Apparent Molar Volume and Compressibility of Tetrabutylphosphonium Bromide in Various Solvents

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The densities of tetra-*n*-butylphosphonium bromide in ethanol, 1-propanol, 1-butanol, acetone, and acetonitrile at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 323.15) K and sound velocities at 298.15 K have been measured. From these data, apparent molar volumes V_Φ at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 323.15) K and the apparent molar isentropic compressibility $K_{S,\Phi}$ at 298.15 K of tetrabutylphosphonium bromide in nonaqueous solvents have been determined.

Introduction

This work is a continuation of our systematic study of the limiting partial molar volumes of the electrolytes in nonaqueous solvents. In previous papers from our laboratory, the volumetric data obtained for transition metal salts,[1–4] as well as tetraalkylammonium salts, have been reported.[5] Hence, it seems quite surprising that such data concerning alkylphosphonium salts are available for very few solvents only, especially since for 20 years tetrabutylphosphonium chloride and bromide have become available in multiton scales. The analogous tetraalkylammonium salts have been deeply investigated and availed in many branches of chemistry. The phosphonium ions have displaced sometimes the ammonium ions with improvement of features of study systems.[6,7]

In this paper, experimental data at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 323.15) K for density and data at 298.15 K for sound velocity for tetrabutylphosphonium bromide in acetonitrile, ethanol, 1-propanol, 1-butanol, and acetone solutions are reported. The apparent molar volume, V_Φ, adiabatic compressibility, κ_S, and apparent molar adiabatic compressibility, $K_{S,\Phi}$, are obtained from the measured properties.

Experimental Section

Tetrabutylphosphonium bromide (Fluka, purum, > 98.0 %) was dried under reduced pressure at 333 K. The purity and the source of the solvents used are summarized in Table 1, along with their measured and literature values of the densities and sound velocities.

Solutions of the salt for the measurements were prepared by weighing diluted stock solutions. All the preparations and manipulations involving anhydrous materials were performed in dryboxes.

The densities of the solutions were measured at a pressure of 0.1 MPa using an Anton Paar DMA 5000 densimeter with precision of $1.0 \cdot 10^{-3}$ kg·m^{-3} and uncertainties of $5.0 \cdot 10^{-3}$ kg·m^{-3} for single measurement. The instrument was equipped with the Peltier-type thermostatting unit, and temperatures were kept constant at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 323.15) K with uncertainties ± 0.001 K.

The sound velocities were measured at a pressure of 0.1 MPa using a sound analyzer OPTIME 1.0 from Optel (Poland) with a precision of 0.05 m·s^{-1} by measuring the time it takes for a pulse of ultrasound to travel from one transducer to another (pitch-catch) or return to the same transducer (pulse-echo). The cell was thermostatted at (298.15 ± 0.005) K and calibrated with double distilled water, and the value 1496.69 m·s^{-1} for the sound velocity in pure water has been used.[8]

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Results and Discussion

The density data for the solutions are given in Table 2. The experimental data for sound velocity and adiabatic compressibility obtained at 298.15 K are presented in Table 3. The concentration dependences of the speed of sound, u, the density, d, and the adiabatic compressibility, κ_S, of solution can be represented by polynomials using molar concentration c (mol·m^{-3})

$$y = A_0 + A_1 \cdot c^{1/2} + A_2 \cdot c \quad (1)$$

The first coefficients of eq 1, A_0, denote the experimental values for the pure solvents (u_0, d_0, or $\kappa_{S,0}$), respectively. The coefficients of the polynomials, their standard deviations, and the residual variance, σ, are given in Tables 4, 5, and 6. As is seen, the speed of sound for the solutions is higher than for the pure solvent and increases with an increase of concentration of the salt for all solvents. Furthermore, the highest increase is observed for ethanolic solutions of tetrabutylphosphonium bromide, whereas the smallest effect takes place for the acetonitrile solutions of the solute. For the solutions in propanol and acetone, the presence of the salt induces almost the same change.

The apparent molar volume V_Φ of a solute is defined as the difference between the volume of the solution and the volume of the pure solvent per mole of solute and is given by

$$V_\Phi = (V - n_1 \cdot V_1^0)/n_2 \quad (2)$$

where V denotes the volume of the solution; n_1 and n_2 are number of moles of the solvent and salt, respectively; and V_1^0 is the molar volume of pure solvent.

