

## CHAPTER VI

### **Ion -Solvent and Ion-Ion Interactions of Sodium Molybdate and Sodium Tungstate in mixtures of Ethane- 1, 2 diol and Water at 298.15, 308.15 and 318.15K.**

#### **6.1. Introduction**

Studies on densities ( $\rho$ ) and viscosities ( $\eta$ ) of electrolyte solutions are of great importance in characterizing the properties and structural aspects of solutions. The addition of an electrolyte to an aqueous organic solution alters the pattern of ion solvation and causes phenomenal changes in the behavior of the dissolved electrolyte. Hence, studies on the limiting apparent molar volume and viscosity- $B$  coefficients of electrolyte provide us valuable information regarding ion-ion, ion-solvent and solvent-solvent interactions [1-3]. It has been found by a number of workers [4-6] that the addition of an electrolyte could either make or break the structure of a liquid. As the viscosity of a liquid depends on the intermolecular forces, the structural aspects of the liquid can be inferred from the viscosity of solutions at various electrolyte concentrations and temperature.

In this paper we have attempted to report the limiting apparent molar volume ( $V_{\phi}^0$ ), experimental slopes ( $S_V^*$ ) and viscosity  $B$ - coefficients for sodium molybdate and sodium tungstate in aqueous binary mixture of ethane-1, 2-diol at 298.15, 308.15 and 318.15K. The mixture of ethane-1, 2-diol with water was chosen because of its diverse application in pharmaceutical and cosmetic. However, the experiment was not performed in pure ethane-1, 2-diol due to the insolubility of the electrolytes. Since both molybdate and tungstate ions have similar structure [9] and sodium ion being a common cation for both the

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electrolyte under investigation, the present work enables us to have a qualitative comparison of the role of anion in aqueous binary mixture of ethane-1,2-diol in terms of various derived parameters obtained from viscosity ( $\eta$ ) and density ( $\rho$ ) measurement.

## **6.2. Experimental section**

### **6.2.1 Materials**

Ethane-1, 2-diol (E.Merck, India) was purified by standard methods [10]. The purity of the solvent was checked by measuring the viscosity ( $\eta$ ) and density ( $\rho$ ) at 298.15K which was in good agreement with the literature values. Doubly distilled, degassed and deionised water with a specific conductance of  $1 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$  was used. Sodium tungstate and sodium molybdate (E.Merck, India) were purified by re-crystallizing twice from conductivity water and then dried in a vacuum dessicator over  $\text{P}_2\text{O}_5$  for 24 hours before use. The purity of the solvents was ascertained by GLC and also by comparing experimental values of viscosity ( $\eta$ ) and density ( $\rho$ ) whenever available with those reported in the literature and are listed in Table 1.

### **6.2.2. Measurements**

Densities ( $\rho$ ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of about  $25 \text{ cm}^3$  and an internal diameter of about 0.1 cm. The measurements were done in a thermostat bath controlled to  $\pm 0.01 \text{ K}$ . Viscosity ( $\eta$ ) was measured by means of suspended Ubbelohde type viscometer, calibrated at 298.15 K with triply distilled water and purified methanol using density and viscosity values from literature. The flow times were accurate to  $\pm 0.1 \text{ s}$ , and the uncertainty in the viscosity measurements was  $\pm 2 \times 10^{-4} \text{ mPas}$ . The mixtures were prepared by mixing known volume of pure liquids in airtight-stopper bottles and each solution thus prepared was distributed into three recipients to perform all the measurements in triplicate, with the aim of determining possible dispersion of the results obtained.

Adequate precautions were taken to minimize evaporation losses during the actual measurements. The reproducibility in mole fractions was within  $\pm 0.0002$ . The mass measurements were done on a Mettler AG-285 electronic balance with a precision of  $\pm 0.01$  mg. The precision of density measurements was  $\pm 3 \times 10^{-4} \text{ g cm}^{-3}$ . Viscosity of the solution,  $\eta$ , is given by the following equation:

$$\eta = \left( Kt - \frac{l}{t} \right) \rho \quad (1)$$

where K and L are the viscometer constants and t and  $\rho$  are the efflux time of flow in seconds and the density of the experimental liquid, respectively. The uncertainty in viscosity measurements is within  $\pm 0.003$  mPas.

Details of the methods and techniques of density and viscosity measurements have been described elsewhere [11-14]. The electrolyte solutions studied here were prepared by mass and the conversion of molality into molarity was accomplished [3] using experimental density values. The experimental values of concentrations (c), densities ( $\rho$ ), viscosities ( $\eta$ ), and derived parameters at various temperatures are reported in Table 2.

### 6.3. Results and discussion

The apparent molar volumes ( $V_\phi$ ) were determined from the solution densities using the following equation [3]:

$$V_\phi = \frac{M}{\rho_0} - \frac{1000(\rho - \rho_0)}{c\rho_0} \quad (2)$$

Where M is the molar mass of the solute, c is the molarity of the solution;  $\rho_0$  and  $\rho$  are the densities of the solvent and the solution respectively. The limiting apparent molar volume ( $V_\phi^0$ ) was calculated using a least -squares treatment to the plots of  $V_\phi$  versus  $\sqrt{c}$  using the following Masson equation [15]:

$$V_{\phi} = V_{\phi}^o + S_V^* \sqrt{c} \quad (3)$$

where  $V_{\phi}^o$  is the apparent molar volume at infinite dilution and  $S_V^*$  the experimental slope. The plots of  $V_{\phi}$  against square root of molar concentration ( $\sqrt{c}$ ) were found to be linear as depicted graphically in Figure (1-6) with negative slopes. Values of  $V_{\phi}^o$  and  $S_V^*$  are reported in Table 3.

