

Heat Capacities of Aqueous Solutions of Acetone; 2,5-Hexanedione; Diethyl Ether; 1,2-Dimethoxyethane; Benzyl Alcohol; and Cyclohexanol at Temperatures to 523 K

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Abstract The heat capacities of aqueous solutions of acetone, 2,5-hexanedione, diethyl ether, 1,2-dimethoxyethane, benzyl alcohol and cyclohexanol at concentrations of 0.1 to 1.0 mol·kg⁻¹ were determined at temperatures of 298.15, 423.15, 473.15 and 523.15 K and pressures up to 28 MPa. The measurements were performed at ambient conditions using the commercial Picker differential flow calorimeter and at high temperatures and pressures with a customized Picker type calorimeter constructed at the Blaise Pascal University, Clermont-Ferrand. Standard molar heat capacities were obtained by weighted extrapolation to the infinite dilution limit. The contributions of –CO–, –O– and –OH groups to the standard molar volume and standard molar heat capacity were determined from the newly determined and literature data. The variation of the three oxygen-containing group contributions with temperature and molecular structure is examined qualitatively.

Keywords Standard molar heat capacity · Apparent molar heat capacity · Standard molar volume · Aqueous solution · Group contribution · Acetone · 2,5-Hexanedione · Diethyl ether · 1,2-Dimethoxyethane · Benzyl alcohol · Cyclohexanol

1 Introduction

Thermodynamic properties of aqueous solutions of organic oxygen containing species over an extended range of temperature and pressure are important for understanding various natural phenomena and industrial processes where phase or chemical equilibria play a role. The following examples can be cited: transfer of hydrophilic and moderately hydrophobic solutes between petroleum and oil field waters, power cycles with a complex chemistry in

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boiler water containing organic admixtures, and wet oxidation of organic waste at moderate or elevated temperatures. The derivative properties such as the standard heats of solution, the standard molar heat capacities and the standard molar volumes are needed for converting the thermodynamic equilibrium constants from the reference conditions of 298.15 K and 0.1 MPa to elevated temperatures and/or pressures. The development of group contribution schemes allowing estimation of the standard thermodynamic properties of a variety of aqueous organic species is therefore of high interest. Predictions can be made for different classes of oxygen containing solutes at ambient conditions thanks to the recent efforts by Plyasunov and collaborators [1–3]. Possibilities of predicting the standard derivative properties at high temperatures and pressures are, however, limited since much less experimental data are available at elevated conditions. Although the amount of volumetric data increased considerably over the past 15 years, due to the operation of high-temperature vibrating-tube densitometers in several laboratories, heat capacity measurements reaching to high temperatures and pressures are less frequent. Rare examples of these data are the results from the University of Delaware for solutions of alcohols [4], and phenol and acids [5], and the values for aqueous phenolic compounds from the Blaise Pascal University Clermont-Ferrand [6, 7]. A considerable amount of heat capacity data for various organic substances in water (including the oxygen containing compounds) was produced in recent years by Woolley and collaborators at the Brigham Young University and published mainly in the *Journal of Chemical Thermodynamics*. The range of their data is, however, limited to 393 K and 0.35 MPa and they cannot be therefore considered as truly high-temperature—high-pressure values.

The main purpose of this paper is to report results of new calorimetric measurements performed with aqueous solutions of selected oxygen containing compounds over a wide range of conditions. The measurements were performed with a commercial Picker differential flow calorimeter at ambient conditions and with the high-temperature Picker-type calorimeter constructed at the Blaise Pascal University [8] at temperatures up to 523 K and pressures to 28 MPa. The compounds were selected to cover different types of molecular structures containing oxygen—ethers, ketones, cyclic and aromatic alcohols—in order to extend the database of experimental results on the standard molar heat capacity for a use in a functional group contribution scheme. This contribution can be considered as a companion paper to that of Schulte *et al.* [9] reporting the volumetric data for these compounds at similar conditions. Such data are then useful for the predictions of the standard Gibbs energies of oxygen containing organic compounds that are necessary for calculating chemical and phase equilibria in aqueous solutions over a wide range of conditions. In the discussion part, the temperature evolution of the contributions for $-O-$, $-CO-$ and $-OH$ groups to the standard molar volume and heat capacity is discussed as a function of the molecular structure of a solute, using the newly determined and literature data.

2 Experimental

2.1 Preparation of solutions

Acetone (purity better than 99%; CAS: 67-64-1), 2,5-hexanedione (purity of 97%; CAS: 110-13-4, the main admixture being 3-methyl-2-cyclopentenone), diethyl ether (purity better than 99%; CAS: 60-29-7), 1,2-dimethoxyethane (purity better than 99%; CAS: 110-71-4), benzyl alcohol (purity better than 99%; CAS: 100-51-6) and cyclohexanol (purity of 98%; CAS: 108-93-0, the main admixture being phenol) were purchased from Acros Organics and

used directly without further purification. Solutions were prepared by mass with deionized water, which was freshly degassed under reduced pressure before use. At least three different concentrations were prepared for each solute. To insure a total dissolution of the solute in water, especially when approaching its solubility limit, solutions were energetically agitated and then placed in ultrasonic bath for at least ten minutes. Solutions were prepared and stored in brown glass bottles with septum caps from which samples were extracted through a metallic needle into a glass syringe to avoid any solute loss by vaporization. A special procedure was used for diethyl ether solution sampling, due to its very high volatility. Small quantities of fresh solutions with a low vapor phase volume (less than 1–3 mL in a 50 cm³ bottle) were prepared just before use. When filling the sample loop of the HT/HP calorimeter, the solution was extracted from the bottle with a glass syringe immediately after mixing in an ultrasonic bath and injected in the sample loop.

The maximum concentration reached was 1 mol·kg⁻¹ for acetone, 0.7 mol·kg⁻¹ for 2,5-hexanedione and 1,2-dimethoxyethane, and 0.5 mol·kg⁻¹ for diethyl ether. Maximum concentrations for benzyl alcohol and cyclohexanol solutions did not exceed 0.32 mol·kg⁻¹, due to the lower solubility of these solutes in water. The uncertainty in solution concentrations is believed to be generally $\pm(2 \times 10^{-3})$ mol·kg⁻¹ according to the balance precision, $\pm(5 \times 10^{-3})$ mol·kg⁻¹ for diethyl ether.

2.2 Measurements of densities

The flow calorimeters used for experiments yield heat capacities per unit volume. For calculation of the specific heat capacities of a solution it is necessary to know the ratio of water to solution densities at temperature of the sample loop and pressure of the experiments (see Eq. (2) below). For that reason we have performed densimetric measurements as a function of pressure at 298.15 K. The densities were obtained at 0.1 MPa with a Picker vibrating tube flow densitometer of Sodev type 03D [10] operating at a low flow rate (1.7×10^{-3} cm³·s⁻¹). The temperature was maintained constant at 298.15 K within 0.005 K using a Picker thermoregulation system and was measured with accuracy of 0.01 K. The oscillation period of the stainless-steel vibrating tube filled with a solution was $\tau = 2.8$ ms with a stability of 0.5 ns.

The measurements at elevated pressures (10 and 28 MPa) were performed at 298.15 K with a HT/HP densitometer constructed at the Blaise Pascal University and described by Hynek *et al.* [11]. It operates with a platinum-rhodium vibrating tube oscillating with a period near 7.6 ms and a stability of 5 ns. The experiments were performed in a flow regime at a constant flow rate near 8.3×10^{-3} cm³·s⁻¹. The temperature inside the densimeter was maintained at $T = (298.15 \pm 0.1)$ K and was measured with a customized 500 Ω Burns Engineering secondary standard calibrated by the manufacturer against the IPTS 90 standard. The pressure was controlled with a stability of ± 0.05 MPa using a Circle Seal back-pressure regulator at the end of the flow system and measured by a DPI 260 Druck electronic pressure gauge with an accuracy of 0.03 MPa. Short-term temperature stability (over one experiment) of the densitometer block was ± 0.01 K.

The density differences between solution, ρ_s , and water, ρ_w , were calculated as

$$\Delta\rho = \rho_s - \rho_w = K(\tau_s^2 - \tau_w^2) \quad (1)$$

where τ_s and τ_w are the oscillation periods of the vibrating tube containing selected solution and pure water, respectively. The calibration constant, K , is only slightly dependent on pressure and was determined from measurements with vacuum against water for the Sodev

densitometer and with 3 mol·kg⁻¹ NaCl solution against water for the HT/HP densitometer. The density of water was calculated from the equation of state by Hill [12] and the density of the NaCl solution was obtained from the correlation by Archer [13]. The expected uncertainties for the calibration constants are 0.05% and 0.15% for the Sodev and high-pressure densitometers, respectively.

2.3 Measurements of heat capacities

The heat capacity measurements at 298.15 K and 0.1 MPa were determined using a Picker flow microcalorimeter (SETARAM) based on the thermal balance principle and operating at a flow rate of 0.01 cm³·s⁻¹. The average temperature was maintained constant within 0.005 K using a Picker thermoregulation ensuring a sensitivity of 10⁻⁴ J·K⁻¹·cm⁻³ when determining the specific heat capacity of the sample. Two cells separated by a delay loop are placed in series and filled with the reference solvent (water) using a peristaltic pump from Gilson. When injecting a solution, one cell is filled with solution while the other contains water. The difference in power needed to maintain the constant temperature rise is then proportional to the ratio of the heat capacity of solution *versus* water. For each measurement the two cells are successively filled with water and solution, and then water again leading to a double determination of the heat capacity of the solution in a run with one sample. The procedure and calibration are classical and well documented in the literature [14].

