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Thermodynamics of the Solubility of Water in 1-Hexanol, 1-Octanol, 1-Decanol, and Cyclohexanol

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Summary. The solubility of water in 1-hexanol, 1-octanol, 1-decanol, and cyclohexanol was determined as a function of water activity by the isopiestic method at 298.2 K. The solubility of water in the alcohol was expressed by a *Setchenov* type of equation and the correlation coefficients were related to the virial coefficients of the *McMillan-Mayer* theory of solution. From the solubility data both the activities and the osmotic coefficients of the alcohols were calculated. The *Henry*'s law constants for the solubility of water in the alcohols are given. They depend linearly on the *Gibbs* energy of hydration. The excess *Gibbs* energy of mixing of water and alcohols is positive as a consequence of the strong intermolecular interactions of the two pure components of the mixture.

Keywords. Alcohols; Excess *Gibbs* energy; Isopiestic measurements; Osmotic coefficients; Solubility.

Introduction

Liquid–liquid solubility data are needed in many separation processes and in the solubilisation of aqueous micellar solutions. In such systems the solubility of water plays a central role. Although the solubility of alcohol in water has been extensively investigated in the past, *e.g.* Ref. [1, 2], the solubility of water in alcohols has hitherto received little attention. Accurate solubility data represent a major problem in analysing an organic solution which contains only a few per cent of water. Another problem arises from the preparation of homogeneous solutions of water in alcohols. As was stated by *Christian et al.* [3], 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 a phase of known water activity and the organic solution. This problem may account for some discrepancies among literature data on the properties of water in dilute solutions.

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The available liquid–liquid solubility data for alcohol–water binary systems, with critical evaluation and smoothed values, are given in two recent surveys, namely by *Barton* [4] and by *Sörensen* and *Arlt* [5].

The molecular complexity of water in dilute solution in alcohols is of especial interest in solution chemistry. Pure alcohols and pure water are extensively associated via hydrogen bonding. Nevertheless, the two types of self-association are quite different. It is generally accepted that aliphatic 1-alcohols and cyclohexanol associate through hydrogen bonds forming linear multimers [6–8]. In liquid water, the water molecules in the bulk form disordered three-dimensional hydrogen-bonded networks [1, 9]. Addition of water to an alcohol ruptures the structure of both components and results in lower molecular complexes of lower dipole moment than those existing in the pure alcohol and which are more dynamic in nature and thus less hindered in reforming bonds [6]. As concerns the molecular complexes between water and alcohol molecules, a tetrahedral structure of the type $H_2O(R\mathrm{OH})_4$ has been postulated with a net dipole moment which is lower than that existing in the pure alcohol [10]. *Backlund et al.* [11] have shown that such a structure cannot be fulfilled for each water molecule since the mean number of alcohol molecules per water molecule is smaller than four.

In the present work we report on the results of solubility measurements of water in some alcohols as a function of water activity. The purpose of this work was to provide a better understanding of those factors that contribute to the thermodynamic properties of the strongly associated mixture. For such studies at nearly unit water activity, the partition or distribution method as well as a directly prepared solution of water in alcohol were applied in the past. In this work the solute isopiestic method was employed to prepare a homogeneous solution of water in alcohols. In addition, studies of such systems at different fixed activities of water were performed.

Results and Discussion

The solubility of water in the investigated alcohols, m ($\mathrm{mol\,kg^{-1}}$), at unit water activity, together with some literature values, are presented in Table 1. An examination of the available literature values shows a great variability of solubility which probably arises from the method of preparation of saturated solutions, as mentioned in the Introduction [3].

From the collected data it can be seen that our values are higher than the recommended data from IUPAC [4], DECHEMA [5], and other authors. From Table 1 it can be seen that the solubility of water in cyclohexanol is surprisingly high compared to 1-hexanol and other alcohols. Since the melting point of cyclohexanol is 298 K, one could expect that self-association of cyclohexanol molecules might be appreciably retained, and that the addition of water would not cause formation of strong hydrogen bonds between alcohol and water molecules. According to *Huyskens et al.* [12], the absorption of water in alcohol is independent of the extent and degree of self-association of the alcohol molecules but rather dependent on the solubility of the alcohol in water. The two alcohols, *i.e.* 1-hexanol and cyclohexanol, greatly differ in their solubility in water at 298.2 K; thus, the solubility of 1-hexanol and cyclohexanol in water is 0.60 per cent and 3.8 per cent [4].

