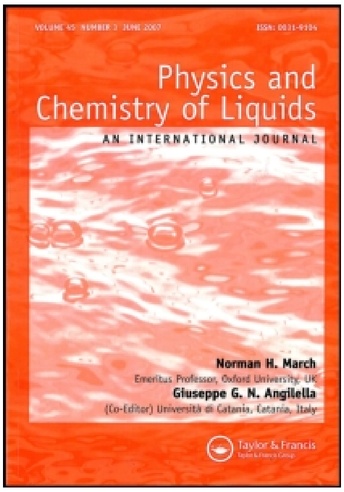

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Ion–solvent and ion–ion interactions of sodium molybdate salt in aqueous binary mixtures of 1,4-dioxane at different temperatures

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Apparent molar volumes and viscosity *B*-coefficients of sodium molybdate in aqueous binary mixtures of 1,4-dioxane have been determined from density and viscosity measurements at 303.15, 313.15 and 323.15 K and at various electrolyte concentrations. Also, adiabatic compressibilities of different solutions have been determined from measurement of ultrasonic speeds of sound at 303.15 K. Experimental density data were evaluated using the Masson equation and the derived parameters interpreted in terms of ion–solvent and ion–ion interactions. Partial molar volumes (ΔV_ϕ^0) and viscosity *B*-coefficients (ΔB) of transfer from water to aqueous 1,4-dioxane mixtures have also been calculated and discussed. The structure-making or breaking capacity of the electrolyte under investigation has been discussed in terms of the sign of $(\delta^2 V_\phi^0/\delta T^2)_\mathrm{P}$.

Keywords: 1,4-Dioxane; Sodium molybdate; Partial molar volumes; Viscosity *B*-coefficients; Adiabatic compressibility; Ion–solvent and ion–ion interactions; Electrostriction

1. Introduction

Partial molar volumes of electrolytes at infinite dilution provide valuable information about ion–ion, ion–solvent and solvent–solvent interactions [1–3]. This information is of fundamental importance for a proper understanding of the behaviour of electrolytes in solution. Measurement of ultrasonic speeds of the solutions also helps in this regard. Recently, we have undertaken a comprehensive programme to study the solvation and association behaviour of some electrolytes [3,4] in different aqueous and non-aqueous solvent media from the measurement of various transport and thermodynamic properties. Aqueous 1,4-dioxane is an important mixed solvent for a number of separation processes and solution studies [5], because of its wide-ranging relative permittivity (2.2–78.3 at 298.15 K). In this article, an attempt has been made to reveal the nature of various types of interactions prevailing in solutions of sodium molybdate

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in aqueous 1,4-dioxane mixtures from volumetric, viscometric and acoustic measurements. Partial molar volumes (ΔV_{ϕ}^{0}) and viscosity *B*-coefficients (ΔB) of transfer from water to aqueous 1,4-dioxane mixtures were determined and are discussed in terms of ion–solvent interactions. Partial molar volumes at infinite dilution have been fitted to a second order polynomial equation in terms of temperature and the structure-making or breaking capacity of the electrolyte has been inferred from the sign of $(\delta^2 V_{\phi}^{0}/\delta T^2)_{\mathrm{P}}$.

2. Experimental

2.1. *Materials*

1,4-Dioxane (Merck, India) was held for several days over potassium hydroxide (KOH), refluxed for 24 h, and distilled over lithium aluminium hydride ($LiAlH_4$). Details have been described earlier [8]. Doubly distilled, degassed and deionised water with a specific conductance of $1 \times 10^{-6}\,\mathrm{ohm^{-1}\,cm^{-1}}$ was used. Sodium molybdate was purified by recrystallising twice from conductivity water and was dried in a vacuum desiccator over P_2O_5 for 24 h before use. Experimental density (ρ_0) and viscosity (η_0) values of pure 1,4-dioxane and different aqueous 1,4-dioxane mixtures at 303.15, 313.15 and 323.15 K are reported in table 1 and are compared with our earlier literature values [3,5,6].

