ACTA CHEMICA SCANDINAVICA 12 (1958) 1015—1023

The Solubility of Nitrogen, Argon and Ethane in Alcohols and Water

J. CHR. GJALDBÆK and H. NIEMANN

Department of Inorganic Chemistry, The Royal Danish School of Pharmacy, Copenhagen, Denmark

The solubility of nitrogen expressed as the Bunsen absorption coefficient is determined at 25°C in the following solvents: *n*-propanol 0.121, *n*-pentanol 0.102, *c*-hexanol 0.0562 and ethylene glycol 0.0140. For argon the following solubilities were determined at 25°C: *n*-propanol 0.231, *n*-butanol 0.220, *n*-pentanol 0.205 and ethylene glycol 0.0317. For ethane at 25°C: methanol 2.14, ethanol 2.52, *n*-propanol 2.60, *n*-butanol 2.61, *n*-pentanol 2.53, *c*-hexanol 1.75, and ethylene glycol 0.215.

Several of the experiments were also carried out at 35°C. A semiempirical explanation of the magnitude of the gas solubilities in the solvents is given using solubility parameters and dielectric constants for the solvents and solubility parameters and polarizabilities for the gases. Solubilities of helium, hydrogen, carbon monoxide, and nitrous oxide have been included in the investigation.

The solubilities of non-polar gases in non-polar liquids can be calculated from the equation

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

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 eqn. (1) reference should be made to Hildebrand and Scott [1].

In a recent paper [2] it was shown that eqn. (1) predicts too small solubilities of gases in polar non-associated solvents. It was, moreover, shown that for oxygen, carbon monoxide, nitrogen, and carbon dioxide the ratios between experimental values and values calculated from eqn. (1) are approximately proportional to the dipole moments of the solvents.

The purpose of the present paper is to examine the solubilities in the associated solvents: water and alcohols. In these solvents, all of which have nearly the same dipole moment (μ about 1.8 Debye), the solubilities vary considerably. The solubilities of nitrogen, argon, and ethane increase in the following order of the solvents: water, ethylene glycol, methanol, ethanol, *n*-propanol, *n*-butanol, *n*-pentanol, see Table 5. The solubility of ethane is about 360 times higher in *n*-pentanol than in water. It will be shown how it is possible to account fairly accurately for the solubilities in methanol, ethanol, *n*-propanol, *n*-butanol, *n*-pentanol, and *c*-hexanol and even obtain a rough estimate for the solubilities in ethylene glycol and water.

MATERIALS AND PROCEDURE

The solubility determinations were carried out by a procedure described in an earlier paper [3].

Nitrogen from "Dansk Ilt- og Brintfabrik" was shown to contain less than 0.13 % oxygen by absorption analysis in an apparatus as described by Christiansen and Wulff [4]. *Argon* and *ethane* were of the same purity as described in a previous paper [5].

Methanol, ethanol, and n-*propanol* were dried by means of magnesium using iodine as a catalyst according to Lund and Bjerrum [6]; these three alcohols were fractionated in a wire gauze column which had about 35 theoretical plates. The fractions used showed the following constants: methanol b. p. 64.60 – 64.63°C and n_D (20°) 1.3285; ethanol b.p. 78.49°C and n_D (20°) 1.3614; *n*-propanol b.p. 97.1 – 97.4°C and n_D (20°) 1.3856. n-*Butanol* was fractionated in the same column and showed a b.p. of 117.75 – 117.83°C and n_D (20°) 1.3995. n-*Pentanol* was fractionated twice in the column at about 115 mm pressure and showed a b.p. of 137.83 – 137.90°C (760 mm) and n_D (20°) 1.412.

c-*Hexanol* was dried by boiling with quicklime and then fractionated in the column at about 115 mm pressure. The bottles containing those fractions which were solid at room temperature were placed upside down in a thermostat; the temperature of the thermostat was slowly increased from 20° to 24°C; slight amounts of liquid impure c-*hexanol*, which were collected in the neck of the bottles, were rejected. By this procedure we obtained samples which were completely solid at 24°C. The melting point reported in the literature [7] is 25.15°C, corresponding to a content of 0.05 % water in our fractions.

Ethylene glycol was fractionated in the column at about 53 mm pressure; the fractions used showed a b.p. of 197.30 – 197.42°C (760 mm) and n_D (20°) 1.4320.