Table 1. Solubility of water at unit water activity in pure alcohols at 298.2 K

Alcohol	m/mol kg^{-1}	m/mol kg^{-1}	(lit. values)			
1-hexanol	4.986	4.2[a] 4.76[b]	3.98[c] 4.76[d]	4.19[e]	4.10[f]	4.32[g]
1-octanol	2.949	2.7[a] 2.79[b]	2.00[c] 2.74[d]	2.91[e]	2.58[f]	2.80[g]
1-decanol	2.412	2.1[a] 2.21[b]	2.30[c]			2.18[g]
cyclohexanol	8.221	7.11[a] 9.04[h]	7.62[c]			

[a] Recommended value from Ref. [4]; [b] the highest value from Ref. [4]; [c] smoothed value from Ref. [5]; [d] the highest value from Ref. [5]; [e] Ref. [14]; [f] Ref. [36]; [g] Ref. [11]; [h] at 299.9 K from Ref. [4]

Table 2. Solubility of water in some alcohols as a function of water activity at 298.2 K

a_2	m/mol kg^{-1}			
	1-hexanol	1-octanol	1-decanol	cyclohexanol
0.1105	0.2070	0.1494	0.1272	0.2570
0.2245	0.4364	0.3226	0.2433	0.6256
0.3300	0.6596	0.4867	0.3859	0.8572
0.4276	0.9530	0.6957	0.4920	1.2729
0.4706	1.0438	0.7531	0.5886	1.4033
0.4997	1.2280	0.8270	0.6313	1.5898
0.5286	1.2983	0.8821	0.6642	1.6248
0.5770	1.4691	1.0356	0.7640	1.9394
0.6183	1.7052	1.1493	0.8664	2.1382
0.7379	2.2619	1.4305	1.1202	2.9245
0.7528	2.3116	1.4922	1.2197	3.0832
0.7710	2.4462	1.5437	1.2501	3.2317
0.7997	2.6214	1.6139	1.3485	3.5200
0.8071	2.6499	1.6679	1.3804	3.7064
0.8426	2.9203	1.7499	1.4572	4.1898
0.8710	3.1357	1.8963	1.6056	4.5560
0.9019	3.4020	2.0859	1.7437	5.0371
0.9248	3.8180	2.2473	1.8632	5.6875
0.9800	4.7576	2.7218	2.2288	7.5197

The solubility of water in alcohols as a function of water activity, a_2, is presented in Table 2. The experimental data presented in Table 2 were analysed by expressing the solubility of water in alcohol by a *Setchenov* type of equation, Eq. (1) [13, 14],

$$\ln(a_2/m) = \lambda_0 + \lambda_1 m + \lambda_2 m^2 \tag{1}$$

Table 3. Correlation coefficients of the *Setchenov* Eq. (3) for the solubility of water in some alcohols at 298.2 K, the regression correlation coefficient *r*, and the standard error of the estimate *s*

Alcohol	$-\lambda_0$	$-\lambda_1$	λ_2	r	s
1-hexanol	0.551 ± 0.011	0.278 ± 0.010	0.0133 ± 0.0019	0.9970	0.017
1-octanol	0.275 ± 0.008	0.272 ± 0.005	–	0.9977	0.015
1-decanol	0.016 ± 0.013	0.365 ± 0.010	–	0.9940	0.027
cyclohexanol	0.817 ± 0.015	0.215 ± 0.009	0.0070 ± 0.0010	0.9958	0.024

where λ_0, λ_1, and λ_2 are correlation coefficients. The values of the correlation coefficients, together with the regression correlation coefficient, *r*, and the standard error of the estimate, *s*, are given in Table 3. For 1-octanol and 1-decanol a linear form of Eq. (1) is sufficient, while for 1-hexanol and cyclohexanol, in which water is the most soluble, a quadratic form must be applied. According to the *McMillan-Mayer* theory of solution [15], the correlation coefficients λ_1 and λ_2 in Eq. (1) can be related to the virial coefficients $g_{22} = \lambda_1\, RT/2$ and $g_{222} = \lambda_2\, RT/3$, which characterise the contributions to the excess *Gibbs* energy due to pair and triplet interactions between solute molecules at a given temperature. So, for the investigated systems a negative value of g_{22} indicates a strong interaction between water molecules, while a positive value of g_{222} is explained by predominantly repulsive forces between solute molecules when they come close together, with the expulsion of solvent [16]. Since for the investigated systems $|g_{22}| > |g_{222}|$ we suppose that strong interactions between water molecules in the alcohol dominate.

At low water activity the solubility of water in alcohol obeys *Henry*'s law [17], Eq. (2),

$$\lim_{x_2 \to 0} \left(\frac{a_2}{x_2} \right) = H_{21} \tag{2}$$

where the *Henry*'s law constant, H_{21}, is related to λ_0 by Eq. (3)

$$H_{21} = \frac{\exp(\lambda_0)}{M_1} \tag{3}$$

where M_1 is the molecular weight of the alcohol. The *Henry*'s law constants for the solubility of water in alcohol are given in Table 4 together with some literature values.

