Measurement and Correlation of Densities, Ultrasonic Velocities, and Compressibilities for Binary Aqueous Poly(ethylene glycol), Disodium Succinate, or Sodium Formate and Ternary Aqueous Poly(ethylene glycol) Systems Containing Disodium Succinate or Sodium Formate at T = (298.15, 308.15, and 318.15) K

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Densities and ultrasonic velocities for binary aqueous solutions of poly(ethylene glycol) 6000, disodium succinate, or sodium formate and ternary aqueous solutions of PEG_{6000} containing disodium succinate or sodium formate have been measured at T = (298.15, 308.15, and 318.15) K. Using the obtained density and ultrasonic velocity data, we also calculated the adiabatic compressibility values for the aforementioned binary systems and fit them to a polynomial equation. Apparent molal volume data calculated from the density data for binary systems were fit to suitable equations to obtain limiting apparent molal volumes. The data for the density, ultrasonic velocity, and adiabatic compressibility for ternary PEG_{6000} + disodium succinate + water and PEG_{6000} + sodium formate + water were correlated with a semiempirical equation.

Introduction

In recent years, the measurement, correlation, and prediction of the thermodynamic properties of aqueous poly(ethylene glycol) (PEG) solutions have been active areas of research. These polymer solutions form two-phase systems with different salts and are extensively employed in biotechnology for chemical partitioning.[1] Although there is a limited amount of information with respect to the volumetric properties of PEG + salt + water systems,[2−4] ultrasonic studies have not been carried out on these aqueous mixtures. In a continuation of our research work on the thermodynamic properties of PEG + salt + water systems, we report here the results of accurate density and ultrasonic velocity measurements for aqueous PEG_{6000} with disodium succinate and sodium formate. As pointed out by Ananthapadmanabhan,[5] aqueous solutions of both of these organic salts form two-phase systems with PEG; therefore, these two-phase systems may be used for the separation of biomolecules. However, for the correlation of these thermodynamic properties for the above ternary systems, we usually need to know the same properties for constituting binary solutions. Although there are many ultrasonic velocity and compressibility data for binary aqueous salt solutions, a limited amount of corresponding data can be found for aqueous polymer solutions in the literature. In the case of binary aqueous disodium succinate or sodium formate solutions, only some volumetric studies have been carried out on aqueous formate solutions.[6] For aqueous PEG solutions, density data have been reported previously;[2] however, ultrasonic velocity or compressibility data have been given only for lower molecular masses of PEG.[7] Therefore, in this work, the density and ultrasonic velocity data were also measured for binary aqueous polymer and salt solutions. From the density data, the apparent molal volumes were calculated for these binary systems, and the results were fit to suitable equations from which the values for limiting apparent molal volume are obtained. Also, from the measured ultrasonic velocity data for the aforementioned binary solutions the corresponding adiabatic compressibility data were calculated, and both the ultrasonic velocity and adiabatic compressibility data were correlated with a polynomial equation. Finally, the applicability of the semiempirical equation proposed in our previous work[2] was examined with respect to the correlation of the density, ultrasonic velocity, and adiabatic compressibility of the ternary PEG_{6000} + disodium succinate + water and PEG_{6000} + sodium formate + water systems.

Experimental Section

Materials. PEG_{6000} was obtained from Merck. The number-average molar mass of the polymer was previously determined[8] to be 5886 g·mol^{-1}. Sodium succinate and sodium formate with a minimum purity of 99% by mass were obtained from Merck. The polymer and salt were used without further purification, and double-distilled deionized water was used.

Apparatus and Procedure. The experimental apparatus employed is essentially similar to the one used previously.[9] The solutions were prepared by mass using an analytical balance (Shimatzu 321-34553, Shimatzu Co., Japan) with a precision of $\pm 1 \times 10^{-4}$ g. The ultrasonic velocity and density of mixtures were measured at different temperatures with a digital vibrating-tube analyzer (Anton paar DSA 5000, Austria) with proportional temperature controller that kept the samples at the working temperature with a precision of 0.001 K. The apparatus was calibrated at each temperature with double-distilled deionized water and dry air. For pure water, the values for the density (997.044, 994.031, and 990.214 kg·m^{-3}) and ultrasonic velocity (1496.92, 1520.37, and 1537.05 m·s^{-1}) were obtained at T = (298.15, 308.15, and 318.15) K. The apparatus was also tested with the density of aqueous NaCl of known molality using the data given by Pitzer et al.[10]

