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Apparent Molar Volume and Expansibility of Cyclohexanol in Benzene and Cyclohexane Solutions

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Summary. The density of solutions of cyclohexanol in benzene and cyclohexane (up to 12.1 and 1.4 mol·kg^{-1}, respectively) was measured at 20, 25, 30, 40, 50, and 60°C. On the basis of the limiting partial molar volume and its temperature dependence, the apparent molar expansibility of cyclohexanol was estimated. The excess molar volume and the excess thermal expansion coefficient of the solute in the studied solvents as well as in water were derived and are discussed on the basis of solute-solvent interactions. In addition, the limiting partial molar volume of the solute is interpreted in terms of the scaled particle theory. The solvent effect on the partial molar volume of the solute was found to be due mainly to cavity formation and intermolecular dispersion forces.

Keywords: Density; Apparent molar volume; Apparent molar expansibility; Cyclohexanol; Benzene; Cyclohexane.

Scheinbares Molvolumen und Expansibilität von Cyclohexanol in Benzol und Cyclohexan

Zusammenfassung. Die Dichte von Lösungen von Cyclohexanol in Benzol und Cyclohexan (bis zu 12.1 bzw. 1.4 mol·kg^{-1}) wurde bei 20, 25, 30, 40, 50 und 60°C bestimmt. Aus dem partiellen Molvolumen und seiner Temperaturabhängigkeit wurde die scheinbare molare Expansibilität von Cyclohexanol abgeschätzt. Das Zusatzmolvolumen und der thermische Expansionskoeffizient von Cyclohexanol in den untersuchten Lösungsmitteln sowie in Wasser wurden hergeleitet und werden im Kontext mit Wechselwirkungen zwischen Lösungsmittel und gelöster Substanz diskutiert. Zusätzlich wird das partielle Molvolumen im Sinn der *scaled particle theory* interpretiert. Der Lösungsmitteleffekt auf das partielle Molvolumen ist hauptsächlich auf die Bildung von Kavitäten und auf intermolekulare Dispersionskräfte zurückzuführen.

Introduction

Volumetric properties of relatively simple organic molecules have proved very useful in the study of molecular and ionic interactions in solution. Thus, the value of partial molar volume at infinite dilution provides information about solute-solvent interactions, and the concentration dependence will reflect solute-solute interactions. The present article is focused on cyclohexanol which may be looked

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upon as an example of a biochemical model compound; therefore, physicochemical investigations of its aqueous and non-aqueous solutions have received considerable attention in recent years [1–9]. It has been found that cyclohexanol molecules undergo self-association *via* hydrogen bond formation. At infinite dilution, monomeric forms of cyclohexanol molecules prevail, whereas with increasing concentration higher oligomeric species with various structures are formed, either linear or cyclic [1–3]. The degree and extent of self-association of alcohol molecules depend on the nature of the solvent as well as on the temperature. However, volumetric investigations give valuable parameters for obtaining a deeper insight into the behaviour of such systems where solute-solute as well as solute-solvent interactions may exist. Surprisingly enough, there are only few studies reporting volumetric data for cyclohexanol solutions, mainly at 25°C, and relatively few data are available at other temperatures, especially for non-aqueous solutions over a wide concentration range.

In this paper we present some volumetric properties of cyclohexanol in two non-polar solvents, comparing them with the volumetric properties of aqueous solutions of cyclohexanol in order to obtain further information on the associative solute-solvent and solute-solute interactions existing in these systems. In addition, the partial molar volume of the solute at infinite dilution is discussed on the basis of scaled particle theory [10–12], *i.e.* in terms of cavity formation and possible shrinking of the cavity.

Results and Discussion

The apparent molar volume of the solute, $V_{2,\Phi}$ ($\mathrm{cm^3 \cdot mol^{-1}}$), is defined [16] as

$$V_{2,\phi} = \frac{V - n_1 V_1^0}{n_2} \tag{1}$$

where V denotes the volume of solution ($\mathrm{cm^3}$), n_1 and n_2 are the amounts (mol) of solvent and solute respectively, and V_1^0 is the molar volume of pure solvent ($\mathrm{cm^3 \cdot mol^{-1}}$). Eq. (1) can be rearranged to read

$$V_{2,\Phi} = 10^3 (v - v_0)/m + vM_2 \tag{2}$$

where M_2 is the molecular weight of solute ($\mathrm{g \cdot mol^{-1}}$), v and v_0 are the specific volumes ($= 1/d$, *i.e.* the reciprocal value of density) of solution and solvent, respectively ($\mathrm{cm^3 \cdot g^{-1}}$), and m is molality ($\mathrm{mol \cdot kg^{-1}}$).

