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Partial Molar Volumes of Selected Aliphatic Alcohols at Infinite Dilution in Water at Temperatures T = (278 to 573) K and Pressures up to 30 MPa

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ABSTRACT: Density data for dilute aqueous solutions of four aliphatic alcohols (2,2-dimethylpropane-1-ol, 2-methylpropane-1,3-diol, 2,2-bis(hydroxymethyl)propane-1-ol, 2,2-bis(hydroxymethyl)butane-1-ol) and one ether alcohol (3,3,7,7-tetrakis(hydroxymethyl)-5-oxanonane) were obtained using both the Anton Paar DSA 5000 vibrating-tube densimeter and the laboratory-made flow densimeter. They are presented together with partial molar volumes at infinite dilution (standard molar volumes) calculated from the measured data. The measurements were performed at temperatures T = (278 to 573) K and at pressures up to p = 30 MPa. Trends in homologous series are discussed, and the group additivity scheme proposed recently is applied to the solutes investigated.

INTRODUCTION

Recently a group contribution method[1] was designed for the estimation of partial molar volumes at infinite dilution (standard molar volumes) of organic solutes in water. Group and structural contributions covering a wide range of temperature from (298 to 573) K and pressures up to 30 MPa were evaluated using data[2−8] measured in our laboratory for aqueous aliphatic derivatives comprising one or two oxygen-containing functional groups (−OH, −O−, >CO). The predictive abilities of the method were examined using a limited number of experimental data available in the literature for extended ranges of temperature and pressure. This examination revealed, however, that intramolecular interactions may occur among multiple functional groups which affect the standard molar volume. This was clearly observed on linear polyhydric alcohols with hydroxyl groups residing on the neighboring carbon atoms (ethane-1,2-diol, propane-1,2-diol, butane-2,3-diol, propane-1,2,3-triol, pentane-1,2,3,4,5-pentanol). Similar effects were indicated by data for solutes with a globular structure derived from 2,2-dimethylpropane (neopentane), namely, 2,2-dimethylpropane-1,3-diol and 2,2-bis(hydroxymethyl)propane-1,3-diol, but a quantitative description of these effects was impossible due to lack of data for other derivatives of this series. Data presented in this work are thus complementary to those available from our previous measurements. Figure 1 shows the structures of the solute molecules investigated here along with three more solutes the data of which have been already published (propane-1,3-diol,[4] 2,2-dimethylpropane-1,3-diol,[6] 2,2-bis(hydroxymethyl)propane-1,3-diol[6]). The arrows between the formulas indicate a particular series of the solutes. Present new data for aqueous 2,2-dimethylpropane-1-ol and 2,2-bis(hydroxymethyl)propane-1-ol make the series of alcohols derived from 2,2-dimethylpropane complete. Data for 2-methylpropane-1,3-diol fill the gap between propane-1,3-diol[4] and 2,2-dimethylpropane-1,3-diol.[6] The molecule of 2,2-bis(hydroxymethyl)butane-1-ol is derived from that of 2,2-bis(hydroxymethyl)propane-1-ol by adding one methylene group. Finally, a large molecule of the fifth solute, 3,3,7,7-tetrakis(hydroxymethyl)-5-oxanonane, is composed of two structures of 2,2-bis(hydroxymethyl)butane-1-ol combined together by the ether-oxygen atom; that is, the hypothetical reaction between two molecules of 2,2-bis(hydroxymethyl)butane-1-ol produces one molecule of water and one molecule of 3,3,7,7-tetrakis(hydroxymethyl)-5-oxanonane. Present new data are also significant for the further development of the group contribution concept applicable over wide ranges of temperature and pressure since one solute only (2,2-dimethylpropane-1,3-diol)

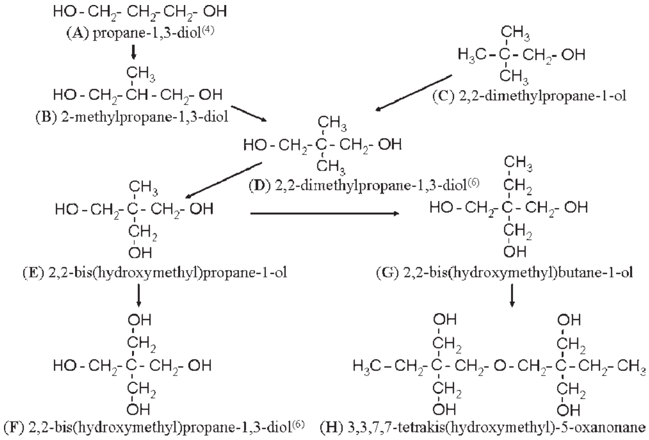

Figure 1. Structures of solute molecules.

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which incorporates the quaternary carbon atom (carbon atom bonded to four other carbon atoms, >C<) was included in the input data set employed for evaluation of contributions.[1] The set of solutes of this type is extended considerably by the present measurements; four of five measured solutes have one or two quaternary carbon atoms in their molecules.

Two vibrating-tube densimeters were used for the measurements. Most of the presented data were obtained using our high-temperature high-pressure flow (HTHP) densimeter[9−11] working in the temperature range from (298 to 573) K and under pressures from ambient up to 30 MPa. Since no cooling system is installed with the HTHP densimeter, the commercial vibrating-tube densimeter DSA 5000 with a glass tube and a built-in thermostat was used for measurements under atmospheric pressure at temperatures down to 278 K; due to air-bubble formation at higher temperatures, the upper temperature limit was 318 K.

EXPERIMENTAL SECTION

The organic solutes were purchased from Sigma Aldrich: 2,2-dimethylpropane-1-ol ($C_5H_{12}O$, CAS RN 75-84-3, stated mass fraction purity 0.99), 2-methylpropane-1,3-diol ($C_4H_{10}O_2$, CAS RN 2163-42-0, stated mass fraction purity 0.99), 2,2-bis(hydroxymethyl)propane-1-ol ($C_5H_{12}O_3$, CAS RN 77-85-0, stated mass fraction purity 0.99), 2,2-bis(hydroxymethyl)butane-1-ol ($C_6H_{14}O_3$, CAS RN 77-99-6, stated mass fraction purity 0.98), and 3,3,7,7-tetrakis(hydroxymethyl)-5-oxanonane ($C_{12}H_{26}O_5$, CAS RN 23235-61-2, stated mass fraction purity 0.97) were used without further treatment. Distilled, demineralized (Millipore RQ) water was used as a calibration fluid for the densimeters and for the preparation of solutions. Nitrogen (Siad, mole fraction purity 0.9999) was used as supplied.

Solutions were prepared by mass using a Precisa 40SM-200A balance (resolution = 10^{-2} mg, uncertainty = ± 0.1 mg) to determine the mass of the solute and a Precisa 2200C SCS balance (resolution = 10 mg, estimated uncertainty = $\pm 2 \cdot 10^{-2}$ percent) to determine the total mass of a solution. The mass of each prepared solution was about 1 kg. Air-saturated water was used for the preparation of solutions measured by the DSA 5000 densimeter. Solutions measured using the HTHP densimeter (see below) were prepared using water saturated with nitrogen and stored in closed bottles under nitrogen atmosphere. The upper concentration limit was selected to be between (0.4 and 0.6) $\text{mol} \cdot \text{kg}^{-1}$; in the case of 2,2-dimethylpropane-1-ol and 3,3,7,7-tetrakis(hydroxymethyl)-5-oxanonane the highest concentrations were limited by the solubility in water. Stop-flow experiments[12] were performed at higher temperatures, and no thermal decomposition of solutes was observed up to the highest experimental temperature.

Densimeter DSA 5000. The vibrating-tube densimeter manufactured by Anton Paar, model DSA 5000, equipped with the autosampler SP-1 m (Anton Paar) was used for the measurements predominantly at temperatures down to 278 K using a built-in thermostat. The highest temperature at which the air-bubble formation had no observable effect and the measurements were possible was 318 K. The densimeter was calibrated with water and air following the instructions and requirements of the manufacturer. All controls, adjustments, and checks were done using manufacturer's software installed in the device. A computer connected to the densimeter enabled us to read the raw data from the device memory and to perform the consequent evaluation.

Several vials filled with air-saturated pure water were included and distributed in the measured sample set. The reproducibility of density of water was usually $\pm 1 \cdot 10^{-3}\ \text{kg} \cdot \text{m}^{-3}$ (slightly worse at higher temperatures), and the average value at each temperature was used for ρ_1 to calculate the density differences $\Delta\rho = \rho - \rho_1$ where ρ and ρ_1 are the densities of the solution and water, respectively.

High-Temperature High-Pressure (HTHP) Densimeter. The HTHP densimeter and the experimental procedure are described in more detail elsewhere,[9−11] and therefore we present here a brief description only. Repeated calibrations of the densimeter were performed at each experimental temperature and pressure using water and nitrogen whose densities were taken from the literature.[13,14] The maximum systematic error of the measured density differences $\Delta\rho = \rho - \rho_1$ resulting from the densimeter calibration was about 0.2 %, and the reproducibility of the measurements was within $\pm 3 \cdot 10^{-3}\ \text{kg} \cdot \text{m}^{-3}$ in most cases. The measurements were performed in the flow regime with the high-pressure pump adjusted to the flow rate of $0.6\ \text{cm}^3 \cdot \text{min}^{-1}$. A pressure vessel of volume 40 dm^3 filled with nitrogen[15] was connected to the end of the pressure line for measurements at pressure 0.5 MPa; at higher pressures a thermostatted back-pressure regulator was used. The total uncertainty of the temperature measurements using a calibrated (ITS 90) platinum resistance thermometer (BURNS Engineering) was estimated to be about ± 20 mK, and the uncertainty in pressure measured using a secondary standard gauge (DIGIQUARTZ-740-6K, Paroscientific Inc.) was less than 0.01 MPa.

