The Evaluation of the Thermodynamic Parameters of Viscous Flow in Dimethylformamide-Water Mixtures for Chlorides and Bromides of Calcium, Strontium and Barium at Different Temperature

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The thermodynamic parameters of viscous flow, namely: ΔE^*, ΔF^* and ΔS^* at 30° and 40°C have been calculated for the chlorides and bromides of calcium, strontium and barium in DMF-water mixtures of various compositions using the method of Nightingale and BencK's equations based on the application of Eyring's theory of absolute reaction rate. The data has been utilised to discuss the ion-solvation in mixed solvent. The value for ΔE^* and ΔF^* increases with the solvent composition and decreases with the rise of temperature for all the electrolyte solutions. ΔS^* value decreases with solvent composition as well as with the rise of temperature for all the electrolyte solutions.

INTRODUCTION

A large number of data[1-7] are available in literature on the applicability of the Jones-Dole equation[8] for electrolyte solutions and Nightingale and BencK[9] have utilised the data to interpret the ion-solvent interaction at 25°C. It is considered worthwhile to examine the behaviour of some alkaline-earth metal halides in DMF-water mixed solvent at 30° and 40°C; although the work on LiCl, LiNO₃ and MClO₄ (M = Li, Na, K) in DMF-water mixture have been reported earlier[10].

EXPERIMENTAL

All the salts used were of AnalaR grade (B.D.H.) except calcium chloride which was prepared by the method of Das[4] by dissolving a sample of calcium carbonate with slightly less than the requisite amount of hydrochloric acid, both being of B.D.H AnalaR quality. The resulting solution was warmed, filtered through glass sintered funnel. They were recrystallised three times by conductance water and were tested by the method of Pinching and Bates[11] to be free from other components. They were dried for 12 hrs at 70°C and were stored in a desiccator over P_2O_5.

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DMF (Reidel) sample[12] was shaken with KOH pellets and was refluxed for several hrs under reduced pressure (5 mm) at 25°–30°C.

DMF-water mixed solvents containing 10, 20 and 40% DMF (by weight) were prepared in conductivity water. All electrolyte solutions were prepared from stock solution of known strength. The ranges of concentration were from 0.0005 to 0.1 M. The measurements of viscosity and density of the solvent and solutions were made as described elsewhere[13-15].

RESULTS AND DISCUSSION

Eyring *et al.*[16] have applied the theory of absolute reaction rate to the phenomenon of viscous flow. The energy of activation for viscous flow ΔE^* is found to be given by

$$\Delta E^* = R \frac{d \ln \eta}{d(1/T)} \tag{1}$$

The free energy of activation for viscous flow ΔF^* is given by

$$\Delta F^* = RT \ln \frac{\eta V}{hN} \tag{2}$$

V being the volume of one mole of solution particles, the other symbols having their usual meaning. Nightingale and BencK[9] have made use of Eyring's idea to interpret the influence of strong electrolytes upon the viscous property of solvents, as summarised in the Jones-Dole equation[8]:

$$h/\eta_0 = 1 + A\sqrt{C} + BC \tag{3}$$

Neglecting the small $\sqrt{C}$ term which has its origin in interionic attraction[17], the Nightingale-BencK equation[9] for activation energy of viscous flow is:

$$\Delta E^* = R \frac{d \ln \eta_0}{d(1/T)} + R \frac{d \ln (1 + BC)}{d(1/T)}$$

or

$$\Delta E^* = R \frac{d \ln \eta_0}{d(1/T)} + \frac{R}{(1 + BC)} \frac{d(1 + BC)}{d(1/T)} \tag{4}$$

while the viscous flow free energy is given by the equation already given (equation 2). Assuming further the activation enthalpy to be approximately equal to the activation energy, the expression for entropy of activation is obtained as

$$\Delta S^* = \frac{\Delta E^* - \Delta F^*}{T} \tag{5}$$

Thus, the temperature coefficient of viscosity B-coefficient of ionic solutions can be made use of to calculate the parameters ΔE^*, ΔF^*, ΔS^* associated with the viscous flow properties of ionic solutions.

