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Limiting Partial Molar Volumes of Water in 1-Hexanol, 1-Octanol, 1-Decanol, and Cyclohexanol at 298.15 K

Nataša Šegatin and **Cveto Klofutar***

Biotechnical Faculty, University of Ljubljana, SLO-1000, Ljubljana, Slovenia

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Summary. From the density of solutions of water in 1-hexanol, 1-octanol, 1-decanol, and cyclohexanol, measured at 298.15 K, the limiting partial molar volume and the excess limiting partial molar volume of water was estimated. The limiting partial molar volume of water in alcohols was discussed in terms of the void space created by the addition of water to alcohol and by the packing density of water. On the basis of the *Kirkwood-Buff* theory and the activity of water in alcohols an average aggregation number of water molecules, as well as the number of the excess alcohol molecules in the surroundings of the water molecule was calculated. The solvation ability of the investigated alcohols was estimated as the difference in the solvation *Gibbs* energy of an alcohol molecule in solution relative to the pure alcohol. The observed difference was mainly ascribed to an indirect effect caused by water molecules on the alcohol structure and to a lesser extent to the hydrogen bonding of water to alcohol molecules. The limiting partial molar volume of water was also interpreted in terms of scaled particle theory and the various volume contributions arising from dispersion, dipole–dipole, and inductive interactions between water and an alcohol molecule were calculated.

Keywords. Water; Alcohols; Limiting partial molar volume; Average aggregation number; Difference in the solvation *Gibbs* energy; Scaled particle theory.

Introduction

Many studies on volumetric properties have been reported in the past for mixtures of various alcohols and water, but only few have been concerned with the volumetric properties of water in the alcohol-rich region [1–4]. It was recognised that many solute–water and even water–water interactions might be better understood if such studies were performed in other solvent systems, especially in some organic solvents, rather than in water. Water molecules could be bound to an organic solvent in a wide variety of ways. As concerns the alcohols, they markedly differ from other organic solvents and also from each other with respect to the extent and

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* Corresponding author. E-mail: natasa.segatin@bf.uni-lj.si

degree of self-association. Little attention has been paid in the past to contributions of the alteration of hydrogen-bonded systems of pure water and alcohol in the mixing process. Since the water–alcohol hydrogen bond is generally stronger than the alcohol–alcohol bond [5], the introduction of water into pure alcohols may break down self-association in the alcohols and new hydrogen bonds may be formed between the alcohols and water molecules. When interpreting the volumetric properties of strongly associated systems, such as alcohol–water mixtures, it is obviously necessary to take into account such effects. With this in mind, we studied the partial molar volume of water in some alcohols in order to provide a better understanding of those factors which contribute appreciably to the volumetric behaviour of strongly associated mixtures. Among many models which are available for describing the properties of strongly non-ideal solutions, *e.g.* Ref. [6], we interpreted the volumetric properties of the investigated systems by the scaled particle theory [7], fluctuation theory [8], and solvation thermodynamics [9].

Results and Discussions

From the density data, d given in Table 1, the apparent molar volume of water at infinite dilution, V^0_{app}, was calculated.

Table 1. Density of solutions of water in 1-hexanol, 1-octanol, 1-decanol, and cyclohexanol at 298.15 K

