

Studies of the Hydrogen Bond

I. Influence of Double Bond on Associates between Ethers and Water

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A comparison of the solubility in water of diethyl ether and the corresponding unsaturated compound, divinyl ether, exhibits a striking difference: at 37° C the solubilities are

diethyl ether ¹	0.632 mole l ⁻¹
divinyl ether ²	0.056 mole l ⁻¹

The low solubility of the unsaturated compound is also found in other cases, *e. g.*

cyclopropyl ethyl ether ³	(27° C) 0.25 mole l ⁻¹
cyclopropyl vinyl ether ⁴	(25° C) 0.08 mole l ⁻¹

A more lipophilic character of divinyl ether is consistent with the fact that it has a higher oil/water distribution coefficient, and that it can anesthetize at a lower concentration than diethyl ether². In this connection its ability to induce liver necrosis is of interest. This ability is not present in diethyl ether but is present in more lipophilic compounds, *e. g.* chloroform⁵, benzene⁶, and furan⁷.

This study comprises an experimental orientation in the properties of the two-component systems diethyl ether — water and divinyl ether — water. From the data collected an attempt will be made to explain the effect of the double bond on the solubility and to elucidate the »hydrogen bond» concept*.

* For the discussion on this point see the following publication⁸.

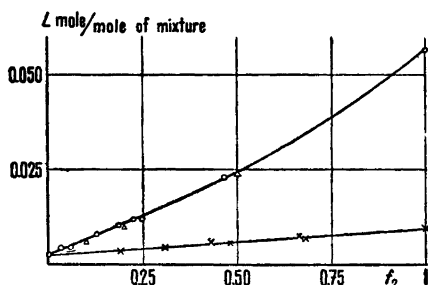


Fig. 1. Solubility of water, L , in benzene—ether mixtures as a function of the mole fraction of ether, f_2 .

× — Benzene—divinyl ether as solvent.

○ — Benzene—diethyl ether as solvent.

○ — Measured values

△ — Values calculated from equ. (3).

SOLUBILITY DETERMINATIONS

The solubility of water in ether—benzene mixtures was determined. In Fig. 1 the solubility of water, L , expressed as moles per mole of mixture, is plotted against the mole fraction of ether, f_2 . The greater solubility of water in the diethyl ether mixtures is noted. Further, it is interesting that the benzene—diethyl ether curve is convex, whereas the benzene—divinyl ether curve cannot be distinguished from a straight line. This fact makes it probable that in the latter case the solubility of water in the two solvent components might be chiefly due to the same causes. In the former case, however, a formation of molecular complexes between the ether and water might explain the curved line. We assume that water, W , and ether, E , form a binary complex, EW , the equilibrium constant of which is

$$K = \frac{a_{EW}}{a_E \cdot a_W} \quad (1)$$

The solubility of (free) water in the mixture, l_w , is assumed to be a linear function of f_2 :

$$l_w - l_{wb} = k_1 f_2 \quad (2)$$

where l_{wb} is the solubility of water in pure benzene and k_1 is a constant [(2) holds in the case of divinyl ether]. If a_E is approximated to f_2 and a_W to l_w we obtain the total solubility:

$$L = a_{EW} + l_w = (K f_2 + 1) (k_1 f_2 + l_{wb}) \quad (3)$$

i. e. an equation of the second degree. The constants in (3) cannot be evaluated with any accuracy without more careful measurements, but using a K -value estimated from the measurements of dipole moments (see below), (3) can be shown to be correct in principle.

The assumption of a binary complex is reasonable because in dilute solutions of HCl and of HBr in ether the phase diagrams show the existence of 1 : 1 complexes⁹⁻¹¹. Further, dimethyl ether and HCl are known to form a rather stable complex 1 : 1^{12, 13, 11}. Complexes E_2W are of course possible but will not be taken into account at present.

