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Partial Molar Volumes and Partial Molar Isentropic Compressions of Three Polyhydric Alcohols Derived from Propane at Infinite Dilution in Water at Temperatures T = (278 to 318) K and Atmospheric Pressure

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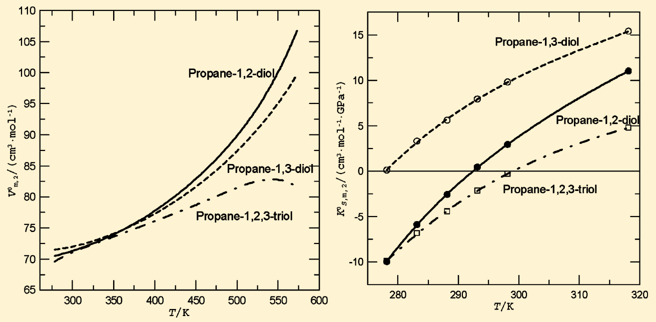
S *Supporting Information*

ABSTRACT: Density and speed of sound data for dilute aqueous solutions of three polyhydric alcohols derived from propane (propane-1,2-diol, propane-1,3-diol, propane-1,2,3-triol) 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. Partial molar volumes at infinite dilution (standard molar volumes) and partial molar isentropic compressions at infinite dilution (standard molar isentropic compressions) were calculated from the measured data.



INTRODUCTION

This work is a part of our systematic study of standard properties of aqueous organic solutes. The aim of this study is to reveal general features of behavior of wide ranges of solutes (hydrophobic, hydrophilic) along with the effort to fill a database with experimental data for properly selected solutes that might be employed for evaluations of related properties (standard chemical potential) and the development of estimation methods.

We have already measured the partial molar volumes at infinite dilution (standard molar volumes) of all aqueous polyhydric alcohols derived from propane in the temperature range from (298 to 573) K and at pressures up to 30 MPa using our high-temperature high-pressure flow densimeter.[1] This device is not equipped with any cooling system, and therefore measurements below the laboratory temperature are not possible. A recently installed vibrating-tube densimeter DSA 5000 (Anton Paar) enabled us to extend the experimental temperature range below the laboratory temperature and thus to enlarge our previous data set on standard molar volumes with new data at temperatures down to 278 K and at atmospheric pressure. Besides that the vibrating tube provides data on sample density, and the model DSA 5000 incorporates also the sound analyzer; thus measurements of speed of sound were also possible, and consequently partial molar isentropic compressions at infinite dilution (standard molar isentropic compressions) were calculated from the measured data. All measurements done with the DSA 5000 device were performed with air-saturated samples and under atmospheric pressure, and therefore the upper temperature limit is given by the formation of air bubbles in measured samples; experimental observation revealed that the highest temperature at which the air-bubble formation had negligible effect on the measurements was about 318 K. Thus the temperature ranges of our present and previous measurements overlap slightly; this enables us to compare the results obtained for the same systems using two different experimental devices (based, however, on the same principle).

EXPERIMENTAL SECTION

The specifications of the organic solutes are summarized in Table 1. Distilled, demineralized (Millipore RQ) water was 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) to determine the mass of the solute and a Precisa 2200C SCS balance (resolution = 10 mg, estimated uncertainty = $\pm\ 2\cdot10^{-2}$ percent) to determine the mass of water. The mass of each prepared solution was about 1 kg. Air-saturated water was used for preparation of solutions. Six solutions in the molality range from (0.1 to 0.6) mol·kg^{-1} were measured for each solute. Molalities were corrected with respect to the content of water in the solute samples (Table 1).

The vibrating-tube densimeter manufactured by Anton Paar, model DSA 5000, with a built-in thermostat and equipped with the autosampler SP-1m (Anton Paar) was used for the measurements. 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.

Measurements were performed in an isothermal mode; that is, the measurements of all prepared solution were done at the same

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Table 1. Specifications of Chemical Samples of Solutes

chemical name	formula	CAS RN	source	mass fraction purity[a]	purification method	mass fraction of water[b]
propane-1,2-diol	$C_3H_8O_2$	57-55-6	Sigma Aldrich	>0.995	used as supplied	0.00033
propane-1,3-diol	$C_3H_8O_2$	504-63-2	Sigma Aldrich	>0.996	used as supplied	0.0012
propane-1,2,3-triol	$C_3H_8O_3$	56-81-5	Sigma Aldrich	0.99	used as supplied	0.0019

[a] Declared by the supplier. [b] Determined by the Fischer method.

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 density of water was usually ± $1 \cdot 10^{-3}$ $\text{kg} \cdot \text{m}^{-3}$ (slightly worse at higher temperatures). The reproducibility of measurements of speed of sound was between ± 0.03 $\text{m} \cdot \text{s}^{-1}$ at 278.15 K and ± 0.06 $\text{m} \cdot \text{s}^{-1}$ at 298.15 K; significantly larger scatter ± 0.2 $\text{m} \cdot \text{s}^{-1}$ was observed at 318.15 K (it is likely that sound waves caused the generation of air microbubbles in the samples). To minimize the effects of both the device drifts and the systematic uncertainties in the calibration, the averages of two values measured for density of water (ρ_1) and those for speed of sound (c_1) at each temperature and for each set of solutions were used to calculate the density differences $\Delta\rho = \rho - \rho_1$ and differences in speed of sound $\Delta c = c - c_1$ where ρ and c are the densities of and speed of sound in the solution, respectively.

