VISCOSITY OF SOME MULTICHARGED ELECTROLYTES IN WATER AND AQUEOUS SULPHURIC ACID

M.L. Parmar and Anita Khanna

Department of Chemistry, Himachal Pradesh University, Shimla - 171 005 (India)

The relative viscosities of solutions of ammonium aluminium sulphate and potassium aluminium sulphate in water and aqueous sulphuric acid (0.01, 0.05, 0.10 and 0.15 N) have been measured at 303°K. The experimental results have been analyzed using the Jones-Dole equation and discussed in terms solute-solvent and solute-solute interactions. Attempt has also been made to determine the transition state parameters.

Solute-solvent interaction studies in electrolytic solutions have been the subject of active interest among physical chemists for the last two decades. The inference regarding the interactions is generally derived either from partial molar volume studies or viscosity studies or conductance studies or from all these properties [1,2]. Since the viscometric method is known to give valuable information regarding ion-solvent interactions, studies on viscosity on ionic solutions are of great help in characterizing the structure and properties of solutions. Although a number of extensive viscometric studies have been made recently in various solvents involving simple electrolytes, literature provides very little information regarding the viscometric studies of the mixtures. Here is reported the results of the study of viscometric properties of ammonium aluminium sulphate and potassium aluminim sulphate in water and aqueous-sulphuric acid.

EXPERIMENTAL

Ammonium aluminium sulphate & potassium aluminium sulphate were of AnalaR grade and used after drying over P_2O_5 without further purification. The sulphuric acid of AnalaR grade was also used without further purification. Water of specific conductance of the order of 10^{-6} Ω^{-1} cm^{-1} was used for making the solutions as well as for all calibration purposes. All solutions of the electrolytes were prepared by weight and conversion of molality to molarity was done by using the following expression [3].

$$C = \frac{d\ m\ 1000}{1000 + mM_2} \qquad \ldots\ldots(1)$$

Where C is the molarity, d the density of solution of the electrolyte, m the moality and M_2 the molecular weight of the electrolyte. Density was measured with an apparatus similar to the one reported by Ward and Millero [4]. The kinematic viscosities were measured with the help of a capillary type Viscometer [5] with a time flow of 283 ± 0.1 seconds for water at 303°K. The relative viscosity of solutions were calculated from the average of 3 readings using the following relation

$$\eta/\eta_o = \frac{d.t}{d_o t_o} \qquad \ldots\ldots(2)$$

Where η and η_o, d and d_o are the viscosity and density of the solution and solvent respectively and t and t_o are their respective flow times. Because all the flow times, were greater than 100 sec, kinetic energy correction was not necessary. The partial molar volumes of solute at infinite dilution were obtained from the Masson's equation [6] as reported in our previous communication [4]. All measurements of viscosity were carried out in air thermostat while those of density in a water bath, whose temperature was kept constant within the range of ± 0.01°C.

RESULTS AND DISCUSSION

The concentration C, density d, relative viscosity η/η_o and $(\eta/\eta_o - 1)/\sqrt{C}$ value of the solutions of ammonium aluminium sulphate and potassium aluminium suphate in water at 303°, 308° and 313° K are given in Table 1 and in various compositions of aqueous sulphuric acid at 303° K are given in Table 2.

It is evident from Table 1 and 2 that the values of relative viscosities of ammonium aluminium sulphate and potassium aluminium sulphate solutions in water and different compositions of aqueous sulphuric acid increase with increasing concentration of the electrolyte and decrease with increasing temperatures. It has been further found that

TABLE 1

CONCENTRATION C, DENSITY d RELATIVE VISCOSITY η/η_o AND $(\eta/\eta_o - 1)/\sqrt{c}$ VALUES FOR AMMONIUM ALUMINIUM SULPHATE AND POTASSIUM ALUMINIUM SULPHATE IN WATER AT 303, 308 AND 313 K.