The values of the apparent molar volumes, V_Φ/m^3·mol^{-1}, were calculated using the equation

$$V_\Phi = M_2/d_0 - (d - d_0)/(m_S \cdot d \cdot d_0) \quad (3)$$

where m_S/mol·kg^{-1} denotes the number of moles of the solute per kilogram of solution (molonity); d/kg·m^{-3} and d_0/kg·m^{-3}

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Table 1. Source and Grade of Solvents, Experimental and Literature Values of Densities *d*, and Speeds of Sound *u* of Ethanol, 1-Propanol, 1-Butanol, Acetone, and Acetonitrile at $T = 298.15$ K and $p = 0.1$ MPa

solvent	source	purity (mass fraction)	d_{exp} / kg·m^{-3}	d_{lit} / kg·m^{-3}	u_{exp} / m·s^{-1}	u_{lit} / m·s^{-1}
ethanol	Chempur	assay > 0.998	785.063	784.93,[9] 785.10[10]	1142.60	1142.6,[11] 1143[12]
1-propanol	Aldrich	assay > 0.998	799.452	799.52,[11] 799.62[13]	1204.90	1205.6,[11] 1204[14]
1-butanol	Aldrich	assay > 0.998, < 0.00005 water	805.659	805.75,[9] 805.64[15]	1239.00	1240,[14] 1239.6[16]
acetone	Aldrich	assay > 0.998, < 0.001 water	784.234	784.29,[17] 784.233[18]	1160.48	1160.6,[19] 1161.65[18]
acetonitrile	Aldrich	assay > 0.999, < 0.0002 water	776.493	775.9,[20] 776.85[21]	1278.28	1277.03,[22] 1280.80[23]

are densities of the solution and the solvent, respectively; and M_2/kg·mol^{-1} is the molar mass of the solute.

The apparent molar volume V_Φ of the tetrabutylphosphonium bromide increases with an increase of the concentration of the salt in all solvents at the measured temperatures. Figure 1 shows the apparent molar volumes V_Φ, plotted against the square root of molarity c, of the salt in ethanol, 1-propanol, 1-butanol, acetone, and acetonitrile solutions at 298.15 K. As is seen, the plots are not linear in the whole range of the measured concentration. However, inspection of the plots shows that for diluted solutions, i.e., for the salt concentrations lower than 0.04 mol·dm^{-3} (40 mol·m^{-3}), the plots are linear, and the Masson equation

$$V_\Phi = V_\Phi^0 + S_V \cdot c^{1/2} \quad (4)$$

may be used to obtain the limiting values of the apparent molar volume, V_Φ^0, of the tetrabutylphosphonium bromide. This is observed for all solvents irrespectively of the temperature. The V_Φ^0 data, S_V coefficients of eq 4, and concentration range obtained for the linear relationship at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 323.15) K are listed in Table 7. Inspection of the data exhibits that the values of the apparent molar volume of the phosphonium salt depend on the nature of the solvent and follow the sequence

butanol > propanol > ethanol > acetonitrile > acetone

The influence of the solvent features on the V_Φ value can also be observed with the change of the temperature of the solutions. An increase in the temperature causes the distinct increase in the values of the apparent molar volume in solutions in propanol and butanol. In the case of the ethanolic solutions, the influence of temperature on the apparent molar volume of the salt depends visibly on the salt concentration; that is, the V_Φ value markedly increases with the temperature for the most concentrated solutions. The effect becomes less distinct with decreasing concentration of the salt, and for the most diluted solutions the inversion of the relation is observed. A very similar effect is observed for the solutions in acetonitrile, but the notable influence of temperature on the V_Φ value is observed for diluted solutions only. The different situation is observed for solutions in acetone. An increase in temperature causes a gentle decrease of the values of the apparent molar volume. The effect becomes less distinct, and even disappears, when the concentration of the phosphonium bromide increases.

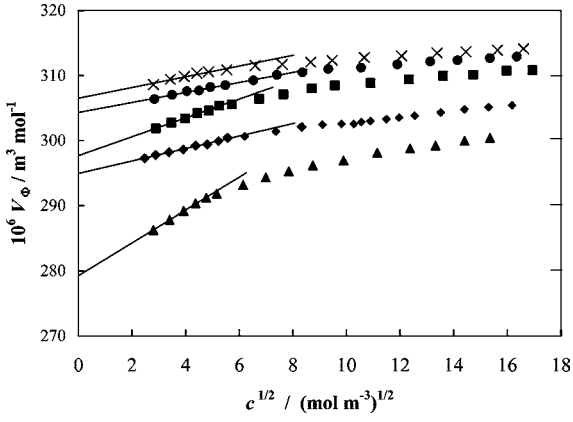

Figure 1. Apparent molar volumes, V_Φ/m^3·mol^{-1}, against the square root of molarity $\sqrt{c}$/(mol·m^{-3})$^{1/2}$, of tetrabutylphosphonium bromide in ■, ethanol; ◆, 1-propanol; ×, 1-butanol; ▲, acetone; and ●, acetonitrile solutions at $T = 298.15$ K. The straight line is fitted to each relation for diluted solutions using the least-squares approach.