2.2. *Apparatus and procedures*

Densities were measured using an Ostwald–Sprengel-type pycnometer having a bulb volume of 25 cm^3 and an internal capillary diameter of ca. 0.1 cm. The pycnometer was calibrated at 298.15, 308.15, and 318.15 K with doubly distilled water and benzene.

Table 1. Physical properties of pure 1,4-dioxane and 1,4-dioxane + water mixtures at different temperatures.

	ρ (g cm^{-3})		η (mPa s)	
Temperature (K)	This work	Literature	This work	Literature
10 mass% of 1,4-dioxane + water				
303.15	1.0058	1.0058 [3]	1.0320	1.0321 [3]
313.15	1.0041	1.0048 [3]	1.0015	1.0014 [3]
323.15	0.9973	0.9973 [3]	0.6895	0.6895 [3]
20 mass% of 1,4-dioxane + water				
303.15	1.0148	1.0148 [3]	1.2014	1.2014 [3]
313.15	1.0100	1.0100 [3]	1.0186	1.0186 [3]
323.15	1.0033	1.0033 [3]	0.8787	0.8787 [3]
30 mass% of 1,4-dioxane + water				
303.15	1.0202	1.0202 [3]	1.3977	1.3977 [3]
313.15	1.0162	1.0162 [3]	1.2493	1.2493 [3]
323.15	1.0103	1.0103 [3]	1.0755	1.0755 [3]
Pure 1,4-dioxane				
303.15	1.0199	1.0222 [5]	1.0886	1.0937 [5]
313.15	1.0144	1.0143 [6]	0.9785	0.9783 [6]
323.15	1.0027	1.0032 [6]	0.8441	0.8443 [6]

The pycnometer with the test solution was equilibrated in a water bath maintained at ±0.01 K of the desired temperatures. The pycnometer was then removed from the thermostatic bath, properly dried, and weighed. Adequate precautions were taken to avoid evaporation losses during the time of actual measurements. An average of triplicate measurements was taken into account. Mass measurements accurate to ±0.01 mg were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The total uncertainty of density is $\pm 0.0001\,\mathrm{g\,cm^{-3}}$ and that of the temperature is ±0.01 K.

Viscosity was measured by means of a suspended Ubbelohde-type viscometer, which was calibrated at 303.15, 313.15 and 323.15 K with triply distilled water and purified methanol using density and viscosity values from the literature. Flow times were accurate to ±0.1 s, and the uncertainty in the viscosity measurements, based on our work on several pure liquids, was within ±0.03% of the reported value. Ultrasonic speeds of sound for the solutions were determined at 298.15 K by a multi-frequency ultrasonic interferometer working at 2 MHz with an uncertainty of $\pm 0.2\,\mathrm{m\,s^{-1}}$, as described earlier [9]. Details of the methods and techniques of density and viscosity measurements have been described earlier [8,9].

The electrolyte solutions studied here were prepared by mass, and the conversion of molality to molarity was accomplished [3] using experimental density values. Experimental values of concentrations (c), densities (ρ), viscosities (η), and derived parameters at various temperatures are reported in table 2.

3. Results and discussion

Apparent molar volumes (V_ϕ) were determined from solution densities using the following equation [3]:

$$V_\phi = \frac{M}{\rho_0} - \frac{1000(\rho - \rho_0)}{c\rho_0} \tag{1}$$

where M is the molar mass of the solute, c the molarity of the solution, ρ_0 and ρ the densities of the solvent and solution, respectively. The limiting apparent molar volumes or partial molar volumes (V_ϕ^0) at infinite dilution were calculated using a least-squares treatment of plots of V_ϕ *versus* $\sqrt{c}$ together with the Masson equation [6]:

$$V_\phi = V_\phi^0 + S_\mathrm{V}^*\sqrt{c} \tag{2}$$

where V_ϕ^0 is the partial molar volume at infinite dilution and S_V^* the experimental slope. Values of V_ϕ^0 and S_V^* along with their standard errors are reported in table 3. Table 3 shows that V_ϕ^0 values are generally positive and increase with a rise in both temperature and amount of 1,4-dioxane in the ternary mixtures. This indicates the presence of strong ion–solvent interactions and these interactions are further strengthened at higher temperatures and higher mass% of 1,4-dioxane in the mixtures, suggesting larger electrostriction at higher temperatures and increased amount of cyclic diether. However, in the case of water, V_ϕ^0 values are positive and decrease with increase in temperature. This may be attributed to a slow desolvation [7,10] and thermal agitation at higher temperature. A perusal of table 3 also reveals that S_V^* values are negative for all the solutions and at all experimental temperatures and S_V^* values decrease as the

