Volumetric properties of dilute aqueous solutions of organic solutes in extended ranges of temperature and pressure: experiment, data, and new observations.

L Hnědkovský, I Cibulka

Institute of Chemical Technology, Technická 5, 166 28 Prague, Czech Republic

ABSTRACT

Several aspects of a study of volumetric properties of dilute aqueous solutions of organic solutes are presented. High-temperature high-pressure vibrating-tube densimetry is discussed as a suitable experimental technique for measurements in wide ranges of temperature and pressure. The treatment of direct experimental data that leads to the standard partial molar volume of a solute is illustrated on selected measurements obtained for the set of solutes so far studied. This set comprises benzene and its mono- and disubstituted derivatives (-CH₃, -OH, -NH₂, -NO₂, -Cl, -COOH, -CN, -CH₂OH, -CH₂CH₂OH) and selected monohydric and polyhydric alcohols derived from alkane hydrocarbon series. It is shown that high accuracy of the measurements and the T-p area densely covered with data allow new observation of phenomena in behaviour of standard partial molar volumes. The relation between an analogue of isothermal compressibility and the molecular structure of a solute, and the phenomenon of the inversion of signs of derivatives of standard partial molar volume with respect to temperature and pressure are discussed as examples.
Introduction

Development of experimental techniques designed for measurements at superambient conditions (elevated temperatures and pressures) led to an increase of published data related to state behaviour of pure liquids and liquid mixtures. Among the systems studied aqueous solutions of both the electrolytes and nonelectrolytes attracted an attention due to their importance in solving environmental problems (distribution of pollutants in the environment and their removal), hydrothermal and geochemical processes, and theoretical aspects of the structure of water and aqueous solutions.

Volumetric properties of dilute aqueous solutions include various quantities: starting from primary experimental quantity as density or specific volume of a solution up to derived properties as partial or apparent molar volumes of a solute (including their limiting values at infinite dilution) and their derivatives with temperature and pressure. Partial molar volumes are the quantities that, along with heat capacities, enable to evaluate chemical potential of the solute as a function of temperature and pressure. This practical application is not the only use of experimental results. If data of sufficient accuracy are available for systematically selected solutes in temperature and pressure ranges densely covered with data then phenomena may be newly observed that direct further investigation to areas where regularities/irregularities in behaviour of solutes can be discovered.

Experimental determination

Vibrating-tube densimeters

Vibrating-tube densimeters are widely used apparatuses for measurement of density of liquids. Since Kratky (1969) published the construction of the first vibrating-tube densimeter many commercially available densimeters and several “laboratory-made” constructions (designed mostly for measurements under superambient conditions) are in use over the world. An extensive overview on the vibrating-tube technique was recently published by Majer (2003). Advantageous features of vibrating-tube densimeters are obvious: (i) small volume of sample, (ii) both the static (batch) and the flow regime of measurements, (iii) measurements in wide ranges of temperature and pressure, (iv) high precision (with sufficient stability of temperature and pressure the resolution $10^{-3}$ kg·m$^{-3}$
can be achieved), and (v) computer control and automation of measurements (see e.g., Ihmels (2000), Hnědkovský (2004)). Nowadays most data on density of liquids are obtained using vibrating-tube technique, measurements by classical methods as pycnometric and dilatometric ones are exceptional.

Assuming harmonic oscillations of the tube the working equation

\[ \rho = K \tau^2 + B \]  

(1)

can be derived where \( \rho \) is the density, \( \tau \) the period of oscillations, and \( K \) and \( B \) are the parameters of the densimeter that must be determined by calibration. As it is shown below, the output experimental quantity necessary for evaluation of partial or apparent molar volumes of a solute (denoted below as component 2) in water (denoted as component 1) is the difference between density of the solution and that of water

\[ \Delta \rho = \rho - \rho_1 = K (\tau^2 - \tau_1^2) \]  

(2)

and thus only parameter \( K \) is needed for the evaluation of the density difference provided the oscillation period for water \( \tau_1 \) is measured.