The limiting values of the apparent molar volume of the solute V_Φ^0, obtained at measured temperatures, are presented in Figure 2. As is seen, the highest values of the parameter are obtained for the solutions in 1-butanol and 1-propanol. Moreover, the values are independent of temperature. Somewhat different effects brought by increasing temperature are observed for solutions in ethanol, acetonitrile, and acetone. The limiting values of the apparent molar volume of the solute V_Φ^0, obtained for (288.15, 293.15, and 298.15) K, that is, for temperatures lower than 300 K, seem to be independent of temperature, but for temperatures higher than 300 K, the values distinctly decrease.

The adiabatic compressibility, defined by the thermodynamic relation

$$\kappa_S = -(1/V)(\partial V/\partial P)_S \quad (5)$$

where V is volume; P is pressure; and S is entropy, is related to the density d/kg·m^{-3} and the sound velocity u/m·s^{-1}, by the Laplace equation

$$\kappa_S = 1/(u^2 \cdot d) \quad (6)$$

providing the link between thermodynamics and acoustics.

The apparent molar isentropic compressibilities, $K_{S,\Phi}$/m^5·(mol·N)$^{-1}$, for tetrabutylphosphonium bromide in acetonitrile, ethanol, 1-propanol, 1-butanol, and acetone solution were calculated according to

$$K_{S,\Phi} = (\kappa_S \cdot d_0 - \kappa_{S,0} \cdot d)/(m_S \cdot d \cdot d_0) + M_2 \cdot \kappa_{S,0}/d_0 \quad (7)$$

where M_2/kg·mol^{-1} is the molecular mass of the salt; m_S/mol·kg^{-1} denotes a number of moles of the solute per kilogram

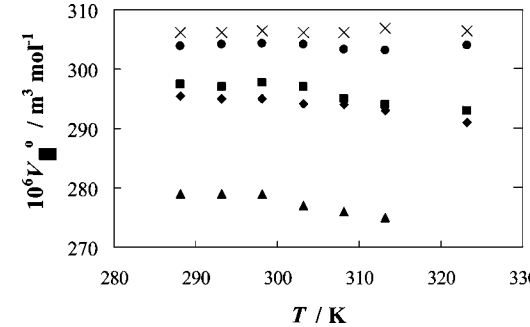

Figure 2. Limiting apparent molar volumes V_Φ^0/m^3·mol^{-1}, against the temperature T/K, of tetrabutylphosphonium bromide in ■, ethanol; ◆, 1-propanol; ×, 1-butanol; ▲, acetone; and ●, acetonitrile solutions.

Table 2. Experimental Densities of Pure Solvents d_0 and Solutions d of Tetrabutylphosphonium Bromide from T = (288.15 to 323.15) K and p = 0.1 MPa