DEGREE OF ASSOCIATION IN PURE ETHERS

In order to elucidate the varying behavior of the ethers towards water it is necessary to know the association in the pure liquids.

Several authors have claimed that ethyl ether is weakly associated. Summing up different data benzene — diethyl ether mixtures are to be regarded as almost ideal solutions:

1. The heat of solution is zero at all concentrations¹⁴ (in decalin — ether solutions it is very small¹⁵).

2. The total vapor pressure is a linear function of the mole fraction (Schmidt¹⁴; Tahvonon¹⁶ finds small positive deviations; *cf.* Schulze¹⁶).

3. The activities of the components, a , calculated from Pickering's¹⁷ and Yamamura's¹⁸ freezing point data and the equation:

$$\ln a_1 = (T - T_0) q/RTT_0$$

are identical with the mole fractions. This keeps within the limits of the uncertainty of $\frac{\partial q}{\partial T}$ (*cf.* Ferche¹⁹, Bridgman²⁰).

4. Löfgren's²¹ surface tension function, $\gamma^{5/6}$, varies linearly with temperature.

5. If an associated liquid is mixed with benzene, it dissociates. As a rule, this leads to a volume expansion (*cf.* Hildebrand²², pp. 59, 115). The very small contraction found by the present authors (Table 1) and by others^{14, 23} might be due to experimental errors through the difficulty of filling the pycnometers without evaporation of ether (*cf.* Niimi²⁴: from his measurements extrapolated value of the partial molar volume of ether 103.3; calc. 103.8). In fact, ether — heptane mixtures, where the components have about the same density, show no contraction²⁵.

6. The molar polarization of ethyl ether, P_2 , determined in the present investigation is nearly constant (Table 1), which is also found by other authors²⁶⁻²⁸ (*cf.* Rolinski²³, who calculates a small association from his P_2 data). In heptane solutions P_2 is independent of the concentration.

As to divinyl ether we found the same degree of constancy in P_2 (*cf.* Smyth

Table 1. Measurements on benzene solutions at 20° C.

f_2	ϵ_{12}	V_{12} cm ³	ΔV_{12} cm ³	P_{12} cm ³	P_2 cm ³
Diethyl ether					
0.05596	2.3834	89.7232	+ 0.0259	28.317	51.71
0.10266	2.4751	90.3905	— 0.0107	29.794	54.82
0.25021	2.7568	92.6380	+ 0.0130	34.214	56.04
0.45907	3.1527	95.3844	— 0.3883	39.850	55.07
0.71658	3.6903	99.2712	— 0.3825	46.934	54.84
1.00000	4.3578	103.9253	—	54.887	54.89
$[P_1 = 26.93 \pm 0.15 \text{ cm}^3; \frac{\partial P_{12}}{\partial f_2} = 28.06 \pm 0.37 \text{ cm}^3; P_2 = 54.99 \pm 0.52 \text{ cm}^3;$ $MR_D = 22.41 \text{ cm}^3;^{46} \mu = 1.23 \pm 0.01 \text{ D}$					
Divinyl ether					
0.10823	2.4337	89.0936	+ 0.0502	28.810	45.70
0.13875	2.4766	89.1784	+ 0.0815	29.415	45.96
0.32035	2.7698	89.4242	+ 0.0095	33.180	46.82
0.47979	3.0173	89.5774	— 0.1164	36.016	46.06
0.49863	3.0799	89.7198	— 0.0070	36.735	46.77
0.72918	3.4970	90.1851	+ 0.0548	40.966	46.24
1.00000	4.1269	90.6042	—	46.240	46.24
$P_1 = 26.75 \pm 0.08 \text{ cm}^3; \frac{\partial P_{12}}{\partial f_2} = 19.50 \pm 0.14 \text{ cm}^3; P_2 = 46.25 \pm 0.21 \text{ cm}^3;$ $MR_D = 21.94 \text{ cm}^3;^{29} \mu = 1.06 \pm 0.01 \text{ D}$					

and Walls²⁹) and a small deviation from the ideal molar volume (Table 1). As will be seen, these deviations are of the same order of magnitude as in the case of diethyl ether and are probably due to the same causes.

