

Thermochemical and sonochemical studies of adenosine–H₂O–DMSO–Ca²⁺/K⁺ systems

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Abstract. Ultrasonic, volumetric and viscometric investigations have been conducted on adenosine base at three different temperatures 303·15, 308·15 and 313·15 K. 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 ΔU , ΔS and ΔH have been calculated. An attempt has been made to explain the changes in water structure when a co-solvent is added. Further, the results of viscosity experiments are tested in terms of transition state theory.

Keywords. Adenosine base; transition state theory; thermodynamic parameters.

1. Introduction

During recent years ultrasonic, volumetric and viscometric techniques have gained much importance in the study of the solution thermodynamics and molecular interactions of biomolecules in aqueous solutions^{1–9}. Some workers^{10–18} have extended such studies to aqueous solutions containing co-solvents such as dioxane, DMSO etc. A number of interesting and useful thermodynamic parameters have been deduced from the experimental values of ultrasonic velocity, density and viscosity. These studies have been extended to aqueous solutions of biomolecules containing ions of salts like Na⁺, K⁺, Ca²⁺ and Mg²⁺¹⁹. We wished to study the various interactions occurring in multicomponent systems containing biomolecules and metal ions in mixed solvents using ultrasonic, volumetric and viscometric techniques. The results obtained are presented here. Earlier^{11,14}, we have reported the results of ultrasonic, volumetric and viscometric studies of adenosine¹¹ and AMP, ADP and ATP¹⁴ in water and water + dioxane mixture. In the present study, the behaviour of adenosine in DMSO–water mixture in presence of K⁺ and Ca²⁺ ions has been compared in terms of ultrasonic, volumetric and viscometric studies at 303·15, 308·15 and 313·15 K. Interaction coefficients (Q), molar volume (V), apparent molal volume (ϕ_v^0), apparent molal compressibility (ϕ_k^0), and Jones–Dole viscosity B coefficient using transition state theory have been deduced.

2. Experimental

Adenosine was supplied by Sigma Chemicals. DMSO was of AR quality and purified before use. KCl used was anhydrous Baker Analysed reagent. 0·01 H of adenosine

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solution was prepared in DMSO. KCl and CaCl₂ stock solutions were prepared in double distilled water. Two sets of ten solutions of adenosine with electrolytes were prepared by varying the composition from 10–75 weight percent of DMSO. These sets A and B consisted of adenosine–DMSO–water in presence of Ca²⁺ and K⁺ respectively.

3. Equations used

Apparent molal volume, ϕ_v , has been calculated using

$$\phi_v = \frac{1000(d_0 - d)}{m \cdot d_0} + \frac{M}{d_0}, \quad (1)$$

where d is the density of the solution, d_0 the density of solvent and m is the molality of the solute. M is the molar mass of solute. Further, (1) can be rewritten as

$$\phi_v = \frac{10(V - V_0)}{m + VM}. \quad (2)$$

The apparent molal volume (ϕ_v^0) at infinite dilution has been obtained using (3) and (4)

$$\phi_v = \phi_v^0 + S_v C^{1/2}, \quad (3)$$

$$\phi_v = \phi_v^0 + S_v I^{1/2}. \quad (4)$$

Isentropic compressibility (k_s) has been obtained from sound velocity (u) and density (d) data using

$$k_s = (u^2 d)^{-1}. \quad (5)$$

Apparent molal compressibility, ϕ_k , is computed using

$$\phi_k = \frac{1000(d_0 K_s - d K_0)}{c \cdot d \cdot d_0} + \frac{K_s M}{d_0}, \quad (6)$$

where K_s and K_0 are the isentropic compressibility coefficients of solution and solvent respectively.

Apparent molal compressibility at infinite dilution, ϕ_k^0 , has been obtained from

$$\phi_k = \phi_k^0 + S_k C^{1/2}, \quad (7)$$

$$\phi_k = \phi_k^0 + S_k I^{1/2}, \quad (8)$$

where I is the ionic strength.

Relative viscosity values, η/η_0 , were analysed in terms of the Jones–Dole equation

$$\eta/\eta_0 = 1 + A\sqrt{C} + BC, \quad (9)$$

where η_0 and η are the viscosity coefficients of solvent and solutions respectively at the given temperature, C is the molar concentration, and A and B are the Falkenhagen and Jones-Dole coefficients.