All the boiling points mentioned were determined by distillation of 30 ml liquid in a boiling point apparatus as described by Baggesgaard Rasmussen and Reimers [8]. At least 90 % of each of the samples distilled in the temperature intervals stated. All the temperatures were recalculated to a pressure of 760 mm, but no thermometer corrections were used. The temperature intervals mentioned are a criterion for the purity of the liquids.

EXPERIMENTAL RESULTS

The results of the solubility determinations are given in Tables 1, 2, and 3. The experiments were carried out at 25°C, and in addition some were carried out at 35°C.

It appears from Table 4 that our values for the solubility of ethane in methanol and ethanol are slightly higher than values given by McDaniel [10]. Our value for the solubility of ethane in *c*-hexanol is about three times as high as the value given by Cauquil[11]. Cauquil found that one liter of *c*-hexanol dissolved 711.5 ml ethane at 26°C and 755 mm corresponding to the Bunsen absorption coefficient $\alpha = 0.64$ at 26°C. If we use the same temperature coefficient for the solubility of ethane in *n*-propanol and in *c*-hexanol our value

Table 1. The solubility of nitrogen. Experimental values expressed in Bunsen absorption coefficients.

Solvent	t°C	α	Mean of α at 25°
n-Propanol	24.91	0.1209	0.121
	24.91	0.1208	
n-Pentanol	24.91	0.1021	0.102
	25.00	0.1013	
c-Hexanol	24.91	(0.0549)	0.0562
	25.00	0.0562	
Ethylene glycol	25.02	0.01428	0.0140
	25.01	0.01374	

Table 2. The solubility of argon. Experimental values expressed in Bunsen absorption coefficients.

Solvent	t°C	α	Mean of α	
			25°.0	35°.0
n-Propanol	24.98	(0.2284)	0.231	
	25.00	0.2315		
	25.01	0.2310		
	35.06	0.2231		0.224
	34.98	0.2249		
	35.00	0.2248		
n-Butanol	24.99	0.2206	0.220	
	25.00	0.2198		
	34.98	0.2156		0.215
	35.00	0.2146		
n-Pentanol	24.97	0.2055	0.205	
	25.00	0.2049		
	35.03	0.2025		0.201
	35.01	0.1993		
Ethylene glycol	24.99	0.0320	0.0317	
	24.99	0.0314		
	35.00	0.0325		0.0320
	35.00	0.0315		

Table 3. The solubility of ethane. Experimental values expressed in Bunsen absorption coefficients.

Solvent	t°C	a	Mean of a	
			25°.0	35°.0
Methanol	25.00 25.01 25.00	2.124 2.161 2.075	2.14	
Ethanol	25.00 25.00	2.523 2.519	2.52	
n-Propanol	25.00 25.01	2.599 2.593	2.60	
	35.00 35.00	2.235 2.239		2.24
n-Butanol	25.00 25.01	2.623 2.597	2.61	
n-Pentanol	25.01 25.00 25.00	2.520 2.565 2.498	2.53	
	35.00 34.99	2.190 2.176		2.18
c-Hexanol	25.00 25.01	1.750 1.747	1.75	
Ethylene glycol	25.01 25.01 25.01	(0.2141) 0.2159 0.2150	0.215	
	34.99 34.99	0.1949 0.1945		0.195

Table 4. Solubilities of nitrogen and ethane expressed in Bunsen absorption coefficients (a) at 25°C. Comparison with older measurements.

	Solvent	Author	a	a present invest.
Nitrogen	*n*-pentanol	Just [9]	0.112	0.102
Ethane	methanol (99 %) ethanol (99.8 %) *c*-hexanol	McDaniel [10] McDaniel [10] Cauquil [11]	1.81 2.10 0.64 *	2.16 2.52 1.75

* 26°C

Table 5. Solubilities of nitrogen, argon and ethane expressed in mole fractions, $x_2 \times 10^4$ at 25°C.

	δ_1	V_1	ε_1*	N_2	A	C_2H_6
H_2O	23.4	18.1	78	0.120 [a]	0.254 [c]	0.339
$(CH_2OH)_2$	17.1	55.9	37.7	0.349	0.792	5.42
CH_3OH	14.35	40.7	32.8	2.75 [b]	4.46 [c]	39.2
C_2H_5OH	12.80	58.7	24.3	3.56 [b]	6.21 [c]	66.3
n-C_3H_7OH	11.95	75.2	21.1	4.06	7.75	87.5
n-C_4H_9OH	11.2	92.0	17.8	4.60 [b]	9.04	107
n-$C_5H_{11}OH$	10.9	109	15.2	4.95	9.95	123
c-$C_6H_{11}OH$	11.7	106	15.0	2.66	5.30 [c]	83.0