Calibration

The method is not absolute one and each densimeter must be calibrated using at least two fluids, e.g. water and nitrogen

\[ K = \frac{(\rho_{\text{water}} - \rho_{\text{nitrogen}})}{(\tau^2_{\text{water}} - \tau^2_{\text{nitrogen}})}, \quad B = \rho_{\text{water}} - K \tau^2_{\text{water}}. \]  

(3)

Basic problems are (i) the validity of the equations (1) and (2) in relation to the width of the calibration interval, and (ii) the dependence of calibration parameters \( K \) and \( B \) on temperature, pressure, and time (ageing of the tube).

The validity of the equations (1) and (2) is sometimes discussed. Some authors, e.g., Delmas (1975), proposed the use of the third calibration fluid and modified the equation (1). The validity of equations (1) and (2) is, however, assumed even for very accurate measurements. We have not observed significant deviations when our densimeter (Hynek (1997)) was calibrated by nitrogen, water, and solutions of sodium chloride with
molality up to 3.0087 mol·kg\(^{-1}\), however, in much wider density intervals it is likely that the deviations may become significant.

Experience and theoretical considerations (Lagourette (1992), Holcomb (1998)) lead to the conclusion that both parameters of the calibration relation (1) are functions of temperature and pressure with the pressure dependence being less pronounced. The attempts to express these dependences analytically might be successful for less accurate measurements, for very accurate measurement repeated calibrations for each experimental temperature and pressure are advisable.

Our experience shows that the value of the parameter \(K\) of our densimeter (Hynek (1997)) determined for a particular \(T\) and \(p\) by repeated calibrations in several years period remains constant within about ±0.1 %. On the other hand the parameter \(B\) exhibits a non-negligible drift in time. Employing equation (2) the effect of the drift of the apparatus can be easily eliminated by repeated measurements of the oscillation period for water, \(\tau_1\), measured between measurements of the solutions. Temperature dependence of \(K\) of our Hasteloy tube is a straight line with a slope about \((\partial K / \partial T)_p = -0.088 \text{ kg·m}^{-3}·\text{ms}^{-2}·\text{K}^{-1}\). Pressure dependence is moderate and the evaluation of our several-years calibrations in the temperature range 298 to 573 K and up to 30 MPa resulted in the value \((\partial \ln K / \partial p)_T = -9.3·10^{-5}\text{ MPa}^{-1}\) valid with sufficient accuracy in the entire temperature and pressure range. Calibration is performed at each temperature and one pressure and \(K\) values for other pressures are obtained using the integrated above equation.

Measurements of small density differences

The vibrating-tube method is perfectly suitable for measurements of small density differences, particularly in those cases when the difference (density of a solution) – (density of a solvent), \(\Delta \rho = \rho - \rho_1\), is measured at given temperature and pressure. Here the equation (2) is employed. In the case of aqueous solutions water is then used not only as a solvent but also as one of the calibrating fluids.

To achieve high accuracy of measured data some additional requirements should be fulfilled. Density difference of dilute solutions is less dependent on temperature and
pressure than density itself since isobaric thermal expansivity and isothermal compressibility of dilute solutions may be assumed to be very close to those of pure water. Therefore the requirements concerning uncertainties in temperature and pressure are not very high. Uncertainties ±0.05 K and ±0.01 MPa are quite acceptable in regions sufficiently distant from the critical point of water. Higher requirements are imposed upon short-time stability of both state variables, i.e., the measurement of the oscillation period for solution \( \tau \) and preceding and consequent measurements of the period for water \( \tau_1 \) should be performed at as constant temperature and pressure as possible. If the density difference should be determined within units of the order \( 10^{-3} \) kg·m\(^{-3} \) then the stability of temperature of measured liquid should be of the order of units of mK and pressure fluctuations should be within the units of kPa. Such parameters can be achieved by a precise temperature regulation (usually using several controlled systems of jackets that encase a vibrating-tube cell) and by perfect pre-thermostating of flowing liquid (Hynek (1997)). The use of the elements that dampen pressure pulses in the pressure line and temperature control of a back-pressure regulator (Hnědkovský (2004)) are also advisable to minimize pressure fluctuations. As it is shown below uncertainty not only in density difference but also uncertainty in solution concentration plays a role. Here the accuracy of weighing of the components during preparation of solutions and purity of solutes should be taken into account. Since impurities (except water) are usually of a similar nature as the main substance, the purities 99 mol per cent and higher are acceptable. If the solute contains a significant amount of water then the Fischer method is a good tool to get the data for corrections. Besides other benefits (minimization of routine work), the automation (Hnědkovský (2004)) may also bring an opportunity for evaluation of concentration corrections due to vaporization of volatile solutes from solutions in storage bottles. Prior to the evaluation of the corrections the values of activity coefficients of solutes in the dilute region (limiting activity coefficients give the information) should be checked and taken into account, if necessary.
Data treatment