1-hexanol		1-octanol		1-decanol		cyclohexanol	
$\frac{m}{\text{mol kg}^{-1}}$	$\frac{d}{\text{g cm}^{-3}}$	$\frac{m}{\text{mol kg}^{-1}}$	$\frac{d}{\text{g cm}^{-3}}$	$\frac{m}{\text{mol kg}^{-1}}$	$\frac{d}{\text{g cm}^{-3}}$	$\frac{m}{\text{mol kg}^{-1}}$	$\frac{d}{\text{g cm}^{-3}}$
0.2070	0.81638	0.1494	0.82038	0.1174	0.82672	0.2570	0.94591
0.4364	0.81718	0.3546	0.82118	0.1272	0.82672	0.6256	0.94607
0.6599	0.81766	0.3695	0.82006	0.2433	0.82688	0.8572	0.94624
0.9530	0.81798	0.4867	0.82134	0.3401	0.82704	1.2729	0.94640
1.0438	0.81830	0.6957	0.82150	0.4920	0.82736	1.4033	0.94673
1.2280	0.81862	0.7531	0.82167	0.5886	0.82768	1.5898	0.94689
1.2983	0.81894	0.8270	0.82183	0.6313	0.82768	1.6248	0.94689
1.4691	0.81926	0.8821	0.82199	0.6642	0.82784	1.9394	0.94705
1.7052	0.81990	1.0356	0.82263	0.7640	0.82800	2.1382	0.94738
2.2619	0.82119	1.1493	0.82295	0.8664	0.82816	2.9245	0.94787
2.3116	0.82151	1.4305	0.82327	1.1202	0.82913	3.0832	0.94803
2.4462	0.82183	1.4922	0.82343	1.2197	0.82929	3.2317	0.94820
2.6214	0.82217	1.5437	0.82359	1.2501	0.82945	3.5200	0.94836
2.6499	0.82231	1.6139	0.82375	1.3485	0.82945	3.7064	0.94836
2.9203	0.82279	1.6679	0.82375	1.3804	0.82961	4.1898	0.94852
3.1357	0.82327	1.7499	0.82455	1.4572	0.82977	4.5560	0.94869
3.4020	0.82391	1.8963	0.82487	1.6056	0.83009	5.0371	0.94885
3.8180	0.82455	2.0859	0.82535	1.7437	0.83025	5.6875	0.94901
4.7576	0.82616			1.8632	0.83041	7.5197	0.94999
4.9860	0.82698			2.2288	0.83105	8.2214	0.95098
				2.4120	0.83163		

The apparent molar volume, V_{app}, of the solute in solution is defined by Eq. (1).

$$V_{app} = \frac{(v - v_1^0)}{m} \tag{1}$$

The specific volume of the solution is $v = (1000 + mM_2)/d$ and the specific volume of the solvent is $v_1^0 = 1000/d_1^0$, while m and M_2 are the molality and molecular weight of solute, respectively. For a sufficiently dilute solution the dependence of V_{app} on solute molality at a definite temperature can be conventionally represented for a non-electrolyte solution as given in Eq. (2) [10], where V_{app}^0 is the apparent molar volume of the solute at infinite dilution, equal to the limiting partial molar volume of solute, $\overline{V}_2^0$, and b_v, b_{vv}… are the virial coefficients, which depend on the solute, solvent and temperature.

$$V_{app} = V_{app}^0 + b_v \cdot m + b_{vv} \cdot m^2 + \cdots \tag{2}$$

By combining Eqs. (1) and (2) the following Eq. (3) can be obtained, from which the values of V_{app}^0 and coefficients b_v, b_{vv}… can be calculated by least squares fitting to Eq. (3).

$$v = v_1^0 + V_{app}^0 \cdot m + b_v \cdot m^2 + b_{vv} \cdot m^3 + \cdots \tag{3}$$

For the investigated systems the experimental data given in Table 1 were treated by a quadratic form of Eq. (3) for 1-hexanol and cyclohexanol, while for 1-octanol and 1-decanol a linear form of Eq. (3) was sufficient. The values of $\overline{V}_2^0$ and b_v are given in Table 2, which also includes some of the literature values. The limiting apparent molar volume is represented to within $0.15\,\mathrm{cm^3\,mol^{-1}}$. In analysing the experimental density data (Table 1) *via* Eq. (3), the v_1^0 values differ by less than 0.03 per cent from the respective values of the pure alcohols calculated from the density data given in Table 8. The apparent molar volume of water in 1-hexanol is within the experimental uncertainty equal to the one calculated from the density data given by *Apelblat* [11], but higher than the one given by *Sakurai et al.* [3]. The value of $\overline{V}_2^0$ of water in 1-octanol is also higher than the one given by *Sakurai et al.* [3], but within the experimental uncertainty equal to that given by *Cabani et al.* [4].