Table 2. Concentration (c), density (ρ), viscosity (η), apparent molar volume (V_ϕ) and $(\eta/(\eta_0-1))/\sqrt{c}$ of sodium molybdate in water and aqueous 1,4-dioxane mixture at different temperatures.

c (mol dm^{-3})	ρ (g cm^{-3})	η (mPa s)	V_ϕ (cm^3 mol^{-1})	$(\eta/(\eta_0-1))/\sqrt{c}$
10 mass% of 1,4-dioxane + water				
$T=303.15$ K				
0.0241	1.0086	1.0336	125.042	0.0103
0.0321	1.0099	1.0356	113.565	0.0195
0.0561	1.0140	1.0433	95.230	0.0464
0.0723	1.0170	1.0491	86.538	0.0617
0.0883	1.0197	1.0555	84.045	0.0767
0.1003	1.0218	1.0606	81.953	0.0875
$T=313.15$ K				
0.0240	1.0057	1.0041	174.568	0.0168
0.0319	1.0066	1.0073	162.912	0.0325
0.0559	1.0096	1.0172	142.974	0.0664
0.0719	1.0123	1.0244	127.380	0.0854
0.0878	1.0148	1.0320	119.592	0.1029
0.0998	1.017	1.0382	112.231	0.1159
$T=323.15$ K				
0.0238	0.9990	0.6986	170.983	0.0856
0.0318	1.0000	0.7036	157.469	0.1144
0.0556	1.0035	0.7193	130.792	0.1836
0.0716	1.0065	0.7301	113.765	0.2201
0.0874	1.0094	0.7413	103.786	0.2544
0.0993	1.0119	0.7498	95.178	0.2774
20 mass% of 1,4-dioxane + water				
$T=303.15$ K				
0.0244	1.0168	1.2032	157.650	0.0096
0.0326	1.0177	1.2090	150.762	0.0349
0.0570	1.0212	1.2257	127.778	0.0846
0.0733	1.0238	1.2379	117.429	0.1123
0.0896	1.0268	1.2523	106.446	0.1416
0.1018	1.0293	1.2625	98.062	0.1595
$T=313.15$ K				
0.0243	1.0115	1.0226	178.437	0.0250
0.0325	1.0125	1.0282	163.393	0.0521
0.0567	1.0160	1.0440	134.782	0.1046
0.0729	1.0187	1.0553	121.394	0.1333
0.0891	1.0219	1.0679	107.319	0.1621
0.1013	1.0247	1.0778	95.878	0.1825
$T=323.15$ K				
0.0242	1.0047	0.8831	183.493	0.0321
0.0323	1.0057	0.8881	167.095	0.0595
0.0564	1.0094	0.9064	133.354	0.1326
0.0724	1.0122	0.9189	118.630	0.1698
0.0886	1.0156	0.9325	102.785	0.2056
0.1006	1.0179	0.9435	96.502	0.2324
30 mass% of 1,4-dioxane + water				
$T=303.15$ K				
0.0228	1.0222	1.4013	151.177	0.0172
0.0304	1.0233	1.4079	137.205	0.0419
0.0532	1.0271	1.4304	110.028	0.1015
0.0684	1.0306	1.4465	88.123	0.1334
0.0835	1.0340	1.4639	75.162	0.1640
0.0950	1.0366	1.4781	67.946	0.1866

(*Continued*)

Table 2. Continued.

