The Solubility of Propane in Non-polar Solvents

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Solubility experiments with propane carried out at 25°C resulted in the following values expressed as Bunsen coefficients: in perfluoroheptane 5.17, hexane 21.6, octane 18.1, benzene 14.7 and in 1,4-dioxane 7.48.

For the solubility parameter of propane, δ_2, the empirical value 6.65 is determined. The theoretical value of δ_2 calculated from the heat of vaporization and the molar volume of propane is 5.95.

In the explanation of the solubility of gases in non-polar solvents the following two equations have been used

$$\log x_2 = \log x_2^i - \frac{\overline{V}_2 \Phi_1^2}{2.303\ RT} (\delta_1 - \delta_2)^2 \tag{1}$$

$$\log \Phi_2 = \log x_2^i - \frac{\overline{V}_2 \Phi_1^2}{2.303\ RT} (\delta_1 - \delta_2)^2 - 0.4343 \left(1 - \frac{\overline{V}_2}{V_1}\right) \Phi_1 \tag{2}$$

The solubility parameter, δ, for the solvents can be calculated from

$$\delta = \sqrt{\frac{\Delta H - P\Delta V}{V}} \sim \sqrt{\frac{\Delta H - RT}{V}} \tag{3}$$

where ΔH is the heat of vaporization and V the molar volume of the solvent. For those gases, which at 25°C are above their critical temperatures, δ_2 (the solubility parameter of the gas) has been empirically determined from the solubility experiments. For gases with a critical temperature higher than 25° a value of δ_2 at 25°C can be calculated from eqn. (3).

The critical temperature of chlorine is about 144°C, and the value of δ_2 for chlorine [2] calculated from eqn. (3) is 8.7 at 25°C.

The experimental values of the solubilities of chlorine in different solvents are generally between the values calculated from eqns. (1) and (2).

For carbon dioxide [3] and ethane [4] the δ_2-values 4.1 and 6.1, respectively, were calculated from eqn. (3). These values inserted in eqns. (1) and (2) gave only poor agreement with the solubility experiments. From these the emperical values of δ_2 are 5.1 and 6.6 [1], respectively.

In order to get a further example of a gas for which we can calculate δ_2 from eqn. (3) we chose to determine some solubilities of propane. Propane at 25°C is about 75° below its critical temperature, while at 25°C carbon dioxide is 6° and ethane 7° below their critical temperatures.

EXPERIMENTAL PROCEDURE AND RESULTS

The solubility determinations were carried out in an apparatus (III) which is described in the preceding paper [1]. The gaschromatographic analyses described below are carried out on a Perkin-Elmer gaschromatograph (154 B) using columns about one metre long and helium as carrier gas.

Propane (research grade, Phillips Petroleum Company) showed by gaschromatographic analysis ("Molecular Sieve 5A", 30°C) 0.1 volume per cent atmospheric air and 0.03 volume per cent ethane (silicagel, 30°C) as impurities; it was used without any purification.

Perfluoroheptane was of the same origin and purity as described in an earlier paper [5].

Hexane ("für Chromatographie", Merck) was purified by gaschromatography on a preparative column (dioctyl phthalate, 75°C, nitrogen as carrier gas). Gaschromatographic analysis (dioctyl phthalate, 50°C) showed only one component. $n_D^{25} = 1.3723$ (Timmermans [6] states $1.3722-1.3723$).

Two products of *octane* were used, partly octane A, which is described in the preceding paper [1] and partly a synthetic product (octane C). The latter product was kindly given us by the Physical-Chemical Institute of the University, Copenhagen. The octane C had a boiling point interval of 0.22°C, *i.e.* a little larger than for octane A (0.02°) determined as described in the preceding paper; the amount of impurity was estimated to be about 0.1 %. The solubility of propane in the two products differed by less than 1 %.

Benzene (Benzolum crystallisable p.a. and "für Chromatographie", Merck) was purified by three times fractionated freezing. The boiling point interval was 0.01° and n_D^{25} 1.4981 (Timmermans [6] states $1.4979-1.4981$). Gaschromatographic analysis (dioctyl phthalate, 52°C) showed only one component.

Half of one litre *1,4-dioxane* (Analar, British Drug House) was frozen; the melted crystals which distilled within 0.05°C and showed n_D^{25} 1.4200 were boiled 7 h with sodium and then distilled. A middle fraction was redistilled with sodium and nine fractions were collected; the last seven were mixed and used for the experiments. Gaschromatographic analysis (diglycerol, 101°C) showed impurities to be about 0.02 % water and traces of two unidentified components. The product melted within 0.30°C and showed $n_D^{25} = 1.4200-1.4201$; the temperature coefficient of the refractive index was measured to be -0.00048 pr. degree between 21 and 27°C. (Timmermans [6] states $n_D^{25} = 1.4201-1.42025$). After two months the purified dioxane was shown to contain some peroxide; it was detected by the appearance of a black sediment produced by shaking with mercury. The peroxide was removed by shaking at intervals for two days with sodium hydroxide, followed by distillation.

