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Partial Molar Volumes of Cyclic Alcohols at Infinite Dilution in Water at Temperatures $T = (298 \text{ to } 373)$ K and Pressure of 0.5 MPa[†]

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Density data for dilute aqueous solutions of six cyclic alcohols (cyclopentanol, cyclohexanol, cycloheptanol, cyclooctanol, cyclohexylmethanol, and 2-cyclohexylethanol) obtained using a flow vibrating-tube densimeter are presented together with partial molar volumes at infinite dilution (standard partial molar volumes) calculated from the measured data. The measurements were performed at temperatures from $T = 298$ K up to $T = 373$ K at pressures close to the atmospheric pressure [(0.4 to 0.5) MPa]. Trends in homologous series are discussed, and group contributions to standard partial molar volume are evaluated. Using the group contributions, standard partial molar volumes of three additional solutes were estimated and compared with data from the literature.

Introduction

This study is a continuation of a systematic investigation of partial molar volumes of organic solutes in dilute aqueous solutions. A study of aliphatic hydroxy derivatives in wide temperature and pressure intervals (from ambient up to 573 K and 30 MPa) has been completed: data for all monohydric alcohols derived from methane through butane,[1,2] selected polyhydric alcohols derived from ethane and propane,[3] butane,[4] and pentane, 2,2-dimethylpropane, and hexane[5] have been published. This paper is an initial study of a group of hydroxy derivatives containing either the hydroxy group bonded directly to a cycle or the cyclohexyl group bonded to an aliphatic chain of an alkanol. Six solutes of the general molecular formula $c\text{-C}_n\text{H}_{2n-1}(\text{CH}_2)_m\text{OH}$ were studied: cyclopentanol ($n = 5$, $m = 0$), cyclohexanol ($n = 6$, $m = 0$), cycloheptanol ($n = 7$, $m = 0$), cyclooctanol ($n = 8$, $m = 0$), cyclohexylmethanol ($n = 6$, $m = 1$), and 2-cyclohexylethanol ($n = 6$, $m = 2$). The present study is focused on the low pressure region, and thus the upper temperature limit is around the normal boiling temperature of water. Due to negligible dependence of standard partial molar volumes on pressure in this temperature range,[1−5] the obtained standard partial molar volumes are fully comparable with published values obtained from measurements at atmospheric pressure.

Experimental

The densimeter and the experimental procedure are described in more detail elsewhere.[6−8] The period of the vibrating tube of the densimeter was measured by means of a counter with an uncertainty of about ± 0.2 ns, which corresponds to $\pm\, 10^{-3}$ $\text{kg}\cdot\text{m}^{-3}$ in density. Repeated calibrations of the densimeter at each experimental temperature and pressure were performed using water and nitrogen whose densities were taken from the literature.[9,10] The maximum systematic uncertainty of the measured density differences $\{\rho(\text{solution}) - \rho(\text{water})\}$ resulting from the densimeter calibration was about 0.2 %, and the reproducibility of the measurements was within $\pm\, 3\cdot10^{-3}$ $\text{kg}\cdot\text{m}^{-3}$ in most cases.

The temperature of the densimeter cell was measured using a calibrated (ITS 90) platinum resistance thermometer (BURNS Engineering), with a resistance $R_0 = 100\ \Omega$ at $T = 273.15$ K, connected to a multimeter in a four-lead configuration. The resolution of the temperature measurements was 0.1 mK. Temperature stability of the cell during one experiment (measurement of one sample) was within 1 mK. The total uncertainty of the temperature measurements was estimated to be about ± 20 mK. The pressure was measured by means of a secondary standard gauge (DIGIQUARTZ-740-6K, Paroscientific Inc.) with an uncertainty of $\pm\, 1\cdot10^{-2}$ MPa.

