been interpolated from the data[8,9] reported in the literature assuming that the presence of uranyl nitrate *bis*-alcohol will have no effect on the heat of solution. ΔH_6 thus estimated for methanol and ethanol complexes, respectively, are 0·42 and 1·5 KJ mol⁻¹. Hence ΔH, for $UO_2(NO_3)_2.2CH_3OH(c)$ and $UO_2(NO_3)_2.2C_2H_5OH(c)$ are −80·8 and −60·6 KJ mol⁻¹, respectively.

Standard heats of formation of uranyl nitrate bis-alcohols — The heats of formation of the *bis*-alcohol compounds have been calculated from the relation (8).
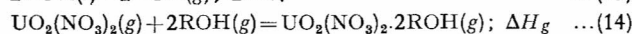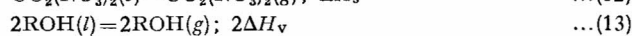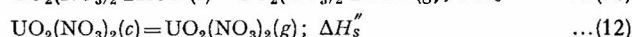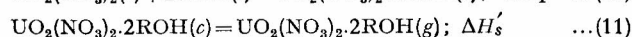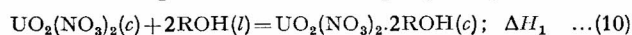
$$\Delta H_1 = \Sigma \Delta H_f^\circ \text{ (products)} - \Sigma \Delta H_f^\circ \text{ (reactants)} \quad \ldots(8)$$

Therefore

$$\Delta H_f^\circ UO_2(NO_3)_2.2ROH(c) = \Delta H_f^\circ UO_2(NO_3)_2(c)$$
$$+ 2\Delta H_f^\circ ROH(l) + \Delta H \quad \ldots(9)$$

By computing $\Delta H_f^\circ UO_2(NO_3)_2(c)$ from Lange[8] and $\Delta H_f^\circ ROH(l)$ from Cox and Pilcher[10], $\Delta H_f^\circ UO_2(NO_3)_2.2CH_3OH(c)$ and $\Delta H_f^\circ UO_2(NO_3)_2.2C_2H_5OH(c)$ come out to be −1935·4 and −1993·2 KJ mol⁻¹, respectively.

The mean bond dissociation energy of uranium-oxygen (alcohol) bond has been calculated from the following well-known[11] steps (10-14):

$$UO_2(NO_3)_2(c) + 2ROH(l) = UO_2(NO_3)_2.2ROH(c); \quad \Delta H_1 \quad \ldots(10)$$

$$UO_2(NO_3)_2.2ROH(c) = UO_2(NO_3)_2.2ROH(g); \quad \Delta H_s' \quad \ldots(11)$$

$$UO_2(NO_3)_2(c) = UO_2(NO_3)_2(g); \quad \Delta H_s'' \quad \ldots(12)$$

$$2ROH(l) = 2ROH(g); \quad 2\Delta H_v \quad \ldots(13)$$

$$UO_2(NO_3)_2(g) + 2ROH(g) = UO_2(NO_3)_2.2ROH(g); \quad \Delta H_g \quad \ldots(14)$$

where $\Delta H_s'$ and $\Delta H_s''$ are the heats of sublimation of uranyl nitrate *bis*-alcohol and uranyl nitrate, respectively; ΔH_v, the heat of vaporization of the alcohol; and ΔH_g, is the gas-phase molecular dissociation energy. Whence, $\Delta H_g = \Delta H_1 + \Delta H_s' - \Delta H_s'' - 2\Delta H_v$.

As pointed out earlier[6] the heats of sublimation data are assumed to be the same for uranyl nitrate and the *bis*-complexes. Hence ΔH_g, for the *bis*-methanol and *bis*-ethanol are −155·6 and −145·8 KJ mol⁻¹; and the uranium-oxygen (alcohol) bond-strength, $E(O-U) = -\Delta H_g/2 = 77·8$ and 72·9 KJ mol⁻¹, respectively for methanol and ethanol adducts. The values compare well with the alcohol and UCl₄ bond strength[11] in $UCl_4.4ROH$ and with the uranium-oxygen (water) bond strength reported earlier[12,13]. The bond strengths in *bis*-alcohol are stronger than the uranium-water bond strengths on account of the electron donating effect of the alkyl groups. It can be seen that the steric effect due to long-chain ethyl group slightly opposes the positive inductive effect of the ethyl group producing a lower bond strength in *bis*-ethanol.