Direct experimental data

Direct experimental data obtained from the densimeter are density differences \( \Delta \rho = \rho - \rho_1 \) for a particular concentration of the solution at particular temperature and pressure. In the case of diluted solutions molality of the solute in the solution, \( m_2 \), is usually used. The dependence of the density difference \( \Delta \rho \) of non-electrolytes solutions on molality can be fitted using the function

\[
\frac{\Delta \rho}{m_2} = \frac{\rho - \rho_1}{m_2} = a + bm_2 + cm_2^2,
\]

(4)

and the adjustable parameters \( a, b, c \) may then be used in further treatment of measured data as it is shown below. Depending on the concentration range, the polynomial expansion (4) may be either extended with further polynomial terms or limited to the straight line \( c = 0 \). The curvature of the dependence \( \Delta \rho/m_2 \) vs. \( m_2 \) is often determined by the solubility of the solute in water at ambient temperature (at which the solution is prepared) or sometimes by the solubility at higher temperatures if the solubility decreases with increasing temperature (to avoid a formation of two phases at experimental temperature higher than ambient one). Even with highly soluble solutes the concentration range is usually selected that the polynomial function (4) is sufficient to describe the measured data.

Partial/apparent molar volumes

The volume of the solution containing one kilogram of solvent (1) is given by

\[
V = \frac{1}{M_1} \bar{V}_1 + m_2\bar{V}_2 = \frac{1 + m_2M_2}{\rho},
\]

(5)

where \( M_1, M_2, \bar{V}_1 \) and \( \bar{V}_2 \) are molar masses and partial molar volumes of the solvent and solute, resp. Combination of relations (4) and (5) gives

\[
V = \frac{1 + m_2M_2}{\rho_1 + am_2 + bm_2^2 + cm_2^3}.
\]

(6)

Partial molar volume of the solute 2 represents a volume change on adding one mole of solute to the infinite amount of the solution at given temperature and pressure and, using eqn (6), is given by the expression
\[
\overline{V}_2 = \left(\frac{\partial V}{\partial m_2}\right)_{T, P, \rho_1} = \frac{\rho_1 M_2 - 2b m_2 - a - m_2^2 M_2 b - m_3^2 M_2 c}{(\rho_1 + a m_2 + b m_2^2 + c m_2^3)^2}.
\]  

(7)

Its limiting value for \(m_2 \to 0\) (standard partial molar volume of the solute) is then

\[
\overline{V}_2^0 = \frac{1}{\rho_1} \left( M_2 - \frac{a}{\rho_1} \right) = \frac{M_2}{\rho_1} - \frac{a}{\rho_1^2}.
\]  

(8)

Another way of the description of a solute behaviour in the solution is the use of apparent molar volume of the solute defined by the equation (\(V\) is, as above, the volume of the solution containing 1 kg of solvent)

\[
V = \frac{1}{M_1} \left( V_1^* + m_2 V_2^{(\text{app})} \right) = \frac{1 + m_2 M_2}{\rho},
\]  

(9)

where \(V_1^* = M_1/\rho_1\) is the molar volume of pure solvent. Apparent molar volume of the solute is then

\[
V_2^{(\text{app})} = \left( \frac{M_2}{\rho} \right) - \left( \frac{\rho - \rho_1}{m_2 \rho \rho_1} \right) = \left( \frac{M_2}{\rho} \right) - \left( \frac{\Delta \rho}{m_2} \cdot \frac{\rho \rho_1}{m_2} \right).
\]  

(10)

In the ideal mixture apparent and partial molar volumes are identical and equal to molar volume of pure solute at given temperature and pressure. Thus the difference from molar volume of pure solute gives information on non-ideality of the solution. As can be easily verified the limiting apparent molar volume is identical with the standard partial molar volume, \(V_2^{(\text{app})}(m_2 \to 0) = \overline{V}_2^0\) but at \(m_2 > 0\) the deviations of apparent molar volume from partial molar volume are significant (see Figure 1).