a*	b*	c*	d*	a*	b*	c*	d*	a*	b*	c*	d*
Temp. 303 η_o = 0.8007 C.P.				Temp. 308 η_o = 0.7225 C.P.				Temp. 313 η_o = 0.6560 C.P.			
Ammonia Aluminium Sulphate											
0.99	0.9974	1.0086	0.0865	0.99	0.9958	1.0072	0.0723	0.99	0.9938	1.0057	0.0575
1.97	0.9993	1.0220	0.1570	1.98	0.9976	1.0202	0.1443	1.97	0.9955	1.0157	0.1115
3.94	1.0033	1.0371	0.1873	3.94	1.0014	1.0408	0.2062	3.93	0.9991	1.0317	0.1602
5.84	1.0077	1.0593	0.2451	5.87	1.0054	1.0613	0.2534	5.96	1.0029	1.0522	0.2157
7.79	1.0129	1.0718	0.2568	7.79	1.0096	1.0811	0.2907	7.98	1.0066	1.0723	0.2599
9.73	1.0172	1.0930	0.2983	9.70	1.0143	1.1001	0.3218	9.68	1.0102	1.0933	0.3000
Potassium Aluminium Sulphate											
0.99	0.9976	1.0111	0.1146	0.99	0.9960	1.0130	0.1306	0.99	0.9940	1.0120	0.1210
1.98	0.9997	1.0271	0.1936	1.98	0.9981	1.0263	0.1870	1.97	0.9961	1.0245	0.1748
3.94	1.0040	1.0486	0.2523	3.93	1.0022	1.0451	0.2275	3.93	1.002	1.0390	0.1971
5.88	1.0085	1.0688	0.3001	5.87	1.0066	1.0688	0.2843	5.96	1.004	1.0580	0.2400
7.81	1.0133	1.0940	0.3478	7.80	1.0115	1.0929	0.3341	7.98	1.002	1.0738	0.2654
9.72	1.0182	1.1193	0.3837	9.70	1.0164	1.1170	0.3765	9.67	1.0141	1.0968	0.3113

where a* = C x 10^2 (mol/dm^3); b* = d (g./Cm^3); c* = η/η_o ; and d* = $(\eta/\eta_o - 1)\sqrt{C}$

plot of η/η_o vs $\sqrt{C}$ is a straight line according to Falkenhagan-Dole equation [7]

$$\eta/\eta_o = 1 + S_\eta \sqrt{C} \qquad \ldots\ldots(3)$$

where S_η is the limiting slope. It is found that Falkenhagan-Dole theory is valid in concentration range reported here in all mixtures of aqueous-sulphuric acid.

The relative viscosities of the electrolytes is represented by Jones-Dole equation [8]

$$(\eta/\eta_o - 1)\sqrt{C} = A + B\sqrt{C} \qquad \ldots\ldots(4)$$

The data has been fitted to this equation. We have not used the extended Jones-Dole equation including the DC^2 term as suggested by Desnoyers and Perron [9] and utilized recently by Bicknell et.al. [10]

The plot of $(\eta/\eta_o - 1)/\sqrt{C}$ vs $\sqrt{C}$ was found to be linear for both the multicharged electrolytes in water as well as in different aqueous sulphuric acid compositions. Sample plots for ammonium aluminium sulphate and potassium aluminium sulphate are shown in Figures 1 and 2 respectively at 303°K in aqueous-sulphuric acid.

