

Water in nonaqueous solvents*

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Abstract - The possibility and usefulness of simple liquid models is reported. The importance of van der Waals forces for liquid water and aqueous solutions is discussed and compared with the solubility of water in nonpolar solvents and as well as of nonpolar solvents in water. Both systems could be understood as equilibrium of few water monomers. The network of H-bonded water molecules seems to be less important for both effects. This conclusion would disagree with the cluster model of liquid water. The polarization of OH groups by unpolar solvents is demonstrated. The carrier effect of polar molecules for the solubility of water in nonpolar solvents is studied with the polyethylenoxides. The change of water solubility in organic phases by changes of the water activity by other solutes is reported. As example for the cooperativity effect of water H-bonds the influence of different cations on the interaction between water and aprotic solvents is studied. This gives a view on the role of water and its cooperativity on biochemical structures.

INTRODUCTION

Water plays an important role in the structure and behaviour of biochemicals; water dissolved in solvents is often a disturbing impurity. Studies of water/solvent mixture could help to optimize our knowledge of the anomalous properties of this unusual compound. In order to understand water/nonpolar solvent mixtures it is necessary to appreciate 1. the structure of nonpolar liquids and, 2. the structure of pure liquid water.

HOW COULD WE DESCRIBE LIQUIDS?

The use of simplified models of the bulk liquid state seems not unreasonable so long as the simplified ideal gas law is used. Such models giving good quantitative results are available for nonpolar liquids (ref. 1, 2) and for H-bonded liquids (ref. 3, 4). Corresponding to the ideal gas an ideal liquid can be defined (ref. 2) as a liquid having a linear relationship of T with decreasing density ρ_L . The ideal gas model is valid as better as higher T is compared with T_c (critical T). The ideal liquid model is better as lower T is compared with T_c or T_B (T_B : boiling T). The linear density - temperature relation is valid for nearly all nonpolar or weak polar liquids in a good approximation at $T < T_B$. The same straight line giving the liquid density at $T < T_B$ is at $T > T_B$ the sum $(\rho_L + \rho_V)$ for real liquids (ρ_V : density of equilibrium vapour). Therefore $x_F = \rho_L / (\rho_L + \rho_V)$ transfers the ideal liquid to a real one easier and more correctly as the real gas correction by van der Waals. This correction corresponds to the hole model of Eyring, but Eyring's model using the statistical thermodynamics is more complicate than our ideal liquid model with its real correction and calculating the mean values of caloric properties. This correction x_F gives a common function on the reduced scale T/T_c valid for most small molecules. It is difficult to understand why this liquid model is not used more often.

Scientists follow often to the fashion. The present fashion of liquid research is dominated by its look for partition functions. But the distribution functions of liquids have the same origin in thermal energy distribution as molecular velocities in gases. Since Boltzmann and Maxwell this gas partition is described by its mean value RT . Why the genial method is not applied on liquids too? T as one of the basic units of the SI system demonstrates the success of the RT -method gifted with genius. Similarly the distribution on the vibration levels of the intermolecular potential E_{11} (Fig. 1) could be averaged by an fictitious vibration level with the height RT . An intermolecular distance distribution corresponds to this average level RT . For orientation dependencies E_{11} depends on two coordinates, the distance r and the angle.

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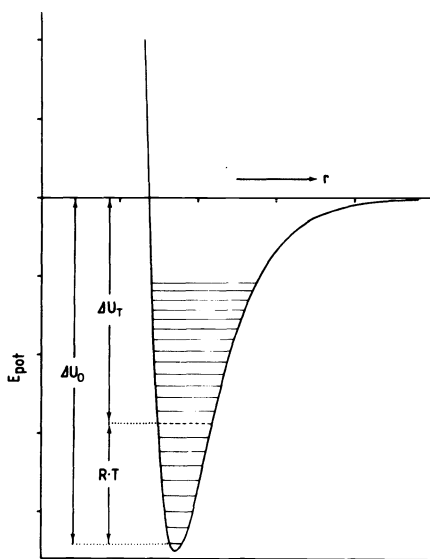


Fig. 1. The distance distribution in liquids described by an averaged level RT (dotted) of the intermolecular vibrations.

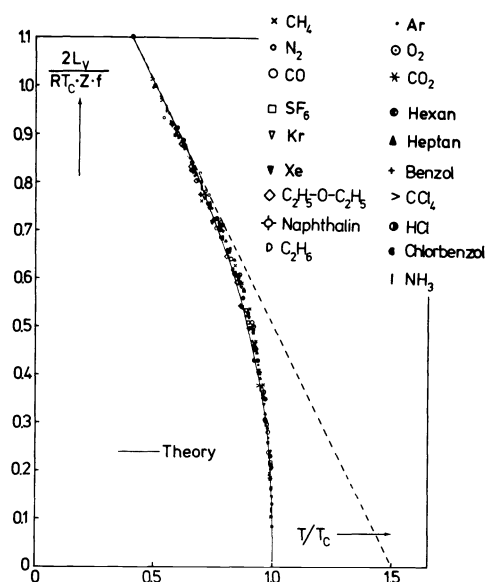


Fig. 2. Heat of vaporization L_v (points: experiments, full line: theory, dotted line: simplified eq. (1)) (ref. 1, 2).

The dissociation energy of an intermolecular dimer is $(E_{11} - RT)$. In condensed phases the interaction potential is given by $Z f' E_{11}/2$ where Z is the number of next nearest neighbours; or as an approximation by $Z f 3 RT_c/2$, with a factor f near 1 expressing the influence of higher next neighbours (ref. 5) and the proportionality between E_{11} and T_c (ref. 1, 2). The intermolecular interaction L_v of an ideal liquid is given by:

$$L_v = Z f R (3 T_c/2 - T)/2 \text{ for } T < T_B, \quad (1)$$

$Z f R/2$ denotes the specific heat of intermolecular degrees of freedom induced by the intermolecular potential curves of every neighbour (ref. 1).

For real liquids in equation (1) Z has to be corrected (ref. 1) when $T > T_B$ (T_B : boiling T) for the deviation of the linearity $(1 - x_p)$. x_p corresponds to the holes in Eyring's (ref. 6) hole model of liquids and can be understood as the simple deviation of the linearity of the ideal liquid. With such a correction equation (1) gives useful reduced formula of the heat of vaporization L_v with one adjusted constant, the coordination number Z (Fig. 2). In condensed media the sum of pair potentials must be taken into account. Such a model is shown in Fig. 3 and assumes 13 molecules at an average symmetric distance r around the centre of the coordination system (σ : molecule size parameter). The action on a central 13th particle as a function of the distance r to an outer-sphere particle gives, for a crystal at 0 K, a potential minimum at $r/\sigma = 1.122$ of size $Z/2 \epsilon$, and at higher T (or higher thermal vibrations expressed by an averaged distance r), a split in 6 minima (two minima plotted in the one dimensional plot of Fig. 3, and 6 in the two dimensional one in Fig. 4). The central particle can oscillate, with small activation energies, from one potential minimum to the neighbouring one. $Z(1 - x_p)$ is the reduction of the potential acting at higher r or higher T respectively (ref. 7). The three dimensional calculation with $Z = 12$ gives similar results. This estimation with nearly constant distance 1.122σ for the potential minima (Fig. 3), nearly the minima of the pair potential, teaches us why X-ray scattering produces a nearly constant distance for the first maximum in the pair distribution curves, and reduced areas of these maxima at higher T (i.e. reduced $Z(1 - x_p)$).