Separate sets of solutions were prepared for measurements performed using the HTHP densimeter. Exceptionally the same solutions were measured using both densimeters. Since the solutions were prepared using nitrogen-saturated water, and because water degassed by boiling was used as a carrier fluid in the flow system,[11] the corrections with respect to the measured difference between density of degassed and nitrogen-saturated water were taken into account.

RESULTS

Direct Experimental Data. The values of the density differences $\Delta\rho = \rho - \rho_1$, where ρ and ρ_1 are the densities of the solution and water, respectively, measured at each experimental temperature and pressure and corrected (where applicable) for measured differences between nitrogen-saturated and degassed water, and the molalities of organic solutes m_2 are available in the Supporting Information (Tables S1 through S5): 526 data points in the range of molality from (0.05 to 0.21) $\text{mol} \cdot \text{kg}^{-1}$ for aqueous 2,2-dimethylpropane-1-ol, 516 data points in the range of molality from (0.10 to 0.41) $\text{mol} \cdot \text{kg}^{-1}$ for aqueous 2-methylpropane-1,3-diol, 779 data points in the range of molality from (0.10 to 0.60) $\text{mol} \cdot \text{kg}^{-1}$ for aqueous 2,2-bis(hydroxymethyl)propane-1-ol, 652 data points in the range of molality from (0.10 to 0.50) $\text{mol} \cdot \text{kg}^{-1}$ for aqueous 2,2-bis(hydroxymethyl)butane-1-ol, and 518 data points in the range of molality from (0.02 to 0.08) $\text{mol} \cdot \text{kg}^{-1}$ for aqueous 3,3,7,7-tetrakis(hydroxymethyl)-5-oxanonane; total 2991 data points.

The dependence of $\Delta\rho/m_2$ on m_2 at constant temperature and pressure was treated as a linear function of m_2 in the composition ranges of measurements; higher polynomial terms were found to be insignificant. The experimental results obtained for each pair of temperature and pressure were fitted with the equation

$$\Delta\rho/m_2 = (\rho - \rho_1)/m_2 = a + bm_2 \tag{1}$$

where a and b are adjustable coefficients. The values of the coefficients were obtained by using a least-squares method with unit weights and are recorded in Table 1.

Table 1. Density ρ_1 of Water,[13] Coefficients a and b of eq 1, and Standard Molar Volumes $V^{o}_{m,2}$ for {2,2-Dimethylpropane-1-ol (2), 2-Methylpropane-1,3-diol (2), 2,2-Bis(hydroxymethyl)propane-1-ol (2), 2,2-Bis(hydroxymethyl)butane-1-ol (2), or 3,3,7,7-Tetrakis(hydroxymethyl)-5-oxanonane (2) + Water (1)}[a]

T	p	ρ_1	a	$\sigma(a)$	b	$\sigma(b)$	$V^0_{m,2}$	$\sigma(V^0_{m,2})$
K	MPa	$kg \cdot m^{-3}$	$kg^2 \cdot m^{-3} \cdot mol^{-1}$	$kg^2 \cdot m^{-3} \cdot mol^{-1}$	$kg^3 \cdot m^{-3} \cdot mol^{-2}$	$kg^3 \cdot m^{-3} \cdot mol^{-2}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$
				2,2-Dimethylpropane-1-ol (aq)				
				DSA 5000 Densimeter				
278.15	0.10	999.966	−12.7545	0.1699	4.4910	0.4391	100.91	0.17
283.15	0.10	999.702	−12.9939	0.1716	4.3100	0.4255	101.18	0.17
288.15	0.10	999.102	−13.1653	0.1714	4.0320	0.4280	101.42	0.17
293.15	0.10	998.207	−13.4373	0.1713	3.7852	0.4298	101.79	0.17
298.15	0.10	997.047	−13.6315	0.1713	3.3631	0.4319	102.12	0.17
308.15	0.10	994.033	−13.9621	0.1661	2.6654	0.4578	102.81	0.17
318.15	0.10	990.212	−14.3512	0.1703	2.1162	0.4313	103.66	0.17
				HTHP Densimeter				
298.19	0.51	997.223	−13.5730	0.2252	2.6238	0.9807	102.04	0.23
318.21	0.53	990.374	−14.6247	0.1828	2.3201	0.7834	103.92	0.19
338.21	0.52	980.703	−15.6379	0.1802	1.4214	0.7842	106.14	0.19
358.16	0.51	968.790	−16.8149	0.1809	0.9270	0.7875	108.90	0.20
373.15	0.52	958.543	−17.6113	0.1829	0.7661	0.7900	111.13	0.20
398.14	2.03	939.946	−19.2810	0.1729	0.8147	0.7411	115.60	0.20
423.15	2.05	917.896	−20.8494	0.1813	0.9555	0.7920	120.78	0.22
448.15	2.04	893.023	−22.2855	0.1820	1.0946	0.7918	126.65	0.23
473.15	2.04	865.029	−24.1567	0.1808	0.6982	0.7822	134.19	0.25
498.13	3.06	834.238	−25.7300	0.1825	−0.4727	0.7881	142.63	0.27
523.18	5.09	800.143	−27.3827	0.1846	−1.6162	0.7947	152.93	0.30
548.15	7.02	760.672	−30.7392	0.1823	1.3925	0.7885	169.01	0.33
573.15	10.22	715.781	−34.3828	0.2112	3.2536	0.9325	190.26	0.43
298.19	15.11	1003.700	−14.3225	0.1832	3.1959	0.8143	102.04	0.18
318.21	15.07	996.626	−14.9611	0.1828	2.2979	0.7847	103.51	0.18
338.21	15.24	987.051	−15.7592	0.1859	1.4171	0.8112	105.48	0.19
358.17	15.11	975.264	−16.7501	0.1777	1.4484	0.7377	107.99	0.19
373.15	15.07	965.235	−17.4280	0.1830	0.8772	0.7904	110.03	0.20
398.14	15.04	946.401	−18.9307	0.1813	0.8108	0.7927	114.28	0.21
423.14	15.01	925.042	−20.2240	0.1806	0.6495	0.7886	118.93	0.22
448.16	15.05	901.161	−21.5066	0.2301	1.3690	0.9999	124.30	0.20
473.15	15.11	874.572	−22.9470	0.1819	0.0616	0.7846	130.79	0.25
498.14	15.10	844.809	−24.2053	0.1815	−0.5132	0.7830	138.26	0.26
523.16	15.04	811.055	−25.3586	0.1816	−2.5520	0.7833	147.23	0.29
548.15	14.99	772.150	−28.4367	0.1846	1.8359	0.7946	161.86	0.32
573.16	15.18	725.889	−31.9032	0.1831	5.9479	0.7864	181.99	0.37
298.22	30.45	1010.300	−14.9343	0.1828	3.2247	0.7995	101.88	0.18
318.21	29.89	1002.800	−15.3714	0.1806	2.6384	0.7858	103.19	0.18
338.21	30.04	993.220	−15.8791	0.1805	1.3367	0.7850	104.85	0.19
358.16	29.84	981.569	−16.7590	0.1913	1.4729	0.8658	107.20	0.20
373.15	30.03	971.836	−17.3120	0.1839	1.0171	0.7949	109.03	0.20
398.14	30.03	953.520	−18.5844	0.1802	0.7508	0.7837	112.89	0.20
423.15	30.03	932.884	−19.6996	0.1817	0.6821	0.7891	117.13	0.21
448.16	30.06	909.965	−20.9918	0.1802	2.0986	0.7853	122.22	0.22
473.16	30.03	884.629	−21.9526	0.1816	0.1524	0.7838	127.70	0.24
498.15	30.01	856.651	−22.7875	0.1819	−0.5897	0.7850	133.95	0.26
523.15	30.08	825.617	−23.5415	0.1821	−1.7815	0.7851	141.30	0.28
548.14	30.03	790.689	−25.4377	0.1842	1.8450	0.7918	152.17	0.31
573.16	30.08	750.754	−27.0498	0.1847	3.8992	0.7736	165.41	0.34

