Thermochimica Acta, 48 (1981) 219—223
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

Note

THERMODYNAMICS OF THE SODIUM CHLORIDE + WATER + SUCROSE SYSTEM FROM VISCOSITY DATA

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(Received 5 March 1981)

Ion—solvent interactions have been a subject of interest for the last two decades [1]. The inference regarding the interactions is derived from viscosity, molar volume, or conductance studies. In the present communication the viscosity of NaCl of aqueous sucrose solutions in the concentration range 0.1—2.0 M is reported. Such a system constitutes a ternary system, which will provide indication of the type of interactions. The theoretical equation of Einstein [2]

$$\eta_r = 1 + 2.5\phi \quad (1)$$

where ϕ is the volume fraction and η_r is the relative viscosity, has been modified by Moullik [3], Thomas [4] and Vand [5] to represent the viscosity of both aqueous solutions of electrolytes and nonelectrolytes at higher concentrations. These equations are

$$\text{Moullik: } \eta_r^2 = M + K'C^2 \quad (2)$$

$$\text{Thomas: } \eta_r = 1 + 2.5\phi + 10.05\phi^2 \quad (3)$$

$$\text{Vand: } \ln \eta_r = \frac{2.5\phi}{1 - Q\phi} \quad (4)$$

where $\phi = C\overline{V}$ (C is the molar concentration, and $\overline{V}$ is the molar volume of the solute); Q is an interaction parameter dealing with mutual interference between the spheres and with their Brownian motion; K_s, M and K' are constants. A comparative study of these equations over a wide concentration range for a number of salts in aqueous solution is reported by Moullik [3].

The B coefficient of the viscosity equation of Jones and Dole [6]

$$\eta_r = 1 + A\sqrt{C} + BC \quad (5)$$

which deals with ion—solvent interaction, is of particular importance in studying the type of interactions taking place in ternary systems. Equation (5) is valid for dilute solutions ($C \leqslant 0.1$ M) but for concentrated solutions ($C \geqslant 0.1$ M), B swamps the effect of A and the following relation holds

$$\eta_r = 1 + BC \quad (6)$$

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0040-6031/81/0000—0000/$02.50

MATERIALS AND METHODS

NaCl was of AnalaR grade. Sucrose AnalaR BDH was used as received. The preparation of solvents and solutions and density and viscosity measurements were the same as described previously [7]. The viscosity and density measurements are accurate up to 0.04% and 4×10^6, respectively. The investigations were carried out at temperatures of 30, 35, 40 and 45 ± 0.01°C.

RESULTS AND DISCUSSION

The B coefficient was obtained using eqn. (6) in the concentration range 0.1—2.0 M. The equation of Thomas and Vand, with some modifications, and Moullik's equation were employed as such to obtain different parameters by both graphical and least squares methods. The B values of the electrolytes are given in Table 1. The values of the other parameters are recorded in Table 2. Rearrangement of eqns. (3) and (4) gives

$$\text{Thomas:} \quad \frac{\eta_r - 1}{C} = 2.5\bar{V} + (K_s \bar{V}^2)C \qquad (7)$$

$$\text{Vand:} \quad \frac{1}{C} = 1.085\bar{V}\frac{1}{\log_r} + K\bar{V} \qquad (8)$$

K and K_s were used instead of Q and 10.05 in eqns. (4) and (3), respectively. Equations (7) and (8) fit well with the viscosity data of NaCl in aqueous sucrose solutions.

Inspection of Table 1 shows that the B values of NaCl decrease with increase in sucrose solution, showing a structure-breaking effect, as the viscosity of aqueous sucrose solutions increases with the increase in sucrose content. A linear relation

$$B = aC + b \qquad (9)$$

where a and b are constants and C is the concentration of sucrose, holds good at all temperatures studied. The values of the B coefficients increase with increasing temperature. This trend is true for aqueous salt solutions [8]. It has been suggested [1,8] that the B coefficient is a measure of the

TABLE 1

B values of the electrolytes (l mole^{-1})

Temp. (°C)	% Sucrose				
	0	5	10	15	20
30	0.3125	0.2600	0.2400	0.2304	0.2200
35	0.3000	0.2700	0.2697	0.2500	0.2245
40	0.2888	0.2800	0.2596	0.2500	0.2347
45	0.2915	0.2823	0.2647	0.2569	0.2396

TABLE 2

Values of different parameters of different viscosity equations

Sucrose (wt.%)	Temp. (°C)	Moullik equation		Thomas equation		Vand equation	
		M	K'	$\overline{V}$ (l mole^{-1})	K_s	$\overline{V}$ (l mole^{-1})	K
0	30	1.22	0.381	0.123	−0.34	0.127	−2.500
	35	1.21	0.375	0.124	0.24	0.122	−2.300
	40	1.22	0.370	0.125	0.25	0.113	−3.350
	45	1.21	0.390	0.127	0.26	0.116	−4.001
5	30	1.20	0.343	0.106	1.112	0.102	−4.41
	35	1.20	0.344	0.107	0.980	0.103	−5.32
	40	1.19	0.345	0.105	0.760	0.107	−5.81
	45	1.19	0.344	0.108	−0.880	0.108	−6.21
10	30	1.19	0.347	0.098	0.225	0.094	−1.37
	35	1.18	0.351	0.099	0.322	0.098	−1.67
	40	1.17	0.352	0.109	0.441	0.100	−1.87
	45	1.19	0.360	0.104	0.343	0.102	−1.90
15	30	1.13	0.260	0.091	0.343	0.090	−3.32
	35	1.13	0.263	0.097	0.358	0.096	−3.12
	40	1.14	0.267	0.100	0.451	0.099	−2.82
	45	1.15	0.271	0.105	0.581	0.103	−3.44
20	30	1.10	0.273	0.086	0.224	0.084	−4.51
	35	1.10	0.270	0.091	0.275	0.090	−4.31
	40	1.12	0.270	0.096	0.331	0.094	−4.12
	45	1.14	0.291	0.098	0.411	0.099	−4.01

