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Partial Molar Volumes of Cyclic Ketones at Infinite Dilution in Water at Temperatures T = (278 to 373) K and Low Pressure†

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Density data for dilute aqueous solutions of four cyclic ketones (cyclopentanone, cyclohexanone, cycloheptanone, and cyclohexane-1,4-dione) obtained using both an Anton Paar DSA 5000 vibrating-tube densimeter and a laboratory-made flow 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 T = (278 to 373) K and at either atmospheric pressure or p = 0.5 MPa. Trends for the homologous series are discussed, and group contributions to the standard partial molar volume are evaluated.

Introduction

This study is a continuation of a systematic investigation of partial molar volumes of organic solutes in dilute aqueous solutions. Our previous recent studies of cyclic compounds were devoted to cycloalkanols[1] and cyclic ethers.[2] The present study is focused on cyclic ketones with one or two carbonyl groups in the cycle. Measurements were performed in the low-pressure region, and thus, the upper temperature limit is around the normal boiling temperature of water. A commercial DSA 5000 vibrating-tube densimeter with a glass tube and a built-in thermostat was used for measurements over the temperature range T = (278 to 318) K and at atmospheric pressure. The measurements on aqueous solutions at atmospheric pressure and elevated temperatures were rather problematic because of the formation of air bubbles. Since the DSA 5000 densimeter makes measurements at sublaboratory temperatures feasible, this device was used at temperatures from 318 K down to 278 K. Measurements at the higher temperatures T = (298 to 373) K were performed using our high-temperature high-pressure (HTHP) flow densimeter[3−5] with the pressure adjusted to a slightly elevated value (0.5 MPa), which ensured that formation of air bubbles did not occur. Because of the modest dependence of standard partial molar volumes on pressure over this temperature range, the results are fully comparable with data obtained at atmospheric pressure. Since measurements using the HTHP densimeter could not be performed at temperatures below the laboratory temperature (no cooling system is installed), the use of the DSA 5000 device significantly extended the experimental temperature range toward low temperatures. Thus, the combination of the data obtained using the two densimeters provides the values of standard partial molar volumes over nearly the entire range of liquid water at low presure.

Experimental Section

The organic solutes, i.e., cyclopentanone (Fluka, puriss., stated mass fraction purity greater than 0.99), cyclohexanone (Sigma-Aldrich, ReagentPlus, stated mass fraction purity 0.998), cycloheptanone (Aldrich, stated mass fraction purity 0.99), and cyclohexane-1,4-dione (Fluka, purum, stated mass fraction purity greater than 0.98) were used without further treatment. Distilled, demineralized (Millipore RQ) water was used as a calibration fluid for the densimeters and for the preparation of solutions. Nitrogen (Siad, mole fraction purity = 0.9999) was used as supplied.

Solutions were prepared by mass using a Precisa 40SM-200A balance (resolution = 10^{-2} mg, uncertainty = ± 0.1 mg) to determine the mass of the solute and a Precisa 2200C SCS balance (resolution = 10 mg, estimated relative uncertainty $\delta m/m = \pm 0.0002$) to determine the total mass of a solution. The mass of each prepared solution was about 1 kg. Air-saturated water was used for preparation of the solutions measured using the DSA 5000 densimeter. Solutions measured using the HTHP densimeter (see below) were prepared using water saturated with nitrogen and stored in closed bottles under a nitrogen atmosphere. Because of the photosensitivity of cyclohexane-1,4-dione, dark-brown glass bottles were used. A small amount of solid impurity insoluble in water was observed in prepared solutions of this solute, and therefore, the solutions were filtered before use. Gravimetric analysis revealed that the mass fraction of this insoluble impurity in the solute sample was about 0.0025, and the concentrations of the prepared solutions were corrected accordingly. Because of the high cost of cyclohexane-1,4-dione, the upper concentration limit was lower than for the other solutes, despite its high solubility in water.

DSA 5000 Densimeter. An Anton Paar model DSA 5000 vibrating-tube densimeter equipped with an SP-1m autosampler (Anton Paar) was used for the measurements at temperatures down to 278 K using a built-in thermostat. The highest temperature at which the formation of air bubbles 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 the 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 perform the consequent evaluation.

