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Viscometric Studies of Concentrated Alkali Halides in Aqueous Acetamide Solution

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The relative viscosity measurements have been reported to explain structural interactions of sodium and potassium halides (0.125 M–3M) in aqueous acetamide solutions at different temperatures. The structural aspects of the alkali halide solutions have been interpreted by the effective flow volume ($\overline{V}$), ionic B-coefficients (B±) and hydration number of ions (n_B). The change in these data is attributed to the structure breaking and structure making extent of various ions present (Na^+, K^+, Cl^-, Br^- and I^-) in the aqueous acetamide solution.

INTRODUCTION

Various physico-chemical methods[1–6] have been used to explain structural phenomenon caused by the added solute in solutions. These solute-solute and solute-solvent interactions have been studied both in binary[7] as well as in ternary[8] systems. Viscosity measurement is one of the physico-chemical methods used in providing informations regarding the structuring effects caused by the electrolytes in a non-electrolytic solution. Structural behaviour of several homogeneous ternary systems have been studied in our laboratory taking sucrose, maltose, xylose, mannitol, urea, dimethyl urea, HMT and glucose as non-electrolytes employing conductance and viscosity measurements[9–14]. In the present investigation, acetamide, a water soluble mono alkyl amide, capable of interacting with electrolytes in solution and possessing three hydrogen bonding sites has been chosen as non-electrolyte while the electrolytes are sodium and potassium halides in aqueous medium.

EXPERIMENTAL

The compounds NaCl, NaBr, NaI, KCl, KBr, KI and acetamide used were of AnalaR grade and were used as such without further purification. Water used for the preparation of solutions was doubly distilled demineralised water having specific conductivity of the order of 10^{-6} mho. The density measurements at different temperatures were carried out with pycnometer in the conventional way. Viscosity measurement at specified temperature was made with the help of a modified Tuan-Fuoss viscometer[15,16]. All the measurements were carried out in a water thermostat having controlling capacity within ±0.05°C temperature.

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RESULTS AND DISCUSSION

The relative viscosity data of alkali metal halide-acetamide-water system was computed using a relation.

$$\eta/\eta_o = dt/d_0t_0 \qquad (1)$$

where η, d, t and η_o, d_o, t_o are viscosity, density and flow time for electrolyte in aqueous acetamide solution and non-aqueous acetamide solution respectively. These relative viscosity data obtained for all the six electrolytes in aqueous acetamide solution (Table 1) have been utilised to calculate B-coefficient values from the relation

$$\eta/\eta_o = 1 + BC \qquad (2)$$

TABLE 1

RELATIVE VISCOSITIES (η/η_o) OF ELECTROLYTES IN AQUEOUS ACETAMIDE SOLUTION AT DIFFERENT TEMPERATURES AND CONCENTRATIONS.

Conc in mole/litre	Temperature °C			
	25	30	35	40
		NaCl		
3.0	1.0900	1.0880	1.0410	0.9352
2.5	1.0030	1.0120	0.9754	0.8740
2.0	0.9552	0.9483	0.9105	0.8260
1.5	0.9050	0.8780	0.8711	0.7851
1.0	0.8640	0.8380	0.8249	0.7541
0.75	0.8466	0.8172	0.8143	0.7375
0.50	0.8229	0.8011	0.7841	0.7114
0.25	0.8165	0.7880	0.7765	0.7014
0.125	0.8090	0.7802	0.7669	0.6900
		NaBr		
3.0	1.0081	1.0601	0.9806	0.8467
2.5	0.9763	0.9636	0.9242	0.8106
2.0	0.9451	0.9056	0.8993	0.7626
1.5	0.9214	0.8746	0.8631	0.7330
1.0	0.8884	0.8502	0.8504	0.7256
0.75	0.8706	0.8384	0.8082	0.7067
0.50	0.8583	0.8375	0.7906	0.6812
0.25	0.8378	0.8070	0.7807	0.6589
0.125	0.8280	0.8078	0.7695	0.6316
		NaI		
3.0	0.9435	0.9268	0.8795	0.7985
2.5	0.9107	0.8887	0.8368	0.7598
2.0	0.8616	0.8541	0.8169	0.7303
1.5	0.8414	0.8631	0.8010	0.7269
1.0	0.8257	0.8216	0.7793	0.6948
0.75	0.8155	0.8100	0.7724	0.6867
0.50	0.8143	0.8104	0.7646	0.6871
0.25	0.8060	0.8001	0.7576	0.6937
0.125	0.8228	0.7955	0.7581	0.6927