ion—dipole interactions between the ions and the solvent molecules, and can be partitioned, assuming that the B coefficients of K^+ and Cl^- are equal. Utilising the B coefficient of Cl^- from our KCl data [9], the B values for Na^+ were determined. For Na^+, dB/dT is positive in sucrose solutions, suggesting that there is a strong interaction between the Na^+ and water dipole. Similarly, dB/dT for Cl^- is also positive and hence the interaction with the water dipole is through hydrogen bonding and the Cl^- have a firm layer of water molecules in their cospheres.

The equation of Moullik in its original form and that of Thomas and Vand in a slightly modified form hold good within certain concentration ranges. It is evident from the results in Table 2 that the viscosity data of the ternary system cannot be explained by a single equation. The values of $\overline{V}$ for NaCl obtained from both Thomas and Vand's equation are in good agreement and these values decrease with increase in sucrose concentration. This may be ascribed to the decrease in the electrostatic attraction between the water dipole and the ion, as a large number of water molecules are not available in the cosphere of the ions.

Breslau and Miller [10] have suggested a relation between $\overline{V}$ and B for a uniunivalent electrolyte. The relation is

$$B = 2.90\,\overline{V} - 0.018\,. \tag{10}$$

Equation (10) has been tried but it does not hold good; however, a linear relation of the type

$$B = a'\overline{V} + b' \qquad (11)$$

where a' and b' are constants, does.

Moullik and Mitra [11] have studied the interaction of the polyhydroxy compounds with salts and organic and inorganic bases and have established sucrose salt interactions in hydroxylic solvents. Hence, in the ternary system water + sucrose + NaCl, the positive value of $dB_{\pm}/dT$ of the ions may be due to the sucrose—salt interaction involving hydroxy groups of the sucrose and the ions. In the case of Cl^-, the interaction may be due to hydrogen bonding or the increase in the interaction of the ion with the water dipole in the microscopic region around the ion in the presence of sucrose.

The interpretation of viscous flow for electrolytic solutions in water according to the theory of absolute reaction has been done by Nightingale and Benck [12], who have calculated the energy of activation, ΔE (which does not differ appreciably from activation enthalpy), free energy of activation, ΔG, and entropy of activation, ΔS, for water and a number of electrolytic solutions. Proceeding in a similar way, ΔE, ΔG and ΔS for NaCl for 0, 5, 10, 15 and 20% (wt.%) sucrose solutions at 35°C only have been calculated and are recorded in Table 3.

It is observed that the energy and entropy of activation for viscous flow are greater than for the solvent (except at 0%) where the free energy of activation is almost unchanged, though it increases slightly with increase in sucrose content. The abnormally large energies and entropies of activation are attributed to the excess energy required to break the hydrogen bond in the solutions.

TABLE 3

Activation flow

% Sucrose	ΔG (kJ mole^{-1})	ΔE (kJ mole^{-1})	ΔS (J K^{-1} mole^{-1})
0			
Solvent	0.050	15.674	21.50
NaCl	9.574	9.612	12.29
5			
Solvent	10.143	7.655	—8.08
NaCl	10.551	10.143	10.31
10			
Solvent	10.492	7.256	—10.50
NaCl	10.981	11.456	12.35
15			
Solvent	11.173	5.805	—19.43
NaCl	11.474	12.581	13.55
20			
Solvent	11.740	5.080	—21.62
NaCl	12.110	12.471	12.85

REFERENCES

1 R.W. Gurney, Ionic Processes in Solutions, McGraw-Hill, New York, 1954, p. 160.
2 A. Einstein, Ann. Phys., 19 (1906) 289.
3 S.P. Moullik, J. Indian Chem. Soc., 49 (1972) 483.
4 D.J. Thomas, J. Colloid Sci., 20 (1965) 267.
5 V. Vand, J. Phys. Colloid Chem., 52 (1948) 277.
6 D. Jones and M. Dole, J. Am. Chem. Soc., 51 (1929) 2950.
7 P.B. Das, Electrochim. Acta, 22 (1977) 1275.
8 M. Kaminsky, Discuss. Faraday Soc., 24 (1957) 71.
9 S. Mohanty, B.K. Das and P.B. Das, Thermochim. Acta, 43 (1981) 385.
10 B.R. Breslau and F.R. Miller, J. Phys. Chem., 74 (1970) 1056.
11 S.P. Moullik and A.K. Mitra, Carbohydr. Res., 23 (1972) 65.
12 E.R. Nightingale, Jr. and R.F. Benck, J. Phys. Chem., 63 (1959) 1777.