Table 1. Continued

T	p	ρ_1	a	$\sigma(a)$	b	$\sigma(b)$	$V^0_{m,2}$	$\sigma(V^0_{m,2})$
K	MPa	$kg \cdot m^{-3}$	$kg^2 \cdot m^{-3} \cdot mol^{-1}$	$kg^2 \cdot m^{-3} \cdot mol^{-1}$	$kg^3 \cdot m^{-3} \cdot mol^{-2}$	$kg^3 \cdot m^{-3} \cdot mol^{-2}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$
2-Methylpropane-1,3-diol(aq)								
DSA 5000 Densimeter								
278.15	0.10	999.966	3.2400	0.0778	0.8526	0.1036	86.88	0.08
283.15	0.10	999.702	3.1351	0.0778	0.7384	0.1032	87.01	0.08
288.15	0.10	999.102	3.0460	0.0779	0.6473	0.1027	87.15	0.08
293.15	0.10	998.207	2.9726	0.0779	0.5343	0.1021	87.30	0.08
298.15	0.10	997.047	2.8924	0.0779	0.4639	0.1015	87.48	0.08
308.15	0.10	994.033	2.7404	0.0778	0.3125	0.1044	87.89	0.08
318.15	0.10	990.212	2.5988	0.0778	0.1600	0.1052	88.36	0.08
HTHP Densimeter								
298.19	0.51	997.223	2.9322	0.1160	0.2945	0.2474	87.42	0.12
338.21	0.53	990.374	2.5471	0.1160	0.1918	0.1255	88.40	0.06
338.21	0.52	980.703	2.1926	0.0578	0.0270	0.1236	89.61	0.06
358.16	0.51	968.790	1.7509	0.0581	0.0314	0.1242	91.16	0.06
373.15	0.52	958.543	1.4549	0.0538	−0.0376	0.1125	92.44	0.06
398.14	2.03	939.943	0.9552	0.0541	−0.0978	0.1129	94.80	0.06
423.15	2.05	917.896	0.4197	0.0562	0.0056	0.1193	97.68	0.07
448.15	2.04	893.023	−0.0253	0.0562	0.0010	0.1192	100.95	0.07
473.15	2.04	865.028	−0.4900	0.0564	0.1145	0.1198	104.84	0.08
498.13	3.06	834.237	−0.8361	0.0543	0.1128	0.1145	109.23	0.08
523.18	5.09	800.142	−1.1005	0.0582	0.1268	0.1240	114.35	0.09
548.15	7.02	760.672	−1.4159	0.0537	0.3028	0.1079	120.92	0.09
573.15	10.22	715.771	−1.5803	0.0637	0.4837	0.1369	128.99	0.12
298.19	15.12	1003.700	2.4536	0.1160	0.4666	0.2474	87.35	0.12
318.21	15.08	996.628	2.2796	0.0580	0.2245	0.1245	88.13	0.06
338.21	15.24	987.051	2.0232	0.0554	0.0549	0.1123	89.23	0.06
358.17	15.10	975.262	1.6531	0.0639	0.0690	0.1398	90.67	0.07
373.15	15.08	965.238	1.4339	0.0533	−0.0490	0.1112	91.83	0.06
398.14	15.04	946.402	0.9937	0.0551	−0.0727	0.1161	94.12	0.06
423.15	15.01	925.042	0.5761	0.0563	−0.0610	0.1195	96.75	0.07
448.16	15.05	901.160	0.1959	0.0563	−0.0362	0.1195	99.76	0.07
473.15	15.11	874.572	−0.1753	0.0542	0.1001	0.1142	103.28	0.07
498.14	15.11	844.818	−0.4206	0.0546	0.0957	0.1152	107.26	0.08
523.16	15.04	811.056	−0.6343	0.0560	0.1348	0.1190	112.08	0.09
548.15	14.99	772.154	−0.8633	0.0500	0.3297	0.0998	118.16	0.08
573.16	15.19	725.891	−1.0586	0.0512	0.4938	0.0980	126.16	0.10
298.22	30.47	1010.300	2.0589	0.0926	0.4605	0.1981	87.19	0.09
318.21	29.90	1002.810	1.9963	0.0597	0.2752	0.1291	87.88	0.06
338.21	30.03	993.218	1.8632	0.0608	0.0443	0.1325	88.85	0.06
358.16	29.85	981.573	1.5687	0.0541	0.0616	0.1122	90.19	0.06
373.15	30.05	971.845	1.3818	0.0532	−0.0200	0.1099	91.27	0.06
398.14	30.04	953.525	1.0378	0.0563	−0.0827	0.1192	93.37	0.06
423.15	30.03	932.884	0.6887	0.0608	−0.0760	0.1311	95.81	0.07
448.16	30.07	909.970	0.3784	0.0570	−0.0342	0.1214	98.58	0.07
473.16	30.03	884.628	0.1042	0.0566	0.0694	0.1209	101.74	0.07
498.15	30.02	856.654	−0.0431	0.0570	0.0472	0.1218	105.26	0.08
523.16	30.08	825.617	−0.1036	0.0550	0.0830	0.1165	109.31	0.08
548.14	30.03	790.689	−0.1185	0.0515	0.2127	0.1039	114.17	0.08
573.16	30.08	750.751	0.0041	0.0518	0.3363	0.1030	120.03	0.09

Table 1. Continued

T / K	p / MPa	ρ_1 / $kg \cdot m^{-3}$	a / $kg^2 \cdot m^{-3} \cdot mol^{-1}$	$\sigma(a)$ / $kg^2 \cdot m^{-3} \cdot mol^{-1}$	b / $kg^3 \cdot m^{-3} \cdot mol^{-2}$	$\sigma(b)$ / $kg^3 \cdot m^{-3} \cdot mol^{-2}$	$V^0_{m,2}$ / $cm^3 \cdot mol^{-1}$	$\sigma(V^0_{m,2})$ / $cm^3 \cdot mol^{-1}$
				2,2-Bis(hydroxymethyl)propane-1-ol(aq)				
				DSA 5000 Densimeter				
278.15	0.10	999.966	18.9820	0.0718	−1.1357	0.0420	101.17	0.07
283.15	0.10	999.702	18.7182	0.0723	−1.1943	0.0418	101.45	0.07
288.15	0.10	999.102	18.4932	0.0727	−1.2355	0.0415	101.73	0.07
293.15	0.10	998.207	18.2983	0.0732	−1.2756	0.0411	102.00	0.07
298.15	0.10	997.047	18.1293	0.0739	−1.3279	0.0407	102.27	0.07
308.15	0.10	994.033	17.8210	0.0711	−1.3576	0.0424	102.83	0.07
318.15	0.10	990.212	17.5744	0.0706	−1.4364	0.0429	103.41	0.07
				HTHP Densimeter				
298.19	0.51	997.222	18.0756	0.0950	−1.3511	0.1573	102.31	0.10
318.22	0.52	990.365	17.5240	0.0469	−1.4597	0.0861	103.45	0.06
338.21	0.52	980.702	17.0830	0.0475	−1.5157	0.0766	104.75	0.06
358.17	0.52	968.789	16.6694	0.0472	−1.4668	0.0750	106.26	0.06
373.15	0.52	958.544	16.4425	0.0471	−1.4835	0.0751	107.45	0.06
398.14	2.03	939.943	16.1034	0.0472	−1.5037	0.0761	109.60	0.06
423.15	2.05	917.903	15.8378	0.0470	−1.4432	0.0759	112.10	0.07
448.15	2.04	893.025	15.7034	0.0476	−1.4053	0.0771	114.85	0.07
473.15	2.05	865.037	15.7003	0.0473	−1.3935	0.0758	117.91	0.08
498.14	3.05	834.223	15.8322	0.0476	−1.3073	0.0764	121.27	0.08
523.18	5.10	800.157	16.2316	0.0492	−1.2815	0.0784	124.80	0.09
548.16	7.00	760.632	16.9610	0.0451	−1.1452	0.0700	128.64	0.10
573.15	10.26	715.852	18.3015	0.0633	−1.0949	0.1061	132.12	0.14
298.19	15.13	1003.710	17.5927	0.0752	−1.2928	0.1209	102.24	0.08
318.22	15.07	996.624	17.1984	0.0473	−1.4081	0.0759	103.24	0.06
338.21	15.20	987.038	16.8371	0.0476	−1.4818	0.0747	104.44	0.06
358.16	15.09	975.258	16.5567	0.0470	−1.4253	0.0752	105.79	0.06
373.14	15.06	965.234	16.3211	0.0465	−1.4835	0.0740	106.96	0.06
398.15	15.04	946.400	16.0341	0.0471	−1.4749	0.0760	109.05	0.06
423.15	15.00	925.037	15.8256	0.0472	−1.3674	0.0761	111.39	0.07
448.15	15.06	901.169	15.7142	0.0473	−1.4107	0.0763	113.97	0.07
473.15	15.10	874.572	15.7380	0.0477	−1.3962	0.0768	116.80	0.07
498.14	15.15	844.843	15.8889	0.0491	−1.3478	0.0795	119.95	0.08
523.16	15.03	811.043	16.2521	0.0493	−1.2998	0.0794	123.43	0.09
548.14	15.00	772.176	16.8924	0.0520	−1.1799	0.0845	127.27	0.10
573.15	15.21	725.949	18.0355	0.0646	−1.0353	0.0969	131.28	0.14
298.22	30.47	1010.300	17.1040	0.0484	−1.2255	0.0780	102.17	0.06
318.21	29.96	1002.830	16.8458	0.0493	−1.3485	0.0861	103.06	0.06
338.21	30.14	993.264	16.6079	0.0489	−1.4677	0.0796	104.13	0.06
358.16	30.07	981.668	16.4020	0.0464	−1.4412	0.0739	105.37	0.06
373.14	30.06	971.852	16.1768	0.0483	−1.4650	0.0778	106.50	0.06
398.15	29.99	953.498	15.9347	0.0476	−1.4595	0.0769	108.48	0.06
423.15	30.06	932.897	15.7712	0.0485	−1.4440	0.0786	110.67	0.07
448.16	30.04	909.954	15.7159	0.0473	−1.4278	0.0764	113.06	0.07
473.15	29.95	884.581	15.7376	0.0477	−1.3896	0.0769	115.71	0.07
498.16	30.03	856.651	15.9080	0.0476	−1.3507	0.0763	118.58	0.08
523.16	30.02	825.560	16.2657	0.0455	−1.3300	0.0728	121.67	0.08
548.14	30.02	790.678	16.8439	0.0497	−1.2790	0.0813	125.01	0.10
573.15	30.00	750.651	17.7353	0.0453	−1.1986	0.0590	128.58	0.10

