

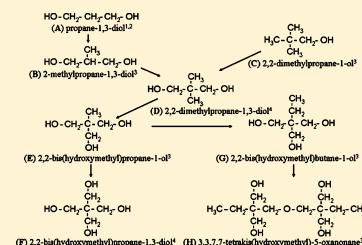
Partial Molar Isentropic Compressions and Partial Molar Volumes of Selected Branched Aliphatic Alcohols at Infinite Dilution in Water at Temperatures from $T = (278 \text{ to } 318) \text{ K}$ and Atmospheric Pressure

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Supporting Information

ABSTRACT: Speed of sound data for dilute aqueous solutions of one monohydric alcohol (2,2-dimethylpropane-1-ol), five polyhydric alcohols (2-methylpropane-1,3-diol, 2,2-dimethylpropane-1,3-diol, 2,2-bis(hydroxymethyl)propane-1-ol, 2,2-bis(hydroxymethyl)propane-1,3-diol, 2,2-bis(hydroxymethyl)butane-1-ol), and one ether alcohol (3,3,7,7-tetrakis(hydroxymethyl)-5-oxanonane) were obtained using the Anton Paar DSA 5000 vibrating-tube densimeter and sound analyzer in the temperature range from (278.15 to 318.15) K and at atmospheric pressure. Standard molar isentropic compressions were evaluated from the measured data. Measured densities of dilute aqueous solutions of 2,2-dimethylpropane-1,3-diol and 2,2-bis(hydroxymethyl)propane-1,3-diol are also presented along with the standard molar volumes of these two solutes calculated from the measured data. Relations between the two standard quantities and molecular structures of the solutes are discussed.



INTRODUCTION

This work is a part of the series devoted to the systematic study of volumetric properties of organic solutes in water. The recent installation of the commercial device DSA 5000 (Anton Paar, Austria) enables simultaneous measurements of density and speed of sound, and thus we can extend our previous density measurements performed in wide temperature and pressure ranges using a flow vibrating-tube technique. This study is predominantly focused on the presentation of experimental speed of sound data measured in the temperature range from (278 to 318) K for dilute aqueous solutions of solutes the density data of which has been already published (with two exceptions, see below). New data make it possible to evaluate the partial molar isentropic compression at infinite dilution (standard molar isentropic compression) in water, though under atmospheric pressure and in a rather limited temperature range only. The solutes studied in this work (except for aqueous propane-1,3-diol the density and speed of sound data of which have been already published^{1,2}) are identical with those considered in our recent paper³ and are summarized in Figure 1. Solute series are incremented by either a methylene group $-\text{CH}_2-$ (series A, B, D and E, G) or a hydroxyl group $-\text{OH}$ (series C, D, E, F). The largest molecule, 3,3,7,7-tetrakis(hydroxymethyl)-5-oxanonane (H), is composed of two structures of 2,2-bis(hydroxymethyl)butane-1-ol (G) combined together by the ether oxygen atom.

The volumetric behavior (density of dilute solutions, standard molar volumes) of the solutes in water has been already studied, and the results are published: propane-1,3-diol^{1,2} (A), 2-methylpropane-1,3-diol³ (B), 2,2-dimethylpropane-1-ol³ (C), 2,2-bis(hydroxymethyl)propane-1-ol³ (E), 2,2-bis(hydroxymethyl)butane-1-ol³ (G), and 3,3,7,7-tetrakis(hydroxymethyl)-5-oxanonane³ (H) in the temperature range

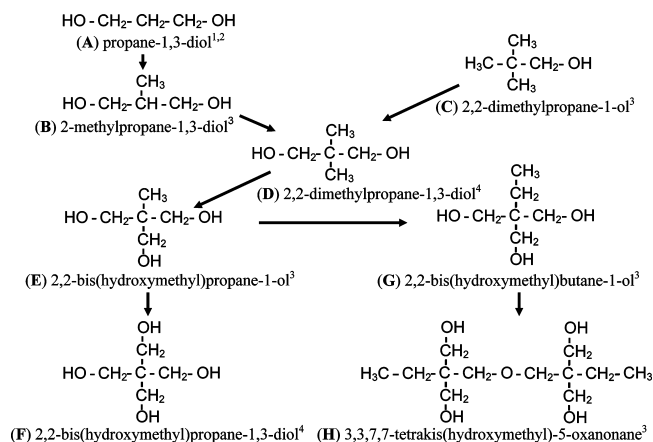


Figure 1. Structures of solute molecules. Reference numbers indicate the sources where the experimental standard molar volumes can be found (ref 3 for the range from (278 to 573) K, ref 4 for the range from (298 to 573) K). Data for aqueous propane-1,3-diol have been published previously (standard molar volumes from (298 to 573) K in ref 1, standard molar volumes and standard molar isentropic compressions from (278 to 318) K in ref 2).

from (278 to 573) K and pressures up to 30 MPa; 2,2-dimethylpropane-1,3-diol⁴ (D) and 2,2-bis(hydroxymethyl)propane-1,3-diol⁴ (F) in the temperature range from (298 to 573) K and pressures up to 30 MPa. Densities at temperatures between (278 and 318 K) and at atmospheric pressure³ were measured using the DSA 5000 vibrating-tube densimeter, and

Received: February 10, 2012

Accepted: April 7, 2012

Published: April 18, 2012

measurements in the range from (298 to 573) K and at elevated pressures^{3,4} were performed by our high-temperature high-pressure flow vibrating-tube densimeter.^{5,6}

Data on speed of sound in dilute aqueous solutions combined with densities either published previously³ or presented in this work for aqueous 2,2-dimethylpropane-1,3-diol (D) and 2,2-bis(hydroxymethyl)propane-1,3-diol (F) enabled us to evaluate the standard molar isentropic compression. The values obtained for aqueous propane-1,3-diol (A) were published recently.² Standard molar volumes of 2,2-dimethylpropane-1,3-diol (D) and 2,2-bis(hydroxymethyl)propane-1,3-diol (F) were also calculated using new density data measured in the range from (278 to 318) K and combined with values for extended ranges of temperature and pressure.⁴ Finally the standard molar isentropic compressions and standard molar volumes presented here in combination with those obtained previously were employed for the discussion of the property–structure relations.

EXPERIMENTAL SECTION

The specifications of the organic solutes are summarized in Table 1. Distilled, demineralized (Millipore RQ) water was

Table 1. Specifications of Chemical Samples of Solute^a

chemical name	formula	CAS RN	mass fraction purity ^b
2-methylpropane-1,3-diol	C ₄ H ₁₀ O ₂	2163-42-0	0.99
2,2-dimethylpropane-1-ol	C ₅ H ₁₂ O	75-84-3	0.99
2,2-dimethylpropane-1,3-diol	C ₅ H ₁₂ O ₂	126-30-7	0.99
2,2-bis(hydroxymethyl)propane-1-ol	C ₅ H ₁₂ O ₃	77-85-0	0.99
2,2-bis(hydroxymethyl)butane-1-ol	C ₆ H ₁₄ O ₃	77-99-6	0.98
2,2-bis(hydroxymethyl)propane-1,3-diol	C ₅ H ₁₂ O ₄	115-77-5	≥ 0.98
3,3,7,7-tetrakis(hydroxymethyl)-5-oxanonane	C ₁₂ H ₂₆ O ₅	23235-61-2	0.97

^aAll samples were from Sigma Aldrich and were used as supplied.

^bDeclared by the supplier.

used as a calibration fluid for the densimeter and for the preparation of solutions. Solutions were prepared by mass using a Precisa 40SM-200A balance (resolution = 10^{−2} mg, uncertainty = ± 0.1 mg, maximum load 200 g) to determine the mass of the solute and an A&D Instruments GF-3000-EC balance (resolution = 10 mg, estimated uncertainty = ± 2·10^{−2} percent, maximum load 3.1 kg) to determine the mass of water. The mass of each prepared solution was about 1 kg. Air-saturated water was used for the preparation of solutions. Four to six solutions in the molality range from (0.1 to 0.6) mol kg^{−1} were measured for each solute; solutions in a lower concentration range were prepared for solutes with a smaller solubility in water.

The vibrating-tube densimeter and sound analyzer manufactured by Anton Paar, model DSA 5000, with a built-in thermostat and equipped with the autosampler SP-1 m (Anton Paar) was used for the measurements. The highest temperature at which the air-bubbles 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 reading the raw data from the device memory and to perform the consequent evaluation.