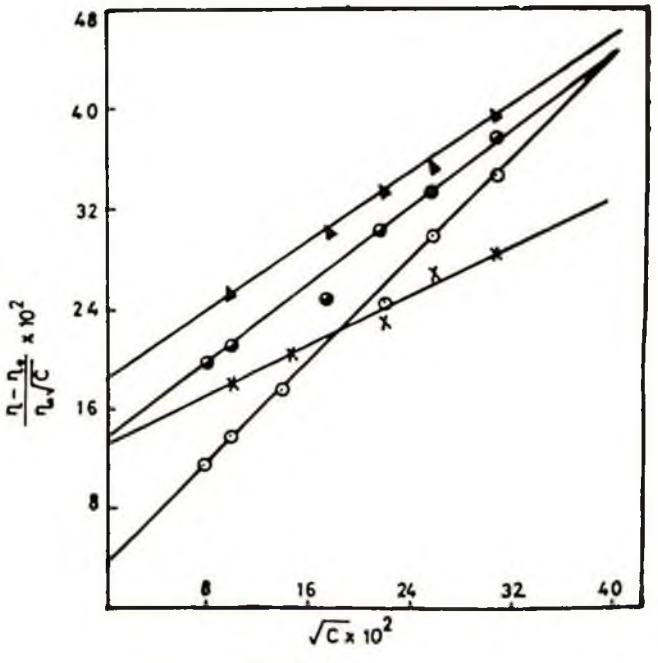


Fig. 1 Plot of $\frac{\eta-\eta_o}{\eta_o\sqrt{C}}$ vs $\sqrt{C}$ for $AlNH_4(SO_4)_2$ 12 H_2O in different compositions of aqueous-sulphuric acid at 303°K

The A and B coefficient of the multicharged electrolytes, obtained as intercepts and

TABLE 2

CONCENTRATION C, DENSITY d, RELATIVE VISCOSITY η/η_o AND $(\eta/\eta_o - 1)/\sqrt{C}$ VALUES FOR ALUMINIUM AMMONIUM SULPHATE AND POTASSIUM ALUMINIUM SULPHATE IN DIFFERENT COMPOSITIONS OF AQUEOUS H_2SO_4 AT 303° K

Ammonium Aluminium Sulphate				Potassium Aluminium Sulphate			
$C \times 10^2$ (mol. dm^{-3})	d (g. cm^{-3})	η/η_o	$(\eta/\eta_o - 1)/\sqrt{C}$	$C \times 10^2$ (mol. dm^3)	d (g.cm^3)	η/η_o	$(\eta/\eta_o - 1)/\sqrt{C}$
			0.01 N H_2SO_4 ; η_o = 8295 cp				
1.00	0.9987	1.0141	0.1423	0.99	0.9988	1.0195	0.1954
1.97	1.0006	1.0248	0.1764	2.92	1.0028	1.0454	0.2600
3.93	1.0060	1.0540	0.2434	4.92	1.0067	1.0638	0.2853
6.85	1.0094	1.0782	0.2989	6.85	1.0103	1.0887	0.3356
9.68	1.0144	1.1084	0.3481	9.67	1.0156	1.1198	0.3853
			0.05 N H_2SO_4 ; η_o = 0.8378 cp				
1.00	0.9997	1.0120	0.1918	0.99	0.9999	1.0181	0.1819
2.97	1.0038	1.0282	0.2043	2.97	1.0041	1.0405	0.2352
4.92	1.0076	1.0433	0.2275	4.92	1.0083	1.0586	0.2642
6.86	1.0112	1.0615	0.2680	6.86	1.0122	1.0741	0.2830
9.72	1.0165	1.0807	0.2828	9.72	1.0179	1.0973	0.3118
			0.1 N H_2SO_4 ; η_o = 0.8384 cp				
1.00	1.0008	1.0255	0.2550	1.00	1.0008	1.0328	0.3285
2.98	1.0051	1.0530	1.3020	2.98	1.0054	1.0650	0.3767
4.94	1.0093	1.0750	0.3356	4.93	1.0097	1.0873	0.3934
6.88	1.0133	1.0936	0.3572	6.88	1.0140	1.1115	0.4252
9.77	1.0190	1.1240	0.3968	9.75	1.0202	1.1442	0.4618
			0.15 N H_2SO_4 ; η_o = 0.8493 cp				
1.00	1.0021	1.0219	0.2154	1.00	1.0021	1.0251	0.2546
2.98	1.0063	1.0430	0.2490	2.98	1.0068	1.0483	0.2798
4.94	1.0113	1.0653	0.2941	4.94	1.0115	1.0676	0.3043
6.88	1.0155	1.0881	0.3360	6.88	1.0158	1.0861	0.3281
9.76	1.0218	1.1126	0.3605	9.76	1.0221	1.1123	0.3610