Table 1. Continued

T / K	p / MPa	ρ_1 / $kg \cdot m^{-3}$	a / $kg^2 \cdot m^{-3} \cdot mol^{-1}$	$\sigma(a)$ / $kg^2 \cdot m^{-3} \cdot mol^{-1}$	b / $kg^3 \cdot m^{-3} \cdot mol^{-2}$	$\sigma(b)$ / $kg^3 \cdot m^{-3} \cdot mol^{-2}$	$V^0_{m,2}$ / $cm^3 \cdot mol^{-1}$	$\sigma(V^0_{m,2})$ / $cm^3 \cdot mol^{-1}$
2,2-Bis(hydroxymethyl)butane-1-ol(aq)								
DSA 5000 Densimeter								
278.15	0.10	999.966	19.9832	0.0761	−1.3892	0.0538	114.19	0.09
283.15	0.10	999.702	19.5970	0.0767	−1.4449	0.0534	114.60	0.09
288.15	0.10	999.102	19.2632	0.0773	−1.4990	0.0529	115.00	0.09
293.15	0.10	998.207	18.9751	0.0782	−1.5768	0.0524	115.37	0.09
298.15	0.10	997.047	18.6980	0.0791	−1.6011	0.0519	115.76	0.09
308.15	0.10	994.033	18.2292	0.0749	−1.7039	0.0546	116.53	0.09
318.15	0.10	990.212	17.8199	0.0740	−1.8096	0.0554	117.33	0.09
HTHP Densimeter								
298.19	0.51	997.224	18.5636	0.1037	−1.4317	0.1934	115.88	0.11
318.22	0.52	990.367	17.6769	0.0520	−1.6343	0.0970	117.46	0.06
338.21	0.52	980.703	16.9207	0.0520	−1.7495	0.0965	119.22	0.06
358.17	0.52	968.790	16.1887	0.0523	−1.6910	0.0962	121.25	0.07
373.15	0.52	958.544	15.7521	0.0505	−1.7281	0.0918	122.83	0.06
398.14	2.03	939.943	15.0453	0.0514	−1.6648	0.0947	125.72	0.07
423.15	2.05	917.903	14.4596	0.0511	−1.5377	0.0941	129.01	0.07
448.15	2.04	893.024	14.0356	0.0511	−1.4504	0.0942	132.65	0.07
473.15	2.05	865.037	13.7637	0.0502	−1.3609	0.0914	136.71	0.08
498.14	3.05	834.226	13.6346	0.0433	−1.2147	0.0781	141.24	0.07
523.18	5.11	800.161	13.7537	0.0509	−1.0812	0.0920	146.20	0.09
548.16	7.00	760.624	14.1693	0.0520	−0.9243	0.0939	151.91	0.10
573.15	10.26	715.863	15.0144	0.0552	−0.7339	0.0972	158.13	0.12
298.19	15.12	1003.710	17.9477	0.0833	−1.3152	0.1556	115.86	0.09
318.21	15.08	996.629	17.2721	0.0528	−1.5419	0.0985	117.24	0.06
338.21	15.21	987.038	16.6303	0.0519	−1.6754	0.0956	118.87	0.06
358.16	15.08	975.258	16.0871	0.0506	−1.6758	0.0920	120.66	0.06
373.14	15.06	965.231	15.6343	0.0506	−1.6905	0.0920	122.23	0.06
398.15	15.04	946.399	15.0158	0.0512	−1.6337	0.0942	125.01	0.07
423.15	15.00	925.035	14.5217	0.0510	−1.5675	0.0938	128.08	0.07
448.15	15.05	901.169	14.1502	0.0511	−1.4556	0.0943	131.47	0.07
473.15	15.10	874.575	13.9623	0.0515	−1.3962	0.0945	135.16	0.08
498.14	15.14	844.844	13.8833	0.0511	−1.2635	0.0936	139.36	0.08
523.16	15.03	811.046	14.0192	0.0515	−1.1474	0.0945	144.12	0.09
548.14	15.00	772.178	14.4079	0.0511	−1.0718	0.0931	149.60	0.10
573.15	15.21	725.950	15.1312	0.0762	−0.8213	0.1373	156.11	0.16
298.22	30.48	1010.310	17.3280	0.0518	−1.2028	0.0964	115.83	0.06
318.21	29.95	1002.830	16.8493	0.0523	−1.4570	0.0978	117.04	0.06
338.21	30.15	993.265	16.3549	0.0527	−1.6318	0.0981	118.51	0.06
358.16	30.09	981.674	15.9065	0.0507	−1.6440	0.0925	120.17	0.06
373.14	30.06	971.853	15.4915	0.0509	−1.6438	0.0926	121.66	0.06
398.15	29.98	953.497	14.9551	0.0515	−1.6068	0.0948	124.27	0.07
423.15	30.06	932.893	14.5301	0.0522	−1.5414	0.0962	127.13	0.07
448.16	30.04	909.954	14.2426	0.0511	−1.4647	0.0937	130.25	0.07
473.15	29.94	884.575	14.0958	0.0504	−1.4022	0.0922	133.67	0.07
498.16	30.03	856.649	14.1032	0.0515	−1.3324	0.0942	137.41	0.08
523.16	30.02	825.564	14.2872	0.0543	−1.2134	0.0998	141.56	0.09
548.14	30.02	790.674	14.7674	0.0506	−1.3165	0.0924	146.07	0.09
573.15	29.99	750.649	15.3719	0.0665	−1.0085	0.1056	151.46	0.13

Table 1. Continued

T / K	p / MPa	ρ_1 / $kg \cdot m^{-3}$	a / $kg^2 \cdot m^{-3} \cdot mol^{-1}$	$\sigma(a)$ / $kg^2 \cdot m^{-3} \cdot mol^{-1}$	b / $kg^3 \cdot m^{-3} \cdot mol^{-2}$	$\sigma(b)$ / $kg^3 \cdot m^{-3} \cdot mol^{-2}$	$V^0_{m,2}$ / $cm^3 \cdot mol^{-1}$	$\sigma(V^0_{m,2})$ / $cm^3 \cdot mol^{-1}$
3,3,7,7-Tetrakis(hydroxymethyl)-5-oxanonane(aq)								
DSA 5000 Densimeter								
278.15	0.10	999.966	34.6939	0.4405	−4.2587	2.7766	215.64	0.44
283.15	0.10	999.702	33.8651	0.4415	−4.0126	2.7678	216.52	0.44
288.15	0.10	999.102	33.2190	0.4424	−4.5260	2.7470	217.28	0.44
293.15	0.10	998.207	32.5972	0.4435	−4.9438	2.7391	218.07	0.44
298.15	0.10	997.047	32.0373	0.4449	−5.4774	2.7308	218.85	0.44
308.15	0.10	994.033	31.0497	0.4390	−5.3044	2.7732	220.41	0.45
318.15	0.10	990.212	30.1215	0.4376	−5.5953	2.7850	222.09	0.44
HTHP Densimeter								
298.19	0.51	997.222	32.2384	0.5692	−8.4155	6.1760	218.61	0.58
318.21	0.53	990.375	29.9166	0.2910	−4.5868	3.1681	222.26	0.30
338.21	0.52	980.703	28.3141	0.2867	−5.2887	3.1141	225.82	0.30
358.16	0.51	968.791	26.7145	0.2861	−3.4871	3.0927	229.93	0.31
373.15	0.52	958.544	25.8460	0.2884	−4.0604	3.1383	233.03	0.32
398.14	2.03	939.945	24.5930	0.3139	−5.1395	3.4853	238.49	0.36
423.15	2.05	917.897	23.3206	0.3037	−2.2061	3.4005	245.05	0.36
448.15	2.04	893.024	22.6556	0.3033	−2.7497	3.4009	251.91	0.38
473.15	2.04	865.026	22.0686	0.1908	−1.1687	1.6479	259.90	0.26
498.13	3.06	834.236	22.0402	0.2732	−2.1256	2.8940	268.40	0.40
523.18	5.09	800.144	22.5267	0.2858	−3.1826	3.0542	277.67	0.45
548.15	7.03	760.675	23.2400	0.2712	−0.3241	2.7976	288.93	0.48
573.15	10.22	715.776	24.7033	0.3384	5.0696	3.4357	301.52	0.67
298.19	15.11	1003.700	30.9120	0.4373	−5.3236	4.6547	218.73	0.44
318.21	15.07	996.626	29.3509	0.3000	−5.2969	3.3051	221.63	0.31
338.21	15.24	987.052	28.0158	0.2843	−6.3578	3.0612	224.86	0.30
358.17	15.11	975.263	26.5186	0.3134	−2.9493	3.4352	228.80	0.33
373.15	15.07	965.232	25.8498	0.2885	−4.2885	3.1457	231.60	0.31
398.14	15.03	946.399	24.6382	0.3037	−4.2948	3.4043	237.00	0.34
423.14	15.01	925.040	23.7720	0.3035	−4.3809	3.4031	242.84	0.36
448.16	15.04	901.155	23.1701	0.3013	−4.2768	3.3469	249.26	0.38
473.15	15.11	874.572	22.6546	0.2689	−1.5535	2.8321	256.62	0.36
498.13	15.10	844.810	22.8450	0.2740	−3.2870	2.9030	264.31	0.39
523.16	15.03	811.049	23.3322	0.2752	−4.3017	2.9096	273.18	0.42
548.15	14.99	772.145	24.2244	0.2797	−3.6668	2.9150	283.57	0.48
573.16	15.19	725.899	25.2439	0.2723	4.0704	2.6697	296.95	0.53
298.22	30.44	1010.290	29.8539	0.4511	−5.3236	4.7528	218.53	0.45
318.21	29.89	1002.810	28.5469	0.2884	−3.8395	3.0900	221.25	0.29
338.21	30.04	993.222	27.6004	0.2873	−6.1706	3.0838	224.06	0.30
358.16	29.83	981.564	26.3245	0.2958	−3.4682	3.2240	227.71	0.31
373.15	30.02	971.830	25.7067	0.2993	−3.9382	3.3045	230.37	0.32
398.14	30.03	953.521	24.7779	0.3056	−5.3794	3.4223	235.28	0.34
423.15	30.02	932.881	24.0341	0.3157	−5.1115	3.5269	240.73	0.37
448.16	30.06	909.966	23.5150	0.3103	−3.8232	3.5026	246.70	0.38
473.16	30.03	884.624	23.1840	0.2703	−2.1348	2.8554	253.36	0.35
498.15	30.01	856.649	23.3783	0.2767	−2.4862	3.0338	260.37	0.38
523.15	30.08	825.618	24.1780	0.2752	−5.2478	2.9096	267.74	0.41
548.14	30.03	790.689	25.0658	0.3058	−3.6358	3.4088	276.51	0.50
573.16	30.08	750.750	26.4122	0.2867	0.6084	3.0523	286.58	0.52