The dependence of $V_{2,\Phi}$ on solute molality at a definite temperature for a non-electrolyte solution is usually nonlinear and can be expressed as a polynomial

$$V_{2,\Phi} = V_{2,\Phi,0} + b_\mathrm{v} m + b_\mathrm{vv} m^2 + \cdots \tag{3}$$

where $V_{2,\Phi,0}$ represents the apparent molar volume of a solute at infinite dilution, equal to the limiting partial molar volume of the solute $\overline{V}_{2,0}$ [17], and b_v, $\mathrm{b_{vv}} \cdots$ are empirical parameters which depend on solvent, solute, and temperature. By combining Eqs. (2) and (3),

$$(10^3 + mM_2)v - 10^3\, v_0 = mV_{2,\Phi,0} + b_\mathrm{v} m^2 + b_\mathrm{vv} m^3 + \cdots \tag{4}$$

Table 1. Density of solutions of cyclohexanol in benzene and in cyclohexane, respectively, in the concentration and temperature ranges studied, and density of pure benzene and pure cyclohexane as a function of temperature[a]

m (mol·kg^{-1})	20°C	25°C	30°C	40°C	50°C	60°C
			Cyclohexanol in benzene			
0.0572	0.8792	0.8738	0.8676	0.8555	0.8431	0.8315
0.1150	0.8795	0.8740	0.8680	0.8558	0.8434	0.8318
0.2325	0.8801	0.8744	0.8686	0.8564	0.8441	0.8325
0.4754	0.8814	0.8756	0.8699	0.8577	0.8454	0.8338
0.7294	0.8827	0.8767	0.8712	0.8592	0.8467	0.8350
0.9952	0.8840	0.8778	0.8725	0.8605	0.8481	0.8363
1.2737	0.8853	0.8790	0.8738	0.8619	0.8494	0.8378
2.8903	0.8923	0.8861	0.8804	0.8696	0.8585	0.8477
5.0132	0.8989	0.8934	0.8879	0.8773	0.8665	0.8566
7.9042	0.9067	0.9011	0.8957	0.8857	0.8753	0.8654
12.0919	0.9143	0.9089	0.9036	0.8942	0.8842	0.8743
			Cyclohexanol in cyclohexane			
0.0456	0.7793	0.7743	0.7693	0.7594	0.7491	0.7390
0.1147	0.7802	0.7751	0.7701	0.7603	0.7503	0.7401
0.1925	0.7812	0.7762	0.7712	0.7612	0.7513	0.7410
0.3241	0.7829	0.7780	0.7729	0.7628	0.7530	0.7428
0.5500	0.7858	0.7808	0.7759	0.7656	0.7559	0.7456
0.6953	0.7877	0.7826	0.7777	0.7674	0.7576	0.7474
0.8817	0.7900	0.7848	0.7801	0.7697	0.7599	0.7497
1.1222	0.7930	0.7877	0.7830	0.7726	0.7627	0.7524
1.4357	0.7967	0.7915	0.7868	0.7765	0.7664	0.7559
			Benzene			
	0.8788	0.8735	0.8673	0.8552	0.8428	0.8312
			Cyclohexane			
	0.7785	0.7737	0.7688	0.7587	0.7488	0.7385

[a] Units: g·cm^{-3}

is obtained from which the values of $V_{2,\Phi,0}$ and the correlation coefficients b_{v}, $b_{\mathrm{vv}}\cdots$ can be estimated by least squares fitting. For all systems investigated, only two parameters ($V_{2,\Phi,0}$ and b_{v}) were sufficient to represent the data adequately. The regression values of the parameters of Eq. (4) are given in Table 2. As can be seen from this table, the values of $V_{2,\Phi,0}$ increase with increasing temperature irrespective of the solvent. This trend is already known for several alcohols in water [18]. Since at infinite dilution only solute-solvent interactions can exist, $\overline{V}_{2,0}$ can therefore provide evidence about the effect of the solute on the structure of the solvent. $\overline{V}_{2,0}$ may be assumed to result from the sum of two contributions: the intrinsic volume of the non-solvated solute molecule and a term which takes into account the volume changes undergone by the solvent molecules during the solvation process [19]. Since the water-alcohol hydrogen bond is generally stronger than the alcohol-alcohol bond [20], the introduction of cyclohexanol into water