* Values from *Int. Crit. Tables* except for ethanol, for which the value is from *Le Fèvre* (1938).
a) Orcutt and Seevers, *J. Biol. Chem.* **117** (1936) 501.
b) Kretschmer, C. B. *et al. Ind. Eng. Chem.* 38 (1946) 506.
c) Lannung [14].

at 26°C is $\alpha = 1.72$. To prove that our ethane was pure it was analyzed by means of gaschromatography, and the absorption spectrum in infrared was determined, see a previous paper [5]. As a further criterion for the purity of ethane we determined the solubility in water. The result was $\alpha = 0.0416$ at 25°C. Winkler [12] found $\alpha = 0.0410$ and Morrison and Billett [13] $\alpha = 0.0391$. It can be mentioned that Cauquil's value for the solubility of argon in c-hexanol ($\alpha = 0.157$ at 26°C) is somewhat higher than the value given by Lannung [14] ($\alpha = 0.112$ at 25°C).

A survey of the solubilities expressed as mole fractions ($x_2 \times 10^4$) at 25°C is given in Table 5 together with some values from the literature.

CORRELATION WITH THEORY

It will be shown in the following how it is possible to account for the solubilities using solubility parameters, molal volumes, and dielectric constants for the solvents together with solubility parameters and polarizabilities for the gases. The solubility parameters of the solvents are calculated from heats of vaporization, which will now be discussed.

The heat of vaporization (ΔH) for *methanol* equal to 9 034 ± 30 cal/mole at 25°C was calculated from vapour pressure measurements by Young [15]; a 1.8 % deviation from ideality of the methanol vapours was used. The value $\Delta H = 9\,000 \pm 140$ at 25°C was estimated by graphical interpolation using calorimetric measurements between 20° and 110°C by Fioch et al.[16] and Bartoszewiczowna [17]. From values given in *Int. Crit. Tables* (V, p. 138) we interpolated $\Delta H = 8\,930$ at 25°C. The value $\Delta H = 9\,000$ cal/mole will be used in the present paper.

ΔH for *ethanol* equal to 10 170 at 25°C was calculated from vapour pressure measurements given by Merriman [18]. A 0.3 % deviation from ideality of the ethanol vapours was used. From calorimetric measurements by Fioch et al.[16] and Bartoszewiczowna [17] we interpolated $\Delta H = 10\,200$ at 25°C; an identical value was found by interpolation of values given in *Int. Crit. Tables* (V, p. 138). We will use the value 10 170 cal/mole, which presumably is valid within an accuracy of about 2 %.

ΔH for n-*propanol* equal to 11 330 at 25°C was calculated from vapour pressure measurements by Young [16]. Bartoszewiczowna [17] gives the calorimetric value 180 cal/g at 20°C corresponding to about 10 740 cal/mole at 25°C. The vapour pressures of propanol and of the alcohols mentioned below are so small, that the vapours can be regarded as ideal for our purpose. The value 11 300 cal/mole will be used in the following.

ΔH for n-*butanol* equal to 13 050 at 25°C was calculated from vapour pressure measurements by Kahlbaum [19]. Heats of vaporization were also calculated from vapour pressure measurements by Dreisbach and Schrader [20]; extrapolation to 25°C resulted in the value 12 100. Bartoszewiczowna [17] gives the calorimetric value 149.5 cal/g at 20°C corresponding to about 11 000 cal/mole at 25°C. We will use the value 12 100 cal/mole, which is estimated to be reliable within 8 %.

For ΔH for n-*pentanol* we use the estimated value 13 500 cal/mole at 25°C. This estimate is based on the approximate linear dependence between heats of vaporization of methanol, ethanol, n-propanol, and n-butanol and the molecular weights of these alcohols. From vapour pressure measurements given in *Int. Crit. Tables* (III, p. 220) we calculated the value 12 200; this result is considered to be rather erroneous due to the low and inaccurate vapour pressure data.

McKinley-McKee and Moelwyn-Hughes [21] have given the formula

$$\Delta H \text{ (cal/mole)} = 24\,357 - 12.48 \cdot RT$$

which is a result of vapour pressure measurements for *ethylene glycol* between 86° and 198°C. If we use this formula at 25°C we get about 17 000 cal/mole.

From vapour pressure data of cyclo*hexanol* given by Nitta [22] we have calculated $\Delta H = 14\,900$ between 28° and 37°C and $\Delta H = 14\,400$ between 40° and 60°C; from these values we get $\Delta H = 15\,000$ cal/mole at 25°C. The vapour pressures vary from only 0.906 mm at 27.9°C to 9.202 mm at 60.0°C, and therefore the calculated value of the heat of vaporization is regarded as being rather inaccurate.

