ACTA CHEMICA SCANDINAVICA 8 (1954) 1398—1413

The Solubility of Carbon Dioxide, Oxygen, Carbon Monoxide and Nitrogen in Polar Solvents

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In recent papers it was shown that the solubility of nitrogen [1], chlorine [2], hydrogen, oxygen and carbon monoxide [3], carbon dioxide [4], helium, argon, methane and ethane [5] in non-polar solvents can be predicted with fair accuracy from the equation

$$-\log x_2 = -\log x_2^i + \log \frac{\overline{V}_2}{V_1} + 0.4343\left(1-\frac{\overline{V}_2}{V_1}\right) + \frac{\overline{V}_2}{2.303\,RT}(\delta_1-\delta_2)^2 \qquad (1)$$

In this equation, x_2 denotes the solubility in mole fraction, x_2^i the "ideal" solubility, $\overline{V}_2$ the partial molal volume of the dissolved gas, V_1 the molal volume of the solvent, δ_1 and δ_2 solubility parameters of solvent and gas, respectively, R the gas constant and T absolute temperature. With regard to the derivation of equation (1) reference should be made to Hildebrand and Scott [6].

Equation (1) is derived on the assumption that the molecules are non-polar and that chemical reactions are absent. If a non-polar gas is dissolved in a polar solvent, we will expect a higher value for the solubility than is calculated from equation (1). A preliminary examination [3] for hydrogen, oxygen and carbon monoxide confirmed this expectation and showed that the difference between experimental values and values calculated from equation (1) was related to the dielectric constant (ε) for the solvent. It is the aim of the present paper to provide a more detailed knowledge of the influence of the polarity of the solvent. For this purpose we have chosen twelve solvents from weakly polar (*e.g.* toluene with $\varepsilon = 2.37$) to strongly polar (*e.g.* nitrobenzene with $\varepsilon = 34.9$) excluding, however, strongly associated solvents, *e.g.* alcohols and water. In the last section, it is shown that among the chosen solvents only acetone is somewhat associated . The other solvents (toluene, chloroform, 1,2-dibromoethane, chlorobenzene, *n*-propyl acetate, aniline, methyl acetate, pyridine, benzyl cyanide, propionitrile and nitrobenzene) are considered to be either non-associated or very little associated.

APPARATUS, MATERIALS AND PROCEDURE

Solubility determinations in the solvents mentioned above have been carried out for the two gases carbon dioxide and carbon monoxide only. The solubility of oxygen and nitrogen was taken from the literature (*cf.* Table 4). The majority of the solubility measurements were carried out in the same apparatus and using the same procedure as described in a previous paper [3]. The solubility of carbon dioxide in chlorobenzene was also determined by titration of the saturated solution, and in the solvents benzyl cyanide and nitrobenzene titration only was used. The procedure was the following: a glass cylinder with the solvent was placed in a water thermostat at 25° C. Carbon dioxide from a cylinder (99.61 % CO_2) was bubbled through until saturation. A portion of the saturated solution (corresponding to about 8 ml 0.2 *M* sodium hydroxide) was drawn off by means of a bended glass tube into a 50 ml measuring glass filled with nitrogen and containing 20.00 ml of 0.2 *M* sodium hydroxide. The amount of saturated solution was determined by weighing. The measuring glass was shaken violently, and the contents were quantitatively transferred to a 500 ml flask filled with nitrogen. After heating to about 80° C, 10.00 ml of 0.2 *M* hydrochloric acid was added and then about a ten percent' excess of barium chloride solution. After cooling to room temperature, the solution was titrated with 0.2 *M* hydrochloric acid in a nitrogen atmosphere. The results were corrected for blank values, which were less than ten percent.

The carbon dioxide used in the volumetric determinations was prepared by adding concentrated sulphuric acid to potassium bicarbonate (analytical reagent, Judex). After being passed through concentrated sulphuric acid, the carbon dioxide was collected in an all-glass gasometer with mercury as closing liquid. The apparatus is described in a previous paper [7]. The gasometer was filled and emptied until sampling showed that the gas was pure. The analyses were carried out in a gas analysis apparatus as devised by Christiansen and Wulff [8]. The carbon dioxide employed contained between 99.8 and 99.9 % CO_2. The solubility determinations were corrected for the small amount of atmospheric air, *cf.* the previous paper [4].

Carbon monoxide was prepared by adding concentrated sulphuric acid to formic acid (analytical reagent, Merck). The carbon monoxide was led through one glass spiral washing bottle containing 40 % sodium hydroxide and another containing concentrated sulphuric acid and was then collected in the mercury gasometer. The gas employed contained between 99.6 and 99.9 % CO. In this case it was superfluous to correct the solubility experiments since carbon monoxide and atmospheric air have nearly the same solubility in the solvents.