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Table 1. Densities ρ and Sound Velocities u for the Aqueous Sodium Succinate System at T = (298.15 to 318.15) K

	T/K					
	298.15	308.15	318.15	298.15	308.15	318.15
m_s/mol·kg^{-1}		ρ/kg·m^{-3}			u/m·s^{-1}	
0.0188	999.052	996.011	992.179	1500.17	1523.19	1539.88
0.0239	999.583	996.544	992.703	1501.06	1524.08	1540.57
0.0336	1000.611	997.550	993.703	1502.72	1525.61	1542.06
0.0373	1000.999	997.934	994.083	1503.37	1526.24	1542.66
0.0452	1001.818	998.747	994.887	1504.86	1527.45	1543.96
0.0489	1002.201	999.130	995.266	1505.36	1528.05	1544.56
0.0546	1002.791	999.711	995.841	1506.32	1528.94	1545.35
0.0593	1003.280	1000.189	996.315	1507.12	1529.68	1546.56
0.0680	1004.182	1001.084	997.197	1508.96	1531.70	1547.51
0.0763	1005.049	1001.939	998.046	1510.55	1532.43	1548.55
0.0864	1006.090	1002.963	999.064	1511.65	1533.94	1549.94
0.0935	1006.823	1003.687	999.785	1512.84	1535.12	1551.21
0.1221	1009.741	1006.557	1002.635	1517.51	1539.46	1555.21
0.2589	1023.441	1020.074	1016.029	1539.79	1560.34	1575.12
0.3292	1030.316	1026.847	1022.730	1550.97	1570.83	1585.21
0.4019	1037.296	1033.746	1029.564	1562.44	1581.56	1595.83
0.4364	1040.568	1036.978	1032.771	1567.81	1586.60	1600.65
0.5252	1048.893	1045.201	1040.919	1581.96	1599.55	1611.98
0.6535	1060.587	1056.741	1052.373	1601.19	1617.79	1629.25
0.7422	1068.470	1064.553	1060.126	1615.07	1630.47	1640.99
0.9099	1083.028	1078.936	1074.414	1639.80	1653.28	1662.74
1.1680	1104.444	1100.126	1095.451	1675.66	1687.50	1694.94
1.4298	1125.040	1120.371	1115.738	1711.25	1720.94	1726.24
1.7483	1148.680	1143.920	1138.952	1752.42	1758.97	1762.50

Table 2. Densities ρ and Sound Velocities u for Aqueous Sodium Formate System at T = (298.15 to 318.15) K

	T/K					
	298.15	308.15	318.15	298.15	308.15	318.15
m_s/mol·kg^{-1}		ρ/kg·m^{-3}			u/m·s^{-1}	
0.0263	998.164	995.129	991.308	1498.60	1521.69	1538.33
0.0331	998.451	995.412	991.587	1499.09	1522.13	1538.80
0.0437	998.896	995.851	992.021	1499.69	1522.71	1539.28
0.0497	999.147	996.099	992.265	1500.09	1523.10	1539.60
0.0570	999.452	996.397	992.559	1500.58	1523.48	1539.95
0.0682	999.921	996.863	993.016	1501.23	1524.17	1540.64
0.0747	1000.198	997.131	993.282	1501.62	1524.55	1540.95
0.0811	1000.463	997.398	993.545	1502.06	1524.92	1541.30
0.0909	1000.875	997.799	993.945	1502.65	1525.46	1541.94
0.0975	1001.153	998.074	994.215	1503.04	1525.88	1542.38
0.1428	1003.035	999.916	996.044	1505.88	1528.46	1544.54
0.2955	1009.333	1006.106	1002.183	1515.09	1536.86	1552.53
0.4697	1016.336	1012.980	1008.947	1525.23	1546.22	1561.20
0.6887	1024.987	1021.489	1017.376	1537.74	1557.73	1572.60
0.8366	1030.689	1027.111	1022.930	1546.05	1565.30	1579.03
0.9653	1035.608	1031.930	1027.664	1553.09	1571.77	1584.91
1.1394	1042.153	1038.379	1034.044	1562.43	1580.37	1593.25
1.2332	1045.633	1041.809	1037.432	1567.47	1584.96	1597.27
1.4958	1055.235	1051.273	1046.787	1581.19	1597.52	1609.20
2.1876	1079.463	1075.153	1070.431	1615.33	1628.82	1638.32
2.7834	1099.170	1094.605	1089.573	1642.77	1653.90	1661.42
3.4585	1120.322	1115.481	1110.109	1671.67	1680.37	1685.66
4.2011	1142.288	1137.225	1131.783	1701.06	1707.21	1709.88
4.9659	1163.546	1158.260	1152.832	1729.12	1732.73	1733.38
6.5612	1204.090	1198.397	1192.369	1779.39	1778.71	1775.66
7.7367	1230.992	1225.045	1218.867	1811.10	1807.59	1802.05
8.5511	1248.266	1242.148	1235.765	1830.55	1825.29	1818.29
10.0471	1277.623	1271.224	1264.599	1862.10	1854.07	1844.61

