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Vapor−Liquid Equilibria, Density, Speed of Sound, and Refractive Index of Sodium Tungstate in Water and in Aqueous Solutions of Poly(ethyleneglycol) 6000

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Vapor−liquid equilibrium data (water activity, vapor pressure, osmotic coefficient, and activity coefficient) of binary aqueous sodium tungstate solutions and ternary aqueous sodium tungstate−poly(ethyleneglycol) (PEG) solutions were obtained through the isopiestic method at $T = 298.15$ K. Density and speed of sound measurements were carried out on sodium tungstate in pure water and in aqueous solution of mass fraction 0.02 PEG at $T = (288.15$ to $308.15)$ K at atmospheric pressure. From the experimental density and speed of sound data, the apparent molar volume and isentropic compressibility values were evaluated and fitted to the Pitzer equation from which the apparent molar volume and apparent molar isentropic compressibility of the solutions at infinite dilution were calculated at each temperature. The results show a positive transfer volume and isentropic compressibility of sodium tungstate from pure water to an aqueous PEG solution. Furthermore, experimental refractive index data were measured for solutions of sodium tungstate in pure water and in aqueous solution of mass fractions 0.02 and 0.04 PEG as well as those for solutions of PEG in pure water and in aqueous solutions of mass fractions 0.02 and 0.04 sodium tungstate at $T = 308.15$ K.

Introduction

Ternary aqueous solutions of sodium tungstate (Na_2WO_4) and poly(ethyleneglycol) (PEG) separate into a sodium tungstate-rich and a PEG-rich phase over part of the composition space.[1] Aqueous two-phase systems of this nature are useful for the separation and purification of biomaterials where the employment of a nonpolar solvent/aqueous phase system would lead to degradation of biological activity.[2,3]

Thermodynamic properties of aqueous polymer−salt systems are necessary for a fundamental understanding of the phase-forming ability and also for the development of theoretical models for the prediction of the partitioning behavior of the two-phase system. In addition to aqueous two-phase systems, aqueous solutions of sodium tungstate are of considerable significance in many other biochemical and chemical processes. Although, with respect to the aqueous sodium tungstate solutions, there are some limited reports on the vapor−liquid equilibria[4−7] of these solutions, however, with respect to other thermodynamic properties of binary aqueous sodium tungstate solutions, very little information can be found in the literature. Furthermore, thermodynamic properties of sodium tungstate in aqueous PEG solutions, which is a very important system with respect to its use in biotechnology, are scarce.

The present work presents experimental data on the vapor−liquid equilibria of binary $Na_2WO_4 + H_2O$ and ternary PEG + $Na_2WO_4 + H_2O$ solutions at 298.15 K. This work also presents the experimental data for density and speed of sound of Na_2WO_4 in pure water and in an aqueous solution of mass fraction 0.02 PEG at $T = (288.15, 293.15, 298.15, 303.15,$ and $308.15)$ K at atmospheric pressure, and the values of apparent molar volume, ϕ_V, and apparent molar isentropic compressibility, ϕ_K, are then calculated from the measured data. Furthermore, experimental refractive index data of solutions of sodium tungstate in pure water and in aqueous solutions of mass fraction 0.02 and 0.04 PEG as well as those for solutions of PEG in pure water and in aqueous solutions of mass fraction 0.02 and 0.04 $Na_2WO_4 \cdot 2H_2O$ at $T = 308.15$ K are also reported.

Experimental Section

Materials. Poly(ethyleneglycol) with a quoted molar mass of 6000 $g \cdot mol^{-1}$ was obtained from Merck. The manufacturer has characterized this polymer with charge/lot number S35317 203. Sodium tungstate ($Na_2WO_4 \cdot 2H_2O$) (> 99 %) and sodium chloride (purity > 99.5 %) were obtained from Merck. The polymer and salts were used without further purification. Double distilled and deionized water was used.

Apparatus and Procedures. The aqueous solutions were prepared by mass, using an analytical balance (Sartorius CP124S) with a precision of $\pm 1 \cdot 10^{-4}$ g. In this study, the isopiestic method was used to obtain the water activity of the aqueous solutions. The isopiestic apparatus used in this work was similar to the one used by Ochs et al.[8] It is based on a phenomenon that different solutions, when connected through the vapor space, approach equilibrium by transferring solvent mass by distillation. Equilibrium has been established once the temperature and pressure are uniform throughout the system, provided that no concentration gradients exist in the liquid phase. At equilibrium, the chemical potentials of the solvent in each of the solutions in the closed system are identical. Equality of the solvent chemical potential implies the equality of the solvent activity. Since the solvent activity is known for one or more standard solutions, it will be known for each solution within the isopiestic system. The apparatus used for determination of water activity in the binary water + Na_2WO_4 solutions consisted of a five-leg manifold attached to round-bottom flasks. Two flasks contained the standard pure NaCl solutions; two flasks contained the pure Na_2WO_4 solutions; and the central flask was used as a water reservoir. However, the apparatus used for determination of water activity in the ternary PEG + Na_2WO_4

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+ water solutions consisted of an eight-leg manifold attached to round-bottom flasks. Two flasks contained the standard pure NaCl solutions; one flask contained the pure PEG solution; one flask contained the pure Na_2WO_4 solution; three flasks contained the PEG + Na_2WO_4 solutions; and the central flask was used as a water reservoir. The apparatus was held in a constant-temperature bath at least 5 days (depending on the salt concentration) for equilibrium. Equilibrations were performed generally within (5 to 10) days for intermediate and concentrated solutions and about 15 days for low molalities. During the equilibration process, the manifold was removed at least once a day, and the samples were agitated. After the third day, the samples were not agitated but left in the bath to approach their final equilibrium conditions. The temperature was controlled to within ± 0.05 K. After equilibrium had been reached, the manifold assembly was removed from the bath, and each flask was weighed with an analytical balance with a precision of $\pm 1 \cdot 10^{-4}$ g. From the weight of each flask after equilibrium and the initial weight of salt and polymer, the mass fraction of each solution was calculated. The water activity for the standard aqueous NaCl solutions at different concentrations and temperatures has been calculated from the correlation of Colin et al.[9] It was assumed that the equilibrium condition was reached when the differences between the mass fractions of each duplicate were less than 1 %. In all cases, averages of the duplicate are reported as the total isopiestic mass fraction. The accuracy of the method depends upon the standard solutions, sample mixing during the equilibrium period, temperature stability, and the time allowed for the equilibrium process. The uncertainty in the measurement of solvent activity was estimated to be $\pm 2 \cdot 10^{-4}$.

The density and speed of sound of the mixtures were measured at different temperatures with a digital vibrating-tube analyzer (Anton Paar DSA 5000, Austria) with proportional temperature control that kept the samples at the working temperature with a precision of 0.001 K. The apparatus was calibrated with double distilled, deionized, and degassed water and dry air at atmospheric pressure. Densities and speed of sounds can be measured to $\pm 10^{-6}$ $g \cdot cm^{-3}$ and $\pm 10^{-2}$ $m \cdot s^{-1}$, respectively, under the most favorable conditions. The uncertainties of density and ultrasonic velocity measurements were $\pm 3 \cdot 10^{-6}$ $g \cdot cm^{-3}$ and $\pm 10^{-1}$ $m \cdot s^{-1}$, respectively.