c (mol dm^{-3})	ρ (g cm^{-3})	η (mPa s)	V_ϕ (cm^3 mol^{-1})	$(\eta/(\eta_0 - 1))/\sqrt{c}$
$T = 313.15$ K				
0.0227	1.0176	1.2553	177.402	0.0321
0.0303	1.0184	1.2622	166.643	0.0595
0.0530	1.0217	1.2874	135.974	0.1326
0.0680	1.0246	1.3046	116.533	0.1698
0.0830	1.0276	1.3233	102.933	0.2056
0.0944	1.0301	1.3385	93.194	0.2324
$T = 323.15$ K				
0.0225	1.0113	1.0790	195.492	0.0220
0.0301	1.0122	1.0859	177.004	0.0559
0.0527	1.0158	1.1087	136.183	0.1346
0.0677	1.0190	1.1254	112.285	0.1783
0.0826	1.0227	1.1421	90.893	0.2154
0.0939	1.0253	1.1582	81.367	0.2510
Pure water				
$T = 303.15$ K				
0.0241	0.9990	0.8028	105.474	0.0444
0.0322	1.0006	0.8083	90.164	0.0769
0.0563	1.0063	0.8262	53.905	0.1530
0.0723	1.0105	0.8395	37.408	0.1967
0.0884	1.0150	0.8542	23.726	0.2401
0.1004	1.0189	0.8654	10.921	0.2695
$T = 313.15$ K				
0.0240	0.9956	0.6577	101.072	0.0465
0.0321	0.9970	0.6625	93.144	0.0815
0.0561	1.0014	0.6781	78.570	0.1625
0.0720	1.0044	0.6878	73.075	0.1986
0.0879	1.0078	0.6988	64.982	0.2368
0.0963	1.0096	0.7059	61.746	0.2613
$T = 323.15$ K				
0.0239	0.9923	0.5547	67.015	0.0931
0.0319	0.9937	0.5586	67.201	0.1209
0.0558	0.9980	0.5704	65.308	0.1829
0.0717	1.0009	0.5793	64.192	0.2222
0.0876	1.0038	0.5873	63.482	0.2500
0.0959	1.0053	0.5920	63.350	0.2667

temperature of the solutions and amount of 1,4-dioxane in the mixtures increases. Since S_V^* is a measure of ion–ion interactions, the results indicate the presence of weak ion–ion interactions in the solutions at all experimental temperatures and these interactions further decrease with a rise in temperature and mass% of 1,4-dioxane in the solutions. This is probably due to more violent thermal agitation at higher temperatures and lower dielectric constants of the aqueous 1,4-dioxane mixtures, resulting in a diminishing force of ion–ion interactions (ionic dissociation) [11]. However, these interactions increase in water at higher temperatures, which results in a decrease in hydration of ions, i.e. more and more solute in accommodated in the void space left in the packing of water molecules [11].

Partial molar volumes (V_ϕ^0) at infinite dilution were fitted to a second order polynomial in terms of absolute temperature (T):

$$V_\phi^0 = a_0 + a_1 T + a_2 T^2. \tag{3}$$

Table 3. Limiting apparent molar volumes (V_ϕ^0) and experimental slopes (S_V^*) for sodium molybdate in different aqueous 1,4-dioxane mixtures at different temperatures.

	V_ϕ^0 (cm^3 mol^{-1})			S_V^* (cm^2 dm$^{1/2}$ mol$^{-3/2}$)		
Mass% of 1,4-dioxane	303.15 K	313.15 K	323.15 K	303.15 K	313.15 K	323.15 K
0 (water)	193.96 (±0.013)	138.28 (±0.013)	71.53 (±0.011)	−578.82 (±0.022)	−246.92 (±0.015)	−26.77 (±0.013)
10	162.66 (±0.014)	232.88 (±0.012)	242.16 (±0.013)	−267.93 (±0.011)	−384.50 (±0.021)	−470.70 (±0.014)
20	215.91 (±0.012)	254.04 (±0.013)	265.30 (±0.012)	−366.91 (±0.014)	−498.57 (±0.013)	−542.25 (±0.011)
30	231.96 (±0.011)	260.93 (±0.015)	305.89 (±0.012)	−538.69 (±0.013)	−547.73 (±0.014)	−740.63 (±0.012)

Standard errors are given in parenthesis.