Table 2. Values of the parameters of Eq. (4) at various temperatures

Parameter	20°C	25°C	30°C	40°C	50°C	60°C
Cyclohexanol in benzene						
$V^{a}_{2,\Phi,0}$	106.51±0.05	107.21±0.16	107.81±0.07	108.67±0.09	109.53±0.17	110.31±0.28
$-b^{b}_{v}$	0.05±0.01	0.06±0.01	0.07±0.01	0.08±0.01	0.07±0.02	0.06±0.03
Cyclohexanol in cyclohexane						
$V^{a}_{2,\Phi,0}$	106.02±0.18	107.45±0.17	108.21±0.25	109.71±0.22	110.37±0.31	110.80±0.17
$-b^{b}_{v}$	0.41±0.03	0.77±0.14	1.01±0.22	1.13±0.20	0.72±0.27	0.01±0.15
Cyclohexanol in water						
$V^{a,c}_{2,\Phi,0}$		103.54±0.03				
$-b^{b,c}_{v}$		2.5±0.2				

Units: ^{a}cm^{3}·mol^{-1}, ^{b}cm^{3}·kg·mol^{-2}; ^{c}Ref. [9]

may break down self-association in the alcohol, and a new hydrogen bond will be formed between the alcohol and water molecules. Considering the negative contribution of hydrogen-bonding to the volumetric properties, therefore, the partial molar volume of cyclohexanol in water is smaller than in both non-polar solvents ($\overline{V}_{2,0} = 103.54\,\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$ at 25°C [9]). Even benzene must be considered in its π-electron system as providing an environment which lowers the energy of a cyclohexanol proton and hence competes with the hydrogen bonding between alcohol molecules. The only solvents which could not be expected to show such effects are those of paraffinic type, *e.g.* cyclohexane. With increasing temperature, the contributions from the cyclohexanol-solvent bonding may be weakened, and the limiting partial molar volume of the alcohol increases significantly with temperature.

According to the *McMillan-Mayer* theory of solutions [21], which proposes a formal separation of the excess thermodynamic functions into contributions arising from the pairs, triplets, *etc*. of the solute particles in a definite medium, it follows from Eq. (4) that $b_v = v_{22}$, $b_{vv} = v_{222}$, *etc*., where v_{22} and v_{222} are the virial coefficients representing the contributions to the excess thermodynamic property due to the pair and triplet interactions among cyclohexanol molecules in benzene or in cyclohexane at a given temperature. However, only the values of v_{22} are given in Table 2, and they are negative in all cases. Moreover, the absolute value of v_{22} increases with temperature, reaches a maximum value at about 40°C in both cases, and then decreases in magnitude with increasing temperature as shown in Fig. 1. The absolute values of the virial coefficient v_{22} for cyclohexanol are higher in cyclohexane than in benzene. In spite of much investigation, however, the situation from the molecular viewpoint of the concentration dependence of the apparent or partial molar volumes, *i.e.* b_v, remains poorly understood [22]. At present we have no clear explanation for the existence of the maximum in Fig. 1.

According to the solvation model proposed by *Wurzburger et al.* [19], the v_{22} values represent the volume changes brought about by the process in which two solvated solute molecules move from infinite distance to proximity. Thereby, the overlap of two solvated cospheres of solvated molecules makes the volume change negative when solvent is released from a cosphere which is more structured than

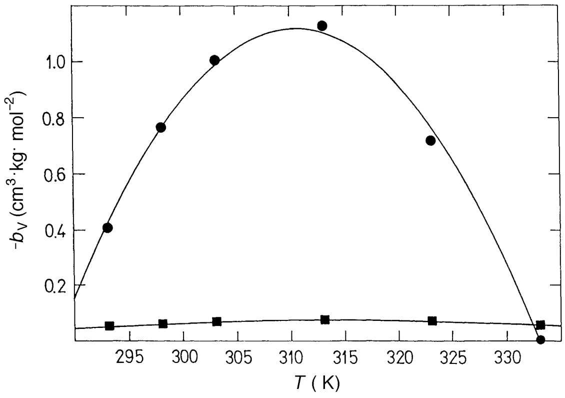

Fig. 1. Temperature dependence of the contribution to the volume originating from cyclohexanol pairing in benzene (■) and cyclohexane (●)

the bulk of the solvent (*i.e.* the solvent in a cosphere has lower density than the amorphous fluid state). From the negative values of v_{22}, given in Table 2, it follows that the investigated solvent molecules are more structured in the cosphere than in the bulk of the solvent. From the higher absolute values of v_{22} for cyclohexanol in cyclohexane than in benzene, the volume changes of the solvation process are higher in the former solvent, being, however, in water as solvent significantly higher than in cyclohexane solutions.