A HT/HP Picker-type differential flow calorimeter constructed at the Blaise Pascal University and described by Hnedkovsky *et al.* [8] was used to measure the specific heat capacities at target temperatures of 423, 473 and 523 K and at a pressure of 10 MPa and also at 28 MPa at the highest temperature. The core of the calorimeter is a temperature controlled massive block housing two identical cells from the platinum-iridium tubing of 2 mm o.d. Each cell is equipped with a wire heater wound around the tube and with the RTDs that detect the temperature rise of the heated fluid compared to the block. The principle of the heat capacity determination is as follows. The electric powers necessary to give the same temperature rise when the sample solution and water are flowing alternately in the sample cell of the instrument are measured. A second (reference) cell is used to equilibrate the temperature bridge and to compensate for possible flow rate and temperature fluctuations in the calorimeter. Because the heat capacities per unit volume are directly measured, the ratio of specific heat capacities of solution and water $c_{p,s}/c_{p,w}$ is related to the difference in the power of the heater $P_s - P_w$ by the relation:

$$c_{p,s}/c_{p,w} = (\rho_w/\rho_s)_{SL} \{1 + f \cdot (P_s - P_w)/P_w\} \quad (2)$$

where $(\rho_w/\rho_s)_{SL}$ is the ratio of water and solution densities at the temperature of the sample loop and pressure of the experiment. The heat loss correction factor, f , was determined by changing the water base flow rate, F_w (near 1.8 cm³·min⁻¹) in the sample cell by ΔF (up to 0.5 cm³·min⁻¹) to mimic the change in heat capacity. The difference ΔP in the base heat power P_w (typically between 0.3 and 0.4 W depending on temperature) necessary to maintain the same temperature rise allows the determination of the factor f as

$$f = \Delta F P_w / (\Delta P F_w) \quad (3)$$

operating at conditions where ΔP is comparable with $P_s - P_w$ during an experiment (up to 0.09 W). The resulting values of f obtained from several pairs of ΔP and ΔF were 1.039

(423 K, 10 MPa), 1.053 (473 K, 10 MPa), 1.071 (523 K, 10 MPa) and 1.049 (523 K, 28 MPa) with an uncertainty typically not exceeding 2.5% (see the detailed discussion below).

The experimental temperature, T , reported for calorimetric measurements represents the average temperature before (assumed to be equal to the temperature of the block, T_{block}) and after the cell heater was used

$$T = T_{\text{block}} + 0.5 \cdot \Delta T_{\text{exp}} \quad (4)$$

with a typical temperature increase of $\Delta T_{\text{exp}} = 2$ K. This variation of temperature corresponds to a compromise allowing measurements of $P_s - P_w$ differences with sufficient precision while avoiding too large heat losses occurring when the temperature rise is too high.

A 500 Ω secondary standard of Burns calibrated by the manufacturer against the IPTS 90 standard was used for measuring the temperature of the block. Considering the possibility of temperature gradients at high temperatures, the uncertainty in the temperature determination increases with temperature from 0.05 to 0.1 K between the lower and upper temperature limits of measurements. The block temperature is regulated by a platinum RTD connected in a Wheatstone bridge control system commanding two cartridge heaters used to produce the power necessary to reach the chosen temperature and to maintain it constant within 0.02 K. This high stability of T_{block} is insured by a system of three concentric jackets and three circular lids surrounding the block, which decrease the probability of any temperature fluctuation. These multiple layers contribute also to the pre-heating of the sample and water before they reach the block. The external can with its lid serves as a vacuum chamber in which the calorimeter is placed. The other two jackets and lids are temperature regulated, using wire and cartridge heaters and platinum RTDs to detect the temperature. The temperature of the block and of the inner jacket are adjusted independently while the temperatures of the outer jacket and of the inner and outer lids are adjusted proportionally to the inner can. The temperatures are set in such a way that there is a difference of about 1 K between the block and the inner jacket, and a similar difference between the inner and the outer jacket. A counter-current heat exchanger, where the two pairs of inlet and outlet transport tubes are silver-soldered together, is used as a first stage of the temperature regulation of the incoming fluids.

The measured solution is supplied to the calorimeter from a sample loop with an internal volume of approximately 20 cm³ placed in a water bath thermostat (LKB-7600) set at 298.15 K. After filling the loop with the solution of interest the shut-off valves on both sides of the filled sample loop are closed and the loop is pre-pressurized to the working pressure by means of a second auxiliary high-pressure pump.

A high-pressure pump (Spectra SERIES, P100) working at a constant volumetric flow rate (flow rate stability <0.25%), was used to supply water or solution to the calorimeter at a typical base flow rate ($F_w = 1.8$ cm³·min⁻¹). Water used as a reference fluid was deionized (SeralPURE AP30) and degassed by boiling under reduced pressure. The pressure in the system was measured with a Bourdon-type pressure gauge (Heise, CM-63961) with an accuracy of 0.1 MPa. The pressure was maintained constant within 0.05 MPa by a back-pressure regulator (Circle Seal, BPR21U) placed at the end of the outlet stream from the calorimeter. After equilibrating the temperature control bridge of the cells with water at $\Delta T_{\text{block}} = 2$ K, which gives the reference power P_w , the sample was injected into the calorimeter by inserting a loaded sample loop into the stream of water. This causes the change in the equilibration of the bridge due to the difference of heat capacity between water in the reference cell and solution in the measuring cell. The new value P_s of power applied to the sample cell allows re-equilibration of the bridge at the same ΔT_{block} .

At each temperature the calorimeter was tested by measuring the heat capacity of a 3 mol·kg⁻¹ NaCl solution. The experimental results obtained were in satisfactory agreement (within 4 J·mol⁻¹·K⁻¹ in the apparent molar heat capacity) with the results of our earlier measurements [8] and with recommended data in the literature [13].

3 Results

Table 1 summarizes parameters A , B , and C obtained by the weighted least-square regression of the density difference, $\Delta\rho$, between the solution and water at 298.15 K as a function of molality and pressure

$$\Delta\rho/m = A + Bp + Cm \quad (5)$$

Parameters of Eq. (5) are valid for the concentration ranges given in the table at a temperature of 298.15 K and at pressures from 0.1 to 28 MPa. The individual parameters were considered only if their values were significant compared to the standard deviation of the parameter at a significance level = 0.05. The standard weighted deviation expresses the quality of the fit compared to the expected error in $\Delta\rho$ that are due to the uncertainty in the calibration constant, K , solution plateau, τ_s , and the water base line, τ_w , as apparent from Eq. (1).

The apparent molar heat capacities $C_{p,\phi}$ were calculated from the measured ratio of the specific heat capacities of the solution $c_{p,s}$ and water $c_{p,w}$ [J·kg⁻¹·K⁻¹]:

$$C_{p,\phi} = c_{p,s} M_s + \frac{c_{p,s} - c_{p,w}}{m} = c_{p,w} [(M_s + 1/m)(c_{p,s}/c_{p,w}) - 1/m] \quad (6)$$

where M_s is the molar mass of solute [kg·mol⁻¹] and m is the concentration of solute [mol·kg⁻¹]. It is useful to describe the ratio of the heat capacity difference $c_{p,s} - c_{p,w}$ and concentration by an equation

$$\frac{c_{p,s} - c_{p,w}}{m} = [(c_{p,s}/c_{p,w}) - 1]c_{p,w}/m = A_0 + A_1m \quad (7)$$

Table 1 Parameters of Eq. (5): $\Delta\rho/m = A + Bp + Cm$ for all solutes at $T = 298.15$ K and $p = 0.1$ –28 MPa

Parameter solute	Valid up to concentration [mol·kg ⁻¹ H ₂ O]	A [kg ² ·mol ⁻¹ ·m ⁻³]	B [kg ² ·mol ⁻¹ ·MPa ⁻¹ ·m ⁻³]	C [kg ³ ·mol ⁻² ·m ⁻³]	S_{yw}
Acetone	1.0	-8.5543	-0.0119	0.4341	0.22
2,5-Hexanedione	0.7	2.3358	-0.012	—	0.34
Diethyl ether	0.7	-16.8392	—	3.5895	1.08
1,2-Dimethoxyethane	0.7	-5.7404	-0.0258	1.8353	0.27
Benzyl alcohol	0.3	7.2609	—	-2.5567	0.54
Cyclohexanol	0.3	-2.8728	—	—	0.41

Note. $\Delta\rho = \rho_s - \rho_w$ (kg·m⁻³); S_{yw} is the standard weighted deviation of correlation. A parameter was not considered if its value was not significant compared to standard deviation of the parameter at a significance level = 0.05.

Because the partial molar heat capacity at infinite dilution, C_p^∞ (the standard molar heat capacity), is equal to the concentration limit of the apparent molar heat capacity, the combination of Eqs. (6) and (7) leads to:

$$C_p^\infty = \lim_{m \rightarrow 0} C_{p,\phi} = c_{p,w}M_s + \lim_{m \rightarrow 0} \left(\frac{c_{p,s} - c_{p,w}}{m} \right) = c_{p,w}M_s + A_0 \tag{8}$$

The parameter A_0 , which plays a decisive role in the determination of C_p^∞ , was obtained by the weighted regression of the experimental data where the weights were determined by taking into account uncertainties in all quantities affecting the heat capacity measurement. For the expected error in the apparent molar heat capacities, $\delta C_{p,\phi}$, it follows from Eq. (6):

$$\delta C_{p,\phi} = c_{p,w} (M_s + 1/m) \delta \left(\frac{c_{p,s}}{c_{p,w}} \right) \tag{9}$$

Using Eq. (2), estimation of the probable error in heat capacity ratio ($c_{p,s}/c_{p,w}$) was performed by calculating the propagation of uncertainties in the density ratio $(\rho_w/\rho_s)_{SL}$, calibration factor, f , and heating powers, P_s and P_w , as follows

$$\delta \left(\frac{c_{p,s}}{c_{p,w}} \right) = [\delta_\rho^2 + \delta_f^2 + \delta_P^2]^{0.5} \tag{10}$$

where symbols δ_ρ , δ_f and δ_P stand for the three uncertainty contributions.