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Viscosity & Apparent Molal Volume of Potassium Chloride in Acetone-, Dioxane- & Methyl Alcohol-Water Mixtures

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The viscosity and apparent molal volume of potassium chloride in acetone-, dioxane- and methyl alcohol-water mixtures containing 10, 20, 30, 40 and 50% (w/w) of the organic components have been measured at 35° and the data analysed in terms of Jones-Dole epuation. The values of the constants *A* and *B* of Jones-Dole equation and the apparent molal volume have been explained in terms of ion-ion and ion-solvent interactions.

VISCOSITY and apparent molal volume (ϕ) of electrolyte solutions in aquo-organic solvents have been studied with a view to understanding the nature of ion-ion and ion-solvent interaction respectively[1-11]. The viscosity and apparent molal volume of KCl in acetone-, dioxane- and methyl alcohol-water mixtures containing 10, 20, 30, 40 and 50% of the organic solvent have now been, measured at concentrations <0·1M at 35°±0·001°.

KCl, acetone, dioxane and methyl alcohol used were of E. Merck (extra pure) qualities. Purification of the solvents and preparation of mixed solvents and solutions were carried out as reported earlier[12]. The procedures for viscosity measurement were the same as described by Prasad *et al.*[13]. The density measurements were made by pyknometer (50 ml) with buoyancy correction and the values are accurate up to 4 in 10⁶. The concentration range was from 0·1 to 0·001M.

The applicability of the Jones-Dole equation[2] is shown by the linear plot of $\eta_r - 1/C^{\frac{1}{2}}$ versus $C^{\frac{1}{2}}$. The values of the constants *A* and *B*, given by the intercept and slope of the plots respectively are given in Table 1. The calculated *B* values are in acceptable agreement with those obtained from these plots.

TABLE 1 — A AND B VALUES FOR DIFFERENT AQUO-ORGANIC SOLVENTS

Organic solvent (w/w, %)	$A \times 10^3$			$B \times 10^2$		
	I	II	III	I	II	III
10	5·0	5·5	6·1	3·2	2·8	0·0
20	6·0	6·2	7·0	6·9	3·9	0·0
30	6·5	7·1	7·8	7·3	5·3	0·0
40	7·5	8·0	8·6	12·6	10·0	2·0
50	9·1	9·7	10·0	13·8	12·6	6·3

The values of A (at 25°) and B (at 25°) are 0·0049 and 0·009 respectively (ref. 17).
I = acetone-water; II = dioxane-water and III = methyl alcohol-water.

TABLE 2 — S_v AND ϕ^0 VALUES FOR DIFFERENT AQUO-ORGANIC SOLVENTS

Organic solvent (w/w, %)	S_v			ϕ^0		
	I	II	III	I	II	III
10	1·08	1·23	1·35	26·00	25·35	24·50
20	1·12	1·20	1·41	25·30	24·25	23·86
30	1·00	1·36	1·48	26·30	22·35	23·23
40	1·03	1·45	1·55	26·70	21·45	22·56
50	1·19	1·51	1·63	25·50	20·75	21·20

The value of ϕ^0 in water at 25° is 26·81 (ref. 17).
I = acetone-water; II = dioxane-water and III = methyl alcohol-water.

The different A values for different mixed solvents indicates its dependence on ionic interaction (Table 1). The values of A in different solvents follow the order: MeOH-H$_2$O > dioxane-H$_2$O > acetone-H$_2$O. It is also seen that the A values increase with the increase in organic solvent in the solvent mixture. This may be attributed to the change in the mobility of the ions with a change in the dielectric constant of the medium.