As the systems under study are characterized by hydrogen bonding, the ion-solvent and ion-ion interactions can be interpreted in terms of structural changes, which arise due to hydrogen bonding between various components of the solvent and solution systems.  $V_{\phi}^o$  can be used to interpret ion-solvent interactions. A perusal of Table 3 reveals that the  $V_{\phi}^o$  values are positive and increases with rise in temperature and decreases with increase in the amount of ethane-1, 2-diol in the solvent mixture. This indicates the presence of strong ion-solvent interactions and these interactions are strengthened with rise in temperature and weakened with an increase in the amount of ethane-1, 2-diol in the solvent mixture under study, suggesting larger electrostriction at higher temperature and in lower amount of ethane-1, 2-diol in the mixture. Similar results were obtained for some 1:1 electrolytes in aqueous dimethylformamide [16] and aqueous tetrahydrofuran [17].

It is evident from Table 3 that the  $S_V^*$  values are negative for all temperatures for aqueous mixtures of ethane-1, 2-diol. Furthermore  $S_V^*$  values decreases with the increase of experimental temperature which may be attributed to more violent thermal agitation at higher temperatures, resulting in diminishing the force of ion-ion interactions (ionic-dissociation) [18]. The  $S_V^*$  values increases with an increase in the amount of ethane-1,2-diol in the aqueous mixture which results in a decrease in solvation of ions, i.e., more and more solute is accommodated in the void space left in the packing of large associated solvent molecules with the addition of ethane-1, 2-diol to the mixture. A quantitative comparison of the magnitude of values shows that  $V_{\phi}^o$

values are much greater in magnitude than those of  $S_V^*$  for all the solutions. This suggests that ion-solvent interactions dominate over ion-ion interactions in all the solutions and at all experimental temperatures.

The variation of  $V_\phi^o$  with temperature of sodium molybdate and sodium tungstate in solvent mixture follows the polynomial,

$$V_\phi^o = a_0 + a_1T + a_2T^2 \quad (4)$$

over the temperature range under study where T is the temperature in K.

Values of coefficients of the above equation for sodium molybdate and sodium tungstate for aqueous ethane-1, 2-diol mixtures are reported in Table 4.

The apparent molar expansibilities ( $\phi_E^o$ ) can be obtained by the following equation:

$$\phi_E^o = \left( \frac{\partial V_\phi^o}{\partial T} \right)_P = a_1 + 2a_2T \quad (5)$$

The values  $\phi_E^o$  of for different solutions of the studied electrolytes at 298.15, 308.15 and 318.15 K are reported in Table 5. From Table it is evident that the values of  $\phi_E^o$  for sodium molybdate increases with a rise in temperature and decreases with the increase in the amount of ethane-1, 2-diol in the mixture which can be ascribed to the absence of caging or packing effects [19]. However for sodium tungstate the  $\phi_E^o$  values were found to be rather complicated to explain.

During the past few years it has been emphasized by a number of workers that  $S_V^*$  is not the sole criterion for determining the structure-making or breaking tendency of any solute. Helper [20] developed a technique of examining the sign of  $(\partial \phi_E^o / \partial T)_P$  for the solute in terms of long-range structure-making and breaking capacity of the electrolytes in the mixed solvent systems. The general thermodynamic expression used is as follows

$$\left(\frac{\partial\phi_E^0}{\partial T}\right)_P = 2a_2 \quad (6)$$

If the sign of  $(\partial\phi_E^0/\partial T)_P$  is positive or small negative [21] the electrolyte is a structure maker and when the sign of  $(\partial\phi_E^0/\partial T)_P$  is negative, it is a structure breaker. As is evident from Table 5, the electrolyte under investigation generally acts as a structure breaker. Thus it may be concluded that the electrolytes are characterized by the absence of caging effect [18, 22].

The viscosity data of solutions for the electrolytes in 0.0312, 0.0677, 0.1106 mole fraction ( $x_1$ ) of ethane-1, 2-diol + water mixtures have been analyzed using Jones-Dole [23] equation:

$$\left(\frac{\eta}{\eta_0} - 1\right)/\sqrt{c} = A + B\sqrt{c} \quad (7)$$

Where  $\eta_0$  and  $\eta$  are the viscosities of the solvent/solvent mixtures and solution respectively.  $A$  and  $B$  are the constants estimated by a least-squares method and are reported in Table 6. From the Table it is evident that the values of the  $A$  coefficient are negative for all the solutions under investigation at all experimental temperatures. These results indicate the presence of weak ion-ion interactions, and these interactions further decrease with the rise of experimental temperatures suggesting an increase in ion-solvation while these interactions increase with an increase of ethane-1, 2-diol in the mixture. Interestingly, values are found to be more negative for sodium molybdate and hence it may be concluded that sodium molybdate is more soluble in aqueous ethane-1,2-diol solutions than sodium tungstate.

The effects of ion-solvent interactions on the solution viscosity can be inferred from the  $B$ -coefficient [24, 25]. The viscosity  $B$ -coefficient is a valuable tool to provide information concerning the solvation of the solutes and their effects on the structure of the solvent. From Table 6 it is evident that the values of the  $B$ -coefficient of sodium molybdate and sodium tungstate in the studied solvent systems are positive, thereby suggesting the presence of strong ion - solvent interactions, and these type of interactions are

strengthened with a rise in temperature and weakened with an increase of ethane-1,2-diol in the mixture. These conclusions are in excellent agreement with those drawn from  $V^{\circ}_{\phi}$  values discussed earlier.

It has been reported in a number of studies [26, 27] that  $dB/dT$  is a better criterion for determining the structure-making/breaking nature of any solute rather than simply the value of the B-coefficient. It is found from Table 6 that the values of the B-coefficient increase with a rise in temperature (positive  $dB/dT$ ) suggesting the structure-breaking tendency of sodium molybdate and sodium tungstate in the solvent systems. A similar result was reported in a study [28] of viscosity of some salts in propionic acid and ethanol mixtures.

