

Volumetric and Viscometric Studies on Sodium Nitrate and Potassium Nitrate in Aqueous and H₂O-urea Solutions

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Summary. Density and viscosity of NaNO₃ and KNO₃ in aqueous and in H₂O-urea solutions were determined as a function of electrolyte concentrations at 308, 313, 318, 323, and 328 K, respectively. The apparent molal volume (ϕ_v) of the electrolytes were found to be linear functions of the square root of the solute molality (b). The ϕ_v and \sqrt{b} data were fitted to the *Masson* equation [1] by the least square method to obtain the apparent molar volume at infinite dilution (ϕ_v°), which is practically equal to the partial molar volume (\bar{v}_2°). The viscosity coefficients A and B were calculated on the basis of the viscosity of the solutions and the solvent concerned using the *Jones–Dole* [2] equation. The activation parameters for viscous flow (ΔG^\ddagger , ΔS^\ddagger , and ΔH^\ddagger) were calculated according to *Eyring* [3]. The values of ($\Delta\mu_1^\ddagger - \Delta\mu_0^\ddagger$) for the two systems were also calculated from B -coefficient data. The results were found to be of opposite nature in the two electrolyte systems. Where sodium nitrate showed structure making behaviour both in aqueous and in H₂O-urea solutions, KNO₃ showed structure breaking behaviour in aqueous solutions and structure making behaviour in 5 molal H₂O-urea solutions in the studied temperature range. The behaviour of these two electrolytes in aqueous binary and in aqueous-urea ternary systems are discussed in terms of charge, size, and hydrogen bonding effects.

Keywords. Apparent molar volume; Partial molar volume; Viscosity coefficient; Activation parameters; Hydrogen bonding.

Introduction

Volumetric, viscometric, and other thermodynamic data provide valuable information regarding solute–solvent, solute–solute, and solvent–solvent interactions [4, 5]. Although volumetric, viscometric, and related thermodynamic parameters in binary systems are abundant, data on ternary systems are limited. Physico-chemical studies on aqueous ternary systems are gaining importance, because sometimes it is difficult to arrive at a definite conclusion regarding structure and properties of solutions from studies on binary systems only. Urea-water and salt-water mixtures

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are of great importance in protein stability and denaturation phenomena [6–8]. The effect of urea and salts on protein structure is now recognized to be more complex than simply disrupt hydrogen bonds and, in particular, cause the breaking of hydrophobic bonds [9–11]. The effects of added urea and salts upon the properties of water are continuously investigated in order to understand the mechanism of protein stability and denaturation by urea and salts. These effects are reported to be intimately connected with the local liquid structure [12, 13]. In this study we made an attempt (a) to interpret the apparent and partial molar volume and the viscosity coefficients A and B in terms of solute–solvent and solute–solute interactions; (b) to study the effect of urea on these interactions; (c) to investigate the structure making/breaking property of the salts; and (d) to discuss the species involved in viscous flow by their characteristic activation parameters (ΔG^\neq , ΔS^\neq , ΔH^\neq and $(\Delta\mu_1^\neq - \Delta\mu_o^\neq)$).

Results and Discussion

Volumetric properties of NaNO_3 and KNO_3 in aqueous and in H_2O -urea solutions were determined at 308, 313, 318, 323, and 328 K, respectively.

The apparent molar volume (ϕ_v) and the partial molar volume (\bar{v}_2) of the electrolytes are shown in Tables 1 and 2 respectively (1 and 3b H_2O -urea data for KNO_3 and 1,3, and 5 molal H_2O -urea data for NaNO_3 are not shown because they are very similar). The concentration dependence of ϕ_v for NaNO_3 and KNO_3 in aqueous and in H_2O -urea solutions at five different temperatures are shown in Fig. 1. The apparent molar volume (ϕ_v) depends on the electrolyte concentration as well as on the temperature in both systems. The increase of ϕ_v with \sqrt{b} is significant in the case of NaNO_3 ; a change of the concentration of KNO_3 is not that significant in aqueous and in 1 and 3 molal H_2O -urea solution systems (Fig. 1; aqueous solutions shown only). Comparatively higher apparent molar volumes (ϕ_v) for the two electrolytes in the H_2O -urea solvent system than in water indicate that electrolytes in H_2O -urea systems are more extensively structured than in the aqueous system. The value of \bar{v}_2 increases with increasing molality of the electrolyte, and the value of \bar{v}_1 (not shown) slightly decreases. This suggests that ion–solvent interactions increase with increasing molality of the electrolytes.