Table 2. The limiting partial molar volume of water in alcohols, $\overline{V}_2^0$ and values of b_v in Eq. (3) at 298.15 K

Solvent	$\frac{\overline{V}_2^0}{\mathrm{cm^3\,mol^{-1}}}$	b_v
1-hexanol	18.10 ± 0.17	0.08 ± 0.03
	18.29[a]	
	17.39[b]	0.22[b]
	17.48[c]	
1-octanol	18.38 ± 0.17	
	17.86[b]	0.05[b]
	18.57[d]	
1-decanol	18.49 ± 0.07	
cyclohexanol	18.18 ± 0.07	0.013 ± 0.009

[a] Calculated from *Apelblat* [11]; [b] Sakurai [2]; [c] Ref. [15]; [d] Ref. [1]

The differences observed between values of $\overline{V}_2^0$ given in Table 2 may be ascribed to the different preparation of solutions of water in alcohols, *i.e.* by the distribution technique [11], mixing of water and alcohol [1, 2, 4] or by isopiestic equilibration as employed in this work. As was stated by *Christian et al.* [12, 13], a homogeneous solution of water in an organic solvent can be achieved only by the isopiestic equilibration technique in which water is distributed by vapour contact between an aqueous solution of known water activity and the organic solution. This problem may account for some discrepancies among literature reports on the properties of water in dilute solutions.

The limiting partial molar volume of water in cyclohexanol is within experimental error equal to that determined in 1-hexanol. It is worth mentioning that the melting point of cyclohexanol is close to 298.15 K. In such a system one has to expect that the self-association of the alcohol might be appreciably retained and that the addition of water could not lead to the formation of very strong water–alcohol hydrogen bonds. The absence of strong solute-solvent interactions brought about a less volume reduction relative to other alcohol systems [7]. The concentration dependence of the apparent molar volume of water for the investigated systems is positive (Table 2). In general, the concentration dependence of any apparent molar quantity has been attributed to solute–solute interactions, *i.e.* in the present case to the water–water or perhaps water–alcohol–water interactions [14].

From the values of $\overline{V}_2^0$ listed in Table 2 it is evident that our values and the values of *Apelblat* [11] and *Berti* [1] are higher than the molar volume of pure water, $\overline{V}_2^0 = 18.068\,\mathrm{cm^3\,mol^{-1}}$, while values of *Sakurai* and *Nakagawa* [2] are substantially lower. So the excess limiting partial molar volume of water ($\overline{V}_{2,0}^{ex} = \overline{V}_2^0 - V_2^0$) is positive, namely 0.03, 0.31, and 0.42 $\mathrm{cm^3\,mol^{-1}}$ for water in 1-hexanol, 1-octanol, and 1-decanol, respectively, as was also observed for higher alcohols by *D'Aprano et al.* [15]. Thus, the more hydrophobic the alkyl chain of the 1-alcohol, the higher is the value of $\overline{V}_2^0$, caused by repulsive interactions between water and the nonpolar residue of the 1-alcohol molecule. A similar behaviour was also observed for the partial molar volume of water in derivatives of benzene [16] and some halogenated hydrocarbon solutions [17].

The volume change upon mixing of two liquids can arise from a variety of origins [18], such as the difference in the size of the component molecules and various interactions between the components. Attractive interactions may arise from hydrogen-bond formation between alcohol–alcohol, alcohol–water and water–water molecules, and repulsive interactions between water and the alkyl group of alcohols. Generally, the attractive interactions are responsible for a reduction of volume, while repulsive interactions are accompanied by opposite changes. From this it may be surmised that the partial molar volume of water increases in hydrophobic solvents and is much larger than the molar volume of pure water. The values of $\overline{V}_2^0$ (Table 2) tend to increase with the molar volume of the pure primary alcohol. In Fig. 1 the limiting partial molar volume of water in 1-alcohols is given as a function of the molar volume of the 1-alcohol. From Fig. 1 it can be seen that when the volumes of the molecules of the 1-alcohol are large, the water molecules fit more or less in the holes between these spheres and $\overline{V}_2^0$ is large mainly due to hydrophobic interactions. So, at infinite dilution the isolated water molecule can