The first term δ_ρ is dependent on the uncertainty in the density difference estimated as $\delta\Delta\rho = 0.15 \text{ kg}\cdot\text{m}^{-3}$ and on the change in density of water due to the possible temperature fluctuations of the bath where the sample loop was thermostated. The maximum expected uncertainty in the density of water is $\delta\rho_w = 0.2 \text{ kg}\cdot\text{m}^{-3}$. It is possible to write

$$\delta_\rho = \left(\frac{c_{p,s}}{c_{p,w}} \right) \left(\frac{\rho_s}{\rho_w} \right)_{SL} \delta \left(\frac{\rho_w}{\rho_s} \right)_{SL} = \left(\frac{c_{p,s}}{c_{p,w}} \right) \left[\left(\frac{\delta\Delta\rho}{\rho_s} \right)^2 + \left(\frac{\Delta\rho}{\rho_s} \right)^2 \left(\frac{\delta\rho_w}{\rho_w} \right)^2 \right]_{SL}^{0.5} \tag{11}$$

The second term in Eq. (10) is calculated as

$$\delta_f = \left(\frac{\rho_w}{\rho_s} \right)_{SL} \left(\frac{P_s - P_w}{P_w} \right) \delta f \tag{12}$$

where the error in the heat loss correction factor, δf , is estimated on the basis of Eq. (3) as

$$\delta f = f \left[\left(\frac{\delta P_w}{P_w} \right)^2 + \left(\frac{\delta F_w}{F_w} \right)^2 + \left(\frac{\delta\Delta F}{\Delta F} \right)^2 + \left(\frac{\delta\Delta P}{\Delta P} \right)^2 \right]^{0.5} \tag{13}$$

The four terms were calculated from the fluctuations in the heating power (typically 0.03 and 0.06 mW with and without use of a lock-in amplifier) and the flow rate (typically 0.2%).

Finally the third term

$$\delta_P = \left(\frac{\rho_w}{\rho_s} \right)_{SL} f \delta \left(\frac{P_s}{P_w} \right) = \left(\frac{\rho_w}{\rho_s} \right)_{SL} f \left(\frac{P_s}{P_w} \right) \left[\left(\frac{\delta P_w}{P_w} \right)^2 + \left(\frac{\delta P_s}{P_s} \right)^2 \right]^{0.5} \tag{14}$$

is dependent on the power fluctuations, δP_w and δP_s , during the passage of water and sample through the measuring cell that were comparable with those relating to the determination of the f factor as stated above.

Experimental results of the heat capacity measurements are presented in Table 2, where besides the heat capacity ratios are also listed the apparent molar heat capacities and their estimated errors calculated from Eqs. (8) and (9), respectively. It can be noted that the differences in the error estimate are in some cases substantial for multiple data points. This is due to the fact that the data were obtained in two experimental campaigns. In the first one (2003) we have encountered serious problems with the functioning of the lock-in amplifier that determines the sensitivity of the temperature regulation of the cells. Therefore, the fluctuations in the powers, P_w and P_s , were much higher than during the second set of measurements carried out in 2005 when the system was functioning with the lock-in amplifier working correctly and better stability of the calorimetric signal was achieved. Otherwise there does not seem to be any systematic gap between the two measurements series. We did not therefore consider it useful to present them separately and the only distinction is the error assignment. The trends in the apparent molar heat capacity data as a function of temperature, pressure and molality are well apparent from the four graphs in Fig. 1. There is not a strong dependence of $C_{p,\phi}$ on concentration for the four solutes presented, the slope being negative in most cases.

The data for diethyl ether solutions should be taken with caution since they can be subject to some systematic errors due to the very high volatility of this solute. Serious difficulties occurred when measuring with solutions of cyclic alcohols at high temperatures. The data were much more scattered compared to the other solutes and the apparent molar heat capacities exhibited an unrealistic steep increase with decreasing concentration. Although the distinct behavior of these two solutes at high temperature was also observed by Schulte *et al.* [9] during their volumetric measurements, we were not able to find a clear explanation for the lack of the data reproducibility during the calorimetric determinations. Partial decomposition catalyzed by the platinum tubing might be an explanation. The data for cyclohexanol and benzyl alcohol are therefore presented only at target temperatures up to 423 and 473 K, respectively.

Table 2 presents the results of the weighted least-squares regression of the heat capacity differences by Eq. (7) and the standard molar heat capacities, C_p^∞ , obtained subsequently from Eq. (8). The standard weighted deviations of the fit, S_{yw} , indicate that the error estimates of individual data points were in most cases realistic. The estimated uncertainty, $\delta(C_p^\infty)$, is identical to the statistical error estimate of parameter A_0 obtained during the fitting procedure; it reflects mainly the scatter of the data. The last column lists the standard molar heat capacities reported in the literature at 298.15 K and 0.1 MPa with expected uncertainties assigned by Plyasunov *et al.* [15]; no data were reported in the literature at superambient conditions. Generally, measured C_p^∞ are in reasonable agreement with the published values within the expected error limits. The standard molar heat capacities are plotted for the six aqueous solutes as a function of temperature in Fig. 2. It is apparent that for ethers and ketones C_p^∞ is an increasing function of temperature. This is an evolution generally encountered for hydrophilic solutes, whereas in the case of cyclic alcohols that can be considered as moderately hydrophobic, a flat minimum seems to occur. This is a similar behavior to that observed earlier for several alkylbenzene derivatives with one hydroxy or amino group [6, 7] (Table 3).

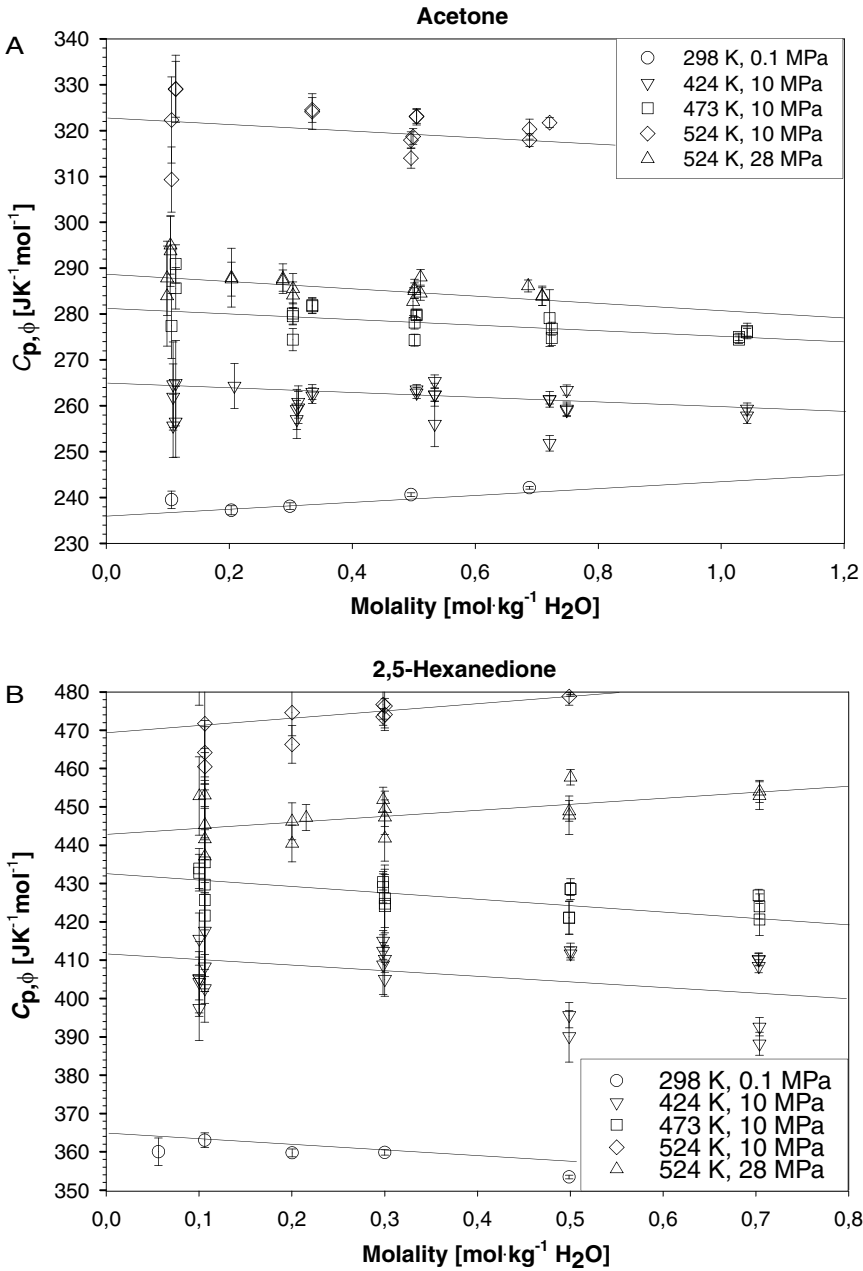


Fig. 1 Apparent molar heat capacity for aqueous solutes at different temperatures and pressures: (a) acetone; (b) 2,5-hexanedione; (c) diethyl ether; (d) 1,2-dimethoxy ethane