The following solvents were purified by fractionated distillation in a wire-gauze column as devised by Klit [9]. The fractions employed showed the following boiling points (760 mm) and index of refraction: *toluene* (analytical reagent, Riedel-de Haën) bp. 110.75°—110.80°, n_D(25.1°) 1.4936—1.4938, *chloroform* (analytical reagent, Merck) bp. 61.15°—61 16°, n_D(20°) 1.4460—1.4461, *chlorobenzene* bp. 131.95°—131.98°, n_D (20°) 1.3840—1.3841, *normal propyl acetate* (Judex chemicals) bp. 101.66°—101.70°, n_D (20°) 1.3846, *methyl acetate* bp. 56.72°—56.85°, n_D (20°) 1.3618, *pyridine* bp. 115.51°—115.55°, n_D (20°) 1.5100—1.5101, *acetone* (analytical reagent, Merck) bp. 56.12°—56.14°, n_D (20°) 1.3588—1.3589 and *propionitrile* (Rubber Industries and Sherman Chemicals) bp. 97.31°—97.35°, n_D (20°) 1.3664—1.3665.

Benzyl cyanide and aniline (puriss Merck) was purified by fractional distillation in vacuum. The fractions used had the following constants: *benzyl cyanide* bp. 233.49°—233.55°, n_D (20°) 1.5233 and *aniline* bp. 184.32°—184.34°, n_D (20°) 1.5864. *Nitrobenzene* was first purified by fractional freezing and then by fractional distillation in vacuum; the fractions employed showed bp. 211.94°—211.95°, n_D (25°) 1.5524—1.5527 and the melting point 5.75° C.

1,2-dibromoethane (Merck) was purified by fractional freezing. The samples employed showed mp. 9.5°—9.8° C, n_D (20°) 1.5390 and the density 2.179 at 20.6° C.

Pertinent data for vapour pressures and densities used in the calculations of the solubility experiments were taken from international Critical Tables.

Table 1. Solubility of carbon dioxide and carbon monoxide. Experimental values expressed in Bunsen absorption coefficient (a) at 25.0° C.

Solvent	Carbon dioxide	Carbon monoxide
Toluene	2.22 2.20	0.172 0.170
Chloroform	3.59 3.58	
1,2-Dibromoethane	2.00 2.00	0.0771 0.0785
Chlorobenzene	$\left.\begin{matrix}2.16\\2.17\end{matrix}\right\}*$ 2.18 2.14 ** 2.16 **	
n-Propyl acetate	4.84 4.80	0.226 0.228
Aniline	1.22 1.18	0.0465 $\left.\begin{matrix}0.0462\\0.0465\end{matrix}\right\}*$
Methyl acetate	6.47 6.39 6.42	
Pyridine	3.38 3.34	0.107 0.107
Benzyl cyanide	2.07 ** 2.03 **	$\left.\begin{matrix}0.0692\\0.0687\end{matrix}\right\}*$ $\left.\begin{matrix}0.0698\\0.0698\end{matrix}\right\}*$
Acetone	6.48 6.45 6.43 6.34 6.49	
Propionitrile	5.39 5.38	0.199 0.199
Nitrobenzene	2.23 ** 2.17 **	$\left.\begin{matrix}0.0819\\0.0823\end{matrix}\right\}*$ $\left.\begin{matrix}0.0808\\0.0805\end{matrix}\right\}*$ $\left.\begin{matrix}0.0814\\0.0808\end{matrix}\right\}*$

* indicates that the equilibrium has been established at different pressures.
** results obtained by titration.

EXPERIMENTAL RESULTS

The results of the solubility determinations for carbon dioxide and carbon monoxide are given in Table 1.

In the calculations of the experimental values for the solubility of carbon dioxide in acetone and methyl acetate, it was necessary to introduce a correction for dissolved gas in the minor amount of solvent which was placed in the gas burette.

It appears from Table 2, which includes solubilities found by other investigators, that the results for *carbon dioxide* in 1,2-dibromoethane, aniline, pyridine and nitrobenzene are a confirmation of results obtained by Just[10] and Kunerth[11]. Our results in toluene, chlorobenzene, methyl acetate, acetone and chloroform were, respectively, about 5, 5, 8, 12 and 15 % higher than the values given by Just.

Our results for the solubility of *carbon monoxide* in aniline and nitrobenzene are about 5 % lower than stated by Just.

The degassing of benzyl cyanide and nitrobenzene was done very carefully since these two solvents have very high boiling points, 234° C and 211° C, respectively. In some experiments the degassing was carried out by evacuation with repeated freezing and melting the solvents; it turned out that experiments in which we did not freeze the solvent resulted in the same experimental value for the solubility.

The solubilities are recalculated into mole fraction in Tables 3 and 4.

CORRELATION WITH THEORY

Hildebrand and Scott[6,p.168] have developed the following expression for the heat of mixing, ΔH^M, for one mole mixture of two polar components

$$\Delta H^M = (x_1 V_1 + x_2 V_2)\,[(\delta_1 - \delta_2)^2 + (\omega_1 - \omega_2)^2]\,\Phi_1 \Phi_2 \qquad (2)$$

Φ_1 and Φ_2 is the volume fraction of solvent and solute, respectively. In equation (2) the δ's no longer have their usual meaning as the square roots of the cohesive energy densities, but must be calculated from

Table 2. Solubility of carbon dioxide and carbon monoxide expressed in Bunsen absorption coefficient at 25° C. Comparison with older measurements.