With these simple ideas the liquid's calorific properties such as, heat of vaporization (Fig. 2), specific heat, enthalpy of liquid or saturated real vapours, surface energy, Troutons rule, Stefans rule, Clausius Clapeyron equation, Nernsts vapour pressure rule etc. can be described nearly quantitatively (ref. 1, 2, 3), demonstrating that a reluctance to use liquid models is overstressed. The proportionality between interaction energy and coordination number Z in eq. (1) implies a cooperative effect (the energy to separate one molecular depends on the number of local defects) which may be the cause of certain stable small clusters of molecules - indicated by mass spectroscopy, and which influences the nucleation process of crystals and liquids.

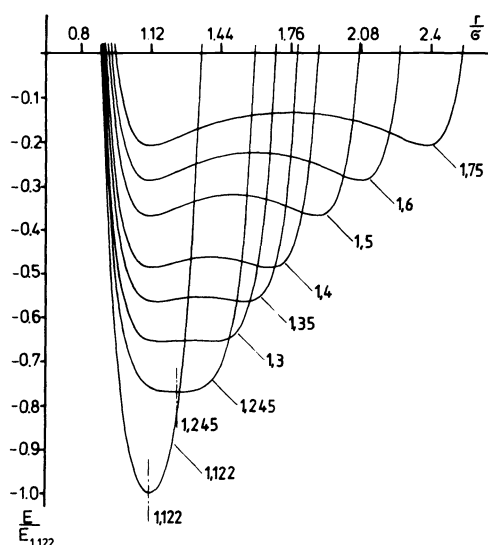


Fig. 3. Sum of 12 neighbours Lennard-Jones potential:

$$\frac{E}{4E_0} = \sum_{i=1}^{12} \left[\left(\frac{r_i}{\sigma} \right)^{-12} - \left(\frac{r_i}{\sigma} \right)^{-6} \right]$$

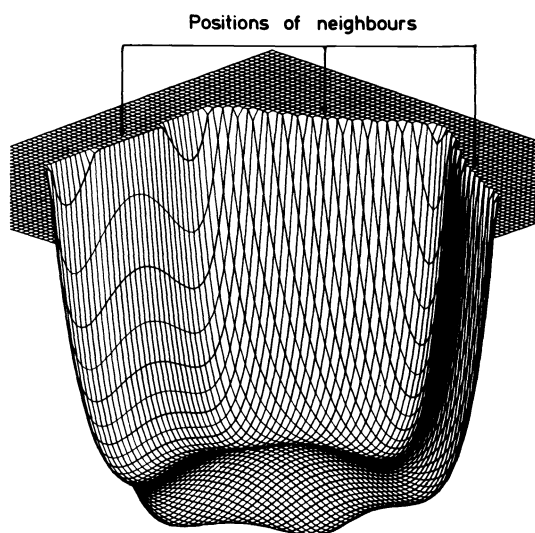


Fig. 4. Two dimensional plot of Fig. 3

For solutions or mixtures the intermolecular potential between different molecules 1 and 2 could be estimated by $E_{12} = (E_{11} E_{22})^{1/2}$ where heats of mixing depend on

$$\left[(E_{11} E_{22})^{1/2} - (E_{11} + E_{22})/2 \right] \cdot \frac{Z}{2} \quad (2)$$

This induces endothermic values for heat of mixing of nonpolar molecules. Since the geometric average (first term) is always smaller than the arithmetic one (second term) if $E_{11} \neq E_{22}$, the difference between both values becomes higher as E_{11} differs more and more from E_{22} . In dilute solutions of the solute 1 in solvent 2, E_{22} determines the energy to produce a "hole" for the solute. This could be the reason that two non-mixable solvents mix at higher T by more similar interaction energies and by $E_{ii} < RT$.

HOW COULD WE DESCRIBE WATER?

For an extremely associated liquid like water with an orientation dependent interaction energy the orientation defects O_F , the number of non-H-bonded OH groups abbreviated with "free OH", are an additional important parameter which determines the properties of liquid water. The density of water changes little up to 200°C; the percentage density change decreases with T as shown in Table 1. The estimated increase of averaged distances are shown in parenthesis.

TABLE 1. Density-, distance- and O_F -change of water

T (°C)	0	50	100	150	200
$-\Delta\rho, (\Delta r)$ (%)	0	1 (0.3)	4 (1.3)	8 (2.8)	14 (5)
O_F (%)	9.5	15.7	21.4	29	36

This means that the orientation defects, which can be determined spectroscopically (ref. 3, 4, 9), dominate the hole defects of nonpolar liquids. With the IR spectroscopically determined O_F values the anomalous properties of liquid water, (ref. 3, 4) or alcohols (ref. 3), 4, 8, 10) such as heat of vaporization, enthalpy, surface energy, specific heat, dielectric constant (ref. 11), density etc., are determinable by simple equations without adjusted parameters. This interesting result, together with the simple model of nonpolar liquids, also indicates that the description of calorific properties seems to be no more difficult

for liquids than for gases; dynamic properties could differ. The calorific properties of H-bonded liquids depend on the concentration O_F of non H-bonded OH, the H-bond energy ΔH_H , and the van der Waals energy ΔW . No adjusted constants are necessary apart from these values. ΔH_H can be determined spectroscopically (ref. 9, 12), and ΔW is available from the total energy, the sublimation energy ΔU_S , and ΔH_H .

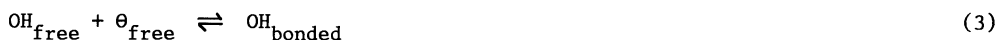
TABLE 2. Energy values in kJ/mol (θ : lone pair electrons)

	ΔH_H	ΔW	$\Delta H_H/\Delta W$	$C_{OH}(\text{mol/l})$	$C_\theta(\text{mol/l})$
Water	31	17	64 %	111	111
CH ₃ OH	16.7	23	42 %	24.7	49.4
C ₂ H ₅ OH	16.7	31	35 %	17.1	34.2
CH ₄	0	8.4	0 %	0	0

The van der Waals interaction energies of Table 2 agree with values from extrapolations of the heats of vaporization of H-(CH_n)_n - X compounds (ref. 13). Van der Waals energies per CH₂ group are nearly constant, about 4.1 kJ/mol (about 6.6 kJ/mol for CH₃). The solubility of water in nonpolar solvents depends on its ability to interact by van der Waals forces. But these are small compared with ΔH_H , the possibility of dissolved water in nonpolar solvents is dependent on the opening of H-bonds: the term E_{11} in eq. (2) is large compared with E_{12} . The different properties of mixtures with H-bond acceptor or donor molecules depend on the possibilities that in eq. (2) the hole production energy can depend on ΔW and ΔH_H but in mixtures nonpolar solvents with H-bonded solutes the interaction solvent-solute depends only on W with the solute, and if the solvent is H-bond acceptor and/or donor its H-bond energy with the solute has to be added. With a coordination number for water, near $Z = 4$ instead of 12, to optimize the H-bond orientation the energetic condition: $\Delta H_H + \Delta W = \Delta H_H + 4 W/2 > 12 W/2$ is expected: the values give 48 kJ/mol < 51 kJ/mol.

Nevertheless $Z = 4$ is preferred because $Z = 12$ would include some repulsion configurations such as OH..HO or $\theta.. \theta$. The H-bonded structure is favoured by both: favoured attractive configurations and non-favoured repulsion ones (ref. 8).

At room temperature the content of O_F in alcohols CH₃OH and C₂H₅OH is about 2.4 % and small compared with the water value of about 12 %. In the equilibrium



the proportion of lone pair electrons in alcohols is always in excess of 50 %, but in water $C_{OH} = C_\theta$ (compare the values in Table 2 at 20°C). The excess of "free" non H-bonded lone pairs of alcohols shifts the equilibrium (3) to the right. This effect has been demonstrated spectroscopically in water-alcohol mixtures at 20°C (Fig. 5). At 1400 nm the extinction coefficient, ϵ , per OH group of the spectrum decreases in a 1 : 1 molar mixture compared with the calculated spectrum.