From the experimental point of view the difference between the two approaches can be seen in the fact that in the case of apparent molar volume the limiting values are usually obtained by extrapolating apparent molar volumes while in the case of partial molar volume the experimental density data are extrapolated and the value of the parameter \(a\) (eqn (4)) is substituted into formula (8). However, for both properties the basic experimental quantity is the density difference \(\Delta \rho\) and the accuracy of partial or apparent molar volumes is predominantly determined by uncertainty in \(\Delta \rho/m_2\). The uncertainties of densities \(\rho, \rho_1\) (eqns (7), (8), (10)) are not critical since they are usually small (\(\rho\) is given by
\( \rho_1 \) through eqn (2) provided a reliable equation of state for water (e.g., Hill (1990)) is used and temperature and pressure are measured with sufficient accuracy.

![Graph](image.png)

**FIGURE 1.** Difference between apparent molar volume and partial molar volume of methanol (Hynčica (2004)). Full line, 298 K, 0.4 MPa; dashed line, 573 K, 10 MPa.

**New observations**

Dependence of standard partial molar volume (see eqn (8)) on state variables (temperature and pressure) is determined (i) by the density of water (i.e., by the state behaviour of water which is, of course, solute-independent) and (ii) by the dependence of the parameter \( a \) on temperature and pressure. The magnitude of \( a \) and the character of its dependence is determined by the nature of the solute. Negative values are usually observed for nonpolar (hydrophobic) solutes (see benzene in Fig.2), when density of solution is lower than that of water, the volume expansion of the hydration shell around the solute molecule occur and negative value of \( a \) leads to an increase of standard partial molar volume. On the other hand, polar solutes exhibit usually positive values of \( a \) (see nitrobenzene in Fig.2), when density of solution is higher than that of water, the volume contraction of the hydration shell around the solute molecule occur and positive value of \( a \)
leads to a decrease of standard partial molar volume. Decrease of $a$ with increasing temperature leads to an increase of partial molar volume and typical dependence is an increasing convex curve. The above considerations are, however, approximate since the value of the parameter $a$ depends also on the mass of the solute molecule (e.g. for small heavy solute molecules the parameter $a$ should tend to large positive values to compensate large term $M_2/\rho_1$ in eqn (8)).

![Figure 2](image_url)

FIGURE 2. Dependence of parameter $a$ on temperature $T$ at pressures close to saturation pressure of water. The lines serve only to join the data. ○, benzene (Hynčica (2003)); ●, nitrobenzene (Hnědkovský (2003)).

On the other hand the solutes that interact strongly with water (e.g., electrolytes) exhibit a decrease of partial molar volume with temperature having a singularity (minus infinity) at the critical point of water. Boric acid, B(OH)$_3$, which is very weak electrolyte, is the solute with strong attractive interactions with water due to three hydroxyl groups. The experiment (Hnědkovský (1995)) showed the increase of standard partial molar volume at ambient temperatures but at higher temperatures boric acid exhibits the electrolyte-like behaviour, i.e. steep decrease of $\bar{V}_2^0$ with temperature. An extrapolation of this observation may lead to the idea that the standard partial molar volume of organic solutes with large
molecular surface of the hydrophilic nature (groups interacting with water via hydrogen bonds like –OH, –NH₂) could exhibit an electrolyte-like behaviour at higher temperatures, i.e. \( (\partial V^o / \partial T) < 0 \). The first indications of such behaviour were observed on data obtained for benzene derivatives with two hydrophilic groups. Standard partial molar volumes of these solutes are monotonously increasing in the experimental temperature range 298 – 573 K (i.e., negative slope \( (\partial V^o / \partial T) \) was not observed), but the character of the dependence of the parameter \( a \) on temperature is different from usual shape. Figure 3 compares \( a(T) \) dependence of nitrobenzene with that of four solutes containing one and two hydrophilic

![Figure 3](image-url)

**FIGURE 3.** Dependence of parameter \( a \) on temperature \( T \) at pressures close to saturation pressure of water. The lines serve only to join the data.

- ○, nitrobenzene (Hnědkovský (2003)); ■, hydroxybenzene (Hynek (1997)); □, 1,4-dihydroxybenzene (Jedelský (1999)); ○, 3-amino-1-hydroxybenzene (Stříteská (2003)); △, 1,2-diaminobenzene (Hynčica (2002)).