m_S	d/kg·m^{-3}							m_S	d/kg·m^{-3}						
mol·kg^{-1}	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	323.15 K	mol·kg^{-1}	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	323.15 K
						Ethanol									
0	793.628	789.354	785.063	780.745	776.392	772.000	763.084	0.07390	799.301	795.066	790.805	786.532	782.224	777.879	769.054
0.01059	794.469	790.202	785.915	781.605	777.266	772.883	763.983	0.09578	800.947	796.718	792.466	788.201	783.906	779.575	770.773
0.01529	794.835	790.569	786.285	781.975	777.642	773.262	764.367	0.1153	802.415	798.195	793.960	789.696	785.405	781.083	772.302
0.02012	795.211	790.945	786.664	782.360	778.029	773.654	764.765	0.1491	805.003	800.793	796.569	792.326	788.054	783.746	775.000
0.02498	795.579	791.314	787.039	782.735	778.405	774.033	765.150	0.1902	808.127	803.940	799.735	795.510	791.254	786.963	778.257
0.03006	795.970	791.710	787.435	783.133	778.811	774.440	765.563	0.2304	811.194	807.016	802.825	798.610	794.369	790.100	781.434
0.03503	796.342	792.084	787.812	783.514	779.185	774.821	765.954	0.2693	814.212	810.050	805.871	801.675	797.452	793.195	784.564
0.04151	796.840	792.586	788.317	784.017	779.692	775.339	766.473	0.3148	817.670	813.522	809.364	805.185	800.979	796.743	788.154
0.05762	798.064	793.819	789.557	785.266	780.958	776.605	767.762	0.3532	820.707	816.572	812.423	808.255	804.069	799.851	791.300
						1-Propanol									
0	807.448	803.460	799.452	795.414	791.344	787.227	778.860	0.06813	812.403	808.443	804.463	800.458	796.411	792.340	784.043
0.008229	808.063	804.080	800.075	796.040	791.980	787.867	779.506	0.08670	813.750	809.793	805.818	801.819	797.792	793.720	785.440
0.01006	808.200	804.217	800.212	796.179	792.120	788.009	779.649	0.1076	815.247	811.298	807.331	803.338	799.313	795.248	786.995
0.01526	808.580	804.599	800.599	796.569	792.510	788.405	780.051	0.1375	817.423	813.485	809.531	805.541	801.524	797.479	789.244
0.02043	808.960	804.977	800.981	796.957	792.896	788.788	780.443	0.1743	820.087	816.159	812.214	808.243	804.242	800.208	792.006
0.02524	809.318	805.330	801.340	797.315	793.259	789.158	780.808	0.2115	822.781	818.864	814.928	810.970	806.982	802.960	794.787
0.03024	809.680	805.698	801.705	797.688	793.626	789.530	781.191	0.2447	825.209	821.300	817.377	813.431	809.450	805.445	797.302
0.03749	810.212	806.230	802.240	798.225	794.174	790.075	781.741	0.2873	828.335	824.437	820.523	816.588	812.630	808.638	800.526
0.05294	811.322	807.354	803.369	799.354	795.307	791.221	782.905	0.3248	831.089	827.205	823.305	819.382	815.432	811.451	803.369
						1-Butanol									
0	813.269	809.472	805.659	801.817	797.945	794.037	786.081	0.09251	819.818	816.049	812.265	808.455	804.620	800.743	792.887
0.009722	813.972	810.179	806.370	802.533	798.665	794.760	786.817	0.1101	821.058	817.297	813.514	809.710	805.879	802.009	794.162
0.01455	814.314	810.525	806.716	802.882	799.017	795.113	787.175	0.1395	823.126	819.370	815.598	811.804	807.981	804.127	796.295
0.01936	814.655	810.867	807.061	803.227	799.366	795.464	787.531	0.1776	825.836	822.089	818.326	814.540	810.729	806.888	799.080
0.02420	814.996	811.209	807.404	803.574	799.712	795.815	787.890	0.2180	828.688	824.949	821.197	817.424	813.625	809.794	802.026
0.02918	815.348	811.563	807.767	803.930	800.070	796.175	788.253	0.2537	831.238	827.510	823.765	820.001	816.210	812.388	804.641
0.03690	815.894	812.109	808.382	804.480	800.621	796.727	788.815	0.2955	834.232	830.511	826.778	823.022	819.242	815.431	807.714
0.05364	817.070	813.293	809.495	805.673	801.825	797.943	790.046	0.3323	836.873	833.160	829.434	825.687	821.922	818.127	810.433
0.07129	818.321	814.549	810.756	806.941	803.095	799.213	791.333								
						Acetone									
0	795.633	789.952	784.234	778.470	772.661	766.799		0.07794	802.136	796.525	790.878	785.191	779.457	773.675	
0.009972	796.516	790.843	785.133	779.385	773.586	767.735		0.09642	803.646	798.046	792.414	786.740	781.022	775.257	
0.01477	796.926	791.257	785.552	779.806	774.015	768.169		0.1230	805.822	800.247	794.640	788.995	783.255	777.557	
0.01959	797.328	791.666	785.967	780.225	774.439	768.597		0.1559	808.487	802.938	797.356	791.736	786.072	780.360	
0.02424	797.711	792.056	786.362	780.624	774.841	769.006		0.1912	811.381	805.858	800.306	794.713	789.077	783.390	
0.02891	798.099	792.447	786.758	781.026	775.247	769.416		0.2209	813.828	808.333	802.798	797.229	791.622	785.970	
0.03385	798.510	792.860	787.178	781.451	775.678	769.850		0.2576	816.813	811.345	805.845	800.309	794.734	789.113	
0.04786	996.73	794.037	788.362	782.648	776.885	771.075		0.2914	819.596	814.151	808.679	803.169	797.619	792.030	
0.06190	800.822	795.195	789.537	783.836	778.088	772.290									
						Acetonitrile									
0	787.275	781.893	776.493	771.067	765.610	760.119	749.031	0.1056	795.783	790.480	785.156	779.812	774.430	769.023	758.107
0.007874	787.927	782.552	777.157	771.738	766.288	760.805	749.733	0.1224	797.155	791.858	786.545	781.208	775.841	770.445	759.553
0.01066	788.155	782.783	777.389	771.974	766.524	761.045	749.978	0.1338	798.088	792.800	787.494	782.156	776.780	771.400	760.532
0.01465	788.477	783.109	777.721	772.308	766.862	761.385	750.325	0.1414	798.688	793.405	788.102	782.773	777.428	772.045	761.174
0.01965	788.885	783.521	778.136	772.724	767.283	761.811	750.761	0.1504	799.412	794.136	788.839	783.514	778.170	772.795	761.945
0.02448	789.275	783.912	778.532	773.125	767.689	762.220	751.178	0.1671	800.758	795.492	790.206	784.900	779.563	774.200	763.372
0.02970	789.700	784.340	778.965	773.559	768.128	762.662	751.631	0.1811	801.879	796.621	791.346	786.047	780.720	775.365	764.561
0.03509	790.132	784.784	779.405	774.005	768.580	763.119	752.095	0.1987	803.297	798.049	792.784	787.498	782.184	776.843	766.064
0.03974	790.506	785.156	779.780	774.389	768.965	763.508	752.488	0.2296	805.781	800.553	795.309	790.042	784.751	779.433	768.697
0.04929	791.273	785.930	780.567	775.178	769.760	764.310	753.307	0.2599	808.220	803.012	797.780	792.541	787.270	781.973	771.277
0.06938	792.879	787.551	782.208	776.834	771.429	765.995	755.023	0.2925	810.865	805.677	800.473	795.247	789.997	784.720	774.075
0.08849	794.411	789.095	783.760	778.399	773.011	767.591	756.649	0.3259	813.591	808.424	803.241	798.038	792.811	787.558	776.962