ΔH for *water* equal to 2 436 joule/g at 25°C (*Int. Crit. Tables* V, p. 138) corresponds to $\Delta H = 10\,490$ cal/mole.

The solubility parameters of the solvents are calculated from

$$\delta_1 = \sqrt{\frac{\Delta H - RT}{V_1}} \tag{2}$$

where ΔH is the heat of vaporization. The results of the calculations at 25°C are given in Table 5 together with values for the molal volumes (V_1) and the dielectric constants (ε) of the solvents.

Table 6. Values of ideal solubilities, solubility parameters, molal volumes and polarizabilities for nitrogen, argon, and ethane at 25°C.

	N_2	A	C_2H_6
$x_2^i \times 10^4$	16.0	21.6	242
δ_2	5.2	5.43	7.55
$\overline{V}_2$	53	46	88
$\alpha \times 10^{25}$	17.6	16.4	44.7

If we calculate the solubilities of the gases in the alcohols, using eqns. (1) and (2) together with the constants x_2^i, δ_2 and $\overline{V}_2$ from Table 6, we get values which are too low. If we use

$$-\log x_2 = -\log x_2^i + 0.4343 \frac{\overline{V}_2}{RT}(\delta_1{}^* - \delta_2)^2 + \log \frac{\overline{V}_2}{\overline{V}_1} + 0.4343\left(1 - \frac{\overline{V}_2}{\overline{V}_1}\right) \qquad (3)$$

where

$$\delta_1{}^* = \delta_1 - (\varepsilon - 1)\,(0.165 - 0.00143\,\alpha \times 10^{25}) \qquad (4)$$

we can account for the experiments with an accuracy which appears from Table 8. The values of

$$\Delta = (-\log x_2)_{\text{calc.}} - (-\log x_2)_{\text{exp.}} = \log \frac{x_{2(\text{exp.})}}{x_{2(\text{calc.})}}$$

are given in Table 8. The antilogarithm of Δ shows how many times the experimental value of the mole fraction is greater than the calculated value.

We have evaluated eqn. (4) in the following manner. By means of eqn. (1) and the experimental values for the solubilities of argon we calculated values δ'_1 for each alcohol and for water. It is shown in Fig. 1 that there is an approximate linear dependence between the difference $\delta_1 - \delta'_1$ and the

Table 7. Polarizabilities for some gases.

Gas	Slope S (see the text)	$\alpha \times 10^{25}$
He	0.163	2.2
H_2	0.150	7.9
N_2	0.144	17.6
A	0.138	16.4
CO	0.136	19.5
N_2O	0.123	30
C_2H_6	0.101	44.7

Table 8. Deviations between calculated and experimental values of the solubilities expressed as $\Delta = (-\log x_2)_{\text{calc.}} - (-\log x_2)_{\text{exp.}}$.

Solvent	N_2	A	C_2H_6
Methanol	0.08	−0.02	−0.12
Ethanol	0.07	0.00	−0.07
n-Propanol	−0.02	−0.04	−0.09
n-Butanol	−0.08	−0.08	−0.11
n-Pentanol	−0.07	−0.06	−0.07
c-Hexanol	−0.07	−0.11	0.00
Ethylene glycol	0.14	−0.01	0.52
Water	−0.35	−0.51	0.35

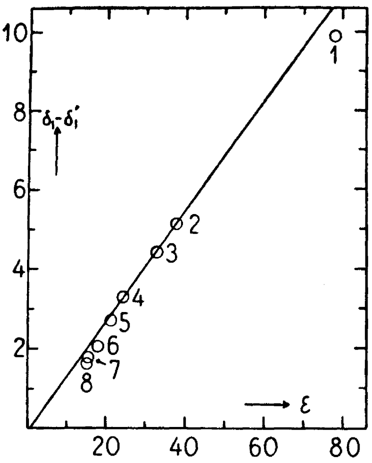

Fig. 1. ($\delta_1-\delta_1'$)-values for *argon* in water (1), ethylene glycol (2), methanol (3), ethanol (4), *n*-propanol (5), *n*-butanol (6), *n*-pentanol (7), and *cyclo*hexanol (8). ε is the dielectric constant of the solvent.

dielectric constant ε. The straight line is drawn through the abscissa value ε—1. The same linear dependence was found for nitrogen, ethane, helium, hydrogen, carbon monoxide, and nitrous oxide. The slopes of the lines are given in Table 7 together with polarizabilities of the gases ($\alpha \times 10^{25}$). The approximate linear dependence between the slopes (S) of these lines and the polarizabilities of the gases is shown in Fig. 2. By means of the slope of the straight line in Fig. 2 (0.00143) and the intersection on the ordinate axis (0.165) we get eqn. (4).

