Table I. Coefficients in Equations 5 and 6 for 2-Butyne (I) and 2,4-Hexadiyne (II) in the Solvents CS_2, CCl_4, and Benzene-d_6 (C_6D_6)

Solute[a]	Solvent	a_1	a_2	a_3	a_4	$b_1 \times 10^3$	$b_2 \times 10^3$	$b_3 \times 10^3$	$b_4 \times 10^3$	Temp range, °C
I	CS_2	1.2916	−0.7304	0.2378	−0.0855	1.450	−0.287	−0.840	0.657	−45 ~ +20
	CCl_4	1.6328	−0.4785	−0.8967	0.4559	1.945	−1.625	2.132	−1.472	−30 ~ +20
	C_6D_6	0.9724	−0.1871	−0.1058	0.3397	1.181	−2.065	4.310	−2.446	−30 ~ +30
II	CS_2	1.2916	−0.7706	0.0898	1.1895	1.450	2.584	−26.67	55.95	+10 ~ +45
	CCl_4	1.6328	−0.7735	−0.0334	−0.0413	1.945	1.275	−9.864	10.87	+10 ~ +65
	C_6D_6	0.9724	−0.1573	0.1004	−0.1746	1.181	0.0367	−3.700	7.333	+10 ~ +75

[a] Concentration range in mole fraction of solute 0–1.0 except for: II in CS_2 (0–0.3); II in CCl_4 (0–0.4); II in C_6D_6 (0–0.4).

Table II. Coefficients in Equations 8 and 9 for 2-Butyne (I) and 2,4-Hexadiyne (II) in the Solvents CS_2, CCl_4, and Benzene-d_6 (C_6D_6)

Solute[a]	Solvent	c_1	c_2	c_3	c_4	d_1	d_2	d_3	d_4	Temp range, °C
I	CS_2	−3.0114	−1.5324	0.2409	+0.0920	590.14	262.02	46.378	−15.127	−45 ~ +20
	CCl_4	−4.5933	1.9797	−3.9211	2.1400	1337.6	−808.17	662.01	−307.92	−10 ~ +20
	CCl_4	−5.0704	4.1076	−6.7271	3.2948	1463.7	−1429.7	1607.7	−758.25	−30 ~ −10
	C_6D_6	−4.7494	2.5123	−4.0857	1.9280	1287.1	−107838.	1296.6	−621.89	−30 ~ +20
II	CS_2	−3.2075	−6.8035	67.338	−156.89	646.53	2314.4	−20500.	48355.	+10 ~ +45
	CCl_4	−4.3113	−2.2438	11.499	−16.436	1255.7	771.06	−4272.8	6322.2	+10 ~ +65
	C_6D_6	−4.7494	1.9563	−9.6528	18.943	1287.1	−287.19	1151.4	−2552.1	+10 ~ +75

[a] Concentration range in mole fraction of solute 0–1.0 except for: II in CS_2 (0–0.3); II in CCl_4 (0–0.4); II in C_6D_6 (0–0.375).

$$D = d_1 + d_2X + d_3X^2 + d_4X^3 \qquad (9)$$

The results are summarized in Table II, giving the c_i's, d_i's, and the temperature range of measurements. The viscosities thus calculated from Equations 7–9 are accurate within 1%.

NOMENCLATURE

h = sum of the scales of both arms of the pycnometer
V_t = vol, ml of the liquid in the pycnometer corresponding to liquid height, h
t = temp, °C
ρ = density of liquid, g/ml
V_o = vol, ml of the liquid in the pycnometer at 22°C
A, B, C, D, E, F, G, = least-square determined parameters
a_i, b_i, c_i, d_i
η = viscosity of liquid, cP

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Solubility of 16 Gases in $(C_4F_9)_3N$ and CS_2

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The solubility of the following gases was measured in $(C_4F_9)_3N$ and CS_2 at 1 atm and over ranges of approximately 30°: He^3, He^4, Ne, Ar, Kr, Xe, H_2, D_2, N_2, CH_4, C_2H_6, c-C_3H_6, CF_4, C_2F_6, c-C_4F_8, and SF_6.

