ELECTROLYTIC CONDUCTIVITY AND WALDEN PRODUCT OF SOME MULTICHARGED ELECTROLYTES IN BINARY ALCOHOL - WATER MIXTURES

M.L. Parmar* and Anita Khanna

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

Conductance measurements are reported for dilute solutions of aluminium ammonium sulphate and potassium aluminium sulphate in different binary alcohol-water mixtures [(Methanol-water (MeOH-H_2O), isopropanol-water (iso PrOH-H_2O) and tert.butanol-water (tert.BuOH-H_2O): 5,10,15, and 20% (w/w)] at 303, 308, 313 and 318°K. The Walden product $\lambda^\circ_m \eta_o$ has been calculated in all media multicharged electrolytes in different compositions of alcohol water. The temperature effect on Walden product in 5% alcohol-water mixtures shows that both the salts behave as structure makers.

Previous studies [1,2] of ion solvent interactions in aqueous organic solvent mixtures have shown the great dependence on the nature of organic component, particularly in investigations involving the hydrogen ion. In order to explain the results, it has been assumed that in water rich region of some binary systems, an enhanced structure occurs which is related to the phenomenon of hydrophobic interactions [3] whereas in other mixed aqueous solvent such as water-acetonitrile mixtures [4] a continuous disruption of the water lattice appears to take place upon the addition of aprotic organic component.

The present studies have been carried out to know about the conductometric behaviour of the highly charged electrolytes like $KAl(SO_4)_2 \cdot 12\ H_2O$ and $AlNH_4(SO_4)_2 \cdot 12\ H_2O$ in aqueous-methanol, aqueous-isopropanol and aqueous tert. butanol. The effect of solvent may be considered as being two fold:

(a) stabilize the pairs due to the H-bond chains in the alcohol,

(b) solvate anions by H-bonding.

The participation of alcohols in ion pair formation should therefore involve both the steric and coulombic effects. On the basis of this approach, the structure modification of alcoholic polymers generated by added solvent should result in variable influence of the alcohol molecules on the ion-pair association of the electrolyte

EXPERIMENTAL

Ammonium aluminium sulphate and potassium aluminium sulphate were of AnalaR grade and used after drying over P_2O_5 without further purification. Methanol, isopropanol and tert. butanol were of AnalaR grade and were dried by refluxing over CaO for several hours and then distilled. Only the middle fractions were collected and stored in glass bottles having Linde type 5A° molecular sieves. Fresh distilled water of specific conductance of the order of $10^{-6}\ \Omega^{-1}\ cm^{-1}$ was used for preparing alcohol-water mixtures.

All alcohol water mixtures and electrolyte solutions were made by weight. Density was measured as per standard method [5,6]. Molarity was calculated using density of the solutions and molecular weight (ammonium alum 453.33 and potash alum 474.44) [7]. Kinematic viscosity was measured with the help of a capillary type viscometer [8] with flow time of 283s for water at 303°K . Runs were repeated until three successive determinations were obtained within 0.1s. Because all the flow times were greater than 100s, kinetic energy correction was not necessary in calculating viscosities.

Conductance measurements were carried out with the help of Naina Digital conductivity meter type NDC 732 at 50 Hz supplied by Naina Electronics (P) Ltd. The conductivity cell having cell constant $4.153 \pm 0.001\ cm^{-1}$ was used for the present study. All measurements were carried out in water thermostat with a temperature control ± 0.01°C.

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RESULTS AND DISCUSSION

The molar conductance λ_m values of aluminium and potassium alums are calculated in different media and plots of λ_m vs $\sqrt{c}$ are made. These are linear. (Typical plots in Fig 1&2).