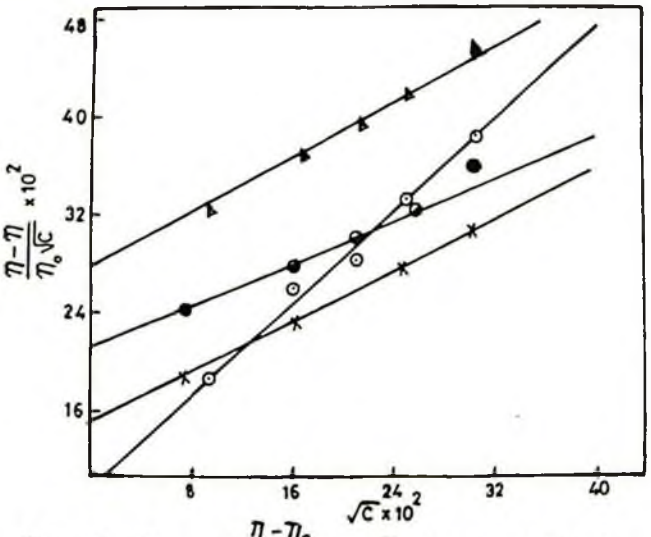


Fig. 2 Plot of $\frac{\eta-\eta_o}{\eta_o\sqrt{C}}$ vs $\sqrt{C}$ for $K\,Al(SO_4)_2\,12\,H_2O$ in different compositions of aqueous sulphuric acid at 303°K

slopes of the straight lines, are given in Table 3.

It is evident from Table 3 that the value of A parameter for both the electrolytes in water is very small and goes on decreasing with the increase of temperature.

B-coefficient may be either positive or negative and is said to be a measure of effective hydrodynamic volume of solvated ions that account for ion-solvent interaction [11]. It is also a measure of order or disorder introduced by ions into the solvent structure. The B-coefficient for both the electrolytes in water is found to be positive and large at all the temperatures thereby suggesting strong solute-solvent interactions.

It has been emphasized by a number of workers that dB/dT is more important criterion [12]

TABLE 3

VALUES OF A AND B PARAMETERS OF THE JONES-DOLE EQUATION FOR ALUMINIUM AMMONIUM SULPHATE AND POTASSIUM ALUMINIUM SULPHATE SOLUTIONS IN WATER AND AQUEOUS SULPHURIC ACID.

Solvent	T	A ($dm^{3/2} mol^{-1/2}$)	B ($dm^3 mol^{-1}$)
Aluminium ammonium sulphate			
Water	303	0.087	0.928
	308	0.012	1.000
	313	-0.046	1.072
0.01N Sulphuric acid	303	0.035	0.983
0.05N Sulphuric acid	303	0.136	0.567
0.10N Sulphuric acid	303	0.186	0.667
0.15N Sulphuric acid	303	0.136	0.723
Potassium aluminium sulphate			
Water	303	0.064	0.909
	308	0.028	1.000
	313	-0.008	1.067
0.01N Sulphuric acid	303	0.099	0.928
0.05N Sulphuric acid	303	0.155	0.529
0.10N Sulphuric acid	303	0.269	0.606
0.15N Sulphuric acid	303	0.217	0.461

for determining the solute-solvent interactions. Viscosity study of a number of solutions has shown that structure makers will have negative values of dB/dT and structure-breakers have positive values. Accordingly, the positive temperature coefficient of B in case of water suggests that both the electrolytes behave like structure breakers. This is in accordance with our earlier conclusion from the study of molar volumes [14] of aluminium sulphate and potassium aluminium sulphate in water.