Refractive index measurements were made by using a refractometer (QUARTZ RS-232, Ceti, Belgium) with an uncertainty of $\pm 1 \cdot 10^{-4}$. The temperature of the refractometer was controlled with water from a large well-regulated water bath to within ± 0.05 K.

Results and Discussion

In the present work, three sets of experiments were carried out to describe thermodynamic properties of binary aqueous Na_2WO_4 solutions and ternary PEG + Na_2WO_4 + H_2O solutions. For the first set of experiments, the osmotic coefficient measurements at $T = 298.15$ K were carried out for Na_2WO_4 + H_2O and PEG + Na_2WO_4 + H_2O solutions to study the vapor−liquid equilibria behavior of these systems. For the second set, density and speed of sound measurements for Na_2WO_4 in pure water and in aqueous solutions of PEG at different salt concentrations were made at $T = (288.15, 293.15, 298.15, 303.15$, and $308.15)$ K to study the variation in apparent molar volumes, compressibilities, and expansibilities with salt concentration and temperature. For the third set of experiments, the refractive index measurements for solutions of Na_2WO_4 in pure water and in aqueous solutions of PEG as well as those for solutions of PEG in pure water and in aqueous solutions of Na_2WO_4 were determined experimentally at $T = 308.15$ K.

Table 1. Isopiestic Equilibrium Molalities, Osmotic Coefficients, Water Activities, and Vapor Pressures of Na_2WO_4 in Water at $T = 298.15$ K

$m_{Na_2WO_4}$ / $mol \cdot kg^{-1}$	m_{NaCl} / $mol \cdot kg^{-1}$	Φ	a_w	p / kPa	γ_w	$\gamma_\pm$
0.0000	0.0000	1.000	1.0000	3.169	1.0000	1.0000
0.1733	0.2871	1.019	0.9905	3.139	0.9998	0.5698
0.2298	0.3617	0.968	0.9880	3.131	1.0003	0.5517
0.2717	0.3992	0.904	0.9868	3.127	1.0013	0.5399
0.2970	0.4388	0.909	0.9855	3.123	1.0013	0.5332
0.3764	0.5038	0.825	0.9834	3.116	1.0034	0.5138
0.4438	0.6004	0.836	0.9802	3.106	1.0037	0.4992
0.4790	0.6482	0.837	0.9786	3.101	1.0039	0.4921
0.5338	0.7223	0.839	0.9761	3.093	1.0042	0.4819
0.5407	0.7278	0.835	0.9759	3.092	1.0044	0.4807
0.5423	0.7297	0.835	0.9758	3.092	1.0044	0.4804
0.5657	0.7651	0.840	0.9746	3.088	1.0044	0.4763
0.6486	0.8665	0.833	0.9712	3.077	1.0053	0.4633
0.7283	0.9634	0.828	0.9679	3.067	1.0060	0.4524
0.8928	1.1817	0.837	0.9604	3.043	1.0067	0.4348
0.9122	1.2033	0.835	0.9597	3.041	1.0070	0.4331
0.9195	1.2249	0.844	0.9589	3.038	1.0066	0.4325
1.0899	1.4436	0.849	0.9512	3.014	1.0072	0.4211
1.1180	1.4779	0.849	0.9500	3.010	1.0074	0.4197
1.3521	1.7921	0.866	0.9387	2.974	1.0073	0.4133
1.4414	1.9373	0.886	0.9333	2.957	1.0061	0.4131
1.5385	2.0632	0.890	0.9287	2.942	1.0059	0.4141
1.7078	2.3069	0.910	0.9195	2.913	1.0043	0.4191
1.7561	2.3688	0.912	0.9171	2.906	1.0041	0.4213
1.8700	2.5682	0.940	0.9094	2.881	1.0013	0.4276
1.8971	2.6136	0.945	0.9076	2.876	1.0007	0.4293
1.9853	2.7302	0.951	0.9030	2.861	0.9999	0.4358
2.0067	2.7602	0.952	0.9019	2.857	0.9997	0.4375
2.0213	2.7810	0.954	0.9010	2.855	0.9995	0.4387
2.1578	2.9866	0.972	0.8928	2.829	0.9970	0.4515
2.3024	3.1917	0.986	0.8845	2.802	0.9946	0.4680

Vapor−Liquid Equilibria Measurements. In the present work, the isopiestic measurements at $T = 298.15$ K were carried out for Na_2WO_4 + H_2O and PEG + Na_2WO_4 + H_2O solutions to study the vapor−liquid equilibria behavior of these systems. For the understanding of interactions in liquids, the activity or osmotic coefficients of the different components are of great interest. They are the most relevant thermodynamic reference data, and they are often the starting point of any modeling.[10−12] At isopiestic equilibrium, the activity of the solvent in the reference and sample solutions must be the same. By definition, the osmotic coefficient Φ is related to the solvent activity a_w as[13]

$$\Phi = -\frac{1000 \ln a_w}{\nu m M_w} \tag{1}$$

where ν is the stoichiometric numbers of the solute; m is the molality of solution; and M_w is the molecular weight of the solvent. The isopiestic equilibrium molalities with reference standard solutions of NaCl in water as reported in Table 1 enabled the calculation of the osmotic coefficient, Φ, of the solutions of Na_2WO_4 in water from[13]

$$\Phi = \frac{\nu^* \Phi^* m^*}{\nu m} \tag{2}$$

where ν^* and ν are the sums of the stoichiometric numbers of anions and cations in the reference solution and the solution of Na_2WO_4, respectively; m is the molality of the Na_2WO_4 solution; m^* is the molality of the reference standard in isopiestic equilibrium with this solution, and Φ^* is the osmotic coefficient of the isopiestic reference standard, calculated at m^*. The necessary Φ^* values at any m^* and temperatures were obtained from the correlation of Colin et al.[9] As can be seen from Table

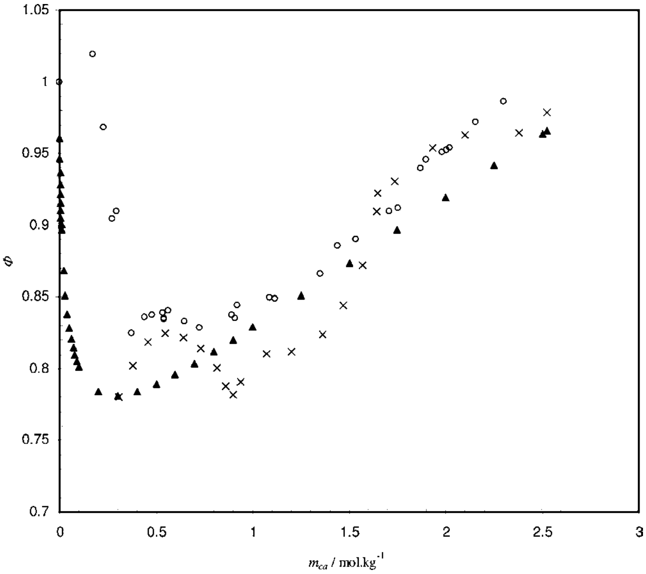

Figure 1. Plot of osmotic coefficient Φ of the $Na_2WO_4 + H_2O$ system against molality of the salt, m_{ca}, at $T = 298.15$ K: ○, this work; ▲, ref 5; ×, ref 7.