In absence of electrolytes, ΔE_0^* for the solvent can be represented as:

$$\Delta E_0^* = R \frac{d \ln \eta_0}{d(1/T)} \qquad (6)$$

ΔE_0^* for solvents (10% DMF-water, 20% DMF-water and 40% DMF-water mixture) are obtained by plotting log η_0 vs 1/T. The curve obtained was not linear and the tangents of the slope when multiplied by 2.303 R, give the value for ΔE_0^* for solvents at various temperatures. Similarly, to calculate ΔE^* for the electrolyte solutions, curves are obtained by plotting $(1 + BC)$ vs 1/T. The values for $\dfrac{d(1 + BC)}{d(1/T)}$ (assuming C = 1 M) are obtained from tangents of the slope. The values then multiplied with $\dfrac{R}{(1 + BC)}$ and added to the ΔE_0^* for the solvent, give ΔE^* for the solution of electrolytes (equation 4). The values obtained for different electrolytes under investigation are recorded in Tables 1 and 2.

TABLE 1

VALUES OF THERMODYNAMIC PARAMETERS FOR VISCOUS
FLOW OF SOLUTE AT 30°C

Solutes	Solvent composition (wt. % of DMF)								
	ΔE^* (Kcals) $\pm$ 0.04			ΔF^* (Kcals)			ΔS^* (e.u.)		
	10	20	40	10	20	40	10	20	40
Solvent	4.306	4.693	4.942	2.336	2.508	2.848	6.498	7.207	6.907
CaCl₂	3.768	3.839	3.987	2.562	2.733	3.122	3.978	3.648	2.853
SrCl₂	3.442	3.516	3.654	2.568	2.751	3.126	2.883	2.523	1.741
BaCl₂	3.115	3.187	3.331	2.514	2.696	3.080	1.979	1.619	0.828
CaBr₂	3.829	3.921	4.059	2.569	2.751	3.129	4.156	3.859	3.067
SrBr₂	3.520	3.592	3.728	2·577	2.754	3.133	3.110	2.764	1.962
BaBr₂	3.192	3.258	3.402	2.520	2.707	3.087	2.216	1.817	1.039

In order to evaluate ΔF^* using equation 2, the volume (in ml) of one mole of solution particles (V) is obtained in the following manner:

$$V = \frac{1000}{n_1 + \Upsilon n_2} \qquad (7)$$

Υ = Number of species into which a solute molecule dissociates,

n_2 = Number of moles of solute per litre of solution (molarity of solution),

n_1 = Number of moles of solvent per litre on the solution.

Again,

$$n_1 = \frac{1000\rho - n_2M_2}{M_1}$$

where M_1 = Molecular weight of solvent,

M_2 = Molecular weight of solute,

ρ = Density of the solution.

The values obtained for the electrolytes under investigation recorded in Table 1 and 2.

ΔS^* are calculated using equation (5) and are placed in Table 1 and 2.

TABLE 2

VALUES OF THERMODYNAMIC PARAMETERS FOR VISCOUS
FLOW OF SOLUTES AT 40°C

| Solutes | Solvent composition (wt. % of DMF) | | | | | | | | |
| | ΔE^* (Kcals) $\pm$ 0.04 | | | ΔF^* (Kcals) | | | ΔS^* (e.u.) | | |
	10	20	40	10	20	40	10	20	40
Solvent	4.226	4.614	4.896	2.278	2.447	2.779	6.224	6.920	6.764
CaCl₂	3.695	3.787	3.919	2.533	2.721	3.096	3.712	3.404	2.628
SrCl₂	3.361	3.459	3.602	2.546	2.734	3.108	2.602	2.315	1.578
BaCl₂	3.047	3.131	3.278	2.505	2.690	3.074	1.730	1.409	0.651
CaBr₂	3.775	3.869	3.999	2.525	2.722	3.099	3.961	3.664	2.875
SrBr₂	3.436	3.532	3.661	2.554	2.737	3.116	2.816	2.538	1.740
BaBr₂	3.132	3.219	3.345	2.507	2.699	3.076	1.997	1.660	0.859

The thermodynamic parameters obtained for the viscous flow has been utilised to understand the phenomena of ion-solvation critically. The plot of ln η vs 1/T is found to be slightly curved which indicates that DMF-water mixed solvent behave as an associated liquid, like water and DMF alone. The evidence for larger association with increasing percentage (%) of DMF in the solvent has also been observed from the nature of curve.