The limiting apparent molar volume (ϕ_v°) which is taken to be the partial molar volume at infinite dilution (\bar{v}_2°) of the electrolytes in aqueous and in H_2O -urea solutions reflect the true volume of the solute and the volume change arising from solute–solvent interactions. The change in the \bar{v}_2° value of the electrolytes can be explained by considering the charge and size of the cations and anions of the electrolytes in aqueous and in H_2O -urea solutions. The salts NaNO_3 and KNO_3 contain the same monovalent anions but different cations. The cations are of very similar nature except for their size. Both ions are hydrated by water. The crystallographic radii of Na^+ and K^+ ions are 0.97 and 1.33 Å, respectively [14]. As the contribution of NO_3^- to \bar{v}_2° is the same in both salt systems, the variation of \bar{v}_2° in the two cases may be due to the difference in ionic radii, charge density, and/or ion–solvent interactions. According to *Vaslows* [15] concept of hydration, small cations normally enhance hydrogen bonded structural grouping in liquid water. As the radius of Na^+ is lower than that of K^+ , the hydration sheath of the former occupies

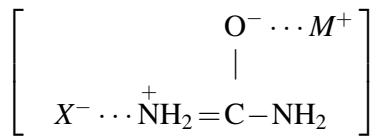
Table 1. Apparent molar volumes (ϕ_v), partial molar volumes (\bar{v}_2), and partial molar volumes at infinite dilution ($\phi_v^\circ \approx \bar{v}_2^\circ$) for sodium nitrate and potassium nitrate in aqueous solutions at 308, 313, 318, 323, and 328 K

$b(\text{mol} \cdot \text{kg}^{-1})$	Sodium nitrate										Potassium nitrate									
	ϕ_v ($\text{cm}^3 \cdot \text{mol}^{-1}$)					\bar{v}_2 ($\text{cm}^3 \cdot \text{mol}^{-1}$)					ϕ_v ($\text{cm}^3 \cdot \text{mol}^{-1}$)					\bar{v}_2 ($\text{cm}^3 \cdot \text{mol}^{-1}$)				
	308 K	313 K	318 K	323 K	328 K	308 K	313 K	318 K	323 K	328 K	308 K	313 K	318 K	323 K	328 K	308 K	313 K	318 K	323 K	328 K
0.0625	27.12	27.25	27.40	27.70	28.03	28.38	28.58	28.78	29.14	29.53	35.41	35.95	36.55	37.05	37.70	35.58	36.13	36.71	37.21	37.86
0.1250	27.82	27.94	28.10	28.32	28.65	29.61	29.84	30.06	30.35	30.77	35.55	36.08	36.69	37.17	37.82	35.80	36.34	36.92	37.40	38.05
0.2500	28.60	28.75	28.90	29.15	29.45	31.12	31.42	31.66	32.03	32.45	35.65	36.19	36.83	37.29	37.94	36.01	36.54	37.15	37.61	38.27
0.5000	29.62	29.80	29.98	30.25	30.55	33.18	33.58	33.88	34.31	34.78	35.79	36.35	36.92	37.42	38.06	36.28	36.85	37.37	37.87	38.52
1.0000	30.95	31.31	31.60	32.05	32.58	35.99	36.65	37.13	37.79	38.57	35.95	36.50	37.05	37.55	38.20	36.64	37.21	37.69	38.19	38.85
$\bar{v}_2^\circ \rightarrow$						25.99	32.05	26.09	26.26	26.48	25.99	26.01	26.09	26.26	26.48	34.67	34.95	35.70	35.99	36.73

Table 2. Apparent molar volumes (ϕ_v), partial molar volumes (\bar{v}_2), and partial molar volumes at infinite dilution ($\phi_v^\circ \approx \bar{v}_2^\circ$) for potassium nitrate in 5 molal aqueous urea solutions at 308, 313, 318, 323, and 328 K

b (mol · kg ⁻¹)	ϕ_v (cm ³ · mol ⁻¹)					\bar{v}_2 (cm ³ · mol ⁻¹)				
	308 K	313 K	318 K	323 K	328 K	308 K	313 K	318 K	323 K	328 K
0.0625	36.49	36.98	37.47	37.94	38.57	37.67	38.20	38.75	39.24	39.83
0.1250	36.97	37.51	37.90	38.53	39.11	38.63	39.23	38.80	40.35	40.89
0.2500	37.58	38.03	38.69	39.15	39.76	39.94	40.46	41.24	41.74	42.29
0.5000	38.49	39.10	39.73	40.25	40.89	41.82	42.53	43.35	43.91	44.46
1.0000	40.05	40.65	41.31	41.85	42.35	44.76	45.50	46.42	47.02	47.41
$\bar{v}_2^\circ \rightarrow$						35.27	35.73	36.17	36.64	37.30

less space than that of the latter. Moreover, the high charge-to-radius ratio of Na⁺ leads to an electrostriction of the water structure. This causes that the limiting apparent molar volumes ϕ_v° of NaNO₃ in aqueous and in H₂O-urea solutions are smaller than those of KNO₃. That is, the interactions of these electrolytes with the water dipole follows the order KNO₃-H₂O > NaNO₃-H₂O. The ϕ_v° values for the two electrolytes are higher in H₂O-urea solution than in water. The variation of ϕ_v° with the molality of urea can be rationalized in terms of cosphere overlap model [16]. According to the model, 'the overlap of the cospheres of two ions or polar groups or an ion with that of a hydrophilic group always produces a positive volume change'. On the other hand, the overlap of the cosphere of an ion with that of hydrophobic groups results in a negative volume change. By the overlap of the cospheres of urea-urea and urea-hydrophilic groups, zwitterion interactions may take place. The overlap of the cospheres of urea gives a positive change in volume due to the relaxation of the electrostricted water molecules from its cosphere to the bulk. The overlap of the cospheres of urea with those of hydrophilic groups of salts results in positive volume changes. The relaxation of the electrostricted water molecules due to strongly localized ion-zwitterion interactions from the cospheres of both salts and urea may cause an increase in volume.