4. Results and discussion

Experimental values of density, ultrasonic velocity and viscosity of the solutions as functions of mole fraction at different temperatures were recorded. Experimental values of apparent molal volume at infinite dilution, ϕ_v^0 and slope S_v for different solutions of adenosine in DMSO-water mixture in presence of K⁺ and Ca²⁺ are summarized in table 1. The values of ϕ_v^0 gradually decrease with increase in temperature from 303.15 K to 313.15 K for the set B and increase with temperature for set A for the entire range of solvent composition of DMSO. The increasing values of partial molal volumes (ϕ_v^0) for set A with increase in temperature are due to the dehydration of adenosine. S_v values decrease with increase in temperature due to the solute-solvent interactions which are affected by the influence of K⁺ (set B) on the structure of DMSO, since interionic attraction is higher in DMSO (dipolar aprotic solvent) than in water, due to the difference in dielectric constant. Negative ϕ_v^0 values due to addition of adenosine in the presence of an electrolyte in DMSO-H₂O lead to some transient structure that enhances the water structure. This is owing to the accommodation of adenosine moiety in the space created by displacement of net water molecule in the interstices.

Table 1. Apparent molal volume at infinite dilution (ϕ_v^0) and experimental slope (S_v) for adenosine-(water-DMSO)-Ca²⁺ (system A) and for adenosine-(water-DMSO)-K⁺ (system B).

Concentration of adenosine = 0.01 M; CaCl₂ = 0.1 M; KCl = 0.1 M

Temperature (K)	(ϕ_v^0) (ml mol ⁻¹ × 10 ²)		S_v	
	System A	System B	System A	System B
303.15	-350.00	-380.00	0.20	0.17
308.15	-270.00	-400.00	0.14	0.16
313.15	-230.00	-410.00	0.09	0.13

Table 2. Apparent molal compressibility at infinite dilution (ϕ_k^0) for adenosine-(water-DMSO) in presence of Ca²⁺ and K⁺ ion.

Concentration of adenosine = 0.01 M; CaCl₂ = 0.1 M; KCl = 0.1 M

Temperature (K)	(ϕ_k^0) (cm ³ , mol ⁻¹ bar ⁻¹ * × 10 ⁻³)	
	System A	System B
303.15	-120.00	-185.00
308.15	-140.00	-186.00
313.15	-150.00	-92.00

*1 bar = 10⁻⁵ Pa

Table 3. Viscosity B coefficient for adenosine – water–DMSO system in presence of Ca^{2+} and K^+ ions.

Temperature (K)	B coefficient ($\text{mol}^{-1} \text{cm}^3$)	
	System A	System B
303.15	-0.0054	-0.0078
308.15	-0.0050	-0.0070
313.15	-0.0045	-0.0056

Table 4. Activation parameters of adenosine–water–DMSO– Ca^{2+} (system A).

Weight % of solvent	Temperature (K)	ΔU^* (k cal)	ΔS^* (k cal)	ΔH^* (k cal)
10.00	303.15	15.66	91.87	12.17
	308.15	15.77	92.08	12.89
	313.15	16.08	92.65	12.91
20.00	303.15	15.81	82.17	9.08
	308.15	16.06	82.64	9.24
	313.15	16.29	83.04	9.70
30.00	303.15	16.00	79.82	7.88
	308.15	16.21	78.09	7.84
	313.15	16.47	78.53	8.11
40.00	303.15	16.21	72.09	5.63
	308.15	16.46	72.34	5.82
	313.15	16.70	72.57	6.01
50.00	303.15	16.45	114.22	18.17
	308.15	16.67	115.12	18.78
	313.15	16.96	116.14	19.39
55.00	303.15	16.55	94.82	12.18
	308.15	16.79	95.45	12.31
	313.15	17.08	96.11	13.20
60.00	303.15	16.67	85.05	9.09
	308.15	16.89	85.33	9.39
	313.15	17.15	85.79	9.67
65.00	303.15	16.82	85.49	9.08
	308.15	17.02	85.77	9.13
	313.15	17.28	86.21	9.58
70.00	303.15	16.86	103.63	14.54
	308.15	17.15	104.12	14.91
	313.15	17.40	105.18	15.52
75.00	303.15	17.17	79.48	6.90
	308.15	17.37	78.31	6.75
	313.15	17.58	79.72	7.37