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Table 1. Density of Water (ρ_1),[6] Coefficients of Equation 1 (a, b, and c), and Extrapolated Values of the Partial Molar Volumes at Infinite Dilution ($V^\circ_{m,2}$) for {Cyclopentanone (2) or Cyclohexanone (2) or Cycloheptanone (2) or Cyclohexane-1,4-dione (2) + Water (1)}; The Estimated Uncertainties $\sigma(a)$, $\sigma(b)$, and $\sigma(c)$ Refer to the Coefficients a, b, and c of Equation 1, and $\sigma(V^\circ_{m,2})$ Represents the Total Estimated Uncertainty in $V^\circ_{m,2}$

T K	p MPa	ρ_1 $kg\cdot m^{-3}$	a $kg^2\cdot m^{-3}\cdot mol^{-1}$	$\sigma(a)$ $kg^2\cdot m^{-3}\cdot mol^{-1}$	b $kg^3\cdot m^{-3}\cdot mol^{-2}$	$\sigma(b)$ $kg^3\cdot m^{-3}\cdot mol^{-2}$	c $kg^4\cdot m^{-3}\cdot mol^{-3}$	$\sigma(c)$ $kg^4\cdot m^{-3}\cdot mol^{-3}$	$V^\circ_{m,2}$ $cm^3\cdot mol^{-1}$	$\sigma(V^\circ_{m,2})$ $cm^3\cdot mol^{-1}$
					Cyclopentanone(aq)					
278.15	0.10	999.966	1.0293	0.0394	1.520	0.133	−0.749	0.136	83.09	0.04
283.15	0.10	999.702	0.5769	0.0395	1.312	0.135	−0.614	0.136	83.56	0.04
288.15	0.10	999.102	0.2004	0.0395	1.033	0.136	−0.421	0.134	83.99	0.04
293.15	0.10	998.207	−0.2011	0.0396	0.977	0.136	−0.441	0.133	84.47	0.04
298.15	0.10	997.047	−0.5535	0.0396	0.818	0.136	−0.344	0.132	84.92	0.04
308.15	0.10	994.033	−1.2603	0.0396	0.733	0.134	−0.361	0.130	85.90	0.04
318.15	0.10	990.212	−1.8828	0.0393	0.504	0.128	−0.227	0.124	86.87	0.04
298.17	0.52	997.231	−0.5735	0.0510	0.811	0.167	−0.338	0.158	84.93	0.05
318.14	0.51	990.396	−1.9263	0.0528	0.548	0.176	−0.233	0.167	86.90	0.05
338.18	0.51	980.714	−3.1556	0.0611	0.384	0.193	−0.247	0.175	89.05	0.06
358.14	0.52	968.807	−4.3383	0.0621	0.269	0.200	−0.196	0.185	91.45	0.07
373.17	0.52	958.531	−5.2118	0.0717	0.139	0.267			93.43	0.08
					Cyclohexanone(aq)					
278.15	0.10	999.966	1.0265	0.0431	2.169	0.175	−1.427	0.212	97.12	0.04
283.15	0.10	999.702	0.4108	0.0447	1.946	0.223	−1.295	0.212	97.76	0.04
288.15	0.10	999.102	−0.1003	0.0448	1.573	0.179	−0.967	0.208	98.33	0.04
293.15	0.10	998.207	−0.6274	0.0448	1.478	0.179	−0.934	0.206	98.95	0.04
298.15	0.10	997.047	−1.0665	0.0448	1.185	0.178	−0.691	0.202	99.51	0.05
308.15	0.10	994.033	−1.9206	0.0448	0.931	0.174	−0.592	0.199	100.68	0.05
318.15	0.10	990.212	−2.7098	0.0441	0.634	0.162	−0.306	0.184	101.88	0.05
298.17	0.52	997.231	−1.0929	0.0426	1.240	0.154	−0.788	0.166	99.51	0.04
318.14	0.51	990.396	−2.7411	0.0593	0.759	0.230	−0.533	0.258	101.89	0.06
338.18	0.51	980.714	−4.2128	0.0827	0.486	0.342	−0.396	0.404	104.45	0.09
358.14	0.52	968.807	−5.5962	0.0806	0.336	0.323	−0.207	0.384	107.27	0.09
373.17	0.52	958.531	−6.5786	0.0808	0.248	0.330			109.55	0.09
					Cycloheptanone(aq)					
278.15	0.10	999.966	0.6379	0.0682	2.434	0.291			111.54	0.07
283.15	0.10	999.702	−0.0052	0.0682	2.327	0.293			112.21	0.07
288.15	0.10	999.102	−0.5131	0.0683	1.881	0.294			112.78	0.07
293.15	0.10	998.207	−1.0242	0.0684	1.704	0.294			113.40	0.07
298.15	0.10	997.047	−1.4933	0.0684	1.507	0.293			114.00	0.07
308.15	0.10	994.033	−2.3403	0.0685	1.071	0.290			115.21	0.07
318.15	0.10	990.212	−3.1265	0.0679	0.688	0.287			116.47	0.07
298.17	0.52	997.231	−1.5336	0.0692	1.811	0.304			114.02	0.07
318.14	0.51	990.396	−3.2357	0.0897	1.167	0.392			116.56	0.09
338.18	0.51	980.714	−4.7320	0.1085	0.824	0.478			119.30	0.11
358.14	0.52	968.807	−6.2345	0.1081	0.785	0.476			122.42	0.12
373.17	0.52	958.531	−7.3011	0.1091	0.707	0.483			124.97	0.12
					Cyclohexane-1,4-dione(aq)					
278.15	0.10	999.966	23.1858	0.1907	−1.668	0.162			88.94	0.19
283.15	0.10	999.702	22.2475	0.1755	−1.254	0.100			89.90	0.18
288.15	0.10	999.102	21.5158	0.1785	−2.057	0.166			90.67	0.18
293.15	0.10	998.207	20.6681	0.1725	−2.105	0.167			91.59	0.17
298.15	0.10	997.047	19.9446	0.1675	−2.435	0.171			92.40	0.17
308.15	0.10	994.033	18.5763	0.1575	−2.264	0.170			94.00	0.16
318.15	0.10	990.212	17.4466	0.1495	−2.804	0.178			95.44	0.15
298.17	0.52	997.231	19.9928	0.1025	−2.919	0.525			92.33	0.14
318.14	0.51	990.396	17.2658	0.0935	−1.653	0.465			95.61	0.16
338.18	0.51	980.714	15.4827	0.1830	−1.276	1.100			98.23	0.22
358.14	0.52	968.807	14.0585	0.1810	−1.037	1.098			100.76	0.22
373.17	0.52	958.531	13.2278	0.1844	−1.160	1.122			102.58	0.22