Table 3. Ultrasonic Velocity u, Adiabatic Compressibility κ_S, and Apparent Molar Compressibility $K_{S,\Phi}$ for Tetrabutylphosphonium Bromide in Ethanol, 1-Propanol, 1-Butanol, Acetone, and Acetonitrile Solutions at $T = 298.15$ K and $p = 0.1$ MPa

solvent	m_S / mol·kg^{-1}	u / m·s^{-1}	$10^{10}\cdot\kappa_S$ / m^2·N^{-1}	$10^{14}\cdot K_{S,\Phi}$ / m^5·N^{-1}·mol^{-1}
ethanol	0.01059	1143.41	9.732	0.158
	0.02012	1144.16	9.710	0.299
	0.03006	1144.90	9.688	0.807
	0.04161	1145.80	9.662	1.042
	0.05762	1146.99	9.627	1.394
	0.07390	1148.28	9.590	1.484
	0.09578	1150.03	9.541	1.641
	0.1153	1151.58	9.498	1.780
	0.1491	1154.02	9.426	2.323
	0.1902	1157.13	9.339	2.712
	0.2304	110.13	9.255	3.107
	0.2693	1163.18	9.172	3.288
	0.3148	1166.56	9.079	3.721
	0.3532	1169.74	8.996	3.808
1-propanol	0.01006	1205.61	8.598	3.642
	0.02524	1206.64	8.571	4.227
	0.05294	1208.61	8.521	4.411
	0.06813	1209.54	8.497	4.964
	0.08670	1210.79	8.465	5.132
	0.1076	1212.19	8.430	5.340
	0.1375	1213.91	8.383	5.871
	0.1743	1216.23	8.323	6.185
	0.2115	1218.41	8.266	6.587
	0.2447	1220.65	8.211	6.664
	0.2873	1223.51	8.141	6.803
	0.3248	1225.72	8.085	7.085
1-butanol	0.01936	1240.12	8.057	6.734
	0.0369	1241.03	8.032	6.933
	0.05364	1242.05	8.008	7.275
	0.07129	1243.05	7.982	7.368
	0.09251	1244.11	7.954	7.733
	0.1101	1245.14	7.929	7.743
	0.1395	1246.69	7.889	7.988
	0.1776	1248.76	7.836	8.169
	0.2180	1251.11	7.780	8.263
	0.2537	1252.93	7.733	8.491
	0.2955	1255.28	7.676	8.616
	0.3323	1257.12	7.629	8.835
acetone	0.009972	1161.12	9.447	−0.145
	0.01959	1161.78	9.426	0.097
	0.03385	1162.70	9.397	0.808
	0.04786	1163.63	9.368	1.072
	0.06190	1164.55	9.339	1.429
	0.07794	1165.66	9.306	1.545
	0.09642	1166.79	9.270	2.022
	0.1230	1168.38	9.218	2.546
	0.1559	1170.43	9.155	3.007
	0.1912	1172.71	9.086	3.291
	0.2209	1174.32	9.033	3.763
	0.2576	1176.62	8.963	4.074
	0.2914	1178.69	8.901	4.353
acetonitrile	0.03974	1280.09	7.826	5.803
	0.04929	1280.50	7.813	5.947
	0.06938	1281.39	7.786	6.157
	0.08849	1282.24	7.760	6.330
	0.1338	1284.11	7.701	6.716
	0.1671	1285.61	7.657	6.876
	0.1987	1287.00	7.615	7.048
	0.2296	1288.30	7.576	7.244
	0.2599	1289.51	7.538	7.465
	0.2925	1290.82	7.498	7.651
	0.3259	1292.25	7.455	7.788

of solution (molonity); and d/kg·m^{-3} and d_0/kg·m^{-3} are the densities of solution and the solvent, respectively. The terms κ_S/m^2·N^{-1} and $\kappa_{S,0}$/m^2·N^{-1} in eq 7 refer to the adiabatic compressibility of the solution and the solvent, respectively, calculated using eq 6. The obtained values of κ_S and $K_{S,\Phi}$ are presented in Table 3. Inspection of the presented data, in Table 3 and Figure 3, shows that an increase in concentration brings