The organic solutes, i.e., cyclopentanol (Fluka, stated mass purity greater than 0.99), cyclohexanol (Fluka, stated mass purity greater than 0.99), cycloheptanol (Aldrich, stated mass purity 0.97), cyclooctanol (Fluka, stated mass purity 0.98), cyclohexylmethanol (Aldrich, stated mass purity greater than 0.99), and 2-cyclohexylethanol (Aldrich, stated mass purity 0.99) were used without further treatment. Distilled, demineralized (Millipore RQ), and degassed water was used as a calibration fluid for the densimeter and as a carrier liquid in the densimeter flow system. Nitrogen (Siad, mole fraction purity = 0.9999) was used as supplied. The 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 total mass of a solution. Distilled and demineralized water saturated with nitrogen was used as a solvent. The mass of each prepared solution was about 1 kg. The solutions were stored in closed bottles under nitrogen, and samples were taken for measurements without opening the bottles.[8] The uncertainty of the solute molality m_2 was estimated to be $\pm\, 2\cdot10^{-5}$ $\text{mol}\cdot\text{kg}^{-1}$.

Results

Direct Experimental Data. 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, corrected[8] for a measured difference between nitrogen-saturated and degassed water and the molalities of organic solutes m_2 at various temperatures and pressures are available as a Supporting Information (83 data

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Table 1. Density ρ_1 of Water,[9] Coefficients *a* and *b* of Equation 1, and Extrapolated Values of the Partial Molar Volumes at Infinite Dilution $V^{o}_{m,2}$ for {Cyclopentanol (2) or Cyclohexanol (2) or Cycloheptanol (2) or Cyclooctanol (2) or Cyclohexylmethanol (2) or 2-Cyclohexylethanol + Water (1)}[a]

T	p	ρ_1	a	$\sigma(a)$	b	$\sigma(b)$	$V^{0}_{m,2}$	$\sigma(V^{0}_{m,2})$
K	MPa	$kg \cdot m^{-3}$	$kg^2 \cdot m^{-3} \cdot mol^{-1}$		$kg^3 \cdot m^{-3} \cdot mol^{-2}$		$cm^3 \cdot mol^{-1}$	
				Cyclopentanol				
298.14	0.45	997.206	−2.6829	0.0612	2.1136	0.1583	89.07	0.06
318.17	0.50	990.377	−3.1524	0.0570	1.1547	0.1396	90.18	0.06
338.16	0.51	980.726	−3.9379	0.0569	0.6907	0.1434	91.92	0.06
358.15	0.51	968.794	−4.9131	0.0708	0.3649	0.1668	94.14	0.08
373.16	0.51	958.532	−5.6201	0.0542	0.1253	0.1370	95.97	0.06
				Cyclohexanol				
298.15	0.47	997.215	−3.1196	0.0586	2.5488	0.1802	103.58	0.06
318.17	0.50	990.377	−3.9717	0.0583	1.4755	0.1923	105.18	0.06
338.15	0.51	980.728	−4.9912	0.0596	0.7439	0.1923	107.32	0.06
358.16	0.51	968.793	−6.0997	0.0561	0.1914	0.1835	109.89	0.06
373.16	0.52	958.536	−7.0014	0.0591	−0.0255	0.1812	112.11	0.06
				Cycloheptanol				
298.15	0.45	997.206	−2.7180	0.0859	4.6153	0.5424	117.24	0.09
318.17	0.50	990.377	−3.8907	0.0871	3.2357	0.5511	119.27	0.09
338.15	0.51	980.728	−5.1181	0.0833	1.9399	0.4972	121.76	0.09
358.16	0.51	968.793	−6.4235	0.0882	1.0254	0.5297	124.71	0.09
373.16	0.52	958.536	−7.3921	0.0870	−0.0536	0.5545	127.18	0.09
				Cyclooctanol				
298.15	0.44	997.201	−2.2843	0.4054	18.2910	11.2183	130.87	0.41
318.17	0.50	990.377	−3.7471	0.4301	14.2630	11.9965	133.28	0.44
338.16	0.51	980.728	−5.1855	0.2872	10.1020	7.6228	136.12	0.30
358.17	0.51	968.783	−6.8128	0.4090	12.8200	11.0031	139.60	0.44
373.16	0.52	958.536	−7.7870	0.4165	7.4758	11.3834	142.23	0.45
				Cyclohexylmethanol				
298.15	0.42	997.192	−4.7148	0.2783	8.1007	4.9302	119.25	0.28
318.17	0.50	990.377	−6.2248	0.2999	10.6780	5.3096	121.65	0.31
338.16	0.51	980.726	−7.5372	0.2739	8.0104	4.8256	124.27	0.28
358.15	0.51	968.794	−9.0963	0.2496	8.3238	4.1733	127.56	0.27
373.16	0.51	958.532	−9.7947	0.2953	−1.1757	5.5460	129.79	0.32
				2-Cyclohexylethanol				
298.14	0.43	997.197	−6.2960	0.3776	–	–	134.90	0.38
318.17	0.50	990.377	−8.4731	0.3898	–	–	138.09	0.40
338.16	0.51	980.726	−10.1552	0.3834	–	–	141.29	0.40
358.15	0.51	968.794	−11.9514	0.6782	–	–	145.07	0.72
373.16	0.51	958.532	−12.9566	0.4217	–	–	147.86	0.46