It was observed that experimental values of ρ_1 and c_1 exhibited systematic deviations from values presented by the National Institute of Standards and Technology (NIST).[2] Experimental densities were slightly higher at low temperatures (by about 0.015 $\text{kg} \cdot \text{m}^{-3}$) and lower at higher temperatures (by 0.004 $\text{kg} \cdot \text{m}^{-3}$), measured speeds of sound were systematically higher (average deviation 0.7 $\text{m} \cdot \text{s}^{-1}$). The effect of these small deviations on the goal quantities (standard molar volumes, standard molar isentropic compressions) is negligible since in the differences $\Delta\rho = \rho - \rho_1$ and $\Delta[(\rho c)^2] = (\rho c)^2 - (\rho_1 c_1)^2$ (see below) these systematic deviations cancel out. Therefore measured differences $\Delta\rho$ and Δc were regarded as direct experimental data. Values ρ_1(NIST) and c_1(NIST) were used for the evaluations of standard molar volumes and standard molar isentropic compressions (see eqs 2 and 8 below) as well as for the calculations of densities and speeds of sound of solutions, that is, $\rho = \Delta\rho(\text{experimental}) + \rho_1(\text{NIST})$ and $c = \Delta c(\text{experimental}) + c_1(\text{NIST})$ as needed for the evaluation of standard molar isentropic compressions. Values ρ_1(NIST) and c_1(NIST) are summarized in Table 2.

Table 2. Density ρ_1 and Speed of Sound c_1 in Water[2]

T	ρ_1	c_1
K	$\text{kg} \cdot \text{m}^{-3}$	$\text{m} \cdot \text{s}^{-1}$
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
318.15	990.213	1536.45

RESULTS

Direct Experimental Data. The values of the density differences $\Delta\rho = \rho - \rho_1$ where ρ and ρ_1 are the measured densities of the solution and water, respectively, and values of the differences in speed of sound $\Delta c = c - c_1$ where c and c_1 are the measured speeds of sound in the solution and water, respectively, along with the molalities of organic solutes m_2 are recorded in Table 3. Triplicate measurements were performed for each solution. Few measured values were excluded due to large deviations from the other measurements, and in those cases there are blank spaces in the table.

Standard Molar Volumes. The dependence of $\Delta\rho/m_2$ on m_2 at constant temperature was treated as a quadratic function of m_2 in the composition ranges of measurements. The experimental results obtained for each temperature were fitted with the equation

$$\Delta\rho/m_2 = (\rho - \rho_1)/m_2 = a_V + b_V m_2 + c_V {m_2}^2 \tag{1}$$

where a_V, b_V, and c_V are adjustable coefficients. The values of the coefficients were obtained by using a least-squares method with unit weights and are recorded in Table 4.

The partial molar volume at infinite dilution ($m_2 \to 0$) of a solute $V^{\circ}_{\text{m},2}$ (named standard molar volume in the following text) is obtained from eq 1 as[3]

$$V^0_{\text{m},2} = \frac{1}{\rho_1}\left(M_2 - \frac{a_V}{\rho_1}\right) \tag{2}$$

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 4. Experimental standard molar volumes were smoothed using a polynomial function described in detail in the Supporting Information.

Standard Molar Isentropic Compressions. Partial molar isentropic compression at infinite dilution (standard molar isentropic compression) is defined as a derivative of standard molar volume with respect to pressure at constant entropy

$$K^0_{S,\text{m},2} = \lim_{m_2 \to 0}\left(\frac{-\partial V^{\text{app}}_{\text{m},2}}{\partial p}\right)_S = -\left(\frac{\partial V^0_{\text{m},2}}{\partial p}\right)_S \tag{3}$$

Apparent molar volume can be expressed as

$$V^{\text{app}}_{\text{m},2} = \frac{M_2}{\rho} - \frac{\rho - \rho_1}{m_2 \rho \rho_1} = \frac{M_2}{\rho} - \frac{1}{m_2}\left(\frac{1}{\rho_1} - \frac{1}{\rho}\right) \tag{4}$$

and thus the apparent molar isentropic compression can be written as

$$\begin{aligned} K^{\text{app}}_{S,\text{m},2} &= -\left(\frac{\partial V^{\text{app}}_{\text{m},2}}{\partial p}\right)_S \\ &= \frac{M_2}{\rho^2}\left(\frac{\partial \rho}{\partial p}\right)_S - \frac{1}{m_2}\left[\frac{1}{\rho_1^2}\left(\frac{\partial \rho_1}{\partial p}\right)_S - \frac{1}{\rho^2}\left(\frac{\partial \rho}{\partial p}\right)_S\right] \end{aligned} \tag{5}$$

Table 3. Experimental Differences $\Delta\rho = \rho - \rho_1$ and $\Delta c = c - c_1$ Measured for Propane-1,2-diol(aq), Propane-1,3-diol(aq), and Propane-1,2,3-triol(aq) at Atmospheric Pressure[a]