Solvent	Carbon dioxide			Carbon monoxide			
	Just[10]	Kunerth[11]	Present investigation	Just[10]	Skirrow[12]	Horiuti[13]	Present investigation
Toluene	2.11		2.21	0.166	0.167		0.171
Chloroform	3.14	3.15	3.58	0.179	0.189		
1,2-Dibromoethane	1.98	1.96	2.00				
Chlorobenzene	2.08		2.17				
Aniline	1.21	1.19	1.20	0.0491	0.0486		0.0464
Methyl acetate	5.95		6.43				
Pyridine	3.35	3.28	3.36				
Acetone	5.77	5.85	6.44	0.204	0.218	0.236	
Nitrobenzene	2.25		2.20	0.0858	0.0852		0.0813

$$\frac{\Delta E^v}{V} = \delta^2 + \omega^2 \tag{3}$$

Equation (3) expresses for each of the components the overall energy of vaporization as a sum of the energy (δ^2) arising from the dispersion forces and the energy (ω^2) arising from the dipole forces. The values of ω^2 are calculated from equation (10) in the next section. Since we are concerned in this paper with gases without permanent dipoles, equation (2) can be written

$$\Delta H^M = (x_1V_1 + x_2V_2)\ [(\delta_1 - \delta_2)^2 + \omega_1^2]\ \Phi_1\Phi_2 \tag{4}$$

Using this equation and the approximations $\Phi_1 = 1$, $x_2 = n_2/n_1$ and $\Phi_2 = x_2\bar{V}_2/V_1$, we find that the solubility can be calculated from equation (1) by adding $\bar{V}_2\omega_1^2/2.303\ RT$. In a previous paper[4] it was shown, that the equation

$$-\log x_2 = -\log x_2^i + \frac{\bar{V}_2}{2.303\ RT}\,(\delta_1 - \delta_2)^2$$

accounts for the experiments somewhat better than equation (1). Consequently we may enquire whether the equation

$$-\log x_2 = \underbrace{-\log x_2^i + \frac{\bar{V}_2}{2.303\ RT}(\delta_1 - \delta_2)^2}_{A} + \underbrace{\frac{\bar{V}_2}{2.303\ RT}\omega_1^2}_{B} \tag{5}$$

is able to account for the experiments. If we use $\delta_1 = \delta'''$, *i.e.* a solubility parameter corrected for dipole attraction (*cf.* next section), we get the A-values given in column 7 in Table 3. The difference (Δ''') between A and the negative logarithm of the experimental value of the solubility is given in column 10. According to equation (5) Δ''' should be equal to B, which is given in the last column of the table. For pyridine and benzyl cyanide we get $B = \Delta'''$, but there are considerable divergences for the other solvents. A corresponding calculation for the solubility of carbon monoxide in the polar solvents gave the same qualitative result. The explanation of the failure of equation (5) may probably be found in the diverse assumptions made in its derivation. The solubility in the "basic" solvents aniline and pyridine will be discussed below.

It will be shown in the following that it is possible to account empirically for the measurements.

Values of A in equation (5) have been calculated (in Table 3) using $\delta_1 = \delta'$ and $\delta_1 = \delta''$, respectively. The differences between A-values and experimental values of $-\log x_2$ are given in column 8 and 9. On the whole these differences (Δ' and Δ'') increase in going from the less polar to the more polar solvents. Fig. 1 showns the Δ''-values as a function of the dipole moments (μ) of the solvents. The μ-values employed are given in Table 8. The points for toluene, chloroform, chlorobenzene, propyl acetate, methyl acetate, benzyl cyanide, propionitrile and nitrobenzene are grouped about a straight line through the zeropoint in the coordinate system.

Table 3. Solubility of carbon dioxide in polar solvents at 25° C. Comparison of experimental and calculated values.

$x_2^i = 0.0230$, $\bar{V}_2 = 47.7$ ml, $\delta_2 = 5.1$.

Solvent	V_1	Exp. value of $x_2 \cdot 10^4$	$-\log x_2$	A in eq. (5) calc. with δ'	δ''	δ'''	Δ'	Δ''	Δ'''	B in eq. (5)
$C_6H_5CH_3$	106.8	105	1.98	2.14	2.20	2.20	0.16	0.22	0.22	0.00
$CHCl_3$	80.7	128	1.89	2.18	2.24	2.17	0.29	0.35	0.28	0.13
1,2-$C_2H_4Br_2$	86.6	77.2	2.11	2.62	2.66	2.58	0.51	0.55	0.47	0.10
C_6H_5Cl	102.2	98.6	2.01	2.33	2.35	2.29	0.32	0.34	0.28	0.12
$CH_3COOC_3H_7$	115.6	245	1.61	2.02	2.09	2.03	0.41	0.48	0.42	0.14
$C_6H_5NH_2$	91.5	49.1	2.31	2.94	3.09	2.98	(0.63)	(0.78)	(0.67)	0.19
CH_3COOCH_3	79.9	226	1.65	2.17	2.32	2.20	0.52	0.67	0.55	0.28
C_5H_5N	80.8	121	1.92	2.60	2.74	2.46	(0.68)	(0.82)	(0.54)	0.55
$C_6H_5CH_2CN$	115.7	105	1.98	2.80	2.96	2.62	0.82	0.98	0.64	0.65
CH_3COCH_3	74.0	211	1.68	2.25	2.36	1.83	0.57	0.68	0.15	1.33
C_2H_5CN	70.9	169	1.77	2.70	2.86	2.02	0.93	1.09	0.25	1.44
$C_6H_5NO_2$	102.7	101	2.00	2.90	3.09	2.35	0.90	1.09	0.35	1.78

The values for *aniline* and *pyridine* are placed above the line showing that the solubilities in these solvents are higher than those corresponding to the dipole moments of the solvents. This higher solubility can be caused by chemical forces between carbon dioxide and the "basic" solvents. This effect is not found for carbon monoxide, and not for nitrogen and oxygen in pyridine.