The accuracy of the instrument is ±0.003kg·m^{-3} for the density and 0.1 m·s^{-1} for the ultrasonic velocity.

Results and Discussion

Volumetric Results for Binary Aqueous Salt and Polymer Solutions. Experimental data for the density of various aqueous disodium succinate or sodium formate and aqueous PEG solutions determined at T = (298.15, 308.15, and 318.15) K are given in Tables 1 to 3. To correlate the density data for binary aqueous salt solutions, we calcu-

Table 3. Densities ρ and Sound Velocities u for Aqueous PEG$_{6000}$ System at T = (298.15 to 318.15) K

	T/K					
	298.15	308.15	318.15	298.15	308.15	318.15
m_p/mol·kg^{-1}		ρ/kg·m^{-3}			u/m·s^{-1}	
0.0036	1000.477	997.353	993.436	1508.15	1529.64	1544.91
0.0186	1013.575	1009.922	1005.571	1552.35	1566.88	1576.24
0.0408	1030.120	1025.751	1020.756	1609.22	1614.19	1615.01
0.0557	1039.721	1034.919	1029.526	1641.77	1641.09	1636.80
0.0881	1057.243	1051.547	1045.141	1697.87	1686.68	1673.22

Table 4. Infinite Dilution Apparent Molal Volume, $\phi^0_{v,s}$, and b_v Values for Aqueous Salt Solutions at T = (298.15 to 318.15) K[a]

salt	$10^6\phi^0_{v,s}$/m^3·mol^{-1}	$10^6 b_v$/m^3·kg·mol^{-2}
	T/K = 298.15	
sodium succinate	53.84 (53.75)*	−0.937 (2.309)
sodium formate	25.14 (25.08)	0.035 (1.118)
	T/K= 308.15	
sodium succinate	54.84 (54.95)	−1.740 (−1.850)
sodium formate	25.73 (25.85)	−0.058 (−1.203)
	T/K = 318.15	
sodium succinate	55.39 (55.56)	−2.579 (−2.946)
sodium formate	25.99 (25.90)	−0.118 (2.100)

[a] Values given in parentheses were obtained using data for the dilute region (m_s < 0.1 mol·kg^{-1}).

Table 5. Infinite Dilution Apparent Molal Volume of Polymer and Monomer ($\phi^0_{v,p}$, $\phi^0_{v,m}$) and h_v Values for Aqueous PEG$_{6000}$ Solutions at T = (298.15 to 318.15) K

$10^6\phi^0_{v,p}$/m^3·mol^{-1}	$10^6\phi^0_{v,m}$/m^3·mol^{-1}	$10^6 h_v$/m^3·kg·mol^{-1}
	T/K = 298.15	
4929.22	37.01	−116.514
	36.92[a]	
	37.0[b]	
	T/K= 308.15	
4976.33	37.36	−32.046
	37.35[a]	
	T/K = 318.15	
5018.20	37.67	135.372
	37.45[a]	