To sum up: both ethers are probably unassociated liquids which form ideal solutions with benzene. If there is any association it is of the same order of magnitude in the two compounds.

THE DIPOLE MOMENTS OF THE ETHERS

From the measurements of the dielectric constant, ϵ , and the specific volume, v , the molar polarization of the mixture, P_{12} , was calculated. P_{12}

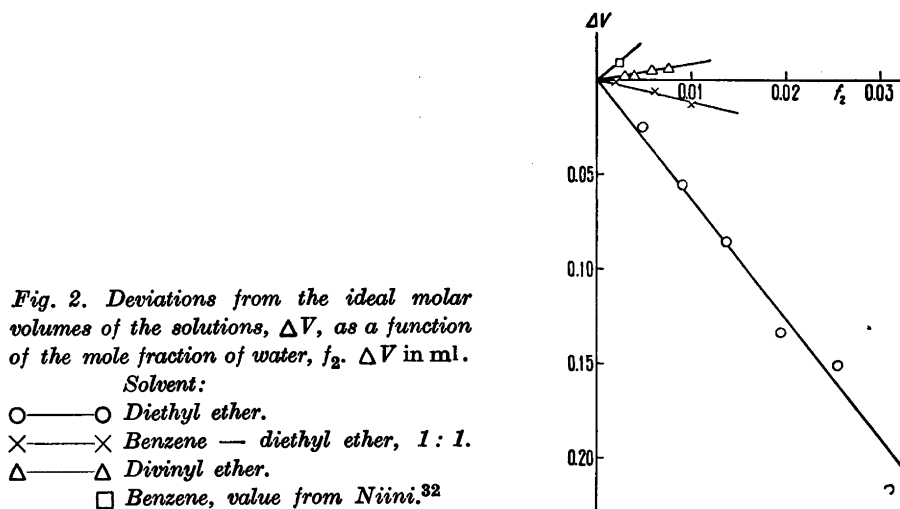


Fig. 2. Deviations from the ideal molar volumes of the solutions, ΔV , as a function of the mole fraction of water, f_2 . ΔV in ml.

Solvent:

- — Diethyl ether.
- × — Benzene — diethyl ether, 1:1.
- △ — Divinyl ether.
- — Benzene, value from Niini.³²

plotted against f_2 gave straight lines, from which P_1 and $\partial P_{12}/\partial f_2$ were obtained by the method of least squares. From

$$P_2 = P_1 + \frac{\partial P_{12}}{\partial f_2}$$

the dipole moments, μ , of the ethers were calculated assuming $P_E + P_A = 1.05 MR_D$ ³⁰. The μ -values (see Table 1) for both ethers agree well with those of earlier measurements, *cf.* Fischer and Ehrenberg⁸, Table 1.

ETHER-WATER SYSTEMS

Partial molar volume

The essential difference between the abilities of the two ethers to dissolve water (*cf.* above) is illustrated in an interesting manner by the partial molar volumes of the ether — water mixtures. If the deviations from the volumes calculated for one mole of ideal mixture, ΔV , are plotted against the mole fraction of water, f_2 , water in diethyl ether exhibits a strong contraction (Fig. 2), the partial molar volume of water, V_2 , being only 11.2 ml (the ideal value at 20° C is 18.0479 ml). A similar contraction is found in water — dioxane and water — tetrahydrofuran mixtures³¹. With benzene — ether mixtures, 1:1, as solvent the contraction is smaller, V_2 being about 16 ml; this value is, however, more uncertain. In divinyl ether, on the other hand, water exhibits a

Table 2. Measurements on ether solutions at 20° C.