The results of the solubility experiments are given in Table 1 expressed as Bunsen coefficients. In the calculation all usual corrections were introduced; moreover we took into account that the vapour pressures of the solvents are decreased by the dissolved gas. In this correction we assumed the lowering of the vapour pressure to be proportional to the mole fraction of the dissolved gas.

Table 1. Solubilities of propane. Experimental values at 25.0°C expressed in Bunsen absorption coefficients.

Solvent	a	Mean of a
Perfluoroheptane	5.07 5.27	5.17
Hexane	21.6 21.5	21.6
Octane	18.0 18.1	18.1
Benzene	14.7 14.7	14.7
1,4-Dioxane	7.55 7.41	7.48

CORRELATION WITH THEORY

The ideal solubility was calculated from

$$x_2^i = f_2/f_2^o \qquad (4)$$

where f_2^o is the fugacity of liquid propane at its vapour pressure and f_2 the fugacity at one atmosphere.

The vapour pressure af propane, equal to 9.50 atm. at 25°C, was interpolated graphically (log p *vs.* $1/T$) from measurements given by Sage *et al.*[7] This value is about 2 % lower than a value given by Francis and Robbins [8] and about 2 % higher than the vapour pressure which can be extrapolated from values given in *Selected Values* (Ref.[9], p. 121) and also about 2 % higher than a value given by Stull [10].

The deviations of propane from an ideal gas have been determined experimentally by Sage *et al.*[7] By interpolation we calculated the ratio between fugacity and pressure at 25°C to be 0.843, hence $f_2^o = 8.01$ atm.

The weight of one litre of propane at 25°C and 1 atm. according to Kemp and Egan [11] is 1.8324 g. From the equation

$$\ln(f/P) = -\omega P/RT \qquad (5)$$

(Lewis and Randall [12]) we got $f_2 = 0.962$. In this equation ω is the difference between the ideal and the real volume of one mole ($\omega = 0.413$ litre), $P = 1$ atm. and $T = 298°K$. The value of the ideal solubility is then

$$x_2^i = 0.962/8.01 = 0.120.$$

The heat of vaporization of propane according to *Selected Values* (Ref.[9], p. 132) is 3605 cal/mole. The value of $P\Delta V$ at 25°C and 9.50 atm. is 453 cal/mole according to Sage *et al.*[7] who also have measured the density of liquid propane (0.4962 at 25°C); the molar volume of liquid propane (V_2) is thus 88.9 ml. These values inserted in eqn. (3) give $\delta_2 = 5.95$.

Table 2. Experimental and calculated values for solubilities ($x_2 \times 10^2$) of propane at 25°C. $x_2^i \times 10^2 = 12.0$, $\overline{V}_2 = 88.9$ ml/mole.

Solvent	V_1 ml/mole	δ_1	exptl.	$\delta_2 = 5.95$		$\delta_2 = 6.65$		
				eqn. (1)	eqn. (2)	eqn. (1)	eqn. (2)	% difference eqn. (1) eqn. (2)
n-C_7F_{16}	226	5.85	5.08	12.0	16.8	11.0	14.2	116 180
n-C_6H_{14}	132	7.30	11.6	9.40	10.3	11.4	12.0	— 2 3
n-C_8H_{18}	164	7.55	12.0	8.46	10.2	10.8	12.3	—10 3
C_6H_6	89.3	9.15	5.68	2.84	2.81	5.15	5.15	— 9 — 9
1,4-Dioxane	85.7	10.0	2.86	1.07	0.091	2.42	2.43	—15 —15

A survey of the solubilities of propane is given in Table 2. The calculations are carried out using eqns. (1) and (2) and the constants $x_2^i = 0.120$, $\overline{V}_2 \sim V_2 = 88.9$ ml/mole and $\delta_2 = 5.95$. It can be seen that the calculated solubility is much too high for propane in perfluoroheptane; the solubilities in hexane and octane are calculated with fair accuracy from eqn. (2) while both equations render much too low values in benzene and dioxane.

Using the empirical value $\delta_2 = 6.65$ both equations represent the experiments rather well exept in the case of perfluoroheptane.

Fig. 1. Correlation between δ_2 calculated from eqn. (2) using solubility experiments and δ_2 calculated from eqn. (3) using heats of vaporization.
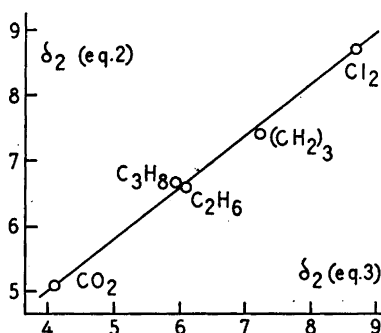
A graph of the relation between empirical solubility parameters and parameters calculated from eqn. (3) is given in Fig. 1. It can be seen that the deviations decrease with increasing critical temperature of the gas.

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