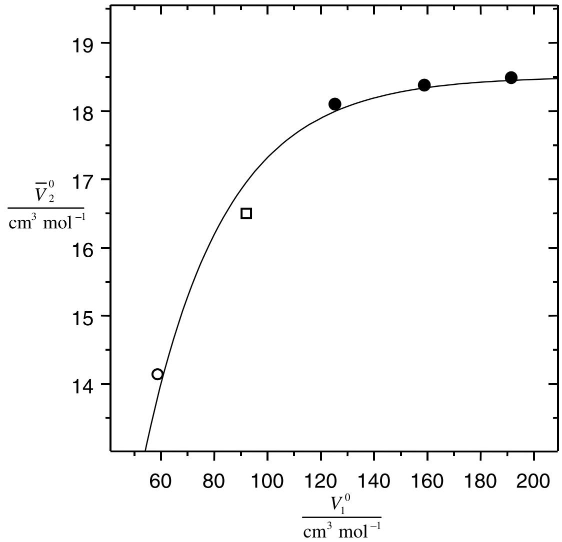

Fig. 1. Limiting partial molar volume of water in some 1-alcohols as a function of the molar volume of 1-alcohols at 298.15 K: ● our values, ○ value for ethanol from Ref. [47], □ value for 1-butanol from Ref. [15]

be considered almost as a hard sphere [19]. The smaller values of $\overline{V}_2^0$ for solutions of water in the lower 1-alcohols can be mainly attributed to strong hydrogen-bond formation between water and such 1-alcohol molecules.

If it is assumed that the *van der Waals* volume of water, $V_W = 12.4\,\text{cm}^3\,\text{mol}^{-1}$ [20], does not change in solution, the difference $(\overline{V}_2^0 - V_W)$ can be taken as the volume of the void space created by the addition of 1.0 mol of water to the solvent [21]. Thus the limiting partial molar volume at infinite dilution can be related to Eq. (4).

$$\overline{V}_2^0 = V_W + \overline{V}_{void} \tag{4}$$

From Table 3 it is evident that $\overline{V}_{void}$ and the ratio of $\overline{V}_{void}$ and V_W almost linearly increase with the increasing molecular weight of the 1-alcohol, *i.e.* with the increasing hydrophobicity of the solvent. In the same Table the packing density of water is also given. The packing density of a solute in solution is defined as the

Table 3. Void space, $\overline{V}_{void}$, the ratio $\overline{V}_{void}/V_W$, and packing density, $V_W/\overline{V}_2^0$, of water in some alcohols at 298.15 K

Solvent	$\overline{V}_{void}/\text{cm}^3\,\text{mol}^{-1}$	$\overline{V}_{void}/V_W$	$V_W/\overline{V}_2^0$
ethanol[a]	1.7	0.14	0.88
1-butanol[b]	4.1	0.33	0.75
1-hexanol	5.7	0.46	0.69
1-octanol	6.0	0.48	0.68
1-decanol	6.1	0.49	0.67
cyclohexanol	5.8	0.47	0.68

[a] Data from Ref. [47]; [b] data from Ref. [15]

ratio of its *van der Waals* volume to its limiting partial molar volume [22]. The packing density of water gradually decreases with increasing molecular weight of a 1-alcohol as a consequence of the increasing void space. *Bernal* and *Finney* [23] found that in a random close packed collection of spheres, the packing density was an average of the densities around individual molecules, the extreme values being 0.57 and 0.70. So the packing density of water in higher 1-alcohols approaches almost its extreme value.