Ditte [15] has shown the formation of a crystalline compound by dissolving carbon dioxide in dry aniline at about 10° C and a pressure of about 50 atm. On the other hand, if carbon dioxide at atmospheric pressure is led into dry aniline at room temperature no carbamate is formed (Faurholt and Ballund Jensen [16]); if some of the saturated solution is added to sodium hydroxide solution, all the carbon dioxide is instantaneously precipitated as carbonate on addition of an excess of barium chloride solution.

The point (10) for *acetone* is placed below the line in accordance with the assumption that acetone is somewhat associated (*cf.* the last section). If we use the molecular weight 75 for acetone — corresponding to a content of about 30 % double molecules — we get the point 10 *A*. This assumption, which influences only the value of x_2, is also able to account for the solubility of carbon monoxide, oxygen and nitrogen in acetone.

A comparison between the experimental and calculated values for the solubilities of oxygen, carbon monoxide and nitrogen is given in Table 4. The calculation is carried out using equation (1) with $\delta_1 = \delta''$. The differences, Δ'', between calculated and experimental values of $-\log x_2$ are (Fig. 1) plotted against the dipole moments of the solvents, and we again find an approximate proportionality. The slope of the lines is greatest for carbon dioxide, almost equal for nitrogen and carbon monoxide and smallest for oxygen. This result is possibly related to the electronic polarization, which for carbon dioxide is 6.6, carbon monoxide 4.9, nitrogen 4.4 and oxygen 4.0 ml, *cf.* Landolt Börn-

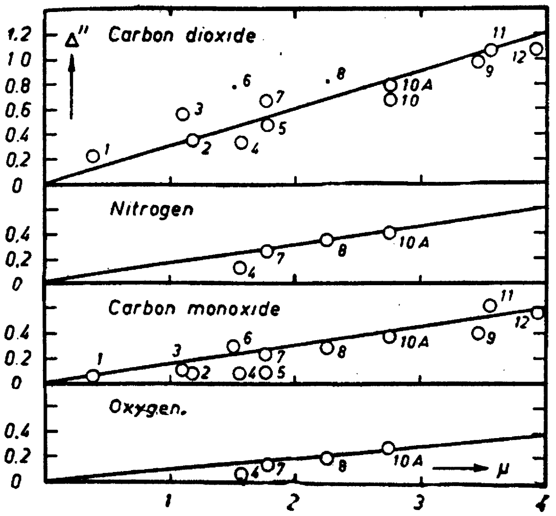

Fig. 1. Δ'' (see the text) plotted against the dipole moments of the solvents. 1. toluene, 2. chloroform, 3. 1,2-dibromoethane, 4. chlorobenzene, 5. n-propyl acetate, 6. aniline, 7. methyl acetate, 8. pyridine, 9. benzyl cyanide, 10. acetone, 11. propionitrile and 12. nitrobenzene. 10 A assuming a mean molecular weight of acetone equal 75.

Table 4. Solubility of carbon monoxide, nitrogen and oxygen in polar solvents at 25° C. Comparison of experimental and calculated values.

	x_2^i	$\bar{V}_2$ ml	δ_2
oxygen	17.6 10^{-4}	46	5.7
carbon monoxide	15.5 10^{-4}	52	5.8
nitrogen	16.0 10^{-4}	53	5.2

Solvent	Oxygen −log x_2			Carbon monoxide −log x_2			Nitrogen −log x_2		
	exp.	eq.(1)	Δ''	exp.	eq.(1)	Δ''	exp.	eq.(1)	Δ''
$C_6H_5CH_3$				3.09	3.14	0.05			
$CHCl_3$				3.17c)	3.23	0.06			
1,2-$C_2H_4Br_2$				3.52	3.61	0.09			
C_6H_5Cl	3.10a)	3.16	0.06	3.20a)	3.28	0.08	3.36a)	3.47	0.11
$CH_3COOC_3H_7$				2.93	3.02	0.09			
$C_6H_5NH_2$				3.72	4.01	0.29			
CH_3COOCH_3	3.05a)	3.19	0.14	3.07a)	3.30	0.23	3.23a)	3.49	0.26
C_5H_5N	3.34b)	3.54	0.20	3.41	3.69	0.28	3.60b)	3.94	0.34
$C_6H_5CH_2CN$				3.44	3.83	0.39			
CH_3COCH_3	2.95a)*)	3.24	0.29	2.99a)*)	3.36	0.37	3.15a)*)	3.55	0.40
C_2H_5CN				3.20	3.82	0.62			
$C_6H_5NO_2$				3.43	3.99	0.56			

a) Horiuti [13], b) Guerry [14], c) Skirrow [12].
* assuming that acetone has the mean molecular weight 75.

stein[17]. It should be noted that the solubility of carbon dioxide in 1,2-dibromoethane is found to be unexpectedly high, and that the four gases have shown smaller solubilities in chlorobenzene than is expected from Fig. 1.