It appears from Table 8, that the calculations of the solubilities of the three gases in water and of ethane in ethylene glycol are very inaccurate. The largest deviation is found for the solubility of argon in water for which the calculated and experimental values are $x_2 = 0.82 \times 10^{-4}$ and 0.25×10^{-4}, respectively. It should be emphasized that the differences Δ in Table 8 are very sensitive to small variations in the δ_1 values. If we use $\delta_1 = 10.64$ for *n*-butanol instead of $\delta_1 = 10.2$ we get $\Delta = 0.04$, $\Delta = 0.03$ and $\Delta = 0.01$

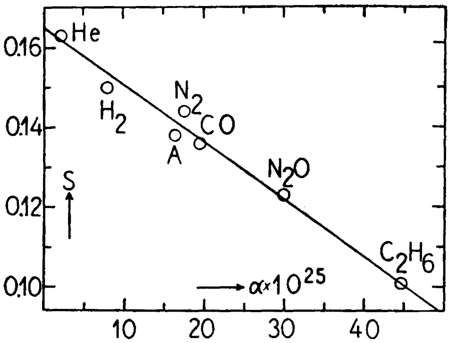

Fig. 2. S (see the text) for different gases. $\alpha \times 10^{25}$ is the polarizability of the gas.

for nitrogen, argon, and ethane, respectively. $\delta_1 = 10.64$ corresponds to the heat of vaporization 13 050 cal/mole (see p. 1020).

Acknowledgements. We wish to express our gratitude to Professor Carl Faurholt, director of the laboratory, for his kind interest in the investigations. Our thanks are also due to lecturer Georg Kilde for many valuable discussions. The financial support from *Statens almindelige Videnskabsfond* is gratefully acknowledged.

REFERENCES

1. Hildebrand, J. H. and Scott, R. L. *Solubility of Non-electrolytes, 3rd Ed., Reinhold Publishing Co., New York* 1950.
2. Gjaldbæk, J. Chr. and Krogh Andersen, E. *Acta Chem. Scand.* **8** (1954) 1398.
3. Gjaldbæk, J. Chr. *Acta Chem. Scand.* **6** (1952) 623.
4. Christiansen, J. A. and Wulff, I. *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **22** (1945) No. 4.
5. Gjaldbæk, J. Chr. and Niemann, H. *Acta Chem. Scand.* **12** (1958) 611.
6. Lund, H. und Bjerrum, J. *Ber.* **64** (1931) 210.
7. Trav. Bur. Int. Et. Phys.-Chim. *J. chim. phys.* **34** (1937) 693.
8. Baggesgaard Rasmussen, H. og Reimers, F. *Dansk Tidsskrift for Farmaci* **16** (1942) 161.
9. Just, G. *Z. physik. Chem.* **37** (1901) 342.
10. McDaniel, A. S. *J. Phys. Chem.* **15** (1931) 587.
11. Cauquil, G. *J. chim. phys.* **24** (1927) 53.
12. Winkler, L. W. *Ber.* **34** (1901) 1409.
13. Morrison, T. and Billett, F. *J. Chem. Soc.* **1952** 3819.
14. Lannung, A. *J. Am. Chem. Soc.* **52** (1930) 68.
15. Young, S. *Sci. Proc. Dublin N.S.* **12** (1910) 374.
16. Fioch, E. F., Ginnings, D. C. and Holton, W. B. *Nat. Bur. Standards* **6** (1931) 881.
17. Bartoszewiczowna, E. *Roczniki Chem.* **11** (1931) 90.
18. Merriman, R. W. *J. Chem. Soc.* **103** (1913) 628.
19. Kahlbaum, G. W. A. *Z. physik. Chem.* **26** (1898) 577.
20. Dreisbach, R. R. and Schrader, S. A. *Ind. Eng. Chem.* **41** (1949) 2879.
21. McKinley-McKee, J. S. and Moelwyn-Hughes, E. A. *J. Chem. Soc.* **1952** 838.
22. Nitta, I. *J. Chem. Soc. Japan, Pure Chem. Sect.* **69** (1948) 141.

Received February 4, 1958.