The positive volume change due to the overlap of the cospheres of urea with those of the hydrophilic groups of salts outweighs the negative volume change due to the overlap of cospheres of urea and hydrophobic groups of salts (negligible), giving a greater ϕ_v° value in urea compared to that in water. The water-water and water-urea interactions are assumed to be the same and do not produce a considerable change in volume. An increase in the molality of urea increases the ion-zwitterion and also the urea-urea interactions, giving rise to increased ϕ_v° values.

The increase of ϕ_v° with temperature in both cases is supposed to be due to (i) an increase in the thermal energy at higher temperature (the relaxation to the bulk of the electrostricted water molecules from the interaction regions of $-\text{CO}^- \cdots M^+$ and $-\text{NH}_2^+ \cdots X^-$ results in a positive volume change); (ii) the fact that an increase

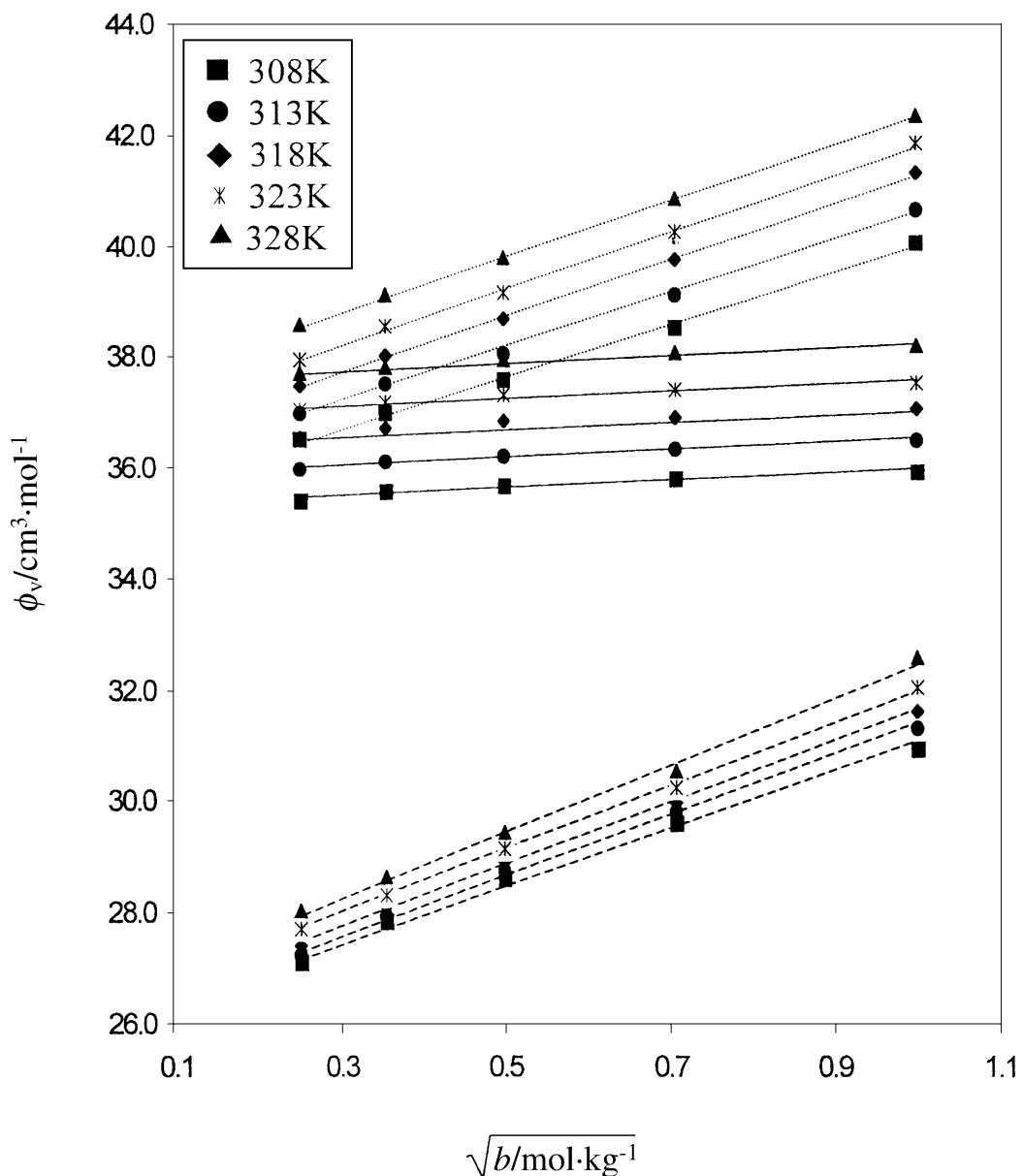


Fig. 1. Plots of apparent molal volumes (ϕ_v) vs. \sqrt{b} for sodium nitrate (dashed line), potassium nitrate (solid line) in aqueous, and potassium nitrate (dotted line) in aqueous 5 molal urea solutions at 308, 313, 318, 323, and 328 K

in temperature renders the salt–salt interactions relatively weaker, thus giving rise to a small negative volume change; (iii) a decrease in salt–water interactions causing a positive volume change; and (iv) the water–water interactions decreasing with increasing in temperature, giving rise to a small negative change in volume.

