

## Viscosities of solutions of some bi-univalent electrolytes in Dimethylsulphoxide (DMSO) at 293.15K, 303.15K and 313.15K

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### Abstract

The apparent molar volumes ( $V_{\phi 0}$ ) at  $T = (293.15K, 303.15K \text{ and } 313.15K)$  of the solutions of bi-univalent electrolytes ( $HgCl_2, SnCl_2, NiCl_2, CoCl_2, MnCl_2$  and  $SrCl_2$ ) have been determined in Dimethylsulphoxide from the measurement of densities and flow time. The partial molar volumes ( $V_{\phi}^0$ ), the coefficients A and B of Jones-Dole equation and activation thermodynamic quantities ( $\Delta\mu_1^{0\#}, \Delta\mu_2^{0\#}, \Delta S_2^{0\#}, \Delta H_2^{0\#}$ ) of viscous flow have been calculated for the equation solutions of these electrolytes in Dimethylsulphoxide (DMSO). The large positive values of  $V_{\phi}^0$  indicate the presence of strong solute solvent interactions while negative value of  $S_v$  indicate the presence of weak ion-ion interactions. Further the positive values of viscosities B coefficient, indicate that all the electrolytes behave as structure makers in DMSO. This is supported by the fact for these electrolytes ( $\Delta\mu_2^{0\#} - \Delta\mu_1^{0\#}) > 0$ .

**Keywords:** viscosities, apparent molar volumes, entropy, enthalpy

### Introduction

Ultrasonic studies leading to isentropic molar compressibility and apparent isentropic molar compressibility data are important for studying ion-solvent interactions and the structural effect of the solute and solvent in solution [1-13]. Dash and co-workers have determined the ultrasonic velocity of Octahedral cobalt complexes. Dash and Pasupulak's have reported the studies of apparent molar volume, sound velocity and velocity in solutions of glycine,  $\alpha$ -alanine and  $\beta$ -alanine in Dimethylsulphoxide (DMSO).

### Materials and methods

All the electrolytes used in the present study were of analytical reagent grade, which were used after drying in a vacuum oven at  $110^\circ C$  for 10-12 h. The reagents were always placed in the desiccator over  $P_2O_5$  to keep them in dry atmosphere. The standard stock solutions of the electrolytes were prepared in water and also in Dimethylsulphoxide (DMSO) mixed solvents. The densities of the solutions were measured at different temperatures (293.15K, 303.15K and 313.15K) using 5 ml pycnometers. The viscosities of the solutions were measured at the desired temperature using an Ostwald's suspended level type viscometer. Since all the flow times were greater than 100 second, the kinetic energy correction was not necessary. The density and viscosity measurement were carried out in thermostat bath, the temperature of which was controlled within accuracy of  $\pm 0.01 K$ . An electronic balance with an accuracy of  $1.0 \times 10^{-4} g$  was used for the mass determination. The present study mainly dealing with the determination of densities, viscosities and apparent molar volumes of the solutions of some bi-univalent electrolytes have been undertaken in the light of the following aspects:

1. Analysis of viscosity data in respect of the solutions of bi-univalent electrolytes in DMSO at different temperatures in the light of Jones-Dole equation [16];

$$\frac{\eta}{\eta_{rel}} = \eta_{rel} = 1 + A\sqrt{C} + BC -$$

2. Ascertain the nature of ion-ion and ion-solvent interactions in DMSO in terms of the values of coefficient A or B of Jones-Dole equation.

3. Determination of apparent molar volume ( $\phi_v$ ) from density data as function of molar concentration of solutions of bi-univalent electrolytes in DMSO at different temperatures and calculation of the values of  $\phi_v^0$  and  $S_v$  by applying Masson's equation vis-à-vis ion-ion and ion solvent interactions [17].

$$\phi_v = \phi_v^0 + S_v\sqrt{C}$$

4. Determination of free energies of activation of viscous flow,  $\Delta\mu_1^{0\#}$  and  $\Delta\mu_2^{0\#}$  per mole of solvent and solute respectively at different temperature and subsequent calculation of entropy and enthalpy of activation i.e.,

$$\Delta S^{0\#} \text{ and } \Delta H_2^{0\#}.$$

5. Ascertain the structure making or making or structure breaking capacities of bi-univalent electrolytes in Dimethylsulphoxide DMSO.

