Thermochimica Acta, 43 (1981) 385—390
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

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# THE THERMODYNAMICS OF THE POTASSIUM CHLORIDE—WATER—SUCROSE SYSTEM FROM VISCOSITY STUDIES

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(Received 11 August 1980)

Ion—solvent interaction studies 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 KCl in aqueous sucrose solutions in the concentration range 0.1—2.0 M is reported. Such a system constitutes a ternary system, which will provide indications regarding the types of interactions. The theoretical equation of Einstein [2]

$$\eta_r = 1 + 2.5\phi \tag{1}$$

(where $\eta_r$ is the relative viscosity and $\phi$ is the volume fraction) has been modified by Thomas [3], Vand [4] and Moullik [5] to represent the viscosity of both aqueous solutions of electrolytes and non-electrolytes at higher concentrations. These equations are

$$\text{Thomas: } \eta_r = 1 + 2.5\phi + 10.05\phi^2 \tag{2}$$

$$\text{Vand: } \ln \eta_r = \frac{2.5\phi}{1 - Q\phi} \tag{3}$$

$$\text{Moullik: } \eta_r^2 = M + K'C^2 \tag{4}$$

In eqns. (1)—(4) $\phi = C\bar{V}$, where $C$ is the molar concentration and $\bar{V}$ is the molar volume of the solute, $Q$ is an interaction parameter dealing with mutual interference between the spheres and with their Brownian motion, $M$ and $K'$ are constants. A comparative study of these equations over a wide concentration range for a number of salts is reported by Moullik [5].

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

$$\eta_r = 1 + A\sqrt{C} + BC \tag{5}$$

deals with ion—solvent interaction and is of particular importance in studying the types of interactions which take place in ternary systems. Equation (5) is valid for dilute solutions ($C \leqslant 0.1$ M), but not for concentrated solutions ($C \geqslant 0.1$ M). $B$ swamps over the effect of $A$ and the equation is reduced

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to

$$\eta_r = 1 + BC \tag{6}$$

## MATERIALS AND METHODS

KCl (AR.B.D.H) and sucrose (AR.BDH) were used as supplied. Calculated amounts of KCl and sucrose were weighed and the volume made up with conductivity water to prepare the experimental solutions. The density and viscosity measurements were as described earlier [7]. The viscosity measurements are accurate up to 0.04% and the density up to 4 in $10^6$. The temperatures used were 30, 35, 40 and 45 ± 0.01°C.

## RESULTS AND DISCUSSIONS

The $B$ coefficients were obtained using eqn. (6) in the concentration range studied (0.1—2.0 M) and are given in Table 1. The different parameters of rearranged Vand [eqn. (7)], Thomas [eqn. (8)] and Moullik equations [eqn. (4)] are obtained by employing both graphical and least-squares methods and these are recorded in Table 2.

$$\frac{1}{C} = 1.085\bar{V}\frac{1}{\log \eta_r} + K\bar{V} \tag{7}$$

$$\frac{\eta_r - 1}{C} = 2.5\bar{V} + (K_s\bar{V}^2)C \tag{8}$$

(In these equations, $K$ and $K_s$ are, respectively, used in place of $Q$ in the Vand equation and 10.05 in the Thomas equation). It is possible to calculate these parameters since the viscosity data for KCl in aqueous solutions of sucrose fit well with these equations [eqns. (7), (8) and (4)].

Inspection of Table 1 shows that the $B$ values of the salt decrease with increasing sucrose percentage, showing a structure breaking effect. A linear relationship

$$B = aW + b \tag{9}$$

TABLE 1

$B$ (l mole$^{-1}$)

| Temp. (°C) | Wt.% sucrose | | | | |
|---|---|---|---|---|---|
| | 0 | 5 | 10 | 15 | 20 |
| 30 | 0.2000 | 0.1750 | 0.1572 | 0.1436 | 0.1375 |
| 35 | 0.2174 | 0.1842 | 0.1786 | 0.1500 | 0.1384 |
| 40 | 0.2083 | 0.2000 | 0.1766 | 0.1500 | 0.1324 |
| 45 | 0.2030 | 0.2030 | 0.1750 | 0.1667 | 0.1500 |

TABLE 2

Values of different parameters in eqns. (4), (7) and (8)

| Wt.% sucrose | Tested salt concn. | Temp. (°C) | Thomas equation | | Vand equation | | Moullik equation | |
|---|---|---|---|---|---|---|---|---|
| | | | $\overline{V}$ (l mole$^{-1}$) | $K_s$ | $\overline{V}$ (l mole$^{-1}$) | $K$ | $M$ | $K'$ (l$^2$ mole$^{-2}$) |
| 0 | 2.0—0.1 | 30 | 0.086 | −0.3545 | 0 080 | −2.50 | 0.21 | 0.375 |
| | | 35 | 0.094 | −0.3245 | 0.085 | −3.53 | 0.21 | 0.412 |
| | | 40 | 0.083 | 0.6970 | 0.087 | −1.15 | 0.20 | 0.382 |
| | | 45 | 0.080 | 0.5675 | 0.080 | −3.13 | 0.20 | 0.368 |
| 5 | 2.0—0.1 | 30 | 0.074 | −0.5945 | 0.078 | −2.56 | 0.20 | 0.333 |
| | | 35 | 0.084 | −0.3570 | 0.080 | −2.88 | 0.20 | 0.375 |
| | | 40 | 0.074 | −0.9130 | 0.085 | −1.76 | 0.20 | 0.400 |
| | | 45 | 0.076 | 1.5455 | 0.084 | −1.55 | 0.180 | 0.428 |
| 10 | 2.0—0.1 | 30 | 0.062 | −0.7246 | 0.072 | −2.78 | 0.18 | 0.344 |
| | | 35 | 0.078 | −0.3741 | 0 074 | −2.70 | 0.18 | 0.316 |
| | | 40 | 0.070 | 1.0200 | 0.075 | −2.67 | 0.16 | 0.308 |
| | | 45 | 0.072 | 1.6100 | 0 076 | −2.76 | 0.18 | 0.300 |
| 15 | 2.0—0.1 | 30 | 0.050 | 6.250 | 0.052 | −6.35 | 0.08 | 0.167 |
| | | 35 | 0.054 | 2 442 | 0.063 | −2.38 | 0.16 | 0.250 |
| | | 40 | 0.078 | −0.901 | 0.066 | −1.97 | 0.18 | 0.250 |
| | | 45 | 0.066 | 0 958 | 0 072 | −2.08 | 0.18 | 0.295 |
| 20 | 2.0—01 | 30 | 0.052 | −1.684 | 0 058 | −3.45 | 0.12 | 0.200 |
| | | 35 | 0.054 | −0.563 | 0.052 | −2.50 | 0.10 | 0.200 |
| | | 40 | 0.062 | −0 541 | 0 055 | −2.36 | 0.12 | 0.200 |
| | | 45 | 0.066 | −0.937 | 0.062 | −3.23 | 0.14 | 0.280 |