Several vials filled with air-saturated pure water were included and distributed in the measured sample set. The reproducibility of the density of water was usually $\pm 1\cdot10^{-3}$ $kg\cdot m^{-3}$ (slightly worse at higher temperatures), and the average value at each temperature was used as the value of ρ_1 in calculating the density differences $\Delta\rho = \rho - \rho_1$, where ρ and ρ_1 are the densities of the solution and water, respectively.

High-Temperature High-Pressure Densimeter. The HTHP densimeter and the experimental procedure are described in more detail elsewhere,[3−5] so here we present brief information only. Repeated calibrations of the densimeter were performed at each experimental temperature and pressure using water and nitrogen, whose densities were taken from the literature.[6,7] The maximum systematic error of the measured density differences $\Delta\rho$ resulting from the densimeter calibration, $\delta(\Delta\rho)/\Delta\rho$, was about 0.002, and the reproducibility of the measurements was within $\pm$ $3\cdot10^{-3}$ $kg\cdot m^{-3}$ in most cases. The measurements were performed in the flow regime with the high-pressure pump set to a flow rate of 0.6 $cm^3\cdot min^{-1}$. A pressure vessel with a volume of 40 dm^3 filled with nitrogen at a pressure of 0.5 MPa was used instead of a back-pressure regulator[5] at the end of the pressure line. Since the volume of water delivered by the pump to the system during one automated run was about 650 cm^3, the pressure increase in the line during the run was negligible ($\delta p/p = 0.016$, i.e., 0.008 MPa). Although the vessel was not thermostatted, small fluctuations in the laboratory temperature had no observable effect on the pressure stability. The total uncertainty in the temperature measurements using a calibrated

(ITS 90) platinum resistance thermometer (Burns Engineering) was estimated to be about ± 20 mK, and the uncertainty in pressure measured using a secondary standard gauge (Digiquartz model 745-6K, Paroscientific, Inc.) was less than 0.01 MPa.

Separate sets of solutions were prepared for measurements performed using the HTHP densimeter. In exceptional cases, the same solution was measured using both densimeters. Since the solutions were prepared using nitrogen-saturated water and water degassed by boiling was used as a carrier fluid in the flow system,[5] corrections with respect to the measured difference between the densities of degassed and nitrogen-saturated water were taken into account. One automated run (18 h) consisted of three cycles over the set of 12 samples of solutions, i.e., each solution was measured three times during the run.

Results

Direct Experimental Data. The values of the density differences $\Delta\rho = \rho - \rho_1$, where ρ and ρ_1 are the densities of the solution and water, respectively, were measured at each experimental temperature and pressure (atmospheric or 0.5 MPa) and corrected[5] (where applicable) for measured differences between nitrogen-saturated and degassed water; the obtained values along with the corresponding molalities of the organic solutes m_2 are available in the Supporting Information [147 data points in the range of molality from (0.10 to 0.64) $\text{mol}\cdot\text{kg}^{-1}$ for aqueous cyclopentanone, 126 data points in the range of molality from (0.09 to 0.51) $\text{mol}\cdot\text{kg}^{-1}$ for aqueous cyclohexanone, 104 data points in the range of molality from (0.05 to 0.20) $\text{mol}\cdot\text{kg}^{-1}$ for aqueous cycloheptanone, and 103 data points in the range of molality from (0.03 to 0.16) $\text{mol}\cdot\text{kg}^{-1}$ for aqueous cyclohexane-1,4-dione (480 data points total)].