Values of the coefficients a_0, a_1 and a_2 for different sodium molybdate solutions along with their standard errors (σ) are reported in table 4. From the values of coefficients the following equations were obtained:

For 10 mass% 1,4-dioxane + 90% water solutions,

$$V_\phi^0 = -30891.740\ (\mathrm{cm^3\,mol^{-1}}) + 194.809T\ (\mathrm{cm^3\,mol^{-1}}) - 0.305T^2\ (\mathrm{cm^3\,mol^{-1}}) \tag{4}$$

For 20 mass% 1,4-dioxane + 80% water solutions,

$$V_\phi^0 = -13694.068\ (\mathrm{cm^3\,mol^{-1}}) + 86.613T\ (\mathrm{cm^3\,mol^{-1}}) + 0.134T^2\ (\mathrm{cm^3\,mol^{-1}}) \tag{5}$$

For 30 mass% 1,4-dioxane + 70% water solutions,

$$V_\phi^0 = 6943.536\ (\mathrm{cm^3\,mol^{-1}}) - 46.374T\ (\mathrm{cm^3\,mol^{-1}}) + 0.080T^2\ (\mathrm{cm^3\,mol^{-1}}) \tag{6}$$

For 100 mass% water solutions,

$$V_\phi^0 = -3372.559\ (\mathrm{cm^3\,mol^{-1}}) + 28.544T\ (\mathrm{cm^3\,mol^{-1}}) - 0.055T^2\ (\mathrm{cm^3\,mol^{-1}}) \tag{7}$$

The partial molar expansibilities (ϕ_E^0) at infinite dilution can be obtained by differentiating equation (3) with respect to temperature:

$$\phi_\mathrm{E}^0 = \left(\frac{\delta V_\phi^0}{\delta T}\right)_\mathrm{P} = a_1 + 2a_2T. \tag{8}$$

Values of ϕ_E^0 for different solutions of the studied electrolyte at 298.15, 308.15, and 318.15 K are reported in table 5. It is found from table 5 that the values of ϕ_E^0 decrease with a rise in temperature as well as an increase in the amount of 1,4-dioxane in the mixtures up to 20 mass% of 1,4-dioxane, however, for 30 mass% of 1,4-dioxane mixtures, the solutions behave in an opposite manner. For aqueous solutions of sodium molybdate, the same trend as observed for the 10 and 20 mass% of 1,4-dioxane

Table 4. Values of the coefficients of equation (3) for sodium molybdate in different aqueous 1,4-dioxane mixtures.

Mass% of 1,4-dioxane	a_0 ($\mathrm{cm^3\,mol^{-1}}$)	a_1 ($\mathrm{cm^3\,mol^{-1}}$)	a_2 ($\mathrm{cm^3\,mol^{-1}}$)
0 (water)	−3372.559	28.544	−0.055
10	−30891.740	194.809	−0.305
20	−13694.068	86.613	−0.134
30	6943.536	−46.374	0.080

Table 5. Limiting partial molar expansibilities (ϕ_E^0) for sodium molybdate in various aqueous 1,4-dioxane mixtures at different temperatures.

	ϕ_E^0 ($\mathrm{cm^3\,mol^{-1}\,K^{-1}}$)			
Mass% of 1,4-dioxane	303.15 K	313.15 K	323.15 K	$(\delta\phi_\mathrm{E}^0/\delta T)_\mathrm{P}$
0 (water)	−4.802	−5.902	−7.002	Negative
10	9.887	3.787	−2.312	Negative
20	5.187	2.501	−0.185	Negative
30	2.069	3.667	5.265	Positive

solutions was observed. This can be ascribed to the absence of caging or packing effect [11,12].