The values for ΔE^* are always positive and increases with the % of DMF in the solvent. These values are higher than the value reported for water at 25°C. The addition of salts in the solvent is accompanied by decrease in ΔE^* values for all % composition of mixed solvent. ΔE^* values also decreases with the increase of temperature. The above observations are related to the phenomena of breaking hydrogen bond in water molecule by the presence of DMF as DMF itself is a better proton acceptor.

Formation of a new bond between water and DMF molecule to give a bulkier three dimensional DMF-water mixed molecule, is the probable explanation for the increase in ΔE^* of water by the addition of DMF in water (Fig. 1).
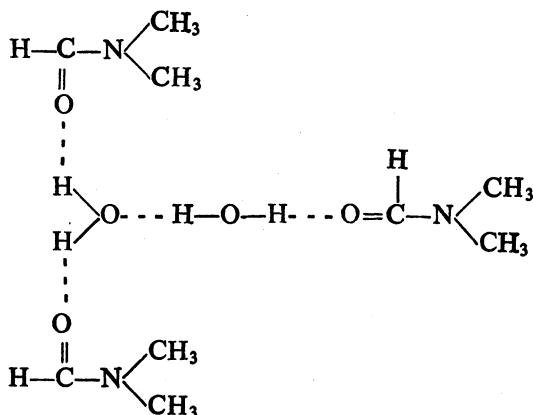
$$H-C-N \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{<}}$$

$$\underset{H}{\overset{H}{>}}O - - - H-O-H- - - O=C-N \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{<}}$$

$$H-C-N \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{<}}$$

Fig. 1   The hydrogen-bonded DMF-water molecule

The addition of salts causes a decrease in ΔE^* values because of the breaking of hydrogen bond present in the solvent (DMF-water mixture). Increase in temperature also breaks the bond as ΔE^* decrease with increase in temperature which is according to Boltzmane distribution *i.e.* the fraction of broken bonds increases with the temperature while fraction required to be broken by the Shearing force in viscous flow decreases with the increase in temperature.

The curve represents the variation of ΔE^* with mole fraction of DMF. The values for 0% (zero) DMF *i.e.* for pure water are obtained by extrapolating the curve and the values are less than that in case of water and of BaCl$_2$ at 25°C as reported by Nightingale and BencK[9]. This indicates further the bond breaking phenomenon is more pronounced at 30°C and 40°C probably because of more thermal agitation. Chlorides decrease more in ΔE^* of solvent in any cases than that of corresponding bromides that indicates that Cl$^-$ ion is more stronger bond breaker than Br$^-$ ion. This is due to smaller size of Cl$^-$ ion.

The values for ΔF^* for salts (Tables 1 and 2) are approximately constant and have slightly higher value than corresponding values at 25°C in water both in cases of solvent and solutions. The increase in ΔF^* value with the mole-fraction of DMF in the solvent at 30°C and 40°C as well as the decrease in ΔF^* value with the increase in temperature also supports bond breaking phenomena in the solvent by presence of electrolytes.

For the data for ΔS^* (Tables 1 and 2) it is evident that they have positive value having similar trends to those of ΔE^* and these can also be

explained according to bond breaking phenomena as in case of ΔE^*. In case of solvent, entropy value ΔS_0^* reaches a maximum in the vicinity of 20% DMF-water mixture at both the temperatures. Therefore, it may be assumed that solvent has the highest degree of structure near this composition. In case of solutions, the highest degree of structure of solvent is in 10% DMF-water mixture.

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