In this region the non-H-bonded OH groups absorb. This decrease, at about 2 %, is similar to that observed when water is cooled to 5°C. The relatively higher concentration of C_θ free may be responsible for the equilibrium shift (3). The complicated spectrum change at higher wavelength corresponds to a change of the simultaneous excitation of two neighbouring OH groups of CH₃OH by one quantum (ref. 12) and CH/OH combination. This effect is favoured by H-bonds. As Fig. 6 demonstrates the viscosity η of these mixtures increases. The viscosity of a 1 : 1 mixtures corresponds to η of water at 5°C too.

H-bonds are cooperative. A second H-bond polarises an OH group and increases its H-bond energy (ref. 15, 16). Némethy and Scheraga (ref. 18) gave a theoretical model of liquid water with a cluster model having, at 273 K, a size of about 125 H-bonded molecules. This assumption seems to agree with the theory of cooperativity of H-bonds (ref. 15). Recently this cooperativity was experimentally established (ref. 16). Assuming an extreme cooperativity we attempted to estimate, together with the experimental values of O_F , the minimum sizes of such clustered H-bond networks. The values obtained were larger than Scheraga and Némethy have assumed, namely about 400 molecules at 273 K (ref. 3, 9).

In describing the solubility of hydrophobic molecules in water by equation (2) we must take into account that E_{11} is proportional to the energy required to produce a hole in water and would depend on $\Delta H_H + \Delta W$, but for the interaction energy with a nonpolar solute in E_{12} only the van der Waals energy of water W need be taken as E_{11}' in $(E_{11}' \cdot E_{22})^{1/2}$. That means $E_{11} \sim 3 \cdot E_{11}'$. As result, at 25°C, the solubility of CH₄ in propane is about 88 times that

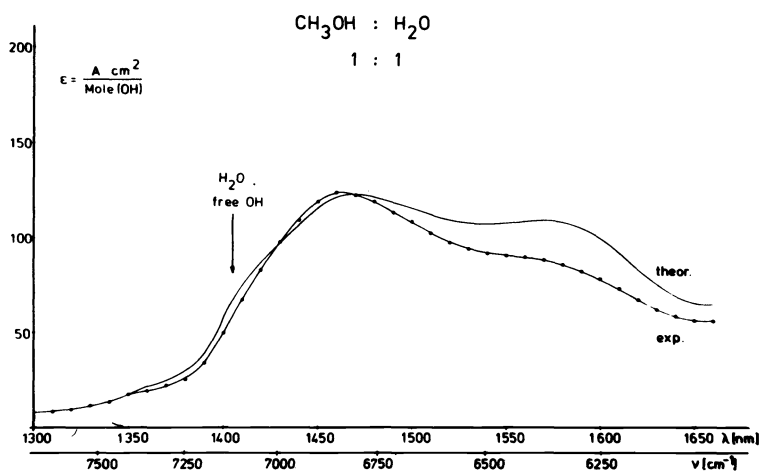


Fig. 5. The reduction of the extinction co-efficient at 1400 nm corresponds to a decrease of non-H-bonded OH groups in 1 : 1 alcohol/water mixtures by the excess of non-H-bonded lone pair electrons of alcohol (ref. 14).

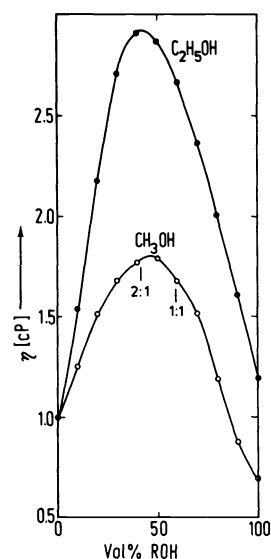


Fig. 6. Viscosity of water/ alcohol mixtures at 20°C.

in water, or 31 times greater in benzene than that in water (ref. 28), than we would predict that the van der Waals energy of OH is greater than that of one CH_2 -group.

The distribution of distances and H-bond angles in liquid water can be taken into account as in the model of nonpolar liquids with the scheme of Fig. 1. If so the intermolecular interaction energy in liquid water is (ref. 3):

$$L_V = \Delta U_S - \Delta H_{\text{H}O_F} - (2 + O_F) RT + RT (1 - x_F) \frac{3}{2} \quad (4)$$

$$\Delta U_S = \Delta H_H + \Delta W$$

The 3rd term corresponds to the average vibration level of the intermolecular degrees of freedom (like the dotted line in Fig. 1) or the heat content of the $Z/2$ intermolecular degrees of freedom with

$$Z = 4 (1 - O_F) + 6 O_F = 4 + 2 O_F \quad (5)$$

Here the term $4 (1 - O_F)$ shows the intermolecular degrees of freedom between H-bonded OH groups and $6 O_F$ of the non-H-bonded OH, assuming a coordination number of 6 around them (ref. 3). The last term in equation (4) corresponds to the excitation of translation in the vapour state and its hindrance in real gas state. This last term is to taken into account near T_c .

SOLUBILITY OF HYDROPHOBIC MOLECULES IN WATER

In consequences of the van der Waals forces of water which we infer in Table 3 for the solubility of small hydrophobic molecules in water at 60°C is proportional to T_c of the solute (Fig. 7). T_c is a measure of the van der Waals interactions (ref. 1, 2, 19). But the solubility of hydrophobic molecules in water depends on two parameters (ref. 20): 1. the pair potential of the hydrophobic solute and 2. its size. These two parameters are indicated by T-dependence of the solubility minimum in mixtures nonpolar solute/water (ref. 17, 20), (Fig. 8). The position of this minimum depends on the pair potential of the solute (Fig. 8). At temperatures below this minimum the solubility decreases normally as the Boltzmann distribution expects. But at higher temperatures the solubility increases again indicating that the higher disturbance of the H-bond network of water favors the acceptance of guest molecules. If the interaction energy of the solute is high this condition is less important. The acceptance of a guest molecule because of relatively low van der Waals interaction energies could be favoured by the formation of a pentagon-dodecahedral group of 20 H-bonded water molecules.

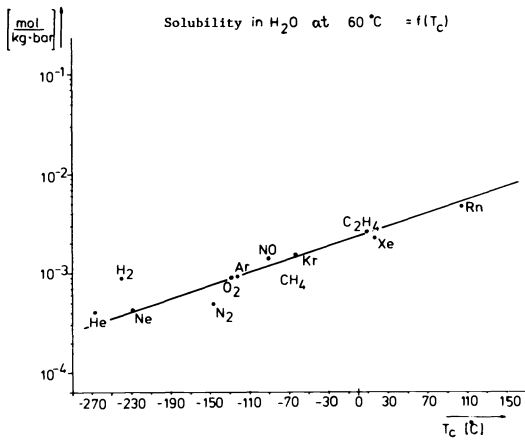


Fig. 7. Solubility coefficient of small molecules in water depends on their T_c (T_c : critical temperature).