According to Hepler [13], the sign of $(\delta^2 V_\phi^0/\delta T^2)_{\mathrm{P}}$ is a better criterion than S_{V}^* in characterising the long-range structure-making and breaking capacity of electrolytes in solution. The general thermodynamic expression used is:

$$\left(\frac{\delta C_{\mathrm{P}}}{\delta P}\right)_{\mathrm{T}} = -\left(\frac{\delta^2 V_\phi^0}{\delta T^2}\right)_{\mathrm{P}}. \tag{9}$$

If the sign of $(\delta^2 V_\phi^0/\delta T^2)_{\mathrm{P}}$ is positive, the electrolyte is a structure-maker and when the sign of $(\delta^2 V_\phi^0/\delta T^2)_{\mathrm{P}}$ is negative, it is a structure-breaker. As is evident from table 5, the electrolyte under investigation is a structure-breaker in all the experimental solvent mixtures except 30 mass% 1,4-dioxane solutions.

Viscosity data of solutions of sodium molybdate in 10, 20 and 30 mass% 1,4-dioxane + water mixtures as well as pure water have been analysed using the Jones–Dole [14] equation;

$$\frac{\eta}{\eta_0} = 1 + A\sqrt{c} + Bc \tag{10}$$

$$\frac{(\eta/(\eta_0 - 1))}{\sqrt{c}} = A + B\sqrt{c} \tag{11}$$

where η_0 and η are the viscosities of solvent/solvent mixtures and solution, respectively. The coefficients A and B were estimated by a least-squares method and are reported in table 6. A perusal of table 6 shows that values of the A coefficient are negative for all the solutions under investigation at all temperatures. These results indicate the presence of weak ion-ion interactions, and these interactions decrease with an increase in the amount of 1,4-dioxane to the mixture.

The *B*-coefficient [15] reflects the effects of ion-solvent interactions on solution viscosity. The viscosity *B*-coefficient is a valuable tool to provide information concerning the solvation of solutes and their effects on the structure of the solvent in the near environment of solute molecules or ions. Table 6 indicates that values of the *B*-coefficient of sodium molybdate in the studied solvent systems are positive, thereby suggesting the presence of strong ion–solvent interactions, and these types of interactions are strengthened with a rise in both temperature and mass% of 1,4-dioxane in the solutions. Similar results were reported earlier by us for resorcinol in aqueous 1,4-dioxane mixtures [3].

A number of studies [16,17] report that $\mathrm{d}B/\mathrm{d}T$ is a better criterion for determining the structure-making/breaking nature of any solute rather than the *B*-coefficient. Table 6 indicates that values of the *B*-coefficients increase with a rise in temperature (positive $\mathrm{d}B/\mathrm{d}T$), suggesting the structure-breaking tendency of sodium molybdate in the studied solvent systems. A similar result has been reported in a study [18] of the viscosity of various salts in propionic acid + ethanol mixtures.

The adiabatic compressibility (β) was evaluated from the following equation:

$$\beta = u^{-2}\rho^{-1} \tag{12}$$

Table 6. Values of *A* and *B* coefficients for sodium molybdate in different aqueous 1,4-dioxane mixtures at different temperatures.

	A ($cm^{3/2} mol^{-1/2}$)			B ($cm^3 mol^{-1}$)		
Mass% of 1,4-dioxane	303.15 K	313.15 K	323.15 K	303.15 K	313.15 K	323.15 K
0 (water)	−0.172 (±0.011)	−0.162 (±0.012)	−0.079 (±0.021)	1.384 (±0.012)	1.356 (±0.013)	1.116 (±0.011)
10	−0.065 (±0.011)	−0.077 (±0.013)	−0.098 (±0.012)	0.478 (±0.011)	0.608 (±0.012)	1.192 (±0.014)
20	−0.132 (±0.011)	−0.122 (±0.023)	−0.0161 (±0.012)	0.909 (±0.011)	0.953 (±0.012)	1.236 (±0.021)
30	−0.145 (±0.011)	−0.162 (±0.014)	−0.195 (±0.013)	1.071 (±0.015)	1.278 (±0.022)	1.439 (±0.011)

Standard errors are given in parenthesis.