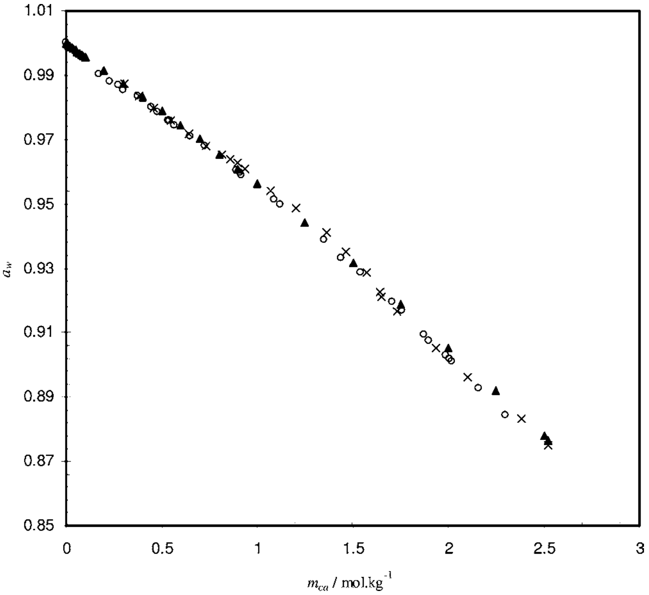

Figure 2. Plot of water actvity a_w of the $Na_2WO_4 + H_2O$ system against molality of the salt, m_{ca}, at $T = 298.15$ K: ○, this work; ▲, ref 5; ×, ref 7.

1, the value of Φ at 0.1733 mol·kg^{-1} is larger than that at pure water. In fact, in dilute electrolyte solutions the osmotic coefficient data are very sensitive to composition, and a small error in composition leads to a large error in osmotic coefficient. From the calculated osmotic coefficient data, the activity of water in the salt solution and the vapor pressure of this solution were determined at isopiestic equilibrium molalities, with the help of the eq 1 and the following relation[14]

$$\ln a_w = \ln\left(\frac{p}{p_w^\circ}\right) + \frac{(B_w^\circ - V_w^\circ)(p - p_w^\circ)}{RT} \qquad (3)$$

where B_w° is the second virial coefficient of water vapor; V_w° is the molar volume of liquid water; and p_w° is the vapor pressure of pure water. The second virial coefficients of water vapor were calculated using the equation provided by Rard and Platford.[14] Molar volumes of liquid water were calculated using the density of water at different temperatures.[15] The vapor pressures of pure water were calculated using the equation of state of Saul and Wagner.[16] In Figures 1 and 2, respectively, comparison of the experimental osmotic coefficient and water activity data for the $Na_2WO_4 + H_2O$ system measured in this work with those taken from refs 5 and 7 has been made at $T = 298.15$ K. Figure 1 shows that these three sets of osmotic coefficient data do not agree well with each other. As can be seen from Figure 3, at the same solute mass fraction, vapor pressure depression for the salt solution is more than those for the polymer solution. This is because the number of moles of ions in the salt solution is more than the number of moles of polymer in the polymer solution with same mass fraction (the vapor pressure depression is a collegative property). The water activity was used to obtain the solvent activity coefficient, γ_w. Calculated water activity coefficients, γ_w, of aqueous solutions of Na_2WO_4 are also given in Table 1. The experimental osmotic coefficients are related to the mean molal activity coefficients, $\gamma_\pm$, at molality m' by the relation[13]

$$\ln \gamma_\pm = \Phi' - 1 + \int_0^{m'} \frac{\Phi - 1}{m} \mathrm{d}m \qquad (4)$$

The calculated values of $\gamma_\pm$ (obtained from eq 4 by using Pitzer's model for Φ) are also given in Table 1.

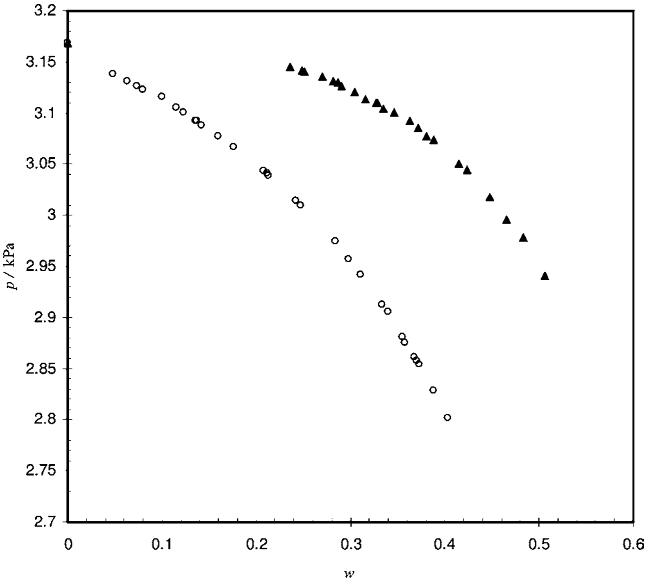

Figure 3. Plot of vapor pressure *p* of $Na_2WO_4 + H_2O$ and $PEG_{6000} + H_2O$ systems against mass fraction of salt or polymer, *w*, at $T = 298.15$ K: ○, $Na_2WO_4 + H_2O$; ▲, $PEG_{6000} + H_2O$.

Table 2 reports the water activities and vapor pressures of the PEG + $Na_2WO_4 + H_2O$ system at $T = 298.15$ K. The lines of constant water activity or vapor pressure of PEG + $Na_2WO_4 + H_2O$ system at $T = 298.15$ K are plotted in Figure 4. As can be seen in Table 2, in fact five points on each line in Figure 4 have a constant water activity or chemical potential, and thus these points are in equilibrium. The line with the lowest water activity must be in the neighborhood of the binodal curve where this system splits into two phases. In Table 3, vapor pressure depression for several PEG + $Na_2WO_4 + H_2O$ solutions along with those for corresponding binary solutions is given at $T = 298.15$ K. This table shows that the vapor pressure depression for a ternary aqueous PEG + Na_2WO_4 system is more than the sum of those for the corresponding binary solutions. In the aqueous solutions, each segment of PEG is hydrated strongly with several water molecules. Such binding will result in a reduction in the free water content and consequently in an