According to Stokes and Mills[14], the viscosity of the dilute electrolyte solution incorporate that of the solvent plus the contribution from three other factors, viz. η^E the viscosity increase due to the shape and size of an ion; η^A the increase due to the alignment or orientation of the polar molecules by the ionic field and η^D the decrease in viscosity due to the distortion of the solvent structure by the ions. In the present case the B values are always positive except for MeOH-H$_2$O mixtures (10, 20 and 30% and where it is zero, B values increase in the order acetone-H$_2$O > dioxane-H$_2$O > MeOH-H$_2$O. Potassium ion with greater crystal radii and smaller charge density would have a weak orienting effect in the first layer. Therefore, η^E and η^A will be small. Hence positive B value indicates that the amount of distortion in the vicinity of such ions, due to the competition between the ionic field and bulk structure is small and consequently η^D will be small. Thus when $\eta^E + \eta^A > \eta^D$, B will be positive. Since B in acetone-H$_2$O is more than in dioxane-H$_2$O, η^D in acetone-H$_2$O is smaller than in dioxane-H$_2$O and in the case of MeOH-H$_2$O mixtures, i.e. up to 30%, $\eta^E + \eta^A = \eta^D$, and hence B is zero. At 40 and 50%, ions start orienting the solvent molecules and $\eta^E + \eta^A$ will begin to increase and so B values increase. In the case of acetone-water and dioxane-water, the B values increase with the increase in the organic solvent content. This may be explained as follows: Addition of small amount of acetone and dioxane enhances the solvent structure, consequently the contribution from $\eta^E + \eta^A$ increase, thereby increasing B values.

Apparent molal volume (ϕ) — The ϕ values calculated from the equation

$$\phi = M/\rho_0 - \left(\frac{\rho - \rho_0}{\rho_0}\right) \times 10^3/C$$

were found to vary linearly with $C^{\frac{1}{2}}$ according to Masson's equation. Masson's plot in different aquo-organic mixtures containing 10% organic components were linear and the values of the limiting apparent molal volume (ϕ^0) in acetone-water, dioxane-water and methyl alcohol-water mixtures at different solvent compositions obtained from the extrapolation of the plot of ϕ versus $C^{\frac{1}{2}}$ to zero concentration are summarised in Table 2 along with the limiting slope (S_v). The limiting experimental slope is positive suggesting electrostatic ion-ion interaction. If the dielectric constant of the solvent is not very high as in mixed solvent or if it is fairly high as in water, and the ions are small, the electrostatic ion-ion interaction will be appreciable and an ion will have strong influence on its neighbour if actual association does not occur. Ion association may be expected in mixed solvents like acetone-H$_2$O, dioxane-H$_2$O and MeOH-H$_2$O but in pure water actual association is very unlikely at moderate concentrations. This effect coupled with ion-solvent interaction seems to be responsible for the positive slope in the ϕ versus $C^{\frac{1}{2}}$ plots in these systems. Also it can be noted from Table 2 that as the dielectric constant decreases with the increase in organic solvent, the S_v values also increase slightly. The S_v values of the three systems are almost same as the dielectric constant do not differ much[15,16] and hence the ion-ion interaction is almost the same.

Further the limiting apparent molal volume (ϕ^0) is found to be dependent on the dielectric constant of the medium as the plot of ϕ^0 versus $1/\epsilon$ is linear and the slope of the plot is of the order MeOH-H$_2$O > dioxane-H$_2$O > acetone-H$_2$O, indicating the order of ion-solvent interaction and solvation. There is strong hydrogen bonding in MeOH and least in acetone and dioxane is in between these two. Hence it can be stated that the ion-solvent interaction increases with the increase in ability of the organic solvent to form hydrogen bond.

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Ion–Solvent Interaction Studies of Chlorides, Bromides & Nitrates of Sodium & Potassium in Dioxane-Water Mixtures at Different Temperatures

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The viscosities of NaCl, NaBr, NaNO₃, KCl, KBr and KNO₃ in 10, 20 and 30% dioxane-water mixtures (w/w) have been measured at 30°, 35°, 40° and 45° and the results analysed in terms of Jones-Dole equation: $\eta_r = 1 + AC^{\frac{1}{2}} + BC$. The coefficients A and B have been obtained graphically from the plot of $\eta_r - 1/C^{\frac{1}{2}}$ versus $C^{\frac{1}{2}}$.