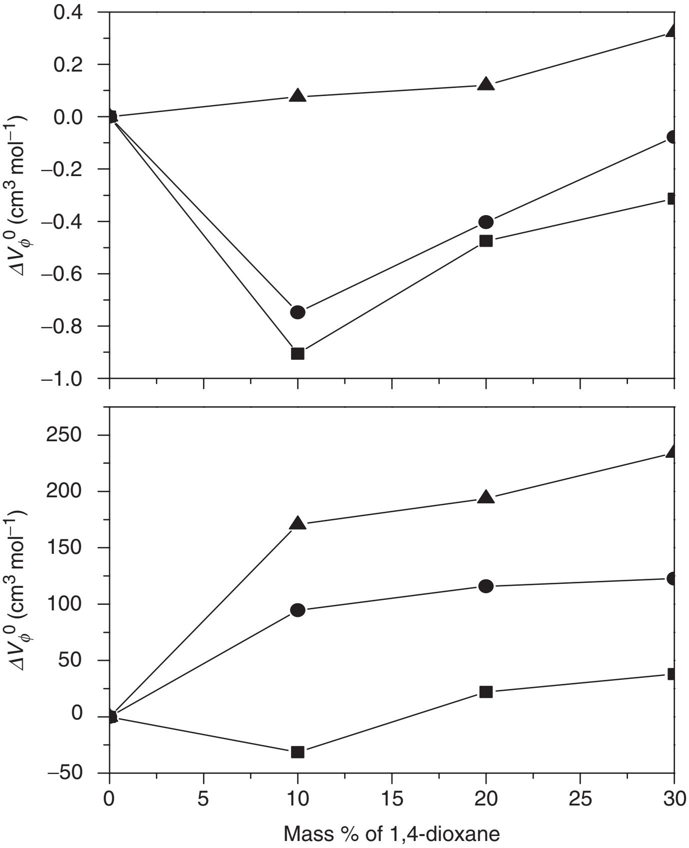

Figure 1. Plots of partial molar volumes (ΔV_{ϕ}^{0}) and viscosity *B*-coefficients (ΔB) of transfer from water to different aqueous 1,4-dioxane mixtures against mass% of 1,4-dioxane in the mixtures at different temperatures. 303.15 K (■); 313.15 K (●); 323.15 K (▲).

where ρ is the solution density and u is the sound speed in the solution. The apparent molal adiabatic compressibility (ϕ_{K}) of the solutions was determined from the relation,

$$\phi_{\mathrm{K}} = \frac{M\beta}{\rho_0} + \frac{1000(\beta\rho_0 - \beta_0\rho)}{m\rho\rho_0} \tag{13}$$

where β_0, β are the adiabatic compressibility of the solvent and solution, respectively and m is the molality of the solution. Limiting partial molal adiabatic compressibilities (ϕ_{K}^{0}) and experimental slopes (S_{K}^{*}) were obtained by fitting ϕ_{K} against the square root of molality of the electrolyte ($\sqrt{m}$) using the method of least squares.

$$\phi_{\mathrm{K}} = \phi_{\mathrm{K}}^{0} + S_{\mathrm{K}}^{*}\sqrt{m} \tag{14}$$

Values of m, u, β, ϕ_{K}, ϕ_{K}^{0} and S_{K}^{*} are presented in table 7. A perusal of table 7 shows that ϕ_{K}^{0} values are positive and S_{K}^{*} values are negative for all the ternary solutions. Since the values of ϕ_{K}^{0} and S_{K}^{*} are measures of ion-solvent and ion-ion interactions,

Table 7. Molality (m), density (ρ), sound speed (u), adiabatic compressibility (β), partial molal adiabatic compressibility (ϕ_K), limiting partial adiabatic compressibility (ϕ_K^0), and experimental slope (S_K^*) of sodium molybdate in different aqueous 1,4-dioxane mixtures at 303.15 K.