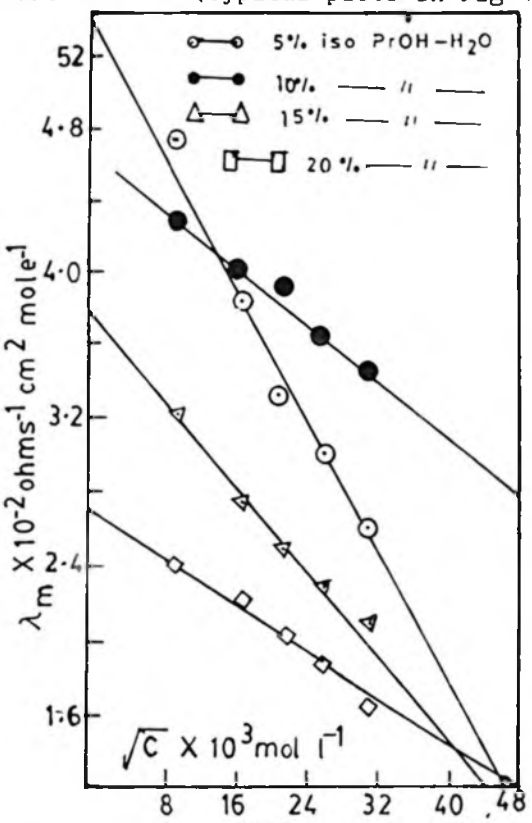


Fig. 1 Plot of λ_m vs $\sqrt{C}$ for $AlNH_4(SO_4)_2 . 12H_2O$ in different compositions of isopropanol - water mixtures at 308°K.

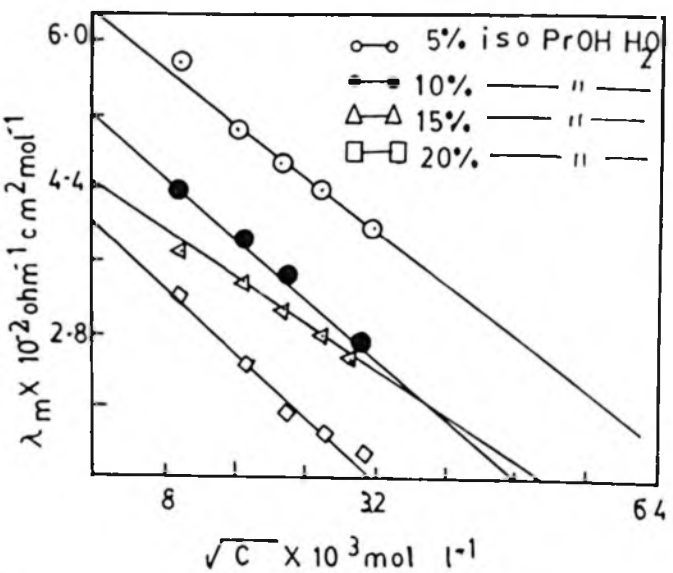


Fig. 2 Plot of λ_m vs $\sqrt{C}$ for $KAl(SO_4)_2 12H_2O$ in different compositions of isopropanol-water mixtures at 308°K.

The values of λ°_m are given in Table 1 and 2 in different compositions of alcohol at 308°K and in 5% alcohol-water mixtures at different temperatures respectively.

In the present case, a more precise estimates [10] of limiting molar conductance λ°_m at infinite dilution has been made from the straight line plots of $1/\lambda_m$ vs $C\lambda_m$. Typical plots for $AlNH_4(SO_4)_2 . 12H_2O$ and $KAl(SO_4)_2$.

TABLE 1

LIMITING MOLAR CONDUCTANCE λ°_m AND WALDEN PRODUCT FOR ALUMINIUM AMMONIUM SULPHATE AND POTASSIUM-ALUMINIUM SULPHATE IN DIFFERENT ALCOHOL-WATER MIXTURES AT 308°K.