The limiting partial molar volume of water in alcohol was also treated by the assumption that water as well as alcohol molecules can be considered as almost hard spheres by the scaled particle theory. According to this theory, the expression for the limiting partial molar volume of the solute is given by Eq. (5) [7, 24, 25].

$$\overline{V}_2^0 = \overline{V}_{cav} + \overline{V}_{\mathrm{int}} + \beta_T^0 \cdot R \cdot T \tag{5}$$

$\overline{V}_{cav}$ and $\overline{V}_{\mathrm{int}}$ are the contributions from the formation of a cavity and from intermolecular interactions, respectively, R is the gas constant, T is the absolute temperature, and β_T^0 is the isothermal compressibility of the solvent. $\overline{V}_{cav}$ in Eq. (5) is by definition a positive contribution to $\overline{V}_2^0$, whereas $\overline{V}_{\mathrm{int}}$ takes into account the attractive intermolecular solute–solute interactions, which cause a shrinking of the cavity. These effects bring a negative contribution to $\overline{V}_2^0$. The cavity volume was calculated by the relation given in Eq. (6) [24, 25], where y is the ratio of the volume occupied by one mole of hard sphere solvent particles to the molar volume of solvent shown in Eq. (7), z is the ratio of the solute σ_2 (nm) and solvent σ_1 (nm) hard sphere diameters (Eq. (8)), and N_A is *Avogadro*'s constant.

$$\overline{V}_{cav} = \beta_T^0 \cdot R \cdot T \left\{ \frac{y}{1-y} + \frac{3 \cdot y \cdot z \cdot (1+z)}{(1-y)^2} + \frac{9 \cdot y^2 \cdot z^2}{(1-y)^3} \right\} + \frac{\pi \cdot \sigma_2^3 \cdot N_A}{6} \tag{6}$$

$$y = \frac{\pi \cdot \sigma_1^3 \cdot N_A}{6} \cdot \frac{1}{V_1^0} \tag{7}$$

$$z = \sigma_2/\sigma_1 \tag{8}$$

From Eq. (6) follows that the cavity contribution to the partial molar volume $\overline{V}_2^0$ depends on the intrinsic size of the solute and solvent molecule, as well as on the isothermal compressibility of the solvent at a definite temperature. $\overline{V}_{\mathrm{int}}$ is defined by the volume contributions due to dispersion, $\overline{V}_{disp}$, the dipole–dipole, $\overline{V}_{dip}$, and inductive interactions, $\overline{V}_{ind}$, *i.e.* as shown in Eq. (9).

$$\overline{V}_{\mathrm{int}} = \overline{V}_{disp} + \overline{V}_{dip} + \overline{V}_{ind} \tag{9}$$

The dispersion interaction volume was calculated from Eq. (10), where E is the energy of an electron, α_1 and α_2 are the electronic polarizabilities, χ_1 and χ_2 are the molecular magnetic susceptibilities of solvent and solute, and $\sigma_{12} = (\sigma_1 + \sigma_2)/2$.

$$\overline{V}_{disp} = \frac{16\pi N_A^2 E \alpha_1 \alpha_2 \beta_T^0}{3 V_1^0 \sigma_{12}^3 (\alpha_1/\chi_1 + \alpha_2/\chi_2)} \tag{10}$$

Table 4. Values of parameters for the scaled particle theory of solvents at 298.15 K

Solvent	$\frac{\sigma_1}{\text{nm}}$	$\frac{\alpha_1 \cdot 10^{24}}{\text{cm}^3}$	$\frac{\mu_1}{\text{D}}$	$\frac{-\chi_1 \cdot 10^6}{\text{cm}^3\,\text{mol}^{-1}}$	$\frac{\beta_T^0 \cdot 10^7}{\text{k Pa}^{-1}}$
1-hexanol	0.593	12.5	2.48	81.6	8.24
1-octanol	0.641	16.2	2.41	105.4	7.64
1-decanol	0.683	19.8	2.17	129.1	7.3
cyclohexanol	0.568	11.6	2.43	75.8	6.6[a]

[a] At 305 K

The dipole–dipole interaction volume was calculated via Eq. (11) where μ_1 and μ_2 are the dipole moments of solvent and solute.

$$\overline{V}_{dip} = -\frac{8\pi N_A^3 \mu_1^2 \mu_2^2 \beta_T^0}{9RTV_1^0 \sigma_{12}^3} \tag{11}$$

