Ion-solvent interaction from viscosity, apparent molar volume and conductivity data of bromates, iodates and sulphates of potassium and sodium in dioxane-water mixtures at different temperatures

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Summary. The viscosity, apparent molar volume and conductivity of $KBrO_3$, $NaBrO_3$, KIO_3, $NaIO_3$, K_2SO_4 and Na_2SO_4 at mass fraction of dioxane (10, 20 and 30%) - water mixtures at 30-45 °C$\pm$0.01 °C have been measured. The ions appear to interact and the ion-solvent interaction is of the order $BrO_3^- > IO_3^- > SO_4^{2-}$.

Viscosity[2], apparent molar volume[2], conductivity[3], activity coefficients[4-6] etc. have been utilised to study ion-solvent interaction of various salts in aqueous and nonaqueous solutions. In the present investigation, viscosity, apparent molar volumes and conductivity of $KBrO_3$, $NaBrO_3$, KIO_3, $NaIO_3$, K_2SO_4 and Na_2SO_4 solutions at mass fraction of dioxane (10, 20 and 30%) - water mixture at 30, 35, 40 and 45 °C$\pm$0.01 °C have been studied, and an attempt has been made to deal with the nature of the ion-solvent interaction and to see the effect of the dielectric constant, temperature and hydrogen bonding on the above properties.

Materials and methods. All the salts used were of E. Merck, extra-pure varieties. The apparatus, technique, preparation of solvents, and solutions were the same as that of Das et al.[2,3]. The concentration range for viscosity and apparent molar volume was from 0.1 to 0.001 moles l^{-1} and 0.01 to 0.001 moles l^{-1} for conductance measurements. The accuracy of the period of flow is 0.2 sec in 20 min. The density data are accurate upto 4 in 10^6. Conductance measured was of an accuracy of $\pm$2 in 1000.

Results and discussions. Viscosity: The viscosity data were analyzed in terms of Jones-Dole equation as the plot of $\zeta_r - 1/C^{1/2}$ vs $C^{1/2}$ is linear. The B values obtained from the slope are tabulated in table 1. According to Stokes and Mill[7], the viscosity of a dilute electrolytic solution incorporates that of the solvent plus the contribution from other sources. They are ζ^E, the positive increase due to the shape and size of an ion; ζ^A, the increase due to the alignment or orientation of the polar molecules by the ionic field and ζ^D, the decrease in the viscosity arising due to the distortion of the solvent structure by the ions. Therefore, B-coefficient can be discussed in terms of these viscosity effects at different temperatures.

The B-coefficients of all the 6 salts increases with the increase in temperature. This indicates that the viscosity decrease due to the solvent structure, i.e., ζ^D is small and hence $\zeta^E + \zeta^A > \zeta^D$ and B is positive. The B value is found to be of the order: $SO_4^{2-} > IO_3^- > BrO_3^-$. The lesser the value of B, the greater is the distortion and hence the ion-solvent interaction. So the ion-solvent interaction is of the order: $BrO_3^- > IO_3^- > SO_4^{2-}$.

Apparent molar volume (Φ): The Φ values calculated in the usual manner[2] were found to vary linearly with $C^{1/2}$. The values of limiting apparent molar volume ($\Phi°$) obtained from the extrapolation of the above plot are reported in table 2. The $\Phi°$ increases with the increase in temperature. This can be explained as follows: The ion-dipole interaction energy in case of dioxane-water mixtures is appreciable[8] and the attachment of the solvent molecules to the ions may not be loose, and at the same time no structure formation would occur around the ion[9]. The net result will be stronger solvation.