Viscosities of NaNO_3 and KNO_3 in aqueous and in H_2O -urea solutions were measured at 308, 313, 318, 323, and 328 K, respectively. The relevant data are shown in Table 3 (1 and 3 molal H_2O -urea data for KNO_3 and 1, 3, and 5 molal

Table 3. Viscosities (η) and the viscosity coefficients B for sodium nitrate and potassium nitrate in solutions at 308, 313, 318, 323, and 328 K

c (mol · dm ⁻³)	308 K		313 K		318 K		323 K		328 K	
	η (cP)	B								
NaNO ₃ in H ₂ O										
0.06	0.7354		0.6662		0.6119		0.5620		0.5156	
0.12	0.7391		0.6705		0.6175		0.5670		0.5198	
0.25	0.7456	+ 0.0324	0.6760	+ 0.0349	0.6225	+ 0.0155	0.5715	+ 0.0230	0.5266	+ 0.0539
0.49	0.7563		0.6865		0.6320		0.5810		0.5375	
1.01	0.7901		0.7132		0.6590		0.6095		0.5625	
KNO ₃ in H ₂ O										
0.06	0.7310		0.6617		0.6030		0.5585		0.5156	
0.12	0.7293		0.6611		0.6025		0.5542		0.5119	
0.25	0.7284	- 0.0499	0.6615	- 0.0258	0.6029	- 0.0069	0.5563	- 0.0383	0.5157	- 0.0367
0.49	0.7260		0.6622		0.6058		0.5573		0.5171	
1.01	0.7275		0.6643		0.6102		0.5634		0.5229	
KNO ₃ in aqueous 5 molal urea										
0.06	0.9104		0.8304		0.7611		0.6998		0.6478	
0.12	0.9118		0.8319		0.7636		0.7019		0.6500	
0.25	0.9134	+ 0.0547	0.8350	+ 0.0647	0.7670	+ 0.0888	0.7047	+ 0.0589	0.6524	+ 0.0515
0.49	0.9184		0.8406		0.7723		0.7118		0.6604	
1.01	0.9332		0.8553		0.7871		0.7278		0.6749	

H₂O-urea data for NaNO₃ are not shown because the data in aqueous solutions were very similar); a representative plot is presented in Fig. 2. The viscosity *vs.* molalilily curves for the two electrolytes are linear in both solvent systems. The value of η increases with increasing molality of NaNO₃. Potassium nitrate shows no significant change in η values in aqueous and in 1 and 3 molal H₂O-urea systems (Fig. 2; aqueous solutions shown only). The viscosity of the two electrolytes is higher in the H₂O-urea system than in the aqueous system, indicating that electrolytes in H₂O-urea systems are more structured than in pure water.

The viscosity coefficient B value is positive for NaNO₃ in both solvent systems and negative for KNO₃ in the aqueous solutions at the studied temperatures (Table 3), indicating that NaNO₃ exhibits structure making behaviour in aqueous and in H₂O-urea systems. The crystallographic radius of Na⁺ is reported to be 0.97 Å [14]. The relatively small size as well as the monovalent nature of the cation and the anion of the electrolyte is in reasonable agreement with its low viscosity.

The negative viscosity coefficient B for KNO₃ in aqueous solutions and its positive value in H₂O-urea systems (Table 3) indicate that KNO₃ behaves as a structure breaker for water in aqueous solutions, but as a structure maker in H₂O-urea systems. The structure breaking tendency of KNO₃ can be rationalized by the consideration of the large size and low charge density of K⁺. Because of the dipole–dipole repulsion between the solution shell molecules, the relatively weak electrostatic field at such ions can cause polarization, immobilization, and

