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THERMODYNAMICS OF ADENINE BASE IN DIOXANE–WATER MIXTURES FROM ULTRASONIC, VISCOSITY AND VOLUMETRIC STUDIES AT 20, 25, 30 AND 35°C

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ABSTRACT

Ultrasonic, volumetric and viscometric investigations have been conducted on adenine base at four different temperatures, 20, 25, 30 and 35 ± 0.01°C. The partial molal volume ϕ_v^0, partial molal compressibility ϕ_k^0, the viscosity coefficient B of the Jones–Dole equation and the solute activation parameters $\Delta\mu^*$, ΔS^* and ΔH^* have been calculated. Attempts have been made to explain the changes in water structure when a co-solvent is added. Results show that the adenine base is less effective in dioxane–water mixtures than in water alone. Further results of viscosity are tested in terms of transition state theory.

INTRODUCTION

Nucleic acid bases belong to one of the most important classes of substances in molecular biology [1]. Ultrasonic studies of the conformational properties of these molecules, the interactions of their various chemical groups with water molecules in aqueous solution and in dioxane–water mixtures and the temperature dependence of these interactions plays a very important role in understanding the thermodynamics of many biochemical processes involving in such species.

In recent years, active interest has been shown in solute–solvent and solute–solute interactions, which are determined by the chemical structure of solute and solvent molecules. Ultrasonic studies are mostly limited to obtaining the hydration number [2–4]. However, Hemmes et al. [5–7] have made successful attempts to study the dependence of solute–solvent interactions on the chemical structure of nucleic acid derivatives.

The electrochemical behaviour of uracil base and the thio and other derivatives has been studied by polarography [8–10], cyclic voltametry

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[11–12], coulometry [13], potentiometry [14–15] and conductimetric pulse radiolysis techniques.

Further, the interaction of bivalent metal ions with uracil, thymine and cytosine have been investigated potentiometrically [16–19].

Several studies on electrolytes and non-electrolytes have been conducted on the solution properties of dioxane–water mixtures [20], since dioxane is particularly suitable for biophysico-chemical processes as it is miscible in all proportions with water and has a relatively high dielectric constant.

The viscosity coefficient *B* for many electrolytes and non-electrolytes (sugars) in dioxane–water mixtures has been reported by Das et al. [21–22]. *B* in the Jones–Dole equation shows that the dioxane–water system breaks down the water structure.

The ion–solvent interaction for electrolytes in water–sulpholane mixtures has been investigated by a viscometric method, and the *B* coefficient of the Jones–Dole equation and the solute activation parameter using Feakins transition state theory have been calculated by Sacco et al. [23]. Results show that the presence of electrolytes in the mixture leads to a breakdown of the three-dimensional water structure at a 0.21 mole fraction of sulpholane.

In the present communication we report the result of volumetric, ultrasonic and viscometric studies on adenine base in dioxane–water mixtures at four different temperatures; 20, 25, 30 and 35 ± 0.01°C. From the above data partial molal volume ϕ_v^0, partial molal compressibility ϕ_k^0, *B* (the coefficient of viscosity) and solute activation parameters have been calculated. Results show that adenine base is less effective in a co-solvent compared to water alone.

EXPERIMENTAL

The adenine used was of the "extra pure" variety. Purity was checked by paper and thin layer chromatography [24].

0.01 M adenine solution was prepared and ten solutions of different concentrations were prepared in double distilled water. Five solutions of 10, 30, 50, 70 and 90% mass fraction by weight were prepared in dioxane–water mixtures. The pH of solutions was maintained in the range 7–8 by a pH meter with a glass electrode. Dioxane (BDH, AR grade) was refluxed with sodium metal under a dry nitrogen atmosphere for 24 h and distilled immediately before use; the first and last 10% were discarded.

Density measurements were performed with a precalibrated pycnometer at 20, 25, 30 and 35 ± 0.01°C. The estimated error was found to be 0.005%.

From the density data, the apparent molal volume of adenine ϕ_v is calculated from eqn. (1)

$$\phi_v = \frac{1000(d_0 - d)}{md_0d} + \frac{M}{d} \tag{1}$$

where ϕ_v is the apparent molal volume of solute, d_0 and d are the densities of solvent and solution respectively, m is the molality and M represents the molecular weight of the solute.

ϕ_v is the linear function of concentration term according to Masson's equation [25]

$$\phi_v = \phi_v^0 + S_v^* \sqrt{C} \qquad (2)$$

where ϕ_v^0 is the partial molal volume at infinite dilution and is a measure of solute–solvent interaction. It is obtained from the linear plot of ϕ_v vs. $\sqrt{C}$ using the least-squares method. S_v^* is the experimental slope and a measure of solute–solute interaction.