[a] The estimated uncertainties $\sigma(a)$and $\sigma(b)$ refer to the coefficients a and b of eq 1; $\sigma(V^0_{m,2})$ represents the total estimated uncertainty.

Table 2. **Comparison of Measured Values of Standard Molar Volumes of 2,2-Dimethylpropane-1-ol at $T = 298$ K (Table 1) with the Values for $T = 298.15$ K and $p = 0.1$ MPa Taken from the Literature**

$V^{\circ}_{m,2}$, this work[a] $\text{cm}^3 \cdot \text{mol}^{-1}$	$V^{\circ}_{m,2}$, lit. $\text{cm}^3 \cdot \text{mol}^{-1}$	dev.[b]	reference
102.08 ± 0.20	102.20 ± 0.04	−0.12	Fenclová et al.[16]
	102.29 ± 0.10	−0.21	Sakurai et al.[17]
	101.87 ± 0.06	0.21	Jolicoeur and Lacroix[18]
	102.32 ± 0.50	−0.24	Roux et al.[19]

[a] The average value from Table 1 is presented since the extrapolation/interpolation from our experimental temperatures close to $T = 298$ K and our experimental pressures to $T = 298.15$ and $p = 0.1$ MPa has a negligible effect which is well below the estimated uncertainties. [b] Deviation/($\text{cm}^3 \cdot \text{mol}^{-1}$) between this work and the literature value.

Standard Molar Volumes. The partial molar volume at infinite dilution ($m_2 \rightarrow 0$) of a solute $V^{\circ}_{m,2}$ (named standard molar volume in the following text) is obtained from eq 1 as[9]

$$V^{0}_{m,2} = \{M_2 - (a/\rho_1)\}/\rho_1 \tag{2}$$

where M_2 is the molar mass of the solute.

The standard molar volumes calculated from the experimental data and their estimated uncertainties are presented in Table 1. The uncertainties in $V^{\circ}_{m,2}$ given in Table 1 include random error estimates, which originate from the scatter associated with eq 1, as well as systematic errors estimated from uncertainties of temperature, pressure, and the calibration constant. Obviously, the uncertainties are highly affected by the width of the experimental concentration range (limited by the solubility in case of 2,2-dimethylpropane-1-ol and 3,3,7,7-tetrakis(hydroxymethyl)-5-oxanonane). Since the density differences obtained using the HTHP densimeter are measured with respect to degassed water,[9,11] an additional uncertainty related to the uncertainty of the measured density difference between degassed and nitrogen-saturated water was taken into account.

Temperature ranges of the two densimeters overlap at low pressures (atmospheric for the DSA5000 densimeter and about 0.5 MPa for the HTHP device). Despite that the experimental temperatures are not identical and pressures differ by about 0.4 MPa, the values of standard molar volumes are comparable. The agreement between values obtained independently using our two densimeters at $T = (298 \text{ and } 318)$ K is excellent (better at 298 K) and well within the estimated uncertainties. Table 2 presents a comparison of our values of standard molar volume of aqueous 2,2-dimethylpropane-1-ol at $T = 298$ K and low pressure with data available in the literature for $T = 298.15$ K and atmospheric pressure. The agreement is within estimated uncertainties in all cases. No other data for solutes investigated here have been found in the literature for a comparison.

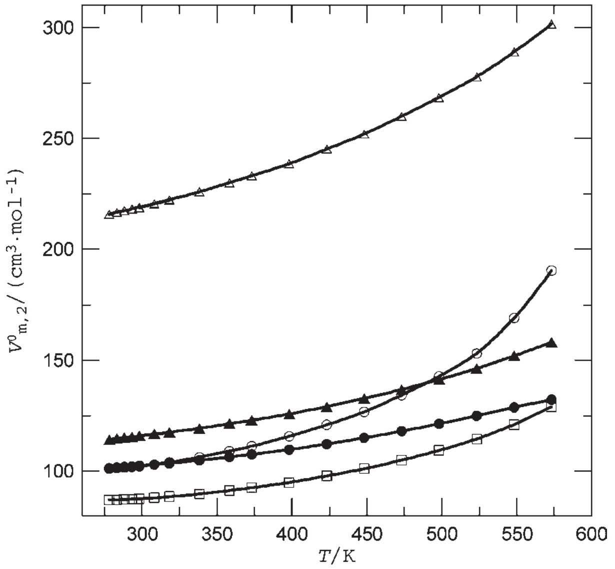

Figure 2. Plots of experimental standard molar volumes at low pressures against temperature. The lines are to aid the eye. ○, 2,2-dimethylpropane-1-ol; □, 2-methylpropane-1,3-diol; ●, 2,2-bis(hydroxymethyl)-propane-1-ol; ▲, 2,2-bis(hydroxymethyl)butane-1-ol; △, 3,3,7,7-tetrakis-(hydroxymethyl)-5-oxanonane.

Experimental standard molar volumes of the five solutes at low pressure (the lowest pressures of each isotherm) are shown in Figure 2. Effects of the molecular structure (hydrocarbon frame, number of hydroxyl groups) on standard molar volume and its evolution with temperature and pressure are analyzed below along with a comparison with our previous observations. To make the analysis and the comparison feasible, the experimental values of standard molar volumes of each solute (experimental surface $V^{\circ}_{m,2}(T,p)$) were smoothed using a polynomial function

$$V^{0}_{m,2}/(\text{cm}^3 \cdot \text{mol}^{-1}) = \sum_{i=1}^{N_T} \sum_{j=1}^{3} a_{ij} (T/\text{K})^{(i-1)} (p/\text{MPa})^{(j-1)} \tag{3}$$

The adjustable parameters a_{ij} were evaluated using the weighted least-squares procedure by minimizing the objective function

$$\phi(\{a_{ij}\}) = \sum_{k=1}^{N} \left\{ \frac{(V^{0(\text{exp})}_{m,2})_k - \sum_{i=1}^{N_T} \sum_{j=1}^{3} a_{ij} T_k^{(i-1)} p_k^{(j-1)}}{\sigma(V^{0(\text{exp})}_{m,2})_k} \right\}^2 \tag{4}$$

Estimated experimental uncertainties were used for the weights $1/[\sigma(V^{0(\text{exp})}_{m,2})_k]^2$. The summation in eq 4 is performed over all experimental data points N reported for a particular solute. Since measurements at three pressures were performed for each isotherm (except for $T < 298$ K), the resulting fits are interpolations in pressure (isotherms are fitted with the second-order polynomials in pressure) while the maximum order of the polynomial with respect to temperature, N_T, was chosen according to the significance of respective parameters. A random distribution of deviations between experimental values and those calculated from eq 1 was adopted as a criterion. Values of parameters along with standard deviations and weighted standard deviations of the fits are presented in the Supporting Information (Table S6). Since extrapolations using a polynomial function are not reliable, the calculations of standard molar volumes from the fits for $T < 298$ K is not recommended for pressures other than 0.1 MPa. Parameters of the fits of data for aqueous propane-1,3-diol,[4] 2,2-dimethylpropane-1,3-diol,[6] and 2,2-bis(hydroxymethyl)propane-1,3-diol[6] taken from our previous paper[1] are also presented in Table S6 of the Supporting Information.