Dymond and Hildebrand (*4*) in 1967 described an apparatus that gave rapid, accurate values of the solubility of gases in liquids. Dymond (*3*) published values of the mole fraction, x_2, of nine gases at 1 atm in c-C_6H_{12} over ranges of temperature of ~40°. Points for log x_2 vs. log T for each gas fell upon straight lines whose slopes, $\Delta \log x_2/\Delta \log T$, multiplied by the gas constant, R, give the entropy of solution, since $\bar{S}_2 = S_2^g = R(\partial \ln x_2/\partial \ln T)_{\Delta F=0}$. The points for the entropy of solution plotted against the solubility expressed as $-R \ln x_2$ gave a straight line whose slope was 1.64 and whose intercept at $-R \ln x_2 = 0$ was −21.0 cal/mol deg. The points for CF_4 and SF_6 were just off the line. Miller (*10*) later added points for C_2F_6, C_3F_8, c-C_4F_8, and $CClF_3$.

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Table I. Solubility, $x_2 \equiv$ Mole Fraction, of Gases at 1 Atm and 25°C, in $(C_4F_9)_3N$ and CS_2

[Effect of temperature, $R(\Delta \log x_2/\Delta \log T)$, cal/mol deg]

	In $(C_4F_9)_3N$		In CS_2	
	$10^4\, x_2$	$R\left(\frac{\Delta \log x_2}{\Delta \log T}\right)$	$10^4\, x_2$	$R\left(\frac{\Delta \log x_2}{\Delta \log T}\right)$
He^3	11.02	4.24	...	...
He^4	11.67	4.13	0.39	...
Ne	16.79	2.76	0.59	~8.0
Ar	61.05	− 1.54	4.87 (*12*)	1.80
Kr	111.5	− 3.30	17.56	−7.30
Xe	215.2	− 5.01	104.2	−9.08
H_2	15.52	3.28	158.9 (*2*, *7*)	5.30
D_2	16.03	3.04	...	...
N_2	42.36	− 0.35	2.22	4.00
			2.23 (*5*)	
CH_4	68.83	− 1.88	12.72	−0.87
C_2H_6	227.4	− 6.36	107.9	−7.55
c-C_3H_6	694.7	−10.30	52.5	...
CF_4	148.1	− 5.35	2.06 (*1*)	4.00
C_2F_6	474.8	− 9.70	...	...
c-C_4F_8	3864	−17.60	22.90	−4.63
SF_6	774.6	−11.60	8.12	0.00
	731	−11.32 (*6*)		

Linford and Hildebrand (*9*) obtained data for five gases in the Freon $CCl_2F \cdot CClF_2$. These data and others obtained by Hiraoka (*6*) and Archer (*1*), when plotted as before, also gave a straight line with intercept at −21.0. Its slope was 1.70, but the points were differently spaced along the lines for this solvent.

The present study was undertaken to secure similarly accurate data for series of gases in two liquids which are at the extremes of solvent power among common nonpolar liquids: CS_2 and $(C_4F_9)_3N$. Data obtained earlier for gases in C_7F_{16} and $C_6F_{11}CF_3$ (*2*, *5*, *8*) had not been determined with the accuracy now possible, and these two liquids are no longer commercially available, so we turned to the perfluorotributylamine, "FC43," made by the 3M Co. Its solvent power is almost identical with that of C_7F_{16}. The electron density on the nitrogen atom is so small that basic character is virtually absent.

The 3M Co. kindly presented us with an adequate amount. We distilled it in a column of many plates and used the portion boiling between 174.7° and 175.5°C. This fraction gave a single peak in vapor-phase chromatography with different columns. Dissolved iodine showed no ultraviolet absorption peak characteristic of hydrocarbon impurities. Its density conformed to $1.8801[1 - 0.0022\,(t - 25)]$ in the range 15–40°C. The carbon disulfide used was the manufacturer's spectrochemical grade. The gases, other than He^3, were manufacturer's research grade. They were dried before use by passing through $CaCl_2$. He^3 was obtained from the Lawrence Radiation Laboratory, Berkeley, through the efforts of B. J. Alder.

The apparatus and operation were those described in ref. 4. Results are given in Table I. Instead of tabulating all measurements, as in the earlier papers, we give only the values of $10^4\, x_2$ at 25°C and of $R(\Delta \log x_2/\Delta \log T)_{P,\,\mathrm{sat}}$ from which solubility at other temperatures can easily be calculated. Duplicate values of $10^4\, x_2$ at the same temperature agreed to within 0.2%. Values of entropy in the tables are considered accurate to 0.1. Earlier measurements made with the perfluoroamine (*8*) are here omitted because the density of the liquid was 1.872 at 25°C instead of 1.880, and the data are less reliable.