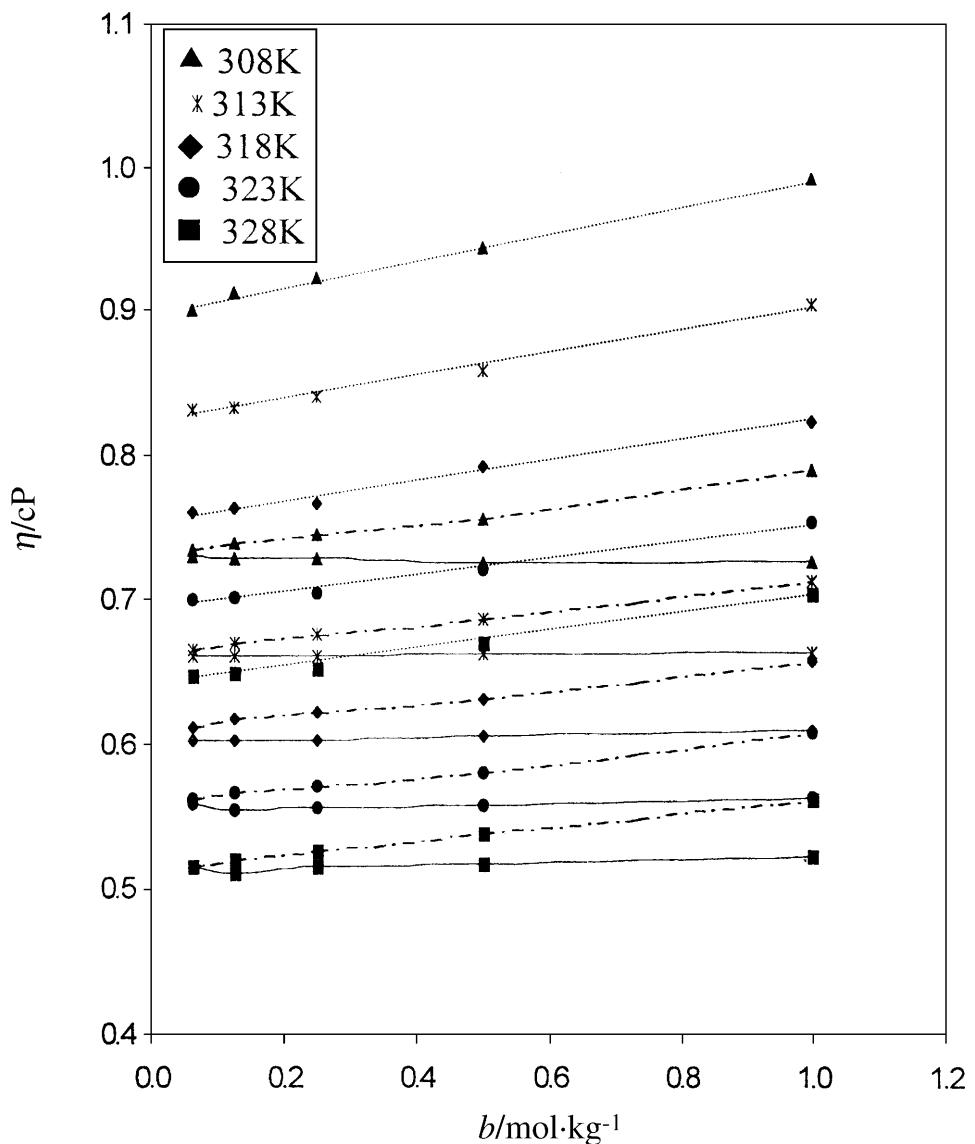


Fig. 2. Plots of viscosity (η) vs. molality (b) for sodium nitrate (long dashed line), potassium nitrate (solid line) in aqueous, and potassium nitrate (dotted line) in aqueous 5 molal urea solutions at 308, 313, 318, 323, and 328 K

electrostriction of the water molecules only in the first layer. Beyond this layer, a strong structure breaking effect persists, *i.e.* a shift in the structure equilibrium in the direction of a smaller degree of ice-likeness. Non-nearest neighbour water molecules in the vicinity of these ions probably become more mobile than those in the pure water. For the interaction of such ions with water, the term 'negative hydration' has been employed [17]. In the view of Gurney [18], there is a critical radius above which the electric field of the ion is too weak to produce order in the water. For an ion to fit into a cavity formerly occupied by a water molecule, its radius must be less than that of the water molecule (1.38 Å). This type of ions

should fit into such a cavity without disruption of the water structures (the primary and secondary hydration layers about this cavity). Potassium ions (1.33 Å [14]) would be expected to disrupt the primary hydration layer slightly. Furthermore, this would also result in a disruption of the secondary hydration layer which should lead to a weakening of the bonds holding this water molecule together in the hydration layer. This disruption is always accompanied by structure breaking effects in the aqueous solution.

The increase of B values of NaNO_3 and KNO_3 with increasing urea molality reveals that these electrolytes gain a progressively more structured environment. In ternary ($\text{H}_2\text{O} + \text{urea} + \text{electrolyte}$) solutions, urea polar group interactions disrupt the less structured region around them, and the water molecules move to the more structured bulk, resulting in an increase in viscosity. The predominance of urea-polar group interactions over urea-hydrophobic group interaction (negligible) gives a net increase in the viscosity. The urea-electrolytes and urea-urea interactions progressively enhance the overall structure of the solution as the molality of urea is increased, reflecting the increase in B -coefficient values.

The viscosity coefficient A represents the solute–solute interactions coupled with the size and shape effect of the solute and, to some extent, solute–solvent interactions. In this study, an irregular variation in the values of A is found (data not shown) which may be due to (i) an incomplete dissociation and ion association of