Measurements were performed in an isothermal mode; that is, the measurements of all prepared solution were done at the same particular temperature, then the temperature was changed, and the measurements were repeated. Several vials filled with air-saturated pure water were included and distributed in the measured sample set. The samples of water preceded and followed each set of solutions of a particular solute; that is, each set of solutions was “bracketed” by pure water. The reproducibility of these doubled measurements of speed of sound was between ± 0.03 m·s^{−1} at 278.15 K and ± 0.06 m·s^{−1} at 298.15 K; significantly larger scatter ± 0.2 m·s^{−1} was observed at 318.15 K (it is likely that sound waves caused the generation of air microbubbles in the samples). The reproducibility of the measurements of density of water was usually ± 1·10^{−3} kg·m^{−3} (slightly worse at higher temperatures). To minimize the effects of both the device drifts and the systematic uncertainties in the calibration the averages of two values measured for speed of sound (c_1) and those for density of water (ρ_1) at each temperature and for each set of solutions were used to calculate the differences in speed of sound $\Delta c = c - c_1$ and the density differences $\Delta \rho = \rho - \rho_1$ where ρ and c are the densities of and speed of sound in the solution, respectively.

It was observed that experimental values of c_1 and ρ_1 exhibited systematic deviations from values presented by the National Institute of Standards and Technology (NIST).⁷ Measured speeds of sound were systematically higher (average deviation 0.7 m·s^{−1}), and experimental densities were slightly higher at low temperatures (by about 0.015 kg·m^{−3}) and lower at higher temperatures (by 0.004 kg·m^{−3}). The effect of these small deviations on the goal quantities (standard molar isentropic compressions, standard molar volumes) is negligible since in the differences $\Delta[(\rho c)^2] = (\rho c)^2 - (\rho_1 c_1)^2$ and $\Delta \rho = \rho - \rho_1$ (see below) these systematic deviations cancel out to a great extent. Therefore measured differences Δc and $\Delta \rho$ were regarded as direct experimental data, and the values c_1 (NIST) and ρ_1 (NIST) were used for the evaluations of standard molar isentropic compressions and standard molar volumes (see below) as well as for the calculations of speeds of sound in and densities of solutions, that is, $c = \Delta c(\text{experimental}) + c_1(\text{NIST})$ and $\rho = \Delta \rho(\text{experimental}) + \rho_1(\text{NIST})$ as needed for the evaluation of standard molar isentropic compressions. The effect on the values $\Delta[(\rho c)^2]/m_2$, that is, on the parameter a_K (see below), compared to the case when $c = \Delta c(\text{experimental}) + c_1(\text{experimental})$ and $\rho = \Delta \rho(\text{experimental}) + \rho_1(\text{experimental})$ was found to be less than 0.06 %. The values c_1 and ρ_1 extracted from the NIST database⁷ are summarized in Table 2.

Table 2. Values of Density ρ_1 of and Speed of Sound c_1 in Water (NIST)⁷ Used in Calculations of Standard Molar Isentropic Compression and Standard Molar Volume

T/K	$\rho_1/\text{kg}\cdot\text{m}^{-3}$	$c_1/\text{m}\cdot\text{s}^{-1}$
278.15	999.967	1426.17
283.15	999.702	1447.27
288.15	999.103	1465.93
293.15	998.207	1482.35
298.15	997.048	1496.70
303.15	995.649	1509.15
308.15	994.033	1519.85
318.15	990.213	1536.45

Table 3. Experimental Differences $\Delta c = c - c_1$ Measured for {2-Methylpropane-1,3-diol (2), 2,2-Dimethylpropane-1-ol (2), 2,2-Dimethylpropane-1,3-diol (2), 2,2-Bis(hydroxymethyl)propane-1-ol (2), 2,2-Bis(hydroxymethyl)propane-1,3-diol (2), 2,2-Bis(hydroxymethyl)butane-1-ol (2), or 3,3,7,7-Tetrakis(hydroxymethyl)-5-oxanonane (2) + Water (1)} at Atmospheric Pressure^a

m_2	$\Delta c/\text{m}\cdot\text{s}^{-1}$							
$\text{mol}\cdot\text{kg}^{-1}$	$T/\text{K} = 278.15$	283.15	288.15	293.15	298.15	303.15	308.15	318.15
2-Methylpropane-1,3-diol(aq)								
0.109745	7.79	7.16	6.63	6.11	5.64		4.83	3.96
0.109745	7.82	7.18	6.65	6.13	5.66			4.12
0.199656	14.15	12.99	12.00	11.07	10.22		8.73	7.30
0.199656	14.19	13.03	12.02	11.09	10.24			7.59
0.309109	21.78	20.00	18.44	17.02	15.72		13.76	11.40
0.309109	21.82	20.06	18.46	17.05	15.74		13.41	11.56
0.398301	27.89	25.63	23.64	21.78	20.10		17.50	14.61
0.398301	27.93	25.68	23.65	21.81	20.13		17.15	14.71
2,2-Dimethylpropan-1-ol(aq)								
0.048498	5.75	5.27	4.81	4.40	4.02		3.46	2.62
0.048498	5.75	5.25	4.77	4.41	4.03		3.21	2.70
0.099947	11.70	10.71	9.81	8.98	8.21		6.74	5.31
0.099947	11.66	10.67	9.77	8.98	8.20		6.58	5.33
0.147155	17.24	15.71	14.32	13.12	11.98		9.88	7.81
0.147155	17.16	15.65	14.28	13.10	11.97		9.67	7.78
0.199879	23.23	21.21	19.30	17.67	16.14		13.06	10.46
0.199879	23.17	21.11	19.24	17.64	16.13		13.02	10.45
2,2-Dimethylpropane-1,3-diol(aq)								
0.100116	9.68	8.88	8.19	7.58		6.46	5.91	5.03
0.100116			8.21	7.57	6.96	6.45	5.97	5.02
0.100116	9.67	8.90	8.22		6.99	6.45	5.90	4.99
0.200606	19.19	17.63	16.29	15.02	13.81	12.78	11.71	9.93
0.200606		17.63	16.24	15.01	13.85	12.77	11.79	9.92
0.200606	19.19	17.66	16.28	14.98	13.90	12.75	11.70	9.9
0.299683	28.32	26.05	24.05	22.16	20.41	18.84	17.30	14.53
0.299683		26.06	24.01	22.16	20.46	18.83	17.38	14.56
0.299683	28.33	26.09	24.04	22.14	20.50	18.83	17.29	14.54
0.402055	37.62	34.59	31.91	29.41	27.07	24.96	22.92	19.18
0.402055	37.59	34.60	31.87	29.40	27.13	24.94	22.99	19.21
0.402055	37.62	34.63	31.90	29.40	27.16	24.97	22.90	19.19
0.500081	46.34	42.59	39.27	36.16	33.30	30.67	28.13	23.49
0.500081	46.35	42.61	39.25	36.16	33.37	30.65	28.21	23.52
0.500081	46.36	42.65	39.27	36.16	33.39	30.71	28.10	23.55
0.600673	55.09	50.63	46.64	42.93	39.53	36.34	33.30	27.75
0.600673	55.11	50.64	46.65	42.92	39.60	36.33	33.36	27.77
0.600673	55.11	50.69	46.66	42.93	39.62	36.41	33.27	27.81
2,2-Bis(hydroxymethyl)propane-1-ol(aq)								
0.099952	7.69	7.14	6.64	6.17	5.74		5.11	4.41
0.099952	7.67	7.13	6.65	6.17	5.77			
0.198504	15.13	14.03	13.07	12.17	11.35		10.05	8.75
0.198504	15.13	14.04	13.08	12.18	11.38			9.06
0.290953	21.99	20.42	19.00	17.71	16.53		14.54	12.67
0.290953	22.00	20.43	19.01	17.72	16.55		14.88	12.52
0.392296	29.43	27.31	25.42	23.72	22.11		19.45	16.89
0.392296	29.43	27.34	25.43	23.74	22.13		19.79	16.72
0.496187	36.94	34.28	31.90	29.75	27.74		24.39	21.17
0.496187	36.94	34.30	31.91	29.76	27.76		24.68	20.98
0.604245	44.53	41.32	38.46	35.84	33.42		29.35	25.49
0.604245	44.54	41.33	38.47	35.86	33.45		29.07	25.28
2,2-Bis(hydroxymethyl)propane-1,3-diol(aq)								
0.100236	6.46	6.02	5.67	5.30	4.98	4.69	4.44	3.92
0.100236	6.48	6.03	5.69	5.31	4.98	4.70	4.41	3.96
0.100236	6.46	6.04	5.68		4.99	4.70	4.45	3.97
0.150101	9.62	8.98	8.44	7.91	7.42	7.01	6.61	5.85
0.150101	9.64	8.99	8.47	7.93	7.42	7.02	6.58	5.91