Table 2. Water Activities and Vapor Pressures for the PEG (p) + Na_2WO_4 (ca) + H_2O (w) System for Different Mass Fraction w at T = 298.15 K

w_p	w_{ca}	w_{NaCl}	a_w	p/kPa	w_p	w_{ca}	w_{NaCl}	a_w	p/kPa
0.3047	0.0000				0.3153	0.0000			
0.1846	0.0341				0.1947	0.0359			
0.0999	0.0591	0.0264	0.9847	3.120	0.1069	0.0632	0.0295	0.9828	3.114
0.0581	0.0721				0.0630	0.0775			
0.0000	0.0897				0.0000	0.0994			
0.3271	0.0000				0.3285	0.0000			
0.1613	0.0526				0.2081	0.0384			
0.0804	0.0803	0.0316	0.9815	3.110	0.1165	0.0686	0.0318	0.9814	3.110
0.0501	0.0909				0.0690	0.0856			
0.0000	0.1089				0.0000	0.1102			
0.3347	0.0000				0.3469	0.0000			
0.2069	0.0422				0.1761	0.0578			
0.1188	0.0716	0.0346	0.9797	3.104	0.0901	0.0899	0.0365	0.9786	3.101
0.0702	0.0889				0.0567	0.1029			
0.0000	0.1155				0.0000	0.1254			
0.36236	0.0000				0.3718	0.0000			
0.2289	0.0468				0.2421	0.0471			
0.1362	0.0821	0.0407	0.9760	3.092	0.1481	0.0842	0.0442	0.9738	3.085
0.0820	0.1039				0.0976	0.1056			
0.0000	0.1393				0.0000	0.1502			
0.3803	0.0000				0.3882	0.0000			
0.2060	0.0676				0.2527	0.0516			
0.1098	0.1095	0.0482	0.9712	3.077	0.1545	0.0932	0.0497	0.9703	3.074
0.0702	0.1273				0.0947	0.1200			
0.0000	0.1628				0.0000	0.1669			
0.4153	0.0000				0.4236	0.0000			
0.2878	0.0532				0.2881	0.0561			
0.1763	0.1043	0.0614	0.9626	3.050	0.1845	0.1049	0.0639	0.9609	3.045
0.1111	0.1377				0.1252	0.1354			
0.0000	0.1993				0.0000	0.2072			
0.4484	0.0000								
0.3091	0.0632								
0.1986	0.1197	0.0760	0.9525	3.018					
0.1267	0.1604								
0.0000	0.2385								

increase in the effective concentration of the salt. Similarly, ionic species in the aqueous solutions are hydrated, and this hydration will result in an increase in the effective concentration of the polymer. Thus, it can be expected that the vapor pressure depression for an aqueous PEG + Na_2WO_4 system will be more than the sum of those for corresponding binary solutions. With an increase in the concentration of the polymer or the salt, the effective concentration will increase, and ultimately, the system could reach a state where, for entropic reasons, the formation of the aqueous two-phase system would become favorable.

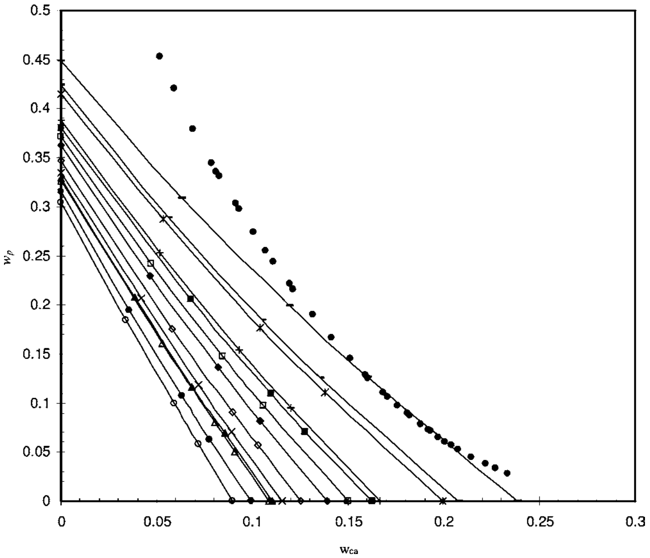

Figure 4. Constant water activity curves for the PEG (p) + Na_2WO_4 (ca) + H_2O (w) system at 298.15 K: ○, 0.9847; ●, 0.9828; △, 0.9815; ▲, 0.9814; ×, 0.9797; ◇,0.9786; ◆, 0.9760; □, 0.9738; ■, 0.9712; +, 0.9703; *, 0.9626; - -, 0.9609; −, 0.9525; ●, binodal curve.

Table 3. Vapor Pressure Depression for Several PEG (p) + Na_2WO_4 (ca) + H_2O (w) Solutions Along with Those for the Corresponding Binary Solutions at T = 298.15 K

		$(p^0 - p)$/kPa		
w_p	w_{ca}	PEG (p) + Na_2WO_4 (ca) + H_2O (w)	PEG (p) + H_2O (w)	Na_2WO_4 (ca) + H_2O(w)
0.3680	0.0716	0.228 (0.122[a])	0.081	0.041
0.3488	0.0644	0.190 (0.108)	0.069	0.039
0.3383	0.0600	0.173 (0.100)	0.064	0.036
0.3091	0.0632	0.151 (0.089)	0.051	0.038
0.2881	0.0561	0.124 (0.075)	0.041	0.034

[a] Sum of vapor pressure depression for the corresponding binary solutions. w is mass fraction.

Volumetric Measurements. Experimental data of density (d) and sound velocity (u) for various sodium tungstate solutions determined at T = (288.15, 293.15, 298.15, 303.15, and 308.15) K are given in Table 4. The apparent molar volumes of the sodium tungstate ϕ_V in aqueous PEG solutions were calculated from the density of the solution by using the following equation[17]

$$\phi_V = \frac{1000(d_0 - d)}{m_{ca} d d_0} + \frac{M_{ca}}{d} \tag{5}$$

where M_{ca} and m_{ca} are the molar mass and molality of the salt, respectively, and d and d_0 are the densities of the solution and solvent, respectively. For ternary systems, the PEG + water is considered as the solvent. We have tested the reliability of the Pitzer equation in the correlation of the experimental apparent

Table 4. Experimental Density $d/(\mathrm{g\cdot cm^{-3}})$ and Speed of Sound $u/(\mathrm{m\cdot s^{-1}})$ of Na_2WO_4 in Water and in Aqueous Solution of Mass Fraction 0.02 PEG at Different Temperatures