This $\Phi°$ has been found to be linear with temperature and

Table 1. B/l · $mole^{-1}$

Mass fraction of dioxane	10%	20%	30%	10%	20%	30%
Temperature in °C	$KBrO_3$			$NaBrO_3$		
30	0.030	0.042	0.062	0.065	0.089	0.104
35	0.043	0.059	0.078	0.089	0.109	0.119
40	0.058	0.076	0.098	0.104	0.122	0.134
45	0.074	0.092	0.114	0.122	0.138	0.146
	KIO_3			$NaIO_3$		
30	0.120	0.145	0.165	0.185	0.212	0.252
35	0.152	0.164	0.175	0.210	0.235	0.264
40	0.165	0.185	0.220	0.235	0.255	0.281
45	0.185	0.205	0.245	0.263	0.278	0.295
	K_2SO_4			Na_2SO_4		
30	0.248	0.275	0.348	0.262	0.291	0.385
35	0.280	0.300	0.380	0.300	0.325	0.410
40	0.305	0.330	0.415	0.330	0.352	0.438
45	0.330	0.358	0.434	0.360	0.378	0.448

Table 2. ∅°/cm^3 · $mole^{-1}$

Mass fraction of dioxane	10%	20%	30%	10%	20%	30%
Temperature in °C	$KBrO_3$			$NaBrO_3$		
30	132.0	138.8	145.6	109.8	115.4	120.8
35	135.3	140.4	147.0	111.2	116.5	121.2
40	137.2	142.5	148.8	112.4	117.0	121.2
45	138.4	143.8	150.6	113.5	118.8	122.0
	KIO_3			$NaIO_3$		
30	166.3	169.3	174.5	130.5	133.0	137.1
35	170.0	173.4	178.0	132.2	135.3	139.0
40	172.8	176.4	182.0	134.2	137.9	141.0
45	175.8	179.0	183.9	135.5	139.6	142.4
	K_2SO_4			Na_2SO_4		
30	123.3	124.4	126.1	71.5	74.2	77.9
35	125.0	125.5	127.0	74.5	76.0	79.5
40	126.3	127.0	129.1	77.2	78.0	81.5
45	128.3	129.0	131.2	79.5	81.0	82.5

Table 3. $\Lambda°\zeta/\Omega^{-1} \cdot cm^2 \cdot poise$

Mass fraction of dioxane	10%	20%	30%	10%	20%	30%
Temperature in °C	$KBrO_3$			$NaBrO_3$		
30	1.171	1.150	1.151	1.057	1.043	1.039
35	1.162	1.151	1.097	1.055	1.041	1.037
40	1.154	1.154	1.140	1.042	1.045	1.032
45	1.159	1.146	1.140	1.051	1.033	1.028
	KIO_3			$NaIO_3$		
30	1.266	1.253	1.245	1.153	1.146	1.137
35	1.259	1.254	1.244	1.149	1.154	1.138
40	1.251	1.257	1.245	1.139	1.149	1.136
45	1.256	1.249	1.248	1.148	1.136	1.136
	K_2SO_4			Na_2SO_4		
30	1.539	1.507	1.367	1.425	1.400	1.259
35	1.522	1.510	1.489	1.423	1.400	1.264
40	1.523	1.495	1.489	1.412	1.387	1.380
45	1.527	1.505	1.492	1.420	1.393	1.381

the decrease of $d\Phi^\circ/dt$ is of the order: $BrO_3^- > IO_3^- > SO_4^{2-}$. Strong electrostatic solvation (primary solvation) is responsible for the decrease of $d\Phi^\circ/dt$[10,11]. So the ion-solvent interaction is of the order: $BrO_3^- > IO_3^- > SO_4^{2-}$.

Further the plot of Φ° vs $1/\varepsilon$ (ε, the reciprocal of the dielectric constant) is found to be linear for all the salts. The slope of the lines are of the order $BrO_3^- > IO_3^- > SO_4^{2-}$.