Since the changes in the solution structure should be very sensitive to temperature, the partial molar expansion could be a reliable and sensitive criterion for the detection of solute-solvent interactions. The apparent molar expansibility of the solute, $E_{2,\Phi} = (\partial V_{2,\Phi}/\partial T)_P$ [16], was calculated for the investigated systems *via* the relation

$$E_{2,\Phi} = E_{2,\Phi,0} + \frac{\partial b_v}{\partial T}\, m \tag{5}$$

which follows from Eq. (3). Here, $E_{2,\Phi,0} = \partial \bar{V}_{2,0}/\partial T = \bar{E}_{2,0}$ is the partial molar expansibility of the solute at infinite dilution.

The value of $E_{2,\Phi,0}$ for our systems was calculated from the temperature dependence of the apparent molar volume at infinite dilution using a second degree polynomial as

$$\overline{V}_{2,0} = \sum_{i=0}^{2} a_i (T - T_0)^i \tag{6}$$

where a_i is an empirical constant, T is the absolute temperature, and $T_0 = 298$ K. In Fig. 2, the temperature dependence of $\overline{V}_{2,0}$ is presented for cyclohexanol in both solvents, including the values from 20 to 60°C. The regression coefficients a_i of Eq. (6), calculated by the method of least squares, are given in Table 3. Thus, $E_{2,\Phi,0} \equiv a_1$ at 25°C. The temperature derivative $\partial b_v/\partial T$ was calculated from b_v (see Table 2) postulating a quadratic relation between b_v and T. Thus, from Eq. (5) it follows that the apparent molar expansibilities of cyclohexanol decrease slightly with increasing molality (up to approximately 40°C, given with the plots in Fig. 3). At

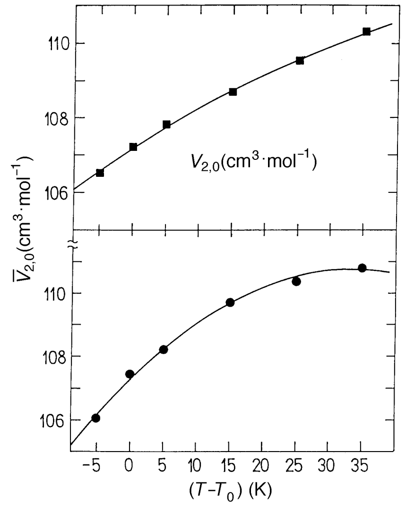

Fig. 2. Temperature dependence of $\overline{V}_{2,0}$ for cyclohexanol in benzene (■) and cyclohexane (●)

Table 3. Regression coefficients of Eq. (6) with the standard deviation, s_s

	a_0	a_1	$-a_2{\cdot}10^3$	s_s
Benzene	107.17±0.04	0.1149±0.0067	0.7±0.2	0.08
Cyclohexane	107.27±0.09	0.2065±0.0137	3.1±0.4	0.16

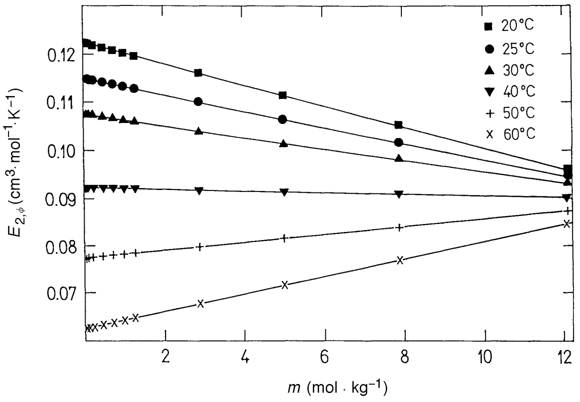

Fig. 3. Variation of the apparent molar expansibility, $E_{2,\Phi}$, with temperature and concentration for cyclohexanol in benzene

all temperatures investigated it can be seen that $E_{2,\Phi,0}$ is positive; at lower temperatures, $E_{2,\Phi}$ becomes more positive, and the decrease with increasing molality is more pronounced. At higher temperatures, the opposite is true; thus, the $E_{2,\Phi}$ values increase significantly with increasing molality. Such behaviour is characteristic for solutions with associated solute species where at low temperature self-association of the solute is important, but with increasing temperature and molality interactions between solute monomers and solvent molecules become a deciding factor.