m_2	$\Delta\rho$	Δc	$\Delta\rho$	Δc	$\Delta\rho$	Δc	$\Delta\rho$	Δc	$\Delta\rho$	Δc	$\Delta\rho$	Δc
mol·kg^{-1}	kg·m^{-3}	m·s^{-1}	kg·m^{-3}	m·s^{-1}	kg·m^{-3}	m·s^{-1}	kg·m^{-3}	m·s^{-1}	kg·m^{-3}	m·s^{-1}	kg·m^{-3}	m·s^{-1}
	T = 278.15 K		T = 283.15 K		T = 288.15 K		T = 293.15 K		T = 298.15 K		T = 318.15 K	
Propane-1,2-diol(aq)												
0.099682	0.563	6.05	0.545	5.58			0.518	4.77			0.461	3.04
0.099682	0.562	5.99	0.546	5.56	0.532	5.16	0.519	4.77	0.506	4.36	0.464	3.12
0.099682	0.562	6.03	0.547	5.56	0.533	5.17	0.519	4.73	0.507	4.45	0.464	3.20
0.200214	1.138	12.07	1.100	11.13	1.071	10.30	1.043	9.52	1.017	8.77	0.925	6.30
0.200214	1.136	12.03	1.101	11.11	1.072	10.29	1.045	9.50	1.019	8.85	0.928	6.38
0.200214	1.136	12.07	1.102	11.11	1.072	10.32	1.046	9.49	1.021	8.77	0.932	6.44
0.300185	1.714	18.01	1.657	16.58	1.609	15.36	1.567	14.18	1.529	13.11	1.385	9.52
0.300185	1.713	17.97	1.657	16.57	1.610	15.33	1.568	14.21	1.531	13.20	1.388	9.60
0.300185	1.712	18.01	1.657	16.59	1.611	15.34	1.571	14.20	1.534	13.10	1.390	9.53
0.400656	2.296	23.90	2.218	22.03	2.152	20.39	2.094	18.80	2.040	17.42	1.846	12.67
0.400656	2.296	23.90	2.219	22.03	2.153	20.35	2.095	18.82	2.041	17.50	1.846	12.66
0.400656	2.296	23.93	2.219	22.03	2.154	20.37	2.095	18.87	2.043	17.40	1.849	12.73
0.500575	2.878	29.70	2.779	27.39	2.694	25.29	2.620	23.39	2.548	21.64	2.303	15.75
0.500575	2.879	29.69	2.781	27.39	2.696	25.34	2.621	23.43	2.550	21.72	2.303	15.80
0.500575	2.879	29.74	2.781	27.40	2.696	25.30	2.622	23.42	2.552	21.60	2.304	15.78
0.600207	3.462	35.46	3.341	32.71	3.235	30.16	3.142	27.90	3.058	25.79	2.754	18.77
0.600207	3.464	35.49	3.342	32.68	3.237	30.22	3.143	27.91	3.060	25.75	2.756	18.81
0.600207	3.463	35.50	3.342	32.69	3.239	30.18	3.143	27.94	3.060	25.88	2.756	18.80
Propane-1,3-diol(aq)												
0.099729	0.461	4.73	0.449	4.32	0.443	4.00	0.438	3.66	0.434	3.36	0.416	2.41
0.099729	0.461	4.73	0.450	4.32	0.444	3.99	0.438	3.70	0.435	3.38	0.416	2.47
0.099729	0.462	4.73	0.451	4.34	0.446	4.04	0.439	3.67	0.436	3.38	0.418	2.44
0.200640	0.930	9.47	0.912	8.67	0.897	7.99	0.883	7.36	0.875	6.79	0.831	4.92
0.200640	0.933	9.47	0.913	8.69	0.898	8.00	0.883	7.36	0.876	6.79	0.831	4.89
0.200640	0.933	9.48	0.914	8.67	0.899	8.05	0.884	7.39	0.876	6.80		
0.299985	1.399	14.12	1.370	12.92	1.346	11.90	1.323	10.99	1.305	10.12	1.240	7.28
0.299985	1.401	14.12	1.373	12.95	1.347	11.95	1.325	10.95	1.305	10.12	1.241	7.38
0.299985	1.402	14.13	1.373	12.93	1.347	11.90	1.325	10.95	1.306	10.12	1.241	7.34
0.400516	1.882	18.80	1.835	17.19	1.803	15.82	1.771	14.58	1.744	13.45	1.645	9.77
0.400516	1.883	18.81	1.837	17.21	1.803	15.78	1.772	14.52	1.745	13.45	1.647	9.75
0.400516	1.884	18.83	1.838	17.20	1.805	15.82	1.772	14.57	1.745	13.44	1.659	9.77
0.499823	2.356	23.36	2.299	21.38	2.251	19.63	2.212	18.05	2.180	16.70	2.059	12.05
0.499823	2.359	23.38	2.300	21.38	2.254	19.61	2.213	18.09	2.180	16.72	2.059	12.12
0.499823	2.360	23.38	2.300	21.39	2.255	19.64	2.215	18.10	2.183	16.71	2.059	12.15
0.599480	2.839	27.91	2.771	25.56	2.709	23.44	2.662	21.59	2.613	19.93	2.466	14.45
0.599480	2.841	27.90	2.773	25.55	2.715	23.44	2.662	21.62	2.613	19.94	2.470	14.40
0.599480	2.843	27.91			2.715	23.47	2.662	21.60	2.614	19.93	2.470	14.43
Propane-1,2,3-triol(aq)												
0.101109	2.260	4.83	2.223	4.52	2.189	4.26	2.163	4.00	2.136	3.82	2.070	2.96
0.101109	2.262	4.82	2.226	4.53	2.194	4.27	2.163	4.00	2.143	3.76	2.073	2.87
0.101109	2.263	4.83	2.225	4.52	2.194	4.26	2.162	3.99	2.141	3.78	2.065	3.31
0.199937	4.440	9.51	4.367	8.91	4.306	8.40	4.251	7.88	4.198	7.36	4.055	5.92
0.199937	4.442	9.49	4.372	8.90	4.309	8.40	4.251	7.88	4.206	7.42	4.059	5.81
0.199937	4.442	9.50	4.372	8.91	4.310	8.39	4.250	7.88	4.204	7.43	4.059	5.94
0.300303	6.630	14.25	6.512	13.31	6.422	12.53	6.339	11.78	6.265	11.09	6.059	8.86
0.300303	6.634	14.24	6.517	13.31	6.425	12.54	6.341	11.78	6.273	11.11	6.058	8.82
0.300303	6.635	14.24	6.517	13.31	6.426	12.54	6.344	11.79	6.273	11.11	6.061	9.03
0.399580	8.754	18.85	8.608	17.65	8.483	16.58	8.375	15.60	8.277	14.69	8.006	11.76
0.399580	8.759	18.87	8.611	17.65	8.491	16.60	8.378	15.60	8.285	14.72	8.010	11.72
0.399580	8.764	18.87	8.614	17.65	8.493	16.60	8.379	15.60	8.285	14.71	8.007	11.93
0.499583	10.884	23.50	10.697	21.98	10.533	20.64	10.399	19.41	10.282	18.29	9.949	14.61
0.499583	10.885	23.48	10.694	21.97	10.535	20.63	10.402	19.41	10.286	18.29	9.952	14.44
0.499583	10.890	23.48	10.701	21.99	10.538	20.64	10.403	19.42	10.287	18.31		
0.599054	12.963	28.03	12.726	26.22	12.549	24.64	12.387	23.17	12.238	21.81	11.840	17.53