CALCULATION OF THE SOLUBILITY PARAMETERS OF THE SOLVENTS

The solubility parameters in question, calculated in different ways, have been summarized in Table 5. δ' and δ'' is calculated from

$$\delta = \sqrt{\frac{\Delta H - RT}{V}} \tag{6}$$

where ΔH is the heat of vaporization at 25° C, R the gas constant, $T = 298.1°$ C and V the molal volume of the solvent at 25° C. In the calculation of δ' is used ΔH-values from

$$\Delta H^{298} = -2950 + 23.7\ T_b + 0.020\ T_b^2 \tag{7}$$

where T_b is the boiling point of the solvent, *cf.* Hildebrand and Scott[6,p.427]. In the calculation of δ'', ΔH-values from the last column in Table 7 are used; these values will be discussed below. It is seen that for each solvent, δ' is less than δ''. δ''' is finally calculated from

$$\delta''' = \sqrt{\frac{\Delta H - \omega_1^2 - RT}{V}} \tag{8}$$

where ω_1^2 is the dipole contribution to the energy of vaporization. In this equation we again have used ΔH-values from the last column in Table 7. In the calculation of ω_1^2 (cal/mole) the following equations given by Böttcher[18] are used:

$$\omega_1^2 = \frac{4\pi}{3}\frac{d}{M}N^2\frac{\varepsilon - 1}{2\,\varepsilon + n_D^2}\frac{n_D^2 + 2}{3}\mu^2 \cdot 2.39 \cdot 10^{-8} \tag{9}$$

$$\omega_1^2 = RT\ \frac{(\varepsilon - 1)(\varepsilon - n_D^2)}{\varepsilon(n_D^2 + 2)} \tag{10}$$

where d is density, M molecular weight, N Avogadros number, ε dielectric constant, n_D refraction index and μ dipole moment for the solvent. For the values for ε and μ used, see Table 8. For non-associated solvents these two equations give nearly the same value for ω_1^2. The results are given in Table 5, where it is seen that equation (9) gives slightly higher or lower values than equation (10). This can be considered as a criterion that the polar liquids in question — with the exception of acetone — are not considerably associated; for associated liquids, equation (9) results in distinctly lower values than equation (10). For acetone we thus calculate ω_1^2 about 22 % less from equation (9) than from (10). Since the two sets of values for ω_1^2 give nearly the same result for δ''' we have only given δ''' calculated by means of equation (10) in Table 5.

Table 5. Solubility parameters (δ) at 25° C.

Solvent	ω_1^2 cal/ml		δ'	δ''	δ'''
	eq. (9)	eq. (10)	eq. (6) a)	eq. (6) b)	eq. (8)
Toluene	0.13	0.11	8.9	9.1	9.1
Chloroform	3.4	3.7	9.05	9.25	9.0
1,2-Dibromoethane	2.7	2.9	10.4	10.5	10.3
Chlorobenzene	3.8	3.6	9.55	9.6	9.4
n-Propyl acetate	4.0	4.0	8.4	8.7	8.45
Aniline	5.4	5.3	11.2	11.55	11.3
Methyl acetate	8.6	7.9	9.0	9.5	9.1
Pyridine	17.1	15.6	10.35	10.7	9.95
Benzyl cyanide	21.0	18.5	10.85	11.25 c)	10.4 c)
Acetone	29.6	37.9	9.3	9.65	7.45
Propionitrile	54.9	50.8	10.6	11.0 d)	8.4 d)
Nitrobenzene	36.6	41.3	11.1	11.55	9.6

a) using ΔH from equation (7)
b) » » » last column in Table (7)
c) calculated from the estimated value $\Delta H = 15.2$ kcal/mole at 25° C.
d) » » » » » $\Delta H = 8.59$ » » 25° C.

As described above, we need values of the heat of vaporization for the solvents at 25° C. For toluene, chloroform and pyridine only calorimetric values at 25° C are found in the literature (*cf.* Table 7) while for most of the solvents values were given at the boiling point.

Several of the calorimetric values at the boiling points — summarized in Table 6 — show considerable disagreement. To check these values, the heat of vaporization is calculated from Clapeyrons formula, partly from values of the pressure dependence of the boiling points (column 3), partly from the temperature dependence of the vapour pressures (column 4). Deviations from ideal gas behavior were calculated from Berthelot's equation

$$P.V = RT\left[1 + \frac{9}{128}\frac{PT_c}{P_cT}\left(1 - 6\,\frac{T_c^2}{T^2}\right)\right] \tag{11}$$

where P_c and T_c is critical pressure and temperature, respectively. These corrections amounted to 2.7—3.7 %.