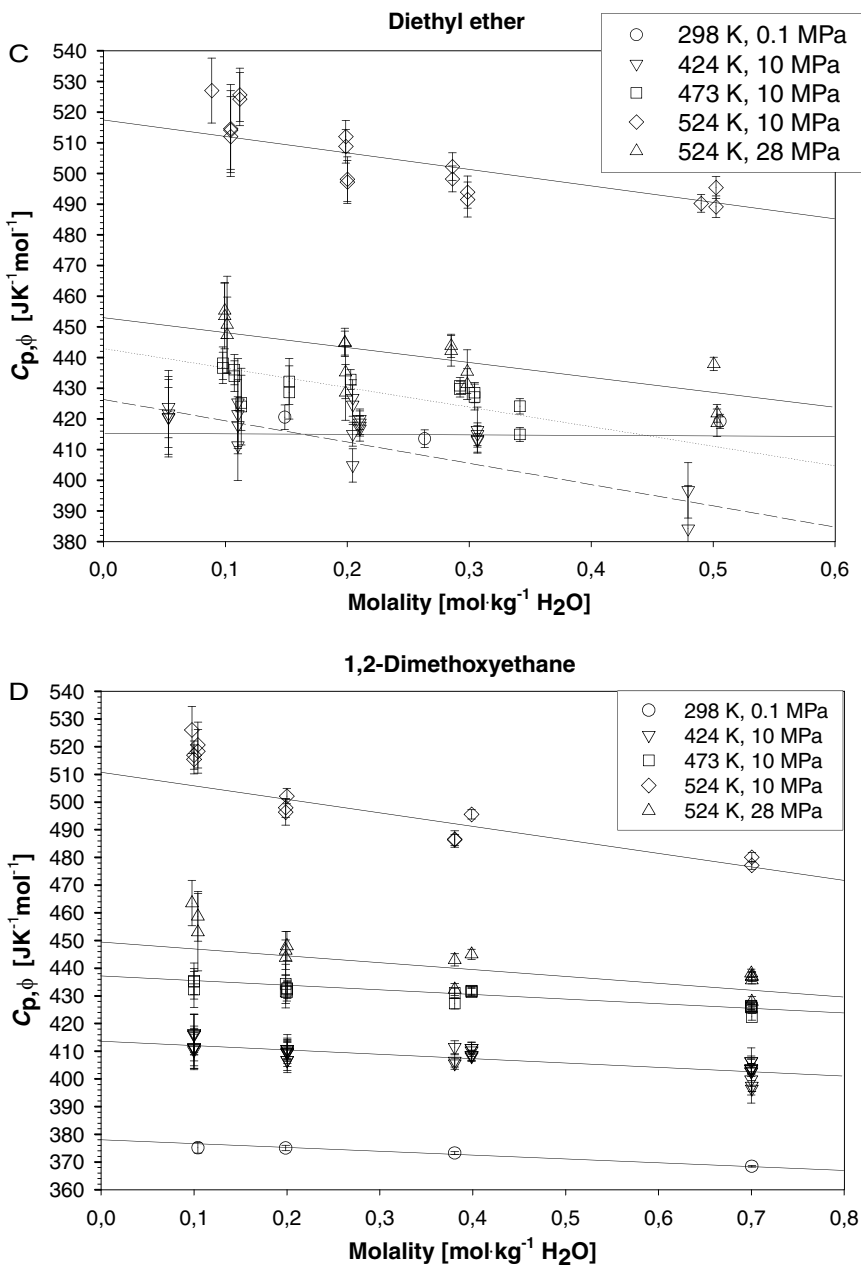


Fig. 1 Continued

4 Discussion and conclusions

The standard molar heat capacity, C_p^∞ , of most organic compounds increases with temperature at conditions remote from ambient despite the possibility of shallow minima near 400 K observed here for cyclohexanol and benzylalcohol. This is consistent with the increasing trend in the standard molar volume, V^∞ , versus temperature reported by Schulte *et al.* [9] for the same solutes. There is universally a rather steep increase in C_p^∞ at 523 K that is suggested by theory [16]: the standard heat capacity of a nonelectrolytic solute typically tends to plus infinity when approaching the critical point of water from below. On the contrary, the heat capacity of electrolytes and a few strongly polar solutes decreases with increasing temperature [17], diverging to minus infinity at the solvent critical point. Because our solutes contain one or two polar functional groups, it is interesting to investigate their effect on the overall hydrophobic behavior. To make such a study more representative, we have combined our results with the standard heat capacities and volumes for ketones, ethers and alcohols reported in the literature at superambient temperatures.

To extract the contributions of oxygen containing functional groups, we employed a similar approach as recently presented for the determination of standard thermodynamic functions of hydration for aqueous hydrocarbons [18]. Under the assumption of functional group additivity any standard thermodynamic property can be expressed as a sum of structural contributions:

$$Y^\infty = Y^{\text{SS}} + \sum_{j=1}^N n_j Y_j^\infty \quad (15)$$

where N is the total number of functional groups in a compound, n_j is the number of occurrences of a specific functional group in a compound, and Y_j^∞ stands for property Y of the j -th group. The term Y^{SS} is the standard state term, which is derived from theory [19] and reflects the contribution of a point mass (*i.e.*, a material point with no functional groups). The value of the standard state term is obtained from the thermodynamic properties of the pure solvent; it increases with temperature and becomes large at high temperatures (infinite at the solvent critical point in the case of V^{SS} and C_p^{SS}). Setting apart the term Y^{SS} is important because this function is certainly not functionally additive (its value is the same for any solute). The appropriate relations for the standard state terms in the case of the standard molar volume and the standard molar heat capacity are given by

$$C_p^{\text{SS}} = RT(2\alpha_w + T(\partial\alpha_w/\partial T)_p) - R/T \quad (16)$$

$$V^{\text{SS}} = RT\kappa_w \quad (17)$$

where α_w and κ_w are the coefficients of thermal expansion and isothermal compressibility of water, respectively. Values of Y^{SS} were in this study computed from the equation of state for water by Hill [12].

Because the original group contribution method [18] was designed for the thermodynamic properties of hydration, our collected standard molar heat capacities were first converted to the heat capacities of hydration $\Delta_{\text{hyd}}C_p^\infty$ by subtracting the heat capacity of solute in the ideal gas state, taken from the compilation of Frenkel *et al.* [20]. Then we subtracted the value of the standard state term, C_p^{SS} . Further, the contributions corresponding to all hydrocarbon

Table 2 Experimental heat capacity ratios $c_{p,s}/c_{p,w}$, apparent molar heat capacities $C_{p,\phi}$ and their estimated error $\delta(C_{p,\phi})$

m (mol·kg ⁻¹)	$c_{p,s}/c_{p,w}$ (-)	$C_{p,\phi}$ (J·K ⁻¹ ·mol ⁻¹)	$\delta(C_{p,\phi})$ (J·K ⁻¹ ·mol ⁻¹)
Acetone: 298.15 K, 0.10 MPa			
0.1063	0.999918	239.5	1.9
0.2035	0.999734	237.2	1.0
0.2988	0.999671	238.1	0.7
0.4957	0.999747	240.6	0.4
0.6884	0.999898	242.1	0.3
Acetone: 423.95 K, 10.30 MPa			
0.1089	1.000407	264.6	9.3
0.1089	1.000181	255.6	6.9
0.1089	1.000340	261.9	7.2
0.1131	1.000210	256.5	7.7
0.1131	1.000432	264.9	9.3
0.2086	1.000763	264.3	4.9
0.3100	1.000605	257.0	4.2
0.3100	1.000766	259.2	4.4
0.3123	1.000883	260.8	3.5
0.3123	1.000800	259.6	3.5
0.3351	1.001119	263.0	1.6
0.3351	1.001055	262.2	1.7
0.5048	1.001722	263.5	1.1
0.5048	1.001642	262.8	1.2
0.5343	1.001686	262.4	2.5
0.5343	1.000918	256.0	4.9
0.5343	1.002038	265.3	1.4
0.5343	1.001685	262.4	1.4
0.7212	1.002074	261.3	0.9
0.7212	1.002096	261.4	1.7
0.7212	1.000538	251.8	1.7
0.7490	1.001821	259.3	1.5
0.7490	1.001773	259.0	1.4
0.7490	1.002507	263.4	1.1
1.0422	1.002136	257.8	1.7
1.0422	1.002495	259.3	1.3
Acetone: 473.24 K, 10.30 MPa			
0.1063	1.000459	277.4	7.1
0.1131	1.000829	290.9	4.2
0.1131	1.000697	285.6	4.5
0.3035	1.001482	280.1	2.3
0.3035	1.001436	279.5	1.9
0.3035	1.001097	274.4	2.4
0.3351	1.001749	281.7	1.6
0.3351	1.001763	281.9	1.7
0.5015	1.002201	278.1	1.4
0.5015	1.001776	274.3	1.3
0.5048	1.002390	279.7	1.1
0.5048	1.002414	279.9	1.1
0.7212	1.003283	279.1	6.2
0.7245	1.002625	274.8	1.7
0.7245	1.002926	276.8	1.4

Table 2 Continued

m (mol·kg ⁻¹)	$c_{p,s}/c_{p,w}$ (-)	$C_{p,s}$ (J·K ⁻¹ ·mol ⁻¹)	$\delta(C_{p,s})$ (J·K ⁻¹ ·mol ⁻¹)
1.0288	1.003703	275.0	0.8
1.0288	1.003568	274.4	0.8
1.0422	1.003955	276.0	0.8
1.0422	1.004024	276.3	1.7
Acetone: 523.89 K, 10.30 MPa			
0.1063	1.000968	322.3	9.4
0.1063	1.000682	309.3	7.1
0.1131	1.001189	329.1	7.3
0.1131	1.001186	329.0	6.1
0.3351	1.003134	324.1	3.9
0.3351	1.003164	324.5	2.7
0.4957	1.003581	314.0	2.2
0.4957	1.003977	317.9	1.8
0.4991	1.004083	318.7	1.7
0.5048	1.004570	323.0	1.8
0.5048	1.004577	323.1	1.5
0.6884	1.005464	317.9	1.4
0.6884	1.005799	320.3	2.2
0.7212	1.006257	321.7	1.1
Acetone: 523.89 K, 28.15 MPa			
0.0990	1.000337	283.9	10.9
0.0990	1.000420	287.8	8.1
0.1047	1.000576	293.7	7.7
0.1047	1.000606	295.0	6.3
0.2037	1.000852	287.6	3.7
0.2037	1.000864	287.9	6.4
0.2873	1.001176	287.3	2.3
0.2873	1.001201	287.7	3.2
0.3038	1.001033	284.1	2.9
0.3038	1.001124	285.5	3.3
0.4991	1.001535	282.7	3.0
0.5012	1.001838	285.5	2.1
0.5012	1.001796	285.1	1.7
0.5113	1.001762	284.5	1.5
0.5113	1.002135	288.0	1.7
0.6861	1.002569	286.1	1.3
0.7090	1.002319	283.8	1.9
0.7090	1.002351	284.0	2.1
2,5-Hexanedione: 298.15 K, 0.10 MPa			
0.0563	0.998433	360.0	3.6
0.1062	0.997136	363.0	1.9
0.2003	0.994501	359.7	1.0
0.3002	0.991854	359.8	0.7
0.4988	0.986031	353.4	0.5
2,5-Hexanedione: 423.95 K, 10.30 MPa			
0.1002	0.998077	405.2	5.6
0.1002	0.998052	404.2	8.0
0.1002	0.998315	415.5	6.8
0.1002	0.997895	397.4	8.4