f_2	ϵ_{12}	v_{12} cm ³ g ⁻¹	P_{12} cm ³	P_2 cm ³
Water in diethyl ether				
0.002565	4.3724	1.4065	55.065	
0.004729	4.3910	1.4062	55.103	63.68
0.009002	4.4420	1.4053	55.276	78.75
0.013886	4.4714	1.4044	55.253	66.96
0.019465	4.5527	1.4032	55.558	79.25
0.031093	4.6353	1.4008	55.547	69.85
$\epsilon_1 = 4.3433 \pm 0.0127$; $\frac{\partial \epsilon_{12}}{\partial f_2} = 10.3 \pm 1.1$; $v_1 = 1.4071 \pm 0.0001$; $\frac{\partial v_{12}}{\partial f_2} = -0.196 \pm 0.005$ $P_{20} = 86 \pm 9$ cm ³ ; $MR_D = 3.75$ cm ³ ; $\mu = 1.99 \pm 0.11$ D				
Water in divinyl ether				
0.002004	4.0132	1.29951	45.572	49.86
0.003165	4.0196	1.29942	45.578	49.98
0.004096	4.0247	1.29934	45.582	49.99
0.005886	4.0348	1.29926	45.594	50.68
0.007650	4.0449	1.29914	45.605	50.91
$\epsilon_1 = 4.0020 \pm 0.0001$; $\frac{\partial \epsilon_{12}}{\partial f_2} = 5.56 \pm 0.03$; $v_1 = 1.29963 \pm 0.00003$; $\frac{\partial v_{12}}{\partial f_2} = -0.0646 \pm 0.0002$ $P_{20} = 51.62 \pm 0.24$ cm ³ ; $MR_D = 3.75$ cm ³ ; $\mu = 1.51 \pm 0.01$ D				

weak expansion, V_2 being 18.9 ml. This should be compared with the expansion exhibited by water in saturated benzene solution (Fig. 2, from Niimi³²). In agreement therewith (Hildebrand²², p. 59) the water vapor pressures over benzene solutions deviate positively from Raoult's law³³. Though such data can only be interpreted with caution (*cf.* Hildebrand²², Chap. VI, Schmidt¹⁴), it is in accordance with the solubility curves above (Fig. 1) to suppose the main reaction of water in benzene or divinyl ether to be its entassociation, whereas in diethyl ether the solvation of the water molecules predominates.

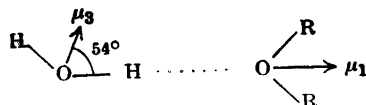
Table 3. Dipole moments measured in different solvents.

Solute	Solvent	<i>t</i> °C	μ recalcd. 10 ⁻¹⁸ e.s.u.	Given originally		Investigator
				P_2 cm ³	μ 10 ⁻¹⁸ e.s.u.	
Water	Gas	—	—	—	1.84	Sanger ⁴⁴
»	Diethyl ether	17	—	—	1.97	Hassel and Uhl ⁴⁵
»	»	10	2.2	67.2	1.71	Linton and Maass ³⁵
»	»	20	1.77	83	1.9	Higasi ²⁶
»	»	20	1.99	86	—	Present invest.
»	Divinyl ether	20	1.51	51.6	—	Present invest.
»	Benzene	25	1.51	—	—	Williams ³⁶
»	Dioxane	25	—	79.1	1.90	Linton and Maass ³⁵
Ethyl alcohol	Diethyl ether	20	1.89	83	1.8	Higasi ²⁶
»	Benzene	20	1.80	76	1.73	Stranathan ⁴⁷
Acetic acid	Diethyl ether	20	—	61.7	—	Smyth and Rogers ³⁷
»	Benzene	20	—	22.8	—	Smyth and Rogers ³⁷