The viscosity data have also been analyzed on the basis of transition state theory of relative viscosity of the electrolytes, suggested by Feakins. et. al [29] using the following equation

$$\Delta\mu_2^{o\ddagger} = \Delta\mu_1^{o\ddagger} + \frac{(1000B + \bar{V}_2^{\circ} - \bar{V}_1^{\circ})RT}{\bar{V}_1^{\circ}} \quad (8)$$

Where  $\bar{V}_1^{\circ}$  and  $\bar{V}_2^{\circ}$  are the partial molar volumes of the solvent and the solute respectively. The contribution per mole of the solute to the free energy of activation of viscous flow ( $\Delta\mu_2^{o\ddagger}$ ) of the solutions was determined from the above relation and are listed in Table 7. The free energy of activation of viscous flow of the pure solvent ( $\Delta\mu_1^{o\ddagger}$ ) is given by the relation:

$$\Delta\mu_1^{o\ddagger} = \Delta G_1^{o\ddagger} = \frac{RT \ln \eta_1 \bar{V}_1^{\circ}}{hN_A} \quad (9)$$

Where N is the Avogadro's number and the other symbols have their usual significance. The values of  $\Delta\mu_2^{o\ddagger}$  and  $\Delta\mu_1^{o\ddagger}$  are reported in Table 7. From Table 7 it is evident that  $\Delta\mu_1^{o\ddagger}$  is practically constant at all the solvent composition and at all temperatures, implying that  $\Delta\mu_2^{o\ddagger}$  is mainly dependent on the viscosity B-coefficients and  $(\bar{V}_2^{\circ} - \bar{V}_1^{\circ})$  terms. Also  $\Delta\mu_2^{o\ddagger}$  values were found to positive at all the experimental temperatures and hence the formation of the

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transition state is less favorable in presence of these anions. A similar result was reported for sodium molybdate and sodium tungstate in aqueous acetonitrile solutions [21]. According to Feakins.et.al [29]  $\Delta\mu_2^{o\ddagger} > \Delta\mu_1^{o\ddagger}$  for electrolytes having positive *B*-coefficients and indicates a stronger ion-solvent interactions, thereby suggesting that the formation of transition state is accompanied by the rupture and distortion of the intermolecular forces in solvent structure [30]. The smaller values of  $\Delta\mu_2^{o\ddagger}$  indicates the increased structure breaking tendency of the electrolyte. Thus from the values of  $\Delta\mu_2^{o\ddagger}$  it can be inferred that both tungstate and molybdate ions have similar structure breaking tendencies. The entropy of activation for electrolytic solutions has been calculated using the following relation [29].

$$-\Delta S_2^{o\ddagger} = \frac{d(\Delta\mu_2^{o\ddagger})}{dT} \quad (10)$$

Where  $\Delta S_2^{o\ddagger}$  has been determined from the negative slope of the plots of  $\Delta\mu_2^{o\ddagger}$  against T by using a least square treatment.

The activation enthalpy ( $\Delta H_2^{o\ddagger}$ ) has been calculated using the relation [29]:

$$\Delta H_2^{o\ddagger} = \Delta\mu_2^{o\ddagger} + T\Delta S_2^{o\ddagger} \quad (11)$$

the value of  $\Delta S_2^{o\ddagger}$  and  $\Delta H_2^{o\ddagger}$  are listed in Table 7 and they are found to be negative for all the electrolytic solutions and at all experimental temperatures suggesting that the transition state is associated with bond formation and increase in order. Although a detailed mechanism for this cannot be easily advanced, it may be suggested that the slip-plane is in the disordered state [29, 31].

#### 6.4. Conclusion

In summary it can be concluded that both sodium molybdate and sodium tungstate shows similar trend of ion-solvent and ion-ion interactions, which can be ascribed to the similar structure of tungstate and molybdate ions [7]. From the values of apparent molar volume ( $V^\circ_\emptyset$ ) and viscosity *B*- coefficients

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it may be concluded that ion-solvent interaction increases with increasing temperature and decreases with increasing amount of ethane-1,2-diol in the aqueous mixture. Also the structure breaking tendencies of the two electrolytes were found to be similar.

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TABLE 1: Density ( $\rho$ ,  $\text{kg m}^{-3}$ ) and viscosity ( $\eta$ ,  $\text{mPa s}$ ) of aqueous binary mixtures of ethane-1, 2-diol in 0.0312, 0.0677, 0.1106 mole fractions ( $x_1$ ) of ethane-1, 2-diol at different temperatures

Temperature (K)	$\rho \times 10^{-3} \text{kg m}^{-3}$		$\eta \text{ mPa s}$	
	This work	Lit	This work	Lit
$x_1=0.0312$				
298.15	1.0110	1.0116 [32]	1.1284	-
308.15	1.0071	1.0080 [32]	0.8922	-
318.15	1.0036	1.0038 [32]	0.7564	-
$x_1=0.0677$				
298.15	1.0238	1.0279 [32]	1.4244	-
308.15	1.0207	1.0239 [32]	1.1371	-
318.15	1.0167	1.0195 [32]	0.9440	-
$x_1=0.1106$				
298.15	1.0372	1.0432 [32]	1.8286	-
308.15	1.0352	1.0390 [32]	1.4302	-
318.15	1.0290	1.0343 [32]	1.1472	-

TABLE 2: Concentration ( $c$ ), density ( $\rho$ ), viscosity ( $\eta$ ), apparent molar volume ( $V_\phi$ ), and  $\alpha = (\eta / \eta_o - 1) / c^{1/2}$  of sodium molybdate and sodium tungstate in different aqueous binary mixtures of ethane-1, 2-diol in 0.0312, 0.0677, 0.1106 mole fractions ( $x_1$ ) of ethane-1, 2-diol at different temperatures