Conc in mole/litre	Temperature °C			
	25	30	35	40
		KCl		
3.0	0.8094	0.8657	0.8373	0.7320
2.5	0.8028	0.8509	0.8193	0.7091
2.0	0.7983	0.8372	0.8075	0.6934
1.5	0.7866	0.8319	0.7925	0.6871
1.0	0.7696	0.8284	0.7861	0.6818
0.75	0.7654	0.8216	0.7837	0.6756
0.50	0.7624	0.8191	0.7791	0.6703
0.25	0.7619	0.8174	0.7766	0.6684
0.125	0.7602	0.8130	0.7740	0.6656
		KBr		
3.0	0.8368	0.8283	0.7108	0.8141
2.5	0.8270	0.8184	0.6978	0.7959
2.0	0.8195	0.8098	0.6830	0.7828
1.5	0.8112	0.8051	0.6740	0.7701
1.0	0.8009	0.8007	0.6647	0.7720
0.75	0.8020	0.8006	0.6658	0.7724
0.50	0.8034	0.8064	0.6681	0.7732
0.25	0.8069	0.8070	0.6695	0.7895
0.125	0.8093	0.8087	0.7212	0.7924
		KI		
3.0	0.8160	0.7884	0.7601	0.7065
2.5	0.8048	0.7688	0.7549	0.6905
2.0	0.7969	0.7543	0.7483	0.6795
1.5	0.7971	0.7581	0.7491	0.6742
1.0	0.7989	0.7652	0.7459	0.6687
0.75	0.8118	0.7691	0.7469	0.6622
0.50	0.8032	0.7746	0.7486	0.6647
0.25	0.8109	0.7870	0.7536	0.6656
0.125	0.8152	0.7928	0.7535	0.6680

where C is 0.1M. It has been found that this relation helds good for all the six solutes in aqueous acetamide solution (0.5 M) upto a concentration of 0.50M. The Moulik equation[17] (eqn 3) has also been applied to test the relative viscosity data

$$(\eta/\eta_o)^2 = M + K\,C^2 \qquad (3)$$

though it is usually valid for concentrated electrolytic solutions only. The values of M and K have been calculated from the intercept and slope of the plots of $(\text{viscosity})^2$ versus $(\text{concentration})^2$. Breslau and Miller equation[18] (eqn 4) yields average effective rigid molar volume ($\overline{V}_e$).

$$\overline{V}_e = \frac{-2.5 + (2.5C)^2 - 4(10.05C^2)(1 - \eta/\eta_o)^{1/2}}{2(10.05)C^2} \qquad (4)$$

A generalised equation had also been utilised to calculate

$$\eta/\eta_o = 1 + a_1C + a_2C^2 + \ldots \tag{5}$$

the coefficient a_1 and a_2 for different values of concentrations. When $V = a_1/2.5$ and $K = a_2/\bar{V}_2$, the average value of $\bar{V}$ and K obtained from above equation is given in Table 2.

TABLE 2
VALUES OF DIFFERENT PARAMETERS (AT ACETAMIDE CONC. = 0.5 AND AT SALT CONC. = 0.5M–3M.

Temp. °C	Calculated from eq. 5		Breslau & Miller eq.	Moulik eq.	
	$\bar{V}$	K	$\bar{V}_e$	M	K
Acetamide-NaCl-Water System					
25	0.1559	10.4368	0.2891	0.68	0.0550
30	0.1770	9.7873	0.3106	0.631	0.0560
35	0.1928	9.5093	0.3336	0.601	0.0507
40	0.3018	4.7905	0.4696	0.611	0.0516
Acetamide-NaBr-Water System					
25	0.1662	9.3216	0.3014	0.725	0.038
30	0.1796	9.5267	0.3231	0.695	0.036
35	0.1957	7.0920	0.3709	0.66	0.032
40	0.3115	3.7500	0.5137	0.475	0.030
Acetamide-NaI-Water System					
25	0.1697	6.4837	0.3358	0.649	0.0269
30	0.1682	6.1443	0.3592	0.650	0.0212
35	0.2056	4.6740	0.4238	0.575	0.0220
40	0.2842	3.3310	0.4956	0.451	0.0200
Acetamide-KCl-Water System					
25	− 0.1529	7.3090	− 0.4379	0.726	0.020
30	− 0.1684	5.4571	− 0.3545	0.747	0.021
35	− 0.2046	4.8091	− 0.4129	0.749	0.020
40	− 0.3019	2.9448	− 0.5092	0.782	0.018
Acetamide-KBr-Water System					
25	0.1775	4.9620	− 0.3730	0.638	0.0071
30	0.1783	4.8182	− 0.3756	0.630	0.0060
35	0.1997	4.2203	− 0.4054	0.576	0.0102
40	0.2850	2.8639	− 0.4995	0.432	0.0070
Acetamide-KI-Water System					
25	0.1821	4.6433	− 0.3695	0.608	0.0058
30	0.2026	3.9220	− 0.4093	0.551	0.0069
35	0.2186	3.7290	− 0.4292	0.543	0.0029
40	0.3061	2.8200	− 0.5198	0.440	0.0076

The results presented in Tables 1 and 2 can well be explained by taking into account, the structural behaviour of acetamide molecules and various ions present in water, the hydrogen bonding capabilities and the hydration properties of non-electrolyte.

A perusal of the data reveals that the B values for all the six alkali metal halides in aqueous acetamide solution increase with increase in temperature. B Values obtained by employing various equations do not agree well with each other but are of the same order. The negative value of B-coefficient are associated with structure breaking effect of the solution.