The dependence of $\Delta\rho/m_2$ on m_2 at constant temperature and pressure was treated as either a quadratic or linear function of m_2 over the composition ranges of the measurements. The experimental results obtained at each temperature and pressure were fitted with the equation

$$\frac{\Delta\rho}{m_2} = \frac{\rho - \rho_1}{m_2} = a + bm_2 + cm_2^{\,2} \tag{1}$$

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

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

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

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 $V^{\circ}_{\text{m},2}$ given in Table 1 include estimates of random errors, which originate from the scatter associated with eq 1, as well as systematic errors estimated from the uncertainties in the temperature, pressure, and calibration constant. Since the density differences obtained from the HTHP densimeter were measured with respect to degassed water,[3,5] additional uncertainty related to the uncertainty of the density difference between degassed and nitrogen-saturated water was taken into account. The larger uncertainties in $V^{\circ}_{\text{m},2}$ for cyclohexane-1,4-dione originate particularly from the larger uncertainties in the molality caused by both the lower purity of the solute samples and the presence of the water-insoluble impurity and its removal.

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

	$V^{\circ}_{\text{m},2}/\text{cm}^3\cdot\text{mol}^{-1}$			
solute	this work[a]	literature	dev.[b]	reference
cyclopentanone	84.92 ± 0.05	84.50 ± 0.30	0.42	Edward[8]
		84.95 ± 0.17	−0.03	Hovorka[9]
cyclohexanone	99.51 ± 0.05	99.70 ± 0.40	−0.19	Edward[8]
		99.56 ± 0.12	−0.05	Hovorka[9]
cycloheptanone	114.01 ± 0.07	113.80 ± 0.20	0.21	Edward[8]
cyclohexane-1,4-dione	92.40 ± 0.17	92.8 ± 0.40	−0.40	Edward[8]

[a] Averages of the values from Table 1 are presented, since the extrapolation/interpolation from our experimental temperatures near $T = 298$ K and our experimental pressures to $T = 298.15$ and $p = 0.1$ MPa has a negligible effect that is much less than the estimated uncertainties. [b] Deviation/($\text{cm}^3\cdot\text{mol}^{-1}$) between this work and the literature value.

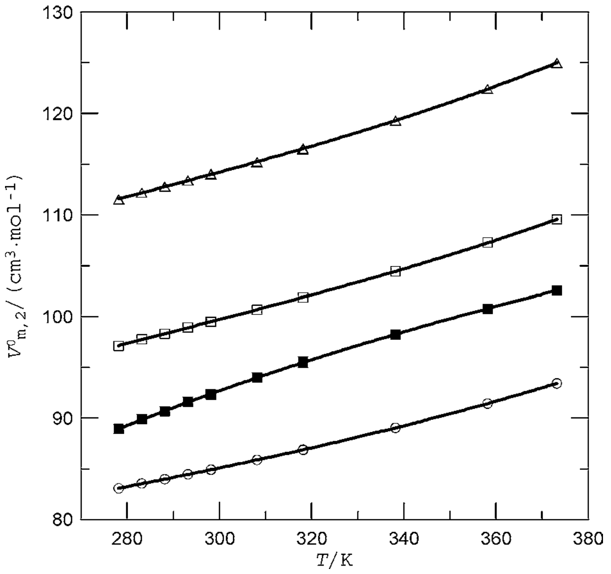

Figure 1. Temperature dependence of the experimental standard partial molar volumes: ○, cyclopentanone; □, cyclohexanone; △, cycloheptanone; ■, cyclohexane-1,4-dione. The lines are polynomial fits using the parameters from Table 3.

The agreement between the values obtained independently using our two densimeters at $T = (298 \text{ and } 318)$ K is excellent (better at 298 K) and well within the estimated uncertainties. Table 2 presents a comparison of our values of the standard partial molar volumes at $T = 298$ K with data available in the literature for $T = 298.15$ K and atmospheric pressure. The deviations from the values reported by Edward et al.[8] are rather large but, except for cyclopentanone, within the limits of the uncertainties. Excellent agreement with the data reported by Hovorka et al.[9] for cyclopentanone and cyclohexanone is observed.

The evolution of the standard partial molar volumes with temperature for the investigated solutes is shown in Figure 1. The experimental standard partial molar volumes were correlated using the third-order polynomial

$$V^{\circ}_{\text{m},2}/(\text{cm}^3\cdot\text{mol}^{-1}) = \sum_{i=0}^{3} a_i (T/\text{K})^i \tag{3}$$

Table 3. Parameters of the Smoothing Polynomial (Equation 3) for the Standard Partial Molar Volumes and Standard Deviations of the Fits (σ_{fit})

solute	a_0	a_1	$10^3 \cdot a_2$	$10^6 \cdot a_3$	σ_{fit} $\text{cm}^3 \cdot \text{mol}^{-1}$
cyclopentanone	44.2365	0.272836	−0.77331	1.05972	0.01
cyclohexanone	13.3061	0.648636	−1.83739	2.11817	0.02
cycloheptanone	33.8745	0.606039	−1.77373	2.15450	0.04
cyclohexane-1,4-dione	−36.9142	0.832965	−1.77027	1.44637	0.06

The set of input experimental data was a combination of the two subsets (DSA 5000 apparatus and HTHP densimeter; see Table 1) for each solute. Values of the adjustable parameters $\{a_i\}$ obtained using the least-squares method are recorded in Table 3 along with standard deviations of the fits. The deviations of the experimental values from the fits are well within the estimated uncertainties (Table 1), i.e., within $\pm\,\sigma(V^\circ_{\text{m},2})$. Higher-order polynomial terms were found to be statistically insignificant.