Table 2 Continued

m (mol·kg ⁻¹)	$c_{p,s}/c_{pw}$ (-)	$C_{p,\theta}$ (J·K ⁻¹ ·mol ⁻¹)	$\delta(C_{p,\theta})$ (J·K ⁻¹ ·mol ⁻¹)
0.1002	0.998073	405.1	9.8
0.1062	0.998266	417.6	10.0
0.1062	0.997898	402.6	8.8
0.1062	0.998036	408.3	9.6
0.2983	0.994883	412.4	2.2
0.2983	0.995054	415.0	2.7
0.2983	0.994637	408.8	7.8
0.3002	0.994350	405.0	4.4
0.3002	0.994707	410.3	3.5
0.4988	0.989172	390.1	6.7
0.4988	0.989770	395.6	3.3
0.5003	0.991615	412.5	1.9
0.5003	0.991529	411.7	1.7
0.7031	0.988100	410.1	1.6
0.7031	0.988131	410.3	1.6
0.7031	0.987850	408.4	1.7
0.7039	0.985432	392.6	2.4
0.7039	0.984758	388.2	3.0
2,5-Hexanedione: 473.24 K, 10.30 MPa			
0.1002	0.998366	433.9	5.2
0.1002	0.998343	432.8	4.8
0.1062	0.998076	425.7	23.9
0.1062	0.997979	421.6	19.8
0.1062	0.998307	435.5	29.8
0.1062	0.998169	429.7	27.2
0.2983	0.994927	429.0	4.1
0.2983	0.995014	430.4	2.1
0.3002	0.994704	426.1	7.6
0.3002	0.994613	424.7	7.6
0.3002	0.994572	424.1	10.7
0.4988	0.990852	421.0	4.3
0.4988	0.990856	421.1	4.3
0.5003	0.991622	428.5	1.7
0.5003	0.991617	428.5	2.7
0.7031	0.988240	426.9	1.6
0.7039	0.987801	424.0	3.3
0.7039	0.987299	420.6	4.2
2,5-Hexanedione: 523.89 K, 10.40 MPa			
0.1002	0.998745	486.2	9.7
0.1002	0.998909	494.1	7.7
0.1002	0.998837	490.7	6.6
0.1062	0.998353	471.7	13.9
0.1062	0.998107	460.5	10.4
0.1062	0.998188	464.2	8.3
0.2002	0.996704	466.3	4.9
0.2002	0.997046	474.6	6.1
0.2983	0.995577	473.5	2.2
0.2983	0.995770	476.7	3.8
0.3002	0.995590	474.1	4.2
0.3002	0.995721	476.3	5.7

Table 2 Continued

m (mol·kg ⁻¹)	$c_{p,s}/c_{p,w}$ (-)	$C_{p,s}$ (J·K ⁻¹ ·mol ⁻¹)	$\delta(C_{p,s})$ (J·K ⁻¹ ·mol ⁻¹)
0.4988	0.993293	478.8	2.3
0.4988	0.993723	483.2	3.4
0.5003	0.993431	480.4	1.5
0.5003	0.993547	481.6	2.3
0.7031	0.992092	488.7	1.2
0.7039	0.991405	483.7	2.1
0.7039	0.991429	483.9	2.8
2,5-Hexanedione: 523.86 K, 28.15 MPa			
0.1002	0.998410	452.8	10.2
0.1062	0.997958	437.1	6.9
0.1062	0.998061	441.6	14.4
0.1062	0.998319	453.0	11.1
0.1062	0.998144	445.3	9.1
0.2002	0.996330	440.4	4.8
0.2002	0.996578	446.2	4.8
0.2153	0.996375	447.2	3.4
0.2983	0.995316	451.9	3.2
0.3002	0.994998	447.3	4.5
0.3002	0.995133	449.5	4.6
0.3002	0.994651	441.8	6.0
0.4988	0.992026	448.9	2.7
0.4988	0.991912	447.8	5.0
0.5003	0.992908	457.7	2.0
0.7039	0.989712	454.0	2.9
0.7039	0.989558	452.9	3.6
Diethyl ether: 298.15 K, 0.10 MPa			
0.1488	1.003895	420.5	4.0
0.2635	1.006411	413.5	2.9
0.5057	1.012754	419.2	2.3
Diethyl ether: 423.99 K, 10.30 MPa			
0.0534	1.001326	423.8	10.0
0.0534	1.001284	420.4	9.8
0.0534	1.001300	421.7	14.1
0.0534	1.001286	420.6	12.2
0.1103	1.002671	421.5	11.2
0.1103	1.002578	417.9	9.3
0.1103	1.002768	425.3	14.3
0.1103	1.002409	411.3	11.4
0.2045	1.005163	426.8	5.9
0.2045	1.005060	424.6	6.4
0.2045	1.004131	404.8	5.4
0.2045	1.004611	415.0	3.9
0.2103	1.004976	419.9	3.3
0.2103	1.004869	417.7	3.3
0.2103	1.004918	418.7	3.9
0.2103	1.004826	416.8	4.1
0.3067	1.006954	416.3	7.5
0.3067	1.006723	413.0	2.2
0.3067	1.006863	415.0	3.7
0.3067	1.006753	413.4	4.3

Table 2 Continued

m (mol·kg ⁻¹)	$c_{p,s}/c_{p,w}$ (-)	$C_{p,\phi}$ (J·K ⁻¹ ·mol ⁻¹)	$\delta(C_{p,\phi})$ (J·K ⁻¹ ·mol ⁻¹)
0.4795	1.007266	384.2	14.0
0.4795	1.008613	396.7	9.0
Diethyl ether: 473.24 K, 10.30 MPa			
0.0980	1.002347	436.6	5.1
0.0980	1.002381	438.1	5.3
0.1074	1.002559	436.0	4.9
0.1074	1.002508	433.9	5.0
0.1131	1.002389	424.0	12.5
0.1131	1.002420	425.2	9.0
0.1524	1.003487	432.2	7.5
0.1524	1.003365	428.6	8.7
0.2028	1.004652	432.8	3.2
0.2925	1.006538	430.8	2.6
0.2925	1.006464	429.7	2.6
0.3045	1.006646	428.5	3.3
0.3045	1.006550	427.1	4.2
0.3416	1.007103	424.1	2.5
0.3416	1.006414	414.9	2.3
Diethyl ether: 523.84 K, 10.40 MPa			
0.0889	1.003170	527.0	10.6
0.1044	1.003449	514.6	14.4
0.1044	1.003394	512.0	13.0
0.1044	1.003439	514.1	12.8
0.1119	1.003948	525.6	8.7
0.1119	1.003915	524.2	8.7
0.1988	1.006414	512.0	5.3
0.1988	1.006283	508.8	5.5
0.2001	1.005845	497.2	7.0
0.2001	1.005883	498.1	7.3
0.2862	1.008600	502.2	4.5
0.2862	1.008369	498.2	4.2
0.2987	1.008317	491.5	5.7
0.2987	1.008463	493.9	5.2
0.4902	1.013336	490.2	2.9
0.5024	1.014178	495.4	3.6
0.5024	1.013541	489.1	3.5
Diethyl ether: 523.86 K, 28.15 MPa			
0.0995	1.002422	455.3	9.1
0.0995	1.002383	453.5	10.7
0.1015	1.002295	447.3	12.4
0.1015	1.002368	450.7	15.8
0.1981	1.004345	444.9	4.6
0.1981	1.004339	444.7	3.9
0.1986	1.003944	435.2	8.6
0.1986	1.003666	428.6	9.1
0.2852	1.006152	443.8	3.8
0.2852	1.006052	442.2	5.0
0.2983	1.005637	431.3	5.0
0.2983	1.005897	435.4	7.1
0.5005	1.010014	437.9	2.2

Table 2 Continued

m (mol·kg ⁻¹)	$c_{p,s}/c_{p,w}$ (-)	$C_{p,s}$ (J·K ⁻¹ ·mol ⁻¹)	$\delta(C_{p,s})$ (J·K ⁻¹ ·mol ⁻¹)
0.5032	1.008372	421.8	2.9
0.5032	1.008047	418.7	4.5
1,2-Dimethoxyethane: 298.15 K, 0.10 MPa			
0.1043	0.999959	375.1	1.9
0.1987	0.999920	375.0	1.0
0.3807	0.999693	373.2	0.5
0.7006	0.998688	368.4	0.3
1,2-Dimethoxyethane: 423.95 K, 10.30 MPa			
0.1001	1.000596	411.3	4.8
0.1001	1.000598	411.3	6.6
0.1001	1.000709	416.1	7.2
0.1001	1.000575	410.3	6.5
0.1001	1.000595	411.2	7.9
0.1001	1.000717	416.5	6.9
0.1001	1.000590	411.0	7.3
0.1001	1.000704	415.9	7.3
0.2004	1.000975	406.7	3.7
0.2004	1.001160	410.7	3.2
0.2004	1.001134	410.2	5.8
0.2004	1.001100	409.4	2.5
0.2004	1.000975	406.7	4.5
0.2004	1.001160	410.7	3.5
0.2004	1.001112	409.7	3.4
0.2004	1.001104	409.5	4.0
0.2004	1.001160	410.7	4.0
0.3807	1.001714	405.5	2.0
0.3807	1.001802	406.5	2.2
0.3807	1.002221	411.4	2.3
0.3989	1.002035	408.1	1.9
0.3989	1.002298	411.1	2.0
0.3989	1.002069	408.5	1.7
0.3989	1.002217	410.2	2.1
0.3989	1.002063	408.5	1.9
0.3989	1.002305	411.1	2.2
0.7000	1.003195	406.3	0.8
0.7000	1.002775	403.6	1.1
0.7000	1.002638	402.7	8.5
0.7000	1.002178	399.7	8.5
0.7000	1.002779	403.6	1.7
0.7000	1.002627	402.6	1.7
0.7000	1.002814	403.8	1.7
0.7000	1.003195	406.3	0.9
0.7000	1.002778	403.6	2.0
0.7006	1.001679	396.4	0.9
0.7006	1.001833	397.4	2.0
1,2-Dimethoxyethane: 473.24 K, 10.30 MPa			
0.1001	1.000774	435.1	4.7
0.1001	1.000711	432.3	6.5
0.1001	1.000777	435.3	6.5
0.1987	1.001369	431.6	6.0