As can be seen the dependences for nitrobenzene and phenol are monotonously decreasing with increasing temperature (with lower absolute value of \( (\partial a / \partial T) \) for phenol) while those for solutes with two hydrophilic groups exhibit flat minima. An extrapolation towards higher temperatures leads to positive value of \( (\partial a / \partial T) \). The increase of \( a \) along
with the decrease of density of water with temperature would increase the second term in eqn (8), \( \frac{a}{\rho_1^2} \). Thus the slope (positive) \( (\frac{\partial V_2^M}{\partial T}) \) would be lower or even might change its sign if the increase of the term \( \frac{a}{\rho_1^2} \) would be greater than that of the term \( \frac{M_2}{\rho_1} \).

An extension of the experimental investigation to the aromatic solutes with more than two hydrophilic groups was impossible due to thermal instability of such solutes at higher temperatures (even dihydroxybenzenes decomposed at temperature above about 470 K, the isomers of aminohydroxybenzene and diaminobenzene other than those shown in Fig. 3 were even less stable). Our investigation therefore turned to mono- and polyhydric derivatives of the aliphatic series which are thermally more stable and offer greater variability of molecular structures.

Fig. 4 presents \( a(T) \) dependences for selected hydroxyderivatives of propane (the differences between isomers are moderate). Obviously, the increasing number of hydroxyl groups leads to a change of both the magnitude of the parameter \( a \) and the shape of its temperature dependence. Contrary to aromatic solutes discussed above, here the increase of the parameter \( a \) of 1,2,3-propanetriol at high temperatures affects the shape of the \( V_2^M(T) \) dependence as shown in Fig. 5. Interestingly, standard partial molar volumes of all three solutes at low temperatures (up to about 350 K) are close to each other. From the point of view of a group contributions approach the contribution of the –OH group is equal to that of hydrogen atom, i.e. the increase of the molecule hard core volume on the replacement of hydrogen atom with larger hydroxyl group is compensated by the contraction of the hydration shell due to strong attractive interactions (H-bonds). The partial molar volumes of the three solutes diverge at higher temperatures where the ratio between hydrophilic (-OH groups) and hydrophobic (hydrocarbon chain) surface plays a role.

The present observations may result in an extrapolation which leads to the conclusion that solutes with more than three hydroxyl groups would exhibit the maximum on the \( V_2^M(T) \) dependence at lower temperatures than 1,2,3-propanetriol. Our recent
FIGURE 4. Dependence of parameter $a$ of the hydroxy derivatives of propane on temperature $T$ at pressures close to saturation pressure of water. The lines serve only to join the data.
○, 1-propanol (Hynčica (2004)); □, 1,3-propanediol (Hynčica (2005)); Δ, 1,2,3-propanetriol (Hynčica (2005)).

FIGURE 5. Dependence of the standard partial molar volume of the hydroxy derivatives of propane on temperature $T$ at pressures close to saturation pressure of water. The lines serve only to join the data.
○, 1-propanol (Hynčica (2004)); □, 1,3-propanediol (Hynčica (2005)); Δ, 1,2,3-propanetriol (Hynčica (2005)).
measurements support this hypothesis. Fig. 6 shows partial molar volumes of solutes derived from \( n \)-pentane (1,2,3,4,5-pentanepentaol) and \( \text{neo} \)-pentane (2,2-dimethyl-1,3-propanediol, 2,2-bis(hydroxymethyl)-1,3-propanediol). Partial molar volumes at low temperatures are again close to each other (here not only independently of number of the hydroxyl groups but also independently of the geometry of the hydrocarbon frame). At higher temperatures we have an expected picture: monotonous dependence for the solute with two hydroxyl groups (2,2-dimethyl-1,3-propanediol) and maxima on curves for solutes with four (globular molecule of 2,2-bis(hydroxymethyl)-1,3-propanediol) and five (chain-like molecule of 1,2,3,4,5-pentanepentaol) hydroxyl groups.