As expected, the temperature dependence of the standard molar volume is affected by the number of hydrophilic carbonyl groups in the cycle relative to the number of hydrophobic methylene groups. While the curves for monoketones are convex, that for cyclohexane-1,4-dione is concave, particularly in the range of low temperatures. The qualitative difference between these two groups of solutes is more obvious in Figure 2a, where values of the analogue of the isobaric thermal expansivity, $\alpha^\circ_{p,2} = (1/V^\circ_{\text{m},2})(\partial V^\circ_{\text{m},2}/\partial T)_p$ (named briefly the isobaric expansivity in the following text), calculated from eq 3 with the parameters recorded in Table 3 are plotted against temperature. For the sake of legibility, the curves in the figure are denoted as *X*-*Y*, where *X* is the number of carbon atoms in the cycle and *Y* the number of carbonyl groups. The expansivities of the solutes with one carbonyl group increase with increasing temperature (cyclohexanone at low temperatures is the exception), while that of cyclohexane-1,4-dione decreases over the entire experimental temperature range. The shape of the temperature dependence of the standard partial molar volume can be further analyzed by evaluation of the second-order temperature derivative, which is related to the derivative of the standard partial molar heat capacity with respect to pressure: $(\partial c^\circ_{p,\text{m},2}/\partial p)_T = -T(\partial^2 V^\circ_{\text{m},2}/\partial T^2)_p$. Figure 2b shows plots of this derivative evaluated for each solute from the fits in Table 3. The plots reveal the character of the evolution (increase or decrease) of the standard partial molar isobaric heat capacity with pressure. Obviously, the $V^\circ_{\text{m},2}(T)$ curve for cyclohexanone shows an inflection point at a temperature of about 290 K, and therefore, $(\partial c^\circ_{p,\text{m},2}/\partial p)_T = 0$ holds at this temperature. The behavior of the derivative quantities observed here for cyclic ketones is similar to that reported for cyclic ethers[10] and confirms that the trends related to the ratio between the hydrophobic and hydrophilic parts of the solute molecule are of a general character.

The dependences of properties within homologous series are usually monotonous. Figure 2 shows that the derivative properties of the higher members of the monoketone series (cyclohexanone and cycloheptanone) exhibit monotonous trends over the entire experimental temperature range, while those of cyclopentanone do not obey these trends in the range of lower temperatures. A similar but less-pronounced phenomenon was observed for the homologous series of cyclic monoethers.[10]