Table 2 Continued

m (mol·kg ⁻¹)	$c_{p,s}/c_{p,w}$ (-)	$C_{p,\phi}$ (J·K ⁻¹ ·mol ⁻¹)	$\delta(C_{p,\phi})$ (J·K ⁻¹ ·mol ⁻¹)
0.1987	1.001488	434.3	7.1
0.2000	1.001369	431.4	3.3
0.2004	1.001431	432.7	2.4
0.2004	1.001413	432.3	3.3
0.3807	1.002530	431.0	1.7
0.3807	1.002216	427.2	1.9
0.3989	1.002720	431.8	1.2
0.3989	1.002709	431.7	1.7
0.3989	1.002681	431.4	1.2
0.7000	1.003851	426.4	0.8
0.7000	1.003835	426.3	1.1
0.7000	1.003786	426.0	1.0
0.7000	1.003761	425.8	1.0
0.7006	1.003743	425.7	1.1
0.7006	1.003252	422.4	1.2
1,2-Dimethoxyethane: 523.89 K, 10.40 MPa			
0.0978	1.001906	526.0	8.5
0.1001	1.001729	515.4	5.2
0.1001	1.001761	516.9	5.1
0.1043	1.001914	520.6	8.3
0.1043	1.001865	518.3	7.9
0.1987	1.002690	497.9	3.4
0.1987	1.002625	496.3	4.7
0.2000	1.002880	502.1	2.8
0.3807	1.004211	486.6	3.0
0.3807	1.004188	486.3	2.0
0.3989	1.005114	495.5	1.7
0.7006	1.006631	480.0	1.7
0.7006	1.006227	477.1	1.4
1,2-Dimethoxyethane: 523.86 K, 28.15 MPa			
0.0978	1.000997	463.5	8.2
0.1043	1.000956	458.7	9.0
0.1043	1.000828	453.0	14.0
0.1987	1.001177	443.8	6.4
0.1987	1.001285	446.4	6.9
0.2000	1.001363	448.0	5.3
0.3807	1.001301	432.3	2.2
0.3807	1.002154	443.0	2.2
0.3989	1.002418	445.0	1.8
0.7000	1.003158	438.1	1.5
0.7006	1.002971	436.8	1.7
0.7006	1.003015	437.1	1.7
0.7006	1.001693	427.9	1.8
0.7006	1.002797	435.6	1.3
Benzylcohol: 298.15 K, 0.10 MPa			
0.1193	0.998528	399.8	1.7
0.1506	0.998099	398.4	1.4
0.1506	0.998096	398.3	1.4
0.1966	0.997566	399.2	1.0
0.3050	0.996014	395.6	0.7

Table 2 Continued

m (mol·kg ⁻¹)	$c_{p,s}/c_{p,w}$ (-)	$C_{p,s}$ (J·K ⁻¹ ·mol ⁻¹)	$\delta(C_{p,s})$ (J·K ⁻¹ ·mol ⁻¹)
Benzylcohol: 423.95 K, 10.3 MPa			
0.0988	0.998261	386.5	8.5
0.0988	0.998237	385.4	9.4
0.0988	0.998133	380.9	6.4
0.0988	0.998248	385.9	8.2
0.0988	0.998236	385.4	11.7
0.0988	0.998126	380.6	11.0
0.1505	0.997073	378.1	10.2
0.1525	0.997293	385.4	3.9
0.1525	0.997293	385.4	4.1
0.2015	0.996435	385.3	4.0
0.2015	0.996429	385.2	4.0
0.2015	0.996435	385.3	4.2
0.2015	0.996430	385.2	4.3
0.2994	0.994610	383.1	3.1
0.2994	0.994659	383.8	2.3
0.2994	0.994610	383.1	3.5
0.3050	0.994064	376.6	3.5
0.3050	0.994453	382.2	2.5
0.3050	0.994675	385.5	3.5
0.3050	0.994678	385.5	3.8
Benzylcohol: 473.24 K, 10.30 MPa			
0.0988	0.998408	408.1	4.8
0.0988	0.998452	410.1	4.9
0.1525	0.997488	406.1	3.2
0.1525	0.997602	409.5	5.2
0.1966	0.995926	386.5	5.9
0.1966	0.996064	389.6	9.6
0.2015	0.996495	401.5	2.6
0.3050	0.993514	382.9	5.7
0.3050	0.994615	399.5	3.6
Cyclohexanol: 298.15 K, 0.10 MPa			
0.0498	1.000943	498.2	6.1
0.1048	1.002013	499.8	2.9
0.1587	1.002995	498.8	2.0
0.2152	1.004279	503.6	1.5
0.2535	1.005120	505.2	1.3
0.2603	1.005016	501.3	1.3
0.3004	1.005793	501.7	1.1
Cyclohexanol: 423.95 K, 10.30 MPa			
0.0978	1.000087	432.3	8.4
0.0978	1.000830	465.1	9.4
0.0978	1.000732	460.8	8.6
0.0978	1.000152	435.2	8.6
0.1497	1.001130	461.3	5.6
0.1497	1.001126	461.1	5.6
0.2013	1.001388	458.6	4.2

Table 2 Continued

m (mol·kg ⁻¹)	$c_{p,s}/c_{p,w}$ (-)	$C_{p,\phi}$ (J·K ⁻¹ ·mol ⁻¹)	$\delta(C_{p,\phi})$ (J·K ⁻¹ ·mol ⁻¹)
0.2013	1.001453	460.0	4.4
0.2152	1.000809	444.9	8.5
0.2152	1.000738	443.5	8.8
0.3001	1.002195	460.7	1.9
0.3134	1.001605	451.1	2.1
0.3134	1.001580	450.7	3.8
0.3134	1.002168	459.0	4.2

functional groups present in the solute molecule were subtracted, their values computed from the Sedlbauer–O’Connell–Wood (SOCW) model [21] using the parameters for hydrocarbon functional groups published by Sedlbauer *et al.* [18]. In the case of polyfunctional solutes the results were finally divided by the number of oxygen containing functional groups present in the given compound to obtain the contribution per one functional group. An analogous procedure was applied for the standard molar volumes, except that there was no need to subtract the property of ideal gas. The standard molar volume is directly the pressure derivative of the Gibbs energy of hydration and has therefore the quality of a hydration property.

Temperature evolution of the –CO–, –O–, and –OH group contributions to V^∞ and $\Delta_{\text{hyd}}C_p^\infty$ are presented in Fig. 3. Comparison of the –OH group contributions calculated from mono- and bi-functional alcohols is made in Fig. 4. Whereas the only data at elevated temperatures for ketones and ethers come from Schulte *et al.* [9] in the case of V^∞ and from this work in the case of $\Delta_{\text{hyd}}C_p^\infty$, there are more studies of the volumetric and calorimetric properties of alcohols up to 623 K reporting data at various pressures. In

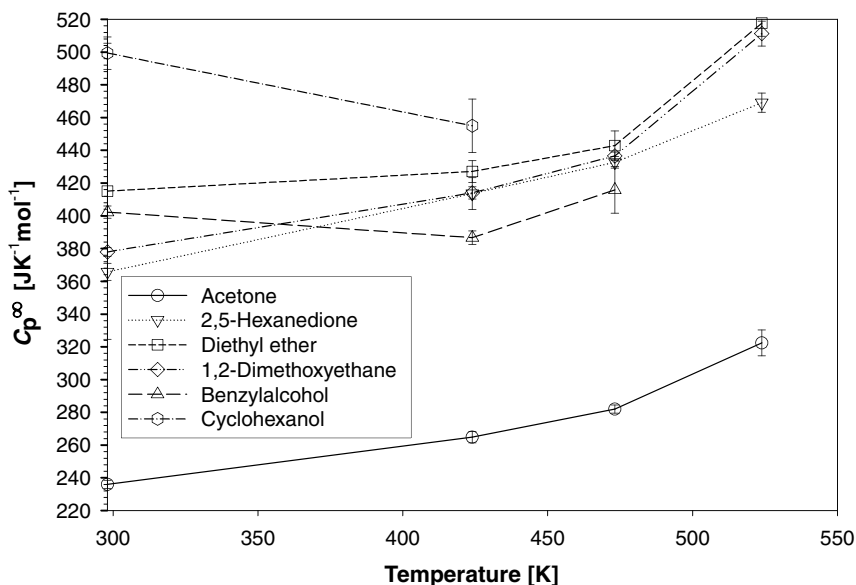


Fig. 2 Standard molar heat capacities as a function of temperature at a pressure of 10 MPa (0.1 MPa at 298.15 K)

Table 3 Results of the data correlation and comparison of the standard molar heat capacities with the literature