From the data collected in Table 3, we also calculated the thermal expansion coefficient of solute at infinite dilution, $\overline{\alpha}_{2,0}$ (K^{-1}), defined as

$$\overline{\alpha}_{2,0} = \frac{1}{\overline{V}_{2,0}} \left(\frac{\partial \overline{V}_{2,0}}{\partial T} \right)_P = \frac{\overline{E}_{2,0}}{\overline{V}_{2,0}} \tag{7}$$

It follows from Eq. (7) that $\overline{\alpha}_{2,0} = a_1/a_0$ at 25°C; the calculated values of $\overline{\alpha}_{2,0}$ at 25°C are $(1.072 \pm 0.001) \cdot 10^{-3}\,K^{-1}$ in benzene and $(1.925 \pm 0.003) \cdot 10^{-3}\,K^{-1}$ in cyclohexane. Taking into account the literature values of $\overline{\alpha}_{2,0}$ for cyclohexanol in water at 25°C ($= 5.8 \cdot 10^{-4}\,K^{-1}$ calculated on the basis of the second degree polynomial dependence of $\overline{\alpha}_{2,0}$ on temperature [8]), one can conclude that the values of $\overline{\alpha}_{2,0}$ increase in the following order of solvents: water < benzene < cyclohexane. On the other hand, the values of $\overline{\alpha}_{2,0}$ for the investigated systems tend to decrease slightly with increasing temperature, as was observed previously for aqueous solutions of compounds having more than one OH group, whereas the opposite effect was observed for monofunctional alcohols [23]. This result emphasizes the significance of solvent-hydroxyl group interactions in determining the solution properties of such solutes.

The difference between $\bar{\alpha}_{2,0}$ and α_2^0($\alpha_2^0 = 7.7 \cdot 10^{-4}\,K^{-1}$ at 25°C [13]), *i.e.* the excess thermal expansion coefficient at infinite dilution, $\alpha_{2,0}^{ex}$, is positive and amounts to $0.30 \cdot 10^{-3}$ and $1.15 \cdot 10^{-3}\,K^{-1}$ in benzene and cyclohexane, respectively. At infinite dilution, where only solute-solvent interactions persist due to the dispersion forces between solute and solvent molecules (in cyclohexane) or are accompanied by weak specific interactions of the type OH-π-electrons (in benzene), $\bar{\alpha}_{2,0}$ is slightly lower than that of the pure solvent. This is in contrast to the pure solute where, besides strong hydrogen bonding forces, dispersive forces are also involved, making α_2^0 much lower than $\overline{\alpha}_{2,0}$. On the contrary, in water $\alpha_{2,0}^{ex}$ was found to be negative, *i.e.* $-0.19 \cdot 10^{-3}\,K^{-1}$ at 25°C [8] on account of the stronger water-alcohol hydrogen bonding.

The excess partial molar volume of solute at infinite dilution can be calculated from

$$\overline{V}_{2,0}^{ex} = \overline{V}_{2,0} - V_2^0 \tag{8}$$

where V_2^0 is the molar volume of pure solute calculated from its density. Figure 3 shows the temperature dependence of the excess limiting partial molar volume of cyclohexanol in the solvents studied as calculated from Eq. (8); the densities of pure cyclohexanol were taken from Ref. [24]. From Fig. 4 it can be seen that the excess partial molar volume of cyclohexanol is positive over the whole range of temperatures studied and is found to be relatively small in both solvents, but always higher in cyclohexane than in benzene. The positive values of $\overline{V}_{2,0}^{ex}$ may be explained by the fact that the solute molecules in their pure state are tightly packed due to the hydrogen bonding between OH groups as well as by the *van der Waals* interactions between cycloalkyl chains, and therefore occupy a relatively smaller volume than in solution at infinite dilution where solute-solvent interactions can exist. It has been suggested [7, 25] that the excess volumes for mixtures containing

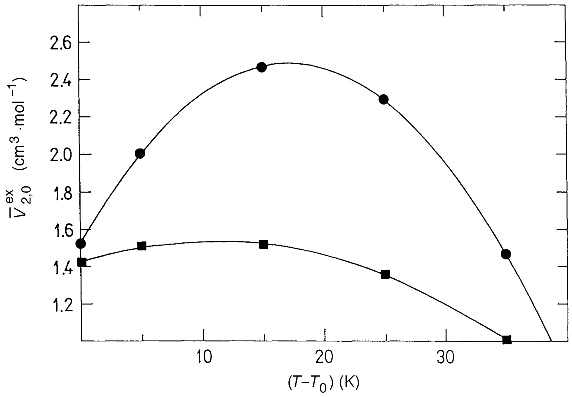

Fig. 4. Excess limiting partial molar volume of cyclohexanol in benzene (■) and cyclohexane (●) as a function of temperature