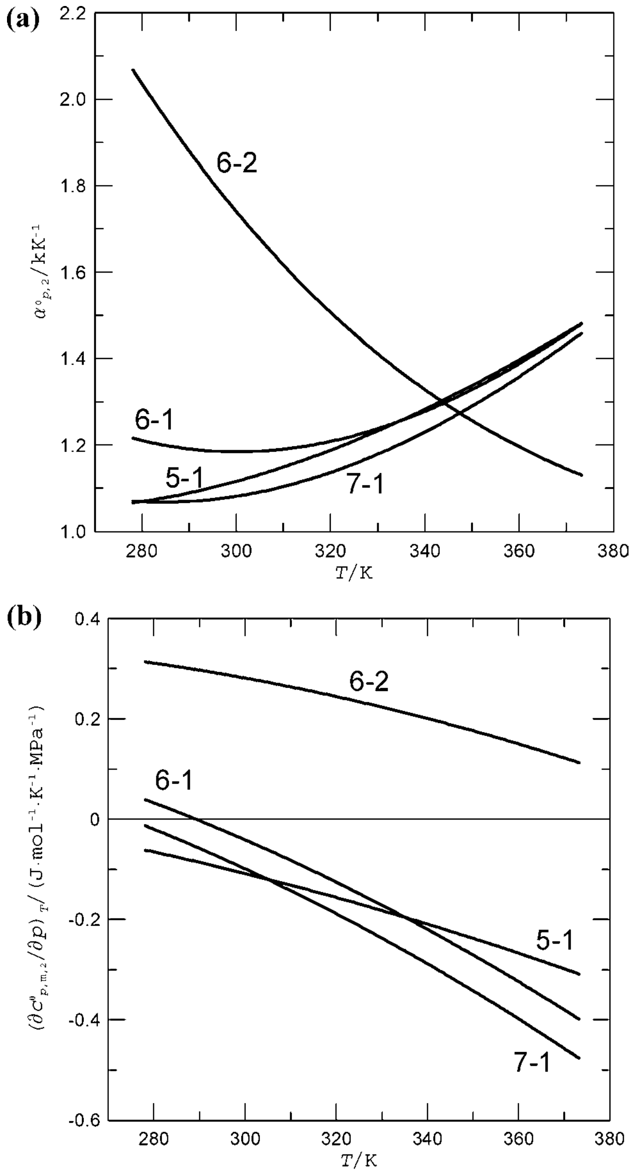

Figure 2. Temperature dependence of quantities related to the derivatives of the standard partial molar volume with respect to temperature: (a) $\alpha^\circ_{p,2} = (1/V^\circ_{\text{m},2})(\partial V^\circ_{\text{m},2}/\partial T)_p$; (b) $(\partial c^\circ_{p,\text{m},2}/\partial p)_T = -T(\partial^2 V^\circ_{\text{m},2}/\partial T^2)_p$. The lines correspond to the fits using the parameters in Table 3: 5-1, cyclopentanone; 6-1, cyclohexanone; 7-1, cycloheptanone; 6-2, cyclohexane-1,4-dione.

Group Contributions. Molecules of the solutes investigated here can be divided into structural segments of two kinds: methylene groups $-\text{CH}_2-$ and carbonyl groups $-\text{CO}-$. Corresponding contributions to the standard partial molar volume, $V^\circ_{\text{m},\text{CH}_2}$ and $V^\circ_{\text{m},\text{CO}}$, can be attributed to each segment. A third contribution that appears naturally for cyclic molecules is the covolume, $V^\circ_{\text{m,c}}$. The covolume is common for all solutes in a particular solvent (i.e., it possesses a nonadditive character) and is related to the partial molar volume of a noninteracting point mass. Despite the fact that theory gives $V^\circ_{\text{m,c}} = \kappa_{T,1}RT$, where $\kappa_{T,1}$ is the isothermal compressibility of the solvent, the covolume was allowed to be an adjustable parameter (for detailed discussion, see, e.g., our previous papers[2,10]). On the basis of the above considerations, the standard partial molar volume of a cyclic ketone with *n* methylene groups and *m* carbonyl groups can be expressed by the formula

$$(V^\circ_{\text{m},2})_{\text{calc}} = V^\circ_{\text{m,c}} + nV^\circ_{\text{m},\text{CH}_2} + mV^\circ_{\text{m},\text{CO}} \qquad (4)$$

The values of the contributions in eq 4 were evaluated for each of the temperatures from (278.15 to 373.15) K in 5 K wide intervals by minimizing the objective function

$$\phi(V^\circ_{\mathrm{m,c}}, V^\circ_{\mathrm{m,CH_2}}, V^\circ_{\mathrm{m,CO}}) = \sum_{i=1}^{4}\left[\frac{(V^\circ_{\mathrm{m,2}})_{\mathrm{exp},i} - (V^\circ_{\mathrm{m,c}} + n_i V^\circ_{\mathrm{m,CH_2}} + m_i V^\circ_{\mathrm{m,CO}})}{\sigma(V^\circ_{\mathrm{m,2}})_{\mathrm{exp},i}}\right]^2 \quad (5)$$

where the summation was performed over all four solutes i with particular values of n_i and m_i. The experimental values $(V^\circ_{\mathrm{m,2}})_{\mathrm{exp},i}$ were represented by smoothed values calculated from the fits given in Table 3, and their uncertainties $\sigma(V^\circ_{\mathrm{m,2}})_{\mathrm{exp},i}$ were obtained by a polynomial interpolation of the experimental uncertainties from Table 1. The uncertainty of each contribution was estimated as the root-mean-square deviation of the deviations of the contribution values calculated for all variations of the smoothed standard partial molar volumes modified by adding or subtracting their respective estimated experimental uncertainties. The values of the contributions along with their estimated uncertainties are recorded in Table S5 in the Supporting Information. The values of the contributions were correlated using eq 3, and the parameters of the fits are given in Table S6 in the Supporting Information.

The standard partial molar volumes calculated from eq 4 for the ketones investigated here yielded good agreement with the input data: the root-mean square deviations (in $\mathrm{cm^3 \cdot mol^{-1}}$) over the experimental temperature range were 0.051 (cyclopentanone), 0.147 (cyclohexanone), and 0.141 (cycloheptanone); the deviations observed for cyclohexane-1,4-dione were of course zero, since data for only one diketone was included in the input data set. The deviations of the predicted standard partial molar volumes at $T = 298.15$ K for cyclic monoketones with $n = 3$, 7, and 8 from the corresponding experimental values[8] were (−0.51, 0.57, and 1.11) $\mathrm{cm^3 \cdot mol^{-1}}$.