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

Table 2. Comparison of Measured Values of Partial Molar Volumes at Infinite Dilution at T = 298 K and p = (0.42 to 0.52) MPa (Table 1) with the values for T = 298.15 K and p = 0.1 MPa Taken from the Literature

	$V^{o}_{m,2}/(cm^3 \cdot mol^{-1})$ [this work][a]	$V^{o}_{m,2}/(cm^3 \cdot mol^{-1})$ [literature]	dev.[b]	ref
cyclopentanol	89.07 ± 0.06	89.06 ± 0.02	0.01	Cabani[11,12]
		88.20 ± 0.40	0.87	Edward[13]
		88.97 ± 0.18	0.10	Hovorka[14]
cyclohexanol	103.58 ± 0.06	103.54 ± 0.03	0.04	Cabani[11,12]
		102.70 ± 0.50	0.88	Edward[13]
		103.51 ± 0.21	0.07	Hovorka[14]
cycloheptanol	117.24 ± 0.09	116.88 ± 0.04	0.36	Cabani[11,12]
		116.90 ± 0.20	0.34	Edward[13]
cyclooctanol	130.87 ± 0.41	129.70 ± 0.40	1.17	Edward[13]
cyclohexylmethanol	119.25 ± 0.28	118.10 ± 0.70	1.15	Edward[13]

[a] The values from Table 1 are 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 have a negligible effect which is well below the estimated uncertainties. [b] Deviation/($cm^3 \cdot mol^{-1}$) between this work and the literature value.

Table 3. Values of the Group Contributions $V^{o}_{m}(-CH_2-)$ and $V^{o}_{m}\{-CH(OH)-\}$ Evaluated at Each Temperature from the Straight Lines $V^{o}_{m,2}\{C_6H_{11}(CH_2)_mOH\} = V^{o}_{m}(-CH_2-)_{aliphatic} \cdot m + V^{o}_{m}(C_6H_{11}OH)$,[a] m = 0, 1, 2; $V^{o}_{m,2}\{C_nH_{(2n-1)}OH\} = V^{o}_{m}(-CH_2-)_{cyclic} \cdot (n-1) + V^{o}_{m}\{-CH(OH)-\}_{cyclic}$, n = 5, 6, 7, 8[b]

T	$V^{o}_{m}(-CH_2-)_{aliphatic}$	$V^{o}_{m}(-CH_2-)_{cyclic}$	$V^{o}_{m}\{-CH(OH)-\}_{cylic}$
K	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$
298.15	15.66 ± 0.16	13.91 ± 0.11	33.71 ± 0.44
318.15	16.46 ± 0.17	14.34 ± 0.12	33.12 ± 0.48
338.15	16.99 ± 0.17	14.71 ± 0.07	33.40 ± 0.28
358.15	17.59 ± 0.32	15.12 ± 0.11	33.92 ± 0.45
373.15	17.87 ± 0.20	15.38 ± 0.12	34.76 ± 0.50

[a] $V^{o}_{m}(C_6H_{11}OH)$ is the adjustable parameter with values (103.58, 105.18, 107.31, 109.91, and 112.05) $cm^3 \cdot mol^{-1}$ (in the order of increasing temperature). The values are within the estimated experimental uncertainties identical with experimental partial molar volumes of cyclohexanol (Table 1) which confirms the linearity of the dependence. [b] Uncertainties were estimated using uncertainties $\sigma(V^{o}_{m,2})$ from Table 1.