alcohols in non-polar solvents result from two opposing effects. A contraction results when a non-polar molecule can be accommodated interstitially within the H-bonded alcohol structure, but the disruption of alkanol multimers through the breaking of H-bonds as well as physical dipole-dipole interactions between alkanol monomers and polymers makes a positive contribution to the excess volume. At low concentrations, the dissociation of the alcohol is more important, and the balance is essentially dependent on the magnitude of positive type contributions. Nevertheless, the relative molecular sizes of the two components being approximately equal in both cases, a negative contribution from the formation of OH-π-electron hydrogen-bonded complexes in benzene makes the net result of contributions lower than in cyclohexane. However, a positive temperature dependence of $\overline{V}^{ex}_{2,0}$ was observed at lower temperatures and a negative one with increasing temperature; these effects, however, cannot be considered to be of significant size at all. On the contrary, it is well known that the excess limiting partial molar volume is extremely negative for alcohols in water [26]. The longer or more branched the alkyl group is, the more negative is the $\overline{V}^{ex}_{2,0}$ value. Therefore, a negative $\overline{V}^{ex}_{2,0}$ value has often been regarded as a criterion of hydrophobic hydration. From the temperature dependence of $\overline{V}^{ex}_{2,0}$ for some higher 1-alcohols, *Sakurai et al.* [27] suggested that the negative excess volume observed for various aqueous systems should be interpreted in principle in terms of the volume change on mixing the different molecular sizes of the components, or in terms of the difference in cohesive density of the components. For comparison with non-polar solvents, the value of the excess limiting partial molar volume for cyclohexanol in water was calculated as $\overline{V}^{ex}_{2,0} = -2.2\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ at 25°C.

Assuming that the molar volume of a pure solute, $\overline{V}_{2,0}$, consists of a volume $N_A v_{2,w}$ where $v_{2,w}$ is the *van der Waals* molecular volume of the solute (calculated from the *van der Waals* increments of atoms in solute molecules [28]) plus a varying amount of empty space between solute molecules, then the ratio of the molecular volume of pure solute to the *van der Waals* volume varies with the properties of the compound. Thus, the empty space in the structure of the pure solute depends on the shapes of the molecules composing it and how well they fit together, their vibrational motion, hydrogen bonding, and other intermolecular interactions. It has been established that for relatively nonpolar substances this ratio $V_2^0/V_{2,\mathrm{w}}$ is *ca.* 1.5 [29], whereas for cyclohexanol this ratio is 1.565 at 25°C. The high value probably arises from the fact that the melting point of cyclohexanol is 25.15°C [13], and hence the hydrogen bonding between cyclohexanol molecules may be weakened (in general, the empty volume will be reduced by hydrogen bonding between molecules which will bring them together). Additionally, when a solid melts, the proportion of empty volume increases, so that translatory motion of the molecules becomes possible. On the other hand, from the ratio $\overline{V}_{2,0}$ to $\overline{V}_{2,\mathrm{w}}$, which is 1.567 in water and 1.623 in the two organic solvents, it follows that the empty space between the polar solute molecules in aqueous solution is roughly the same as the empty volume associated with these molecules in the solid or liquid state at ordinary temperatures because of their strong attraction for the polar water molecules. In contrast, less polar molecules such as benzene or, even better, cyclohexane, do not attract alcohol molecules strongly, and so alcohol molecules have large empty volumes associated with them in these types of solvents.

The volume properties of cyclohexanol in different solvents were also analyzed by the scaled particle theory. According to this theory, the expression for the partial molar volume of a solute at infinite dilution is [10–12].

$$\overline{V}_{2,0} = \overline{V}_{\mathrm{cav}} + \overline{V}_{\mathrm{int}} + \beta_{\mathrm{T}}^0 \mathrm{R}T \tag{9}$$

where $\overline{V}_{\mathrm{cav}}$ and $\overline{V}_{\mathrm{int}}$ are the contributions from the formation of a cavity and from intermolecular interactions, respectively, β_{T}^0 is the isothermal compressibility of the solvent, R is the gas constant, and T is the absolute temperature. The creation of a cavity is by definition a positive contribution to the partial molar volume of a solute, whereas the attractive intermolecular solute-solvent interactions cause a negative contribution by shrinking the cavity. The quantity $\overline{V}_{\mathrm{cav}}$ is calculated by the theoretical equation [30]