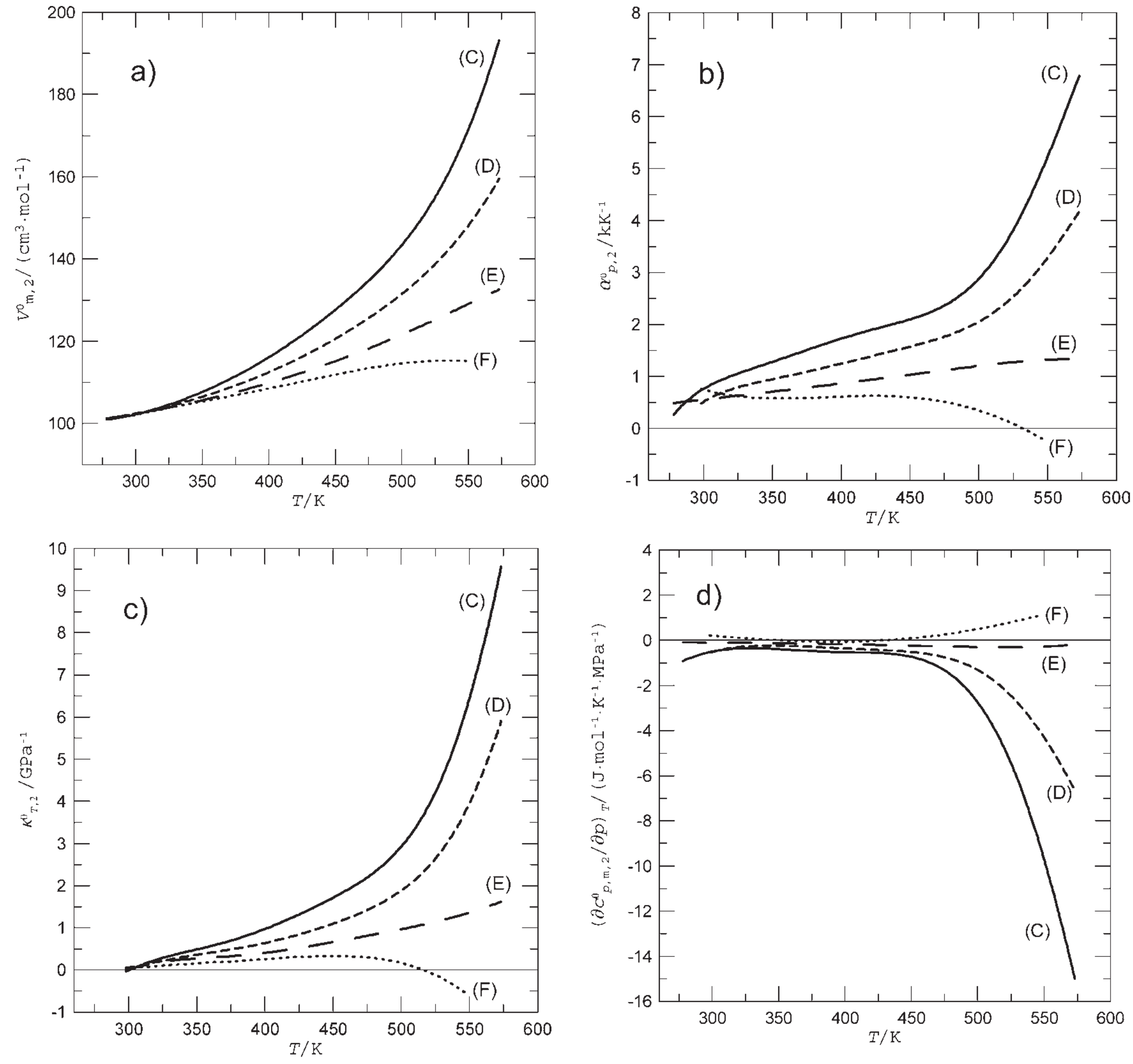

Figure 3. Plots of smoothed quantities calculated from the fits (3) for alcohols derived from 2,2-dimethylpropane along the saturation line of water against temperature. (a) Standard molar volume $V^0_{m,2}$; (b) isobaric expansivity $\alpha^0_{p,2} = (1/V^0_{m,2})(\partial V^0_{m,2}/\partial T)_p$; (c) isothermal compressibility $\kappa^0_{T,2} = -(1/V^0_{m,2})(\partial V^0_{m,2}/\partial p)_T$; (d) derivative of standard heat capacity with respect to pressure $(\partial c^0_{p,m,2}/\partial p)_T = -T(\partial^2 V^0_{m,2}/\partial T^2)_p$. Solid line, (C) 2,2-dimethylpropane-1-ol; short dashed line, (D) 2,2-dimethylpropane-1,3-diol;[6] long dashed line, (E) 2,2-bis(hydroxymethyl)propane-1-ol; dotted line, (F) 2,2-bis(hydroxymethyl)propane-1,3-diol.[6]

Derived Quantities. Smoothing functions make the mutual comparison feasible not only for standard molar volumes but also for some derived quantities. The derived quantities considered below for a comparison are: the relative change of standard molar volume per unit change of temperature, $\alpha^0_{p,2} = (1/V^0_{m,2})(\partial V^0_{m,2}/\partial T)_p$ (named shortly isobaric expansivity in the following text), negative relative change of standard molar volume per unit change of pressure, $\kappa^0_{T,2} = -(1/V^0_{m,2})(\partial V^0_{m,2}/\partial p)_T$ (named shortly isothermal compressibility in the following text), and the change of standard heat capacity per unit change of pressure, $(\partial c^0_{p,m,2}/\partial p)_T = -T(\partial^2 V^0_{m,2}/\partial T^2)_p$. Values plotted in the following graphs are calculated for pressures 0.1 MPa at $T \leq 373.15$ K and for saturated vapor pressure of water at higher temperatures; this pressure set is called the saturation line of water.

Figure 3 presents a mutual comparison of the standard molar volume and derived quantities of all four aqueous alcohols having the hydrocarbon frame of 2,2-dimethylpropane. As it is already indicated in Figure 2, standard molar volumes of 2,2-dimethylpropane-1-ol (one hydroxyl group) and 2,2-bis(hydroxymethyl)propane-1-ol (three hydroxyl groups) at temperatures around 298 K are nearly identical. Experimental curves $V^0_{m,2}(T)$ at low pressure intersect each other at about 308 K (volumes $V^0_{m,2}(T = 308.15\text{ K}, p = 0.1\text{ MPa})$ are (102.81 and 102.83) cm^3·mol^{-1} for 2,2-dimethylpropane-1-ol and 2,2-bis(hydroxymethyl)propane-1-ol, respectively, see Table 1), and the temperature of the intersection point at 30 MPa is somewhat higher being about 312 K. Figure 3a reveals that this observation holds for all four alcohols, that is, that the substitution of the hydrogen atom in the methyl group with the hydroxyl group has no effect on the standard molar volume in this temperature range. The deviations of standard molar volumes of individual alcohols at $T = 298.15$ K from the average value are, independently of pressure, within ± 0.2 cm^3·mol^{-1}, which is the value close to experimental uncertainties. The effect of the number of hydroxyl groups becomes significant as the temperature increases. As it is shown in Figures 3a through d, the dependences on the ratio between hydrophilic part of the molecule (hydroxyl groups) and hydrophobic part (hydrocarbon frame which remains unchanged