[a] Obtained for aqueous PEG$_{6000}$ in the previous work.[3] [b] Given by Zana.[13]

lated the apparent molal volumes of salts, $\phi_{v,s}$, at each molality, m_s, from the following relation

$$\phi_v = \left[\frac{M}{\rho} + \frac{1}{m}\left(\frac{1}{\rho} - \frac{1}{\rho_0}\right)\right] \tag{1}$$

and the results were fit to the Redlich−Mayer equation[11]

$$\phi_{v,s} = \phi^0_{v,s} + S_v\sqrt{m_s} + b_v m_s \tag{2a}$$

where b_v is an empirical parameter and S_v is defined as

$$S_v = k\left[\frac{1}{2}\left(\sum_i \nu_i z_i^2\right)\right]^{3/2} \tag{2b}$$

In these equations, ρ and ρ_0 are the density of the solution and that of pure water in kg·m^{-3}, respectively. ϕ_v is the apparent molal volume of the solute (polymer, $\phi_{v,p}$, or salt, $\phi_{v,s}$) in m^3·mol^{-1}, M is the molar mass of solute in kg·mol^{-1}, and $\phi^0_{v,s}$ and m_s are the limiting apparent molal volume and the molality of the salt, respectively. ν_i and z_i are the stoichiometric number and absolute charge of ion i, respectively. For the limiting theoretical slope k, the values

Table 6. Correlation Parameters of Equation 5 and Average Relative Deviations σ for Aqueous Sodium Succinate System at T = (298.15 to 318.15) K

	A	B	C	D	$10^2\sigma$
			T/K = 298.15		
u/m·s^{-1}	1.784×10^2	−28.945	13.777	−7.837	0.01
β/Pa^{-1}	-1.5541×10^{-10}	2.2086×10^{-11}	3.1036×10^{-11}	-9.4709×10^{-12}	0.02
			T/K = 308.15		
u/m·s^{-1}	1.617×10^2	−14.495	2.046	−4.179	0.01
β/Pa^{-1}	-1.3897×10^{-10}	1.0471×10^{-11}	3.5933×10^{-11}	-1.0827×10^{-11}	0.01
			T/K = 318.15		
u/m·s^{-1}	1.562×10^2	−14.253	−5.220	0.323	0.01
β/Pa^{-1}	-1.3261×10^{-10}	1.2621×10^{-11}	3.2888×10^{-11}	-1.0567×10^{-11}	0.02

Table 7. Correlation Parameters of Equation 5 and Average Relative Deviations σ for the Aqueous Sodium Formate System at T = (298.15 to 318.15) K

	A	B	C	D	$10^2\sigma$
			T/K = 298.15		
u/m·s^{-1}	62.712	−1.607	−3.422	0.411	0.01
β/Pa^{-1}	-6.0660×10^{-11}	1.0019×10^{-11}	2.5006×10^{-12}	-5.7517×10^{-13}	0.03
			T/K = 308.15		
u/m·s^{-1}	56.725	−0.431	−3.622	0.447	0.00_4
β/Pa^{-1}	-5.4145×10^{-11}	7.7830×10^{-12}	2.6668×10^{-12}	-5.6124×10^{-13}	0.04
			T/K = 318.15		
u/m·s^{-1}	53.919	−1.357	−3.225	0.421	0.01
β/Pa^{-1}	-5.0823×10^{-11}	7.5525×10^{-12}	2.3240×10^{-12}	-4.9908×10^{-13}	0.04

Table 8. Correlation Parameters of Equation 7 and Average Relative Deviations σ for the Aqueous PEG$_{6000}$ System at T = (298.15 to 318.15) K

	A	B	C	$10^2\sigma$
		T/K = 298.15		
u/m·s^{-1}	3.175×10^3	-1.058×10^4	4.854×10^3	0.00_2
β/Pa^{-1}	-2.3073×10^{-9}	1.4568×10^{-8}	-4.2834×10^{-8}	0.01
		T/K= 308.15		
u/m·s^{-1}	2.666×10^3	-9.140×10^3	3.442×10^3	0.00_4
β/Pa^{-1}	-1.9160×10^{-9}	1.1543×10^{-8}	-3.1785×10^{-8}	0.01
		T/K = 318.15		
u/m·s^{-1}	2.271×10^3	-9.294×10^3	1.205×10^4	0.00_4
β/Pa^{-1}	-1.6365×10^{-9}	1.0095×10^{-8}	-2.9084×10^{-8}	0.01