The *Henry*'s law constant for the system 1-octanol + water is, within experimental uncertainties, equal to the literature value, while the value for the system

Table 4. *Henry*'s law constants for the solubility of water in some alcohols H_{21} at 298.2 K

Alcohol	H_{21}	H_{21} (Ref. [14])
1-hexanol	5.64 ± 0.06	6.71
1-octanol	5.83 ± 0.05	5.82
1-decanol	6.22 ± 0.08	
cyclohexanol	4.41 ± 0.07	

1-hexanol + water is much lower. The observed difference between the *Henry*'s law constants may be ascribed to the different preparation of the saturated solutions of water in 1-hexanol, *i.e.* by the distribution technique [14] or by isopiestic equilibration applied in this work. As seen from Table 4, the *Henry*'s law constant for 1-alcohols increases for each additional methylene group. This effect of alkyl groups is the manifestation of the hydrophobic interaction of alcohol molecules and water. It was found that the *Henry*'s law constants depend linearly on the *Gibbs* energy of hydration of the alcohol, ΔG_h^* [18] with an intercept of (10.0 ± 0.2) and a slope of (0.24 ± 0.01). The values of ΔG_h^* for 1-hexanol, 1-octanol, and cyclohexanol were taken from *Cabani et al.* [19]. The value of $\Delta G_h^* = -15, 3\,\mathrm{kJ\,mol^{-1}}$ for 1-decanol was calculated from its solubility in water [4] and the *Gibbs* energy of solvation of its vapour condensing into 1-decanol [20]. The observed difference in the *Henry*'s law constant or in the solubility of water in the system of 1-alcohol and water and cyclohexanol + water must arise from specific interactions between water and alcohol. Since the solubility of water in an alcohol is independent of the extent and degree of self-association of the alcohol molecules [12], it follows from the observed linear relation that the limiting solubility of water in alcohol primarily depends on the *Gibbs* energy of hydration of the alcohol.

The experimental data presented in Table 2 were analysed as a binary alcohol + water system via the *Gibbs-Duhem* equation, Eq. (4),

$$x_2 \mathrm{d} \ln a_2 + x_1 \mathrm{d} \ln a_1 = 0 \tag{4}$$

where x_2 and x_1 are the mole fractions and a_2 and a_1 are the activities of water and alcohol, respectively. The integral form of the *Gibbs-Duhem* Eq. (4) is given in Eq. (5).

$$\ln a_1 = -\int_0^{a_2} \frac{x_2}{1 - x_2} \mathrm{d} \ln a_2 \tag{5}$$

Taking into account Eqs. (1) and (5) and that $m = x_2/[M_1(1 - x_2)]$, the activity of alcohol in solution is given by Eq. (6).

$$\ln a_1 = -M_1 m \left(1 + \frac{\lambda_1}{2} m + \frac{2\lambda_2}{3} m^2\right) \tag{6}$$

The practical molar osmotic coefficient of solution, ϕ, which is defined as outlined in Eq. (7)

$$\ln a_1 = -M_1 m \phi \tag{7}$$

is given by Eq. (8)

$$\phi = \left(1 + \frac{\lambda_1}{2} m + \frac{2\lambda_2}{3} m^2\right) \tag{8}$$

from which it follows that $\lim_{m \to 0} \phi = 1$. Relation (8) is a typical form representing the dependence of ϕ on molality for a non-electrolyte [21]. The calculated values of molal osmotic coefficients for the water + alcohol system at rounded molalities are presented in Table 5. These values are accurate to within 5%. From Table 5 it is evident that the values of the molal osmotic coefficients are

Table 5. Osmotic coefficient ϕ, activity coefficient of water ln $\gamma_{2,m}$, and excess *Gibbs* energy of mixing $\Delta_{\text{mix}}G^{\text{E}}$ for water + alcohol systems at 298.2 K

m/mol kg^{-1}	ϕ	$-\ln\gamma_{2,m}$	$\Delta_{\text{mix}}G^{\text{E}}$/kJ mol^{-1}
1-hexanol			
0.5	0.933	0.136	0.203
1.0	0.870	0.264	0.378
1.5	0.812	0.387	0.529
2.0	0.758	0.502	0.659
2.5	0.708	0.611	0.771
3.0	0.663	0.714	0.868
4.0	0.586	0.899	1.026
1-octanol			
0.5	0.932	0.136	0.262
1.0	0.864	0.272	0.483
1.5	0.796	0.409	0.669
2.0	0.728	0.545	0.826
2.5	0.660	0.681	0.957
1-decanol			
0.5	0.909	0.183	0.323
1.0	0.817	0.365	0.583
1.5	0.726	0.548	0.792
2.0	0.635	0.730	0.958
cyclohexanol			
0.5	0.947	0.106	0.17
1.0	0.897	0.208	0.32
1.5	0.849	0.307	0.45
2.0	0.804	0.402	0.57
2.5	0.760	0.494	0.67
3.0	0.720	0.582	0.76
4.0	0.645	0.748	0.90
5.0	0.579	0.900	1.01
6.0	0.523	1.038	1.10
7.0	0.477	1.162	1.16
8.0	0.439	1.271	1.21

relatively low and decrease with increasing molality of the solution. The value of $d\phi/dm$ increases with the hydrophobic character of the alkyl chain in the 1-alcohol.