$$\overline{V}_{\mathrm{cav}} = \beta_{\mathrm{T}}^0 \mathrm{R}T\left(\frac{y}{1-y} + \frac{3yz(1+z)}{(1-y)^2} + \frac{9y^2 z^2}{(1-y)^3}\right) + \frac{\pi\sigma_2^3 N_{\mathrm{A}}}{6} \tag{10}$$

where y represents the ratio of the volume occupied by one mole of hard sphere solvent particles to the molar volume of the solvent,

$$y = \frac{\pi\sigma_1^3 N_{\mathrm{A}}}{6\,V_1^0}, \tag{11}$$

and z is the ratio of the solute, σ_2 (nm) and solvent, σ_1 (nm) hard sphere diameters,

$$z = \frac{\sigma_2}{\sigma_1} \tag{12}$$

Thus, from Eq. (10) it follows that the cavity contribution to $\overline{V}_{2,0}$ depends on the intrinsic sizes of the solute and solvent molecule as well as on the isothermal compressibility of the solvent.

The hard sphere diameter of the solute molecule ($\sigma_2 = 0.575\,\mathrm{nm}$), solvent molecule, σ_1, as well as the packing parameter y, all at 25°C, were taken from Refs. [12, 31], whereas the values of β_{T}^0 for the solvents studied were taken from Refs.

Table 4. Solvent data for the scaled particle theory and internal pressure of the solvents at 25°C

	V_1^0 (cm^3·mol^{-1})	β_T^0RT (cm^3·mol^{-1})	σ_1 (nm)	y	P_i (atm)
Water	18.07	1.122	0.272[a]	0.349[a]	1656
Benzene	89.41	2.39	0.501[b]	0.443[b]	3695
Cyclohexane	108.78	2.82	0.561[b]	0.517[b]	3149

[a] Ref. [12]; [b] Ref. [31]

[13, 14]. The values of y and σ_1 used are given in Table 4, as well as the internal pressure of the solvents, P_i. This macroscopic property is related to the cohesive forces and molecular order of liquids and defined as [32]

$$P_i \approx T\frac{\alpha_1^0}{\beta_T^0} \tag{13}$$

P_i mainly reflects non-chemical interactions (*e.g.* polar or non-polar forces), whereas it does not seem to reflect chemical interactions (hydrogen bonding and very strong non-specific interactions) which restrict the free rotation of molecules. The values of α_1^0 for the solvents studied were taken from Refs. [13, 14]. However, from Tables 4 and 5 it is seen that P_i can be related to the volume of cavity formation in the liquid and the volume associated with the solute-solvent interactions. Thus, the lowest P_i corresponds the lowest $\overline{V}_{cav}$ (in water). On the other hand, the exceptionally small P_i value of the solvent water results in a big $\overline{V}_{int}$ term in Table 5. In addition, one can also conclude that the solvent effect on the $\overline{V}_{int}$ term is attributable to the difference in solvent compressibilities. That is to say, the negative $\overline{V}_{int}$ contribution can be considered to decrease in magnitude with the compressibility of the solvent.

In the simplest case, the interaction volume $\overline{V}_{int}$ is determined by the volume contributions from dispersion, dipole-dipole, and inductive interactions, *i.e.* [12]

$$\overline{V}_{int} = \overline{V}_{disp} + \overline{V}_{dip} + \overline{V}_{ind} \tag{14}$$

Thus, the dispersion interaction volume was calculated from the relation

$$\overline{V}_{disp} = \frac{16\pi N_A^2 E\alpha_1\,\alpha_2\,\beta_T^0}{3\,V_1^0\sigma_{1,2}^3(\alpha_1/\chi_1 + \alpha_2/\chi_2)} \tag{15}$$

where E is the energy of the electron, α_1 and α_2 are the distortion polarizabilities of solvent and solute molecules, χ_1 and χ_2 are the magnetic susceptibilities of solvent and solute molecules, and $\sigma_{1,2} = (\sigma_1 + \sigma_2)/2$.

The dipole-dipole interaction volume was calculated *via* the relation [12]

$$\bar{V}_{dip} = -\frac{8\pi N_A^3\,\mu_1^2\,\mu_2^2\,\beta_T^0}{9\,\mathrm{R}TV_1^0\sigma_{1,2}^3} \tag{16}$$

where μ_1 and μ_2 are the dipole moments of the solvent and solute.