Table 4. Parameters of Equation 1 for Speed of Sound (and Standard Deviation) for Tetrabutylphosphonium Bromide in Ethanol, 1-Propanol, 1-Butanol, Acetone, and Acetonitrile Solutions at $T = 298.15$ K and $p = 0.1$ MPa

solvent	u_0 / m·s^{-1}	$10^2\cdot A_1$ / (m^5·s^{-2}·mol^{-2})$^{1/2}$	$10^3\cdot A_2$ / m^4·s^{-1}·mol^{-1}	σ / m·s^{-1}
ethanol	1142.60	4 ± 1.8	92 ± 1.4	0.084
1-propanol	1204.90	9 ± 2.8	73 ± 2.5	0.11
1-butanol	1239.00	4 ± 2.1	64 ± 1.8	0.078
acetone	1160.48	7 ± 2.7	73 ± 2.7	0.097
acetonitrile	1278.28	6 ± 2.5	50 ± 1.5	0.071

Table 5. Parameters of Equation 1 for Density d (and Standard Deviation) for Tetrabutylphosphonium Bromide in Ethanol, 1-Propanol, 1-Butanol, Acetone, and Acetonitrile Solutions from $T =$ (288.15 to 323.15) K and $p = 0.1$ MPa

solvent		d_0 / kg·m^{-3}	$10^2\cdot A_1$ / (kg·m^{-3}·mol^{-1})$^{1/2}$	$10^3\cdot A_2$ / kg·m^6·mol^{-1}	σ / kg·m^{-3}
ethanol	288.15 K	793.628	3.3 ± 0.42	91.5 ± 0.30	0.021
	293.15 K	789.354	3.5 ± 0.45	92.4 ± 0.37	0.024
	298.15 K	785.063	3.7 ± 0.48	93.2 ± 0.39	0.024
	303.15 K	780.745	3.9 ± 0.52	94.2 ± 0.42	0.027
	308.15 K	776.392	4.3 ± 0.52	95.0 ± 0.38	0.027
	313.15 K	772.000	4.6 ± 0.54	95.9 ± 0.41	0.028
	323.15 K	763.084	5.1 ± 0.62	98.0 ± 0.48	0.032
1-propanol	288.15 K	807.448	2.6 ± 0.32	86.1 ± 0.25	0.017
	293.15 K	803.460	2.7 ± 0.38	86.9 ± 0.32	0.018
	298.15 K	799.452	2.8 ± 0.43	87.6 ± 0.33	0.019
	303.15 K	795.414	3.0 ± 0.45	88.3 ± 0.30	0.020
	308.15 K	791.344	3.2 ± 0.39	89.1 ± 0.30	0.020
	313.15 K	787.227	3.4 ± 0.49	89.9 ± 0.37	0.023
	323.15 K	778.860	3.7 ± 0.56	91.8 ± 0.45	0.028
1-butanol	288.15 K	813.269	2.1 ± 0.41	83.7 ± 0.30	0.019
	293.15 K	809.472	2.3 ± 0.40	84.3 ± 0.30	0.020
	298.15 K	805.659	2.6 ± 0.51	84.8 ± 0.38	0.025
	303.15 K	801.817	2.6 ± 0.50	85.6 ± 0.35	0.023
	308.15 K	797.945	2.7 ± 0.48	86.3 ± 0.38	0.024
	313.15 K	794.037	2.8 ± 0.43	87.0 ± 0.42	0.025
	323.15 K	786.081	3.3 ± 0.59	88.6 ± 0.48	0.028
acetone	288.15 K	795.633	5.2 ± 0.63	97.2 ± 0.53	0.030
	293.15 K	789.952	5.4 ± 0.67	98.7 ± 0.57	0.032
	298.15 K	784.234	5.6 ± 0.72	100.3 ± 0.59	0.033
	303.15 K	778.470	5.9 ± 0.77	101.9 ± 0.61	0.035
	308.15 K	772.661	6.1 ± 0.72	103.6 ± 0.63	0.033
	313.15 K	766.799	6.4 ± 0.81	105.4 ± 0.70	0.038
acetonitrile	288.15 K	787.275	3.6 ± 0.71	97.3 ± 0.57	0.039
	293.15 K	781.893	3.8 ± 0.71	98.6 ± 0.59	0.040
	298.15 K	776.493	4.0 ± 0.73	100.0 ± 0.59	0.042
	303.15 K	771.067	4.2 ± 0.77	101.4 ± 0.62	0.043
	308.15 K	765.610	4.4 ± 0.81	102.9 ± 0.63	0.044
	313.15 K	760.119	4.6 ± 0.80	104.4 ± 0.68	0.046
	323.15 K	749.031	5.1 ± 0.88	107.4 ± 0.75	0.049