Measurements of ultrasonic velocity were performed with an ultrasonic interferometer. Details of the apparatus are reported elsewhere [26].

Partial molal compressibility has been deduced from the isentropic apparent molar compressibility ϕ_k using eqn. (4)

$$\phi_{k(s)} = \frac{1000(\beta_s - \beta_0)}{md_0} + \phi_v \beta_s \qquad (4)$$

β_s, β_0 are the compressibilities of solution and solvent respectively, d_0 is the density of the medium, ϕ_v represents apparent molal volume and m is the molality of the solution in g l^{-1}. Partial molal compressibility ϕ_k^0 have been deduced from the linear plot of ϕ_k vs. $\sqrt{C}$. Accuracy in ultrasonic velocity measurements was $\pm 0.05\%$.

Viscosity measurements were carried out using a precalibrated Ostwald viscometer at 20, 25, 30 and 35 ± 0.01°C. A time of flow of water in the range of 50–230 s was selected. Different solutions of adenine base were prepared and placed in the viscometer such that the time of flow for the most dilute solution was always at least 25 s more than the time of flow for water. Each solution was measured 3–4 times and an average of these readings taken. This procedure ensures reproducibility of results and the final readings were an average of these two sets. To check the efficiency of the viscometer the data for sucrose solution at 30°C were compared with the literature. A correlation within 1% was recorded. However, the uncertainties of measured viscosities were within 0.03% at 30 ± 0.01°C. Ten solutions of adenine base in the concentration range 0.001–0.01 M were prepared in water and five solutions of mass fraction 10, 30, 50, 70 and 90% in dioxane–water have been analysed in terms of the Jones–Dole equation (5)

$$\eta/\eta_0 = 1 + A\sqrt{C} + BC \qquad (5)$$

where η/η_0 is the viscosity of the adenine solution relative to that of the solvent. A and B are constants characteristic of the electrolyte. A represents the contribution from interionic electrostatic forces and B measures the order or disorder introduced by ion into the solvent structure. This constant is specific and an approximately additive property of ions of an electrolyte at a given temperature, although no satisfactory theoretical treatment has yet been given. On plotting $(\eta/\eta_0 - 1)/\sqrt{C}$ vs. $\sqrt{C}$ the coefficients A and B can be obtained [29].

Viscosity data have further been utilized for the calculation of solute activation parameters [30]. The free energy of activation for viscous flow is given by [31,32]

$$\Delta\mu^* = RT \ln \frac{V}{hN}$$

where h is the Planck constant and N is the Avogadro number. V may be regarded as the volume of one mole of solute particles and is given by

$$V = \frac{1000}{n_1 + \nu_{n_2}} \text{cm}^3$$

where ν is the number of species into which a solute molecule dissociates and n_2 is the number of moles of solute per litre of solution. The number of moles n_1 of solvent per litre of solution is given by

$$n_1 = \frac{1000\rho - n_2 M_2}{M_1}$$

where M_1 and M_2 are the molecular weights of solvent and solute respectively. Furthermore, by measuring B at different temperatures, enthalpies and entropies of activation can be obtained using equations

$$\Delta S^* = -\mathrm{d}(\Delta\mu^*)/\mathrm{d}T$$

and

$$\Delta H^* = \Delta\mu^* + \Delta S^*$$

RESULTS AND DISCUSSION

Calculated values of apparent molal volumes ϕ_v from density data have been found to be in agreement with Masson's equation, as the plot of ϕ_v vs. $\sqrt{C}$ is linear. Calculated values of partial molal volume ϕ_v^0 are summarized in Tables 1 and 2. Results show that the values increase considerably with temperature. ϕ_v^0 values in the dioxane–water system are comparatively low compared to those of pure water; this is attributed to the fact that dioxane penetrates the three-dimensional structure of water. Negative values of ϕ_v indicate that this severely restricts molecular motion within the solution. However, this significant type of behaviour is not proven.

S_v^* values obtained from the slope of ϕ_v vs. $\sqrt{C}$ are incorporated in Table 3 together with the values of partial molal volumes. Results of the experimental slope S_v^* revealed that solute–solute interaction increases with rise in temperature. Values are comparatively low in dioxane–water system com-

TABLE 1

Partial molal volumes (ϕ_v^0) of adenine base in water at different temperatures

Concentration (mol l^{-1})	$-\phi_v^0(\times 10^2$ ml mol$^{-1})$			
	20°C	25°C	30°C	35°C
0.001	137.01	200.03	204.04	218.04
0.002	137.02	200.03	204.06	218.06
0.003	137.05	200.04	204.07	218.07
0.004	137.06	200.05	204.08	218.08
0.005	137.07	200.06	204.09	218.09
0.006	137.08	200.06	204.09	218.10
0.007	137.08	200.07	204.10	218.11
0.008	137.09	200.07	204.11	218.12
0.009	137.09	200.08	204.12	218.12
0.01	137.10	200.08	204.13	218.14