Finally, the inductive interaction volume was calculated from Eq. (12).

$$\overline{V}_{ind} = -\frac{4\pi N_A^2 \left(\mu_1^2 \alpha_2 + \mu_2^2 \alpha_1\right) \beta_T^0}{3V_1^0 \sigma_{12}^3} \tag{12}$$

Data for the solvent and solute parameters needed for calculation of the various volume contributions collected in Table 4 were obtained as follows. The values of σ_1 for 1-alcohols were calculated from the *Stearn-Eyring* relation [26], which is recommended for larger solvent molecules [27], while the value of 0.275 nm for water was taken from Ref. [28]. The electronic polarizability of alcohol molecules was calculated using the *Lorenz–Lorentz* relation from the molar volume and refractive index [29, 30]. A value of $1.45 \cdot 10^{-24}$ cm^3 was taken for the water molecule [31]. The dipole moment of alcohols was calculated using the *Kirkwood* relation [32] from the respective electrical permittivity data [29, 31]. For the *Kirkwood* correlation factor g a value of 2.57 was used. This was obtained for alcohols which are associated chain-wise through hydrogen bonds [33]. The dipole moment of the water molecule $\mu_2 = 2.42$ D was taken from Ref. [34]. The magnetic susceptibility of alcohols was calculated from the respective atomic contributions [35], while for water a value of $-12.97 \cdot 10^{-6}$ cm^3 mol^{-1} was used [36]. The values for isothermal compressibility of 1-hexanol, 1-octanol, and cyclohexanol were taken from Refs. [29] and [37]. The isothermal compressibility of 1-decanol was obtained by extrapolation of the relation $\ln \beta_T^0 = \ln \beta^0 + An^{-1/2}$, where β^0 and A were obtained from the values of β_T^0 for 1-alcohols from 1-propanol to 1-octanol given in Ref. [29], and n is the number of carbon atoms in the 1-alcohol. The calculated contributions to the limiting partial molar volume of water in various alcohols are collected in Table 5.

From Table 5 it may be seen that $\overline{V}_{cav}$ is greater than the molar volume of pure water and that it decreases with increasing molecular weight of 1-alcohol. Just the opposite is true for the limiting partial molar volume of water. This may be explained by the fact that with decreasing size of the cavity, the water molecule fits into the cavity just as a monomeric water molecule [1] and the observed expansion of $\overline{V}_2^0$ occurs due to an environment which is exclusively hydrophobic in nature. Among volume contributions to $\overline{V}_{\text{int}}$ the intermolecular dispersion and

Table 5. Volume contributions to the limiting partial molar volume of water in various alcohols at 298.15 K in $\text{cm}^3\,\text{mol}^{-1}$

Solvent	$\overline{V}_{cav}$	$-\overline{V}_{disp}$	$-\overline{V}_{dip}$	$-\overline{V}_{ind}$	$-\overline{V}_{\text{int}}$	$\overline{V}_2^0$	
						calc.	expt.
1-hexanol	28.45	4.55	7.14	1.00	12.69	17.80	18.10
1-octanol	24.62	3.66	4.19	0.78	8.63	17.88	18.38
1-decanol	22.36	3.12	2.35	0.65	6.12	18.06	18.49
cyclohexanol	28.79	4.36	7.11	0.97	12.44	17.99	18.28

dipolar contributions are significant while inductive interactions are relatively small.

On the basis of the fluctuation theory of *Kirkwood* and *Buff* [38], the aggregation number of water in alcohol solution at infinite dilution can be obtained from the activity coefficient and limiting partial molar volume of water. According to this theory, the dimensionless parameter N_{22}, a measure of the aggregation number, representing the total excess of solute molecules in the surroundings of a solute molecule at infinite dilution, is given by Eq. (13) [8].

$$N_{22} = \rho_{m,2}\beta_T^0 RT + \frac{V_1^0}{V_2^0}(1 + K_2) - \frac{2\overline{V}_2^0}{V_2^0} \tag{13}$$