points for five solutions in the range of molality from (0.04 to 0.40) $mol \cdot kg^{-1}$ for aqueous cyclopentanol, 75 data points for five solutions in the range of molality from (0.05 to 0.29) $mol \cdot kg^{-1}$ for aqueous cyclohexanol, 67 data points for four solutions in the range of molality from (0.05 to 0.10) $mol \cdot kg^{-1}$ for aqueous cycloheptanol, 56 data points for three solutions in the range of molality from (0.010 to 0.028) $mol \cdot kg^{-1}$ for aqueous cyclooctanol, 45 data points for three solutions in the range of molality from (0.014 to 0.045) $mol \cdot kg^{-1}$ for aqueous cyclohexylmethanol, 49 data points for three solutions in the range of molality from (0.006 to 0.011) $mol \cdot kg^{-1}$ for aqueous 2-cyclohexylethanol; total of 375 data points). The highest concentrations of solutes other than cyclopentanol were limited

Table 4. Comparison of Predicted Values of Standard Partial Molar Volumes of Selected Solutes at T = 298.15 K with Experimental Data[a]

	$V^o_{m,2}/(cm^3 \cdot mol^{-1})$			
		predicted[a]		
		cyclobutanol	cyclopropylmethanol	cyclopentylmethanol
source solute[a] (Table 1)		$x = 4$, $y = 0$	$x = 3$, $y = 1$	$x = 5$, $y = 1$
cyclopentanol; $n = 5$, $m = 0$	89.07	75.16	76.91	104.73
cyclohexanol; $n = 6$, $m = 0$	103.58	75.76	77.51	105.33
cycloheptanol; $n = 7$, $m = 0$	117.24	75.51	77.26	105.08
cyclooctanol; $n = 8$, $m = 0$	130.87	75.23	76.98	104.80
cyclohexylmethanol; $n = 6$, $m = 1$	119.25	75.77	77.52	105.34
2-cyclohexylethanol; $n = 6$, $m = 2$	134.90	75.76	77.51	105.33
mean predicted value		75.53	77.28	105.10
experimental value[13]		75.6 ± 0.1	76.0 ± 0.2	103.6 ± 0.4
deviation (predicted − exptl)		−0.07	1.28	1.50

[a] Calculations were performed using a general formula. $V^o_{m,2}\{c\text{-}C_xH_{(2x-1)}(CH_2)_yOH\} = V^o_{m,2}\{c\text{-}C_nH_{(2n-1)}(CH_2)_mOH\} + (x - n)\cdot V^o_m(-CH_2-)_{cyclic} + (y - m)\cdot V^o_m(-CH_2-)_{aliphatic}$ where $V^o_m(-CH_2-)_{cyclic} = 13.91\ cm^3\cdot mol^{-1}$ and $V^o_m(-CH_2-)_{aliphatic} = 15.66\ cm^3\cdot mol^{-1}$ (Table 3).

by solubility in water at ambient conditions and were selected to prevent any formation of two liquid phases at experimental conditions.

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. The experimental results obtained for each pair of temperature and pressure were fitted with the equation

$$\Delta\rho/m_2 = (\rho - \rho_1)/m_2 = a + bm_2 \qquad (1)$$

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. Due to the very low solubility of 2-cyclohexylethanol, no composition dependence was evaluated for this solute, and the parameter a was obtained as an arithmetic mean of the experimental values $\Delta\rho/m_2$.

Partial Molar Volumes. The partial molar volume at infinite dilution ($m_2 \rightarrow 0$) of a solute $V^o_{m,2}$ (standard partial molar volume) is obtained from eq 1 as[6]

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

where M_2 is the molar mass of the solute.

The standard partial molar volumes calculated from the experimental data and their estimated uncertainties are presented in Table 1. The uncertainties in $V^o_{m,2}$ 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 calibration constant. Since the density differences are measured with respect to degassed water,[6,8] additional uncertainty related to the uncertainty of the density difference between degassed and nitrogen-saturated water was taken into account.

Table 2 presents a comparison of our values of standard partial molar volume at T = 298 K and low pressure (up to 0.5 MPa) with data available in the literature for T = 298.15 K and atmospheric pressure. The comparison is possible since the effects of small variations in experimental temperature and pressure on standard partial molar volumes are within the estimated uncertainties. The differences between our partial molar volumes and those taken from the literature are within the estimated experimental uncertainties for cyclopentane and cyclohexane (data from papers by Cabani et al.[11,12] and Hovorka et al.[14]). Rather large deviations are observed when compared with data published by Edward et al.[13] Their values are systematically lower than our data and, with the exception of cycloheptanol, are also lower than other values available in the literature (cyclopentanol and cyclohexanol).