System	λ_m 1	λ_m 2	$\eta_o \times 10^3$ (P)	$\lambda^\circ_m \eta_o$
Aluminium ammonium sulphate				
	methanol-water system.			
5% $MeOH-H_2O$	552.0	552.4	8.477	4.68
10% $MeOH-H_2O$	664.0	666.2	9.336	6.22
15% $MeOH-H_2O$	704.0	704.0	9.603	6.72
20% $MeOH-H_2O$	833.0	833.0	10.870	8.42
	isopropanol-water system			
5% iso $PrOH-H_2O$	544.0	543.8	8.098	4.40
10% iso $PrOH-H_2O$	466.0	463.0	9.721	4.50
15% iso $PrOH-H_2O$	376.0	373.1	10.512	3.92
20% iso $PrOH-H_2O$	270.0	272.1	12.423	3.32
	tert.butanol-water system			
5% tert.$BuOH-H_2O$	520.0	500.0	8.595	4.30
10% tert.$BuOH-H_2O$	494.0	490.0	10.130	4.96
15% tert.$BuOH-H_2O$	470.0	469.5	11.733	5.51
20% tert.$BuOH-H_2O$	442.4	442.4	13.954	6.17
Potassium aluminium sulphate				
	Methanol-water system			
5% $MeOH-H_2O$	588.0	585.0	8.477	4.96
10% $MeOH-H_2O$	576.0	574.8	9.336	5.30
15% $MeOH-H_2O$	558.0	561.7	9.603	5.40
20% $MeOH-H_2O$	546.0	541.0	10.870	5.47
	isopropanol-water system			
5% iso $PrOH-H_2O$	632.0	630.7	8.098	5.11
10% iso $PrOH-H_2O$	520.0	520.0	9.721	5.05
15% iso $PrOH-H_2O$	452.0	454.9	10.512	4.79
20. iso $PrOH-H_2O$	384.0	384.6	12.423	4.77
	tert.butanol-water system			
5% tert.$BuOH-H_2O$	624.0	625.0	8.595	5.37
10% tert.$BuOH-H_2O$	604.0	609.0	10.130	6.38
15% tert.$BuOH-H_2O$	544.0	543.5	11.733	6.17
20% tert.$BuOH-H_2O$	444.0	441.4	13.954	6.15

1. Values from Onsager plots
2. Values from $1/\lambda_m$ vs $C\lambda_m$ plots

TABLE 2

LIMITING MOLAR CONDUCTANCE λ°_m AND WALDEN PRODUCT FOR $AlNH_4(SO_4)_2.12H_2O$ AND $KAl(SO_4)_2.12H_2O$ IN 5% ALCOHOL-WATER MIXTURES AT DIFFERENT TEMPERATURES

Temperature	λ°_m 1	λ°_m 2	$\eta_0 \times 10^3$ (P)	$\lambda_m \eta_0$
Aluminium ammonium sulphate				
	5% methanol-water			
303	472	471.7	9.290	4.38
308	552	552.4	8.477	4.68
313	684	684.9	7.099	4.86
318	820	819.7	6.228	5.11
	5% isopropanol-water			
303	460	458.7	9.401	4.31
308	544	543.0	8.098	4.40
313	600	602.4	7.569	4.56
318	664	666.6	7.102	4.67
	5% tert.butanol-water			
303	432	429.2	9.795	4.02
308	520	500.0	8.595	4.30
313	572	571.4	7.701	4.40
318	662.4	662.4	6.791	4.50
Potassium aluminium sulphate				
	5% methanol-water			
303	528	529.1	9.290	4.92
308	588	585.0	8.477	4.96
313	724	724.6	7.099	5.14
318	824	826.4	6.228	5.18
	5% isopropanol-water			
303	544	543.2	9.401	5.11
308	636	636.7	8.098	5.15
313	688	684.9	7.569	5.18
318	766	775.9	7.102	5.43
	5% tert.butanol-water			
303	468	469.0	9.795	4.59
308	624	625.0	8.595	5.37
313	634	636.9	7.701	4.90
318	742	740.7	6.791	5.03