The density of water is $\rho_{m,2}$ ($\text{mol}\,\text{cm}^{-3}$), V_1^0 and V_2^0 are the molar volume of alcohol and water and K_2 is given by Eq. (14).

$$K_2 = -\left(\frac{\partial \ln \gamma_{2,x}}{\partial x_2}\right)_{P,T}^{\infty} \tag{14}$$

The activity coefficient of the water according to the symmetric convention for normalisation is $\gamma_{2,x}$. The parameter H_{12}^{∞}, as a measure of the excess solvent molecules in the surroundings of a water molecule at infinite dilution, is given by Eq. (15), where $\rho_{m,1}$ is the density of the pure alcohol ($\text{mol}\,\text{cm}^{-3}$).

$$H_{12}^{\infty} = \rho_{m,1}(\beta_T^0 RT - \overline{V}_2^0) \tag{15}$$

Equations (13) and (15) allow to estimate N_{22} and H_{12}^{∞} from experimentally measurable quantities, *i.e.* from the activity coefficient of water in alcohol, the limiting partial molar and molar volumes of water and alcohol. An analysis of possible errors in the calculation of N_{22} and H_{12}^{∞} clearly indicates that error is introduced through the values of K_2 (Eq. (13)) and $\overline{V}_2^0$ (Eq. (15)). The value of K_2 was calculated from the activity a_2 and solubility x_2 (mole fraction) of water in alcohol at infinite dilution [39]. Table 6 shows the values of the limiting derivative of the activity coefficient of water, the excess water molecules, and the excess alcohol molecules.

In the calculation of N_{22} and H_{12}^{∞}, the products $\rho_{m,2}\beta_T^0 RT$ and $\rho_{m,1}\beta_T^0 RT$ are negligible due to the small values of isothermal compressibility of the alcohols. From Table 6 it can be seen that the parameter N_{22} increases with increasing chain length of the 1-alcohol molecule. This indicates that clustering in these systems is caused by the accumulation of water molecules near a central water molecule. The

Table 6. Limiting derivatives, K_2, total excess solute molecules, N_{22}, and excess solvent molecules H_{12}^{∞}, at 298.15 K

Solute	K_2	N_{22}	$-H_{12}^{\infty}$
1-hexanol	1.91 ± 0.24	18 ± 2	0.128 ± 0.001
1-octanol	2.10 ± 0.25	25 ± 2	0.104 ± 0.001
1-decanol	2.00 ± 0.29	30 ± 3	0.087 ± 0.001
cyclohexanol	1.25 ± 0.40	11 ± 2	0.156 ± 0.001

main conclusion is that separate clusters of water are formed and that clustering increases with the chain length of the 1-alcohol molecule, as was also observed earlier for lower 1-alcohols up to 1-butanol [46]. Furthermore, from Table 6 it can be seen that the value of H_{12}^{∞} is small and increases with the increasing chain length of the 1-alcohol molecule, as was also observed by *Liu* and *Ruchenstein* [8]. From the values of H_{12}^{∞} it is also evident that the number of excess alcohol molecules in the surroundings of a water molecule at infinite dilution is negligibly small.

The solvation ability of the alcohol molecules can be estimated by the approach of *Ben-Naim* [9]. According to this theory, the difference in the solvation *Gibbs* energy of a solvent molecule in solution ΔG_l^{*l} relative to the pure solvent ΔG_A^{*p}, $\Delta\Delta G_l^{*}$ (J molecule^{-1}), is given by Eq. (16).

$$\Delta\Delta G_l^{*} = \Delta G_l^{*l} - \Delta G_A^{*p} = kT \ln\left(\frac{C_1^0 a_1}{C_1}\right) \tag{16}$$

C_1^0 and C_1 are the number density of pure solvent in pure solvent and of solvent in solution (molecules cm^{-3}), a_1 is the activity of solvent in solution, and k is the *Boltzmann* constant. The ratio C_1^0/C_1 was obtained from the respective densities of pure solvent and solution and the weight fraction of solvent in solution. The activity of the solvent was obtained from Ref. [39]. The values of $\Delta\Delta G_l^{*}$ (J mol^{-1})