Table 3. continued

m_2 mol·kg ⁻¹	$\Delta c/\text{m}\cdot\text{s}^{-1}$							
	$T/\text{K} = 278.15$	283.15	288.15	293.15	298.15	303.15	308.15	318.15
2,2-Bis(hydroxymethyl)propane-1,3-diol(aq)								
0.150101	9.63	9.01	8.46		7.45		6.58	5.93
0.200125	12.82	11.96	11.23	10.52	9.90	9.32	8.78	7.80
0.200125	12.82	11.96	11.25	10.54	9.91	9.33	8.77	7.88
0.200125	12.83	11.98	11.25	10.50	9.92	9.31	8.76	7.89
0.250294	16.00	14.90	13.96	13.13	12.34	11.62	10.94	9.72
0.250294	15.96	14.91	14.00	13.14	12.35	11.64	10.93	9.80
0.250294	15.97	14.93	14.01	13.10	12.36	11.62	10.92	9.83
0.300478	19.14	17.83	16.69	15.70	14.80	13.90	13.10	11.62
0.300478	19.09	17.84	16.74	15.71	14.80	13.92	13.08	11.71
0.300478	19.11	17.86	16.74	15.67	14.79	13.92	13.06	11.74
0.350045	22.21	20.72	19.38	18.24	17.16	16.14	15.21	13.49
0.350045	22.16	20.72	19.43	18.25	17.17	16.18	15.21	13.58
0.350045	22.18	20.75	19.44	18.21	17.18	16.19	15.18	13.62
2,2-Bis(hydroxymethyl)butane-1-ol(aq)								
0.099736	9.88	9.16	8.55	7.94	7.39		6.64	5.73
0.099736	9.91	9.18	8.55	7.95	7.40		6.32	5.56
0.199810	19.49	18.07	16.83	15.65	14.57		12.88	11.11
0.199810	19.51	18.10	16.83	15.67	14.59		12.55	10.97
0.299981	28.92	26.84	24.96	23.22	21.62		19.01	16.35
0.299981	28.95	26.86	24.96	23.25	21.63		18.68	16.22
0.396143	37.79	35.06	32.59	30.32	28.20		24.73	20.96
0.396143	37.82	35.10	32.60	30.35	28.22		24.45	21.14
0.504794	47.61	44.14	41.03	38.14	35.47		31.02	26.33
0.504794	47.63	44.17	41.04	38.17	35.50		30.70	26.54
3,3,7,7-Tetrakis(hydroxymethyl)-5-oxanonane(aq)								
0.019719	3.62	3.35	3.07	2.82	2.62		2.31	1.77
0.019719	3.60	3.33	3.08	2.83	2.62		2.13	1.88
0.041050	7.45	6.87	6.35	5.83	5.40		4.67	3.76
0.041050	7.48	6.86	6.34	5.85	5.41		4.48	3.87
0.060452	10.89	10.03	9.28	8.53	7.89		6.79	5.54
0.060452	10.90	10.02	9.29	8.55	7.91		6.59	5.64
0.079001	14.17	13.01	12.03	11.08	10.23		8.78	7.20
0.079001	14.14	13.01	12.03	11.07	10.23		8.57	7.32

^aStandard uncertainties are $u(T) = 0.01 \text{ K}$, $u(m_2) = 3 \cdot 10^{-5} \text{ mol}\cdot\text{kg}^{-1}$, and the combined expanded uncertainty is $U_c(\Delta c) = 0.3 \text{ m}\cdot\text{s}^{-1}$ at $T = 318.15 \text{ K}$ and $U_c(\Delta c) = 0.1 \text{ m}\cdot\text{s}^{-1}$ at lower temperatures (level of confidence = 0.95).

The vapor space in the flasks used for the preparation and storage of the solutions gradually increased as the samples were withdrawn for measurements, and thus the evaporation might affect the concentrations. Measurements were started with full storage flasks at the temperature 298.15 K, and after measurements at all of the other temperatures were completed then the measurements at 298.15 were repeated. No effects of evaporation on density and speed of sound were observed.

RESULTS

Direct Experimental Data. The values of the differences in speed of sound $\Delta c = c - c_1$ where c and c_1 are the speeds of sound in the solution and water, respectively, along with the molalities of organic solutes m_2 are recorded in Table 3 (solutes B, C, D, E, F, G, H). New experimental values of the density difference $\Delta\rho = \rho - \rho_1$, where ρ and ρ_1 are the measured densities of the solution and water for aqueous 2,2-dimethylpropane-1,3-diol (D) and 2,2-bis(hydroxymethyl)propane-1,3-diol (F) are recorded in Table 4. Duplicate or triplicate measurements were performed for each solution. Few measured values that deviated from the other measurements

(probably due to formation of air bubbles) were excluded; in those cases there are blank spaces in the tables. At $T = 303.15 \text{ K}$ the solutions of 2,2-dimethylpropane-1,3-diol (D) and 2,2-bis(hydroxymethyl)propane-1,3-diol (F) only were measured.

Standard Molar Isentropic Compressions. The partial molar isentropic compression at infinite dilution (standard molar isentropic compression) of the solute 2 is defined as the derivative of standard molar volume $V_{m,2}^0$ with respect to pressure at constant entropy

$$K_{S,m,2}^0 = \lim_{m_2 \rightarrow 0} \left(\frac{-\partial V_{m,2}^{\text{app}}}{\partial p} \right)_S = - \left(\frac{\partial V_{m,2}^0}{\partial p} \right)_S \quad (1)$$

where $V_{m,2}^{\text{app}}$ is the apparent molar volume and m_2 is the molality of the solute. Based on this definition it is possible to derive² the expression for standard molar isentropic compression

$$K_{S,m,2}^0 = \frac{1}{(\rho_1 c_1)^2} \left(M_2 - \frac{a_K}{(\rho_1 c_1)^2} \right) \quad (2)$$

Table 4. Experimental Differences $\Delta\rho = \rho - \rho_1$ Measured for {2,2-Dimethylpropane-1,3-diol (2) or 2,2-Bis(hydroxymethyl)propane-1,3-diol (2) + Water (1)} at Atmospheric Pressure^a

m_2 mol·kg ⁻¹	$\Delta\rho/\text{kg}\cdot\text{m}^{-3}$							
	$T/\text{K} = 278.15$	283.15	288.15	293.15	298.15	303.15	308.15	318.15
2,2-Dimethylpropane-1,3-diol(aq)								
0.100116	0.285	0.266	0.247	0.228	0.215	0.201	0.183	0.155
0.100116	0.284	0.265	0.248	0.231	0.216	0.201	0.182	0.154
0.100116	0.285	0.265	0.247	0.233	0.213	0.200	0.183	0.155
0.200606	0.603	0.558	0.520	0.481	0.451	0.418	0.382	0.318
0.200606	0.602	0.557	0.520	0.483	0.451	0.418	0.382	0.319
0.200606	0.603	0.560	0.520	0.486	0.451	0.417	0.383	0.320
0.299683	0.941	0.872	0.808	0.749	0.696	0.644	0.591	0.488
0.299683	0.941	0.872	0.810	0.751	0.697	0.645	0.588	0.487
0.299683	0.942	0.872	0.810	0.753	0.694	0.644	0.591	0.488
0.402055	1.318	1.215	1.126	1.038	0.965	0.889	0.812	0.670
0.402055	1.316	1.215	1.126	1.043	0.965	0.890	0.812	0.669
0.402055	1.318	1.216	1.126	1.045	0.967	0.889	0.814	0.669
0.500081	1.696	1.560	1.442	1.329	1.232	1.132	1.034	0.847
0.500081	1.696	1.561	1.444	1.334	1.231	1.132	1.032	0.844
0.500081	1.697	1.563	1.444	1.336	1.234	1.132	1.035	0.845
0.600673	2.101	1.930	1.781	1.639	1.512	1.387	1.264	1.029
0.600673	2.100	1.931	1.781	1.642	1.511	1.388	1.263	1.028
0.600673	2.102	1.934	1.782	1.644	1.514	1.387	1.265	1.028
2,2-Bis(hydroxymethyl)propane-1,3-diol(aq)								
0.100236	3.577	3.528	3.488	3.452	3.423	3.396	3.371	3.332
0.100236	3.578	3.529	3.486	3.451	3.421	3.396	3.371	3.332
0.100236	3.579	3.530	3.489	3.454	3.419	3.395	3.369	3.330
0.150101	5.328	5.257	5.195	5.143	5.097	5.057	5.019	4.963
0.150101	5.329	5.257	5.195	5.142	5.097	5.057	5.020	4.963
0.150101	5.330	5.261	5.198	5.146	5.099	5.058	5.020	4.964
0.200125	7.077	6.979	6.901	6.829	6.767	6.716	6.664	6.593
0.200125	7.078	6.980	6.903	6.828	6.767	6.716	6.665	6.593
0.200125	7.082	6.985	6.907	6.833	6.771	6.714	6.667	6.595
0.250294	8.800	8.683	8.581	8.494	8.419	8.354	8.292	8.197
0.250294	8.803	8.684	8.582	8.493	8.419	8.353	8.293	8.197
0.250294	8.805	8.690	8.587	8.499	8.424	8.353	8.295	8.199
0.300478	10.508	10.367	10.244	10.142	10.051	9.973	9.899	9.785
0.300478	10.511	10.369	10.248	10.141	10.052	9.973	9.902	9.785
0.300478	10.515	10.375	10.252	10.146	10.057	9.973	9.905	9.788
0.350045	12.185	12.021	11.880	11.761	11.655	11.564	11.480	11.346
0.350045	12.187	12.020	11.881	11.759	11.652	11.566	11.487	11.346
0.350045	12.189	12.027	11.886	11.764	11.661	11.568	11.486	11.350