Table 3. continued

m_2	$\Delta\rho$	Δc	$\Delta\rho$	Δc	$\Delta\rho$	Δc	$\Delta\rho$	Δc	$\Delta\rho$	Δc	$\Delta\rho$	Δc
$mol·kg^{-1}$	$kg·m^{-3}$	$m·s^{-1}$	$kg·m^{-3}$	$m·s^{-1}$	$kg·m^{-3}$	$m·s^{-1}$	$kg·m^{-3}$	$m·s^{-1}$	$kg·m^{-3}$	$m·s^{-1}$	$kg·m^{-3}$	$m·s^{-1}$
						Propane-1,2,3-triol(aq)						
0.599054	12.959	28.01	12.729	26.22	12.548	24.62	12.386	23.15	12.244	21.76	11.830	17.44
0.599054	12.965	28.01	12.734	26.22	12.552	24.64	12.389	23.17	12.246	21.84	11.846	17.23

[a] Standard uncertainties are $u(T) = 0.01$ K, $u(m_2) = 3·10^{-5}$ mol·kg^{-1}, and the combined expanded uncertainties are $U_c(\Delta\rho) = 2·10^{-3}$ kg·m^{-3}, $U_c(\Delta c) = 0.3$ m·s^{-1} at $T = 318.15$ K, and $U_c(\Delta c) = 0.1$ m·s^{-1} at lower temperatures (level of confidence = 0.95).

Table 4. Coefficients a_V, b_V, and c_V of Equation 1, Standard Molar Volumes $V^{\circ}_{m,2}$, Coefficients a_K and b_K of Equation 7, and Standard Molar Isentropic Compressions $K^0_{S,m,2}$ for {Propane-1,2-diol (2), Propane-1,3-diol (2), or Propane-1,2,3-triol (2) + Water (1)}. The Uncertainties $\sigma(V^0_{m,2})$ and $\sigma(K^0_{S,m,2})$ Represent the Combined Expanded Uncertainties

T	a_V	b_V	c_V	$V^0_{m,2} \pm \sigma(V^0_{m,2})$	$a_K·10^{-12}$	$b_K·10^{-12}$	$K^0_{S,m,2} \pm \sigma(K^0_{S,m,2})$
K	$kg^2·m^{-3}·mol^{-1}$	$kg^3·m^{-3}·mol^{-2}$	$kg^4·m^{-3}·mol^{-3}$	$cm^3·mol^{-1}$	$kg^3·m^{-4}·s^{-2}·mol^{-1}$	$kg^4·m^{-4}·s^{-2}·mol^{-2}$	$cm^3·mol^{-1}·GPa^{-1}$
				Propane-1,2-diol(aq)			
278.15	5.6017	0.4115	−0.2229	70.49 ± 0.04	0.1961	−0.0011	−10.0 ± 0.2
283.15	5.4554	0.2446	−0.0947	70.66 ± 0.04	0.1852	−0.0024	−5.9 ± 0.2
288.15	5.3306	0.1173	−0.0212	70.82 ± 0.04	0.1752	−0.0040	−2.6 ± 0.2
293.15	5.1903	0.1535	−0.1293	71.02 ± 0.04	0.1646	−0.0032	0.4 ± 0.2
298.15	5.0722	0.1177	−0.1335	71.22 ± 0.04	0.1550	−0.0038	2.9 ± 0.2
318.15	4.6533	−0.0993	−0.0116	72.10 ± 0.04	0.1172	0.0006	11.0 ± 0.5
				Propane-1,3-diol(aq)			
278.15	4.593	0.2777	−0.0531	71.50 ± 0.03	0.1544	−0.0003	0.1 ± 0.2
283.15	4.4858	0.3404	−0.1984	71.63 ± 0.03	0.1449	−0.0006	3.3 ± 0.2
288.15	4.4488	0.1363	−0.0193	71.71 ± 0.03	0.1375	−0.0036	5.6 ± 0.2
293.15	4.3883	0.0828	0.0034	71.83 ± 0.03	0.1287	−0.0025	7.9 ± 0.2
298.15	4.3728	−0.0927	0.1231	71.92 ± 0.03	0.1209	−0.0018	9.8 ± 0.2
318.15	4.1963	−0.3098	0.3023	72.57 ± 0.03	0.0937	−0.0018	15.4 ± 0.5
				Propane-1,2,3-triol(aq)			
278.15	22.5104	−1.4429	−0.0188	69.58 ± 0.07	0.2284	−0.0023	−9.9 ± 0.2
283.15	22.1525	−1.5027	0.0050	69.96 ± 0.07	0.2228	−0.0035	−6.9 ± 0.2
288.15	21.8572	−1.5765	0.0937	70.28 ± 0.07	0.2181	−0.0053	−4.5 ± 0.2
293.15	21.5340	−1.3742	−0.0992	70.65 ± 0.07	0.212	−0.0044	−2.2 ± 0.2
298.15	21.3329	−1.5469	−0.0899	70.91 ± 0.07	0.2066	−0.0047	−0.3 ± 0.2
318.15	20.5883	−1.3960	0.0464	72.01 ± 0.07	0.1877	−0.0081	4.8 ± 0.5