N_{points} (—)	T (K)	p (MPa)	A_0 (J·K ⁻¹ · mol ⁻¹)	A_1 (J·kg· mol ⁻²)	S_{wy}	C_p^∞	$\delta(C_p^\infty)$ (J·K ⁻¹ · mol ⁻¹)	C_p^∞ lit ^b	Ref. (—)
Acetone									
5	298.1	0.1	-6.82	9.06	0.12	236.0 ^a	2.5	240.0 ± 5	24
								225.0 ± 15	33
								240.5 ± 5	34
								240.0 ± 10	36
26	424.0	10.3	16.33	-6.19	1.52	264.8	3.5		—
19	473.2	10.3	23.8	-7.58	1.43	281.9	2.5		—
14	523.9	10.3	43.81	-5.45	1.58	322.2	7.9		—
18	523.9	28.1	20.16	-5.99	0.71	288.3	2.8		—
2,5-Hexanedione									
5	298.1	0.1	-111.41	-10.89	1.43	365.7 ^a	5.2	357 ± 15	25
22	424.0	10.3	-74.85	-1.38	2.51	413.5	9.7		—
18	473.2	10.3	-74.61	-1.46	0.75	432.6	3.6		—
19	523.9	10.4	-77.96	31.35	1.4	469.0	5.9		—
17	523.9	28.1	-83.06	24.71	1.1	443.8	5.5		—
Diethyl ether									
3	298.1	0.1	105.16	-0.79	1.63	415.0 ^a	90.4	423 ± 15	35
23	424.0	10.3	109.88	-53.04	0.87	427.7	6.7		—
16	473.2	10.3	113.45	-64.52	1.34	442.8	8.9		—
17	523.8	10.4	162.5	-65.37	1.13	517.6	8		—
15	523.9	28.1	110.18	-50.45	1.66	452.3	11.6		—
1,2-Dimethoxy ethane									
4	298.1	0.1	1.15	-12.76	0.74	377.9 ^a	2.7	364 ± 15	31
								380 ± 10	32
37	424.0	10.3	28.41	-16.8	1.75	413.9	3.7		—
19	473.2	10.3	36.01	-17.47	0.96	436.5	2.4		—
13	523.9	10.4	79.38	-52.11	1.96	511.2	7.6		—
14	523.9	28.1	33.39	-21.74	2.05	449.4	10.1		—
Benzyl alcohol									
5	298.1	0.1	-49.83	-15.3	0.75	402.2 ^a	3.7	396.0 ± 10	26
20	424.0	10.3	-75.98	-3.61	0.57	386.6	4.1		—
9	473.2	10.3	-64.74	-64.29	1.49	415.8	14.2		—
Cyclohexanol									
7	298.1	0.1	80.62	4.01	1.41	499.3 ^a	9.9	463 ± 20	27
								501 ± 5	28
								483 ± 20	29
								523 ± 20	30
14	424.0	10.3	26.44	1.2	1.72	454.9	16.3		—

Note. A_0 and A_1 are parameters of Eq. (7); S_{wy} the standard weighted deviation of correlation; C_p^∞ the standard molar heat capacity; $\delta(C_p^\infty)$ the statistical error in the C_p^∞ value.

^aMeasured with Picker flow microcalorimeter; otherwise with HT/HP Picker-type differential flow calorimeter.

^bUncertainties as estimated in reference [15].

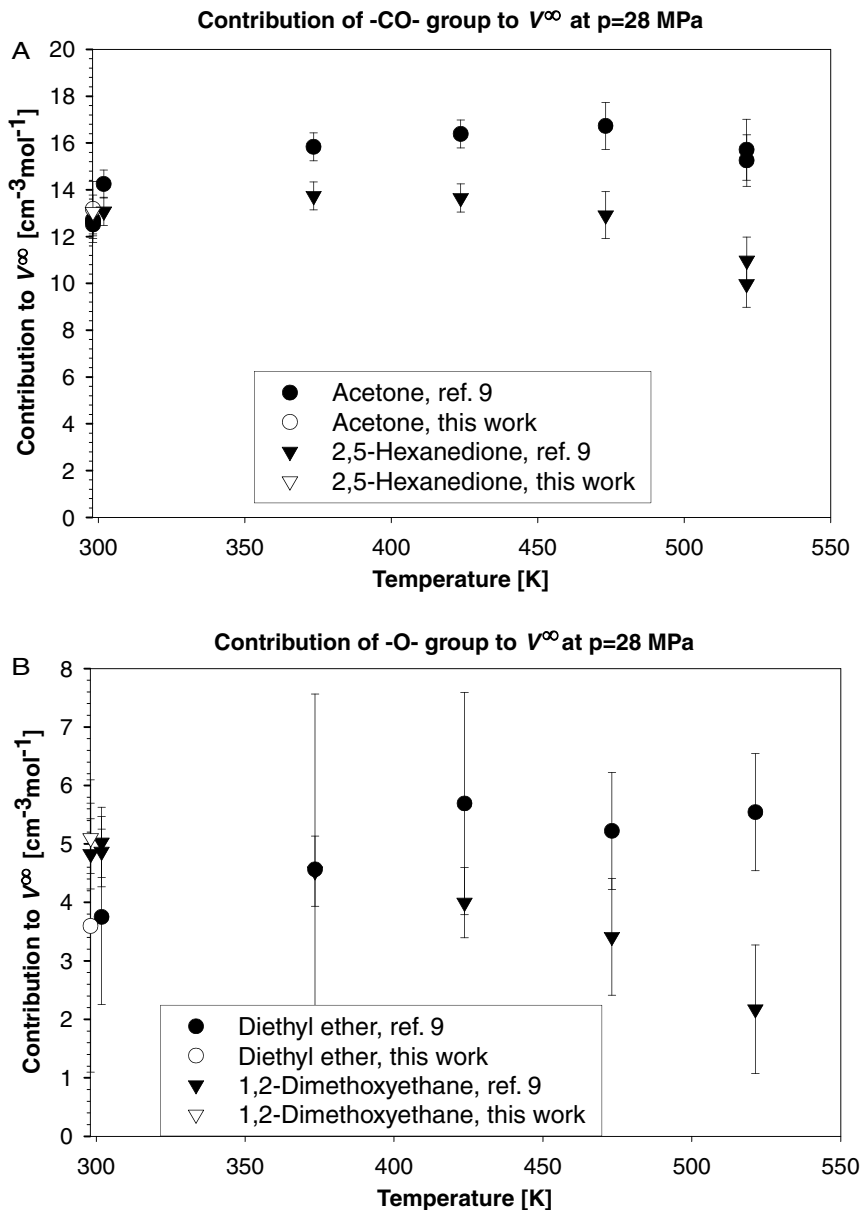


Fig. 3 Temperature dependence of the -CO- , -O- , -OH group contributions for V^∞ (a, b, c) and C_p^∞ (d, e, f)

order to use these results for comparison of the -OH group values obtained from the results for different compounds we had to convert the data to a common pressure, which was selected as 28 MPa. Only at 298.15 K are the results presented at normal pressure (0.1 MPa); the pressure effect is not, however, very important at this temperature. The parameters of the SOCW model for the -OH group were tentatively determined earlier [18] so it was

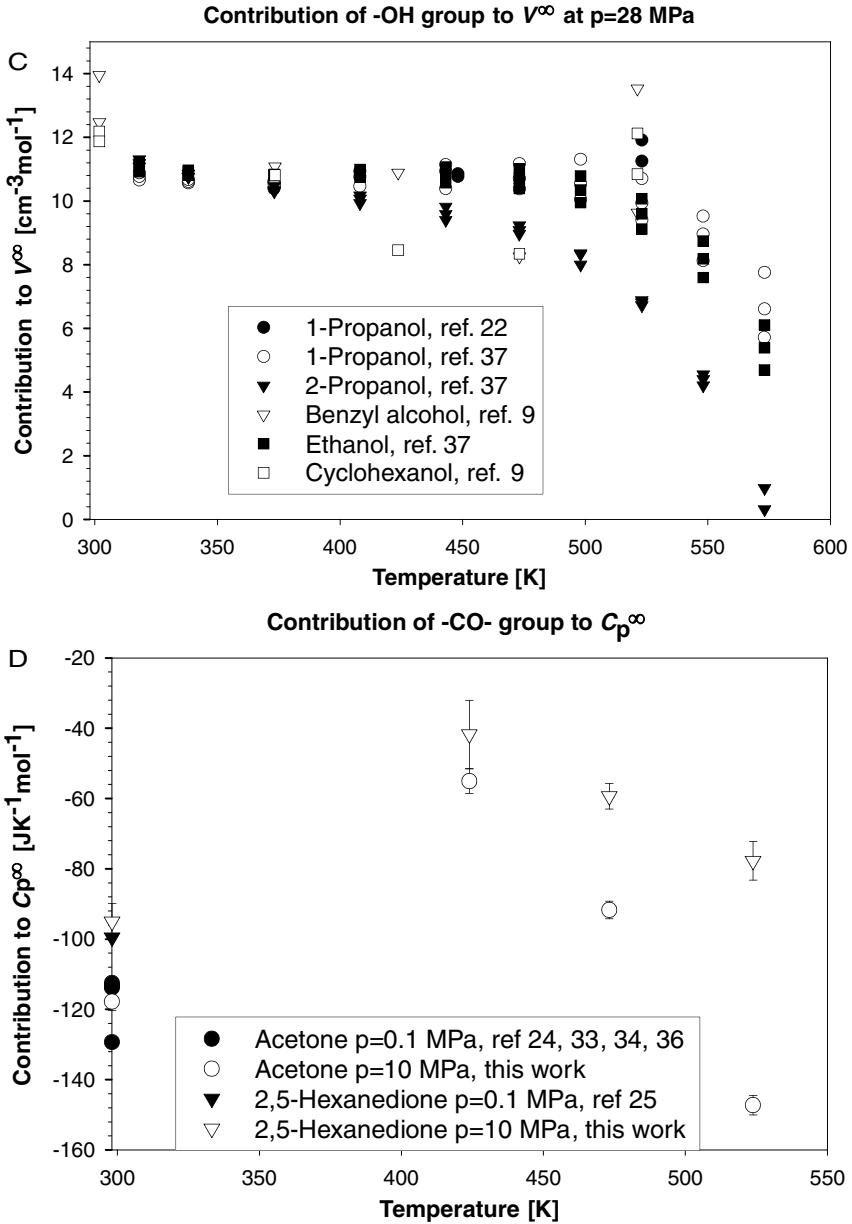


Fig. 3 Continued

possible to calculate the pressure correction (from experimental pressure to 28 MPa) again with the SOCW equation of state. Experimental results at elevated temperatures were taken from the following sources: for volumes from Schulte *et al.* [9]; Criss and Wood [22]; Hynicka *et al.* [37] and for heat capacities from Inglese and Wood [4]; Origlia-Luster and Woolley [23] and from this study. Error bars in Figs. 3(c, f) and 4(a, b) depicting hydroxy compounds