![Graph showing the dependence of the standard partial molar volume of the hydroxyderivatives of pentane on temperature \( T \) at pressures close to saturation pressure of water. The lines serve only to join the data.](image)

All these experimental observations may help to answer the question of Amend (2001) concerning the temperature dependence of standard partial molar volumes of saccharides (\( C_5 \) and \( C_6 \) aldoses and ketoses): can we expect a maximum on the \( \overline{V}_2^0(T) \)
curve for these solutes at high temperatures? Based on theoretical considerations (a semiempirical extrapolation of existing data at lower temperatures towards higher temperatures) the authors incline to the conclusion that there should be a maximum. Despite that the structure of saccharides is rather different from our solutes, the high number of hydroxyl groups leads to the conclusion that the Amend’s prediction is probably correct.

The examples of data presented above show the results obtained at pressures not far from the saturation pressure of water. Usually measurements for eleven temperatures and at least for three pressures on each isotherm are performed. Typical picture of pressure dependences of standard partial molar volume at selected temperatures is shown in Fig.7. At low temperatures the dependence $V^0_2(p)$ is moderate and linear, the slope $(\partial V^0_2 / \partial p)_T$ becomes more negative as temperature increases and the dependence takes a convex shape. A different picture is obtained in the case of 1,2,3,4,5-pentanepentaol (Fig.8), the solute that exhibits the inversion of the sign of $(\partial V^0_2 / \partial T)$. Here the positive slope $(\partial V^0_2 / \partial p)_T$ is observed at higher temperatures where the slope $(\partial V^0_2 / \partial T)$ becomes negative, and, as follows from Fig.9 where isotherms $T = 573$ K are plotted for four selected solutes (the curve for 1,3-propanediol is shown for a comparison), their values seem to be interrelated: the more negative slope $(\partial V^0_2 / \partial T)$, the more positive slope $(\partial V^0_2 / \partial p)_T$.

The quantity

$$\kappa^0_{T,z} = -\frac{1}{V^0_2} \left( \frac{\partial V^0_2}{\partial p} \right)_T$$

represents a relative change of standard partial molar volume caused by a unit change in pressure and is an analogue of isothermal compressibility (it should not be named as “partial molar isothermal compressibility” since it cannot be derived from its non-existing extensive property). This quantity is suitable for a comparison of pressure behaviour of standard partial molar volumes of various solutes with different molecular size, i.e.,
FIGURE 7. Dependence of the standard partial molar volume of 1-propanol (Hynčica (2004)) at selected temperatures on pressure $p$. The lines serve only to join the data.

○, 298 K; ●, 373 K; □, 473 K; ■, 523 K; ▲, 573 K.

FIGURE 8. Dependence of the standard partial molar volume of 1,2,3,4,5-pentanepentaol (Hnědkovský (2005)) at selected temperatures on pressure $p$. The lines serve only to join the data.

○, 298 K; ●, 373 K; □, 473 K; +, 498 K; ■, 523 K; ▲, 573 K.
FIGURE 9. Dependence of the standard partial molar volume of the selected hydroxyderivatives on pressure $p$ at temperature 573 K. The lines serve only to join the data.

$\bullet$, 1,3-propanediol (Hynčica (2005)); $\bigcirc$, 1,2,3-propanetriol (Hynčica (2005));
$\square$, 2,2-bis(hydroxymethyl)-1,3-propanediol (Hnědkovský (2005));
$\Delta$, 1,2,3,4,5-pentanepentaol (Hnědkovský (2005)).

different partial molar volumes ($\left(\frac{\partial V^0}{\partial T}\right)_p$ depends on the magnitude of $V^0$). Besides that it is highly affected by the precision of measurements; an error analysis of our measurements showed that the uncertainty of $\kappa_{T,2}^\circ$ is lower than $0.5 \times 10^{-3}$ MPa$^{-1}$.

Figure 10 shows $\kappa_{T,2}^\circ$ for several solutes, two of them without the sign inversion of $\left(\frac{\partial V^0}{\partial T}\right)$ and three solutes with the sign inversion. It is observed that the temperature at which the slope $\left(\frac{\partial V^0}{\partial p}\right)_T$ changes its sign corresponds approximately with the temperature of maximum on the $\bar{V}^0_2(T)$ curve (see Figs. 5 and 6).