Using the combination of the definition of isentropic compressibility $\kappa_S = 1/\rho(\partial\rho/\partial p)_S$ with the Newton−Laplace equation $\kappa_S = 1/(\rho c^2)$ eq 5 can be further rearranged as

$$K^{\mathrm{app}}_{S,m,2} = \frac{M_2}{(\rho c)^2} - \frac{1}{m_2}\left[\frac{1}{(\rho_1 c_1)^2} - \frac{1}{(\rho c)^2}\right] = \frac{1}{(\rho c)^2}\left[M_2 - \frac{\Delta[(\rho c)^2]}{m_2(\rho_1 c_1)^2}\right] \quad (6)$$

where $\Delta[(\rho c)^2] = (\rho c)^2 - (\rho_1 c_1)^2$.

For evaluation of isentropic compression, the experimental data were fitted with an equation

$$\frac{\Delta[(\rho c)^2]}{m_2} = \frac{(\rho c)^2 - (\rho_1 c_1)^2}{m_2} = a_K + b_K m_2 \quad (7)$$

The limit of infinite dilution ($m_2 \to 0$) gives $(\rho c)^2 \to (\rho_1 c_1)^2$ and $\Delta[(\rho c)^2]/m_2 \to a_K$, and eq 6 turns into the expression for standard molar isentropic compression

$$K^0_{S,m,2} = \frac{1}{(\rho_1 c_1)^2}\left(M_2 - \frac{a_K}{(\rho_1 c_1)^2}\right) \quad (8)$$

with the form analogous to eq 2 for standard molar volume. The values of the coefficients a_K and b_K were obtained from measured data (Table 3) by using a least-squares method with unit weights and are recorded in Table 4 along with calculated values of $K^0_{S,m,2}$. Uncertainties $\sigma(K^0_{S,m,2})$ are affected mainly by the uncertainty in speed of sound which was estimated to be about ± 0.1 m·s^{-1} at temperatures from (278 to 298) K and ± 0.3 m·s^{-1} at 318 K.

■ DISCUSSION

Comparison with Published Data. Comparison of experimental standard molar volumes with values taken from the literature is presented in Table 5. Most of data published in the literature were obtained at atmospheric pressure and at temperatures from 298.15 K upward. The detailed comparison of our data measured previously for $T \geq 298.15$ K using our high-temperature high-pressure flow densimeter with available data from the literature was already presented,[1] and satisfactory agreement was observed. Our new values obtained here for the temperature range from (298.15 and 318.15) K agree well with our previous data.[1] The differences in standard molar volumes caused by small differences in experimental temperatures and pressures (see Table 5) are well below experimental uncertainties; maximum values of $[\partial \ln(V^{\circ}_{m,2})/\partial T]_p$ and $[-\partial \ln(V^{\circ}_{m,2})/\partial p]_T$ evaluated from the fits described in the Supporting Information

Table 5. A Comparison of Measured Values of Standard Molar Volume with the Values Taken from the Literature

this work		literature				
T	$V^0_{\mathrm{m,2}}$	T	p	$V^0_{\mathrm{m,2}}$		dev.[a]
K	$\mathrm{cm^3 \cdot mol^{-1}}$	K	MPa	$\mathrm{cm^3 \cdot mol^{-1}}$	ref	$\mathrm{cm^3 \cdot mol^{-1}}$
			Propane-1,2-diol(aq)			
298.15	71.22 ± 0.04	298.21	0.64	71.23 ± 0.03	1	−0.01
318.15	72.10 ± 0.04	318.17	0.50	72.14 ± 0.03	1	−0.04
			Propane-1,3-diol(aq)			
278.15	71.50 ± 0.03	278.15	0.1	71.40	4	0.10
			0.1	71.40 ± 0.05	5	0.10
283.15	71.63 ± 0.03	283.15	0.1	71.51 ± 0.05	5	0.12
293.15	71.83 ± 0.03	293.15	0.1	71.44	6	0.39
		293.15	0.1	71.93 ± 0.05	5	−0.10
298.15	71.92 ± 0.03	298.15	0.1	71.89	4	0.03
		298.22	0.64	71.93 ± 0.02	1	−0.01
313.15	72.41[b]	313.15	0.1	72.29	6	0.12
		313.15	0.1	72.39 ± 0.05	5	0.02
318.15	72.57 ± 0.03	318.15	0.1	72.55	4	0.02
		318.17	0.49	72.62 ± 0.02	1	−0.05
			Propane-1,2,3-triol(aq)			
298.15	70.91 ± 0.07	298.21	0.64	70.93 ± 0.04	1	−0.02
318.15	72.01 ± 0.07	318.17	0.47	72.05 ± 0.04	1	−0.04