m_{ca}	T = 288.15 K		T = 293.15 K		T = 298.15 K		T = 303.15 K		T = 308.15 K	
$(\mathrm{mol\cdot kg^{-1}})$	d	u	d	u	d	d	u	d	u	d
					in pure water					
0.0000	0.999099	1466.25	0.998203	1482.66	0.997043	1497.00	0.995645	1509.44	0.994029	1520.12
0.0397	1.009651	1469.11	1.008702	1484.89	1.007494	1498.88	1.006055	1511.03	1.004403	1521.53
0.0737	1.018629	1471.19	1.017632	1486.73	1.016387	1500.51	1.014914	1512.44	1.013234	1522.76
0.1057	1.027054	1473.13	1.026016	1488.46	1.024736	1502.02	1.023232	1513.80	1.021523	1523.93
0.1483	1.038205	1475.65	1.037117	1490.69	1.035784	1504.01	1.034240	1515.64	1.032495	1525.52
0.2055	1.053143	1479.19	1.051982	1493.84	1.050591	1506.76	1.048990	1517.99	1.047197	1527.64
0.2792	1.072296	1484.13	1.071039	1497.97	1.069599	1510.48	1.067957	1521.39	1.066095	1530.91
0.3424	1.088612	1487.87	1.087289	1501.48	1.085739	1513.55	1.084039	1524.05	1.082130	1533.04
0.3949	1.101838	1491.02	1.100459	1504.41	1.098874	1516.19	1.097105	1526.38	1.095156	1535.10
0.5505	1.141032	1500.88	1.139492	1513.34	1.137764	1524.25	1.135864	1533.67	1.133800	1541.68
0.7258	1.184565	1512.72	1.182858	1524.04	1.180982	1533.94	1.178947	1542.42	1.176764	1549.60
0.9538	1.239619	1528.32	1.237722	1538.26	1.235670	1546.94	1.233479	1554.34	1.231150	1560.57
					in aqueous solution of mass fraction 0.02 PEG					
0.0000	1.002450	1478.77	1.001477	1493.90	1.000247	1507.31	0.998784	1518.92	0.997108	1528.87
0.0118	1.005588	1479.57	1.004599	1494.63	1.003353	1507.92	1.001881	1519.44	1.000195	1529.32
0.0906	1.026423	1484.49	1.025333	1498.96	1.023999	1511.75	1.022447	1522.88	1.020694	1532.35
0.1227	1.034926	1486.34	1.033792	1500.73	1.032422	1513.31	1.030840	1524.25	1.029058	1533.57
0.1907	1.052710	1490.56	1.051492	1504.42	1.050049	1516.59	1.048400	1527.15	1.046561	1536.11
0.2575	1.069899	1494.71	1.068601	1508.04	1.067090	1519.84	1.065379	1529.99	1.063486	1538.61
0.3282	1.088058	1499.06	1.086680	1511.96	1.085097	1523.31	1.083324	1533.08	1.081374	1541.38
0.4393	1.116573	1506.09	1.115078	1518.29	1.113386	1528.96	1.111516	1538.15	1.109478	1545.87
0.4811	1.127161	1508.74	1.125621	1520.65	1.123892	1531.07	1.121986	1540.03	1.119918	1547.59
0.5588	1.146374	1513.65	1.144759	1525.14	1.142962	1535.11	1.140996	1543.66	1.138872	1550.82
0.6967	1.180388	1522.51	1.178644	1533.13	1.176732	1542.34	1.174662	1550.21	1.172443	1556.79
0.9125	1.232651	1536.94	1.230727	1546.20	1.228648	1554.26	1.226428	1561.09	1.224074	1566.72
0.9733	1.247401	1540.94	1.245425	1549.97	1.243302	1557.72	1.241041	1564.26	1.238748	1569.66

Table 5. Pitzer's Model Parameters and the Corresponding Absolute Relative Deviation, ARD, for Apparent Molar Volume and Isentropic Compressibility of Na_2WO_4 in Water and in Aqueous Solution of Mass Fraction 0.02 PEG at Different Temperatures[a]

	ϕ_V^0					$\phi_K^0\cdot 10^4$				
T/K	$\mathrm{cm^3\cdot mol^{-1}}$	$\beta_V^0\cdot 10^4$	$\beta_V^1\cdot 10^3$	$C_V\cdot 10^5$	ARD·10^2	$\mathrm{cm^3\cdot mol^{-1}\cdot kPa^{-1}}$	$\beta_K^0\cdot 10^9$	$\beta_K^1\cdot 10^9$	$C_K\cdot 10^{10}$	ARD·10^2
					in pure water					
288.15	26.576	6.5780	−2.2537	−4.7696	0.457	−1.6115	−0.90098	−16.9320	−4.0473	−0.376
293.15	27.683	5.7010	−2.2764	−3.6002	0.440	−1.4567	−2.4596	−3.9798	0.17539	−0.145
298.15	28.620	5.8165	−2.6224	−4.9234	0.439	−1.3601	−3.5556	3.1049	3.8010	−0.112
303.15	29.362	6.1157	−3.0275	−6.2918	0.491	−1.2848	−4.2359	8.1260	6.0406	−0.135
308.15	29.843	5.9184	−3.1375	−6.5488	0.462	−1.2393	−3.9910	8.3693	5.8211	−0.200
					in aqueous solution of mass fraction 0.02 PEG					
288.15	28.201	16.916	−6.0912	−33.581	0.624	−1.5102	−2.6455	−6.1557	0.13517	−0.135
293.15	29.292	16.180	−6.1646	−32.759	0.614	−1.4337	−2.3321	−5.6494	0.14984	−0.180
298.15	30.353	17.017	−6.8609	−35.888	0.612	−1.3444	−3.5904	1.5942	4.3418	−0.197
303.15	30.717	14.799	−6.1360	−30.811	0.585	−1.2726	−4.5122	7.5201	7.0794	−0.202
308.15	31.150	14.716	−6.2338	−31.786	0.592	−1.2258	−4.1714	7.8094	6.5143	−0.228

[a] ARD = $(1/NP)\sum[(|\phi_{exp} - \phi_{cal}|)/(\phi_{exp})]$.

molar volume data for the investigated aqueous solutions at different temperatures. The Pitzer equation has the form[18]

$$\phi_V = \phi_V^0 + \nu|z_c z_a|\left(\frac{A_V}{2b}\right)\ln(1 + bI^{1/2}) + 2RT\nu_c\nu_a[B_V m_{ca} + \nu_c z_c C_V m_{ca}^2] \quad (6)$$

where ν_c and ν_a are the number of cations and anions and $\nu = \nu_c + \nu_a$; the subscripts c and a are used for the cation and anion, respectively; z_c and z_a are the number of charges on cations and anions, respectively; I is total ionic strength; R is the gas constant; T are thermodynamic temperatures; A_V is the Pitzer−Debye−Hückel limiting slope (A_V values at different temperatures were taken from the literature[18]); and B_V is defined by the following equation[18]

$$B_V = \beta_V^0 + \beta_V^1\left(\frac{2}{\alpha^2 I}\right)[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})] \quad (7)$$

where β_V^0, β_V^1, and C_V are pressure derivative parameters of Pitzer's ion interaction parameters for the osmotic coefficient expression. The parameter b is given the value 1.2 $\mathrm{kg^{1/2}\cdot mol^{-1/2}}$ for all electrolytes, and α is 2.0 for all 1:1 and 2:1 electrolytes;[18,19] b and α are taken as temperature independent.