Dipole moment

The dielectric constants and the specific volumes of the ether — water mixtures were determined (Table 2). The dipole moment of water was calculated according to the method of Halverstadt and Kumler³⁴: $\frac{\partial \epsilon_{12}}{\partial f_2}$, $\frac{\partial v_{12}}{\partial f_2}$, ϵ_1 and v_1 are calculated by the method of least squares using the points for the solutions and omitting those for the pure solvent, whereby moisture and other impurities of the solvent are regarded. Earlier measurements of the dipole moment of water in diethyl ether solution^{26, 35} were recalculated by the same method (Table 3). The values obtained in this manner agree rather well with ours. The difference between the P_2 values of water when dissolved in different solvents is striking. P_{20} ³⁴ in diethyl ether is significantly higher than P_{20} in divinyl ether. The latter value agrees well with P_2 in benzene (Table 3; Williams'³⁶ μ value recalculated regarding the diminished density found by Niini³²). The variation of P_2 with f_2 in divinyl ether is probably due chiefly to the formation of complexes: $n \text{H}_2\text{O} = (\text{H}_2\text{O})_n$, and P_{20} is the polarization of free water molecules. The higher P_{20} value in diethyl ether is consistent with the existence of a certain proportion of ether-water complexes: $\text{W} + \text{E} = \text{EW}$, assumed above. In this case the equilibrium constant might be calculated from the dipole moments, if the dipole moment of the complex can be estimated. $\mu_w = \mu_3$ is supposed to be 1.51 D (the value in divinyl ether or ben-

zene), $\mu_{\text{E}} = \mu_1 = 1.23$ D, and a complex is supposed to be formed through a hydrogen bond:



for which $\mu_4 = 2.44$ D is calculated. If f_1 is the mole fraction of ether, f_3 that of water, and f_4 that of the complex, we get from equation (1), as

$$f_3 + f_4 = f_2 \text{ and } f_4 \ll f_1:$$

$$f_3 = \frac{f_2}{K+1}; \quad f_4 = \frac{f_2 K}{K+1}; \quad f_1 = 1 - f_2.$$

If these values are put into the expression for the total polarization

$$P_{134} = f_1 P_1 + f_3 P_3 + f_4 P_4$$

we obtain

$$P_{134} = P_1 + f_2 \left(-P_1 + \frac{1}{K+1} P_3 + \frac{K}{K+1} P_4 \right),$$

and, because the molar refraction, R , is additive,

$$P_{134} = P_1 + f_2 \left[-P_1 + R_2 + A \left(\frac{1}{K+1} \mu_3^2 + \frac{K}{K+1} \mu_4^2 \right) \right] \quad (4)$$

where A is a constant $= 4 \pi N / 9 k T$. Now we have measured

$$P_{12} = P_1 + f_2 \left(-P_1 + R_2 + A \mu_{\text{eff}}^2 \right) \quad (5)$$

where μ_{eff} is the dipole moment calculated for water in diethyl ether (1.99 D). As P_{134} is approximately equal to P_{12} , P_{12} being calculated from values extrapolated to infinite dilution, K can be estimated from

$$\mu_{\text{eff}}^2 = \mu_3^2 \frac{1}{K+1} + \mu_4^2 \frac{K}{K+1}$$

to 0.833. If this value is put into equation (3) above (k_1 being computed from the solubility in pure ether), the theoretical solubility curve can be constructed.

Table 4. Work of adhesion between some organic liquids and water at 20° C.

Organic liquid	γ_A dyn cm ⁻¹	γ_{AB} dyn cm ⁻¹	W_{AB} dyn cm ⁻¹
Diethyl ether	16.99	10.44	79.30
Divinyl ether	17.94	24.15	66.54
Benzene ³⁹	28.88	35.00	66.63
<i>n</i> -Octyl alcohol ³⁹	27.5	8.5	91.8

The calculated points of Fig. 1 and the curvature of the line agree well with the experimental ones. Hence, the assumptions made and the order of magnitude of the constants seem to be reasonable.

It is interesting that water has a still higher μ -value when dissolved in dioxane, which is totally miscible with water ³⁵ (Table 3).