[a] Deviation between this work and the literature value. [b] Calculated for p = 0.1 MPa from eq S1 presented in the Supporting Information.

in the range from (298 to 318) K are $7 \cdot 10^{-4}$ $\mathrm{K^{-1}}$ and $3 \cdot 10^{-4}$ $\mathrm{MPa^{-1}}$, respectively, for the aqueous solutes investigated. Data on standard molar volumes for $T < 298$ K were found in the literature for aqueous propane-1,3-diol only and are compared with our values in Table 5. Except for data by Alexander[6] which are systematically lower than our values the agreement with other data[4,5] can be regarded as very satisfactory, mostly within the estimated experimental uncertainties.

A comparison of measured standard molar isentropic compressions with data from the literature is presented in Table 6.

Table 6. A Comparison of Measured Values of Standard Molar Isentropic Compression with the Values at p = 0.1 MPa Taken from the Literature

this work		literature		
T	$K^0_{\mathrm{S,m,2}}$	$K^0_{\mathrm{S,m,2}}$		dev.[a]
K	$\mathrm{cm^3 \cdot mol^{-1} \cdot GPa^{-1}}$	$\mathrm{cm^3 \cdot mol^{-1} \cdot GPa^{-1}}$	ref	$\mathrm{cm^3 \cdot mol^{-1} \cdot GPa^{-1}}$
		Propane-1,2-diol(aq)		
298.15	2.9 ± 0.2	5.6	7	−2.7
308.15	7.2[b]	15.4	7	−8.2
318.15	11.0 ± 0.5	19.7	7	−8.7
		Propane-1,3-diol(aq)		
278.15	0.1 ± 0.2	−0.7	5,8	0.8
283.15	3.3 ± 0.2	1.8	5	1.5
293.15	7.9 ± 0.2	7.0	5	0.9
298.15	9.8 ± 0.2	−0.3	7	10.1
		9.5	8	0.3
308.15	12.8[b]	8.0	7	4.8
313.15	14.1[b]	14.5	5	−0.4
318.15	15.4 ± 0.5	10.9[c]	7	4.5
		15.2	8	0.2

[a] Deviation between this work and the literature value. [b] Interpolated using a cubic function of temperature. [c] Probably typographical errors were observed in speed of sound data.[7]

No data were found for aqueous propane-1,2,3-triol. In the case of propane-1,3-diol our values at higher temperatures agree well with data by Høiland[5] and Nakajima et al.,[8] while larger deviations are observed at lower temperatures. Values calculated from density and speed of sound data measured by George and Sastry[7] for both diols deviate largely from ours. It should be, however, pointed out that measurements[7] were performed in the entire concentration range, and we have calculated the compressions from the data subset in the dilute region (the solute molality range m_2 from (0.27 to 1.74) $\mathrm{mol \cdot kg^{-1}}$). Beside that, standard molar volumes evaluated from data[7] for (298.15 and 318.15) K (not included in Table 5) differ significantly from our results, being up to 1.8 $\mathrm{cm^3 \cdot mol^{-1}}$ (propane-1,2-diol) and 0.75 $\mathrm{cm^3 \cdot mol^{-1}}$ (propane-1,3-diol) lower than our values.

Dependences on Temperature and Derived Quantities. Standard molar volumes presented in this work were combined with data obtained previously,[1] and a polynomial function of temperature and pressure was fitted to the entire set as described in the Supporting Information. The fits represent the experimental standard molar volumes obtained in this work (Table 4) with root-mean-square deviations (rmsd) (0.01, 0.02, and 0.02) $\mathrm{cm^3 \cdot mol^{-1}}$ for propane-1,2-diol, propane-1,3-diol, and propane-1,2,3-triol, respectively. Derivative quantities (see below) were evaluated by analytical differentiation of these polynomial fits. Smoothed dependences $V^0_{\mathrm{m,2}}(T)$ at p = 0.1 MPa for $T \leq 373.15$ K and at saturation pressure of pure water for $T > 373.15$ K (this pressure set is named "low pressure") are shown in Figure 1. Our new measurements confirm a general behavior observed already for aqueous cyclic ethers,[9,10] cyclic ketones,[11,12] and some other polyhydric alcohols,[13,14] that is, that the shape of $V^0_{\mathrm{m,2}}(T)$ of highly hydrophilic solutes becomes concave at low temperatures. This can be clearly seen on the $V^0_{\mathrm{m,2}}(T)$ curve of propane-1,2,3-triol. Consequently an analogue of isobaric thermal expansivity, $\alpha^0_{p,2} = (1/V^0_{\mathrm{m,2}})(\partial V^0_{\mathrm{m,2}}/\partial T)_p$ (named shortly "isobaric expansivity" in the following text), is larger compared to less hydrophilic solutes and decreases in this temperature range (see Figure 2). In cases of highly hydrophilic solutes the isobaric expansivity may even become negative[12−14] at very high temperatures, as shown for propane-1,2,3-triol[1] in Figure 2. This behavior is likely to be related to the increase in