It is also evident from Table 3 that the value of A parameter for both the electrolytes in aqueous-sulphuric acid is positive and large as compared to water at the same temperature. Also the value of A parameter goes on increasing with acid content upto 0.10 N sulphuric acid and decreases at higher concentration. This indicates that ion-ion interactions are lower at lower as well as at higher concentrations.

It is also evident from Table 3 that the values of the B-coefficient of sulphuric acid are positive and do not change considerably with the change in composition of sulphuric acid thereby suggesting that solute-solvent interactions remain more or less constant. The positive values of B-coefficient also indicate that both the electrolytes behave as structure makers/promoters in aqueous-sulphuric acid which in accordance with our earlier conclusion from the study of molar volumes[4].

Viscosity data have also been analysed on the basis of a transition state treatment of the relative viscosity of electrolytic solutions as suggested by Feakins et al [13].

The application of this theory gives rise to the following equation:

$$B = \frac{\bar{V}_1^\circ - \bar{V}_2^\circ}{1000} + \frac{\bar{V}_1^\circ}{1000} \cdot \frac{\Delta \mu_2^{\circ\#} - \mu_1^{\circ\#}}{RT} \quad \ldots(5)$$

where $\bar{V}_1^\circ$ and $\bar{V}_2^\circ$ are the partial molar volumes of solvent and solute (at infinite dilution) respectively, $\Delta \mu_2^{\circ\#}$ is the contribution per mole of solute to the free energy of activation for viscous flow of the solution. $\Delta \mu_1^{\circ\#}$, the free energy of activation per mole of the pure solent, is given by [14]

$$\Delta \mu_1^{\circ\#} = \Delta G_1^{\#} = RT \ln (\eta_\circ \bar{V}_1^\circ / hN) \quad \ldots\ldots(6)$$

where h is the Plank constant & N is the Avogadro constant, $\eta_\circ$ is the viscosity of the solvent.

Now equation (5) can also be written as

$$\Delta \mu_2^{\circ\#} = \Delta \mu_1^{\circ\#} + \frac{RT}{\bar{V}_1^\circ} \left[1000\, B - (\bar{V}_1^\circ - \bar{V}_2^\circ)\right] \quad \ldots(7)$$

$\Delta \mu_1^{\circ\#}$ parameter was calculated from relation(6) and its values are given in Table 4 for different compositions of aqueous-sulphuric acid at 303° K. The values of $\bar{V}_2^\circ$, the partial molar volumes at infinite dilution, for both the electrolytes were determined as described earlier [4] and are also recorded in Table 4. The partial molar volume $\bar{V}_1^\circ$ of sulphuric acid at infinite dilution was found to be 17.50 cm^3 $mole^{-1}$ at 303° K.

The $\Delta \mu_2^{\circ\#}$ values obtained from (7) are also given in Table 4 for different compositions of sulphuric acid at 303k. The $\Delta \mu_1^{\circ\#}$ values were practically constant in all the range of solvent composition (Table 4). It is also clear from tables 3 and 4 that the behaviour of $\Delta \mu_2^{\circ\#}$ is quite similar to that of B in all the solvent compositions and no regular trend has

TABLE 4

VALUES OF $\bar{V}_2^\circ$, $\Delta\mu_1^{\circ\#}$ AND $\Delta\mu_2^{\circ\#}$ IN AQUEOUS-SULPHURIC ACID AT 303°K

Systems	$\bar{V}_2^\circ$ ($Cm^3\ mol^{-1}$)	$\Delta\mu_1^{\circ\#}$ ($K\ J\ mol^{-1}$)	$\Delta\mu_2^{\circ\#}$ ($K\ J\ mol^{-1}$)	$\bar{V}_2^\circ$ ($Cm^3\ mol^{-1}$)	$\Delta\mu_1^{\circ\#}$ ($K\ J\ mol^{-1}$)	$\Delta\mu_2^{\circ\#}$ ($K\ J\ mol^{-1}$)
	Ammonium Aluminium Sulphate			Potassium Aluminium Sulphate		
0.01N H SO	249.0	9.055	183.88	262.0	9.055	177.84
0.05N H SO	235.5	9.078	122.08	244.5	9.078	117.96
0.10N H SO	218.5	9.083	134.06	233.0	9.083	127.31
0.15N H SO	202.0	9.115	139.78	221.0	9.115	104.77

been observed suggesting thereby that the flow rate is influenced to a considerable extent by the presence of the multicharged electrolyte.