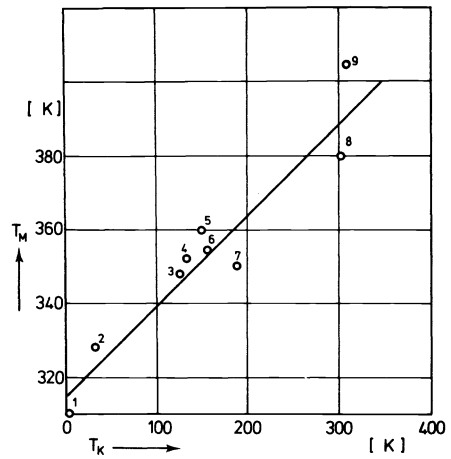


Fig. 8. T_M : solubility-minimum $\frac{da}{dT} = 0$

1 He 2 H₂ 3 N₂
4 CO 5 Ar 6 O₂
7 CH₄ 8 CO₂ 9 N₂O

This requires only a small deviation of the maximum H-bond angle if the axis of protons and lone pair electrons are antiparallel. In the pentagon-dodecahedron (see Fig. 9) water forms five membered rings instead of the six membered rings of the ideal ice tridymite structure. These pentagon-dodecahedron, known by X-ray scattering of gas-hydrates, form holes of a size similar to those of the Stuart - Briegleb models in while one benzene molecule could be included. Within such holes guest molecules would have a coordination number $Z = 20$ to H₂O, thus favouring the solubility energy. Table 3 demonstrates the decrease of solubility of saturated organic molecules with increasing size of solutes (Fig. 10).

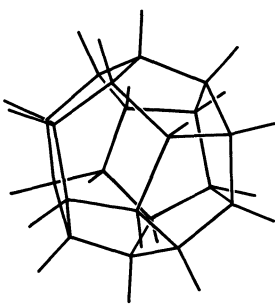


Fig. 9. Model of the pentagon-dodecahedron, arrangement of 20 H₂O in gashydrates.

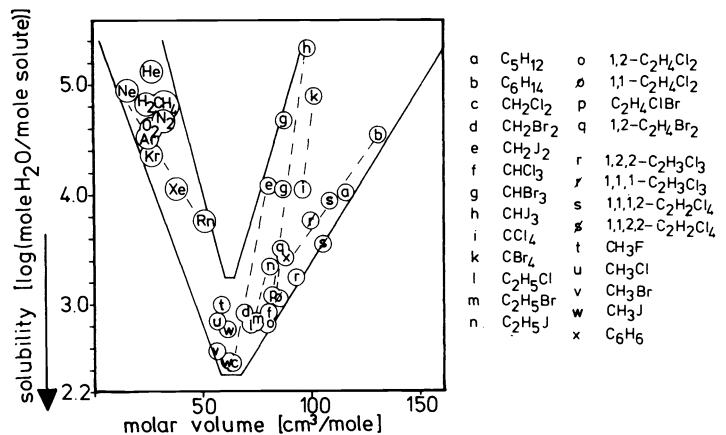





Fig. 10. Reciprocal solubility of non-polar molecules in water (20°C) as function of the molar volume of the solvent (ref. 31).

In Fig. 10 the log of the reciprocal solubility of hydrophobic molecules in water (log (mole H₂O/mole solute)) at 20°C as function of the molar volume of the solute is plotted (ref. 31). To compare solubility and interaction energies the logarithm of the solubility has to be taken by its proportionality with the free energy. Below the minimum (maximum solubility) the solubility depends mainly on the van der Waals potential of the solute. Above the minimum the work to produce bigger holes may dominate the solubility mechanism. The position of the minimum in Fig. 10 corresponds to a molecular size of about $4.5 \cdot 10^{-8}$ cm; the diameter of the hole of the pentagon-dodecahedron (Fig. 9) is also about $4.5 \cdot 10^{-8}$ cm. Above a certain molecular diameter the solubility decreases strongly (ref. 31, 32).

TABLE 3. Solubility solvents (1) in water

	Solute	T(°C)	$x_1 \cdot 10^6$	$C_c (\text{Mol/l}) \cdot 10^3$	Reference
C ₂ H ₆	CH ₃ -CH ₃	25	36	1.1	(34)
C ₆ H ₁₄	CH ₃ -CH ₂ -C-(CH ₃) ₃	25	4.97	0.276	(22)
C ₆ H ₁₄	CH ₃ -(CH ₂) ₄ -CH ₃	20	2.95	0.162	(21)
C ₇ H ₁₆	CH ₃ -(CH ₂) ₅ -CH ₃	20	3.07	0.17	(22)
C ₈ H ₁₈	(CH ₃) ₂ -(CH ₂) ₂ -CH ₂ -CH-(CH ₃) ₂	25	0.362	0.0202	(23)
C ₈ H ₁₈	(CH ₃) ₂ -C-CH ₂ -CH ₂ (CH ₃) ₂	25	0.323	0.018	(23)
C ₈ H ₁₈	CH ₃ ² -(CH ₂) ₆ -CH ₃	25	0.134	0.0074	(23)
C ₉ H ₂₀	CH ₃ -C-(CH ₂) ₂ -CH-(CH ₃) ₂	25	0.0758	0.0041	(24)
C ₆ H ₁₀		20	48	2.68	(21, 22)
C ₈ H ₁₀	 -CH ₂ -CH ₃	25	30	1.66	(23)
C ₆ H ₆		25	131	7.3	(27)

Double bonds act as weak H-bond acceptors, and groups like Cl with higher interaction energies increase the solubility (Table 3). The solubility of small hydrophobic molecules in water at 20°C (in 10^{-3} mol/l, CH₄:1.44; C₂H₆: 2.05; C₃H₈: 1.6) is in the range of the concentration of water molecules in saturated H₂O vapour i.e. $1.28 \cdot 10^{-3}$ mol/liter at 25°C. The solubility of such small molecules in water could be imagined as an exchange process between water monomers and perhaps some small water aggregates. The low solubilities of nonpolar molecules in water do not agree well with the cluster model of water. If the non-H-bonded OH groups of water were concentrated on the surface of H-bonded clusters we might expect a better solubility of hydrophobic molecules in these defect areas. We could assume that the non-H-bonded OH groups are distributed in the H-bonded network and therefore the energy to produce hole for guest molecules in water depends not only on ΔW but also on ΔH_H .

The solubility of CH₄ in water is about 1/88 of its solubility in C₃H₈ or 1/33 of in benzene. This is not a lag of Waals forces of water but the necessity of opening H-bonds of water for the solute. The solubility of Ar at 25°C in CH₃OH or C₂H₅OH is similar to that in acetone or benzene about $1.1 \cdot 10^{-2}$ mol/l, but $1.5 \cdot 10^{-3}$ mol/l in water⁶ (20°C). In alcohols guest molecules could be included between the hydrophobic CH groups without opening H-bonds.

The content O_F of non-H-bonded OH groups is such that there is a probability that one OH group of H₂O is non H-bonded. The probability that all 4 possible H-bonds of one H₂O are not bonded (monomers) could be assumed (Stanley) as O_F . These values, the fraction of monomers in liquid water N_{liq}/N_{liq}^{mo} are plotted as dotted line in Fig. 11. At 25°C we get with the spectroscopic O_F -value: $O_F^{mo} = 0.00029 \cdot 55.5 \text{ Mol/l} = 0.016 \text{ Mol/l}$. Full line in Fig. 11 also contains the ratio of molecules N_{vap} to N_{liq} in the saturated vapour state. If we assume $N_{vap}/N_{liq}^{mo} = \rho_{vap}/(\rho_{vap} \cdot O_F^{mo}) = \exp(\Delta H_{mo}^{vap}/RT)$ we can estimate from the Fig. 11 the heat of vaporization of water monomers as $\Delta H_{mo}^{vap} \approx 7.6 \text{ kJ/mol}$.

In Eyring's hole model the N_{vap} is equal to the hole concentration in the liquid (ref. 2, 6). In a solubility model we can assume that these holes accept solute. Naturally this simplified model must be corrected by the heats of solution. On the other hand we can assume that water monomers are in equilibrium with other solvents and are correlated to the water solubility in the solvent. In this simplified assumption we assume that the network of H-bonded molecules has little influence on the water solubility only the few monomers and dimers etc. can take part.