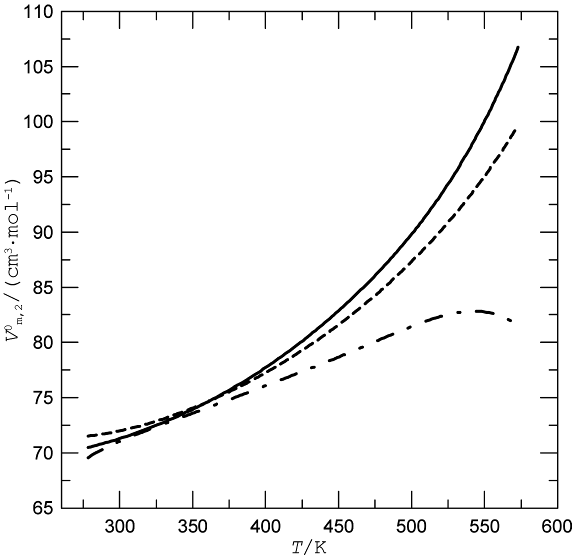

Figure 1. Plot of smoothed standard molar volumes $V^0_{\mathrm{m},2}$ at low pressures against temperature. Full line, propane-1,2-diol; dashed line, propane-1,3-diol; dot-and-dash line, propane-1,2,3-triol.

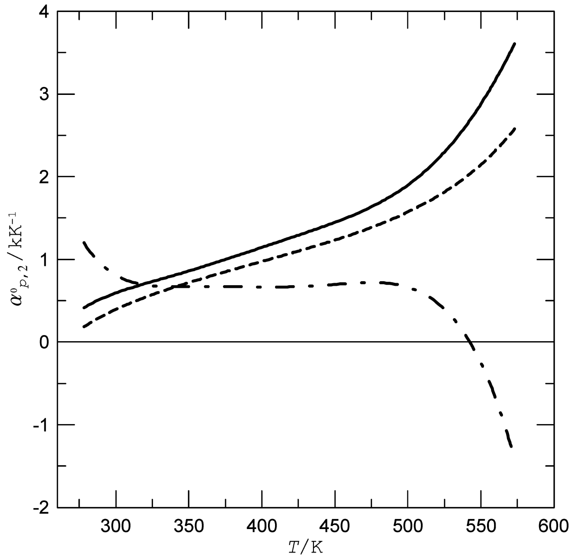

Figure 2. Plot of isobaric expansivity, $\alpha^0_{p,2} = (1/V^0_{\mathrm{m},2})(\partial V^0_{\mathrm{m},2}/\partial T)_p$, calculated for low pressures from smoothing polynomials against temperature. Full line, propane-1,2-diol; dashed line, propane-1,3-diol; dot-and-dash line, propane-1,2,3-triol.

compressibility of water in both the low and the high temperature ranges (at atmospheric pressure the isothermal compressibility of water exhibits a minimum at about 333 K). This leads to more compressible bulk water as well as the hydration shell around the solute molecule and thus to a lower standard volume due to attractive interactions between water and hydrophilic parts of the solute molecule (hydroxyl groups in this case). The concave shape of $V^0_{\mathrm{m},2}(T)$ curve leads to a negative second derivative of $V^0_{\mathrm{m},2}$ with respect to temperature, and consequently positive values of $(\partial c^0_{p,\mathrm{m},2}/\partial p)_T = -T(\partial^2 V^0_{\mathrm{m},2}/\partial T^2)_p$ are observed for highly hydrophilic aqueous solutes as it is shown in Figure 3 for propane-1,2,3-triol. Less hydrophilic diols exhibit negative values of $(\partial c^0_{p,\mathrm{m},2}/\partial p)_T$.

Two diols investigated here are structural isomers which differ in the mutual position of the hydroxyl groups. Obviously the position of the hydroxyl groups affects the standard molar volumes (Figure 1). At low temperatures the standard molar volume of propane-1,2-diol (the solute with a close vicinity of the two hydroxyl groups) is lower than that of propane-1,3-diol while the opposite relation is observed at higher temperatures. Thus the present measurements in the temperature range extended to low temperatures confirm our recent evaluation of group and structural contributions[15] which showed that the structural contribution related to two hydroxyl groups residing on the neighboring carbon atoms is negative at low temperatures and becomes positive as the temperature increases. This means that at low temperatures propane-1,2-diol is more hydrophilic (lower standard molar volume) than propane-1,3-diol, and at high temperatures the structure with two separated hydroxyl groups (propane-1,3-diol) is more hydrophilic than that with two adjacent hydroxyl groups (propane-1,2-diol). This is confirmed even by $(\partial c^0_{p,\mathrm{m},2}/\partial p)_T$ as it is shown in Figure 3 where the lines for the two diols cross each other at the temperature about 350 K.

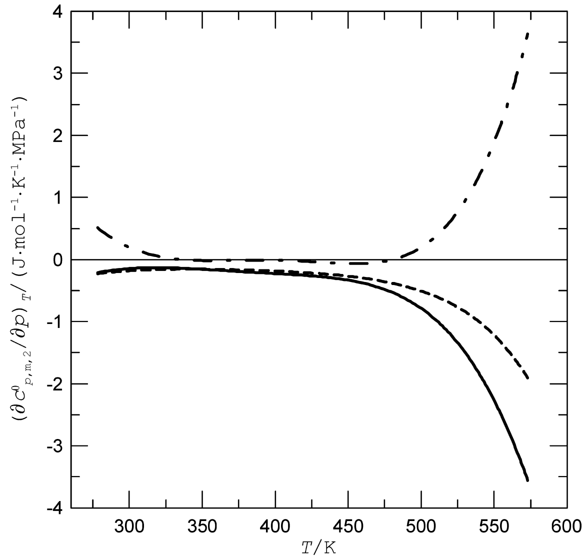

Figure 3. Plot of pressure derivative of standard heat capacity, $(\partial c^0_{p,\mathrm{m},2}/\partial p)_T = -T(\partial^2 V^0_{\mathrm{m},2}/\partial T^2)_p$, calculated for low pressures from smoothing polynomials against temperature. Full line, propane-1,2-diol; dashed line, propane-1,3-diol; dot-and-dash line, propane-1,2,3-triol.