^aStandard uncertainties are $u(T) = 0.01 \text{ K}$, $u(m_2) = 3 \cdot 10^{-5} \text{ mol}\cdot\text{kg}^{-1}$, and the combined expanded uncertainty is $U_c(\Delta\rho) = 2 \cdot 10^{-3} \text{ kg}\cdot\text{m}^{-3}$ (level of confidence = 0.95).

where a_K is the adjustable parameter of the fit of experimental values of the differences $\Delta[(\rho c)^2] = (\rho c)^2 - (\rho_1 c_1)^2$ in the form

$$\frac{\Delta[(\rho c)^2]}{m_2} = \frac{(\rho c)^2 - (\rho_1 c_1)^2}{m_2} = a_K + b_K m_2 \quad (3)$$

The values of the coefficients a_K and b_K were obtained from measured data (Tables 3 and 4) by using a least-squares method with unit weights and are recorded in Table 5 along with calculated values of $K_{S,m,2}^0$. Density values were either taken from our previous measurements³ (solutes B, C, E, G, H) or evaluated from data in Table 4 (solutes D, F). Uncertainties $\sigma(K_{S,m,2}^0)$ are affected mainly by the uncertainty in the speed of sound which was estimated to be about $\pm 0.1 \text{ m}\cdot\text{s}^{-1}$ at temperatures from (278 to 298) K and $\pm 0.3 \text{ m}\cdot\text{s}^{-1}$ at 318 K.

Standard Molar Volumes. The partial molar volume at infinite dilution ($m_2 \rightarrow 0$) of a solute $V_{m,2}^0$ (standard molar volume) can be calculated from the equation⁵

$$V_{m,2}^0 = \lim_{m_2 \rightarrow 0} (V_{m,2}^{\text{app}}) = \frac{1}{\rho_1} \left(M_2 - \frac{a_V}{\rho_1} \right) \quad (4)$$

where M_2 is the molar mass of the solute and a_V is an adjustable parameter of the fit of experimental values $\Delta\rho/m_2$

$$\frac{\Delta\rho}{m_2} = \frac{\rho - \rho_1}{m_2} = a_V + b_V m_2 + c_V m_2^2 \quad (5)$$

The values of the coefficients a_V , b_V , and c_V obtained for aqueous 2,2-dimethylpropane-1,3-diol (D) and 2,2-bis-(hydroxymethyl)propane-1,3-diol (F) by using a least-squares method with unit weights are recorded in Table 6 along with the standard molar volumes. Due to lower concentration range (lower solubility) the linear function ($c_V = 0$) was found to be sufficient for 2,2-bis(hydroxymethyl)propane-1,3-diol (F).

Table 5. Coefficients a_K and b_K of eq 3 and Standard Molar Isentropic Compressions $K_{S,m,2}^0$ for {2-Methylpropane-1,3-diol (2), 2,2-Dimethylpropane-1-ol (2), 2,2-Dimethylpropane-1,3-diol (2), 2,2-Bis(hydroxymethyl)propane-1-ol (2), 2,2-Bis(hydroxymethyl)propane-1,3-diol (2), 2,2-Bis(hydroxymethyl)butane-1-ol (2), or 3,3,7,7-Tetrakis(hydroxymethyl)-5-oxanonane (2) + Water (1)}. The Uncertainties $\sigma(K_{S,m,2}^0)$ Represent the Combined Expanded Uncertainties

T K	$a_K \cdot 10^{-12}$ $\text{kg}^3 \cdot \text{m}^{-4} \cdot \text{s}^{-2} \cdot \text{mol}^{-1}$	$b_K \cdot 10^{-12}$ $\text{kg}^4 \cdot \text{m}^{-4} \cdot \text{s}^{-2} \cdot \text{mol}^{-2}$	$K_{S,m,2}^0 \pm \sigma(K_{S,m,2}^0)$ $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1}$	T K	$a_K \cdot 10^{-12}$ $\text{kg}^3 \cdot \text{m}^{-4} \cdot \text{s}^{-2} \cdot \text{mol}^{-1}$	$b_K \cdot 10^{-12}$ $\text{kg}^4 \cdot \text{m}^{-4} \cdot \text{s}^{-2} \cdot \text{mol}^{-2}$	$K_{S,m,2}^0 \pm \sigma(K_{S,m,2}^0)$ $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1}$
2-Methylpropane-1,3-diol(aq)				2,2-Dimethylpropane-1-ol(aq)			
278.15	0.2173	−0.0004	−8.2 ± 0.4	278.15	0.2871	−0.0174	−26.1 ± 0.4
283.15	0.2033	−0.0007	−3.3 ± 0.4	283.15	0.2605	−0.0238	−17.3 ± 0.4
288.15	0.1915	−0.0043	0.4 ± 0.4	288.15	0.2344	−0.0244	−9.8 ± 0.4
293.15	0.1791	−0.0045	3.8 ± 0.4	293.15	0.2117	−0.0313	−3.9 ± 0.4
298.15	0.1675	−0.0048	6.7 ± 0.4	298.15	0.1876	−0.0270	1.8 ± 0.3
308.15	0.1454	−0.0005	11.6 ± 0.3	308.15	0.1450	−0.0565	10.8 ± 0.3
318.15	0.1238	−0.0021	15.8 ± 0.3	318.15	0.0998	−0.0399	19.5 ± 0.3
2,2-Dimethylpropane-1,3-diol(aq)				2,2-Bis(hydroxymethyl)propane-1-ol(aq)			
278.15	0.2895	−0.0125	−18.8 ± 0.2	278.15	0.2981	−0.0082	−13.0 ± 0.2
283.15	0.2703	−0.0126	−11.9 ± 0.2	283.15	0.2866	−0.0093	−8.0 ± 0.1
288.15	0.2527	−0.0137	−6.4 ± 0.2	288.15	0.2756	−0.0101	−3.9 ± 0.2
293.15	0.2358	−0.0147	−1.6 ± 0.2	293.15	0.2644	−0.0093	−0.3 ± 0.1
298.15	0.2193	−0.0143	2.5 ± 0.2	298.15	0.2541	−0.0100	2.7 ± 0.1
303.15	0.2041	−0.0161	6.1 ± 0.2	308.15	0.2382	−0.0149	6.9 ± 0.7
308.15	0.1885	−0.0161	9.4 ± 0.2	318.15	0.2187	−0.0171	11.1 ± 0.8
318.15	0.1605	−0.0193	15.0 ± 0.2				
2,2-Bis(hydroxymethyl)propane-1,3-diol(aq)				2,2-Bis(hydroxymethyl)butane-1-ol(aq)			
278.15	0.3320	−0.0081	−13.3 ± 0.2	278.15	0.3671	−0.0193	−22.8 ± 0.2
283.15	0.3241	−0.0076	−8.9 ± 0.2	283.15	0.3509	−0.0196	−16.0 ± 0.2
288.15	0.3182	−0.0122	−5.7 ± 0.5	288.15	0.3364	−0.022	−10.6 ± 0.2
293.15	0.3100	−0.0093	−2.5 ± 0.3	293.15	0.3213	−0.0219	−5.7 ± 0.2
298.15	0.3027	−0.0076	0.1 ± 0.3	298.15	0.3069	−0.0223	−1.6 ± 0.2
303.15	0.2962	−0.0096	2.2 ± 0.3	308.15	0.2813	−0.0249	4.8 ± 0.2
308.15	0.2895	−0.0113	4.1 ± 0.3	318.15	0.2567	−0.0315	10.1 ± 0.2
318.15	0.2767	−0.0119	7.2 ± 0.3				
3,3,7,7-Tetrakis(hydroxymethyl)-5-oxanonane(aq)							
278.15	0.6682	−0.0174	−38.5 ± 0.6				
283.15	0.6350	−0.0238	−25.3 ± 0.6				
288.15	0.6017	−0.0244	−14.1 ± 0.6				
293.15	0.5699	−0.0313	−4.5 ± 0.6				
298.15	0.5426	−0.027	3.0 ± 0.6				
308.15	0.4836	−0.0565	16.8 ± 0.6				
318.15	0.4217	−0.0399	29.4 ± 0.6				