Table 7. Dependence of $\Delta\Delta G_1^{*}$ on molality for solutions of water in some alcohols at 298.15 K

$\frac{m}{\text{mol kg}^{-1}}$	$\frac{-\Delta\Delta G_1^{*}}{\text{J mol}^{-1}}$			
	1-hexanol	1-octanol	1-decanol	cyclohexanol
0.5	100	132	159	96
1.0	184	242	283	180
1.5	254	330	371	253
2.0	311	396	423	315
2.5	358	441		368
3.0	395			411
4.0	449			475
5.0				514
6.0				535
7.0				545
8.0				551

calculated for the investigated systems are given in Table 7 at rounded molalities. From Table 7 follows that the values of $\Delta\Delta G_l^*$ are negative and decrease with increasing molality and chain length of the 1-alcohol molecule. According to *Ben-Naim* [9] it is not possible to state categorically whether the observed values of $\Delta\Delta G_l^*$ are due to direct solute-solvent interactions or to indirect changes of the structure of the solvent environment induced by addition of the solute. The *Gibbs* energy of solvation of alcohols in their pure liquids at 298.15 K are negative ($\Delta G_A^{*p} = -30.11$, -35.62, -40.08, and $-31.42\,\mathrm{kJ\,mol^{-1}}$ for 1-hexanol, 1-octanol, 1-decanol, and cyclohexanol, respectively [9]). From the values obtained for $\Delta\Delta G_l^*$ it can be concluded that the addition of water to pure solvent makes the solvation *Gibbs* energy of alcohol molecules in solution more negative relative to the corresponding value of the pure alcohol. From qualitative reasoning the observed effect may be mainly ascribed to the indirect effect of water molecules on the structure of alcohols. Straight chain 1-alcohols and cyclohexanol in their pure state contain an appreciable number of predominantly linear multimers [40, 41]. By introduction of water into a pure alcohol rupturing of self-associated molecules occurs and consequently lower molecular aggregates are formed than those existing in the anhydrous alcohol. These aggregates may be further hydrogen bonded to water molecules and a maximum of four alcohol molecules bonded to each water molecule was postulated [42]. These processes are intensified with the lengthening of the alkyl chain in the 1-alcohol molecule.

Experimental

1-Decanol (Fluka, puriss, 99.5%), 1-octanol (Riedel de Haën, puriss, 99.5%), 1-hexanol (Kemika, p.a. 98%), and cyclohexanol (Riedel de Haën, puriss, 99.0%) were dried over anhydrous $CaCl_2$ and then vacuum distilled and stored in an desiccator over P_2O_5 [29]. The purity of the alcohols was checked by measurements of their densities at 298.15 K. The values obtained are presented in Table 8 together with literature values.

The solutions of water in alcohols were prepared by the isopiestic method [43] using saturated aqueous salt solutions of known water activity at 298.15 K [44]. The amount of water in alcohol was determined with an automatic Karl Fischer titrator, Aquatest II, with an accuracy of $\pm 10\,\mu$g water per cm^3 of solution.

The density, ($g \cdot cm^{-3}$), of solutions was measured at 298.15 K ± 0.02 K using an oscillating – tube densimeter (*Anton Paar*, DMA 10), as described before [45].

Table 8. Experimental densities of pure alcohols at 298.15 K compared with literature data

Alcohol	$d_1^0/\mathrm{g\,cm^{-3}}$	
	Exptl.	Lit.
1-hexanol	0.81558	0.81534[a], 0.8155[b], 0.81509[c], 0.8150[d]
1-octanol	0.81990	0.82157[a], 0.82086[c], 0.82172[e], 0.82169[h]
1-decanol	0.82664	0.82652[f]
cyclohexanol	0.94575	0.9454[g]

[a] Ref. [29]; [b] Ref. [11]; [c] Ref. [2]; [d] Ref. [15]; [e] Ref. [1]; [f] Ref. [48]; [g] calculated from the molar volume given in Ref. [49]; [h] Ref. [4]

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