Conductance. The equivalent conductance of all the 6 salts are found to be linear with $C^{1/2}$, which indicates that the Debye-Huckel-Onsager theory of electrolytic conductivity is applicable to these ions. The walden product $\Lambda^\circ\zeta_0$, which can be employed for the study of ion-solvent interaction is recorded in table 3. The plots of $\Lambda^\circ\zeta_0$ vs temperature are found to be linear and negative temperature coefficient is observed. This suggests[12,13] that the ion-solvent interaction is of the order: $BrO_3^- > IO_3^- > SO_4^{2-}$ and is in accordance with that of viscosity and apparent molar volume measurements.

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Protein methylase from calf liver nuclei: Enzyme characterization and stimulation by serum albumins

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Summary. A protein methylase from calf-lifer nuclei was partially purified by sonication of the nuclear pellet at high ionic strength, chromatin removal and ammonium sulphate fractionation of the solubilized activity.

Enzymic methylation is one of the post-synthetic modifications of macromolecules. Methylation of a protein is a common biochemical reaction occurring on different substrates and catalyzed by different enzymes[3]. Utilizing S-adenosyl-L-methionine, a common donor in methylation reactions, it is possible to methylate the guanidino groups of arginine[4], the carboxyl groups of dicarboxylic amino acid residues[5,6] and the ε-amino group of lysine of proteins[7]. The significance of protein methylation is not clear as yet; however, naturally occurring macromolecules are modified differently after their primary structures are established. Acetylation, and phosphorylation of proteins are some other examples of these modification phenomena.

This paper reports the characteristics of a partially purified protein methylase which methylates its endogenous protein. The enzyme activity has a pH optimum of 8.0 and a K_m of 0.95×10^{-5} M for S-adenosyl-L-methionine, and is stimulated by bovine and human serum albumins.

Experimental. Materials and methods. Fresh calf liver: from the local slaughter-house. S-adenosyl-L-[Me^{14}C]methionine, sp.act. 55 mCi/mmole, in dilute sulphuric acid (pH 3.5): from the Radiochemical Centre, Amersham. Crystallized bovine serum albumin and human serum albumin were from Pentex, Kankakee (Illinois, USA). Glutamate dehydrogenase and phosphoglucomutase: from Boehringer, Mannheim (Germany). Carboxypeptidase A: from Worthington (New Jersey, USA). Lysozyme: from Schwarz/Mann, New York (USA). γ-globulins from rabbit, chicken and hog: from NBC, Cleveland (Ohio, USA). All other chemicals used were of analytical grade quality. Sonication was carried out with a Branson model 5-177A sonicator (Branson Sonic Power, USA).

Buffers. Buffer A: 20 mM Tris-HCl pH 7.9, 10 mM $MgCl_2$, 1.66 M sucrose, 10 mM dithiothreitol; buffer B: 50 mM Tris-HCl pH 7.9, 25% (v/v) glycerol, 5 mM $MgCl_2$, 0.10 mM EDTA, 2 mM dithiothreitol; dialysis buffer: 20 mM $(NH_4)_2SO_4$ in buffer B.

Preparation of nuclei. Nuclei were isolated by continuous flow ultracentrifugation in high density sucrose as described elsewhere[8].

Protein determination. Protein was determined by one of the following procedures: the method of Lowry et al.[9] and the turbidimetric method of Layne[10], using crystalline potassium ferricyanide. Nucleic acids were determined spectrophotometrically at 260 nm.

Assay of protein methylase activity. The enzymic activity was expressed as pmoles of the methyl groups incorporated into an acid precipitable product/min/mg of added pro-

Table 1. Partial purification of protein methylase from calf liver

	Protein (mg/ml)	Total protein (mg)	Specific activity*	Total activity	Purification (-fold)	Yield (%)
Intact nuclei	160	26,900	2.82	75,800	1	100
Lysed nuclei	48	5,130	11.2	57,600	4	76
Supernatant I	10	2,900	16.0	46,400	5.7	61
Supernatant II	57	1,250	34.1	42,600	12.1	56

For assay conditions see Materials and methods. Values are given for 1600 g of calf liver. * pmoles of methyl groups incorporated into an acid insoluble product/min/mg of protein