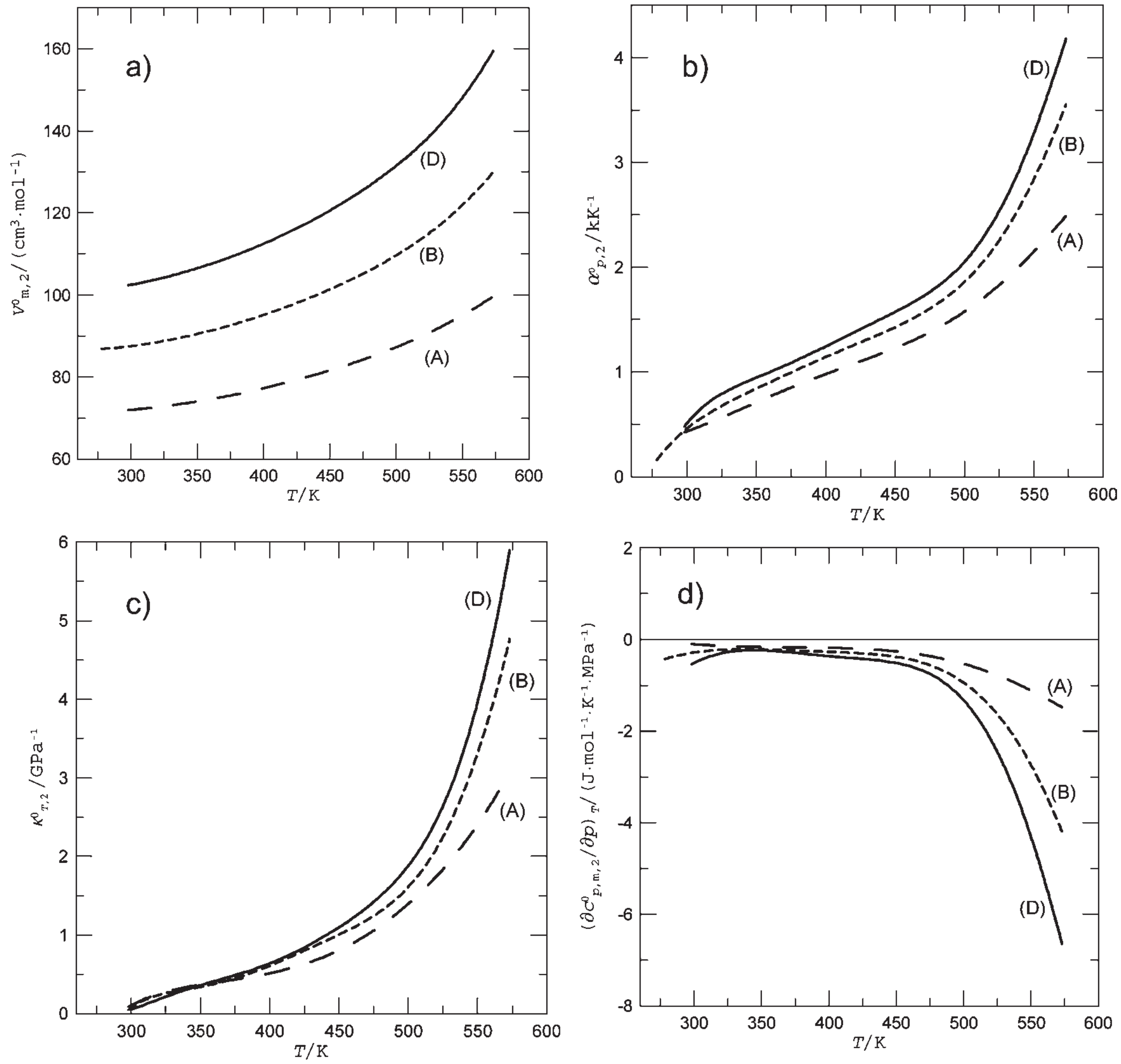

Figure 4. Plots of smoothed quantities calculated from the fits (3) for diols along the saturation line of water against temperature. (a) Standard molar volume $V^0_{m,2}$; (b) isobaric expansivity $\alpha^0_{p,2} = (1/V^0_{m,2})(\partial V^0_{m,2}/\partial T)_p$; (c) isothermal compressibility $\kappa^0_{T,2} = -(1/V^0_{m,2})(\partial V^0_{m,2}/\partial p)_T$; (d) derivative of standard heat capacity with respect to pressure $(\partial c^0_{p,m,2}/\partial p)_T = -T(\partial^2 V^0_{m,2}/\partial T^2)_p$. Solid line, (D) 2,2-dimethylpropane-1,3-diol;[6] short dashed line, (B) 2-methylpropane-1,3-diol; long dashed line, (A) propane-1,3-diol.[4]

within this series) are strictly monotonous for all quantities investigated, even for $(\partial c^0_{p,m,2}/\partial p)_T$ which is determined by the second derivative of standard molar volume with respect to temperature and thus more sensitive to the quality of experimental data. Same effects can be observed for the series of propane-1,3-diol and its 2-methyl derivatives (Figure 4). Here the number of hydroxyl groups remains constant, and the size of the hydrophobic part increases from propane-1,3-diol (A) to 2,2-dimethylpropane-1,3-diol (D). Naturally, standard molar volumes differ by the volume contribution of the methylene group (Figure 4a), but three other quantities (Figures 4b through d) are affected by the ratio between hydrophilic and hydrophobic part of the solute molecule and monotonous dependences on this ratio, similar as with the series above, are observed. A note should be given concerning the low temperature range. As it is obvious in Figures 3b and 4b the dependence of the isobaric expansivity on the hydrophilic/hydrophobic ratio is inversed compared to that at higher temperatures. All above observations are in perfect accordance with analyses performed for other aliphatic alcohols[20] and other classes of aqueous organic solutes (cyclic ethers,[21,22] cyclic ketones[15,23]) and confirm a general character of this behavior.

Group Contributions. Figure 5 shows a comparison of the volume increment related to the methylene group $-CH_2-$ obtained by subtracting standard molar volumes of various pairs of solutes under investigation. The full line in Figure 5 represents the contribution obtained from the group additivity scheme[1] in which all methylene segments were regarded equivalent and independent of neighboring groups (first-order group contribution scheme). The methylene groups in molecules of most solutes the data of which were used for the evaluation of group contributions[1] were located in the linear nonbranched chains. The contribution that corresponds to the insertion of the methylene group between quaternary carbon atom and the methyl group of 2,2-bis(hydroxymethyl)propane-1-ol (E) resulting in 2,2-bis(hydroxymethyl)butane-1-ol (G), $V^0_{m,2}(G) - V^0_{m,2}(E)$, is significantly lower (by 2.3 $cm^3 \cdot mol^{-1}$ in average, see the dotted line in Figure 5) than the contribution obtained from the group contribution method.[1] Thus it seems likely that the methylene

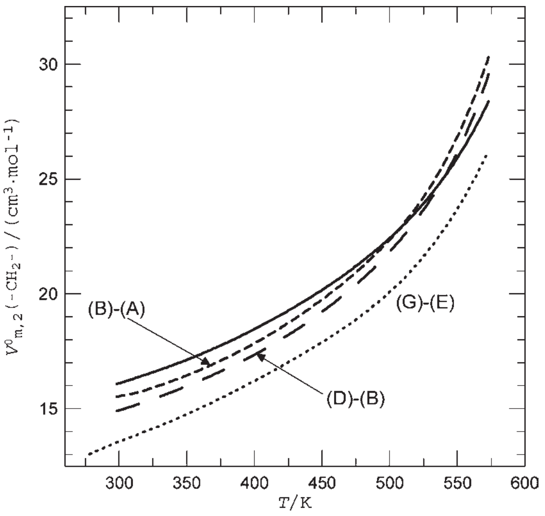

Figure 5. Plots of the contribution of the methylene group ($-CH_2-$) along the saturation line of water calculated from smoothed standard molar volumes of various pairs of solutes against temperature. For the solutes and their molecular structures substituted here by the uppercase letters see Figure 1. Solid line, group contribution method;[1] short dashed line, $V^0_{m,2}(B) - V^0_{m,2}(A)$; long dashed line, $V^0_{m,2}(D) - V^0_{m,2}(B)$; dotted line, $V^0_{m,2}(G) - V^0_{m,2}(E)$.

group hidden in the globular structure of the carbon frame of 2,2-bis(hydroxymethyl)butane-1-ol is less accessible to the hydrophobic interactions with water and consequently contributes less to the standard molar volume of the solute in comparison with the methylene group in a linear chain that is more exposed to interactions with water molecules. An analogous case can be observed with quaternary carbon atom whose volume contribution is significantly lower than would correspond to the value obtained by subtracting contributions of two hydrogen atoms from the contribution of the methylene group as can be verified using the group contributions.[1]

On the other hand the volumes of the methylene segment evaluated from standard molar volumes of the solute pairs {2-methylpropane-1,3-diol (B) and propane-1,3-diol (A)} (short-dashed line in Figure 5) and {2,2-dimethylpropane-1,3-diol (D) and 2-methylpropane-1,3-diol (B)} (long-dashed line in Figure 5) are much closer to those resulting from the group contribution method.[1] The fact that the methylene increment $V^0_{m,2}(D) - V^0_{m,2}(B)$ is lower than $V^0_{m,2}(B) - V^0_{m,2}(A)$ supports the explanation concerning the values $V^0_{m,2}(G) - V^0_{m,2}(E)$ given above; the steric hindrance of the methylene group in the side chain of 2,2-dimethylpropane-1,3-diol(D) is greater than that in the side chain of 2-methylpropane-1,3-diol (B). It should be noted, however, that these methylene segments are related to the insertion of the $-CH_2-$ group into the bond C−H, and the resulting structure $-CH_2-H$ is regarded as a combination of two groups (a methylene group and a hydrogen atom). On the other hand, in the group contribution method[1] the combination $-CH_2-H$ stands for the methyl group $-CH_3$. Thus the methylene group in the structure $-CH_2-H$ is not equivalent to the methylene group of the group contribution method[1] which corresponds to the structures $X-CH_2-Y$ where X and Y are groups or atoms other than hydrogen.