Table 6. Parameters of Equation 1 for Adiabatic Compressibility (and Standard Deviation) for Tetrabutylphosphonium Bromide in Ethanol, 1-Propanol, 1-Butanol, Acetone, and Acetonitrile Solutions at $T = 298.15$ K and $p = 0.1$ MPa

solvent	$\kappa_0\cdot 10^{11}$ / m^2·N^{-1}	$10^{13}\cdot A_1$ / (m^7·N^{-2}·mol^{-1})$^{1/2}$	$10^{13}\cdot A_2$ / m^5·N^{-1}·mol^{-1}	$10^{12}\cdot\sigma$ / m^2·N^{-1}
ethanol	97.57	−2.7 ± 0.74	−2.50 ± 0.059	0.35
1-propanol	86.16	−2.5 ± 0.61	−1.84 ± 0.046	0.23
1-butanol	80.85	−1.5 ± 0.48	−1.58 ± 0.038	0.20
acetone	94.68	−2.5 ± 0.80	−2.27 ± 0.068	0.28
acetonitrile	78.81	−1.8 ± 0.57	−1.52 ± 0.049	0.21

an increase in the adiabatic compressibility of the bromide solutions and the linear equation

$$K_{S,\Phi} = K^0_{S,\Phi} + S_K\cdot c^{1/2} \quad (8)$$

which is analogous to the Masson equation and satisfactorily describes the concentration dependence. $K^0_{S,\Phi}$ and S_K denote the apparent molar adiabatic compressibility of the bromide at infinite dilution and the slope, respectively. The coefficients of eq 8, their standard deviations, and the respective values of the residual variance, σ, are given in Table 8. The positive values

Table 7. Parameters of Equation 4 (and Standard Deviation) for Tetrabutylphosphonium Bromide in Ethanol, 1-Propanol, 1-Butanol, Acetone, and Acetonitrile Solutions from T = (288.15 to 323.15) K and p = 0.1 MPa

solvent (the range of the salt concentration/mol·kg^{-1})		$10^6 \cdot V_\Phi^0$ / m^3·mol^{-1}	$10^6 \cdot S_V$ / m^3·mol^{-1}·M$^{1/2}$	$10^6 \cdot \sigma$ / m^3·mol^{-1}
ethanol (0.01059; 0.03503)	288.15 K	297.5 ± 0.88	1.4 ± 0.21	0.15
	293.15 K	297 ± 1.1	1.5 ± 0.29	0.18
	298.15 K	297.7 ± 0.61	1.4 ± 0.19	0.11
	303.15 K	297 ± 1.3	1.6 ± 0.31	0.20
	308.15 K	295 ± 1.6	2.0 ± 0.38	0.26
	313.15 K	294 ± 1.6	2.1 ± 0.35	0.24
	323.15 K	293 ± 1.7	2.3 ± 0.40	0.26
1-propanol (0.01006; 0.06819)	288.15 K	303.7 ± 0.76	0.7 ± 0.17	0.22
	293.15 K	304.2 ± 0.84	0.8 ± 0.20	0.26
	298.15 K	304.3 ± 0.38	0.78 ± 0.070	0.11
	303.15 K	304.2 ± 0.33	0.82 ± 0.063	0.11
	308.15 K	303.3 ± 0.88	1.0 ± 0.20	0.28
	313.15 K	303 ± 1.1	1.0 ± 0.25	0.33
	323.15 K	304.0 ± 0.76	1.0 ± 0.16	0.25
1-butanol (0.009722; 0.0369)	288.15 K	306.1 ± 0.96	0.7 ± 0.27	0.18
	293.15 K	306.1 ± 0.64	0.8 ± 0.18	0.11
	298.15 K	306.5 ± 0.95	0.8 ± 0.25	0.18
	303.15 K	306.2 ± 0.65	1.0 ± 0.20	0.12
	308.15 K	306.2 ± 0.39	1.03 ± 0.090	0.069
	313.15 K	306.9 ± 0.31	0.96 ± 0.069	0.053
	323.15 K	306.4 ± 0.63	1.1 ± 0.18	0.11
acetone (0.009972; 0.02891)	288.15 K	279 ± 1.6	2.8 ± 0.38	0.19
	293.15 K	279.2 ± 0.83	2.6 ± 0.25	0.11
	298.15 K	279.3 ± 0.60	2.5 ± 0.17	0.071
	303.15 K	277 ± 2.1	3.0 ± 0.56	0.26
	308.15 K	276 ± 1.5	3.0 ± 0.33	0.15
	313.15 K	274 ± 1.7	3.1 ± 0.34	0.16
acetonitrile (0.007874; 0.03974)	288.15 K	295.5 ± 0.69	0.9 ± 0.18	0.19
	293.15 K	295.0 ± 0.71	1.0 ± 0.22	0.21
	298.15 K	294.9 ± 0.40	0.96 ± 0.087	0.11
	303.15 K	294.2 ± 0.43	1.1 ± 0.12	0.12
	308.15 K	294.1 ± 0.47	1.0 ± 0.15	0.13
	313.15 K	293.0 ± 0.50	1.2 ± 0.13	0.14
	323.15 K	291.0 ± 0.56	1.4 ± 0.14	0.16