$C$ mol dm <sup>-3</sup>	$\rho \times 10^{-3}$ kg m <sup>-3</sup>	$\eta$ mPas	$V_\phi \times 10^6$ m <sup>3</sup> mol <sup>-1</sup>	$\alpha$	$c$ mol dm <sup>-3</sup>	$\rho \times 10^{-3}$ kg m <sup>-3</sup>	$\eta$ mPas	$V_\phi \times 10^6$ m <sup>3</sup> mol <sup>-1</sup>	$\alpha$
Sodium molybdate $x_1=0.0312$					Sodium tungstate $x_1=0.0312$				
298.15 K					298.15 K				
0.0250	1.0143	1.1429	109.228	0.0650	0.0250	1.0163	1.1471	116.278	0.1050
0.0350	1.0159	1.1493	101.895	0.0900	0.0350	1.0186	1.1582	110.767	0.1410
0.0450	1.0174	1.1549	97.665	0.1050	0.0450	1.0210	1.1669	106.845	0.1610
0.0550	1.0191	1.1619	93.236	0.1267	0.0550	1.0233	1.1750	104.213	0.1760
0.0750	1.0223	1.1748	90.621	0.1502	0.0750	1.0281	1.1902	100.921	0.2000
0.0850	1.0239	1.1820	89.663	0.1630	0.0850	1.0305	1.1998	99.7900	0.2170
308.15 K					308.15 K				
0.0249	1.0099	0.9044	127.605	0.0870	0.0249	1.0120	0.9094	133.908	0.1220
0.0348	1.0115	0.9102	114.742	0.1080	0.0349	1.0143	0.9173	121.999	0.1507
0.0448	1.0131	0.9183	107.597	0.1380	0.0448	1.0167	0.9245	115.189	0.1711

0.0548	1.0147	0.9256	103.106	0.1598	0.0548	1.0191	0.9325	110.818	0.1929
0.0747	1.0178	0.9383	98.545	0.1889	0.0747	1.0238	0.9472	105.575	0.2255
0.0846	1.0195	0.9442	94.498	0.2003	0.0846	1.0262	0.9543	103.732	0.2391
318.15K					318.15K				
0.0248	1.0060	0.7672	144.585	0.0910	0.0248	1.0081	0.7724	149.569	0.1346
0.0347	1.0076	0.7743	125.053	0.1273	0.0347	1.0105	0.7799	130.293	0.1667
0.0447	1.0093	0.7801	114.206	0.1485	0.0446	1.0130	0.7868	119.589	0.1903
0.0547	1.0110	0.7867	105.545	0.1712	0.0546	1.0154	0.7937	112.722	0.2110
0.0747	1.0144	0.7991	96.4701	0.2065	0.0744	1.0204	0.8076	104.345	0.2484
0.0847	1.0161	0.8047	92.9767	0.2195	0.0844	1.0228	0.8146	101.635	0.2649
Sodium molybdate $x_1=0.0677$					Sodium tungstate $x_1=0.0677$				
298.15K					298.15K				
0.0250	1.0274	1.4451	94.8690	0.0100	0.0250	1.0306	1.4460	101.479	0.0960
0.0350	1.0290	1.4527	91.4636	0.1130	0.0350	1.0331	1.4553	97.1661	0.1158
0.0450	1.0307	1.4633	86.8985	0.1350	0.0450	1.0355	1.4646	96.866	0.1330
0.0550	1.0324	1.4720	82.8316	0.1480	0.0550	1.0380	1.4738	94.961	0.1479
0.0750	1.0357	1.4906	81.3094	0.1746	0.0750	1.0428	1.4934	95.189	0.1770
0.0850	1.0374	1.4997	79.8219	0.1860	0.0850	1.0453	1.5016	94.153	0.1860

308.15K					308.15K				
0.0249	1.0236	1.1540	115.626	0.0960	0.0249	1.0267	1.1563	131.329	0.1070
0.0349	1.0252	1.1630	106.010	0.1236	0.0349	1.0292	1.1653	118.732	0.1330
0.0448	1.0268	1.1710	100.402	0.1419	0.0448	1.0317	1.1732	111.443	0.1500
0.0548	1.0283	1.1788	96.9554	0.1578	0.0548	1.0341	1.1797	107.973	0.1600
0.0747	1.0315	1.1940	93.3839	0.1841	0.0747	1.0390	1.1992	103.259	0.1998
0.0846	1.0330	1.2033	91.9710	0.2010	0.0847	1.0415	1.2065	101.803	0.2097
318.15K					318.15K				
0.0248	1.0193	0.9583	136.063	0.0950	0.0248	1.0224	0.9608	139.942	0.1130
0.0347	1.0208	0.9667	120.549	0.1280	0.0347	1.0248	0.9694	127.007	0.1444
0.0446	1.0223	0.9739	113.695	0.1487	0.0446	1.0272	0.9763	119.833	0.1619
0.0546	1.0240	0.9808	105.996	0.1659	0.0546	1.0297	0.9840	113.528	0.1816
0.0744	1.0271	0.9947	99.814	0.1962	0.0744	1.0346	0.9988	107.263	0.2127
0.0843	1.0287	1.0019	97.666	0.2104	0.0843	1.0371	1.0068	104.668	0.2290
Sodium molybdate $x_1=0.1106$					Sodium tungstate $x_1=0.1106$				
298.15K					298.15K				
0.0250	1.0410	1.8517	85.2862	0.0940	0.0250	1.0446	1.8553	85.2862	0.0924