The coefficients of these equations along with the corresponding absolute relative deviation for ϕ_V at each temperature are given in Table 5. The values of the infinite dilution apparent molar volume, ϕ_V^0, of Na_2WO_4 in water and in aqueous PEG solutions have also been given in Table 5. From the infinite dilution partial molar volume of ions WO_4^{2-} and Na^+ reported by Millero[17] and using the additivity principle at infinite dilution, we can obtain the values 23.28 $\mathrm{cm^3\cdot mol^{-1}}$ for the infinite dilution apparent molar volume of Na_2WO_4 in pure water at T = 298.15 K, which does not agree well with the value (28.620 $\mathrm{cm^3\cdot mol^{-1}}$) obtained in this work. At infinite dilution, each ion is surrounded only by the solvent molecules and being infinitely distant from other ions. It follows, therefore, that the infinite dilution apparent molar volume is unaffected by ion + ion interaction, and it is a measure only of the ion + solvent interaction.[17,20] In Figure 5, the concentration dependence of ϕ_V of Na_2WO_4 in pure water has been given at T = (288.15,

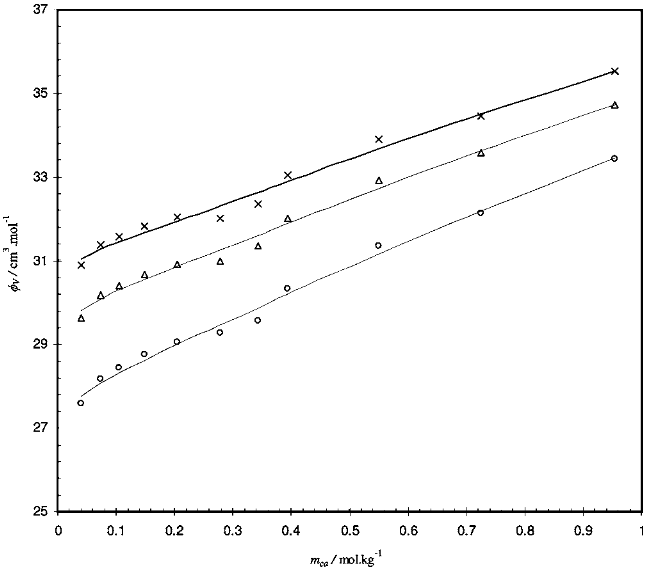

Figure 5. Plot of the apparent molar volume of Na_2WO_4, ϕ_V, in water against molality of the salt, m_{ca}, at different temperatures: ○, $T = 288.15$ K; △, $T = 298.15$ K; ×, $T = 308.15$ K; —, calculated by eq 6.

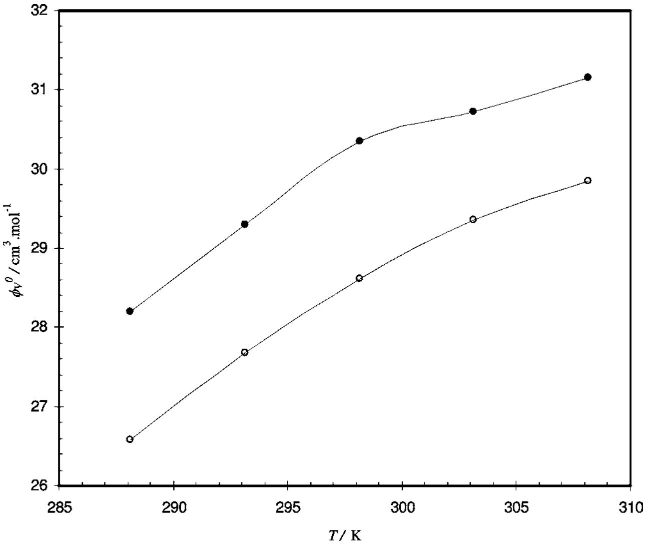

Figure 6. Plot of infinite dilution apparent molar volume of Na_2WO_4, ϕ_V^0, against temperature, T: ○, in water; ●, in aqueous solution of mass fraction 0.02 PEG.

298.15, and 308.15) K. From Figure 5, it can be seen that the apparent molar volumes of Na_2WO_4 in water (and also in aqueous PEG solution) increase with an increase in the salt molality. By increasing the salt concentration, the ion−ion interaction increases and the positive initial slope of ϕ_V against salt concentration is attributed to these interactions. In the electrolyte solutions, the solute−solute interactions are characterized by positive slopes of ϕ_V versus concentration plots.[17] This is attributed to the phenomenon, described in terms of destructive overlap of cospheres,[21,22] resulting in a net decrease of solvation, thereby increasing the solute volume. The effect of temperature on the ϕ_V^0 of Na_2WO_4 in water and in aqueous PEG solutions has been shown in Figure 6. As can be seen from Figure 6, the infinite dilution apparent molar volume of Na_2WO_4 increases with increasing temperature. The infinite dilution apparent molar volume of ions can be expressed as the sum of two contributions[23]

$$\phi_V^0(\text{ion}) = \phi_V^0(\text{int}) + \phi_V^0(\text{elect}) \tag{8}$$

where $\phi_V^0(\text{int})$ is the intrinsic (related to the size of the ions) apparent molar volume and $\phi_V^0(\text{elect})$ is the electrostriction apparent molar volume related to ion−solvent interactions (i.e., the decrease in volume due to hydration). The term $[(\partial\phi_V^0(\text{int}))/\partial T]$ contributes negligibly to the overall temperature dependence of $\phi_V^0(\text{ion})$, and therefore an increase in the ϕ_V^0 by increasing temperature occurs with a loss of hydration.

Figure 6 shows a positive transfer volume of Na_2WO_4 from an aqueous solution to an aqueous PEG solution. This indicates that the sodium tungstate ions in aqueous PEG solutions are larger than those in aqueous solutions. The larger values of ϕ_V for Na_2WO_4 in aqueous PEG solutions are attributed to the three factors: (1) The strong attractive interactions due to the hydrogen-bond formations between PEG and water molecules

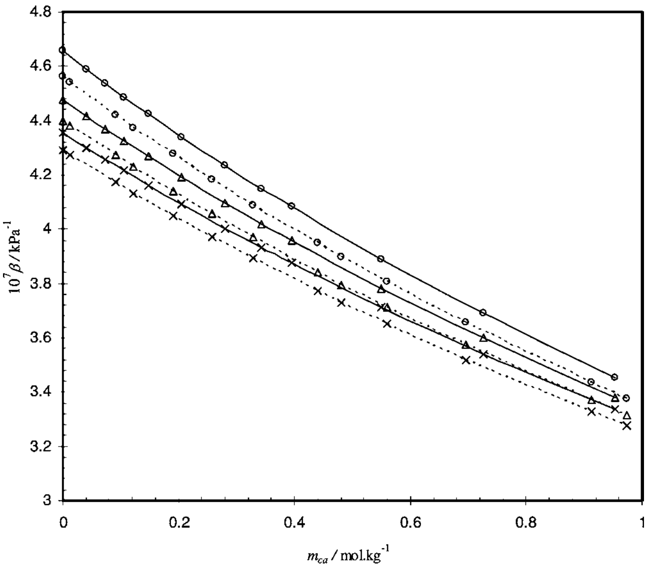

Figure 7. Plot of isentropic compressibility, β, of solutions of Na_2WO_4 in pure water (solid line) and in aqueous solution of mass fraction 0.02 PEG (dotted line) against molality of the salt, m_{ca}, at different temperatures: ○, $T = 288.15$ K; △, $T = 298.15$ K; ×, $T = 308.15$ K.