Apparent molal compressibilities, ϕ_k^0 , increase with rise in temperature for set A, while for set B, except at 313.15 K, the values of ϕ_k^0 are comparatively low with solvent

composition changing from 10 to 75 weight percentage, i.e. it is negative at all temperatures (table 2). Physico-chemical studies of DMSO-water mixtures led to the conclusion that reinforcement of H₂O structure in the neighbourhood of DMSO molecules in dilute solution must have taken place. This is due to the fact that at higher temperatures, the ordering effect of K⁺ on the structural compressibility of the solvent is comparatively less as compared to that of Ca²⁺ (set A) that is reflected by the ϕ_k^0 value at 313.15 K in set B. Viscosity data are analysed in terms of the Jones-Dole equation. Values of B are displayed in table 3 for three different temperatures. Positive B values for both the sets show 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 the temperature. These values

Table 5. Activation parameters of adenosine-water-DMSO-K⁺ (system B).

Weight % of solvent	Temperature (K)	ΔU^* (k cal)	ΔS^* (k cal)	ΔH^* (k cal)
10.00	303.15	15.71	64.77	3.91
	308.15	16.07	64.66	3.84
	313.15	16.09	64.41	4.07
20.00	303.15	15.92	72.94	6.18
	308.15	16.03	72.78	6.38
	313.15	16.24	72.98	6.60
30.00	303.15	16.02	75.68	6.91
	308.15	16.30	76.07	7.13
	313.15	16.44	76.09	7.37
40.00	303.15	16.23	79.21	7.99
	308.15	16.59	79.48	7.88
	313.15	16.64	79.96	8.15
50.00	303.15	16.45	83.32	8.79
	308.15	16.69	83.47	8.97
	313.15	16.85	84.41	9.57
55.00	303.15	16.59	83.86	8.82
	308.15	16.75	83.96	9.11
	313.15	16.97	84.28	9.41
60.00	303.15	16.71	84.56	8.91
	308.15	16.88	84.71	9.21
	313.15	17.11	85.03	9.50
65.00	303.15	16.79	86.02	9.27
	308.15	17.00	86.30	9.58
	313.15	17.19	86.53	9.89
70.00	303.15	16.91	87.61	9.63
	308.15	17.13	88.14	10.02
	313.15	17.34	88.24	10.27
75.00	303.15	17.04	89.24	9.99
	308.15	17.41	90.07	10.33
	313.15	17.46	89.92	10.68

are due to many factors such as pyrimidal shape of DMSO with 2 C atoms, one O atom and one S atom at the vertices and it being a dipolar aprotic solvent.

The analysis of solute activation parameters is presented in tables 4 and 5.

The activation energy of a reaction is defined as the additional energy which reactant molecules must acquire in order to form the intermediate activated complex for the reaction. The reacting molecules possessing sufficient energy approach one another and form bonds so that the activated complex acquires the energy to form the intermolecular bonds. It is evident from tables 4 and 5 that the free energy of activation $\Delta\mu_2^{0\ddagger}$ is positive for all the solvent compositions and at all temperatures under the present investigation. The results show that adenosine with higher free energy, i.e. formation of transition state, is less favourable for reaction, characteristic of adenosine in DMSO–water mixture from 10 to 75 weight percent of DMSO–water co-solvent in the presence of K^+ or Ca^{2+} ions. Similarly, other parameters for adenosine, like ΔH^* and ΔS^* of activation, show negative contribution in DMSO–water mixture, suggesting that entropies (ΔS^*) are less effective in the presence of K^+ or Ca^{2+} ions and, therefore, the net amount of order created by cations in DMSO–water mixture is more. This shows that DMSO interacts strongly with cations.

Solute activation parameters show that entropies (ΔS^*) and enthalpies (ΔH^*) of activation for sets A and B are negative and increase with increase in composition from 10 to 50 weight percent of DMSO–water indicating that the average transition state associated with bond-making increases in this order, while it decreases with increase from 55 to 75 weight percent, showing that the transition state for viscous flow is accompanied by breaking and distortion of the intermolecular bonds. At all temperatures, the free energy of activation ΔU^* is positive for all solvent compositions.

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