0.0350	1.0428	1.8624	81.6000	0.1108	0.0350	1.0471	1.8648	81.6000	0.1057
0.0450	1.0443	1.8731	80.7124	0.1253	0.0450	1.0498	1.8760	80.7124	0.1221
0.0550	1.0462	1.8845	76.2873	0.1401	0.0550	1.0520	1.8874	76.2873	0.1370
0.0750	1.0495	1.9066	74.7013	0.1640	0.0750	1.0572	1.9109	74.7013	0.1643
0.0850	1.0513	1.9190	73.6711	0.1775	0.0850	1.0603	1.9214	73.6711	0.1740
Sodium molybdate $x_1=0.1106$					Sodium molybdate $x_1=0.1106$				
308.15K					318.15K				
0.0249	1.0385	1.4522	105.289	0.1070	0.0249	1.0240	1.4521	105.289	0.0976
0.0349	1.0401	1.4597	99.2167	0.1184	0.0349	1.0447	1.4615	99.2167	0.1170
0.0449	1.0416	1.4695	95.8562	0.1368	0.0449	1.0471	1.4687	95.8562	0.1270
0.0548	1.0431	1.4793	95.3671	0.1532	0.0549	1.0496	1.4798	95.3671	0.1480
0.0748	1.0460	1.5002	93.5430	0.1847	0.0748	1.0544	1.4979	93.5430	0.1731
0.0848	1.0483	1.5096	84.7810	0.1960	0.0847	1.0570	1.5089	84.7810	0.1892
318.15K					318.15K				
0.0248	1.0321	1.1679	114.771	0.1148	0.0248	1.0356	1.1660	114.771	0.1040
0.0347	1.0336	1.1756	105.395	0.1330	0.0347	1.0380	1.1746	105.395	0.1282
0.0446	1.0353	1.1840	98.2377	0.1520	0.0446	1.0405	1.1831	98.238	0.1483
0.0545	1.0369	1.1924	93.4467	0.1686	0.0545	1.0430	1.1914	93.447	0.1651
0.0743	1.0401	1.2106	90.0550	0.2029	0.0743	1.0479	1.2075	90.055	0.1928
0.0842	1.0418	1.2193	87.2167	0.2166	0.0842	1.0505	1.2157	87.217	0.2059

TABLE 3: Limiting apparent molar volumes ( $V_{\phi}^o$ ) and experimental slopes ( $S_V^*$ ) of sodium molybdate and sodium tungstate in different aqueous binary mixtures of ethane-1, 2-diol in 0.0312, 0.0677, 0.1106 mole fractions of ethane-1,2-diol at different temperatures

Mole fraction of ethane-1,2- diol	$V_{\phi}^o \times 10^6 (\text{m}^3 \text{mol}^{-1})$			$S_V^* \times 10^6 (\text{m}^3 \text{mol}^{-3/2} \text{dm}^{3/2})$		
	298.15K	308.15K	318.15K	298.15K	308.15K	318.15K
Sodium molybdate						
0.0312	129.27	159.40	196.73	-142.44	-229.13	-370.98
0.0677	112.07	138.58	174.46	-114.37	-167.67	-275.93
0.1106	98.401	123.80	142.76	-87.05	-124.49	-197.92
Sodium tungstate						
0.0312	133.53	163.74	196.65	-119.91	-215.01	-341.53
0.0677	107.08	159.28	176.10	-46.15	-207.53	-254.70
0.1106	95.53	134.31	146.72	-31.66	-141.55	-180.09

TABLE 4: Values of the coefficients of equation (4) for sodium molybdate and sodium tungstate in different aqueous binary mixtures of ethane-1, 2-diol in 0.0312, 0.0677, 0.1106 mole fractions of ethane-1,2-diol.

Mole fraction of ethane-1,2-diol	$a_0(\text{m}^3\text{mol}^{-1})$	$a_1(\text{m}^3\text{mol}^{-1}\text{K}^{-1})$	$a_2(\text{m}^3\text{mol}^{-1}\text{K}^{-2})$
Sodium molybdate			
0.0312	2538.441	-18.8138	0.0360
0.0677	3630.617	-25.7845	0.0469
0.1106	-3617.255	22.0628	-0.0322
Sodium tungstate			
0.0312	473.1154	-5.164	0.0135
0.0677	17701.946	112.475	-0.1769
0.1106	-13169.706	83.788	-0.1318

TABLE 5: Limiting partial molar expansibilities for sodium molybdate and sodium tungstate in different aqueous binary mixtures of ethane-1, 2-diol in 0.0312, 0.0677, 0.1106 mole fractions of ethane-1, 2-diol at different temperatures

Mole fraction of ethane-1,2-diol	$\emptyset_E^0(\text{m}^3\text{mol}^{-1}\text{K}^{-1})$			$(\partial\emptyset_E^0/\partial T)_P$ ( $\text{m}^3\text{mol}^{-1}\text{K}^{-2}$ )
	298.15K	308.15K	318.15K	
Sodium molybdate				
0.0312	2.6530	3.3730	4.0930	0.0720
0.0677	2.1820	3.1200	4.0580	0.0938
0.1106	-2.8619	-2.2179	-1.5739	-0.0644
Sodium tungstate				
0.0312	2.8861	3.1561	3.4261	0.0270
0.0677	6.9890	3.4510	0.0870	-0.3538
0.1106	5.1957	2.5597	-0.0763	-0.2636

TABLE 6: Values of  $A$  and  $B$  coefficients for sodium molybdate and sodium tungstate in different aqueous binary mixtures of ethane-1, 2-diol in 0.0312, 0.0677, 0.1106 mole fractions of ethane-1,2-diol at different temperatures.

Mole fraction of ethane 1,2-diol	$A, \text{dm}^{3/2}\text{mol}^{-1/2}$			$B, \text{dm}^3\text{mol}^{-1}$		
	298.15 K	308.15K	318.15K	298.15K	308.15K	318.15K
Sodium molybdate						
0.0312	-0.0478	-0.0504	-0.0535	0.7272	0.8746	0.9493
0.0677	-0.0067	-0.0211	-0.0329	0.6606	0.7610	0.8445
0.1106	-0.0056	-0.0083	-0.0108	0.6226	0.6977	0.7792
Sodium tungstate						
0.0312	-0.0118	-0.0145	-0.0165	0.7891	0.8733	0.9720
0.0677	-0.0122	-0.0135	-0.0176	0.6842	0.7678	0.8494
0.1106	-0.0102	-0.0126	-0.0139	0.6311	0.6834	0.7608

TABLE 7: Values of  $\bar{V}_1^o$ ,  $\bar{V}_2^o$ ,  $\Delta\mu_1^{o\neq}$ ,  $\Delta\mu_2^{o\neq}$ ,  $T\Delta S_2^{o\neq}$  and  $\Delta H_2^{o\neq}$  for sodium molybdate and sodium tungstate in different aqueous binary mixtures of ethane-1,2-diol in 0.0312, 0.0677, 0.1106 mole fractions ( $x_1$ ) of ethane-1,2-diol at different temperatures.

