

Viscosity of Solutions of Sodium Bromate and Potassium Iodate at 30°, 35° and 40° ; Calcium Chloride at 35°, 40° and 45° and Barium Chloride at 30°, 40° and 45°

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Viscosity of solutions of sodium bromate, potassium iodate, calcium chloride and barium chloride between 30°-45° have been studied. The change of 'B' values of Jones-Dole equation with temperature was examined and the 'B' values for sodium bromate are $B_{30}=0.1070$, $B_{35}=0.1142$, $B_{40}=0.1233$, for potassium iodate are $B_{30}=0.1483$, $B_{35}=0.1525$, $B_{40}=0.1628$, for calcium chloride are $B_{35}=0.2900$, $B_{40}=0.2880$, $B_{45}=0.2840$ and for barium chloride are $B_{30}=0.2300$, $B_{40}=0.2880$, $B_{45}=0.2970$. The free energy (ΔF), energy of activation for viscous flow (ΔE) and the entropy of activation (ΔS) with respect to the solvent have been calculated.

A large number of data¹⁻⁴ are available in literature on the applicability of the Jones-Dole equation for electrolytic solutions and Nightingale⁵ has utilised the data to interpret the ion-solvent interaction at 25°. It is considered worthwhile to examine the behaviour of some electrolytes like barium chloride, calcium chloride, potassium iodate and sodium bromate where no viscosity data exists in literature at higher temperature.

Experimental

All the salts of BDH AnalaR quality were recrystallised, dried and used, except calcium chloride which was prepared by dissolving a sample of calcium carbonate with slightly less than the requisite amount of hydrochloric acid, both being of BDH AnalaR quality.

The resulting solution was warmed, filtered through glass sintered funnel, diluted and estimated. All solutions were prepared from stock solutions of known strength. The range of concentrations studied were from 0.001 to 0.100 molar. Viscosity measurements were made as described previously⁶.

Discussion

For all solutions at all temperatures, the relative viscosity can be expressed by Jones-Dole equation: $\frac{\eta}{\eta_0} = 1 + A\sqrt{C} + BC$, where the terms have their usual significance and the values of 'A' and 'B' were found in the usual manner. The values of 'A' and 'B' for the electrolytes studied, at different temperatures are presented in Table-1. The data for barium chloride⁷ at 35° and for potassium and sodium chloride have been calculated from the published data. The value of 'B' is found in all cases to be positive at the temperatures studied and it increases with temperature except in case of calcium chloride solution where a decrease in the value of 'B' is noticed as the temperature increases from 35° to 45°. The magnitude of 'B' in case of calcium chloride is larger than that of barium chloride, so also is the case of potassium iodate compared to sodium bromate.

Lately, Moulik⁸ has analysed the viscosity data, at higher concentration, for both electrolytes and non-

TABLE—1

Electrolyte	Temperature °C	'A' Value	'B' Value
KIO ₃	30	0.0067	0.1483
	35	0.0070	0.1525
	40	0.0072	0.1628
NaBrO ₃	30	0.0069	0.1070
	35	0.0072	0.1142
	40	0.0075	0.1233
CaCl ₂	35	0.0171	0.2900
	40	0.0160	0.2880
	45	0.0140	0.2840
BaCl ₂	30	0.0226	0.2300
	40	0.0153	0.2880
	45	0.0073	0.2970

electrolytes, available in literature and has tried to make out a relation between 'B' of the Jones - Dole equation and 'K' of his equation (i. e. $(\eta/\eta_0)^2 = M + K'C^2$). The present data were tested in the similar lines as has been done by Moulik but was found that no satisfactory relation can be drawn by using Vand⁹ and Thomas¹⁰ equations and hence \bar{V} , the molar volume cannot be

The conclusions, so arrived at, can be easily visualised by utilising the data to calculate the activation energy of viscous flow (ΔE), free energy of activation (ΔF) and entropy of activation (ΔS) for the salts in the manner worked out by Nightingale and are recorded in Table 2, together with the data at 25°, given in brackets, available in literature⁵. Comparison of the

TABLE 2

Solvent	ΔE in K cal ± 0.03	ΔF in K cal	ΔS in e.u.
KIO ₃	3.765 (4.01)	2.134 (2.19)	5.30 (6.1)
NaBrO ₃	3.528 —	2.221 —	4.24 —
CaCl ₂	3.490 —	2.200 —	4.19 —
BaCl ₂	3.721 —	2.290 —	4.60 —
KCl	2.915 (3.10)	2.288 (2.30)	2.00 (2.70)
NaCl	3.485 (3.56)	2.140 (2.18)	4.37 (4.60)
	3.764 (3.81)	2.184 (2.20)	5.13 (5.40)

obtained in this way. However, a straight line can be obtained by plotting the data as has been done by Moulik for his equation. No satisfactory relationship could be established between the Moulik's constants and 'B' of Jones-Dole equation. This is because the contribution of 'A' term cannot be neglected in comparison with the 'B' term in the cases studied, for instance for 0.1 concentration of barium chloride at 30°, the contributions of A/C term and BC term are 0.0072 and 0.0230 respectively, as has been done by Moulik, Vand and Thomas.

Kaminsky¹¹, Gurney¹² have suggested that 'B' (in Jones-Dole equation) is a measure of ion-dipole interaction between the ion and the solvent molecules and have supported the idea of partitioning the 'B' coefficients to their ionic components assuming that the 'B' components of potassium and chloride ions are equal in potassium chloride. When such interaction is considered, the magnitude of 'B' is dependent on the manner and the extent to which the ions orient the water dipole in their cospheres at a particular temperature. The larger value of 'B' for calcium chloride than that of barium chloride is due to the calcium ion where the charge density is larger, promoting greater interaction between the calcium ion and water dipole, than the case of barium ion with smaller charge density leading to lesser interaction between the ion and water dipole. In case of such ions, like calcium and sodium the $\frac{dB}{dT}$ is negative where-

as $\frac{dB}{dT}$ is positive for ions like barium and potassium.

In case of the anions again the interaction between the solvent and the ions will be through hydrogen bonding and hence a symmetrical ion like chloride ion is likely to have a firmer layer of water molecule in its cosphere than that of bromate or iodate ions.

data for the activation energy of viscous flow between barium chloride and calcium chloride clearly indicates that barium ion requires less activation energy than that of calcium ion, so is the case between potassium chloride and sodium chloride. The value of ΔE for sodium bromate is slightly less than that of potassium iodate. These two electrolytes are known to be promoting ion-pair formation and therefore the actual process of ion-solvent interaction is more complicated than in case of simple electrolytes, as the ion-pairs contribute to the total viscosity of solution.

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