Table 4. Activation parameters for the viscous flow of sodium nitrate and potassium nitrate in solutions at 308, 313, 318, 323, and 328 K

b (mol · kg $^{-1}$)	ΔG^\neq (kJ · mol $^{-1}$)					ΔS^\neq (J · mol $^{-1}$ · K $^{-1}$)	ΔH^\neq (kJ · mol $^{-1}$ · K $^{-1}$)
	308 K	313 K	318 K	323 K	328 K		
NaNO ₃ in H ₂ O							
0.0625	8.97	8.86	8.79	8.70	8.61	17.69	14.41
0.1250	8.98	8.88	8.81	8.73	8.63	17.16	14.26
0.2500	9.01	8.91	8.84	8.75	8.67	16.65	14.13
0.5000	9.05	8.95	8.88	8.80	8.74	15.75	13.90
1.0000	9.18	9.07	9.01	8.95	8.88	14.51	13.64
KNO ₃ in H ₂ O							
0.0625	8.95	8.85	8.75	8.69	8.61	17.11	14.21
0.1250	8.95	8.85	8.75	8.67	8.59	17.97	14.48
0.2500	8.96	8.86	8.76	8.69	8.62	17.83	14.13
0.5000	8.96	8.87	8.78	8.71	8.64	17.80	13.88
1.0000	8.99	8.91	8.83	8.76	8.71	17.36	13.41
KNO ₃ in aqueous 5 molal urea							
0.0625	9.82	9.74	9.67	9.61	9.55	13.17	13.87
0.1250	9.83	9.75	9.69	9.62	9.57	12.84	13.77
0.2500	9.83	9.76	9.70	9.64	9.58	12.56	13.70
0.5000	9.86	9.80	9.74	9.68	9.63	11.54	13.40
1.0000	9.93	9.87	9.82	9.77	9.72	10.24	13.08

electrolytes in aqueous and in H_2O -urea systems and (ii) the size of the ions which causes differences in the degree of hydration or in solvation [18].

The decrease of A with rising temperature is probably due to the greater thermal agitation and reduction of attractive forces between the ions. The increase in A value can be explained by the inter-penetration effect, which brings the ions closer together [19]. It is found that A -values are negative in H_2O -urea solutions and positive in aqueous solutions. This indicates that in aqueous solutions ion-ion interactions are not as severely prevented by the solvent (relatively low structured) as in H_2O -urea systems (relatively high structured).

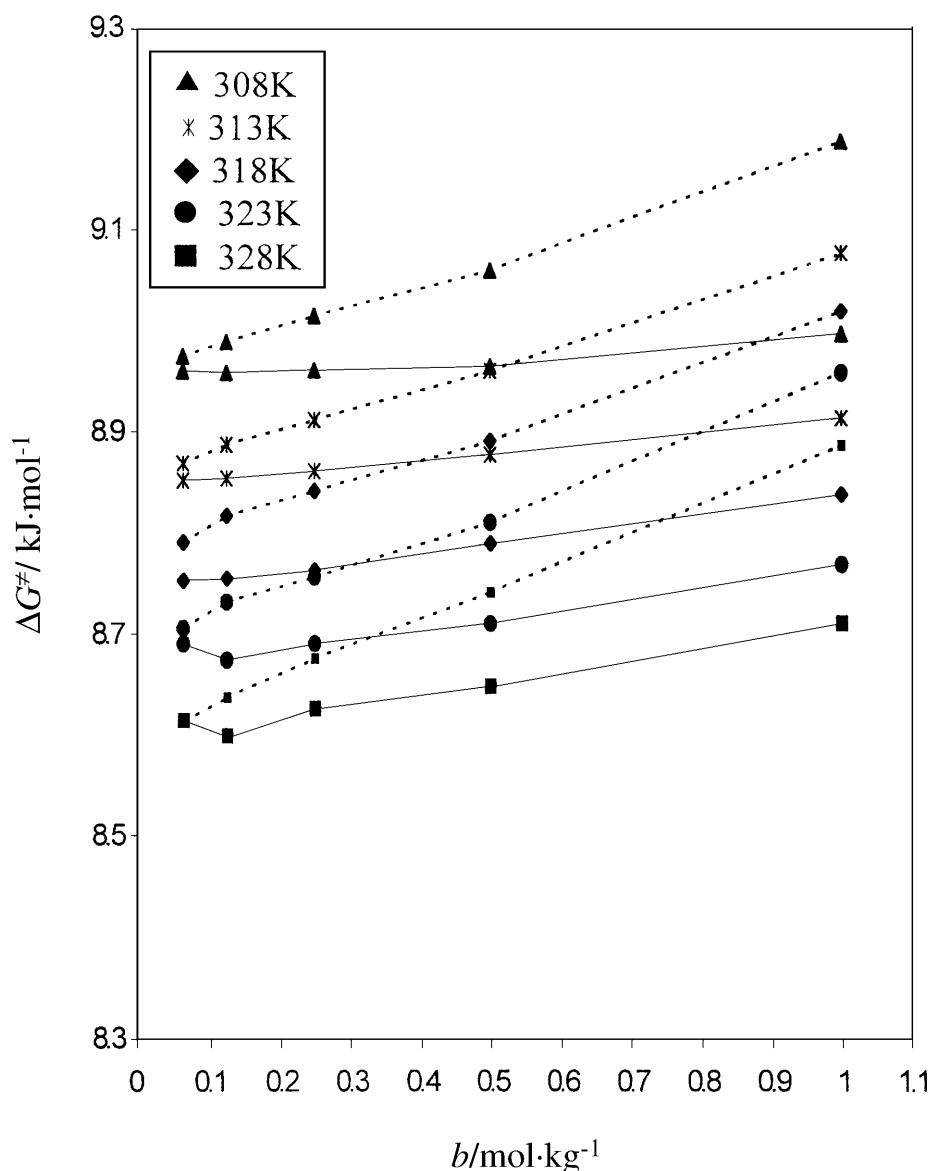


Fig. 3. Plots of free energy of activation (ΔG^\ddagger) vs. molality (b) for sodium nitrate (dashed line) and potassium nitrate (solid line) in aqueous solutions at 308, 313, 318, 323, and 328 K