The ionic molar volumes ($\overline{V}\pm$) can be obtained from the ionic ($B\pm$) coefficient employing the relation.

$$B\pm = 2.5\,\overline{V}\pm \qquad (6)$$

The hydration number n_B of ions can be calculated from the equation

$$\overline{V}\pm = \overline{V}^{o}_{ion} = n_B\,\overline{V}^{o}_{s} \qquad (7)$$

where $V^{o}_{ion_3}$ is free ion volume which can be calculated from the relation $\overline{V}^{o}_{ion}$ 2.53 r^{o} where r^{o} is radius in Å taken from Gourary-Adrian radii, $\overline{V}^{o}_{s}$ is volume of water equal to 6.62 $cm^3\ mol^{-1}$ taking radius of water 1.38 (Pauling).

Thus the hydration number of ions are given by the relation

$$n_B = \frac{\overline{V}\pm - \overline{V}^{o}_{ion}}{\overline{V}^{o}_{s}} \qquad (8)$$

In substituting the values of $\overline{V}\pm$ from eq. (6) in (8), we get,

$$n_B = \frac{0.4\,B\pm\,V^{o}_{ion}}{\overline{V}^{o}_{s}} \qquad (9)$$

The results obtained from equation (9) are given in Table 3.

The thermodynamic properties of aqueous solutions can be described by multiplyer hydration model of Gurney[19] and Eigen and Wicke[20]. Through this model for solute-water interaction, the value of $\overline{V}\pm$ can be attributed to different components like crystal partial molar volume, electrostriction partial molar volume, voidspace or disordered partial molar volume and caged or structural partial molar volume. Thus on the basis of above arguments, it is convenient to divide the ions into three classes as to which region is predominent; (a) electrostrictive structure-making ions (b) disordered structure-breaking ions and (c) hydrophobic structure making ions.

The ionic molar volume ($\overline{V}\pm$) slightly increases with increase in temperature in aqueous acetamide solution except in the case of Na^+, where the $\overline{V}\pm$ values remain constant on temperature increase. Our results are similar to that of Curthoys and Mathesion's[21]. Thus it can be concluded that K^+, Cl^-, Br^- and I^- are disordered structure-breaking ions or negative hydrating ions and the structure breaking behaviour is in the order $I^- > Br^- > Cl^- > K^+ > Na^+$ in aqueous acetamide solution.

TABLE 3
VALUES OF VARIOUS IONIC PARAMETERS AT DIFFERENT TEMPERATURES

Ion	$\gamma^{a}_{\pm}$	$\overline{V}_e$ ($cm^3 mol^{-1}$)	$B_\pm$ (Lit mol^{-1})	$\overline{V}_\pm$ ($cm^3 mol^{-1}$)	n_B
25°C					
Na^+	1.17	4.04	0.095	38	5.1209
K^+	1.49	8.34	– 0.085	– 34	– 6.3950
Cl^-	1.64	11.12	– 0.085	– 34	– 6.9660
Br^-	1.80	14.70	– 0.045	– 18	– 4.9390
I^-	2.05	21.70	– 0.185	– 74	– 14.4561
30°C					
Na^+	1.17	4.04	0.105	42	5.7340
K^+	1.49	8.34	– 0.095	– 38	– 7.0000
Cl^-	1.64	11.12	– 0.095	– 38	– 7.4190
Br^-	1.80	14.70	– 0.145	– 58	– 10.9800
I^-	2.05	21.70	– 0.205	– 82	– 15.6696
35°C					
Na^+	1.17	4.04	0.077	30.8	4.0422
K^+	1.49	8.34	–0.110	– 44.0	– 7.9063
Cl^-	1.64	11.12	– 0.137	– 54.8	– 10.9980
Br^-	1.80	14.70	– 0.163	– 74.4	– 11.7820
I^-	2.05	21.70	– 0.237	– 94.8	– 17.5981
40°C					
Na^+	1.17	4.04	0.045	18.0	2.1087
K^+	1.49	8.34	– 0.165	– 66.0	– 11.2296
Cl^-	1.64	11.12	– 0.165	– 66.0	– 11.6495
Br^-	1.80	14.70	– 0.255	– 102.0	– 17.6280
I^-	2.05	21.70	– 0.315	– 126.0	– 22.3111

The negative and positive signs of hydration numbers are assigned to the structure breaking and struture making behaviours of K^+ and Na^+ ions respectively. The hydration number of Na^+ ions remain constant with increase in temperature, while hydration numbers of other ionic moities increase with increase in temperature, indicating that these ions show structure breaking/negative hydrating tendencies in aqueous acetamide solution. In other words we can say that the exchange of molecule of water nearest the ions occurs more frequently than the exchange of water molecule in bulk[22].

The hydration number and B-coefficient (B±) correlations show that hydration number of positive and negative ions have different linear relationships with their B± coefficient supporting the idea[23] that structure making ions have positive ionic molar volume, positive hydration number and positive entropy change while structure breaking ions have reverse values.

In conclusion we can say that the magnitudes of hydration number and other parameters indicate that the structure making behaviour of various ions, present in the alkali metal halides-acetamide-water system are in the order

$$Na^+ > K^+ > Cl^- > Br^- > I^-.$$

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