The heat of vaporization were also calculated from Hildebrand's empirical equation [6,p.427]

$$\Delta H^b = 17.0\ T_b + 0.009\ T_b^2 \tag{12}$$

where T_b is the boiling point in absolute temperature. This equation, which is only valid for non-polar liquids, gives too low values for polar liquids. The heats of vaporization for the liquids in question — with the exception of nitrobenzene — are only between 2 and 10 % higher than calculated from equation (12). We thus see that the boiling points include to a high degree the effect of the dipole attraction. No vapour pressure data for nitrobenzene allowing a calculation of the heat of vaporization at the boiling point (210.8° C) was found in the literature. The calorimetric value, 7.94 kcal/mole, is considered to be much too low, since it is 2.4 kcal lower than that calculated from equation (12). The most satisfactory heats of vaporization are given in the last column of the table. For benzyl cyanide we found no data allowing a calculation of ΔH at the boiling point.

These heats of vaporization have been recalculated to 25° C (see Table 7) by means of Kirchhoff's law

$$\Delta H^{298} = \Delta H^{b} + \int_{298}^{T_b} \Delta c_p dT \tag{13}$$

Table 6. Heats of vaporization (ΔH) at the boiling point, kcal/mole.

Solvent	Calorimetric values	Calc. by us from			Chosen value
		$\frac{dt}{dp}$[27]	vapour pressures	eq(12)	
Toluene	7.70[1] 7.83[2] 7.99[3] 7.96[4]	8.00		7.85	8.00
Chloroform	6.97[5] 7.02[4] 7.09[6] 7.08[7]	7.01		6.69	7.01
1,2-Dibromoethane	8.69[4] 8.23[8] 8.51[4]	8.65		8.35	8.69
Chlorobenzene	8.73[4] 8.54[9]	8.46	8.55[10]	8.36	8.54
n-Propyl acetate	7.89[1] 8.20[4] 8.21[11] 8.15[9] 8.49[12]	8.20		7.63	8.20
Aniline	9.71[13] 10.20[14] 10.60[15] 10.60[16]	10.43	10.54[17]	9.66	10.4
Methyl acetate	6.96[1] 7.26[4] 7.18[12] 7.28[11]	7.36	7.29[10]	6.59	7.28
Pyridine	8.49[4] 8.48[18]	8.93	8.41[19] 8.54[20]	7.97	8.48
Acetone	7.09[4] 7.27[21] 7.27[22]	7.12	7.09[23] 7.14[24]	6.57	7.14
Propionitrile		8.05	7.79[25] 7.84[26]	7.53	7.84
Nitrobenzene	7.94[13]	12.35		10.33	12.3

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where Δc_p is the difference between the molal heat capacity of the liquid and the vapour. Considering Δc_p to be independent of the temperature as a first approximation we get from equations (7), (12) and (13)

$$\Delta c_p \sim 10 + 0.011\ T_b \tag{14}$$

Even if equation (14) can give Δc_p with an accuracy of 10—20 % only, the error in the calculated value of ΔH at 25° C is estimated to be few percent. The agreement with the heats of vaporization calculated from vapour pressures (column 4) is satisfactory.

Heats of vaporization at 25° C have also been calculated from equation (7) (see Table 7) , and in the last column of this table we have chosen such values of the heat of vaporization, which we believe are most reliable. These values — with the exception of the value for nitrobenzene — are estimated to be reliable to within 2—3 %. The calorimetric values for toluene and pyridine are in accordance with the values in column 3 and 4, while the calorimetric value for chloroform is estimated to be too high.

Table 7. Heats of vaporization (ΔH) at 25° C, kcal/mole.

Solvent	Calorimetric values	Calculated by us from			Chosen value
		eq(13)	vapour pressures	eq(7)	
Toluene	9.07[1]	9.21	9.12[4]	9.09	9.12
Chloroform	7.97 (20°)[2]	7.50	7.40[5] 7.48[6] 7.10[7]	7.21	7.48
1,2-Dibromoethane		10.30	10.1[5]	9.92	10.1
Chlorobenzene		10.08	9.99[8]	9.93	10.0
n-Propyl acetate		9.27	9.33[9]	8.74	9.33
Aniline		12.8	12.79[10] 12.84[11]	12.08	12.8
Methyl acetate		7.72	7.81[12]	7.05	7.81
Pyridine	9.71 (20°)[3]	9.76	9.84[13]	9.28	9.84
Acetone		7.56	7.50[14] 7.39[15] 7.75[16] 7.45[6]	7.02	7.5
Nitrobenzene		15.1	14.3[17]	13.20	14.3

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7 and 17 are cited from Timmermans (*cf.* Table 6, Ref.[21]).