1. value from Onsager plot
2. value from $1/\lambda_m$ vs $C\lambda_m$ plot

$12H_2O$ in different compositions of isopropanol water mixtures at 308°K are shown in Figs. 3 and 4. The values of λ°_m thus obtained from the extrapolation of these plots are also given in Tables which indicate an excellent agreement between λ°_m values otained from the two methods. In other words, this method can be used as an accurate method to give good

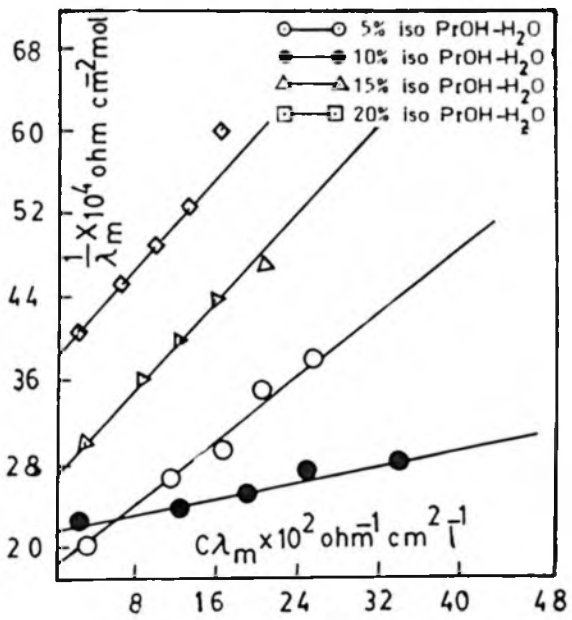


Fig. 3 Plot of $\frac{1}{\lambda_m}$ vs $C\lambda_m$ for $AlNH_4(SO_4)_2\,12H_2O$ in different isopropanol-water mixtures at 308°K

precision of extrapolation to the conductance at zero concentration for highly charged electrolytes.

It is seen from Table 1 that the value of limiting molar conductance, λ°_m decreases with the increase of alcohol content in all cases except for aluminium alum in methanol-water system. Here it increases with the increase in methanol content. This may be due to decreasing association of aluminium ammonium sulphate with methanol content. The Table 1 also shows a change in the value of Walden product with composition of alcohol.

Effect of Temperature

Since the behaviour of both the multicharged electrolytes was found to be identical in the different alcohol-water mixtures at a particular temperature, only 5% composition of different alcohol-water was selected to know the effect of the temperature on the structure of solvent. The limiting molar conductance λ°_m alongwith Walden product $\lambda^\circ_m \eta_0$ is given in Table 2. It is found that the value of the limiting molar conductance λ°_m increases with increase of temperature.

The positive temperature coefficient of the Walden product can be attributed to the

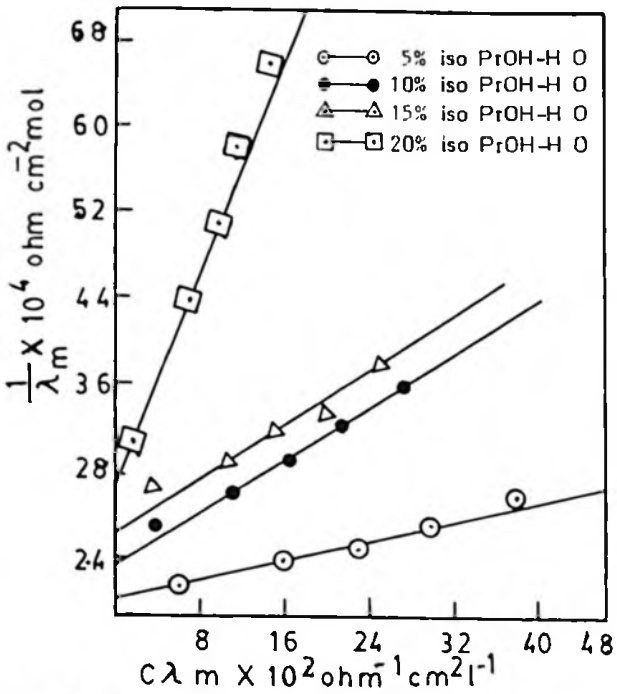


Fig. 4 Plot of $1/\lambda_m$ vs $C\lambda_m$ for $KAl(SO_4)_2\ 12H_2O$ in different compositions of iso PrOH-H_2O mixtures at 308°K