recommended by Millero[6] were used. The limiting apparent molal volume of disodium succinate and sodium formate in water solutions, $\phi^0_{v,s}$ (equal to the partial molal volume at infinite dilution, $V_2°$) obtained from the fitting of apparent molal volume data for the aqueous salt solutions, along with the b_v values are given in Table 4. The limiting apparent molal volume for disodium succinate has not been reported previously. However, for sodium formate the $\phi^0_{v,s}$ value at T = 298.15 K may be estimated to be 25.06×10^{-6} m^3·mol^{-1} (by applying the additivity rule and using the values of the ionic partial molal volume at infinite dilution reported by Millero[6] for sodium and formate ions) and may be compared with our result, 25.08×10^{-6} m^3·mol^{-1}.

Similarly, for aqueous binary PEG solutions the apparent molal volumes, $\phi_{v,p}$, were calculated from eq 1, and the results were fit to the following equation[12]

$$\phi_{v,p} = \phi^0_{v,p} + h_v m_p \tag{3}$$

where m_p is the molality of the polymer. The obtained infinite dilution apparent molal volumes of polymer and monomer ($\phi^0_{v,p}$ and $\phi^0_{v,m}$) along with h_v values at working temperatures are given in Table 5. The values obtained for $\phi^0_{v,m}$ are comparable with those reported previously[2] as shown in Table 5. Also, at T = 298.15 K our infinite dilution apparent molal volume for the monomer is in good agreement with the value of 37×10^{-6} m^3·mol^{-1} given by Zana.[13]

Ultrasonic Velocity and Compressibility Results for Binary Aqueous Salt and Polymer Solutions. The experimental ultrasonic velocity values u for binary aqueous salt solutions reported at working temperatures are collected in Tables 1 and 2. Using the density and ultrasonic velocity values for aqueous salt solutions, we calculated the adiabatic compressibility values β with the help of the Laplace equation

$$\beta = \frac{1}{u^2\rho} \tag{4}$$

The obtained adiabatic compressibility values and the experimental ultrasonic velocity data of Tables 1 and 2 were correlated with the following equation

$$F_{sw} = F_w + Am_s + Bm_s^{3/2} + Cm_s^{2} + Dm_s^{5/2} \tag{5}$$

where F_{sw} is u or β for aqueous salt solutions and F_w is the corresponding value for pure water. The results of fitting the ultrasonic velocity and compressibility values for aqueous disodium succinate or sodium formate solutions together with the average relative deviations σ are presented in Tables 6 and 7. Average relative deviations between the calculated, F_i^{calcd}, and experimental, F_i^{exptl}, values have been estimated by using

$$\sigma = \frac{1}{N}\left[\sum_{i=1}^{N}\frac{|F_i^{calcd} - F_i^{exptl}|}{F_i^{exptl}}\right] \tag{6}$$

Table 9. Infinite Dilution Adiabatic Apparent Molal Compressibilities of Polymer and Monomer ($\phi^0_{k,p}$, $\phi^0_{k,m}$) and h_k Values for Aqueous PEG$_{6000}$ Solutions at T = (298.15 to 318.15) K

$10^{15}\phi^0_{k,p}$/ m^3·mol^{-1}·Pa^{-1}	$10^{15}\phi^0_{k,m}$/ m^3·mol^{-1}·Pa^{-1}	$10^{15}h_k$/ m^3·kg·mol^{-2}·Pa^{-1}
	T/K = 298.15	
−119.38	−0.90	4271.770
	−0.75[a]	
	T/K= 308.15	
237.74	1.78	3025.131
	T/K = 318.15	
493.90	3.71	2723.139
	3.75[a]	

[a] From reference Harada et al.[14]

Table 10. Densities ρ and Sound Velocities u for the Aqueous PEG_{6000}–Sodium Succinate System at T = (298.15 to 318.15) K