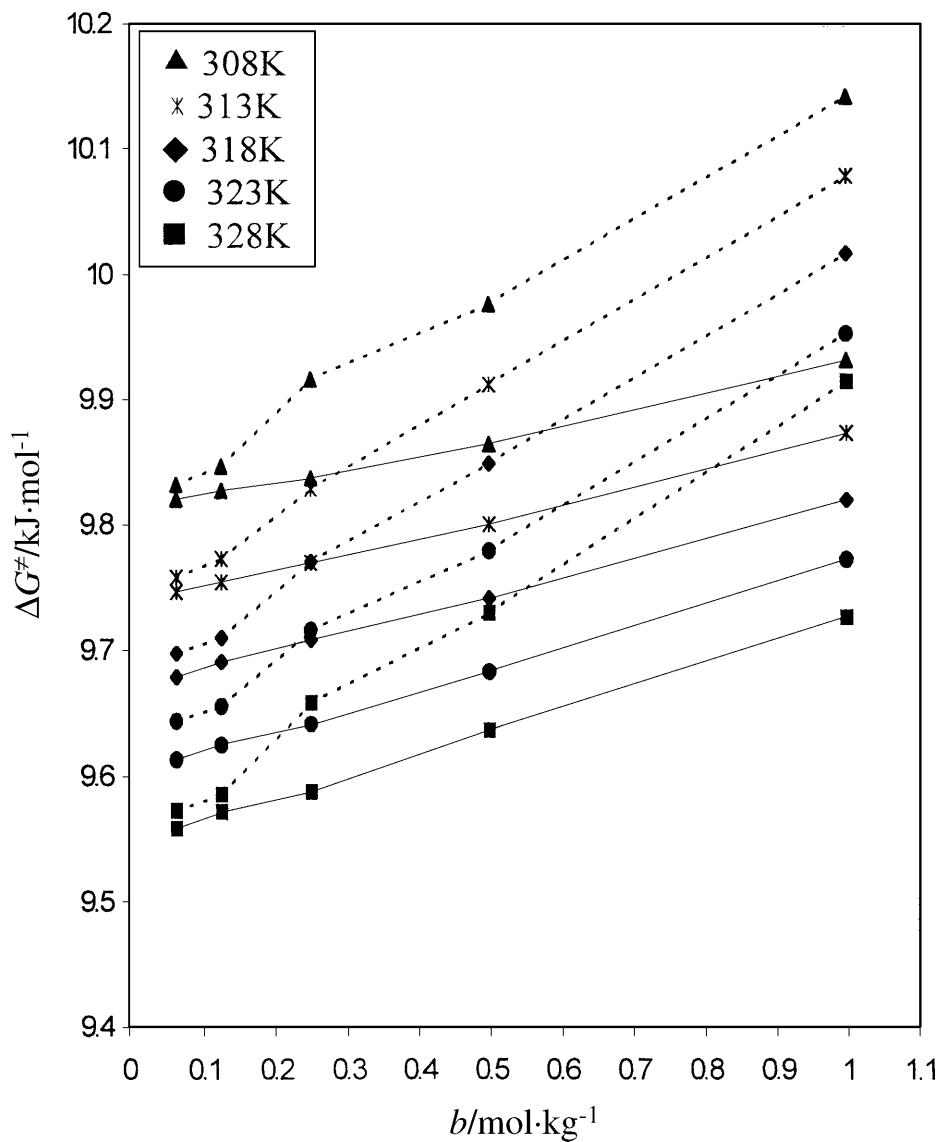


Fig. 4. Plots of free energy of activation (ΔG^\ddagger) vs. molality (b) for sodium nitrate (dashed line) and potassium nitrate (solid line) in 5 molal aqueous urea solutions at 308, 313, 318, 323, and 328 K

The thermodynamic properties of NaNO_3 and KNO_3 in aqueous and in H_2O -urea solutions were calculated at the mentioned temperatures and are shown in Table 4 and Figs. 3 and 4. It is obvious that the ΔG^\ddagger values of electrolytes in aqueous and in H_2O -urea solutions increase with electrolyte concentration and decrease with increasing temperature. ΔG^\ddagger is positive for the two electrolytes; this may be due to the kinetic species involved in forming cavities or holes in the liquid medium and is given by the work required for forming the hole against the surface tension of the solution. For NaNO_3 , the increase in ΔG^\ddagger with the molality of the electrolyte is significant in both solvent systems. This indicates that NaNO_3 acts as a structure maker for water and H_2O -urea solvent systems. The variation of the enthalpy and entropy of activation (ΔH^\ddagger and ΔS^\ddagger) with the