ACKNOWLEDGEMENT

One of the authors (A.K.) is grateful to C.S.I.R New Delhi(India) for the award of Senior Research Fellowship.

REFERENCES

1. J.M. McDowali and C.A. Vincent, *J. Chem. Soc., Farady Trans. I.* **70** (1974) 1862.

2. M.R.J. Dack, K.J. Bird and A.J. Parker, *Aust. J. Chem.*, 28 (1975) 955.

3. D.P. Shoemaker and C.W. Garland, *"Experiments in Physical Chemistry"*, **Mc Graw Hill, New York** (1967) p. 131.

4. G.K. Ward and F.J. Millero, *J. Soln. Chem.*, 3 (1974) 417. M.L. Parmar and Anita Kundra, *Electrochimica Acta*, 28 (1983) 1655.

5. R.L. Blokhra and M.L. Parmar, *Aust. J. Chem.*, 27 (1974) 1407.

6. D.O. Masson, *Phil. Mag.* 8 (1929) 218.

7. H. Falkenbagan and M. Dole, *Physik. Z.*, 33 (1929) 611.

8. G. Jone and M. Dole, *J. Am. Chem. Soc.* **51** (1929) 2950.

9. J.E. Desnoyers and G. Parron, *J. Soln. Chem.* **1**(1972) 199.

10. R.T.M. Bicknell, K.G. Lawrence and D. Feakins, *J.Chem. Soc. Faraday, I.* **76** (1980) 637.

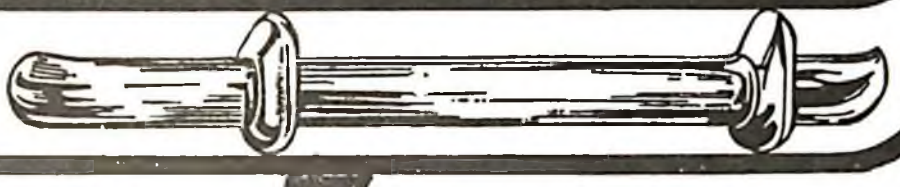
11. E.R. Nightingale, *"Chemical Physics of Ionic Solution"*, **Wiley, Inc. New York** (1966) p.92

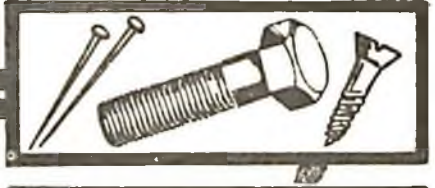
12. T.S. Sarma and J.C. Ahluwalia, *Rev. Chem. Soc*, 2 (1973) 217.

13. D. Feakins, D.J. Freemantle and K.G. Lawrence, *J. Chem. Soc. Faradey Trans. I*, **70** (1974) 795.

14. S. Glasstone, K.J. Laidler and H. Eyring, *"The theory of Rate Processes"*, **Mc Graw Hill New York** (1941) p.477.

ELECTROPLATERS & ANODISERS







ELECTROPLATING :-

Chrome, Nickel, Silver, Bronze, Brass, Tin, Zinc, Copper, Cadmium, Chromate Processing, Barrel plating etc.

Auto Motor Bumpers & Guards a speciality. Remember, it is the quality that counts! Work carried out to I.S., B.S. & ASTM Specifications.

ALUMINIUM ANODISING :-

Specialists in Industrial & Structural Anodising.

KOHINOOR ELECTRO GILDERS

(Estd. 1932)

Khotwadi 10th Lane, Bombay-4. Phone : 351780