		T/K					
		298.15	308.15	318.15	298.15	308.15	318.15
m_p/mol·kg^{-1}	m_s/mol·kg^{-1}		ρ/kg·m^{-3}			u/m·s^{-1}	
0.0022	0.7921	1074.067	1070.028	1065.515	1627.32	1641.75	1651.17
0.0064	0.7288	1070.857	1066.764	1062.160	1628.62	1641.71	1649.80
0.125	0.6916	1070.892	1066.675	1061.960	1637.69	1648.45	1654.43
0.0173	0.7052	1074.471	1070.112	1065.279	1650.41	1658.94	1662.92
0.0332	0.5402	1069.275	1064.609	1059.479	1662.31	1665.91	1665.36
0.0409	0.3293	1056.920	1052.221	1047.021	1651.97	1654.45	1652.83
0.0463	0.4886	1071.678	1066.728	1061.265	1680.91	1680.03	1675.45
0.0829	0.3909	1080.395	1074.596	1068.385	1725.34	1713.92	1699.76
0.1015	0.3399	1083.885	1077.711	1071.225	1741.54	1725.63	1707.82

Table 11. Densities ρ and Sound Velocities u for the Aqueous PEG_{6000}–Sodium Formate System at T = (298.15 to 318.15) K

		T/K					
		298.15	308.15	318.15	298.15	308.15	318.15
m_p/mol·kg^{-1}	m_s/mol·kg^{-1}		ρ/kg·m^{-3}			u/m·s^{-1}	
0.0021	3.0622	1108.719	1103.981	1098.886	1659.28	1668.66	1674.09
0.0067	2.9567	1106.902	1102.202	1097.002	1664.05	1672.12	1675.90
0.0128	2.6354	1099.101	1094.336	1089.173	1662.60	1669.37	1672.13
0.0169	2.5645	1098.448	1093.575	1088.314	1667.64	1673.01	1674.59
0.0218	2.3062	1092.466	1087.637	1082.374	1666.62	1671.08	1671.80
0.0331	2.2243	1094.219	1089.163	1083.691	1683.25	1684.15	1681.40
0.0471	2.1152	1096.121	1090.755	1085.031	1701.41	1698.10	1691.55
0.0575	1.1330	1073.541	1068.193	1062.543	1685.94	1682.00	1674.88
0.0642	1.9323	1096.939	1091.301	1085.244	1719.05	1711.28	1700.60
0.0841	2.1382	1107.334	1101.176	1094.811	1745.26	1732.11	1716.51

Table 12. Correlation Parameters of Equation 10 and Relative Deviation σ for Densities of the Investigated Ternary Aqueous Systems at T = (298.15 to 318.15) K

A/kg^2·m^{-3}·mol^{-1}	$10^{-2}B$/kg^3·m^{-3}·mol^{-2}	$10^2\sigma$
PEG_{6000} + Sodium Succinate + H_2O		
T/K = 298.15		
−19.15416	−3.107229	0.03
T/K= 308.15		
−8.313644	−3.518496	0.04
T/K = 318.15		
−31.15459	−2.266047	0.03
PEG_{6000} + Sodium Formate + H_2O		
T/K = 298.15		
−16.79563	−1.233078	0.03
T/K= 308.15		
−14.51826	−1.238241	0.04
T/K = 318.15		
−14.89063	−1.185537	0.03

where N is the number of experimental points. On the basis of the reported average relative deviations, we conclude that eq 5 is a suitable equation for representing the experimental u and β values for the studied aqueous salt solutions at three temperatures.

Similarly, for the aqueous PEG solutions the experimental ultrasonic velocity data presented in Table 3 and the adiabatic compressibility values calculated from the eq 4 were satisfactorily correlated with eq 7:

$$F_{pw} = F_w + Am_p + Bm_p^{\ 2} + Cm_p^{\ 3} \tag{7}$$

In eq 7, F_{pw} is u or β for aqueous polymer solutions. The obtained correlative coefficients, together with the average relative deviations for the ultrasonic velocity and the adiabatic compressibility of aqueous PEG solutions at three temperatures, are collected in Table 8.