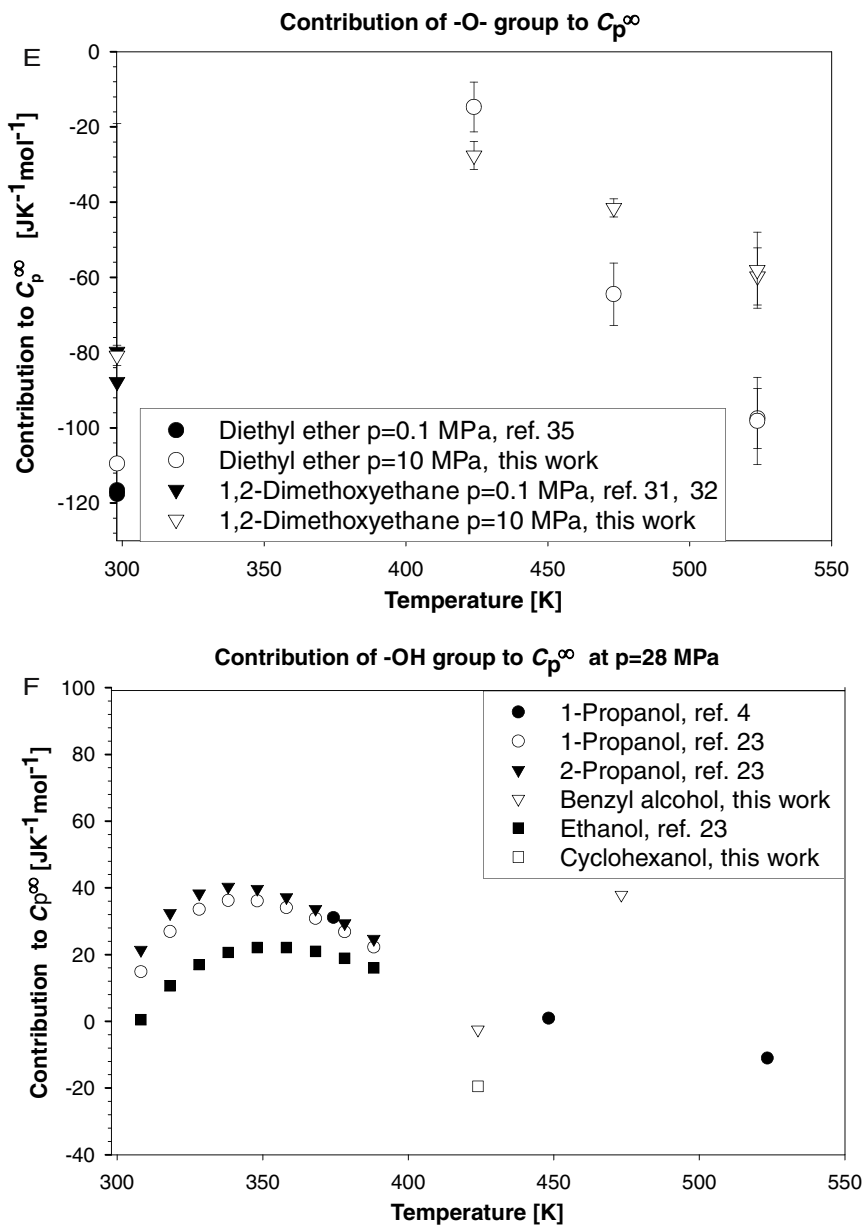


Fig. 3 Continued

are not presented due to the larger amount of data points and uncertain comparison or error estimates from the several data sources.

It follows from Figs. 3 and 4 that oxygen containing functional groups generally exhibit polar-like behavior, since their values decrease at high temperatures. The contributions calculated at the same conditions from different compounds keep the same trends, although

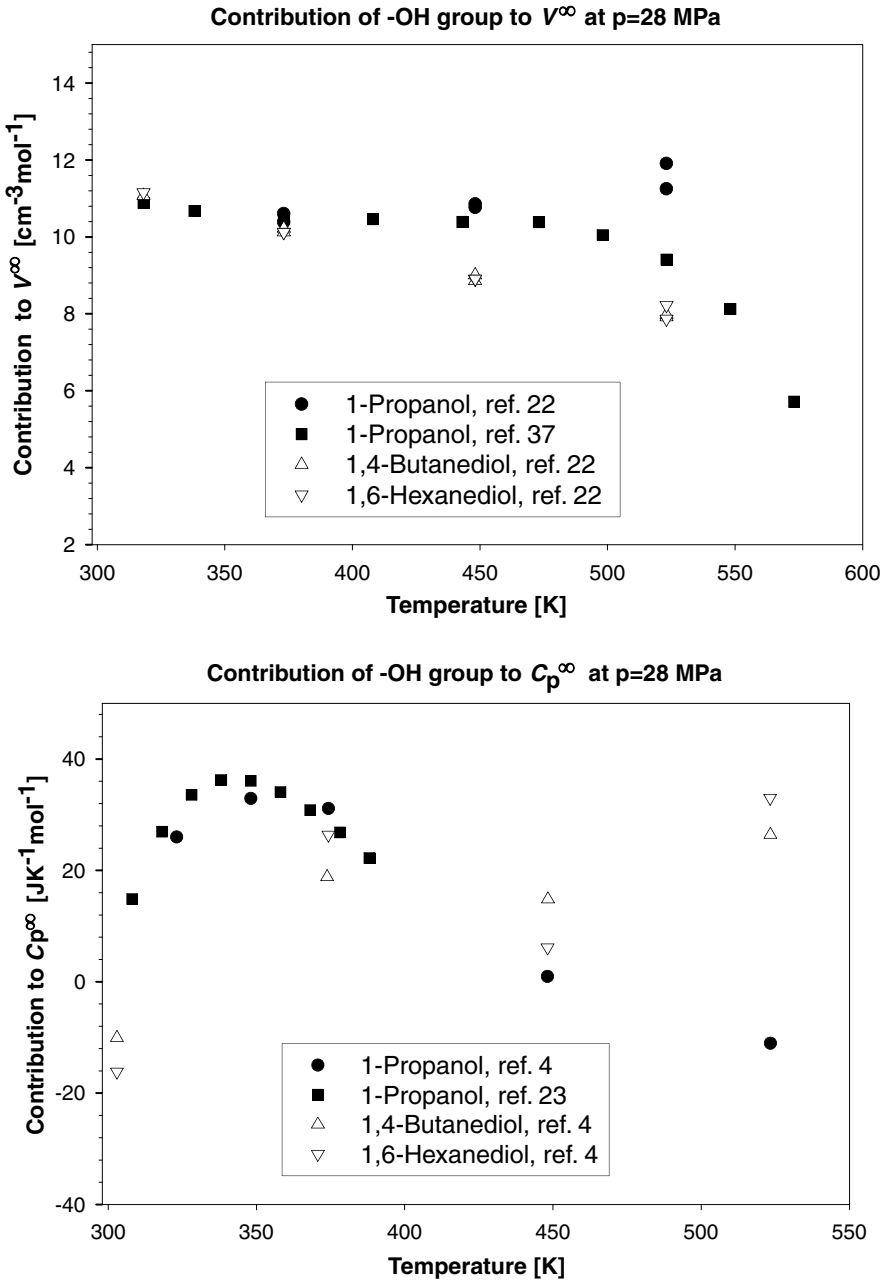


Fig. 4 Temperature dependence of the –OH group contribution for (a) V^∞ and (b) C_p^∞ at 28 MPa; comparison of mono- and bi-functional solutes

they do not have quite the same values. Group contributions evaluated from bi-functional ketones, ethers and alcohols have, in the case of V^∞ , consistently lower values than single groups and higher values in the case of $\Delta_{\text{hyd}}C_p^\infty$. The difference is in most cases larger than experimental uncertainty of a given experimental result, indicating the need for polyfunctional correction in the group contribution method, especially if the two polar groups are in close proximity. For alcohols this effect is weaker and probably insignificant compared to combined experimental and model errors (see below for discussion). On the other hand, the hydroxy group in secondary alcohols deviates from the primary alcohols, which suggests a need of a higher-order correction for this structure in the group contribution approximation. Other structures such as in cycloalcohols probably do not require steric corrections to the first-order group additivity scheme; their calculated contributions exhibit marked differences only at highest temperatures, where their values are, however, subject to larger experimental uncertainty.

When examining the group contribution values plotted in Figs. 3 and 4, several factors connected with the procedure should be kept in mind. First, there is the experimental error of the original data, which is in some cases already comparable to the differences between group contributions calculated from different solutes. Second, additional uncertainty stems from application of the group contribution scheme and from using the SOCW model for calculating hydrocarbon group contributions. This error was estimated by Sedlbauer *et al.* [18] to be about 2% of V^∞ and 5–7% of C_p^∞ , which is again in some cases comparable to our observed differences. Third, in the case of the heat capacities of hydration one has also to consider the propagation of error in the ideal gas heat capacity used for conversion from the standard molar heat capacity. Nevertheless, the above analysis is useful for tracing at least semiquantitatively the insufficiency of the first-order group contribution assumption, which is very likely responsible for systematic deviations that appear between mono- and bi-functional or polyfunctional compounds and primary and secondary alcohols.

The differences among contributions derived from different compounds are relatively large, but often systematic. The results suggest the need for (i) including a correction for the presence of several polar functional groups in a solute molecule, and (ii) considering a correction for the primary or secondary position of the polar group in the molecule. The data on the standard hydration properties resulting from densitometric and calorimetric measurements presented here and in earlier papers thus suggest a possibility to apply a functional group contribution scheme for the description of aqueous alcohols, ketones and ethers in a wide range of conditions and provide some indications for this planned extension.

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