Table 6. Coefficients a_V , b_V , and c_V of eq 5, Standard Molar Volumes $V_{m,2}^0$ for {2,2-Dimethylpropane-1,3-diol (2) or 2,2-Bis(hydroxymethyl)propane-1,3-diol (2) + Water (1)}. The Uncertainties $\sigma(V_{m,2}^0)$ Represent the Combined Expanded Uncertainties

T	a_V	b_V	c_V	$V_{m,2}^0 \pm \sigma(V_{m,2}^0)$	T	a_V	b_V	$V_{m,2}^0 \pm \sigma(V_{m,2}^0)$
K	$\text{kg}^2 \cdot \text{m}^{-3} \cdot \text{mol}^{-1}$	$\text{kg}^3 \cdot \text{m}^{-3} \cdot \text{mol}^{-2}$	$\text{kg}^4 \cdot \text{m}^{-3} \cdot \text{mol}^{-3}$	$\text{cm}^3 \cdot \text{mol}^{-1}$	K	$\text{kg}^2 \cdot \text{m}^{-3} \cdot \text{mol}^{-1}$	$\text{kg}^3 \cdot \text{m}^{-3} \cdot \text{mol}^{-2}$	$\text{cm}^3 \cdot \text{mol}^{-1}$
2,2-Dimethylpropane-1,3-diol(aq)					2,2-Bis(hydroxymethyl)propane-1,3-diol(aq)			
278.15	2.6729	1.7637	−0.6520	101.48 ± 0.06	278.15	36.0493	−3.5240	100.10 ± 0.08
283.15	2.4975	1.5347	−0.5639	101.68 ± 0.06	283.15	35.5601	−3.4636	100.61 ± 0.08
288.15	2.3479	1.3210	−0.4846	101.89 ± 0.06	288.15	35.1453	−3.4187	101.06 ± 0.08
293.15	2.1886	1.2027	−0.4945	102.14 ± 0.06	293.15	34.7864	−3.3911	101.48 ± 0.08
298.15	2.0409	1.1074	−0.5226	102.40 ± 0.06	298.15	34.4703	−3.3382	101.88 ± 0.08
303.15	1.9199	0.8859	−0.3953	102.67 ± 0.06	303.15	34.2100	−3.3508	102.23 ± 0.08
308.15	1.7372	0.9226	−0.5227	103.02 ± 0.06	308.15	33.9489	−3.2716	102.61 ± 0.08
318.15	1.4936	0.5392	−0.2913	103.65 ± 0.06	318.15	33.5750	−3.3032	103.25 ± 0.08

DISCUSSION

Comparison with Published Data. Our values of standard molar isentropic compression obtained for aqueous 2,2-dimethylpropane-1,3-diol (C) are compared with data reported by Sakurai et al.⁸ in Table 7. The agreement is within the

experimental uncertainties at higher temperatures, and larger deviations are observed at low temperatures. Standard molar volumes measured in our laboratory at (298 and 318) K for 2,2-dimethylpropane-1,3-diol (D) and 2,2-bis(hydroxymethyl)propane-1,3-diol (F)⁴ using the flow densimeter agree with

Table 7. Comparison of Measured Values of Standard Molar Isentropic Compression at $p = 0.1$ MPa with the Values Taken from the Literature

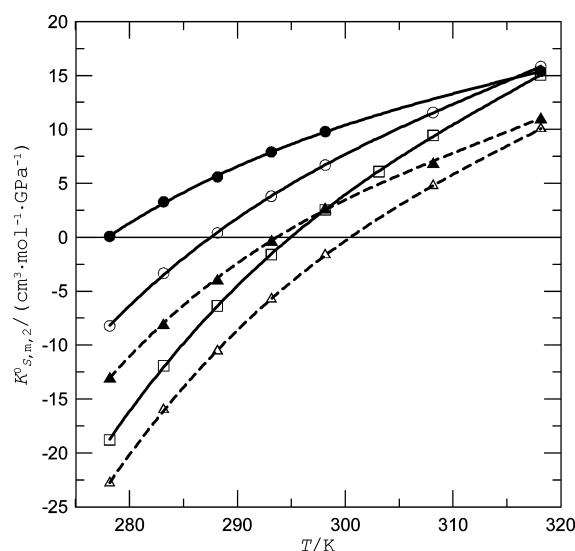
this work		literature		
T	$K_{S,m,2}^0$	$K_{S,m,2}^0$		dev. ^a
K	cm ³ ·mol ⁻¹ ·GPa ⁻¹	cm ³ ·mol ⁻¹ ·GPa ⁻¹	ref.	cm ³ ·mol ⁻¹ ·GPa ⁻¹
2,2-Dimethylpropane-1-ol(aq)				
278.15	-26.1 ± 0.4	-27.84 ± 0.07	8	1.8
288.15	-9.8 ± 0.4	-11.03 ± 0.07	8	1.2
298.15	1.8 ± 0.3	0.69 ± 0.07	8	1.1
308.15	10.8 ± 0.3	10.50 ± 0.07	8	0.3
318.15	19.5 ± 0.3	19.26 ± 0.06	8	0.2

^aDeviation between this work and the literature value.

the present data within the estimated uncertainties (Table 8). Small differences in experimental temperatures and pressures play no role due to moderate variations of standard molar volumes with temperature and pressure in this range; maximum values of $[\partial \ln(V_{m,2}^0)/\partial T]_p$ and $[-\partial \ln(V_{m,2}^0)/\partial T]_p$ evaluated in the range from (298 to 318) K from the fits described in the Supporting Information are $8 \cdot 10^{-4}$ K⁻¹ and $2 \cdot 10^{-4}$ MPa⁻¹, respectively, for the aqueous solutes investigated.

Dependences of Standard Isentropic Compression on Temperature. Experimental values of standard isentropic compressibility of two series of solutes are plotted against temperature in Figure 2. The figure shows the effect of changes in the size (and consequently in the shape) of the hydrocarbon frame of the solute molecule within the series of diols (full lines) and triols (dashed lines). Obviously the lower ratio between hydrophilic (hydroxyl groups) and hydrophobic (hydrocarbon frame) parts of the solute molecule leads to (i) lower standard molar isentropic compression in the experimental temperature range and (ii) larger slope of the dependence. Consequently the curves tend to cross each other at a particular temperature (around 320 K for both solute groups). The order of magnitudes is likely to be reversed above this temperature.

Molecules of the pairs of the solutes A–B, B–D, and G–E (for structures of solute molecules, see Figure 1) differ by one methylene group –CH₂–, and therefore the distances between curves within each series shown in Figure 2 correspond to the contribution of the methylene group to the standard isentropic molar compression. Figure 3 shows the values obtained as differences between respective pairs of solutes, that is, $K_{S,m,2}^0(B) - K_{S,m,2}^0(A)$, $K_{S,m,2}^0(D) - K_{S,m,2}^0(B)$, and $K_{S,m,2}^0(G) - K_{S,m,2}^0(E)$. The full lines plotted in the figure for a comparison represent the values calculated from data measured for linear aliphatic (C₃ to C₆) 1-alkanols, 2-alkanols, and α ,

**Figure 2.** Plot of experimental standard molar isentropic compressions against temperature. The lines are to aid the eye. Full lines, diols; dashed lines, triols. ●, propane-1,3-diol² (A); ○, 2-methylpropane-1,3-diol (B); □, 2,2-dimethylpropane-1,3-diol (D); ▲, 2,2-bis(hydroxymethyl)propane-1-ol (E); △, 2,2-bis(hydroxymethyl)-butane-1-ol (G).

ω -alkanediols^{9,10} and values obtained as the limiting ones for long chain linear 1-alkanols and α,ω -alkanediols¹¹ (there is an obvious error in Table 2 of ref 11; the value for 298.15 K should be (-1.8, not 1.8) cm³·mol⁻¹·GPa⁻¹). Obviously the methylene group contribution in the short side branches of hydrocarbon frame is smaller (more negative) than that in long linear chains. The fact that in cases of solute pairs A–B and B–D the methylene group is inserted between the carbon atom and hydrogen resulting in the methyl group –CH₃ affects the methylene group contribution compared to long straight chains.^{9–11} Surprisingly the contribution of the methylene group inserted between the quaternary carbon atom and the methyl group in the molecule of 2,2-bis(hydroxymethyl)propane-1-ol (E), that is, for the pair E–G, is nearly identical to that when the methylene group is inserted between the tertiary carbon atom and the hydrogen atom in the molecule of 2-methylpropane-1,3-diol (B), that is, for the pair B–D.