### Results and discussion

Viscosities of solutions of some bi-univalent electrolytes, viz,  $HgCl_2, SnCl_2, NiCl_2, CoCl_2, MnCl_2$  and  $SrCl_2$  in Dimethylsulphoxide (DMSO) have been determined as a function of molar concentration at different temperatures and result are presented in Table-1. Analysis of viscosity data in the light of Jones-Dole equation shows that the plots of  $(\eta_{rel} - 1)/\sqrt{C}$  versus  $\sqrt{C}$  are linear in each case as shown in Figure -1. The values of coefficient A and B have been

obtained from these plots by the method of least squares and results presented in Table -2.

It is seen that the values of A are negative for all the electrolytes, which indicate the presence of weak ion-ion interactions. On the other hand the values of B are positive which show the presence of strong ion-solvent interaction in DMSO. Further, the increasing trend in the values of B with the rise of temperature indicates that ion-solvent interactions become some what stronger at elevated temperature, which may be ascribed to increased solutions of the ions. The positive values of B also indicate<sup>[18]</sup> that HgCl<sub>2</sub>, SnCl<sub>2</sub>, NiCl<sub>2</sub>, CoCl<sub>2</sub>, MnCl<sub>2</sub> and SrCl<sub>2</sub> act as structure – makers in solvent Dimethylsulphoxide (DMSO).

The apparent molar volume ( $\phi_v$ ) as a function of molar concentration has been determined from density data different temperatures and the results have been presented in Table – 3. The  $\phi_v$  data have been analysed in the light of the Masson's equation and the values of constant  $\phi_v^0$  and  $S_v$  have been obtained from the linear plot of  $\phi_v$  versus  $\sqrt{c}$ , as shown in Figure- 2 by Least Squares method and results are presented in Table -4. It is seen that the values of  $\phi_v^0$  are positive and large for all the bi-univalent electrolyte, which show the presence of strong ion-solvent interactions in DMSO. Further with the rise of temperature and the values

of  $\phi_v^0$  are rendered increasingly larger which suggest that the ion-solvent interactions become increasing stronger at elevated temperatures.

Thus the identical conclusions in regard to the nature of ion-ion and ion-solvent interactions in solutions of bi-univalent electrolytes in DMSO are obtained on the basis of coefficient A and B of Jones – Dole equation and those on the basis of the constants,  $\phi_v^0$  and  $S_v$  of Masson's equation. The free energies of activation of viscous flow,  $\Delta\mu_1^{0\#}$  and  $\Delta\mu_2^{0\#}$  per mole of solvent (DMSO) and solute (bi-univalent electrolytes) respectively have been determined at different temperatures and the volumes presented in Table-5.

It is seen that the values of  $\Delta\mu_2^{0\#}$  are larger as compared to those of  $\Delta\mu_1^{0\#}$  for all the bi-univalent electrolytes and that  $(\Delta\mu_2^{0\#} - \Delta\mu_1^{0\#}) > 0$ . This suggests that all the bi-univalent electrolytes under discussion behave as structure makers<sup>[19]</sup>. It is evident that both entropy and enthalpy of activation are negative for all the bi-univalent electrolytes and that in each case  $(\Delta H_2^{0\#} > T\Delta S_2^{0\#})$ , thereby suggesting that ion-solvent interactions for these electrolytes are nearly complete in the ground state. Further, the negative values  $(\Delta H_2^{0\#} \text{ and } T\Delta S_2^{0\#})$  suggest that the transition state is associated with bond breaking and increase in order<sup>[20]</sup>.

**Table 1:** Viscosities of solutions of bi-univalent electrolytes in Dimethylsulphoxide (DMSO) at different temperatures.