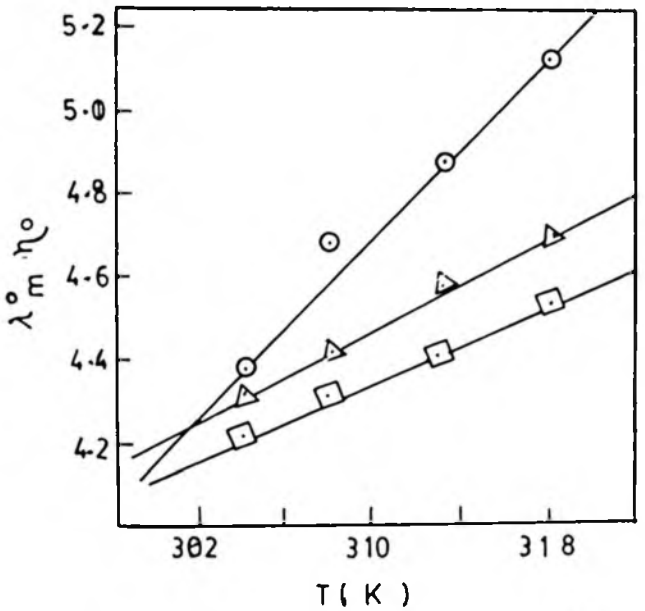


Fig. 5 Plot of $\lambda^\circ_m \eta_o$ vs T for $AlNH_4(SO_4)_2\ 12H_2O$ in 5% alcohol-water mixtures

5% MeOH-H_2O 5% iso PrOH-H_2O
5% tert Bu OH-H_2O

structure making [11] characteristic of both the multicharged electrolytes in different alcohol-water mixtures. These conclusions are in excellent agreement with those drawn from volumetric and transport properties, for these multicharged electrolytes, reported earlier [13]. Structure making may be attributed to the positive solvation and the greater slope of the plots of $\lambda^\circ_m \eta_o$ vs T in case of methanol + water for both the multicharged electrolytes suggests that greater solvation takes place in case of methanol-water and which in turn may be attributed to the preferential solvation of ions by methanol. The order of solvation for both the multicharged electrolytes in different alcohol-water mixtures is as follows:

MeOH > iso. PrOH > tert. BuOH.

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REFERENCES

1. G. Dauheret, *Bull Soc. Chim Fr.*, (1966) 513; (1968) 3122; (1971) 2393.

2. C. Moreau and G. Wouheret, *J. Chem. Phys.*, 74 (1974) 1313.

3. F. Franks and D.J.G. Ives, *Rev. Chem. Soc.*, 66 (1966) 1.

4. C. Moreau and G. Douheret, *Thermochim. Acta*, 13 (1975) 385; *J. Chem. Thermodyn*, 8 (1976) 403.

5. G.K. Ward and F.J. Millero, *J. Soln. Chem.* 3 (1974) 417.

6. M.L. Parmar and Anita Kundra, *Electrochimica Acta*; 28 (1983) 1655.

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

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

9. R.A. Robinson and R.H. Stokes, *Electrolytic solutions* chapters 5 & 7 (Butterworths, London, 2nd rev. ed.) 1965.

10. R.L. Blokhra and M.L. Parmar, *J. Electroanal. Chem.* 59 (1975) 226.

11. R.L. Blokhra and P.C. Verma, *Electrochimica Acta*, 22 (1977) 485.

12. M.L. Parmar and Anita Khanna, *Indian J. Chem.*, 25A (1986) 1044; *J. Phys. Soc. Japan*, 35 (1986) 4122; *Indian Nat. Sci. Acad.*, (comuunicated 1986).