Analogous behavior concerning the magnitudes and slopes of the $K_{S,m,2}^0(T)$ dependences observed in Figure 2 is exhibited by the series of all four hydroxyderivatives of 2,2-dimethylpropane (neopentane) as shown in Figure 4. The intersection temperature is about 295 K. Contrary to Figure 2 the values of standard molar isentropic compression are close to zero at

Table 8. Comparison of Measured Values of Standard Molar Volume at $p = 0.1$ MPa with the Values Taken from the Literature

this work		literature			
T	$V_{m,2}^0$	T	p	$V_{m,2}^0$	dev. ^a
K	cm ³ ·mol ⁻¹	K	MPa	cm ³ ·mol ⁻¹	cm ³ ·mol ⁻¹
2,2-Dimethylpropane-1,3-diol(aq)					
298.15	102.40 ± 0.06	298.17	0.33	102.37 ± 0.03	0.03
318.15	103.65 ± 0.06	318.26	0.47	103.68 ± 0.03	-0.03
2,2-Bis(hydroxymethyl)propane-1,3-diol(aq)					
298.15	101.88 ± 0.08	298.17	0.77	101.95 ± 0.06	0.07
318.15	103.25 ± 0.08	318.26	0.47	103.35 ± 0.09	-0.10

^aDeviation between this work and the literature value.

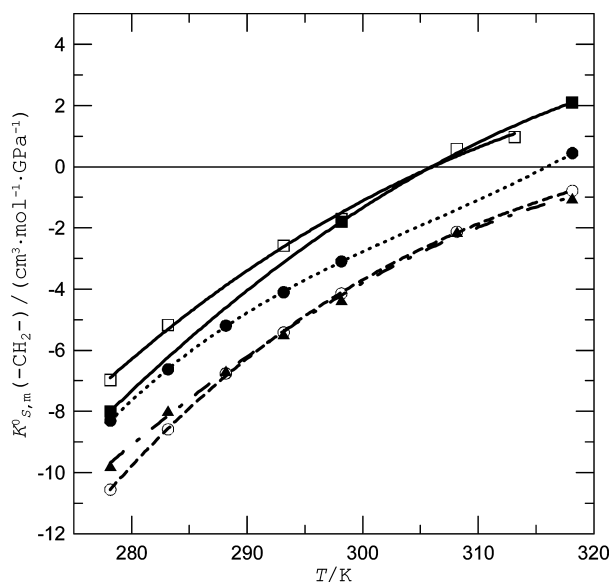


Figure 3. Plot of the contribution of the methylene group $-\text{CH}_2-$ to standard molar isentropic compression against temperature. The lines are to aid the eye. ●, $K^0_{S,m,2}(\text{B})-K^0_{S,m,2}(\text{A})$; ○, $K^0_{S,m,2}(\text{D})-K^0_{S,m,2}(\text{B})$; ▲, $K^0_{S,m,2}(\text{G})-K^0_{S,m,2}(\text{E})$; □, Høiland and Vikingstad;^{9,10} ■, Nakajima et al.¹¹ Solutes are denoted by letters according to Figure 1.

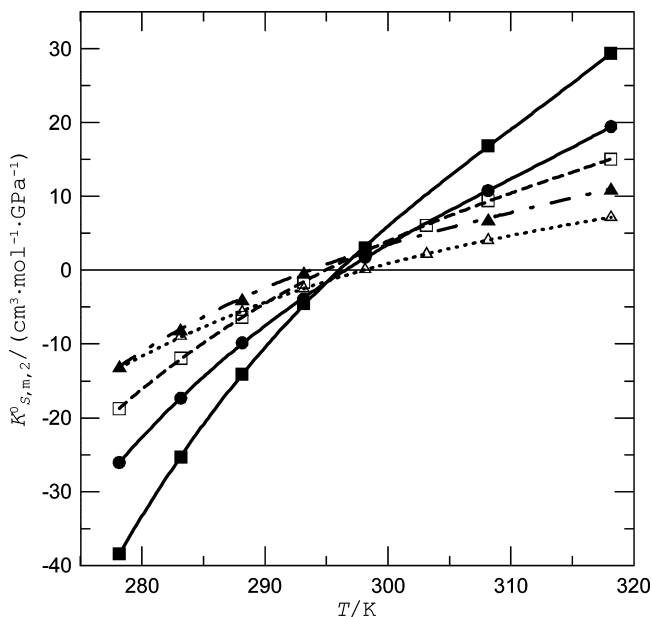


Figure 4. Plot of experimental standard molar isentropic compressions of aqueous alcohols derived from 2,2-dimethylpropane (neopentane) against temperature. The lines are to aid the eye. ●, 2,2-dimethylpropane-1-ol (C); □, 2,2-dimethylpropane-1,3-diol (D); ▲, 2,2-bis(hydroxymethyl)propane-1-ol (E); △, 2,2-bis(hydroxymethyl)propane-1,3-diol (F); ■, 3,3,7,7-tetrakis(hydroxymethyl)-5-oxanonane (H).

this temperature. Above the intersection temperature the magnitudes of the compression are decreasing in the order $C > D > E > F$, that is, in the order of increasing ratio between hydrophilic and hydrophobic parts of the solute molecule. The opposite order is observed at temperatures below the intersection temperature (with the exception of solutes E and F). As in Figure 2 the lower ratio between hydrophilic and hydrophobic parts of the solute molecule leads to a larger slope

of the dependence in the entire experimental temperature range. Surprisingly the large molecule of 3,3,7,7-tetrakis(hydroxymethyl)-5-oxanonane (H) follows the behavior of neopentane derivatives, and one might deduce that it is the most hydrophobic solute among those shown in Figure 4. Probably the size of the molecule may play a role here. The molar compression is an absolute quantity (absolute volume change per unit change of pressure) when compared to a relative quantity such as isentropic compressibility (relative volume change per unit change of pressure). Figure 5 presents

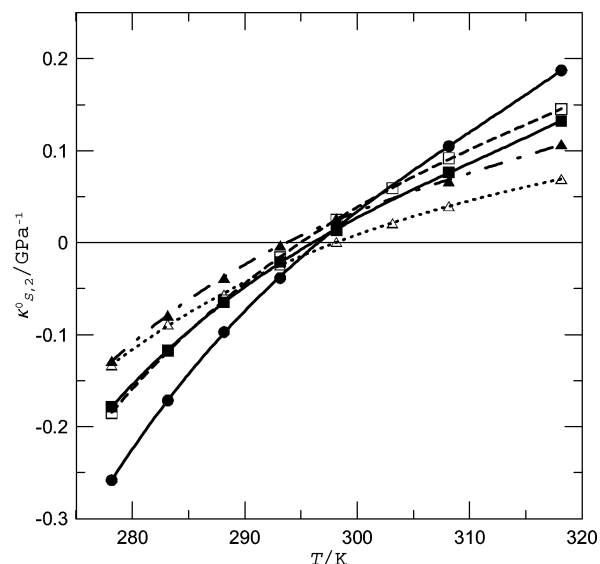


Figure 5. Plot of the analogue of isentropic compressibility $\kappa^0_{S,2} = K^0_{S,m,2}/V^0_{m,2}$ of aqueous alcohols derived from 2,2-dimethylpropane (neopentane) against temperature. The lines are to aid the eye. ●, 2,2-dimethylpropane-1-ol (C); □, 2,2-dimethylpropane-1,3-diol (D); ▲, 2,2-bis(hydroxymethyl)propane-1-ol (E); △, 2,2-bis(hydroxymethyl)propane-1,3-diol (F); ■, 3,3,7,7-tetrakis(hydroxymethyl)-5-oxanonane (H).

the plots for an analogue of isentropic compressibility $\kappa^0_{S,2} = K^0_{S,m,2}/V^0_{m,2}$ for the same solutes as in Figure 4. Obviously $\kappa^0_{S,2}$ of 3,3,7,7-tetrakis(hydroxymethyl)-5-oxanonane (H), the molecule of which is composed of two branched diol segments of 2,2-bis(hydroxymethyl)butane-1-ol (G) connected by the ether oxygen, is close to that of 2,2-dimethylpropane-1,3-diol (D). For other solutes (derivatives C, D, E, F of 2,2-dimethylpropane) we see a picture similar to that in Figure 4.