Parameter	mole fraction of ethane-1,2-diol $x_1=0.0312$			mole fraction of ethane-1,2-diol $x_1=0.0677$			mole fraction of ethane-1,2-diol $x_1=0.1106$		
	298.15K	308.15K	318.15K	298.15K	308.15K	318.15K	298.15K	308.15K	318.15K
$\bar{V}_1^o \times 10^6$ $\text{m}^3\text{mol}^{-1}$	19.1855	20.8527	22.8122	18.9456	20.5749	22.5182	18.7008	20.2867	22.2491
$\Delta\mu_1^{o\neq}$ , KJ $\text{mol}^{-1}$	27.0272	27.5454	28.2401	27.5736	28.1325	28.7919	28.1606	28.6840	29.2758
Sodium molybdate									
$\bar{V}_2^o \times 10^6$ $\text{m}^3\text{mol}^{-1}$	129.27	159.40	196.73	112.07	138.58	174.46	98.401	123.80	142.76
$\Delta\mu_2^{o\neq}$ , KJ $\text{mol}^{-1}$	42.1900	45.6418	49.5068	40.6222	43.7739	47.6317	39.5501	42.6376	44.5292
$T\Delta S_2^{o\neq}$ , KJ $\text{mol}^{-1}$	-109.122	-112.782	-116.442	-104.501	-108.006	-111.511	-74.239	-76.729	-79.2193
$\Delta H_2^{o\neq} \times 10^3$ KJ $\text{mol}^{-1}$	-66.9329	-67.1411	-66.936	-63.8793	-64.2326	-63.8798	-34.6889	-34.0914	-34.6901

Sodium tungstate									
$\bar{V}_2^o \times 10^6$ $\text{m}^3\text{mol}^{-1}$	133.53	163.74	196.65	107.08	159.28	176.10	95.53	134.31	146.72
$\Delta\mu_2^{o\ddagger}, \text{KJ}$ $\text{mol}^{-1}$	42.8203	46.1784	49.5238	40.0002	46.3599	47.8301	39.1810	43.9108	44.9781
$T\Delta S_2^{o\ddagger}, \text{KJ}$ $\text{mol}^{-1}$	-99.8802	-103.230	-106.580	-116.427	-120.332	-124.237	-86.3144	-89.2094	-92.1044
$\Delta H_2^{o\ddagger} \times 10^3$ $\text{KJ mol}^{-1}$	-57.0599	-57.0518	-57.0519	-76.4273	-73.9726	-76.4074	-47.1334	-45.2986	-47.1263

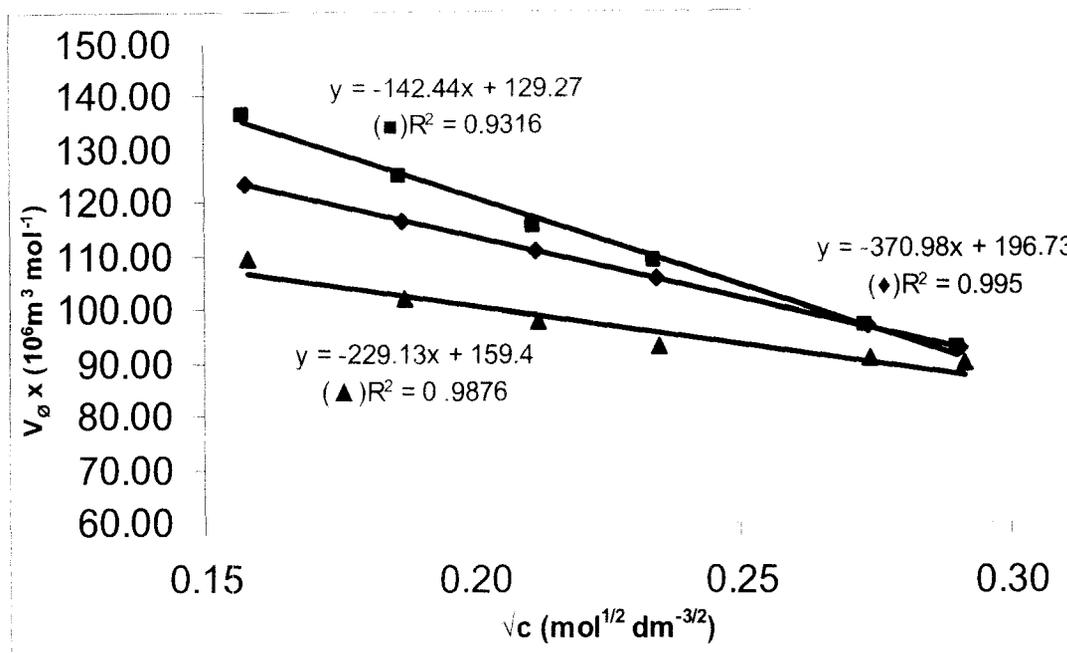


FIGURE 1. The apparent molar volume ( $V_{\phi}^0$ ) of sodium molybdate in the mixture of aqueous ethane-1, 2-diol ( $x_1 = 0.0312$ ) as a function of square root of concentration ( $\sqrt{c}$ ) at 298.15(▲), 308.15(◆) and 318.15 K(■). The lines represent the linear fits.