Table 5. Contributions to the limiting partial molar volume of cyclohexanol at 25°C

	V^{a}_{cav}	$-V^{a}_{disp}$	$-V^{a}_{dip}$	$-V^{a}_{ind}$	$-V^{a}_{int}$	$\overline{V}^{a}_{2,0}$	
						calc.	expt.
Water	98.96	16.94	9.29	2.17	28.39	71.69	103.54[b]
Benzene	119.48	19.81		0.33	20.14	101.73	107.17
Cyclohexane	165.13	18.84		0.35	19.19	148.76	107.27

[a] Units: mol·cm^{-3}; [b] Ref. [9]

Finally, the inductive interaction volume was calculated from Eq. (17) [12]:

$$\overline{V}_{\mathrm{ind}} = -\frac{4\pi N_{\mathrm{A}}^{2}(\mu_{1}^{2}\alpha_{2} + \mu_{2}^{2}\alpha_{1})\beta_{\mathrm{T}}^{0}}{3\,V_{1}^{0}\sigma_{1,2}^{3}} \tag{17}$$

The data for the solute and solvent distortion polarizability was taken from Ref. [33] and those for the magnetic susceptibility of solute and solvent from Ref. [34]. For a cyclohexanol molecule in benzene, a value for the dipole moment of 1.75 D from Ref. [5] was used, whereas in cyclohexane or water as solvent, no effects of the polar solvent on the dipole moment of the cyclohexanol molecule could be taken into account because of the lack of corresponding literature data; therefore, the value of cyclohexanol molecule in the gas phase was used, *i.e.* 1.86 D [13].

From Table 5 it is seen that when $\overline{V}_{\mathrm{cav}}$ becomes less positive, the $\overline{V}_{\mathrm{int}}$ term becomes more negative on account of the increasing attractive intermolecular solute-solvent interactions. Since in the investigated systems two solvents are apolar and water is slightly polar as well as the solute itself, it may be concluded that the contribution to $\overline{V}_{\mathrm{int}}$ arises primarily from the intermolecular dispersion forces.

Experimental

Materials

Cyclohexanol (Riedel de Häen) was dried over anhydrous calcium chloride, purified by vacuum distillation, and stored over a 4 Å molecular sieve in a closed container. Benzene (Riedel de Häen) was shaken first with concentrated sulfuric acid, then with a 10% aqueous solution of sodium carbonate. The purified benzene was dried over calcium chloride, distilled under normal pressure, and kept over 4 Å molecular sieves. Cyclohexane (Merck) was shaken first with a mixture of concentrated nitric and sulfuric acid (1:4) and then with distilled water. Purified cyclohexane was distilled and stored over 4 Å molecular sieves.

The purity of the liquid components was checked by measurement of their refractive indices and densities at 25°C or 30°C. The values obtained are presented in Table 6 together with literature values [13]. From the purified solvents, stock solutions of cyclohexanol in benzene or cyclohexane (5.0 mol·dm^{-3} and 1.0 mol·dm^{-3}, respectively) were prepared; by successive dilution, solutions with concentrations varying from 0.0500 to 4.0000 mol·dm^{-3} (in benzene) and from 0.0354 to 0.8000 mol·dm^{-3} (in cyclohexane) were obtained. The molalities of the solutions, m (mol·kg^{-1}), were calculated using the known molar concentration and the densities of the solutions at 20°C.

Table 6. Experimental density and refractive index of the component liquids and their comparison with literature data at 25 and 30°C

	d_0 (25°C)	d_0 (30°C)	d_0 (25°C)	d_0 (30°C)	n_D (25°C)	n_D (30°C)	n_D (25°C)	n_D (30°C)
	(g·cm^{-3})		(g·cm^{-3})					
	expt.		lit.[a]			expt.		lit.[a]
Cyclohexanol		0.9416	0.9684	0.94155		1.4628		1.4629
Benzene	0.8735		0.87360		1.4983		1.49792	
Cyclohexane	0.7737		0.77389		1.4235		1.42354	

[a] Ref. [13]

Density measurements

Density measurements were carried out using an *A. Paar* digital densimeter (Model DMA 10) in the temperature range of 20–60°C. The thermal stability of the measuring cell was controlled by a quartz thermometer (Hewlet-Packard HP 2804 A) to better than ±0.02°C. At each temperature studied, the densimeter was calibrated with water [14] and dry air [15]. The accuracy of the density values was $2 \cdot 10^{-4}$ g·cm^{-3}.

Refractive index measurements

Refractive indices were measured at 25 and 30°C with a Carl Zeiss Abbé refractometer (32-G 110e) with a precision of $1 \cdot 10^{-4}$ at a wavelength of 589 nm.

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