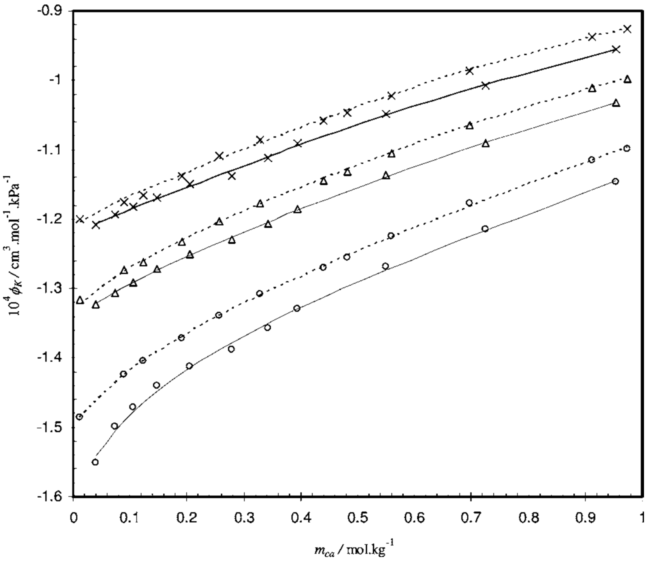

Figure 8. Plot of apparent molar isentropic compressibility, ϕ_K, of Na_2WO_4 in pure water (solid line) and in aqueous solution of mass fraction 0.02 PEG (dotted line) against molality of the salt, m_{ca}, at different temperatures: ○, $T = 288.15$ K; △, $T = 298.15$ K; ×, $T = 308.15$ K; —, calculated by eq 11.

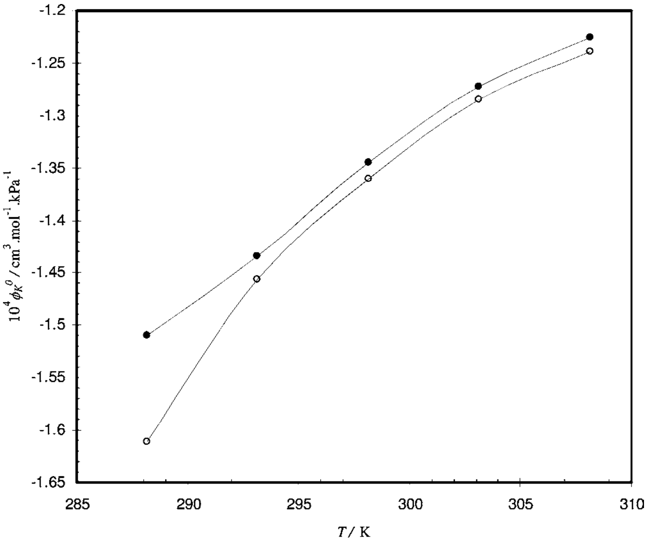

Figure 9. Plot of infinite dilution apparent molar isentropic compressibility of Na_2WO_4, ϕ_K^0, against temperature, T: ○, in water; ●, in aqueous solution of mass fraction 0.02 PEG.

induce the dehydration of ions and therefore increase the ϕ_V. (2) Repulsive interactions between the anion and the anionic-like polyether group of PEG increase the apparent molar volume of sodium tungstate. (3) A particular complication, which occurs in many nonaqueous solvents (PEG + water) whose relative permittivities are significantly lower than that of water, is the effect of ion pairing. The ion-pairing effect arises because in general the sum of the molar volume values of free (dissociated) ions is smaller than that of their ion pair due to the greater electrostrictive effect of the ions on the solvent molecules.

On the basis of the speed of sound and density values, the isentropic compressibility, β (kPa^{-1}), values were calculated for the investigated mixtures from the Laplace−Newton equation[23]

$$\beta = d^{-1}u^{-2} \tag{9}$$

where u (m·s^{-1}) is the speed of sound. In Figure 7, the salt concentration dependence of the isentropic compressibilities is shown for sodium tungstate in pure water and in aqueous PEG solutions at T = (288.15, 298.15, and 308.15) K. From Figure 7, it can be seen that the values of β decrease by increasing salt concentration and temperature. In fact, for low electrolyte concentration, the compressibility of an aqueous electrolyte solution is mainly due to the effect of pressure on the bulk (unhydrated) water molecules. As the concentration of the electrolyte increases and a large portion of the water molecules are electrostricted, the amount of bulk water decreases causing the compressibility to decrease. Also, in the temperature range investigated in this work, the compressibility of water decreases with temperature, and therefore the values of β of the investigated electrolyte solutions also decrease with temperature. In fact, it has been shown that[24] the compressibility of water decreases with temperature to a minimum β value near 337.15 K and then increases gradually. It has been postulated[25] that this is due to the existence of two structural types of water aggregates at a given temperature. The $(\partial\beta/\partial T)$ term for the structured form is negative, while it is positive for the less-structured form. Also, Figure 7 shows that the concentration dependence of β becomes greater as temperature decreases. This is because at higher temperatures ion−solvent interactions are weakened, and therefore the number of water molecules affected by the ions decrease.[23] Figure 7 shows that at each temperature at a constant salt concentration the values of β decrease as the concentration of PEG increases. This effect can be attributed to the strong attractive interactions due to the hydration of polymer segments and therefore decreasing the amount of bulk water and also incorporation of ionic species into the PEG chain.

Similar to the apparent molar volume, the apparent molar isentropic compressibility of the Na_2WO_4, ϕ_K, in water and in aqueous PEG solutions was calculated from the density and sound velocity experimental data according to the following equation[23]

$$\phi_K = \frac{1000(\beta d_0 - \beta_0 d)}{m_{ca} d d_0} + \frac{M_{ca}\beta}{d} \tag{10}$$

where β and β_0 are the isentropic compressibility of the solution and solvent, respectively. For systems containing both sodium tungstate and PEG, PEG + water is considered as the solvent. In Figure 8, the salt concentration dependence of the ϕ_K is shown for sodium tungstate in pure water and in aqueous PEG solutions at T = (288.15, 298.15, and 308.15) K. The apparent molar isentropic compressibility can also be expressed by the following Pitzer equation[18]

Table 6. Experimental Refractive Index, n, of Na_2WO_4 in Pure Water and in Aqueous Solution of Mass Fraction 0.02 and 0.04 PEG Along with Those for Solutions of PEG in Pure Water and in Aqueous Solution of Mass Fraction 0.02 and 0.04 $Na_2WO_4 \cdot 2H_2O$ at T = 308.15 K