Concentration (c) of electrolyte (mol dm <sup>-3</sup> )	$\eta$ (mpa.s)	$\frac{\eta_{res}^{-1}}{\sqrt{c}}$	$\eta$ (mpa.s)	$\frac{\eta_{res}^{-1}}{\sqrt{c}}$	$\eta$ (mpa.s)	$\frac{\eta_{res}^{-1}}{\sqrt{c}}$
	293.15 K		303.15 K		313.15 K	
HgCl <sub>2</sub>						
0.00	2.0900	-	1.8900	-	1.7500	-
0.02	2.1025	0.0423	1.8940	0.0149	1.7555	0.0223
0.04	2.1148	0.0594	1.8998	0.0258	1.7640	0.0400
0.06	2.1298	0.0777	1.9140	0.0519	1.7767	0.0624
0.08	2.1447	0.0925	1.9283	0.0717	1.7902	0.0811
0.10	2.1753	0.1290	1.9425	0.0878	1.8034	0.0965
SnCl <sub>2</sub>						
0.00	2.0900	-	1.8900	-	1.7500	-
0.02	2.0940	0.0137	1.8991	0.0042	1.7533	0.0133
0.04	2.1019	0.0284	1.8991	0.0240	1.7633	0.0380
0.06	2.1157	0.0503	1.9125	0.0487	1.7758	0.0602
0.08	2.1299	0.0675	1.9263	0.0679	1.7885	0.0777
0.10	2.1439	0.0815	1.9400	0.0837	1.8011	0.0924

**Table 2:** Values of coefficients A and B of Jones-Dole equation for bi-univalent electrolytes in Dimethylsulphoxide (DMSO) at different temperatures.

Electrolyte	(dm <sup>3/2</sup> mol <sup>-1/2</sup> )			B (dm <sup>3</sup> mol <sup>-1</sup> )		
	293.15 K	303.15 K	313.15 K	293.15 K	303.15 K	313.15 K
MnCl <sub>2</sub>	-0.2475	-0.2699	-0.2757	0.8449	0.8489	0.8971
CoCl <sub>2</sub>	-0.3097	-0.3288	-0.3531	0.6957	0.6993	0.8052
NiCl <sub>2</sub>	-0.0819	-0.0906	-0.0919	0.8709	0.9025	0.9942
SrCl <sub>2</sub>	-0.1213	-0.1434	-0.1458	0.7428	0.8286	0.8597
SnCl <sub>2</sub>	-0.1243	-0.1305	-0.1494	0.6915	0.7046	0.8362
HgCl <sub>2</sub>	-0.0761	-0.1355	-0.1566	0.6320	0.7383	0.8686

**Table 3:** Densities ( $\rho$ ) and Apparent Molar Volumes ( $\phi_v$ ) of solutions of bi-univalent electrolytes in Dimethylsulphoxide (DMSO) at different temperatures.

Concentration (c) of electrolyte (mol dm <sup>-3</sup> )	$\rho$ (g. cm <sup>-3</sup> )	$\phi_v$ (cm <sup>3</sup> mole <sup>-1</sup> )	$\rho$ (g. cm <sup>-3</sup> )	$\phi_v$ (cm <sup>3</sup> mole <sup>-1</sup> )	$\rho$ (g. cm <sup>-3</sup> )	$\phi_v$ (cm <sup>3</sup> mole <sup>-1</sup> )
	293.15 K		303.15 K		313.15 K	
HgCl <sub>2</sub>						
0.00	1.014	-	1.0974	-	1.0834	-
0.02	1.1032	166.80	1.8940	181.59	1.0847	188.66
0.04	1.1050	164.00	1.8998	179.09	1.0864	182.00