SOLUBILITY OF WATER IN SOLVENTS

Solubility of water in hydrophobic solvents

To solve water (ref. 11) in unpolar solvents (ref. 21) instead eq. (2) the solution energy is $\sim Z_{12}(E_{22}W_{11})^{1/2}/2$ but the energy to produce holes is $\sim(Z'E_{22}/2) + Z''(\Delta H_H + W_{11})$. The table 4 shows the solubility of water in some organic hydrophobic solvents at 20°C or 25°C. The table demonstrates that the molefraction x_2 of water in a mixture is not a good measure of solubility but the molar concentration of water. We get similar values of about $3 \cdot 10^{-3}$ mol water/liter solvent and in nearly all cases in the table water interacts similarly to CH₂ or CH₃ groups. The averaged solubility of table 4 is not far from the equilibrium vapour concentration of $p = 1.28 \cdot 10^{-3}$ Mol/l (25°C). We might assume that the monomers in liquid water namely determine the solubility equilibria. The network of H-bonded molecules can be assumed not to be involved much in the solubility.

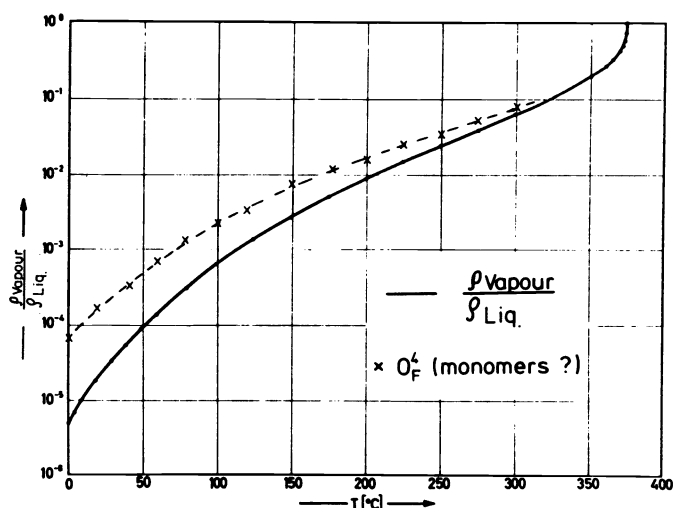


Fig. 11. Dotted: O_F^4 (monomers of water ?)

Full line: $\frac{\rho_{\text{vap}}}{\rho_{\text{liq}}}(\text{H}_2\text{O}) = \frac{N_{\text{MO}}}{N_{\text{liq}}}$

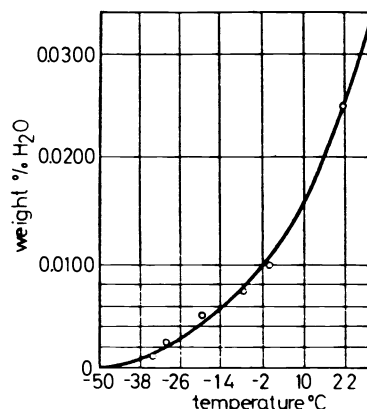



Fig. 12. Solubility (weight-%) H_2O in $\text{CHCl}_3 = \text{CCl}_2$ (ref. 33, 34).

TABLE 4. Solubility H_2O (2) in solvents

Solvent	$T(^{\circ}\text{C})$	$x_2 \cdot 10^4$	$C_{\text{H}_2\text{O}}(\text{Mol/l}) \cdot 10^3$	Reference
C_6H_{12} 	25	3.5	2.9	(25)
C_6H_{12} $(\text{CH}_2)_7\text{-CH-CH}_2\text{-CH}_3$	20	3.7	3.21	(26)
C_6H_{14} $\text{CH}_3\text{-(CH}_2)_4\text{-CH}_3$	25	3.7	2.85	(21)
C_6H_{14} $\text{CH}_3\text{-CH}_2\text{-C(CH}_3)_2$	25	4.02	3.02	(23)
C_8H_{18} $(\text{CH}_2)_2^2(\text{CH})_2\text{-CH}_3\text{-CH-(CH}_3)_2$	25	4.69	2.95	(23)
C_8H_{18} $\text{CH}_3\text{-(CH}_2)_3\text{-CH}_3$	25	4.8	4.18	(26)
C_7H_{16} $\text{CH}_3\text{-(CH}_2)_5\text{-CH}_3$	25	5.06	3.42	(24)
C_6H_{18} $\text{CH}_3\text{-(CH}_2)_6\text{-CH}_3$	25	5.01	3.07	(23)
C_8H_{18} $(\text{CH}_2)_3\text{-C-CH}_2\text{-CH-(CH}_3)_2$	25	5.07	3.06	(23)
C_9H_{20} $(\text{CH}_2)_3\text{-C-(CH}_2)_2\text{-C-(CH}_3)_6$	25	5.34	2.95	(23)
C_9H_{20} $\text{CH}_3\text{-(CH}_2)_7\text{-CH}_3$	25	5.6	3.15	(24)
$\text{C}_{10}\text{H}_{22}$ $\text{CH}_3\text{-(CH}_2)_8\text{-CH}_3$	25	5.7	2.92	(24)

In the temperature range 0 to 25°C the solubility of water in other solvents increases with T , reflecting the increase of the monomer content in liquid water, or p_s of water. In agreement with this simplified solubility model the solubility moles of water s per liter of $\text{CHCl}_3 = \text{CCl}_2$ at 20°C is equal to the water vapour concentration p_s in mole/l, and the T -dependence of the solubility of water in $\text{CHCl}_3 = \text{CCl}_2$ is nearly the same as the T -dependence of p_s (Fig. 12) (ref. 33, 34).

Molecular polarization by intermolecular interactions






Simple estimations of intermolecular effects with E_{12} etc. suppose the molecules to be rigid but this is not really the case. Using infrared intensities in the fundamental and overtone regions we have calculated (ref. 29) the first and second dipole moment derivatives $\partial\mu/\partial q$ and $\partial^2\mu/\partial q^2$. We expect the same effects on the OH groups of water or the butanol OH oscillator. Both derivatives change by simple van der Waals solvent effects.

$\partial\mu/\partial q$ increases with increasing van der Waals forces of the solvent, and $\partial^2\mu/\partial q^2$ decreases similarly (in table 5 the more probable \pm solution is taken). The integrated I.R. intensity of the OH fundamental stretching band of monomeric *t*-butanol increases (ref. 29, 30) from the vapour state to the solution in CCl_3CH_3 from $0.84 \cdot 10^6$ to $5.62 \cdot 10^6$ (cm mol^{-1}). Both effects are caused by polarization of the OH by the solvents. Parallel to the intensity change a frequency shift is observed (ref. 30), due to a change of the OH bond potential. This observation corresponds to the known solvent effect on chemical reactions usually described in chemistry by solvent parameters. The OH frequency shift of alcohols by solvents in the region $100 \text{ K} < T < 360 \text{ K}$ is: $\Delta\nu = \Delta\nu_0 - aT$ corresponding eq. (1) (ref. 30, 35).