IN continuation of our earlier work[1] on the viscosity of electrolyte solution in aquo-organic mixtures, the viscosity of NaCl, NaBr, NaNO₃, KCl, KBr and KNO₃ in different dioxane-water mixtures have been measured at 30°, 35°, 40° and 45° and the data analysed on the basis of Jones-Dole equation[1] to know the nature of ion-ion and ion-solvent interaction in solution[2-8].

All the salts used were of E. Merck (extra pure) quality. The viscometric apparatus and technique were similar to those employed by Chackravarty and Prasad[9]. The densities of the solvents and solutions were determined with a pycnometer (50 ml) with buoyancy correction and were the same as those of Srinivasan and Prasad[10]. Necessary precautions were taken to prevent evaporation of the solvent[11]. The viscosities of the electrolyte solutions were measured in the dioxane-water mixtures containing 10, 20 and 30% of dioxane (w/w). The concentration range was from 0·1 to 0·001M.

From the conductance measurements (unpublished) electrolytes were found to be almost completely dissociated and hence the modified equation proposed by Das[12] was not applicable. The results have been analysed in terms of Jones-Dole equation since the plots of $\eta_r - 1/C^{\frac{1}{2}}$ versus $C^{\frac{1}{2}}$ were linear. The intercepts and the slopes of the plots gave respectively the coefficients of A and B. The coefficient B thus obtained for various salts at different temperatures are given in Table 1. The calculated values[13] of A are in good agreement with the experimental values. The relative viscosity values calculated from the values of A and B thus obtained are found to be in fair agreement with the experimental values.

The values of A coefficients for different electrolytes are positive indicating dependence of ionic interactions on the nature of the electrolytes. The radii of the anions Cl⁻, Br⁻ and NO₃⁻ are almost of the same order[14]. Hence the ion-ion interaction is expected to be same and this is found to be true. The electrostatic ion-ion interaction and hence the value of A is found to increase with the decrease in dielectric constant of the medium, i.e. with an increase in dioxane content in the solvent mixture. As expected the values of A decrease with the rise in temperature for all the salts.

According to Stokes and Mill[4], the viscosity of a dilute electrolytic solution incorporates that of the solvent plus the contribution from other factors viz. (i) η^E, the positive increase due to the shape and size of an ion (ii) η^A, the increase due to the alignment or orientation of the polar molecules by the ionic field and (iii) η^D, the decrease in the viscosity due to distortion of the solvent structure by the ions. Therefore the B coefficients can also be discussed in terms of the viscosity effects at different temperatures. With increase in temperature, η^D decreases because the competition between ionic field and bulk structure is less. η^E remains fairly constant and η^A decreases slowly, so that B is positive. The negative temperature coefficient of B is due to the fact that the oriented solvent molecules in the secondary layer will be less rigidly held due to the increased thermal motion. This will give a significant decrease in the value of η^A. Also with increase in temperature, the water structure is broken down and the fluidity is increased (i.e. η^D is large). The mobility of the ion to the first approximation is dependent on the fluidity of the medium in its immediate surroundings and hence there is a decrease in the B value.

In the present case, the B coefficients of the salts containing Cl⁻ and NO₃⁻ increase with the increase in temperature (though the increase is less in case

TABLE 1 — VALUES OF COEFFICIENT B AT DIFFERENT TEMPERATURES AND [DIOXANE]

Temp. °C	$B \times 10^2$ in dioxane-water mixtures (%, wt/wt)					
	10	20	30	10	20	30
	NaCl			KCl		
30	8·1	10·0	15·5	1·9	3·4	4·8
35	9·1	11·2	16·6	2·0	4·0	5·2
40	14·0	15·0	20·0	3·3	5·0	6·1
45	15·0	16·2	22·0	3·6	5·8	6·9
	NaBr			KBr		
30	9·7	12·0	15·1	2·8	4·7	5·1
35	11·5	12·4	17·0	3·4	5·1	6·2
40	6·6	11·2	14·5	2·2	6·2	5·8
45	6·5	10·8	13·7	2·1	5·1	5·6
	NaNO₃			KNO₃		
30	7·1	9·6	13·0	1·1	3·2	4·2
35	8·5	10·9	14·2	1·5	3·9	5·0
40	10·2	11·5	15·3	1·8	4·3	5·7
45	11·2	12·5	16·0	1·9	4·7	6·1