TABLE 2

Partial molal volume (ϕ_v^0) of adenine base in water–dioxane mixtures at different temperatures and mass fractions of dioxane

Temperature (°C)	Mass fraction of dioxane (%)				
	10	30	50	70	90
20	32.01	32.02	32.03	32.05	32.10
25	53.02	53.04	53.06	53.08	53.17
30	98.03	98.05	98.07	98.12	98.23
35	126.04	126.08	126.12	126.19	126.37

TABLE 3

Experimental slope S_v^* for adenine base at different temperatures

Temperature (°C)	S_v^*	
	Adenine–water–dioxane	Adenine–water
20	0.3448	0.4500
25	0.5714	0.8200
30	0.7692	1.2700
35	1.2500	1.3600

pared to water alone, which indicates that any adenine–adenine interaction is maximum at 35°C in the adenine–water system.

Partial molal compressibilities ϕ_k^0 obtained from the linear plot of ϕ_k vs. $\sqrt{C}$ are shown in Table 4 for various temperatures. Results show that the values are comparatively high in dioxane–water compared to water alone. Negative

TABLE 4

Partial molal compressibility ϕ_k^0 of adenine base at different temperatures

Temperature (°C)	ϕ_k^0 (ml mol^{-1} bar^{-1} $\times 10^{-2}$)	
	Adenine–water–dioxane	Adenine–water
20	−182	−21
25	−240	−32
30	−260	−34
35	−312	−38

values of ϕ_k^0 are attributed to loss of structural compressibility of the solvent molecules due to the increased population of four-bonded water molecules in the water–dioxane mixture i.e. structural disruption is less effective in the water–dioxane mixture than water alone [27,28]. The results in Table 4 show a greater loss of structural compressibility for water, implying a greater ordering effect by adenine on the dioxane–water system.

Viscosity data are analysed in terms of Jones–Dole equation. Values of B are displayed in Table 5 for four different temperatures. Positive B values indicate a strong alignment of solvent molecules with ions, which reveals the "structure forming" behaviour of water. B values decrease with rise in temperature showing that ion–solvent interactions are influenced gradually by temperature. The behaviour of adenine in the dioxane–water mixture can be analysed by observing the B value. Table 5 reveals that the adenine base in the mixture has a low positive B value and is slightly influenced by variation in temperature between 20–35°C. Therefore, we can state that positive B values for adenine base are due exclusively to anions. For this reason, ions present in the solution of adenine are defined as "structure maker". On the other hand, the behaviour of adenine in dioxane–water systems shows a lower value of B indicating that it is strongly solvated in dioxane and behaves as a "structure maker". On the basis of the behaviour of adenine in water and in dioxane mixtures, the noticeable decrease in B observed for all mixtures as the percentage of dioxane increases can be

TABLE 5

Coefficient B of the Jones–Dole equation for adenine base at different temperatures

Temperature (°C)	B (mol^{-1})	
	Adenine–water–dioxane	Adenine–water
20	0.661	1.20
25	0.550	1.17
30	0.500	0.514
35	0.100	0.439

explained by supposing that interaction between ion–dioxane molecule becomes more and more important.

This type of behaviour can be explained if one bears in mind that the structure making ability of adenine generally increases with increasing size of solvent molecule, and if one assumes that dioxane can "form" the water structure. Thus, as the percentage of dioxane in the solvent increases, the adenine becomes a more effective structure maker.

The analysis of solute activation parameters are presented in Tables 6 and 7. Results reveal that ΔS^* and ΔH^* are negative for dioxane–water systems and increase gradually with increase in the percentage of water–dioxane present. This indicates that in mixtures of water–dioxane the average transition state is associated with bond making and increases in order. On the other hand, with an increase in the percentage of dioxane, the values of ΔH^* and ΔS^* are increasingly less negative. In the latter case and with 90% dioxane–water mixture we can suppose that the transition state for viscous flow is accompanied by the breaking and distortion of intermolecular bonds. However, irregular changes in values of the adenine base activation parame-

TABLE 6

Activation parameters for adenine base in dioxane–water mixtures at four temperatures