TABLE 5. The dipolemoment derivatives of monomeric t-butanol in solvents (ref. 29).

	vapour (35°C)	Hexane	Cyclohexane	CCl ₄	Cl ₃ C-CH ₃
$\partial\mu/\partial q$ (10°C)	0.47	0.86	0.89	1.00	1.14
$\partial\mu/\partial q$ (60°C)		0.80	0.81	0.95	1.10
$\partial^2\mu/\partial q^2$ (10°C)	-1.01	-0.95	-0.84	-0.77	-0.64
$\partial^2\mu/\partial q^2$ (60°C)		-0.94	-0.84	-0.78	-0.64
T _c (K) (Solvent)		507.6	553.5	556.3	

TABLE 6. Water solubility in weak H-bond acceptor liquids

	Liquid	T(°C)	x ₂ ·10 ³	C _{H₂O} (Mol/l)·10 ²	Reference
C ₆ H ₁₂	H ₂ C=CH-(CH ₂) ₃ -CH ₃	20	1.6	1.08	(21)
C ₇ H ₈		20	1.8	1.8	(26)
C ₆ H ₁₀		20	1.9	1.9	(21)
C ₈ H ₁₀		25	2.5	2.1	(23)
C ₈ H ₁₀		25	2.6	2.3	(23)
C ₆ H ₁₀	H ₂ C=CH-(CH ₂) ₂ -CH=CH ₂	20	4.37	3.68	(27)
C ₇ H ₁₄	H ₂ O=CH-(CH ₂) ₄ -CH ₃	25	5.68	3.7	(27)
C ₆ H ₆		23	3.02	2.98	(28)

The amplitudes of the OH vibrations of H₂O change with different H-bond acceptors (Fig. 15); parallel reactivities change.

Solubility in solvents with weak H-bond acceptors

Double bonds or aromatic systems are known as weak H-bond acceptors. Corresponding by the water solubility in such solvents is higher because of the bigger interaction energies compared with nonpolar solutes (see Table 6). (To $(E_{11}E_{22})^{1/2}$ in eq. (2) the H-bond energy ΔH_{12} water/H-bond acceptor has to be added).

Double bonds, which act as weak H-bonds acceptors increase the solubility by a factor of about 10 (compare table 4 and 6). They reduce the energy lag between the water H-bond network in liquid state and the nonpolar solvent. Contrary to table 5 in weak H-bond acceptor liquids the water concentration (table 6) does not describe the water solubility better than x₂. The increase of the unsaturated solvent solubility in water is parallel to the increased solubility of water in the same solvent. The reason is that the same pair interaction E₁₂ is an important factor in both cases. The water solubility in solvent is usually bigger than that of the solvent in water because of the greater energy needed to produce a hole in the water H-bond system larger enough to include a relatively big organic molecule.

Solubility of water in hydrophilic solvents

A still higher solubility increase of water could be induced by stronger H-bond acceptor groups. If both components 11 and 22 are H-bond donors in eq. (2) the hole production energy is now $\sim [Z'/2 W_{11} + \Delta H_{11} + Z''/2 + \Delta H_{22}]$. Fig. 13 demonstrates this solubility increase (n = mol H₂O / mol solvent) at 25°C from toluene (n = 0.0025), to valeronitrile (n = 0.07), to CH₃-n-pfopylketone (n = 0.13), to pentanol (n = 0.65) up to the mixible system water / diethylamine. The band maxima shift to smaller frequencies ν , corresponds to the so called Badger-Bauer rule: $\Delta\nu \sim \Delta H_H$. Fig. 13 shows that: $n \sim \Delta H_H$.

The water solubility n in different alcohols (Fig. 14 at the bottom with log scale at the left) depends on the size of hydrophobic chains (increasing from the left to the right). In ternary-alcohols (upper dotted curve at the bottom of Fig. 14) n is bigger compared with secondary or primary-alcohols. In ternary-alcohols the content of H-bonds is lower compared with other alcohols because of steric hinderance. The non H-bonded OH groups in ternary-alcohols induce a high negative part of the solubility energy of water of forming H-bonds in water / ternary-alcohol. The Fig. 14 is an other example of the parallelism between

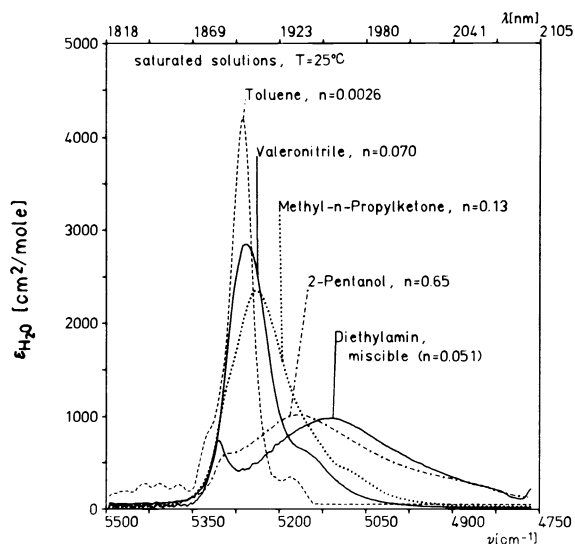


Fig. 13. Overtone OH band shifts $\Delta\nu$ of H_2O saturated in solvents is parallel to ΔH_{H} and to the water solubility n in solvents (ref. 31).

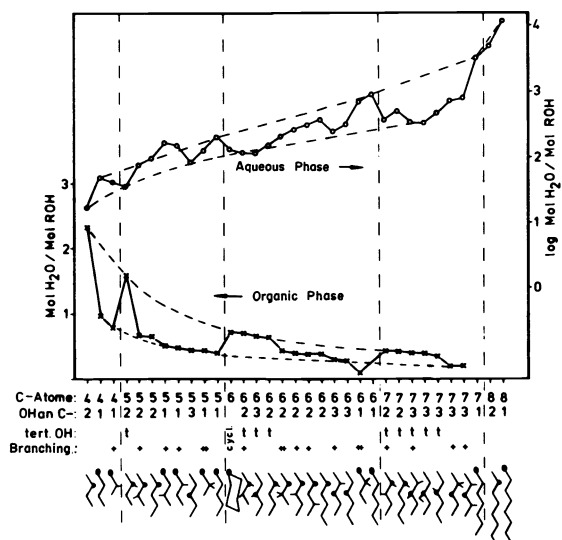


Fig. 14. Water solubility in solvents (at the bottom and left log-scale) and reciprocal solubility of solvent in water (at the top and right log-scale) have mirror symmetry (ref. 31).

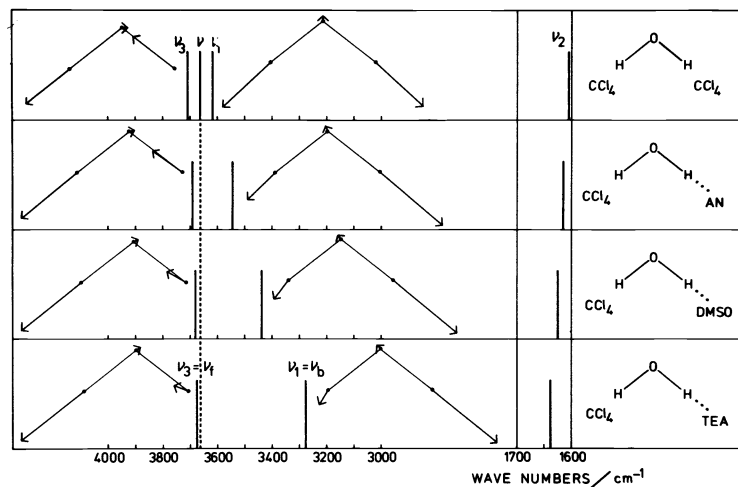


Fig. 15. As the figure demonstrates in ternary systems/water/hydrophilic H-bond acceptors/ CCl_4 with small solvent concentrations: 1:1 complexes with only 1 OH H-bonded exists. In this case the ν_1 band shifts to smaller ν_1 proportional to ΔH_{H} , and the amplitude of the vibration motion becomes unsymmetric (ref. 36, 37). The ν_3 -band shifts less but amplitude becomes unsymmetric also. A different reactivity of H_2O could be the consequence.

good solubility of water in solvents to good solubility of solvents in water (in Fig. 14 curves at the top and right scale give the reciprocal solubility of alcohols in water in mole H_2O per mole alcohol).