The dependences of the contributions on temperature are shown in Figure 3a (solid lines). Curves related to contributions obtained from data for some other homologous series of solutes (dashed curves) are plotted in the figure for comparison. The group contribution of the methylene group is close to that evaluated from data for cyclic ethers.[2,10] On the other hand, the contribution of the carbonyl group for the cyclic ketones is surprisingly much smaller than that for linear aliphatic ketones,[11] and the covolume term is much larger than that obtained for cyclic ethers.[10] It is therefore evident that the covolume term here includes a structural effect related to the presence of two carbonyl groups in cyclohexane-1,4-dione. The carbonyl group exhibits a keto−enol equilibrium that is not much affected by cyclization of the aliphatic part of a molecule. Interestingly, the content of the enol form is significantly higher in cyclohexanone than in cyclopentanone and cycloheptanone.[12,13] No information on the keto−enol equilibrium in cyclic diketones was found in the literature, but it is likely that the presence of the two carbonyl groups at the 1 and 4 positions in cyclohexane-1,4-dione might favorably affect the formation of the enol form; if both carbonyl groups were to be transformed into the enol form, then two conjugated double bonds would appear in the six-membered cycle. Consequently, the presence of the hydroxyl groups of the enol form would lead to larger compression of the hydration shell and thus to a lower standard partial molar volume. The smaller values of the contribution of the carbonyl group lead to values of the covolume that are about 1.5 times larger than that obtained for cyclic ethers. This is in contradiction to the theoretical significance of the covolume, which should be determined by properties of the solvent only and thus should have a common value for all solutes in the same solvent.

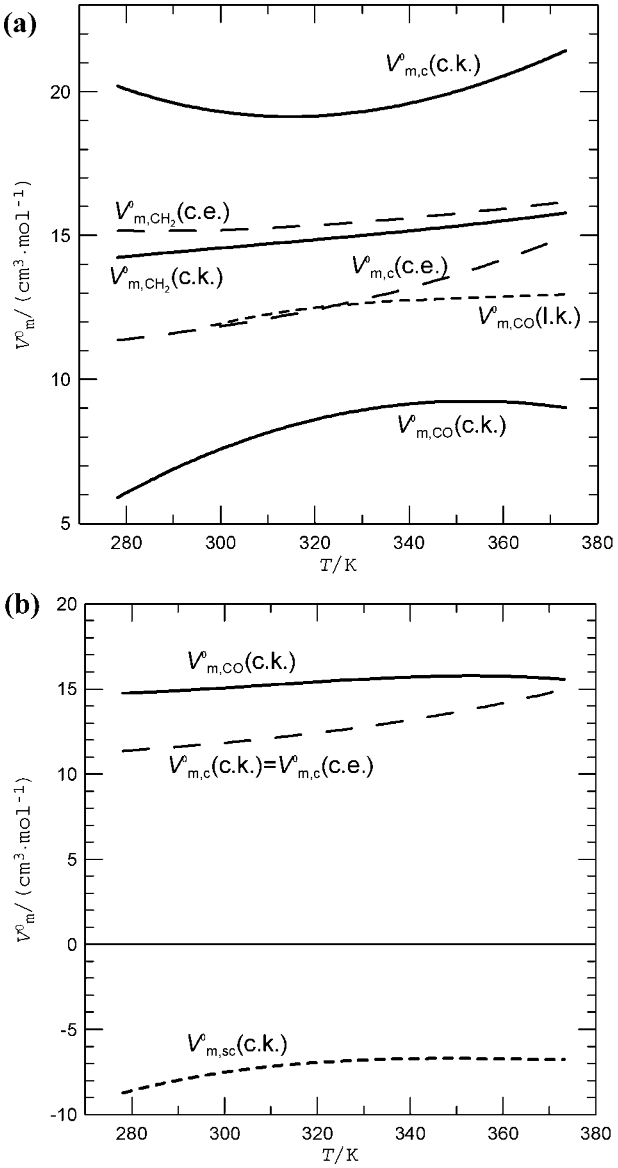

Figure 3. Temperature dependence of covolume and group contributions to the standard partial molar volumes. (a) Contributions in eq 4 for cyclic ketones and selected contributions obtained for other classes of solutes (linear ketones, cyclic ethers). (b) Contributions in eq 6 for cyclic ketones: c.k., cyclic ketones (this work); l.k., linear ketones (ref 11); c.e., cyclic ethers (ref 10). The lines are guides to aid the eye.