concentration of the electrolytes is noted in Table 4. The $\Delta S^\#$ and $\Delta H^\#$ values for the flow process are positive in all cases but do not follow any specific pattern. The values in the H_2O -urea system are lower than those in aqueous system, indicating that in H_2O -urea systems the electrolytes are more structured than in the aqueous system. The positive values of $\Delta H^\#$ indicate that positive work has to be done to overcome the energy barrier for the flow process. That is, the viscous flow is not thermodynamically favoured for the systems studied. The change of chemical potential values ($\Delta\mu_1^\# - \Delta\mu_0^\#$) indicates the solute–solvent interactions in the solution. A positive and high value of ($\Delta\mu_1^\# - \Delta\mu_0^\#$) indicates a strong interaction between ions and solvents; low and negative value of ($\Delta\mu_1^\# - \Delta\mu_0^\#$) indicates structure disorder [21]. Calculated values obtained from the *B*-coefficient data for the studied electrolytes are presented in Table 5. An examination of the data indicates that positive values of ($\Delta\mu_1^\# - \Delta\mu_0^\#$) are obtained for NaNO_3 systems.

Table 5. Change of chemical potential ($\Delta\mu_1^\# - \Delta\mu_0^\#$) for sodium nitrate and potassium nitrate in solutions at 308, 313, 318, 323, and 328 K

T (K)	Molality of urea, <i>b</i> (mol · kg ⁻¹)	Concentration of salt, <i>c</i> (mol · dm ⁻³)	$(\Delta\mu_1^\# - \Delta\mu_0^\#)$ (kJ · mol ⁻¹)	
			NaNO_3	KNO_3
308	0.00	0.06	5998	-5120
		0.12	5860	-4100
		0.24	5894	-4380
		0.48	6157	-4376
	5.00	0.96	6249	-4150
		0.06	35347	9795
		0.13	34385	9161
		0.26	33951	9095
		0.51	33346	9082
		1.01	32687	9094
313	0.00	0.6	6633	-1471
		0.12	6379	-589
		0.24	6425	-894
		0.49	6638	-844
	5.00	0.96	6734	-614
		0.06	24269	10459
		0.13	23716	10258
		0.26	23607	10105
		0.51	22909	9905
		1.01	22411	9819
318	0.00	0.06	3870	-1584
		0.12	3716	-2202
		0.24	3728	-1926
		0.48	3975	-1964
	5.00	0.95	4150	-2207
		0.06	29608	12981
		0.13	28967	12510
		0.26	28455	12110

(continued)

Table 5 (continued)

T (K)	Molality of urea, <i>b</i> (mol · kg ⁻¹)	Concentration of salt, <i>c</i> (mol · dm ⁻³)	$(\Delta\mu_1^\# - \Delta\mu_0^\#)$ (kJ · mol ⁻¹)	
			NaNO ₃	KNO ₃
323	0.00	0.51	28154	11927
		1.01	27554	11502
		0.06	4836	-3369
		0.12	4853	-2386
		0.24	4865	-2645
	5.00	0.48	5141	-2591
		0.95	5325	-2344
		0.06	19688	9825
		0.13	18960	9705
		0.26	18541	9219
328	0.00	0.51	18145	9097
		1.01	17804	9023
		0.06	9969	-2779
		0.12	9459	-2010
		0.24	9542	-2303
	5.00	0.48	9777	-2257
		0.95	9814	-1985
		0.06	21009	9605
		0.13	20905	9510
		0.26	20219	9320
		0.51	19926	9055
		1.01	19517	8978

However, for KNO₃, negative values are obtained which decrease with increasing of concentration of urea and become positive at higher concentrations of urea (≥ 5 molal). This indicates that the structure disordering properties of KNO₃ also diminish in the presence of urea. The thermodynamic data are in excellent agreement with those obtained from density and viscosity measurements.

Conclusions

A volumetric and viscometric study on NaNO₃ and KNO₃ in aqueous and in H₂O-urea solutions at 308–328 K reveals the following:

- (i) Sodium nitrate and potassium nitrate interact with water differently.
- (ii) Both urea and sodium nitrate in water behave as structure makers, whereas potassium nitrate acts as structure breaker.
- (iii) The structure breaking tendency of KNO₃ is counteracted by the structure making tendency of urea in aqueous solutions.
- (iv) At and above a concentration of 5 molal, urea may overcome the structure breaking effect of KNO₃.

Experimental

Urea (99%), NaNO₃ (>98%), and KNO₃ (99.5%) were purchased from Merck. The chemicals were dried first in an oven at 110°C and then at room temperature in vacuum over P₂O₅ for at least 24 h before use. Doubly distilled H₂O was used for making up solutions; densities were measured using a 10 cm³ bicapillary pycnometer previously calibrated with H₂O. Viscosities were measured by a calibrated U-type Ostwald viscometer of the British standard institution with sufficiently long efflux time to avoid for kinetic energy corrections; the time of flow was recorded by a timer accurate up to ± 0.01 s. A Mettler PM-200 electronic balance with an accuracy of ± 0.0001 g was used for weighing. Temperature was controlled to $\pm 0.1^\circ\text{C}$ by a thermostatted water bath.

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