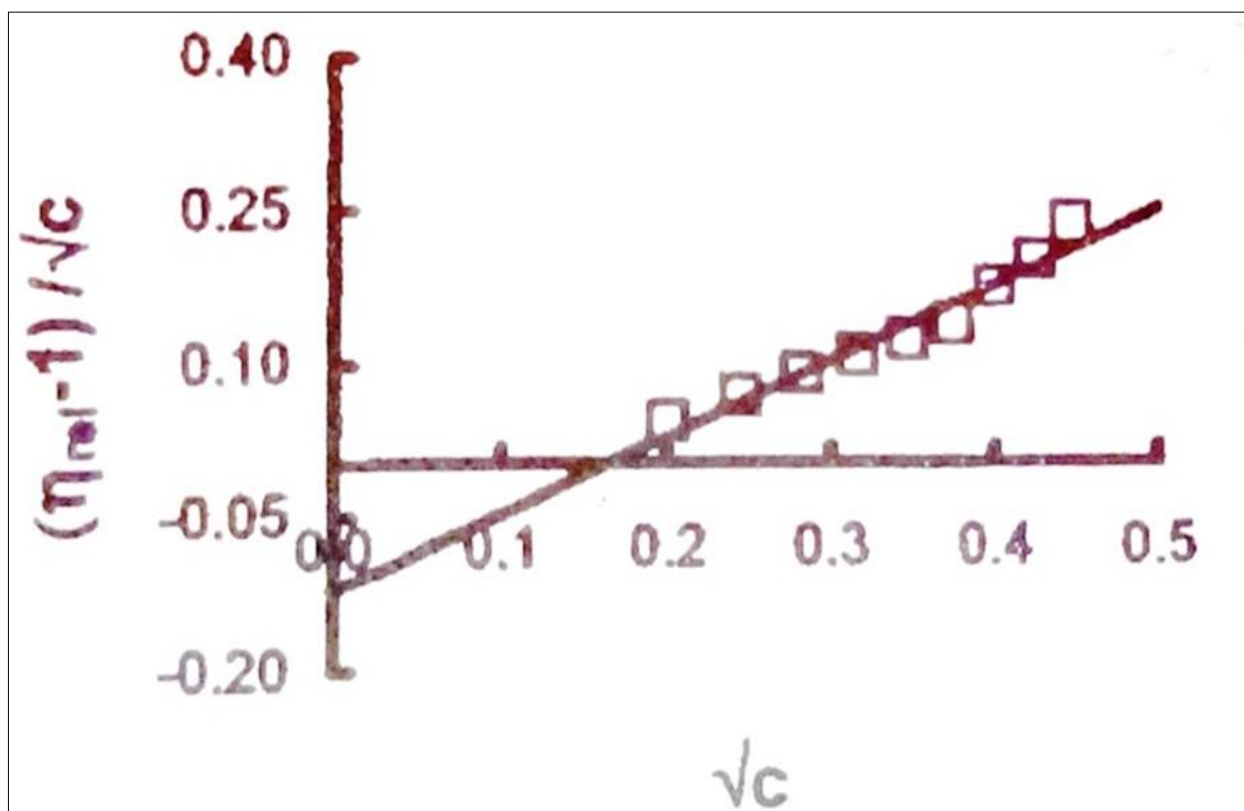
0.06	1.1070	161.02	1.9140	173.79	1.0880	180.00
0.08	1.1090	106.04	171.14	171.14	1.0900	174.30
0.10	1.1111	158.00	170.38	170.38	109.19	172.00
SnCl <sub>2</sub>						
0.00	1.1014	-	1.0974	-	1.0834	-
0.02	1.1027	145.06	1.0986	148.85	1.0846	152.76
0.04	1.1041	144.52	1.1000	146.65	1.0859	150.00
0.06	1.1055	142.53	1.1014	145.04	1.0874	146.53
0.08	1.1071	140.06	1.1029	142.63	1.0890	143.77
0.10	1.1086	139.45	1.9263	141.24	1.0905	142.49

**Table 4:** Values of limiting apparent molar volume ( $\phi^0 v$ ) and experimental slope ( $S_v$ ) of bi-univalent electrolytes in Dimethylsulphoxide (DMSO) at different temperatures.

Electrolyte	$\phi^0 v$ (cm <sup>3</sup> mol <sup>-1/2</sup> )			$S_v$ (cm <sup>3</sup> dm <sup>1/2</sup> mol <sup>-3/2</sup> )		
	293.15 K	303.15 K	313.15 K	293.15 K	313.15 K	313.15 K
MnCl <sub>2</sub>	143.03	150.41	164.58	81.23	-91.56	-102.00
CoCl <sub>2</sub>	115.52	132.01	136.03	64.39	-67.30	-67.35
NiCl <sub>2</sub>	136.90	149.38	152.73	212.59	-240.70	-249.13
SrCl <sub>2</sub>	150.49	170.11	180.64	146.57	-153.32	-171.68
SnCl <sub>2</sub>	155.11	158.10	161.81	50.70	-54.39	-61.16
HgCl <sub>2</sub>	179.25	195.30	202.79	69.16	-83.44	-98.14