TABLE 3

Viscosity (cPoise) of sucrose solutions

| Temp. (°C) | Wt.% sucrose | | | | |
|---|---|---|---|---|---|
| | 0 | 5 | 10 | 15 | 20 |
| 30 | 0.7982 | 1.2297 | 1.5423 | 2.0071 | 2.5061 |
| 35 | 0.7350 | 1.2023 | 1.5263 | 1.9378 | 2.4831 |
| 40 | 0.6510 | 1.1152 | 1.5067 | 1.8890 | 2.4112 |
| 45 | 0.5960 | 1.1110 | 1.4989 | 1.8727 | 2.3784 |

(where $a$ and $b$ are constants and $W$ is the weight % of sucrose) holds good at all the temperatures studied. The values of $B$ coefficients increase with increasing temperature. This trend in the increase of $B$ coefficients is also noticed for aqueous salt solutions [8]. It has been suggested [8] that the $B$ coefficient is a measure of the ion—dipole interactions between the ions and the solvent molecules, and can be partitioned assuming that the $B$ components of $K^+$ and $Cl^-$ are equal in KCl. In the case of $K^+$, $dB/dT$ is positive in sucrose solutions, suggesting that there is strong interaction between $K^+$ and the water dipole. Similarly, the $Cl^-$ ion has a positive $dB/dT$ value. So, for an anion the interaction with the water dipole is through hydrogen bonding. The positive value of $dB/dT$ shows that $Cl^-$ ions have a firm layer of water molecules in their cospheres. However, the $B$ coefficient decreases with increase in sucrose content, which indicates that either sucrose or KCl are structure breakers. But since the viscosity of sucrose solutions increases with sucrose content (Table 3), it is true that sucrose is a structure maker. Hence it is obvious that $K^+$ or $Cl^-$ are structure breakers.

The equations of Vand and Thomas in slightly modified forms and Moulik's equation in its original form hold good for the solutions of KCl reported here. It is evident from the results of Table 2, that the viscosity data of the ternary system cannot be explained by a single equation. The values of $\bar{V}$ of KCl obtained by the equations of Vand and Thomas agree well with each other 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 large numbers of water molecules are not available in the cosphere of the ions.

Breslau and Miller [9] have suggested a method of calculating the viscosity of concentrated aqueous salt solutions from a knowledge of their $B$ coefficient and have put forward the empirical relations [eqn. (10)] between $\bar{V}$ and $B$ for uni-univalent electrolytes.

$$B = 2.90\bar{V} - 0.018 \tag{10}$$

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

$$B = a'\bar{V} + b' \tag{11}$$

(where $a'$ and $b'$ are constants) does.

TABLE 4

Thermodynamic parameters for viscous flow

| | $\Delta G$ (kJ mole$^{-1}$) | $\Delta E$ (kJ mole$^{-1}$) | $\Delta S$ (J K$^{-1}$ mole$^{-1}$) |
|---|---|---|---|
| *0% Sucrose* | | | |
| Solvent | 9.050 | 15.674 | 21.50 |
| KCl | 9.378 | 10.050 | 13.89 |
| *5% Sucrose* | | | |
| Solvent | 10.143 | 7.655 | − 8.08 |
| KCl | 10.433 | 13.978 | 11.51 |
| *10% Sucrose* | | | |
| Solvent | 10.492 | 7.256 | −10.50 |
| KCl | 10.753 | 15.010 | 14.86 |
| *15% Sucrose* | | | |
| Solvent | 11.173 | 5.805 | −17.43 |
| KCl | 11.365 | 15.240 | 12.58 |
| *20% Sucrose* | | | |
| Solvent | 11.740 | 5.080 | −21.62 |
| KCl | 11.893 | 16.020 | 13.40 |

Moullik and Mitra [10] 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—KCl, the positive value of $dB_{\pm}/dT$ of the ions may be due to a sucrose—salt interaction involving the 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 rates has been done by Nightingale and Benck [11] and they have calculated the energy of activation, $\Delta E$ (which does not differ appreciably from activation enthalpy), free energy of activation, $\Delta G$, and entropy of activation, $\Delta S$, for water and a number of electrolytic solutions. Proceeding along similar lines, $\Delta E$, $\Delta G$ and $\Delta S$ for KCl in 0, 5, 10, 15 and 20 weight % sucrose solution have been calculated and the results are recorded in Table 4. It is observed that the energy and entropy of activation for viscous flow is greater than that of the solvent (except for pure water), but 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 necessary to break the hydrogen bonding in the solutions.

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