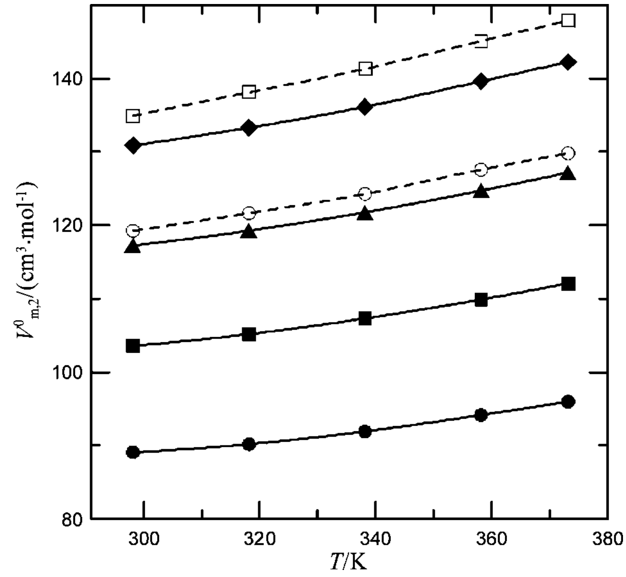

Figure 1. Plot of partial molar volume $V^o_{m,2}$ of cyclic alcohols as a function of temperature T. The lines are to aid the eye. ●, cyclopentanol; ■, cyclohexanol; ▲, cycloheptanol; ◆, cyclooctanol; ○, cyclohexylmethanol; □, 2-cyclohexylethanol.

Schulte et al.[15] presented the value $V^o_{m,2}$ = (103.8 ± 1.4) $cm^3\cdot mol^{-1}$ for aqueous cyclohexanol at T = 301.80 K and p = 0.13 MPa. Our value $V^o_{m,2}(T = 301.80\ K, p = 0.5\ MPa)$ = (103.83 ± 0.06) $cm^3\cdot mol^{-1}$ obtained from our partial molar volumes by a polynomial interpolation is identical within the combined experimental uncertainties.

Evolution of standard partial molar volumes with temperature for the investigated solutes is shown in Figure 1. As can be expected for monohydric alcohols, the lines are smooth and slightly convex curves in this temperature range. The distances between curves correspond to the contribution of the methylene group ($-CH_2-$) to the standard partial molar volume. Two types of the methylene group can be distinguished: either the aliphatic $-CH_2-$ group in the homologous series of cyclohexanol, cyclohexylmethanol, 2-cyclohexylethanol, i.e., $c\text{-}C_nH_{(2n-1)}\text{-}(CH_2)_mOH$ for fixed n = 6 and m = 0, 1, 2, or the cyclic $-CH_2-$ group in the homologous series of cyclopentanol, cyclohexanol, cycloheptanol, and cyclooctanol, i.e., $c\text{-}C_nH_{(2n-1)}\text{-}(CH_2)_mOH$ for n = 5, 6, 7, and 8 and fixed m = 0. It was observed that the isothermal dependencies of the standard partial molar volume on the respective variable (m or n) within each