System: water/polyethylenoxides

Polyethylenoxides with hydrophobic endgroups are important industrial compounds as surfactants, dyeing levelling agents (ref. 38, 39), protective colloids etc. They are an interesting system for the study of the two phase formation of water / hydrophilic solvents (ref. 40). These compounds are water soluble at low temperature because of the H-bonds between water and the ether groups and the OH end-group. Depending from the hydrophilic / hydrophobic balance determined by the number n of ethyleneoxides groups above a turbidity temperature T_K , a separation into two phases occurs. In Fig. 17 T_K of aqueous solutions without salts is given. The position of T_K is sensitive to ionic additives and corresponds to the position of the ions in the Hofmeister or lyotropic ion series (ref. 40). This series can be identified spectroscopically as a series changing the H-bond system of liquid water (ref. 41). Ions which weaken the H-bonds of water (ref. 41) (structure breakers) increase T_K , corresponding to an increase of non H-bonded or weak H-bonded OH groups (ref. 41). Increasing O_{F} means increasing the solubility behaviour of water, i.e. water becomes more hydrophilic. Ions which strengthen the H-bonds (ref. 41) decrease T_K , corresponding to a smaller content of free OH in water and reducing the solubility property of water.

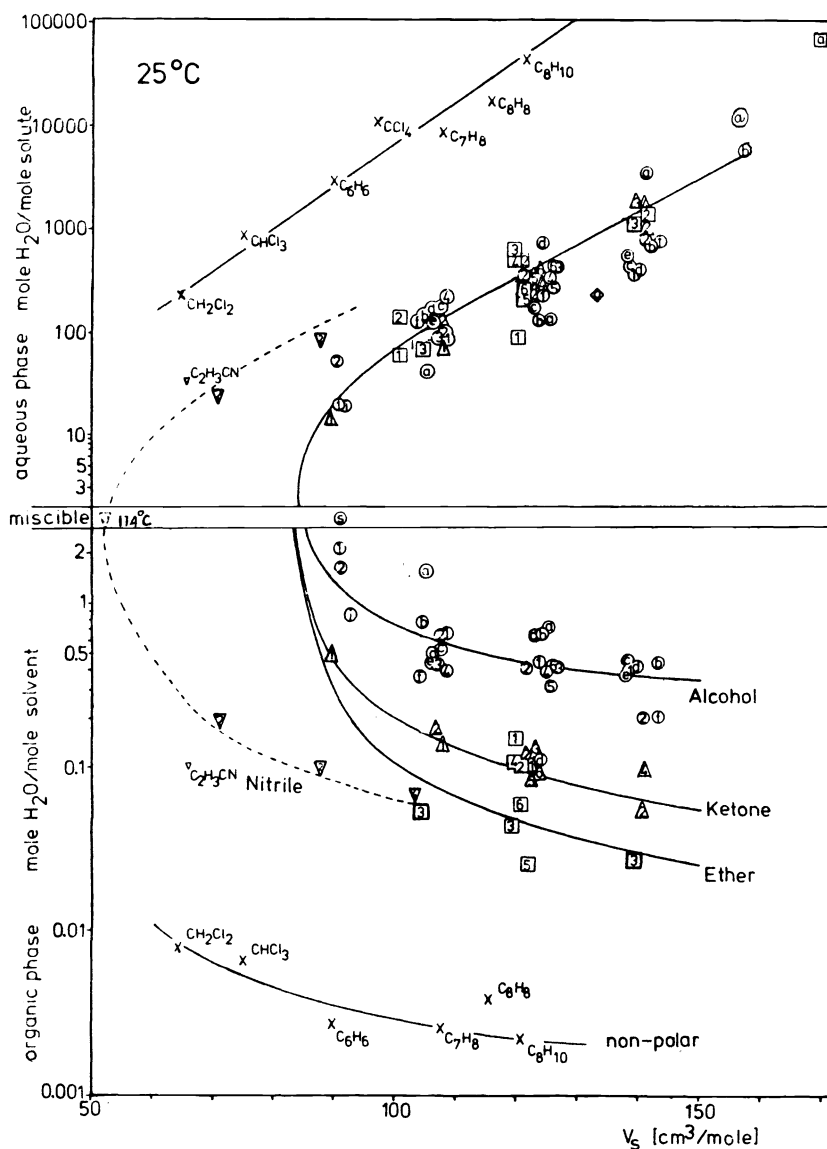


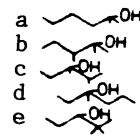
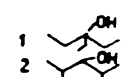
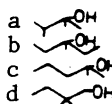
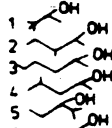
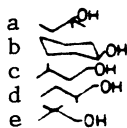
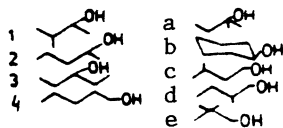
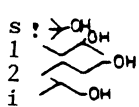
Fig. 16. Other examples of mirror symmetry between the water solubility in organic solvents (at the bottom) and the reciprocal solubility of the same solvents in water (at the top) as a function of the molar volume V_s of the solvent. The symbols for different V_s are as follows:

V_s - 91 cm³/mole

V_s - 105 cm³/mole

V_s - 123 cm³/mole

V_s - 140 cm³/mole



These symbols defined for C-O-H are also valid for C=O and -O- (ref. 31).

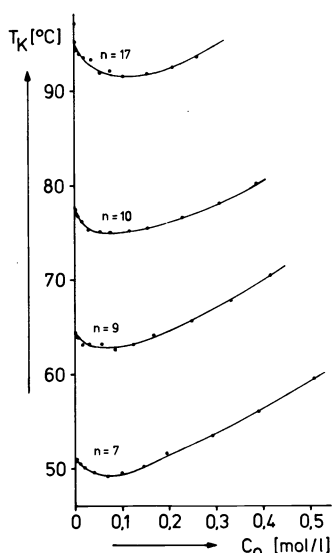


Fig. 17. Turbidity point T_K of $\text{iso-C}_8\text{H}_{17}\text{-C}_6\text{H}_4\text{-(O-CH}_2\text{-CH}_2\text{)}_n\text{-OH}$ in water

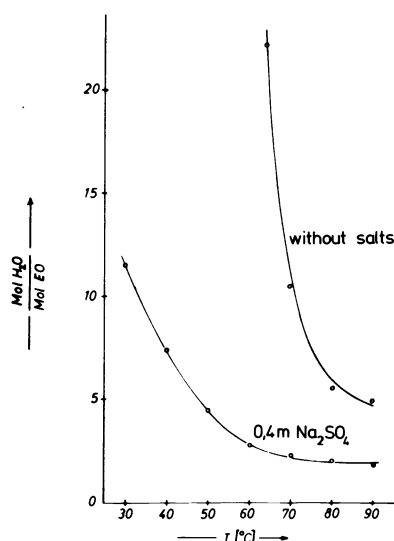


Fig. 18. Water content of the organic phase of $\text{i-C}_8\text{H}_{17}\text{-C}_6\text{H}_4\text{-(OCH}_2\text{CH}_2\text{)}_n\text{OH (ON)}$ without and in presence of Na_2SO_4

The water content of the organic phase above T_K decreases with T , going asymptotic to a water content of 2 H_2O per ether oxygen (Fig. 18). This asymptotic value of the dihydrate is obtained by increasing the concentration of structure-making ions (ref. 40). Heusch (ref. 42) has observed different stoichiometric hydrates of aqueous solutions of *p*-isononyl-phenol-decaglycolether already. Below T_K liquid crystal type structures of different H_2O /ether stoichiometries depend on T and the solute concentration.