When comparing “isothermal compressibility” $\kappa_{T,2}^\circ$ for various solutes an interesting “structure-related” phenomenon was observed. As shown in Fig.11 the value of $\kappa_{T,2}^\circ$ is not affected by the number of carbon atoms nor the structure of the hydrocarbon part.
in an alkanol molecule for alkanols C\textsubscript{1} through C\textsubscript{4} (no data are available for higher alkanols). 2-Methyl-2-propanol (\textit{tert}-butanol) is the exception, $\kappa_{T,2}^0$ is much higher at high temperatures than for other monohydric alcohols. For high pressures a similar picture is obtained with values of $\kappa_{T,2}^0$ slightly lower at high temperatures. The rule holds also for solute pairs (benzene, toluene) and (phenylmethanol, 2-phenylethanol) differing in the number of $-\text{CH}_2-$ groups as shown in Fig.12. The effect of two hydroxyl groups seems, however, to be inter-correlated and the above mentioned rule fails for diols. Figure 13 presents the plots of $\kappa_{T,2}^0$ for four diols derived from \textit{n}-alkane series with $-\text{OH}$ groups bonded to the terminal carbon atoms of the hydrocarbon chain. Contrary to monohydric alcohols there is a monotonous dependence on the length of the molecule chain at higher temperatures as shown in Fig.14.

![Figure 10](image_url)

**FIGURE 10.** Dependence of $\kappa_{T,2}^0$ on temperature $T$ at pressures close to saturation pressure of water. The lines serve only to join the data.

$\bullet$, 1-propanol (Hynčica (2004)); $\blacksquare$, 1,3-propanediol (Hynčica (2005)); $\bigcirc$, 1,2,3-propanetriol (Hynčica (2005)); $\square$, 2,2-bis(hydroxymethyl)-1,3-propanediol (Hnědkovský (2005)); $\triangle$, 1,2,3,4,5-pentanepentaol (Hnědkovský (2005)).
FIGURE 11. Dependence of $\kappa_{T_2}$ of monohydric alcohols on temperature at pressures close to saturation pressure of water. The line is to aid the eye.
- $\bigcirc$, methanol; $\square$, ethanol; $\triangle$, 1-propanol; $\diamond$, 2-propanol; $\bullet$, 1-butanol; $\blacksquare$, 2-butanol;

FIGURE 12. Dependence of $\kappa_{T_2}$ of benzene, toluene, phenylmethanol, and 2-phenylethanol on temperature at pressures close to saturation pressure of water. The lines are to aid the eye.
- $\bigcirc$, benzene (Hynčica (2003)); $\square$, toluene (Hynčica (2003)); $\bullet$, phenylmethanol (Stříteská (2004)); $\blacksquare$, 2-phenylethanol (Stříteská (2004)).
FIGURE 13. Dependence of $\kappa_{T,2}^\circ$ of selected diols on temperature at pressures close to saturation pressure of water. The lines are to aid the eye.

○, 1,2-ethanediol (Hynčica (2005)); □, 1,3-propanediol (Hynčica (2005)); ●, 1,4-butanediol (Hynčica (2005)); ■, 1,6-hexanediol (Hnědkovský (2005)).

FIGURE 14. Dependence of $\kappa_{T,2}^\circ$ of diols HO(CH$_2$)$_n$OH at 573 K on number of carbon atoms $n$. The lines are to aid the eye. Data from Hynčica (2005) ($n = 2, 3, 4$) and Hnědkovský (2005) ($n = 6$).

○, 10 MPa; ●, 30 MPa.
Conclusions

Presented summary of recent experimental investigation of dilute aqueous solutions of organic solutes clearly indicates that it is worth to invest the experimental effort to accurate systematic measurements in wide temperature and pressure intervals with rather narrow temperature and pressure steps. The result is a well described surface $V^m(T, p)$ for a given solute and this makes possible a comparison of the surfaces and derived properties of various solutes. New conclusions, some of them presented here for the first time, may then be drawn from the experimental data.

Acknowledgment. Support from the fund MSM6046137307 is acknowledged.

References

Hnědkovský L, Cibulka I, 2004 *Int. J. Thermophys.* 25, 1135-1142
Hnědkovský L, Cibulka I, 2005 *unpublished results*
Holcomb C D, Outcalt S L, 1998 *Fluid Phase Equilib.* 150-151, 815 - 827
Hynčica P, 2005 *PhD Disertation*, Institute of Chemical Technology, Prague

