_h^0)_2$ at the temperatures *T*₁ and *T*₂ we may then write,

$$(-\bar{S}_h^0)_2 - (-\bar{S}_h^0)_1 = b(T_2 - T_1) \quad (7)$$

$$\text{or } (-\bar{S}_h^0)_2 = (-\bar{S}_h^0)_1 + b(T_2 - T_1) \quad (7a)$$

It may be mentioned that by combining the scaled particle theory of Mayer⁶ and Born's theory⁷, Sen⁸ developed an equation which can predict with

† The solutions were assumed to be dilute throughout and their concentration *C* was taken as near about 0.1 *M*. ‡ In equation (4), $h = (h_+) + (h_-)$, where *h*₊ and *h*₋ represent the hydration numbers of the cations and anions, respectively, and similarly $\phi = (\phi_+) + (\phi_-)$, their respective apparent molal volumes.

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fair accuracy the variation of $(-\bar{S}_h^0)$ with temperature. His equation⁸ may be written as

$$-\Delta S_h^0 = S_{\text{cavity}} + S_{\text{Born}} + \alpha_p RT - R \quad (\text{XIII})$$

where, $\alpha_p = [(1/\bar{V})\delta\bar{V}/\delta T]$ and it represents the thermal expansibility of the solvent. For further details including calculation of the terms on the right-hand side of the equation, author's paper⁸ may be consulted. It may be pointed that $-\Delta S_h^0$ used by Sen⁸ is the same as $(-\bar{S}_h^0)$ used by the author in this paper.

Processing of the data in the Tables: Under the head miscellaneous are mentioned the equation used and the values of its constants; T represents

temperature in the absolute scale. In Table 1, the values of $(h - \phi/18)$ and those of the viscosity B -coefficient have been collected from the previous paper¹ of the author. In Table 2, the values of $(-\bar{S}_h^0)$ of the electrolytes have been collected from the literature⁹. The data for BaCl_2 in Table 3 have been collected partly from two separate publications^{9,10} and T above 373.2 K. In Table 4 $(-\bar{S}_h^0)_{273.2}$ and $(-\bar{S}_h^0)_{298.2}$ are the same respectively as $(-\bar{S}_h^0)_2$ and $(-\bar{S}_h^0)_1$ of equation (7) or (7a).

Discussion

The data recorded in Table 1 show that the values of $(-\bar{S}_h^0)$ calculated by using equation (1)

TABLE 1—VARIATION OF $(-\bar{S}_h^0)$ WITH $(h - \phi/18)$ AND ALSO WITH VISCOSITY B -COEFFICIENT AT 25°

Miscellaneous	Electrolyte	$(h - \phi/18)^*$	Value of $(-\bar{S}_h^0)$		B -Coefficient	Value of $(-\bar{S}_h^0)$	
			Exptl.	Calcd. Eqn. (1)		Exptl.	Calcd. Eqn. (2)
Eqn. (1)	LiCl	4.63	51.5	51.3	0.142	51.5	51.5
$m=4.45$	NaCl	3.14	44.4	44.6	0.086	44.4	44.6
$C=30.5$	KCl	1.47	35.5	37.0	-0.008	35.5	37.0
Eqn. (2)	CsCl	0.20	31.9	31.4	-0.052	31.9	31.9
$m_0=101$							
$C_0=37.7$							
*Ref. 1.							

TABLE 2—VARIATION OF $(-\bar{S}_h^0)$ OF ELECTROLYTE SOLUTIONS WITH TEMPERATURE (T)

Miscellaneous	T K	Value of $(-\bar{S}_h^0)$		T K	Value of $(-\bar{S}_h^0)$	
		Exptd.	Calcd.		Exptl.	Calcd.
LiCl						
Eqn. (7)	298.2	51.5	51.5	373.2	57.1	57.1
$(-\bar{S}_h^0)=51.5$	333.2	54.5	54.1	423.2	60.4	60.9
$T_1=298.2$						
$b=0.076$						
NaCl						
Eqn. (7)	298.2	44.4	44.6	423.2	54.7	54.1
$(-\bar{S}_h^0)=44.6$	333.2	47.2	47.3	473.2	60.9	60.9
$T_1=298.2$	373.2	50.1	50.2			
$b=0.076$						
KCl						
Eqn. (7)	298.2	35.5	35.5	373.2	43.4	43.3
$(-\bar{S}_h^0)=35.5$	333.2	40.0	39.2	423.2	48.3	48.6
$T_1=298.2$						
$b=0.205$						
CsCl						
Eqn. (7)	298.2	31.9	31.9	373.2	40.5	40.5
$(-\bar{S}_h^0)=31.9$	333.2	36.2	35.9			
$T_1=298.2$						
$b=0.115$						
MnCl ₂						
Eqn. (7)	298.2	101.7	101.7	373.2	121.6	121.6
$(-\bar{S}_h^0)=101.7$	333.2	113.5	111.0			
$T_1=298.2$						
$b=0.266$						
BaCl ₂						
Eqn. (7)	298.2	95.9	95.9	373.2	118.0	112.8
$(-\bar{S}_h^0)=95.9$	333.2	105.1	103.8	423.2	123.8	124.3
$T_1=298.2$						
$b=0.225$						