In the case of alcohols there seems also to be a similar complex formation with diethyl ether (Table 3). Confer also the fact that acetic acid has a higher P_2 -value in diethyl ether than in benzene ³⁷.*

Surface tension

The surface tensions of the pure ethers, γ_A , and the ether—water interfacial tensions, γ_{AB} , were determined. These measurements we obtained by the courtesy of Mr. L. E. Tammelin, Assistant at Tekniska Högskolan, Stockholm. Methods of measuring and calculation were those used by Tammelin and Löfgren ³⁸. Using a tabulated value of the surface tension of water ³⁹, $\gamma_B = 72.75$ dyn cm⁻¹, the work of adhesion ⁴⁰, $W_{AB} = \gamma_A + \gamma_B - \gamma_{AB}$, was calculated (Table 4). For comparison tabulated values of benzene and *n*-octyl alcohol ³⁹ are given. The values show clearly a similarity between divinyl ether and benzene, while the behavior of diethyl ether is intermediate between the hydrocarbon and the alcohol. These results are in accordance with the assumption made above that diethyl ether but not divinyl ether forms complexes with water to a measurable extent.

* We must also refer to the most interesting paper by Weith, Hobbs, and Gross⁴⁷, which did not become known to us until the present paper was in press. They found a large positive increment of the dipole moments of HF, HCl, and HBr when measured in dioxane solution compared to measurements in hydrocarbon solutions. They also found μ_{H_2O} in dioxane to be 1.89 D (cf. our Table 3).

EXPERIMENTAL

Diethyl ether (Abs. ether from AB Syntes, Nol, Sweden) and

Divinyl ether (»Vinethene» from Merck and Co. Inc. N. J., containing 3.5 % ethanol and 0.01 % phenyl- α -naphthylamine) were purified through treatment with and distillation over freshly cut sodium pieces in dry N₂ atmosphere.

Benzene (Baker's Analyzed, thiophene free) was dried through the same procedure.

The solubility determinations were performed principally as done by Marie and Lejeune⁴¹. Freshly redistilled water was titrated from a microburette (scale division 0.0002 ml) into stoppered flasks, containing weighed amounts of benzene and ether in different proportions, until the mixtures, after vigorous shaking, became opalescent in transmitted light. The temperature was kept at 20 ± 0.5 °C. The flasks were weighed after the titrations were completed. From the weight loss and the vapor pressures of the components the alteration of the mole fractions could be estimated. However, the errors due to evaporation were insignificant. — Because of the tendency of water to form larger drops in pure diethyl ether, the method failed to give a correct value for this case. Instead, Niini's refractometrically determined value³² is used.

The dielectric constants were measured at a frequency of 2000 kilocycles with a crystal controlled heterodyne beat apparatus built in this laboratory according to a design published by Hudson and Hobbs⁴². The measuring condenser was a modification of one described by Arrhenius⁴³. The difference between two settings of the condenser was determined with an accuracy of 0.05 %. The details of apparatus and calibration will appear in a later publication. The solutions were made up of freshly distilled liquids, care being taken to avoid moisture and evaporation. For the density measurements, performed on the same solutions as the dielectric constant measurements, an Ostwald-Sprengel pycnometer fitted with carefully ground caps was used. The temperature was kept constant at 20.00 ± 0.05 °C.

CONCLUSIONS

Diethyl ether and divinyl ether are uni-molecular liquids. Data from measurements of solubility, partial molar volume, and dipole moment of water dissolved in the ethers and of surface and interfacial tensions are explained by the assumption that diethyl ether associates with water, about 50 % of the water molecules in diethyl ether solution being present as a (hypothetical) binary complex with $\mu = 2.44$ D, whereas divinyl ether in this respect is more like benzene, forming no obvious complex with water. Probably, this different behavior depends on different ability to form hydrogen bonds (see the following publication⁸).

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