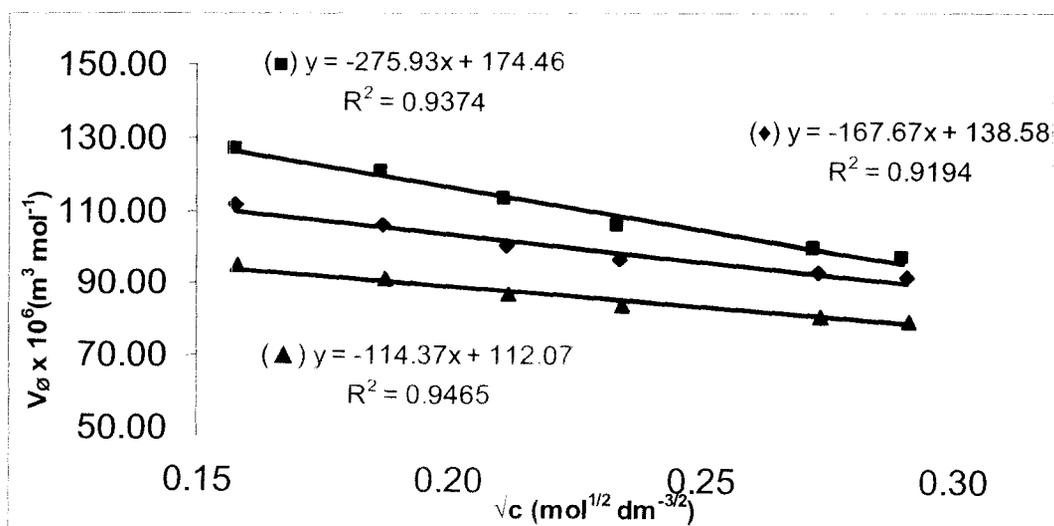


FIGURE 2. The apparent molar volume ( $V_{\phi}^0$ ) of sodium molybdate in the mixture of aqueous ethane-1,2-diol ( $x_1 = 0.0677$ ) as a function of square root of concentration ( $\sqrt{c}$ ) at 298.15(▲), 308.15(◆) and 318.15 K(■). The lines represent the linear fits.

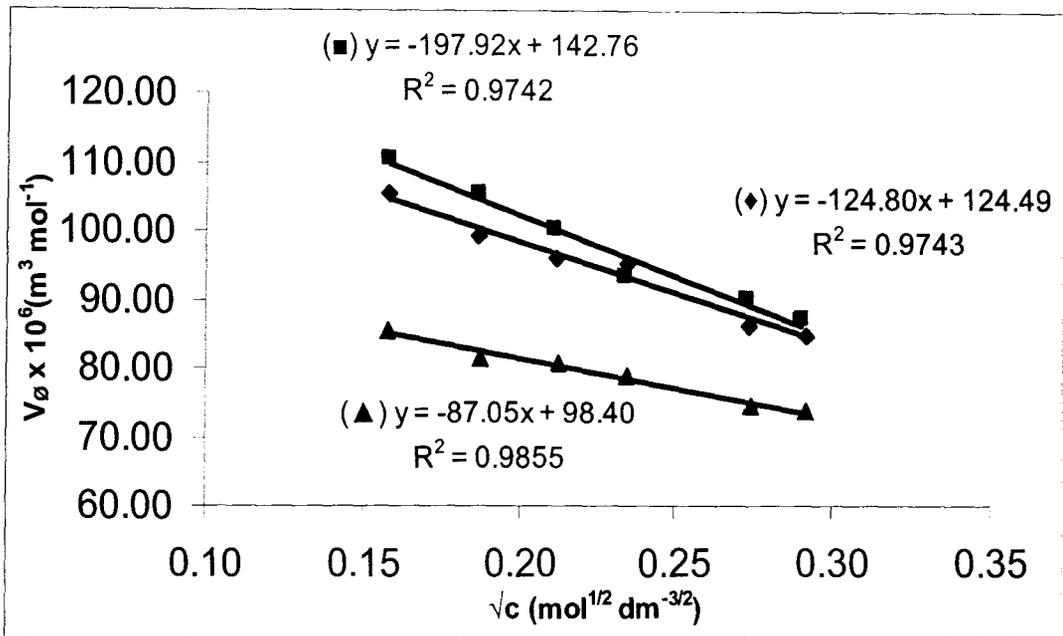


FIGURE 3. The apparent molar volume ( $V_{\phi}^o$ ) of sodium molybdate in the mixture of aqueous ethane-1,2-diol ( $x_1= 0.1106$ ) as a function of square root of concentration ( $\sqrt{c}$ ) at 298.15(▲), 308.15(◆) and 318.15 K(■).The lines represent the linear fits.

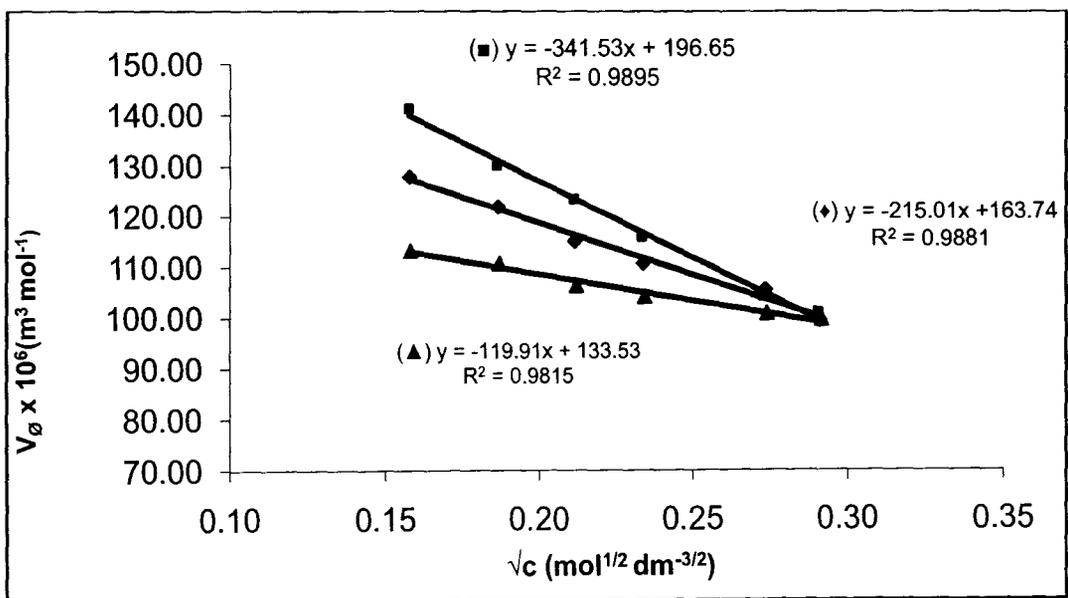


FIGURE 4. The apparent molar volume ( $V_{\phi}^o$ ) of sodium tungstate in the mixture of aqueous ethane-1,2-diol ( $x_1= 0.0312$ ) as a function of square root of concentration ( $\sqrt{c}$ ) at 298.15(▲), 308.15(◆) and 318.15 K(■).The lines represent the linear fits.