The pairs of the solutes C–D, D–E, and E–F differ by the oxygen atom inserted between the hydrogen atom and the carbon atom of the methyl group. Figure 6 shows the temperature dependence of the contribution of the oxygen atom (however, as a part of the hydroxyl group) to the standard molar isentropic compression. Values of the contribution were calculated for the above-mentioned solute pairs as $K^0_{S,m,2}(\text{D})-K^0_{S,m,2}(\text{C})$, $K^0_{S,m,2}(\text{E})-K^0_{S,m,2}(\text{D})$, and $K^0_{S,m,2}(\text{F})-K^0_{S,m,2}(\text{E})$. Obviously, the contribution strongly depends on the number of hydroxyl groups in the molecule, particularly at low temperatures. It is likely that the extent of the hydrophilic character of the solute molecule plays a role, at least in the present temperature range. The contributions evaluated from data for pairs of 1-alkanols and α,ω -alkanediols^{10,11} with the same length of the hydrocarbon chain are plotted in the figure for a comparison. It is evident that there is a strong dependence on

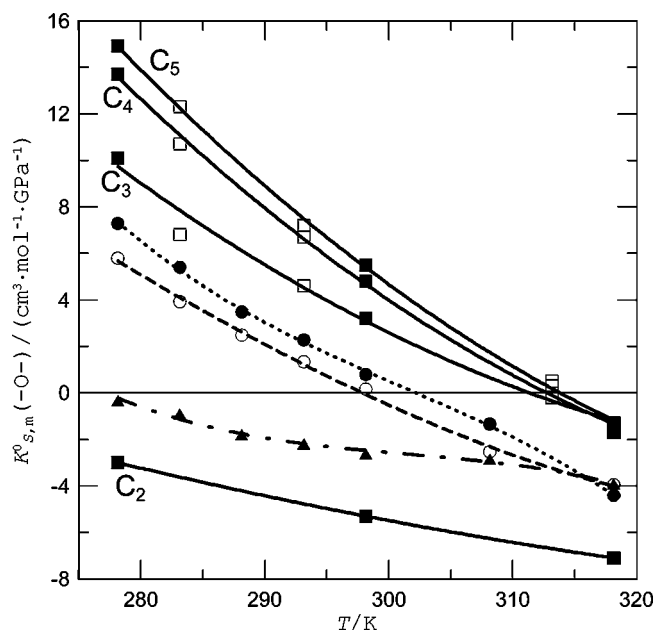


Figure 6. Plot of the contribution of the oxygen atom $-O-$ in the hydroxyl group to standard molar isentropic compression against temperature. The lines are to aid the eye. \bullet , $K^0_{S,m,2}(D) - K^0_{S,m,2}(C)$; \circ , $K^0_{S,m,2}(E) - K^0_{S,m,2}(D)$; \blacktriangle , $K^0_{S,m,2}(F) - K^0_{S,m,2}(E)$. Solutes are denoted by letters according to Figure 1. Full lines marked with C_n ($n = 2, 3, 4, 5$) correspond to the differences $K^0_{S,m,2}\{\text{HO}-(\text{CH}_2)_n-\text{OH}\} - K^0_{S,m,2}\{\text{H}-(\text{CH}_2)_n-\text{OH}\}$ evaluated from data by Høiland¹⁰ (\square) and Nakajima et al.¹¹ (\blacksquare).

the chain length which decays with increasing length (C_6 -line obtained from data by Høiland¹⁰ is nearly identical with the depicted C_5 -line). This behavior indicates that not only the ratio between hydrophilic and hydrophobic part of the molecule but also the distribution of the hydroxyl groups (their mutual distance) affect the contribution of the oxygen atom. There are two analogous pairs in both series: linear alcohols propane-1-ol and propane-1,3-diol, and branched alcohols 2,2-dimethylpropane-1-ol (C) and 2,2-dimethylpropane-1,3-diol (D). The respective curves (C_3 -line and dotted line) are close each other; the effect of two methyl branches is, however, clearly visible.

Dependences of Standard Molar Volumes and Derived Quantities on Temperature. Experimental standard molar volumes obtained in this work for 2,2-dimethylpropane-1,3-diol (D) and 2,2-bis(hydroxymethyl)propane-1,3-diol (F) were combined with data measured in the ranges from (298 to 573 or 548) K and (0.1 to 30) MPa,⁴ and the entire set of each solute was smoothed using a polynomial function of temperature and pressure. The fitting procedure is described in the Supporting Information where the values of adjustable parameters are given. Parameters of the fits for the other solutes considered here can be found in our previous papers.^{2,3}

Similarly, as the contributions of the methylene group to the standard molar isentropic compression are shown in Figure 3, smoothed contributions to the standard molar volume are plotted in Figure 7. Standard molar volumes were calculated from smoothing polynomials for $p = 0.1$ MPa in the temperature range up to 373.15 K and for the saturation pressure of water for higher temperatures (this pressure set is named “low pressures”). The line that represents the contribution evaluated from group contribution scheme¹² is plotted for a comparison. Figure 7 is the extension down to the temperature 278 K of Figure 5 in our previous paper⁴ where the discussion can be found.

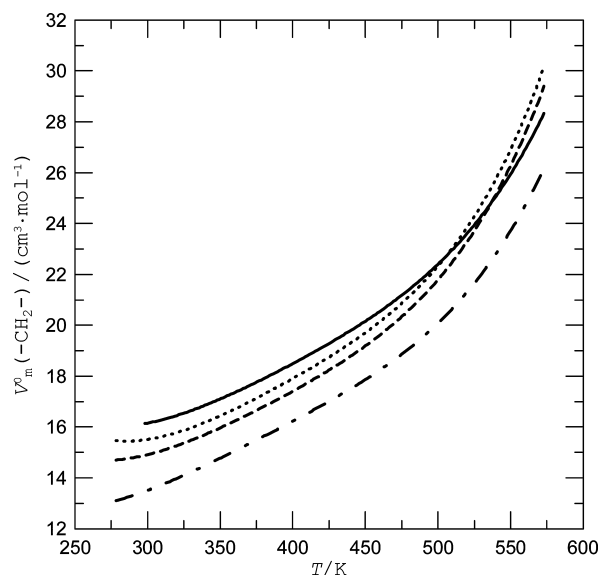


Figure 7. Plot of the smoothed contribution of the methylene group $-\text{CH}_2-$ to standard molar volume at low pressure against temperature. Dotted line, $V^0_{m,2}(B) - V^0_{m,2}(A)$; dashed line, $V^0_{m,2}(D) - V^0_{m,2}(B)$; dot-and-dash line, $V^0_{m,2}(G) - V^0_{m,2}(E)$; full line, group contribution method.¹² The solutes are denoted by letters according to Figure 1.

Dependences of standard molar volume on temperature and pressure in the entire experimental temperature region (up to 573 K) have been analyzed in our previous paper.⁴ Employing new data obtained in this work for low temperatures we focus at the temperature range from (278 to 373) K to observe the regularities in more detail. The following figures are based on values of standard molar volumes and derived quantities calculated for $p = 0.1$ MPa from smoothing polynomials (refs 2 and 3 and the Supporting Information).

Figures 8 and 9 present smoothed derivative quantities (the analogue to isobaric expansivity $\alpha^0_{p,2} = (1/V^0_{m,2})(\partial V^0_{m,2}/\partial T)_p$ and

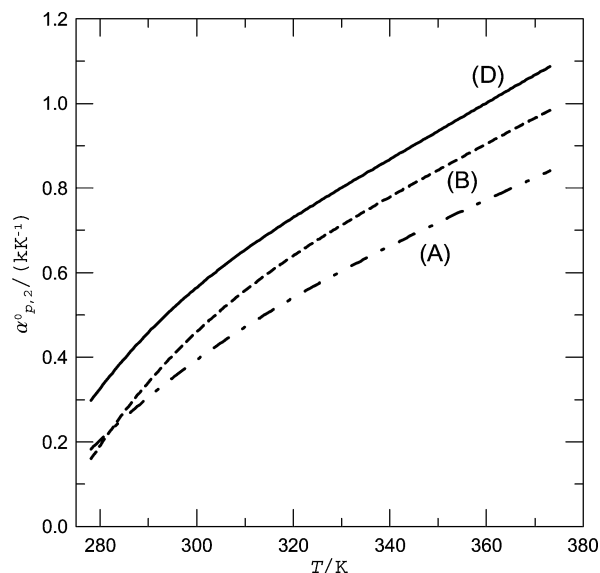


Figure 8. Plot of smoothed isobaric expansivities $\alpha^0_{p,2} = (1/V^0_{m,2})(\partial V^0_{m,2}/\partial T)_p$ at $p = 0.1$ MPa against temperature. Full line, 2,2-dimethylpropane-1,3-diol (D); dashed line, 2-methylpropane-1,3-diol³ (B); dash-and-dot line, propane-1,3-diol² (A).