Klein (ref. 14, 43) observed by I.R. overtone spectra, frequency shifts of the water combination band with an optimal shift at 25°C of the hydrate: 4 H_2O per ether and at 60°C at water concentration of the dihydrate. The *para*-isooctyl-phenol-nonaglycolether has a high viscosity maximum in aqueous solutions of the tetrahydrate at 30°C, and the dihydrate at 60°C (ref. 40). The I.R. spectra of such solutions show a decrease of water bands due to strong H-bonds, and an increase of bands due to medium strength H-bonds (ref. 43). With the Badger-Bauer rule we would expect with this decrease of the H-bond interaction energies that these solutions, like many solutions of organic solutes in water, should be endothermic. The entropy effect should dominate this solubility. Correspondingly Lauffer has called phenomena like demixing at higher temperature "entropy driven processes" (ref. 44, review ref. 45). Such processes, favoured at higher temperature, may be of importance in some biochemical observations like: polymerisation of tobacco mosaic protein (ref. 46), or sickle cell protein (ref. 46), deviation of fertilized eggs, formation of pseudopodia (ref. 46) or gelformation of collagen, rabbit skin tropocollagen soluble in water at 4°C, and forming collagen-fibres at 37°C (ref. 46, 47), or transition temperature of 0.5 % ribonuclease (ref. 48). This transition T is sensitive to electrolytes like the turbidity point of poly-ethylenoxides and corresponds to the Hofmeister ion series. Similar salt effects are known on the solubility of thymine, adenine (ref. 49), poly-proline (ref. 50, 51) transition- T of DNA (ref. 40, 52, 53) etc.

Ion effects

Added salts change the mutual solubility of water / octylphenol-nonaglycolether (ON) in the two phase region (ref. 58). The "mirror symmetry" of both solubilities is also observed in these systems "Structure breaking" ions increase the mutual solubility in both phases above T_K by a weakening of the H-bond structure. Structure makers decrease the solubility of the solute in both phases (ref. 58).

Anions act on water in a similar way to H-bonds (ref. 56). Cationic interactions are mainly stronger than anionic ones. This can be determined in the systems water / aprotic solvent / salt in the stoichiometric ratio 1 : 2 : ca. 100 (ref. 16). Cations induce higher water / aprotic solvent H-bonding by polarization of the OH group (ref. 16) (H-bond cooperativity). The relative frequency shifts $\Delta\nu/\nu$ of the water OH-bonded to the solvent (measured in binary systems) depend on the cations for the cooperative part $\Delta\Delta\nu/\nu$ (Fig. 19). These cation induced effects are (in per cent of $\Delta\nu/\nu$): Mg^{2+} (140); Li^+ (69); Ba^{2+} (65); Na^+ (45); K^+ (10).

This specific cation induced amplification of H-bonds water / solvents may play a role in biological systems. Cations could induce specific strengthening of the biopolymer hydration. Poisonous effects of heavy metal cations could be correlated to its too by strengthening of the hydrates.

Anions effects on ethylenoxides may act mainly through changes in the water H-bonds. Anions determine the turbidity point T_K of ON. Cations may influence the hydration of ON to give a second order effect on T_K in °C of the ON. ON solubility in water is the sum of the small solubility of the monomers (at 25°C, $5.5 \cdot 10^{-3}$ mol/l of octylphenol-25-glycoether; $7.1 \cdot 10^{-5}$ of 0-40-gly) and the micell concentration which starts about $2.2 \cdot 10^{-3}$ mol/l of 0-25-gly and at $3.3 \cdot 10^{-5}$ mol/l of 0-40-gly (ref. 38, 39). The hydrophobic micell nucleus can solubilize other hydrophobic solutes (ref. 38, 39).

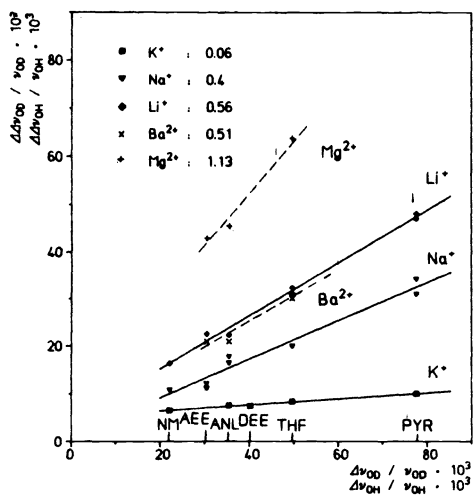


Fig. 19. Cation induced strengthening $\Delta\Delta v/v$ of the H-bond shift $\Delta v/v$ of binary systems water / aprotic solvents. 25°C (ref. 57).

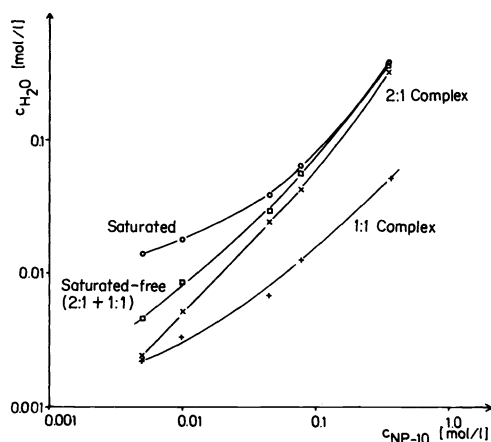


Fig. 20. Curve at the top total H_2O solubility in CCl_4 / NP 10. 2nd curve from the top hydration water of NP 10. 25°C (ref. 43).

Carrier effect for water solubility in unpolar solvents by H-bond acceptors

The water solubility in nonpolar solvents can be increased by hydrophilic molecules like p-isononyl-phenol-decaglycoether (NP 10). It increases the water solubility in CCl_4 at 25°C from $0.93 \cdot 10^{-2}$ mol/l by formation of some complexes $2 H_2O : 1 NP 10$. (see Fig. 20 third curve from the top, see the dihydrate in the preceding chapter) and some $1 H_2O : 1 NP 10$ (Fig. 20 lowest curve) (ref. 49). Unexpectedly the 10 ether groups of NP 10 solubilize in CCl_4 , not more than $1 H_2O$ per $1 NP 10$ (ref. 43). Probably the second OH group of H_2O induces difficulties for the NP 10 carrier effect.

Preferred di- or tetrahydrates (ref. 40) of NP 10 can be shown too by density or IR spectra (ref. 43). They may be stabilized by preferred H-bond angles and by less disturbances of the H-bands in the neighbourhood of hydrophobic CH_2 -groups. Such preferred hydrates seem to be a general phenomena which is not recognized enough: so in the two phase region of water-nicotine two H_2O are per nicotine in the organic phase; solubility of water : cyclohexanol is at 0°C 1:2; Fig. 6 shows a $2 H_2O : 1 CH_3OH$ complex; M.Symons demonstrated stoichiometric hydrates of Et PO, Me_2CO , $M\acute{E}CN$ at the Leuven conference.

Water in polymers

Water in polymers is a broad field of its own. Some indicators are given: Water acts in 6-nylon as plasticizer for dyestuff diffusion (ref. 39); the water diffusion in nylon is concentration dependent (ref. 58). For water in collagen or in cellulose acetate membranes it could be shown, two different water forms: 1. hydrate water as polymer monolayer and 2. liquid like water as higher water layers (ref. 58, 62, 64). The liquid like water seems to be of importance for the photosynthesis or for growing processes in biopolymers etc. The separation process of sea water desalination membranes seems to depend on the smallness of the liquid like water layer, thin enough that the big hydration shell of ions have not room enough. Spectra of solid hydrates have demonstrated that the ion-water interaction is not far from the water - water interaction (ref. 63), meaning that the hydration energies of ions are given by a group of water molecules in the hydrate sphere. This group of H_2O determines the salt-solubilities.

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