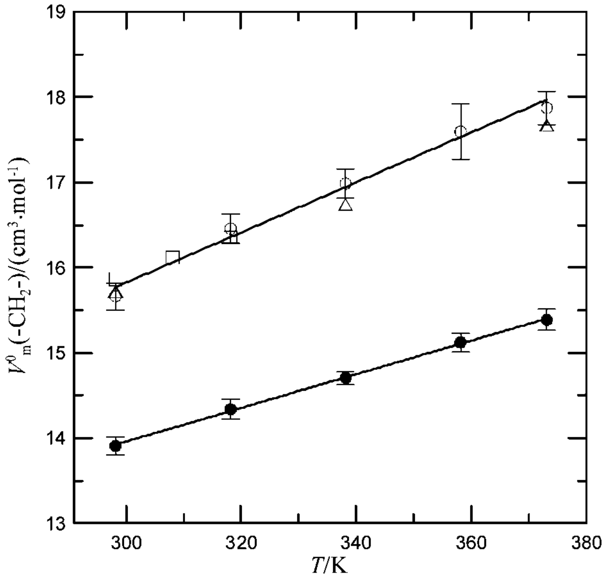

Figure 2. Plot of the $-CH_2-$ group contribution $V^o_m(-CH_2-)$ as a function of temperature evaluated from following straight lines. ●, this work, $V^o_{m,2}(c\text{-}C_nH_{(2n-1)}OH) = V^o_m(-CH_2-) \cdot (n-1) + V^o_m\{-CH(OH)-\}$, $n = 5, 6, 7, 8$; ○, this work, $V^o_{m,2}\{c\text{-}C_6H_{11}(CH_2)_mOH\} = V^o_m(-CH_2-) \cdot m + V^o_m(C_6H_{11}OH)$, $m = 0, 1, 2$; Δ, Hynčica,[1,2] $V^o_{m,2}\{H(CH_2)_mOH\} = V^o_m(-CH_2-) \cdot m + V^o_m(HOH)$, $m = 2, 3, 4$; □, Sakurai,[17] $V^o_{m,2}\{H(CH_2)_mOH\} = V^o_m(-CH_2-) \cdot m + V^o_m(HOH)$, $m = 2, 3, 4, 5, 6$. The lines are to aid the eye. Error bars correspond to the estimated uncertainties.

homologous series can be represented by straight lines which indicates that the group volumes of the methylene group (aliphatic, cyclic) are independent of both the length of the aliphatic chain and the size of the cycle. The slopes of these straight lines are the group contributions of the methylene group to the standard partial molar volume at each temperature. Values of the slopes along with their estimated uncertainties are summarized in Table 3 and shown in Figure 2. The dependencies of the methylene group contributions on temperature can be, within the estimated uncertainties, represented by straight lines.

Despite the fact that the standard partial molar volumes at 298.15 K by Edward et al.[13] exhibit systematic deviations from our values (Table 2), the group contribution of the cyclic methylene group at 298.15 K evaluated from their data is very close to our value $\{(13.91 \pm 0.11)\ cm^3 \cdot mol^{-1}$, see Table 3$\}$: the value 13.69 $cm^3 \cdot mol^{-1}$ results from the straight-line plot of $V^o_{m,2}(c\text{-}C_nH_{(2n-1)}OH)$ vs $(n-1)$ for $n = 4, 5, 6, 7$, and 8, and the plot $V^o_{m,2}(c\text{-}C_nH_{(2n-1)}(CH_2)OH)$ vs $(n-1)$ for $n = 3$, 5, and 6 gives 14.00 $cm^3 \cdot mol^{-1}$ (surprisingly, this dependence is linear even though it includes the smallest alicyclic group).

Group contribution for the aliphatic methylene group evaluated from Edward's[13] data at $T = 298.15$ K for cyclopentane and cyclopentylmethanol $\{(15.40 \pm 0.57)\ cm^3 \cdot mol^{-1}\}$, and cyclohexane, and cyclohexylmethanol $\{(15.40 \pm 0.86)\ cm^3 \cdot mol^{-1}\}$ agrees within the combined uncertainties with our value $\{(15.66 \pm 0.16)\ cm^3 \cdot mol^{-1}$, see Table 3$\}$ and with the value 15.8 $cm^3 \cdot mol^{-1}$ presented by Cabani et al.[16] Figure 2 shows a comparison of our values with the volume of the aliphatic methylene group evaluated from standard partial molar volumes of 1-alkanols: ethanol to 1-butanol (Hynčica et al.[1,2] for pressures up to 0.5 MPa at $T < 373$ K and 2 MPa at 373 K) and ethanol to 1-hexanol (Sakurai et al.[17] for atmospheric pressure). The agreement is surprisingly good. This fact indicates that the influence of the large cycloalkyl group (cyclohexyl in our case) on the group volume of the aliphatic methylene group is negligible, even for short aliphatic chains. It should be pointed out that methanol (although data are also available[1,2,17]) was excluded from the evaluation since it was observed that its partial molar volumes are significantly out of the straight lines constructed using data for higher 1-alkanols at various temperatures.