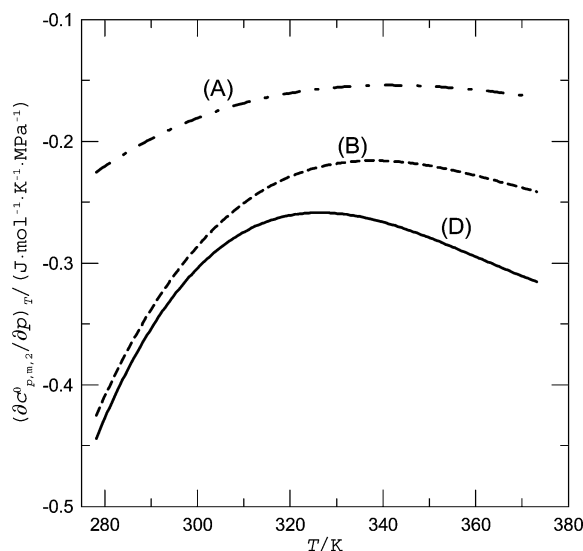


Figure 9. Plot of smoothed derivatives of heat capacity with respect to pressure $(\partial c_{p,m,2}^0 / \partial p)_T = -T(\partial^2 V_{m,2}^0 / \partial T^2)_p$ at $p = 0.1$ MPa against temperature. Full line, 2,2-dimethylpropane-1,3-diol (D); dashed line, 2-methylpropane-1,3-diol (B); dash-and-dot line, propane-1,3-diol (A).

the derivative of standard isobaric heat capacity with respect to pressure $(\partial c_{p,m,2}^0 / \partial p)_T = -T(\partial^2 V_{m,2}^0 / \partial T^2)_p$ for the series of three diols with the ratio between the hydrophilic and the hydrophobic part of the solute molecule increasing in the order 2,2-dimethylpropane-1,3-diol (D), 2-methylpropane-1,3-diol (B), and propane-1,3-diol (A). Obviously the dependence $V_{m,2}^0(T)$ becomes less convex (Figure 8) with lower curvature (Figure 9) when the solute molecule becomes more hydrophilic. This confirms a general behavior observed for several other series^{13,14} consisting of solutes with various degrees of hydrophilic character. The dependence $V_{m,2}^0(T)$ may even become concave for highly hydrophilic solutes as it is clearly seen in Figure 10 for the series of four alcohols derived from

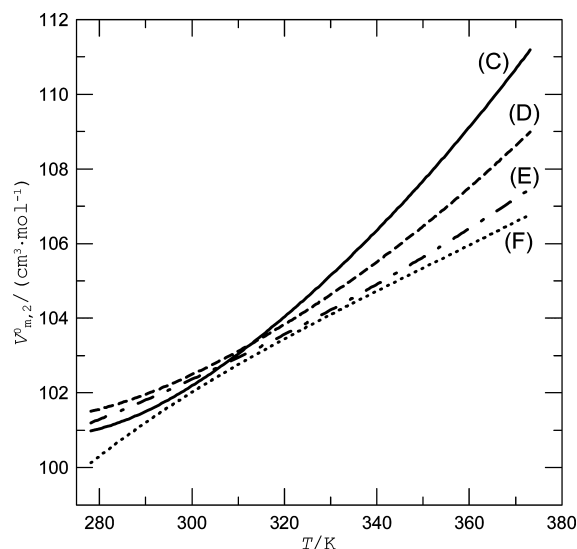


Figure 10. Plot of smoothed standard molar volumes $V_{m,2}^0$ at $p = 0.1$ MPa against temperature. Full line, 2,2-dimethylpropane-1-ol (C); dashed line, 2,2-dimethylpropane-1,3-diol (D); dash-and-dot line, 2,2-bis(hydroxymethyl)propane-1-ol (E); dotted line, 2,2-bis(hydroxymethyl)propane-1,3-diol (F).

2,2-dimethylpropane, that is, (in the order of increasing hydrophilic character) 2,2-dimethylpropane-1-ol (C), 2,2-dimethylpropane-1,3-diol (D), 2,2-bis(hydroxymethyl)propane-1-ol (E), and 2,2-bis(hydroxymethyl)propane-1,3-diol (F). In the range of low temperatures the dependence is concave for the most hydrophilic solute (F), and consequently its expansivity $\alpha_{p,2}^0$ is decreasing in this temperature range (Figure 11). The magnitude and sign of the second derivative $(\partial^2 V_{m,2}^0 / \partial T^2)_p$ correspond to the various shapes of the $V_{m,2}^0(T)$ dependences as can be deduced from Figure 12.

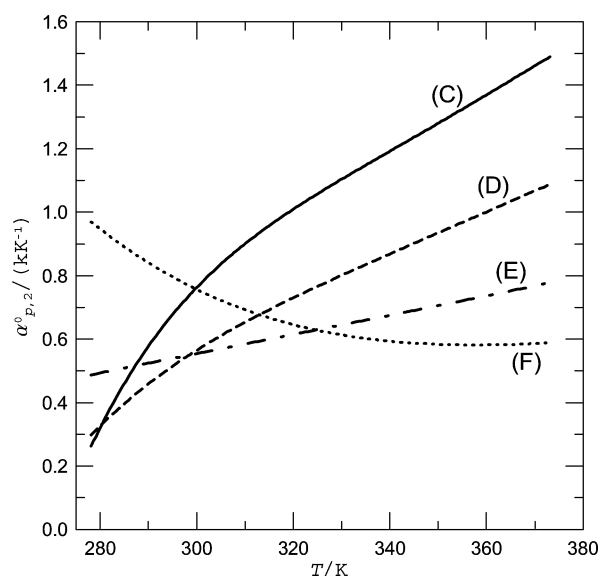


Figure 11. Plot of smoothed isobaric expansivities $\alpha_{p,2}^0 = (1/V_{m,2}^0)(\partial V_{m,2}^0 / \partial T)_p$ at $p = 0.1$ MPa against temperature. Full line, 2,2-dimethylpropane-1-ol (C); dashed line, 2,2-dimethylpropane-1,3-diol (D); dash-and-dot line, 2,2-bis(hydroxymethyl)propane-1-ol (E); dotted line, 2,2-bis(hydroxymethyl)propane-1,3-diol (F).

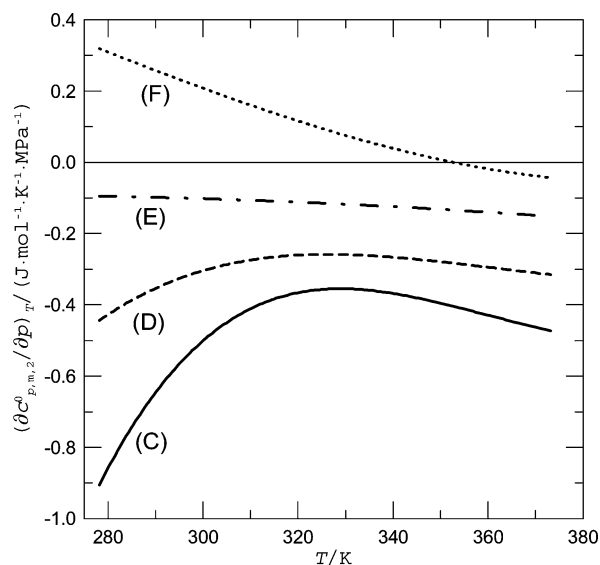


Figure 12. Plot of smoothed derivatives of heat capacity with respect to pressure $(\partial c_{p,m,2}^0 / \partial p)_T = -T(\partial^2 V_{m,2}^0 / \partial T^2)_p$ at $p = 0.1$ MPa against temperature. Full line, 2,2-dimethylpropane-1-ol (C); dashed line, 2,2-dimethylpropane-1,3-diol (D); dash-and-dot line, 2,2-bis(hydroxymethyl)propane-1-ol (E); dotted line, 2,2-bis(hydroxymethyl)propane-1,3-diol (F).

CONCLUSIONS

New data on speed of sound are reported for the series of aqueous aliphatic alcohols with a branched hydrocarbon frame. New density data were also measured for solutions of two of those solutes, and standard molar volumes were evaluated. Combined experimental data on speed of sound and density were then employed for the evaluation of standard molar isentropic compression of the solutes in the temperature range (278 to 318) K. Standard molar isentropic compression and the standard molar volume are strongly affected by the structure of solute molecule, but clear regularities are observed within the homologous series in the range of low temperatures. These regularities are predominantly governed by the ratio between hydrophilic (hydroxyl groups) and hydrophobic (hydrocarbon frame) parts of the solute molecule. Contributions of the methylene group and the oxygen atom in the hydroxyl group to the standard molar isentropic compression and the contribution of the methylene group to the standard molar volume were also evaluated and compared with values obtained from data available for other homologous series in the literature.

ASSOCIATED CONTENT

Supporting Information

Description of the procedure of fitting the combined set of standard molar volume data (this work and ref 4) of 2,2-dimethylpropane-1,3-diol(aq) and 2,2-bis(hydroxymethyl)propane-1,3-diol(aq) using a polynomial function of temperature and pressure and adjustable parameters of the smoothing polynomial for the two aqueous solutes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Funding

Support from the Ministry of Education, Youth and Sports of the Czech Republic (fund MSM6046137307) is acknowledged.

Notes

The authors declare no competing financial interest.

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