of $K_{S,\Phi}$ are an indication of the more compressible structure of the solution than those of the pure solvent. This effect is more noticeable in the solvent with the lower isothermal compressibility, and $K_{S,\Phi}^0$ values follow the sequence

butanol > acetonitrile > propanol > ethanol > acetone

It is easy to note that the highest values of the volumetric data, V_Φ, as well as the compressibilities, $K_{S,\Phi}$, are observed for the solutions in 1-butanol. It seems to be due to the change in the structure of the solvent which is sensitive toward the perturbation related to the solute−solvent interactions. The formation of the high free volumes in the solvent network is the factor responsible for the high compressibility. The smallest values of the volumetric parameters are observed for the acetone solutions, and the conclusion follows that the presence of the solute does not disturb the structure of the solvent significantly.

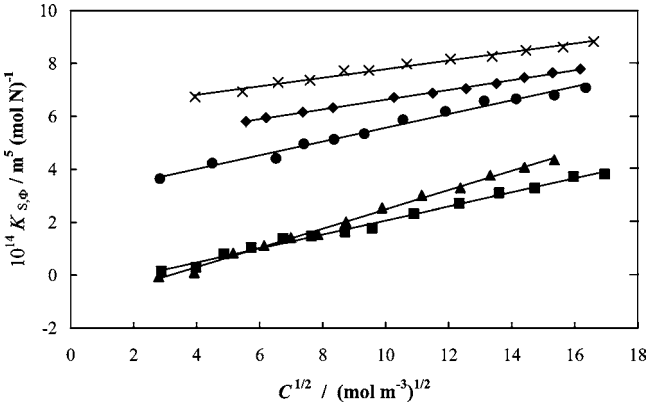

Figure 3. Apparent molar adiabatic compressibility, $K_{S,\Phi}$/m^5·(N·mol)$^{-1}$, against the square root of molarity, $\sqrt{c}$/(mol·m^{-3})$^{1/2}$, of tetrabutylphosphonium bromide in ■, ethanol; ◆, 1-propanol; ×, 1-butanol; ▲, acetone; and ●, acetonitrile solutions at T = 298.15 K. The straight line is fitted to each relation using the least-squares approach.

Table 8. Parameters of Equation 8 and Standard Deviation for Tetrabutylphosphonium Bromide in Ethanol, 1-Propanol, 1-Butanol, Acetone, and Acetonitrile Solutions at T = 298.15 K and p = 0.1 MPa

solvent	$10^{14} \cdot K_{S,\Phi}^0$ / m^5·N^{-1}·mol^{-1}	$10^{15} \cdot S_K$ / (m^{13}·N^{-2}·mol^{-3})$^{1/2}$	$10^{14} \cdot \sigma$ / m^5·N^{-1}·mol^{-1}
ethanol	−0.6 ± 0.18	2.6 ± 0.15	0.12
1-propanol	3.0 ± 0.28	2.6 ± 0.23	0.15
1-butanol	6.2 ± 0.16	1.6 ± 0.16	0.086
acetone	−1.1 ± 0.18	3.6 ± 0.18	0.11
acetonitrile	3.0 ± 0.28	1.85 ± 0.063	0.033

Conclusion

Precise determination of the density at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15 and 323.15) K and the velocity of sound at 298.15 K permitted thermodynamic analysis of volumetric and compressibility properties of tetra-n-butylphosphonium bromide in ethanol, 1-propanol, 1-butanol, acetone and acetonitrile. The value of the obtained $K_{S,\Phi}$ and V_Φ data depend strongly on the features of the solvent. Temperature characteristic of the limiting apparent molar volume shows probably the lack of the electrostriction effect in 1-butanol and 1-propanol solutions due to the constant values of the $V_\Phi{}^0$.

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