We attempted to correct this drawback by tentatively adjusting the values of the standard molar volume of cyclohexane-1,4-dione to get covolume values identical with those obtained for cyclic ethers.[10] The adjusted volumes are significantly larger than the experimental ones, and the difference is equal to a structural correction $V^\circ_{\mathrm{m,sc}}$ (which has a negative value) that should be introduced into eq 4 for cyclohexane-1,4-dione:

$$(V^\circ_{\mathrm{m,2}})_{\mathrm{calc}} = V^\circ_{\mathrm{m,c}} + nV^\circ_{\mathrm{m,CH_2}} + mV^\circ_{\mathrm{m,CO}} + kV^\circ_{\mathrm{m,sc}} \quad (6)$$

where $k = 0$ for monoketones ($m = 1$, $n = 4$, 5, 6) and $k = 1$ for cyclohexane-1,4-dione ($m = 2$, $n = 4$). The plots of the contributions in eq 6 obtained after the covolume was a priori set to that evaluated for cyclic ethers[10] [i.e., $V^\circ_{\mathrm{m,c}}$(cyclic ketones, this work) = $V^\circ_{\mathrm{m,c}}$(cyclic ethers, ref 10)] are shown in Figure 3b. The contribution of the methylene group (not plotted in Figure 3b) is determined by the volumes of monoketones and therefore remained unchanged. The contribution of the carbonyl group increased, but the values significantly exceed those reported for linear ketones (see Figure 3a), which may raise the question of whether the covolume obtained for cyclic ethers is a "true" covolume that is transferrable to other classes of organic solutes. The answer is obvious: an empirical group-additivity scheme applied to a limited set of data is not capable of accounting for all of the structural effects, and consequently, the resulting covolume term is necessarily affected by the structural characteristics of a particular class of solutes.

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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; group contributions; and parameters of the smoothing polynomial. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Cibulka, I.; Hnědkovský, L. Partial molar volumes of organic solutes in water. XIX. Cyclic alcohols(aq) at temperatures $T = 298$ to 573 K and at pressures up to 30 MPa. *J. Chem. Thermodyn.* **2009**, *41*, 489–498.
(2) Cibulka, I. Partial molar volumes of organic solutes in water. XXII. Cyclic ethers at temperatures $T = 298$ to 573 K and pressures up to 30 MPa. *J. Chem. Thermodyn.* **2010**, *42*, 502–512.
(3) Hynek, V.; Hnědkovský, L.; Cibulka, I. A new design of a vibrating-tube densitometer and partial molar volumes of phenol(aq) at temperatures from 298 to 573 K. *J. Chem. Thermodyn.* **1997**, *29*, 1237–1252.
(4) Hnědkovský, L.; Cibulka, I.; Hynek, V. Partial molar volumes of organic solutes in water. VI. *o*- and *p*-Chlorophenols at temperatures $T = (298$ to $573)$ K and pressures up to 30 MPa. *J. Chem. Thermodyn.* **2001**, *33*, 1049–1057.
(5) Hnědkovský, L.; Cibulka, I. An automated vibrating-tube densimeter for measurements of small density differences in dilute aqueous solutions. *Int. J. Thermophys.* **2004**, *25*, 1135–1142.
(6) Wagner, W.; Pruss, A. The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use. *J. Phys. Chem. Ref. Data* **2002**, *31*, 387–535.
(7) Jacobsen, R. T.; Stewart, R. B.; Jahangiri, M. Thermodynamic Properties of Nitrogen from the Freezing Line to 2000 K at Pressures to 1000 MPa. *J. Phys. Chem. Ref. Data* **1986**, *15*, 735–909.
(8) Edward, J. T.; Farrell, P. G.; Shahidi, F. Partial Molar Volumes of Organic Compounds in Water. Part 1.—Ethers, Ketones, Esters and Alcohols. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 705–714.
(9) Hovorka, S.; Roux, A. H.; Roux-Desgrandes, G.; Dohnal, V. Limiting Partial Molar Excess Heat Capacities and Volumes of Selected Organic Compounds in Water at 25 °C. *J. Solution Chem.* **1999**, *28*, 1289–1305.
(10) Cibulka, I.; Alexiou, C. Partial molar volumes of organic solutes in water. XXI. Cyclic ethers at temperatures $T = 278$ to 373 K and at low pressure. *J. Chem. Thermodyn.* **2010**, *42*, 274–285.
(11) Cibulka, I.; Hnědkovský, L.; Marek, T. Partial molar volumes of organic solutes in water. XVII. 3-Pentanone(aq) and 2,4-pentanedione(aq) at temperatures $T = 298$ to 573 K and at pressures up to 30 MPa. *J. Chem. Thermodyn.* **2007**, *39*, 1286–1291.
(12) Gero, A. Studies on Enol Titration. III. Enol Content of Cycloalkanones. *J. Org. Chem.* **1961**, *26*, 3156–3157.
(13) Keeffe, J. R.; Kresge, A. J.; Schepp, N. P. Keto−Enol Equilibrium Constants of Simple Monofunctional Aldehydes and Ketones in Aqueous Solutions. *J. Am. Chem. Soc.* **1990**, *112*, 4862–4868.

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