TABLE 3—VARIATION OF $(-\bar{S}_h^0)$ OF BaCl_2 SOLUTION WITH TEMPERATURE

Miscellaneous	T K	Value of $(-\bar{S}_h^0)$		
		Exptl.	Sen's eqn (XIII)	Author's eqn. (7)
BaCl_2	298.2	88.9	95.6	83.9
Eqn (7)	323.2	90.4	94.9	90.9
$(-\bar{S}_h^0)=83.9$	333.2	92.8	95.0	92.1
$T_1=298.2$	348.2	96.0	95.1	95.9
$b=0.24$	373.2	101.4	102.6	101.9
	398.2	106.8	108.8	107.9
	423.2	111.9	114.9	113.9
	448.2	117.8	121.2	117.9
	473.2	124.9	127.0	125.9

TABLE 4—RELATION BETWEEN $(-\bar{S}_h^0)_{273.2}$ AND $(-\bar{S}_h^0)_{298.2}$

Miscellaneous	Electrolyte	$(-\bar{S}_h^0)_{298.2}$	Value of $(-\bar{S}_h^0)_{273.2}$		Value of m
			Exptl.	Calcd. (Eqn. 8)	
Eqn. (8)	LiCl	51.5	57.1	61.8	1.11
Tangent $m=1.2$	NaCl	44.4	50.1	53.2	1.13
Intercept=0	KCl	35.5	43.4	42.6	1.22
	CsCl	31.9	40.5	39.3	1.21
	CaCl_2	95.9	113.0	115.1	1.18
	SrCl_2	93.3	112.0	112.0	1.20
	BaCl_2	83.9	101.4	100.7	1.21
	MnCl_2	101.7	121.6	122.0	1.20
				Average	1.18

agree well with those found experimentally for the electrolytes LiCl, NaCl, KCl and CsCl. Hence it may be concluded that $(-\bar{S}_h^0)$ varies linearly with $(h-\phi/18)$ at 25°. The data recorded in Table 1 also show that $(-\bar{S}_h^0)$ varies linearly with the modified viscosity B -coefficient.

Substituting in equation (5) the values of m , m_0 , C and C_0 as recorded in Table 1 and simplifying we get the following equation,

$$B = \frac{4.45}{101} \left[(h - \phi/18) + \frac{(30.5 - 37.7)}{4.45} \right]$$

$$= 0.044[(h - \phi/18) - 1.6]$$

$$= 0.044[(h - \phi/18) - \phi_s/18] \quad (5a)$$

where, $1.6 = \phi_s/18 = a$ constant. It may be pointed out that the relation between B and $(h - \phi/18)$ is the same as that deduced in the previous paper¹.

The data recorded in Table 2 show that for the electrolytes mentioned therein, the values of $(-\bar{S}_h^0)$ calculated by using equation (7) or (7a) agree well with those observed in the temperature range 298.2–473.2 K.

In Table 3, the values of $(-\bar{S}_h^0)$ of BaCl_2 solution calculated by Sen have been recorded for comparison. The values, calculated by the author using equation (XIII)¹⁰ agree with those observed. This should be considered highly encouraging as the primary data which the author could collect from the literature were, in some cases, not of a high order of accuracy. The agreement between the observed values and those calculated by using equation (7) also appears to be satisfactory.

Using the data recorded in Table 4, it has been found that plots of $(-\bar{S}_h^0)_{273.2}$ vs $(-\bar{S}_h^0)_{298.2}$ yield a straight line which can be represented by the equation,

$$(-\bar{S}_h^0)_{273.2} = 1.2(-\bar{S}_h^0)_{298.2} \quad (8)$$

The agreement of the experimental values with those calculated by using equation (8) supports the aforesaid conclusion. It may be noted that the intercept of the straight line represented by equation (8) is zero. It also follows from equation (7a) that a plot of $(-\bar{S}_h^0)_{273.2}$ vs $[(\bar{S}_h^0)_{298.2} + b(T_2 - T_1)]$ should yield a straight line with zero intercept. Hence the question arises whether the straight line represented by the equations (8) and (7a) are the same or different. The value of the tangent, m , of the straight line represented by equation (7a) should be found from the following expression,

$$m(-\bar{S}_h^0)_{298.2} = [1 + b(T_2 - T_1)] / (-\bar{S}_h^0)_{298.2} (-\bar{S}_h^0)_{298.2}$$

The value of m thus calculated have been recorded in the last column of Table 4. It will be noticed that the average value of $m=1.18$. Hence it is to be concluded that the two straight lines are identical or both the equations (7a) and (8) yield the same straight line.

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