Predictions. Group contributions from our previous work[1] were employed for predictions of standard molar volumes of the solutes investigated in this work. The deviations between predicted and smoothed experimental values along the saturation line of water are shown in Figure 6. Similar curves can be obtained for higher pressures, and the deviations decrease with increasing pressure, particularly in the high temperature range where for p = 30 MPa the negative deviations do not exceed -0.6 $cm^3 \cdot mol^{-1}$ for diols (compare with -1 $cm^3 \cdot mol^{-1}$ in Figure 6a) and -7 $cm^3 \cdot mol^{-1}$ for other solutes (compare with -11 $cm^3 \cdot mol^{-1}$ in Figure 6b). Positive deviations of 2-methylpropane-1,3-diol (B, Figure 6a) and those at lower temperature range in Figure 6b remain nearly unchanged with increasing pressure. Deviations for 2,2-dimethylpropane-1,3-diol (D) are zero since in the set of solutes, the data of which were used for the evaluation of group contributions,[1] this solute was the only one with the quaternary carbon atom in the molecule. The curve shown for propane-1,3-diol (Figure 6a, curve A) does not represent the prediction since experimental data of this solute were included in the data set used for the evaluation of contributions.[1]

Figures 6a,b show that standard molar volumes of solutes with one and two hydroxyl groups are predicted very satisfactorily, and the deviations are within 1 $cm^3 \cdot mol^{-1}$ (2-methylpropane-1,3-diol, (B), Figure 6a) and -1.5 $cm^3 \cdot mol^{-1}$ (2,2-dimethylpropane-1-ol, (C), Figure 6b), respectively, in the entire temperature and pressure ranges. Large deviations are observed for solutes with more than two hydroxyl groups (Figure 6b). The deviation curves have similar shapes. In the lower temperature range the deviations are positive and turn out to be negative when temperature increases. The deviations depend distinctly on the number of hydroxyl groups; their magnitudes increase with the increasing number of hydroxyl groups in both the positive (low temperatures) and the negative (higher temperatures) directions as can be clearly seen on the curves (E) (2,2-bis(hydroxymethyl)propane-1-ol, three −OH groups) and (F) (2,2-bis(hydroxymethyl)propane-1,3-diol, four −OH groups). This observation indicates that the intramolecular interactions of hydroxyl groups on the globular molecular surface increase the hydrophilic character of the solute molecule (resulting in smaller standard molar volume) at low temperatures while at high temperatures the hydrophilic character is being depressed (resulting in greater standard molar volume). This is in a perfect accordance with the character of the structural contribution (correction) (OH)∼(OH) attributed to the close vicinity of two hydroxyl groups,[1] that is, to the pair of hydroxyl groups residing on neighboring carbon atoms of nonbranched linear hydrocarbon chains. This structural contribution is negative at lower temperatures and increases to positive values as the temperature increases. The present observation indicates that hydroxyl groups on the surface of the molecules of globular polyhydric alcohols derived from 2,2-dimethylpropane affect the character of the solute in the same manner as close hydroxyl groups on the linear aliphatic chain.

The deviation curve (G) in Figure 6b (2,2-bis(hydroxymethyl)butane-1-ol, three −OH groups) has a similar shape as the curve (E) (2,2-bis(hydroxymethyl)propane-1-ol, three −OH groups), but it is shifted by about (1 to 2) $cm^3 \cdot mol^{-1}$ upward. This is obvious consequence of the fact that the contribution of the "hidden" methylene group of the ethyl substituent in 2,2-bis-(hydroxymethyl)butane-1-ol is lower than larger contribution resulting from linear or moderately branched carbon chains[1] used for the prediction (see also the discussion related to Figure 5 above).

The deviation curve (H) (3,3,7,7-tetrakis(hydroxymethyl)-5-oxanonane, dotted line in Figure 6b) has a similar shape as those for other polyhydric alcohols. Two pairs of hydroxyl groups are located on both globular ends of this large molecule, but due to the flexibility of the connection chain the intramolecular OH∼OH interactions may occur. The effect of these interactions on the character of this solute is likely to be similar as that of

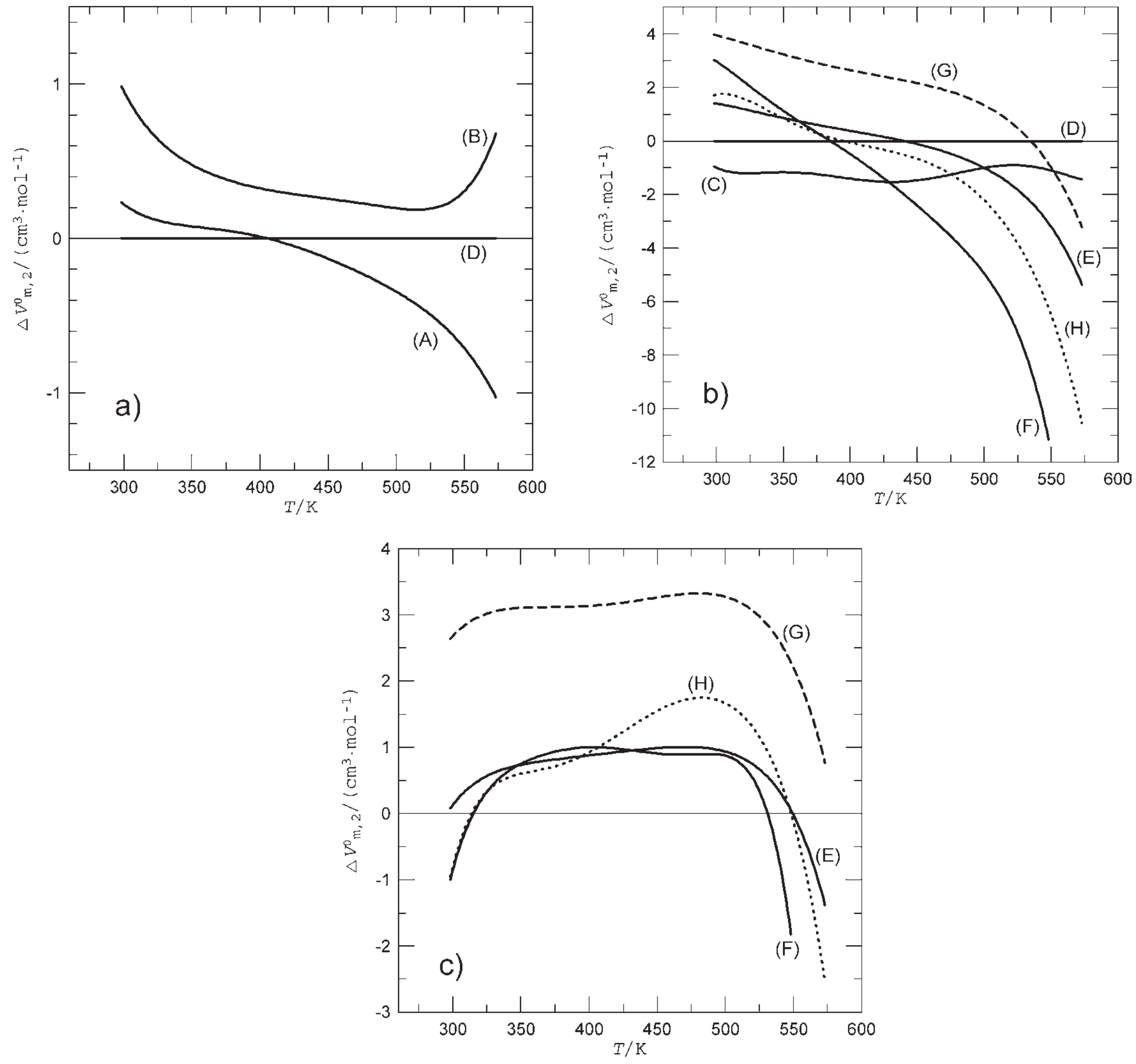

Figure 6. Plots of deviations of predicted standard molar volumes from smoothed experimental values, $\Delta V^0_{m,2} = V_{m,2}{}^0$(predicted) $-$ $V^0_{m,2}$(experimental) along the saturation line of water against temperature. (a) Diols; (b) solutes with quaternary carbon atom(s); (c) polyols with quaternary carbon atom(s) corrected using (OH)~(OH) structural correction. (A) Propane-1,3-diol; (B) 2-methylpropane-1,3-diol; (C) 2,2-dimethylpropane-1-ol; (D) 2,2-dimethylpropane-1,3-diol; (E) 2,2-bis(hydroxymethyl)propane-1-ol; (F) 2,2-bis(hydroxymethyl)propane-1,3-diol; (G) 2,2-bis(hydroxymethyl)butane-1-ol; (H) 3,3,7,7-tetrakis-(hydroxymethyl)-5-oxanonane.

multiple hydroxyl groups on the surface of molecules of polyhydric alcohols derived from 2,2-dimethylpropane.

The similar character of the dependences (E), (F), (G), and (H) in Figure 6b indicates that a common structural contribution (correction) could be introduced into future versions of the group contribution schemes. Here we have tentatively applied the (OH)~(OH) structural contribution which resulted from our group contribution method[1] and is based on data for diols with neighboring hydroxyl groups (ethane-1,2-diol, propane-1,2-diol, butane-2,3-diol). One structural contribution (OH)~(OH) was added to 2,2-bis(hydroxymethyl)propane-1-ol (E) and 2,2-bis(hydroxymethyl)butane-1-ol (G), two same contributions were added to 3,3,7,7-tetrakis(hydroxymethyl)-5-oxanonane (H), and three contributions were added to 2,2-bis(hydroxymethyl)propane-1,3-diol (F). Deviation plots for these corrected estimates are shown in Figure 6c. Obviously the estimations are significantly improved. The curves of similar shapes are obtained; that for 2,2-bis(hydroxymethyl)butane-1-ol (G) is shifted upward by about 2 cm^3·mol^{-1} as a consequence of the difference between the contributions of "hidden" methylene group and that issuing from the group contribution method (see Figure 5 and the related discussion above). The improved estimates, despite that they were obtained in a purely empirical way, indicate that there is a chance for the introduction of a proper structural contribution describing the effects of the multiple hydroxyl groups on the surface of the globular carbon frame. Thus the group contributions[1] are worth to be updated using new, possibly even more extended experimental data.

■ ASSOCIATED CONTENT

Supporting Information. Measured values of the density differences $\Delta\rho = \rho - \rho_1$ where ρ and ρ_1 are the densities of the solution and water, respectively, and the molalities of organic solutes m_2 at various temperatures and pressures. The parameters of the smoothing polynomial (eq 3) for the aqueous solutes under investigation. This material is available free of charge via the Internet at http://pubs.acs.org.

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