Since an n-member cycle of a cycloalkanol molecule consists of $(n-1)$ $-CH_2-$ groups and one $-CH(OH)-$ group, the plot $V^o_{m,2}(c\text{-}C_nH_{(2n-1)}OH)$ vs $(n-1)$ enables us to evaluate the group contribution of the $-CH(OH)-$ group bonded as one member of the cycle. Obtained values are given in Table 3. One should keep in mind that these values are very sensitive to the uncertainty of partial molar volumes used for the evaluation. The temperature dependence of $V^o_m(-CH(OH)-)$ is not monotonous, but when a straight line is used for the fit, then its slope is lower $(0.0147\ cm^3 \cdot mol^{-1} \cdot K^{-1})$ in this temperature range compared to the value obtained for the cyclic $-CH_2-$ group $(0.0197\ cm^3 \cdot mol^{-1} \cdot K^{-1})$.

Since all investigated solutes comprise one trivalent $(=CH-)_{cyclic}$ group and one $-OH$ group (either directly bonded as in cycloalkanols or separated by one or two aliphatic $-CH_2-$ groups as in cyclohexylalkanols), the group volume of the hydroxyl group cannot be evaluated from the present data without any data from other sources. However, it seems likely that the group contribution of the hydroxyl group directly bonded to the cycle is close to that of the hydroxyl group bonded to the aliphatic chain. This conclusion is supported by the fact that the intercepts of the straight lines $V^o_{m,2}\{c\text{-}C_6H_{11}(CH_2)_mOH\}$ vs m $(m = 0, 1, 2)$ are nearly identical with the experimental standard partial molar volumes of cyclohexanol (for numerical values, see footnote to Table 3). Even the extrapolations using experimental partial molar volumes for cyclohexylmethanol $(m = 1)$ and 2-cyclohexylethanol $(m = 2)$ to $m = 0$ (cyclohexanol) give values that differ by (0.02, 0.02, −0.07, 0.16, and −0.39) $cm^3 \cdot mol^{-1}$ (in the order of increasing temperature) from experimental partial molar volumes of cyclohexanol. This observation leads to the statement that the group contribution of the $\{-CH(OH)-\}_{cyclic}$ group is equal to the sum of the group contributions of the $(=CH-)_{cyclic}$ and $(-OH)_{aliphatic}$ groups.

Contributions of the groups that contain the $-OH$ group evaluated from Edward's data are $V^o_m(-CH(OH)-) = 34.17\ cm^3 \cdot mol^{-1}$ (our value is 33.71 $cm^3 \cdot mol^{-1}$, Table 3) and $V^o_m(-CH(CH_2OH)-) = 47.9\ cm^3 \cdot mol^{-1}$. The difference between these two values $(13.77\ cm^3 \cdot mol^{-1})$ corresponds to the group contribution of the aliphatic $-CH_2-$ group but does not agree with the value obtained directly from experimental partial molar volumes $(15.40\ cm^3 \cdot mol^{-1}$, see above). This disagreement is obviously a consequence of different slopes of the dependencies $V^o_{m,2}(c\text{-}C_nH_{(2n-1)}OH)$ and $V^o_{m,2}(c\text{-}C_nH_{(2n-1)}\text{-}(CH_2)OH)$ vs $(n-1)$.

Partial molar volumes at $T = 298.15$ K of selected solutes (cyclobutanol, cyclopropylmethanol, and cyclopentylmethanol) were estimated using our values of partial molar volumes obtained for all solutes investigated here ("source solute") and group contributions of methylene groups (aliphatic, cyclic) from Table 3. Results of the predictions are shown in Table 4. Calculations starting from different source solutes yielded the predicted values within the interval 0.61 $cm^3 \cdot mol^{-1}$ wide (the standard deviation of the mean predicted values is 0.28 $cm^3 \cdot mol^{-1}$), which confirms good internal consistency and supports the approximation that the group volume of the hydroxyl group directly bonded to the cycle is close to that of the hydroxyl group bonded to the aliphatic chain. The agreement between the predicted and experimental[13] standard partial molar volumes of cyclobutanol is within the experimental uncertainty, and the deviations of mean values predicted for cyclopropylmethanol and cyclopentylmethanol are positive and rather large. These deviations might be, however, partly caused by the fact already mentioned above that Edward's values are mostly lower than ours and other literature data. With this in mind, the perfect agreement in the case of cyclobutanol might seem to be rather accidental.

Supporting Information Available:

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. This material is available free of charge via the Internet at http://pubs.acs.org.

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