The activity coefficient of water, $\gamma_{2,m}$, was obtained from the osmotic coefficient via the *Bjerrum* relation given by Eqs. (9) and (10).

$$d[(1-\phi)m] + m\,d\ln\gamma_{2,m} = 0 \tag{9}$$

$$\ln\gamma_{2,m} = \lambda_1 m + \lambda_2 m^2 \tag{10}$$

The activity coefficients of water in the alcohols investigated are given in Table 5.

The excess *Gibbs* energy of mixing of water and alcohols, $\Delta_{\mathrm{mix}}\mathrm{G}^{\mathrm{E}}$, on the symmetric scale of normalisation is given by Eq. (11).

$$\Delta_{\mathrm{mix}}\mathrm{G}^{\mathrm{E}} = RT\left[x_2 \ln\left(\frac{a_2}{x_2}\right) + (1 - x_2)\ln\left(\frac{a_1}{1 - x_2}\right)\right] \tag{11}$$

The values of $\Delta_{\mathrm{mix}}\mathrm{G}^{\mathrm{E}}$ are positive and are given in Table 5. Positive values of $\Delta_{\mathrm{mix}}\mathrm{G}^{\mathrm{E}}$ for the system water + alcohol were also obtained by *Apelblat* [14] from solubility data of water in some alcohols, and by *Mikhailov* and *Grigoreva* [22] from the coligative properties of solutions.

The positive values of $\Delta_{\mathrm{mix}}\mathrm{G}^{\mathrm{E}}$ given in Table 5 can be explained in terms of intermolecular forces [23]. In the mixing process the water and alcohol molecules are dispersed in each other. This process is endothermic while the association of water and alcohol molecules is an exothermic process. Since for the investigated systems the energy of interaction between water molecules is very much greater than the interaction between water and alcohol molecules or between alcohol molecules [24, 2], these systems show positive deviations from *Raoult*'s law, what can be also seen from $\gamma_{1,x}$ and $\gamma_{2,x}$, which are greater than one. Consequently for such systems a limiting miscibility exists and phase separation takes place [23].

The above arguments suggest that the behaviour of these systems is rather nonideal, with relatively low osmotic coefficients and positive excess *Gibbs* energy of mixing.

Experimental

1-Decanol (Fluka, puriss., 99.5%), 1-octanol (Riedel de Haën, puriss., 99.5%), 1-hexanol (Kemika, p. a. 99.0%), and cyclohexanol (Riedel de Haën, puriss., 99.0%) were dried over anhydrous $CaCl_2$ and then vacuum distilled and stored in a dessicator over P_2O_5 [25]. The purity of the alcohols was checked by measurements of their densities at 298.15 K. The values obtained are close to the literature values (better than 0.1%) [25–28].

The solubility of water in alcohols was determined at 298.2 K by the isopiestic method described previously [29–31] using saturated aqueous salt solutions of known water activity at 298.2 K [32]. For isopiestic equilibration 10 cm^3 of saturated salt solution with solid phase were introduced into an outer part of the glass equilibrator and 10 cm^3 of pure alcohol into the inner part. Equilibration was allowed to take place for 2 days with the entire apparatures immersed in a water bath held at a constant temperature of 298.2 ± 0.2 K. The amount of water in the alcohol was determined with an automatic Karl Fischer titrator, Aquatest II, with an accuracy of $\pm 10\,\mu$g of water per cm^3 of sample. At least five replicate measurements were made for each determination. The uncertainty of the solubility determination was between 0.1 and 1.6%. In the determination of the activity of water in alcohol we assumed that the solubility of the investigated alcohol in saturated salt solutions is negligible; the solubility of alcohols in water is low [4] and in salt solutions salting out also occurs.

The accuracy of the isopiestic procedure was checked by the determination of the solubility of water in benzene at various water activities. The value obtained for the solubility of water in benzene at 298.2 K and a water activity $a_2 = 1$ was $0.0348 \pm 0.0006\,\mathrm{mol\,dm^{-3}}$ which is close to the values of *Masterton* [33] of $0.0347\,\mathrm{mol\,dm^{-3}}$ and *Roddy* [34] of $0.0363\,\mathrm{mol\,dm^{-3}}$. The "best" value given by the recent compilation of IUPAC [35] is $0.0350 \pm 0.0008\,\mathrm{mol\,dm^{-3}}$.

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