% Wt. (Dioxane–water)	Temperature (°C)	$\Delta\mu^*$ (kcal)	$-\Delta S^*$ (kcal)	$-\Delta H^*$ (kcal)
10	20	15.59	77.41	6.51
	25	15.79	77.72	6.56
	30	16.07	77.52	7.30
	35	16.00	78.24	7.38
30	20	15.69	85.81	9.55
	25	15.95	86.33	9.72
	30	16.23	86.34	9.93
	35	16.13	86.94	10.27
50	20	15.90	96.25	12.30
	25	16.10	96.71	12.71
	30	16.41	97.23	13.74
	35	16.35	97.53	13.59
70	20	16.12	97.95	13.0
	25	16.65	98.63	13.44
	30	16.32	99.93	13.89
	35	16.57	99.43	14.37
90	20	16.36	113.67	16.94
	25	17.41	114.68	16.76
	30	16.90	115.69	18.15
	35	16.91	115.79	18.75

TABLE 7

Activation parameters for adenine base in water

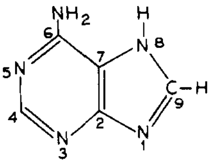
Concentration (mol/l^{-1})	Temperature (°C)	$\Delta\mu^*$ (kcal)	$-\Delta S^*$ (kcal)	$-\Delta H^*$ (kcal)
0.001	20	15.34	75.31	6.58
	25	15.52	75.33	6.72
	30	15.69	75.42	6.75
	35	15.88	75.42	6.92
0.002	20	15.36	75.49	6.97
	25	15.56	75.66	7.13
	30	15.69	75.71	7.18
	35	15.88	75.84	7.41
0.003	20	15.36	79.22	7.82
	25	15.57	79.79	8.15
	30	15.76	80.19	8.45
	35	15.95	80.84	8.54
0.004	20	15.36	81.57	8.69
	25	15.57	81.81	8.81
	30	15.76	81.81	8.84
	35	15.96	82.01	8.88
0.005	20	15.56	82.35	8.97
	25	15.58	82.35	9.09
	30	15.76	82.55	9.14
	35	15.97	83.98	9.22
0.006	20	15.37	82.79	9.25
	25	15.58	83.06	9.37
	30	15.77	83.22	9.40
	35	15.97	83.24	9.48
0.007	20	15.37	83.95	9.64
	25	15.58	84.18	9.67
	30	15.79	84.38	9.76
	35	15.99	84.60	9.91
0.008	20	15.38	85.35	9.95
	25	15.60	85.69	10.05
	30	15.80	85.95	10.28
	35	16.00	86.25	10.95
0.009	20	15.38	94.66	12.36
	25	15.61	95.13	12.75
	30	15.81	95.50	12.94
	35	16.02	96.00	13.01
0.01	20	15.39	95.26	13.16
	25	15.62	95.72	13.36
	30	15.84	96.21	13.59
	35	16.05	96.67	13.78

ters found in water–dioxane mixtures confirms the structure enhancement of water by the addition of dioxane. In fact, when the water structure is increased by addition of co-solvent, maxima or minima for values of the activation parameters of viscous flow are obtained, as observed for electrolytes in water–methanol and water–acetone systems.

Free energy of activation $\Delta\mu^*$ are recorded in Tables 6 and 7. The results show positive values at all solvent compositions and at all temperatures, indicating that adenine is a higher free energy state in dioxane–water mixtures than in water alone, suggesting that water has more affinity for adenine than in a water–dioxane mixture. Similarly, other activation parameters for adenine base, such as ΔH^* and ΔS^*, show negative values at all solvent compositions of dioxane–water, thereby suggesting that entropies in dioxane–water mixtures are less effective than pure water and hence the net order created by salts in a dioxane–water mixture is greater than in pure water.

EFFECT OF CO-SOLVENT ON ADENINE BASE

Adenine is a weak base and less acidic than water because of the electron-releasing tendency of the amino group at position 6 and the free nitrogen present at positions 1, 3, 5 and 8. Similarly, dioxane is also more basic and less acidic than water i.e. the methylene group is electron-releasing, and therefore the water molecule forms a hydrogen-bond with the oxygen of dioxane and also with the nitrogen of the adenine base. The addition of adenine base to the dioxane–water mixture leads to the conclusion that adenine is less effective at disrupting the structure of the solution because of H-bonding with the oxygen of dioxane and with the nitrogen of adenine, and therefore a comparatively strong interaction compared to water alone. Hence the adenine molecule is stable in a mixture of co-solvents.



Adenine base

In conclusion, dioxane has two main effects;

(i) If dioxane is accommodated in the solvent structure it may strengthen the water structure as it is a better proton acceptor.

(ii) If dioxane cannot be accommodated because of its bulky size, then it may cause a breakdown of the three-dimensional water structure.

It is seen from the above studies that the values of ϕ_v^0, ϕ_k^0 and the coefficient B are lower in the dioxane–water mixture, and it is concluded, therefore, that dioxane does not disrupt the three-dimensional water structure as dioxane is better proton acceptor. Therefore, the additivity rule is expected to hold good in the water–dioxane system.

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