Na_2WO_4 in pure water		Na_2WO_4 in aqueous solution of PEG (0.02)		Na_2WO_4 in aqueous solution of PEG (0.04)		PEG in pure water		PEG in aqueous solution of $Na_2WO_4 \cdot 2H_2O$ (0.02)		PEG in aqueous solution of $Na_2WO_4 \cdot 2H_2O$ (0.04)	
w_{ca}	n	w_{ca}	n	w_{ca}	n	w_p	n	w_p	n	w_p	n
0.0038	1.3315	0.0045	1.3346	0.0043	1.3370	0.0049	1.3316	0.0049	1.3342	0.0049	1.3364
0.0088	1.3321	0.0095	1.3352	0.0088	1.3375	0.0099	1.3323	0.0100	1.3348	0.0099	1.3370
0.0130	1.3326	0.0134	1.3356	0.0134	1.3380	0.0149	1.3330	0.0148	1.3356	0.0142	1.3376
0.0160	1.3330	0.0167	1.3359	0.0175	1.3385	0.0197	1.3337	0.0193	1.3362	0.0202	1.3384
0.0259	1.3342	0.0267	1.3370	0.0264	1.3395	0.0298	1.3351	0.0303	1.3376	0.0299	1.3397
0.0350	1.3353	0.035	1.3379	0.0340	1.3404	0.0402	1.3366	0.0390	1.3387	0.0401	1.3410
0.0438	1.3363	0.0437	1.3389	0.0442	1.3416	0.0496	1.3380	0.0495	1.3401	0.0481	1.3422
0.0530	1.3375	0.0488	1.3394	0.0510	1.3424	0.0598	1.3394	0.0586	1.3414	0.0599	1.3438
0.0626	1.3385	0.0607	1.3408	0.0616	1.3436	0.0705	1.3410	0.0685	1.3428	0.0698	1.3450
0.0679	1.3391	0.0701	1.3420	0.0717	1.3448	0.0805	1.3425	0.0810	1.3446	0.0702	1.3450
0.0696	1.3393	0.0783	1.3430	0.0792	1.3457	0.0906	1.3438	0.0876	1.3455	0.0896	1.3476
0.0885	1.3415	0.0785	1.3430	0.0865	1.3465	0.0984	1.3448	0.0980	1.3470	0.0999	1.3490
0.0973	1.3426	0.0958	1.3451	0.0975	1.3477	0.1103	1.3465	0.1063	1.3481	0.1101	1.3505
0.1103	1.3443	0.1077	1.3467	0.1142	1.3494	0.1284	1.3491	0.1181	1.3496	0.1306	1.3536
						0.1474	1.3518				

$$\phi_K = \phi_K^0 - \nu|z_c z_a|\left(\frac{A_K}{2b}\right)\ln(1 + bI^{1/2}) - 2RT\nu_c\nu_a[B_K m_{ca} + \nu_c z_c C_K m_{ca}^2] \quad (11)$$

where B_K is binary interaction parameter which is defined as

$$B_K = \beta_K^0 + \beta_K^1\left(\frac{2}{\alpha^2 I}\right)[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})] \quad (12)$$

The values of b and α in eqs 11 and 12 are same as those in eqs 6 and 7. The results of fitting ϕ_K values to eq 11 are also given in Table 5. The values of the infinite dilution apparent molar isentropic compressibility, ϕ_K^0, of Na_2WO_4 in the investigated solvents at different temperatures are also given in Table 5 and shown in Figure 9. The values of the apparent molar isentropic compressibility of Na_2WO_4 are negative and increase by increasing temperature, concentration of electrolyte, and polymer. The negative values of the apparent molar isentropic compressibility (loss of compressibility of the medium) imply that the water molecules around the solute are less compressible than the water molecules in the bulk solutions. In fact, the negative values of ϕ_K of the investigated solutions are attributed to the strong attractive interactions due to the hydration of ions at low temperatures. By increasing temperature, ion−water interactions are weakened, and therefore some water molecules are released into the bulk, thereby making the medium more compressible. By increasing the salt concentration, the ion−ion interaction increases, resulting in a net decrease of solvation, thereby increasing the amount of bulk water and making the medium more compressible. In fact, on ion association, some water molecules associated with the ions are released into the bulk, thereby making the medium more compressible. The hydrogen-bond interactions between PEG and water molecules induce the dehydration of ions and therefore increase bulk water molecules. Furthermore, as mentioned above, in aqueous PEG solutions because of the ion-pairing effect, the number of water molecules affected by the ions decreases.

Refractive Index Measurements. The results of refractive index measurements for solutions of the Na_2WO_4 in pure water and in aqueous PEG solutions along with those for solutions of the PEG in pure water and in aqueous Na_2WO_4 solutions at $T = 308.15$ K are collected in Table 6 and are shown in Figure 10.

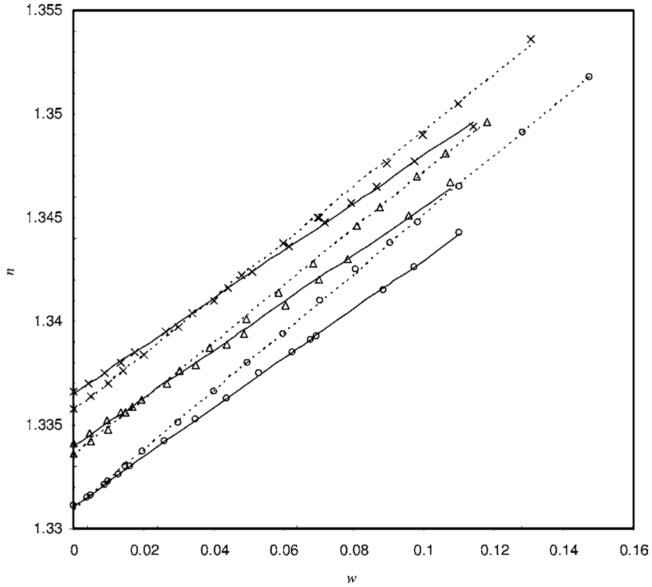

Figure 10. Plot of refractive index, n, of solutions of Na_2WO_4 in aqueous solutions of PEG (solid line) along with those for solutions of PEG in aqueous solutions of Na_2WO_4 (dotted line) against mass fraction, w, at $T = 308.15$ K: ○, in pure water; △, in aqueous solution of mass fraction 0.02 PEG or $Na_2WO_4 \cdot 2H_2O$; ×, in aqueous solution of mass fraction 0.04 PEG or $Na_2WO_4 \cdot 2H_2O$.

Conclusions

Precise water activity, density, speed of sound, and refractive index measurements have been carried out on sodium tungstate in aqueous solutions of PEG. The results show that the vapor pressure depression for a ternary aqueous PEG + Na_2WO_4 system is more than the sum of those for the corresponding binary solutions. The apparent molar volume of Na_2WO_4 in aqueous PEG solutions is larger than those in pure water and increases by increasing both salt concentration and temperature. The values of the isentropic compressibility of solutions of Na_2WO_4 in aqueous PEG solutions are smaller than those in pure water and decrease by increasing both salt concentration and temperature. The apparent molar isentropic compressibility of sodium tungstete in both binary and ternary solutions has negative values and increases by increasing temperature, concentration of electrolyte, and concentration of polymer.

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