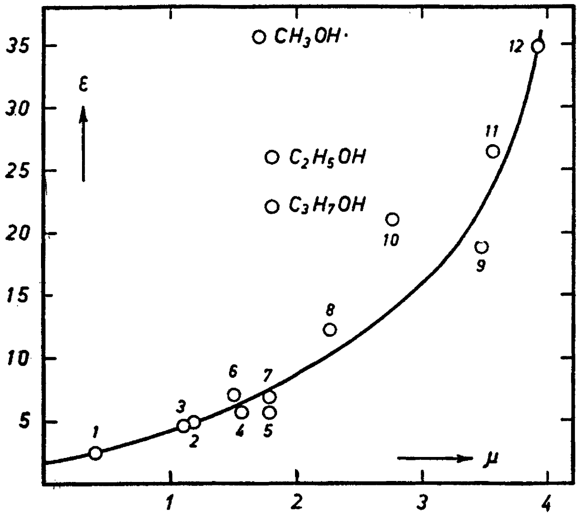

Fig. 2. The dielectric constants (ε) of polar liquids plotted against the dipole moments (μ). 1. toluene, 2. chloroform, 3. 1,2-dibromoethane, 4. chlorobenzene, 5. n-propyl acetate, 6. aniline, 7. methyl acetate, 8. pyridine, 9. benzyl cyanide, 10. acetone, 11. propionitrile, and 12. nitrobenzene.

The values of dielectric constants and dipole moments for the solvents used in this work are given in Table 8 columns 2 and 5, respectively. To get reliable values for the dielectric constants we plotted values given in the literature against the temperature; the temperature coefficients are given in the table. $d\varepsilon/dt$ as a whole increases with increasing values of ε. The values of μ in column 5 for eleven of the solvents were obtained from measurements in benzene; the value for 1,2-dibromoethane originates from a measurement in gas phase. Moreover we have reproduced the lowest and highest stated value of μ for each of the solvents, values which include measurements both in gas phase and in non-polar solvents.

ON ASSOCIATION IN THE SOLVENTS

In this section we wish to estimate the extent of association of the solvents. Pauling [19] has given the following criterion for association in liquids. If the dielectric constants are plotted against the dipole moments, for non-associated liquids the points lie close to a simple curve, while the points for associated liquids lie above the curve. The points for the present solvents are shown in Fig. 2 together with points for the associated solvents methanol, ethanol and propanol. Since the point for acetone is placed distinctly over the curve, this solvent is considered to be associated. We get a confirmation of this estimate by regarding Yamamura's [20] freezing point measurements for mixtures of acetone and benzene.

Yamamura's measurements have been compared (Fig. 3) with the freezing points for solutions of carbon tetrachloride, carbon disulphide, *cyclo*hexane and nitrobenzene in benzene (data from *Int. Crit. Tables*). The experimental freezing point lowering is plotted against the mole percent of the solute. The curve

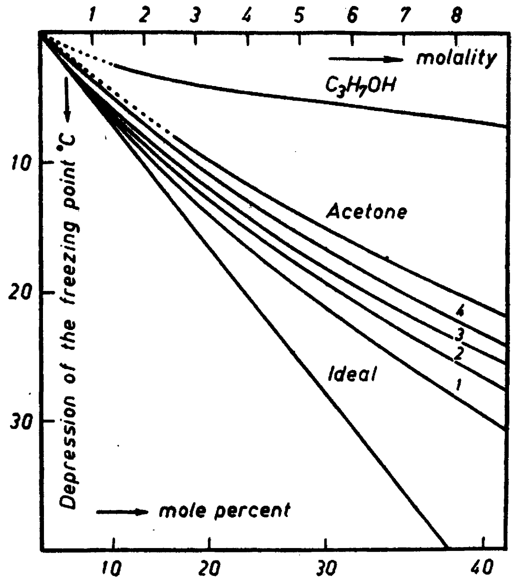

Fig. 3. Freezing point depression of benzene solutions. Solutes: 1. carbon tetrachloride, 2. carbon disulphide, 3. cyclohexane and 4. nitrobenzene.

marked "ideal" is drawn using the cryoscopic constant for benzene (5.1°). It is seen from equation (1) that the departure from ideality for molecules with molal volumes not too different from that of benzene is given by

$$\frac{\bar{V}_2}{2.303\,RT}\,(\delta_1-\delta_2)^2$$

Using solubility parameters from Hildebrand and Scott [6, appendix 1] we calculate the following values of this term:

carbon tetrachloride	0.026
carbon disulphide	0.028
*cyclo*hexane	0.080

These numbers are in accordance with the experimental fact that the deviation from ideality is smallest for carbon tetrachloride and largest for *cyclo*hexane. Using $\delta_1 = 9.25$, for acetone we get the value 0.011, *i.e.* the curve for acetone is expected to lie near the curve for carbon tetrachloride. The much higher position cannot be explained from the polarity of acetone, *cf.* the position of the curve for the more polar nitrobenzene. An explanation would be to assume association in acetone. The curve for propanol dissolved in benzene is shown for comparison.

Finally some older criterions for association in liquids shall be mentioned.

Walden [21] has investigated the connection between the surface tension (σ) and internal pressure (K) for many liquids at their boiling point. The internal pressure was calculated from the heat of vaporization. Both the values of σ and K give information on the forces of attraction in the liquids. Walden put forward the following empirical rules:

1) The ratio between the surface tension at the boiling point and the critical pressure (p_k) for "normal" liquids is nearly constant ($\sigma/p_k \sim 0.45$, lying between 0.42 and 0.47)

2) The ratio between the internal pressure at the boiling point and the critical pressure for "normal" liquids is nearly constant ($K/p_k \sim 34$, lying between 32 and 35).