Table 13. Correlation Parameters of Equation 10 and Average Relative Deviations σ for the Ultrasonic Velocity and Compressibility of the Investigated Ternary Aqueous Systems at T = (298.15 to 318.15) K

	A	B	$10^2\sigma$
PEG_{6000} + Sodium Succinate + H_2O			
T/K = 298.15			
u/m·s^{-1}	1.001	-8.824×10^2	0.01
β/Pa^{-1}	7.1193×10^{-11}	5.5685×10^{-10}	0.32
T/K= 308.15			
u/m·s^{-1}	3.147	-8.142×10^2	0.01
β/Pa^{-1}	5.5228×10^{-11}	5.2003×10^{-10}	0.27
T/K = 318.15			
u/m·s^{-1}	−8.464	-7.305×10^2	0.02
β/Pa^{-1}	5.0973×10^{-11}	4.6992×10^{-10}	0.23
PEG_{6000} + Sodium Formate + H_2O			
T/K = 298.15			
u/m·s^{-1}	−9.329	-3.343×10^2	0.04
β/Pa^{-1}	4.8424×10^{-11}	2.1124×10^{-10}	0.46
T/K = 308.15			
u/m·s^{-1}	−7.967	-2.998×10^2	0.04
β/Pa^{-1}	3.8298×10^{-11}	1.9231×10^{-10}	0.38
T/K = 318.15			
u/m·s^{-1}	−14.020	-2.610×10^2	0.03
β/Pa^{-1}	3.4722×10^{-11}	1.7098×10^{-10}	0.31

For aqueous polymer solutions, the apparent adiabatic compressibility, ϕ_k, values may be calculated from the relation

$$\phi_k = \left[\frac{(\beta - \beta_0)}{m_p\rho_0} + \beta\phi_v\right] \tag{8}$$

where β_0 represents the adiabatic compressibility for pure water. At low PEG concentrations (m_p < 0.1 mol·kg^{-1}), there is linear relationship between ϕ_k and polymer concentration, so ϕ_k values at low concentrations were fit to the following equation:

$$\phi_{k,p} = \phi^0_{k,p} + h_k m_p \quad (9)$$

Equation 9 allows one to obtain the limiting apparent adiabatic compressibility ϕ^0_k for the polymer and the monomer ($\phi^0_{k,p}$ and $\phi^0_{k,m}$), as presented in Table 9. As shown in Table 9, the calculated $\phi^0_{k,m}$ values at T = (298.15 and 318.15) K for the monomer, CH_2CH_2O, are in very good agreement with those reported by Harada et al.[14] $\phi^0_{k,m}$ (CH_2CH_2O) increases from negative to positive values with an increase in temperature, which can be interpreted in terms of the release of structured water molecules from around the CH_2CH_2O group with increasing temperature as pointed out by Harada et al.[14]

Density, Ultrasonic Velocity, and Compressibility Results for Ternary Aqueous Polymer−Salt Systems. The experimental density and ultrasonic velocity data for ternary aqueous PEG + disodium succinate or PEG + sodium formate systems at working temperatures are collected in Tables 10 and 11. For the correlation of density, ultrasonic velocity, and compressibility data of ternary PEG_{6000} + disodium succinate + water and PEG_{6000} + disodium formate + water systems, we use the following general equation:

$$F_{mix} - F_w = (F_{sw} - F_w) + (F_{pw} - F_w) + A(m_s m_p)^{1/2} + B(m_s m_p) \quad (10)$$

Previously, it was shown[2,3] that eq 10 can be satisfactorily used to represent the density, activity of water, and refractive index of some aqueous polymer + salt solutions. To examine the reliability of this general equation in representing the ultrasonic velocity and compressibility as well as density data for the investigated aqueous polymer−salt solutions, we fit the obtained experimental data for these ternary systems to eq 10. As can be seen from the obtained average relative deviations reported in Tables 12 and 13, this general equation can be satisfactorily used to represent the ultrasonic velocity or compressibility as well as the density of the studied ternary systems.

Conclusions

Accurate densities and ultrasonic velocities for binary aqueous solutions of PEG_{6000}, disodium succinate, or sodium formate and ternary aqueous solutions of PEG_{6000} containing disodium succinate or sodium formate have been measured at T = (298.15, 308.15, and 318.15) K. A general semiempirical equation was satisfactorily applied to correlate ultrasonic velocity or adiabatic compressibility as well as density for the studied ternary systems.

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