**Table 5:** Value of  $\Delta\mu_1^{0\#}$  for bi-univalent electrolytes in Demethylsulphoxide (DMSO) at different temperatures

Electrolyte	$(\Delta\mu_1^{0\#} \text{ KJ mol}^{-1})$		
	293.15 K	303.15 K	313.15 K
HgCl <sub>2</sub>	25.51	30.61	36.16
SnCl <sub>2</sub>	26.72	28.10	33.51
NiCl <sub>2</sub>	32.27	34.80	38.90
CoCl <sub>2</sub>	25.50	26.98	31.46
MnCl <sub>2</sub>	31.59	32.94	35.81
SrCl <sub>2</sub>	28.33	32.92	35.04



**Fig 1:** Variation of  $(\eta_{rel} - 1) / \sqrt{c}$  for the solutions of HgCl<sub>2</sub> in Dimethyl sulphoxide (DMSO) at 293.15 K

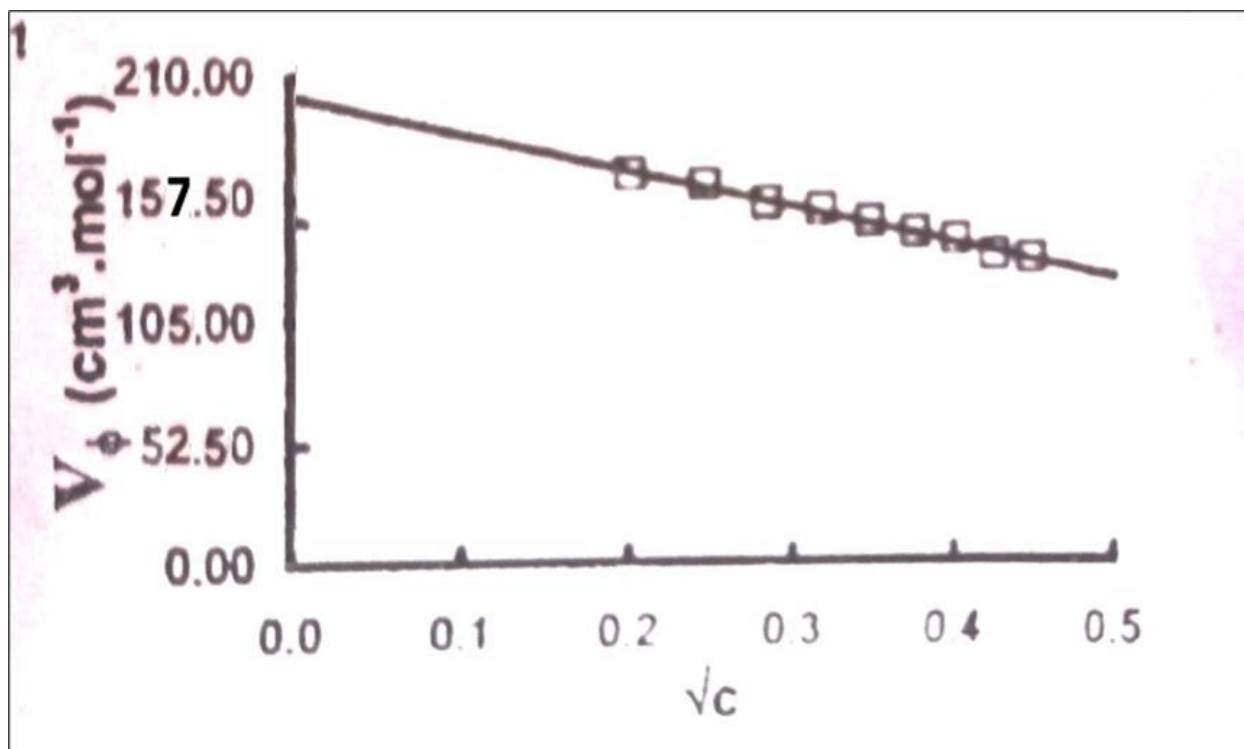


Fig 2: Variation of  $\phi_v$  with  $\sqrt{c}$  for the solutions of  $\text{HgCl}_2$  in Dimethyl sulphoxide (DMSO) at 293.15 K

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