Experimental dependences of standard molar isentropic compression of all three solutes on temperature are depicted in Figure 4. It seems likely that the close vicinity of hydroxyl groups plays a significant role, and as a result it decreases the standard molar isentropic compression. Høiland[5] has published an extensive experimental data set on standard molar isentropic compression for 12 aqueous aliphatic alcohols (1-alkanols, 2-alkanols, α,ω-alkanediols) derived from *n*-alkanes C_3 to C_6 at (278.15, 283.15, 293.15, and 313.15) K. We have tentatively evaluated the group contributions of the second-order method (contributions $-CH_3$, $-CH_2-$, $-CH(OH)-$, $-CH_2(OH)$) from these data. Back calculations over all 12 input solutes and all four temperatures resulted in the overall root-mean-square deviation (rmsd) of 1.1 $\mathrm{cm^3 \cdot mol^{-1} \cdot GPa^{-1}}$ (1.8 $\mathrm{cm^3 \cdot mol^{-1} \cdot GPa^{-1}}$ for propane-1,3-diol) between calculated and experimental values which indicates satisfactory internal consistency of the method. On the other hand, the predictions of standard molar isentropic compression performed in the temperature range from (278 to 313) K for aqueous solutes with close vicinity of hydroxyl groups in the molecule failed, largely resulting in much higher predicted

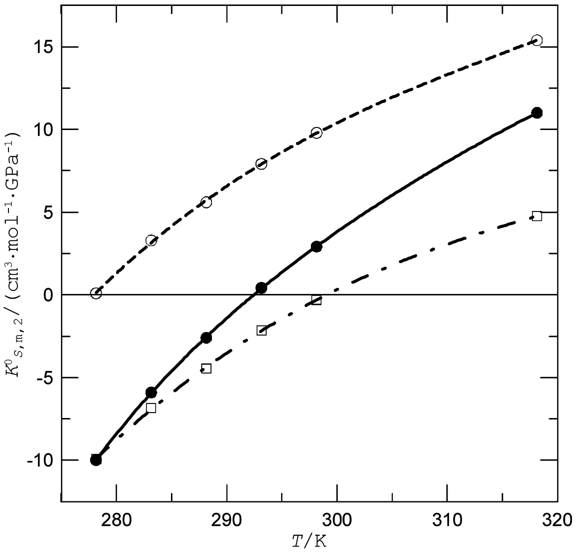

Figure 4. Plot of experimental standard molar isentropic compressions against temperature. The lines are to aid the eye. ●, full line, propane-1,2-diol; ○, dashed line, propane-1,3-diol; □, dot-and-dash line, propane-1,2,3-triol.

values compared to the experiment: rmsd's of (8.7 and 19.1) cm^3·mol^{-1}·GPa^{-1} were obtained for propane-1,2-diol and propane-1,2,3-triol, respectively. Similarly the data for aqueous α,ω-alkanediols (from C_2 to C_6) measured by Nakajima et al.[8] at (278.15, 298.15, and 318.15) K show that values obtained for ethane-1,2-diol are significantly lower than would correspond to a smooth dependence (at each temperature) within this homologous series. The effect of the first member of the series may play a role here, but it is likely that the influence of the neighboring hydroxyl groups is dominant. Measurements on aqueous diols with proper distributions of hydroxyl groups on the hydrocarbon chain might bring more light into the explanation of this behavior.

■ CONCLUSIONS

Standard molar volumes and standard molar isentropic compressions of three aqueous polyhydric alcohols derived from propane were evaluated from experimental data on density and speed of sound measured for dilute aqueous solutions at atmospheric pressure in the temperature range (278.15 to 318.15) K. Values obtained for standard molar volumes were combined with those reported previously for extended ranges of temperature and pressure and analyzed. It was clearly observed that the various degrees of hydrophilic character of the solute molecules (lower for propanediols, larger for propane-1,2,3-triol) affect the standard molar volumes and derived properties (the first and second derivatives with respect to temperature) in the same manner as observed for other classes of aqueous organic solutes. New experimental standard molar volumes of propanediols at low temperatures also confirm that the close vicinity of the hydroxyl groups on the hydrocarbon chain; that is, the structure −CH(OH)−CH(OH)− increases the hydrophilic character of the solute in this temperature region, while the opposite effect is observed at high temperatures. Standard molar isentropic compression is strongly affected by the structure of the solute molecule (number of hydroxyl groups and their distribution on the hydrocarbon frame), but data for other solutes are needed to reveal general relations between the compression and the structure of the solute molecule. The measurements to get such data are in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Description of the procedure of fitting the combined set of standard molar volume data (this work and ref 1) using a polynomial function of temperature and pressure and adjustable parameters of the smoothing polynomial 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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Notes

The authors declare no competing financial interest.

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