For "associated" liquids he found σ/p_k less than 0.42 and K/p_k greater than 35. Such ratios have been reproduced for several of the solvents in Table 8, and using Walden's rules, it is seen that only acetone behaves abnormally. It should be emphazised that the departure from ideal behavior decreases with increasing temperature and that Walden's rules only give information on possible association at the boiling point of the liquid.

Eötwös[22] has given the following relation between surface tension, molal volume (V) and temperature (t):

$$\sigma \cdot V^{2/3} = A - k_E \cdot t$$

Table 8. Some constants for the twelve polar solvents.

Solvent	ε 25° C	$\frac{d\varepsilon}{dt}$	μ-limits[12]	μ[12]	Eötwös constant k_E[13]	Values at the boiling point for	
						σ/p_k	K/p_k
Toluene	2.37[1]	0.005	0.34–0.39	0.39	2.2	0.44	33
Chloroform	4.77[1]	0.018	1.15–1.18	1.18	2.1		
1,2-Dibromoethane	4.70[2]	0.008	0.79–1.10	1.10	2.2		
Chlorobenzene	5.61[3]	0.016	1.55–1.70	1.57	2.2	0.45	34
n-Propyl acetate	5.6[4]	(0.02)	1.78–1.96	1.78	2.3	0.47[a]	34[a]
Aniline	6.86[5]	0.023	1.48–1.75	1.51	2.1	0.45	34
Methyl acetate	6.68[6]	0.030	1.74–1.78	1.78	2.2		
Pyridine	12.2[7]	0.029	2.10–2.26	2.26	2.3		
Benzyl cyanide	18.8[8]	0.064	3.47–3.56	3.47	2.2		
Acetone	20.9[9]	0.10	2.71–2.85	2.76	1.9	0.39[b]	41[b]
Propionitrile	26.3[10]	0.13	3.56–4.03	3.56	1.6	0.43	
Nitrobenzene	34.9[11]	0.18	3.93–4.30	3.93	2.2		

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a) $p_k = 32.9$ atm.
b) $p_k = 47$ atm.

where A is a constant depending on the liquid in question. k_E (Eötwös' constant) was found to be about 2.12 for many liquids. Values of k_E for the twelve solvents have been summarized in Table 8. It is seen that k_E for propyl acetate and pyridine is somewhat higher than 2.12, while k_E for acetone and propionitrile is lower than 2.12. Later on it has been proved that k_E even for 'normal' liquids is not a constant, but depends on the molecular weight of the liquid, *cf.* Glasstone [23]. Among the twelve solvents just acetone and propionitrile have the lowest molecular weights, and therefore we are not able to draw any conclusion on association in these two solvents. Neither did an examination of the temperature dependence of k_E enlighten the question: values of k_E in many temperature intervals between 0° and 100° C were calculated for the twelve solvents. In no case was an essential increase of k_E with increasing temperature found (*cf.* Glasstone [23]). For acetone, aniline and pyridine we found an increase of about 10 %, for propyl acetate a decrease of about 16 %, while there was no clear variation in k_E for the other solvents.

SUMMARY

1. The solubility of *carbon dioxide* expressed as the Bunsen absorption coefficient is determined at 25° C in the following solvents: toluene 2.21, chloroform 3.58, 1,2-dibromoethane 2.00, chlorobenzene 2.17, normal propyl acetate 4.82, aniline 1.20, methyl acetate 6.43, pyridine 3.36, benzyl cyanide 2.05, acetone 6.44, propionitrile 5.39 and nitrobenzene 2.20.

For *carbon monoxide* the following solubilities were determined at 25° C: toluene 0.171, 1,2-dibromoethane 0.778, normal propyl acetate 0.227, aniline 0.0464, pyridine 0.107, benzyl cyanide 0.0694, propionitrile 0.199 and nitrobenzene 0.0813.

These solubilities are compared with previous measurements in Table 2.

2. If the solubility of *carbon dioxide* is calculated from

$$-\log x_2 = -\log x_2^i + \frac{\bar{V}_2}{2.303\,RT}(\delta_1-\delta_2)^2$$

we get values less than the experimental ones. The difference between the calculated and experimental values of $-\log x_2$ is shown to be approximately proportional to the dipole moment of the solvent, *cf.* Fig. 1.

The solubilities of *oxygen, carbon monoxide* and *nitrogen* are calculated from equation (1), and the same dependence of the dipole moments of the solvents was found to be valid (*cf.* Fig. 1). The different slopes of the lines in this figure are held to depend on the electronic polarization of the gases.

3. A comparison between calorimetric values of the heat of vaporization for the solvents and values calculated from the temperature dependence of the vapour pressure is given in Table 6 and 7.

4. Different criteria for association in liquids are discussed. Acetone is the only one among the twelve solvents which is assumed to be associated (*cf.* Figs. 2 and 3). It is shown that the solubility of the four gases in acetone can be explained by assuming a mean molecular weight of acetone equal to 75.

We wish to express our gratitude towards the chief of the laboratory, Professor *Carl Faurholt* for the unfailing interest he has shown our work. Also we wish to thank *Det teknisk-videnskabelige Forskningsråd,* Copenhagen, for financial support.

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Received May 18, 1954.