m (mol kg^{-1})	u (m s^{-1})	$\beta \times 10^{10}$ (Pa^{-1})	$\phi_K \times 10^{10}$ (m^3 mol^{-1} Pa^{-1})	$\phi_K^0 \times 10^{10}$ (m^3 mol^{-1} Pa^{-1})	$S_K^* \times 10^{10}$ (m^3 mol$^{-3/2}$ Pa^{-1} kg$^{1/2}$)
10 mass% of 1,4-dioxane + water					
0.0240	1530.1	4.2349	−1.134	0.051 (±0.012)	−7.770 (±0.024)
0.0320	1532.5	4.2160	−1.353		
0.0561	1541.5	4.1504	−1.807		
0.0724	1548.5	4.1006	−2.034		
0.0884	1557.2	4.0442	−2.224		
0.1005	1564.9	3.9963	−2.416		
20 mass% of 1,4-dioxane + water					
0.0242	1572.2	3.979	0.390	1.599 (±0.011)	−7.901 (±0.013)
0.0323	1573.2	3.970	1.650		
0.0567	1577.0	3.977	−3.080		
0.0729	1580.3	3.911	−5.240		
0.0891	1584.5	3.879	−7.450		
0.1013	1588.6	3.850	−9.200		
30 mass% of 1,4-dioxane + water					
0.0224	1579.9	3.919	0.400	1.756 (±0.024)	−9.159 (±0.011)
0.0299	1580.4	3.913	0.182		
0.0524	1584.1	3.880	−0.380		
0.0674	1586.4	3.855	−0.640		
0.0824	1590.0	3.826	−0.864		
0.0937	1593.4	3.799	−1.030		
Pure water					
0.0243	1510.2	4.389	−2.960	−1.454 (±0.012)	−9.829 (±0.011)
0.0324	1515.0	4.354	−3.250		
0.0567	1529.9	4.246	−3.770		
0.0729	1542.7	4.158	−4.150		
0.0891	1555.8	4.070	−4.410		
0.1012	1564.9	4.008	−4.540		

Standard errors are given in parenthesis.

Table 8. Partial molar volumes (ΔV_ϕ^0) and viscosity B-coefficients (ΔB) of transfer from water to different aqueous 1,4-dioxane mixtures for sodium molybdate at different temperatures.

Mass % of 1,4-dioxane	V_ϕ^0	ΔV_ϕ^0	B	ΔB
303.15 K				
0 (water)	193.96 (±0.013)	0.00	1.384 (±0.012)	0.00
10	162.66 (±0.014)	−31.30	0.478 (±0.011)	−0.906
20	215.91 (±0.012)	21.95	0.909 (±0.011)	−0.475
30	231.96 (±0.011)	38.00	1.071 (±0.015)	−0.313
313.15 K				
0 (water)	138.28 (±0.013)	0.00	1.356 (±0.013)	0.00
10	232.88 (±0.012)	94.60	0.608 (±0.012)	−0.748
20	254.04 (±0.013)	115.76	0.953 (±0.012)	−0.403
30	260.93 (±0.015)	122.65	1.278 (±0.022)	−0.078
323.15 K				
0 (water)	71.53 (±0.011)	0.00	1.116 (±0.011)	0.00
10	242.16 (±0.013)	170.63	1.192 (±0.014)	0.076
20	265.30 (±0.012)	193.77	1.236 (±0.021)	0.120
30	305.89 (±0.012)	234.36	1.439 (±0.011)	0.323

respectively, the results are in good agreement with those drawn from the values of V_ϕ^0 and S_V^* discussed earlier.

Partial molar volumes (ΔV_ϕ^0) and viscosity *B*-coefficients (ΔB) of transfer from water to aqueous 1,4-dioxane solutions have been determined using the relations [19,20],

$$\Delta V_\phi^0 = V_\phi^0(\text{Aqueous 1,4-dioxane solution}) - V_\phi^0(\text{Water}) \tag{15}$$

$$\Delta B = B(\text{Aqueous 1,4-dioxane solution}) - B(\text{Water}). \tag{16}$$

The value of ΔV_ϕ^0 is by definition free from ion–ion interactions and therefore provides information regarding ion–solvent interactions [19]. As can be seen from figure 1, the value of ΔV_ϕ^0 is negative at 303.15 K for 10 mass% of 1,4-dioxane solution but becomes positive at higher temperatures. ΔV_ϕ^0 is positive and increases monotonically with mass% of 1,4-dioxane in the remaining mixtures. These results further confirm the presence strong ion–solvent interactions in the chosen solvent mixtures for sodium molybdate. ΔB values [20] shown in table 8 and figure 1 also support the results obtained from ΔV_ϕ^0 values.

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