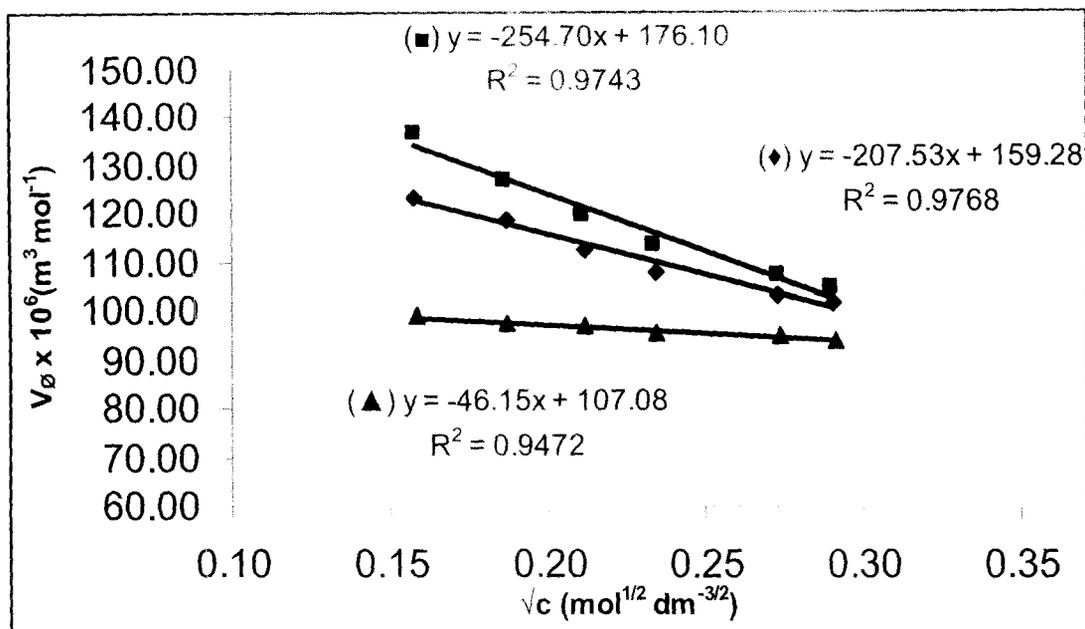


FIGURE 5. The apparent molar volume ( $V_{\phi}^0$ ) of sodium tungstate in the mixture of aqueous ethane-1,2-diol ( $x_1= 0.0677$ ) as a function of square root of concentration ( $\sqrt{c}$ ) at 298.15( $\blacktriangle$ ), 308.15( $\blacklozenge$ ) and 318.15 K( $\blacksquare$ ).The lines represent the linear fits.

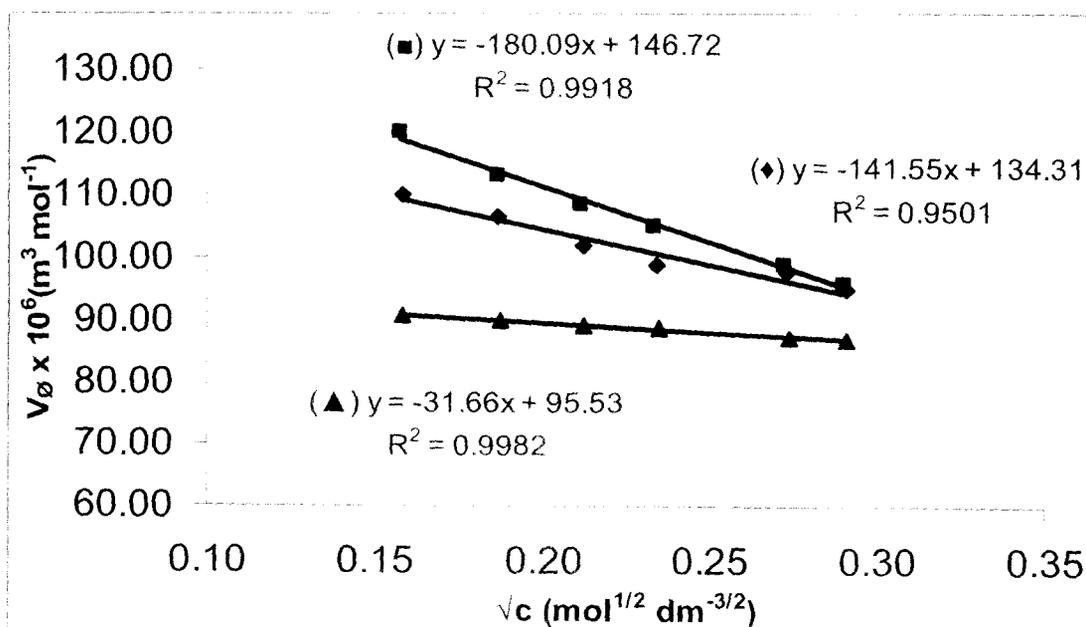


FIGURE 6. The apparent molar volume ( $V_{\phi}^0$ ) of sodium tungstate in the mixture of aqueous ethane-1,2-diol ( $x_1= 0.1106$ ) as a function of square root of concentration ( $\sqrt{c}$ ) at 298.15( $\blacktriangle$ ), 308.15( $\blacklozenge$ ) and 318.15 K( $\blacksquare$ ).The lines represent the linear fits.