The data are plotted in Figure 1 as $\bar{S}_2 - S_2^g$ vs. $-R \ln x_2$ at 25°C as in the earlier papers.

The results presented in this paper and those previously published are being used by J. H. Hildebrand, who suggested this study, in a comprehensive, factual, and theoretical survey of solubility of gases in liquids. The solubility of He^3 in $(C_4F_9)_3N$ was utilized in a recent paper on a quantum enhancement of diffusion of quantum gases by Powell and Hildebrand (*11*).

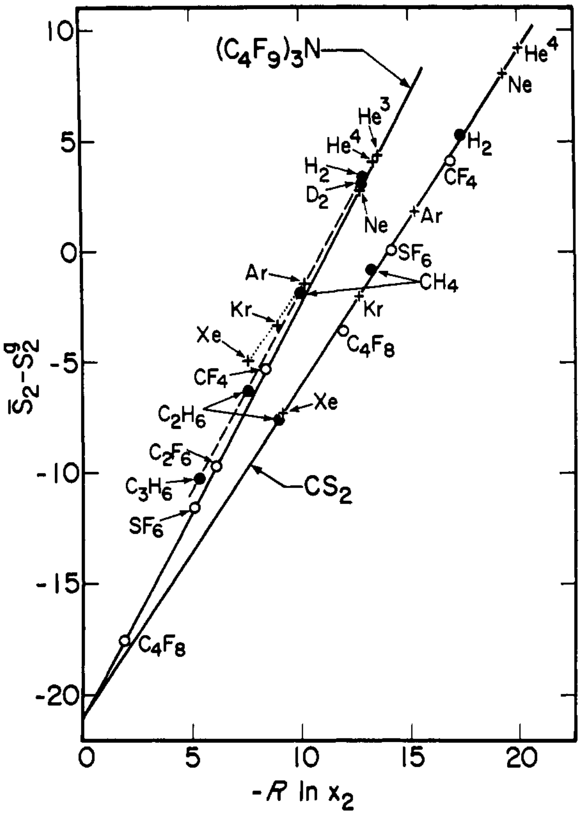

Figure 1. Entropy of solution of gases at 25°C and 1 atm, $\bar{S}_2 - S_2^g$, cal/mol deg, calculated from $R(\Delta \log x_2/\Delta \log T)$ plotted against the solubility expressed as $-R \ln x_2$

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Solubility of Urea in Water–Alcohol Mixtures

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The solubility of urea in water, methyl alcohol, ethyl alcohol, isopropyl alcohol, and mixtures thereof was experimentally measured over a temperature range from about 0–60°C. The data were correlated by an exponential function of the form:

$$\log_e S = A + Bt$$

The actual data and constants for the correlating equation are reported.

Many of the processes concerned with nucleation and crystallization of urea are not well understood. In addition, the solubilities of urea in water–alcohol mixtures, which have to be known to study the nucleation process, have not been measured to any great extent. The data available in the literature are quite scattered and in some cases believed to be unreliable.

The object of this investigation (*2*) was to determine systematically the solubility of urea in water, methanol, ethanol, isopropanol, and their mixtures. The results were compared with some literature values existing for the pure solvents.

EXPERIMENTAL

Saturated solutions of urea in 12 different solvents were prepared at temperatures from about 0–60°C. The particular solvent and an excess amount of urea were added to a 300-ml round-bottomed flask. The flask with urea and solvent was then placed in the constant-temperature bath at a predetermined temperature, controlled to within ±0.05°C. For bath temperatures below room temperature, cooling was provided from a coolant reservoir. A constant flow cooler made by Blue M (Model No. PLL-24SSA-2) was used to maintain the temperature in the coolant reservoir. The solution in the flask was agitated by a glass rod stirrer for at least 6 hr to reach saturation as previously determined (*3*). Dirnhuber and Schutz (*1*) have established that conversion to ammonium cyanate amounts to about 0.1% when held for periods of less than 2 days. After saturation, the solution was allowed to settle for about 1 hr. The top part of the clear solution was transferred by means of a 50-ml syringe and an 18-gauge needle to a tared sealed bottle stored in an oven at a temperature a few degrees higher than the saturation temperature.

About 3–5 ml of saturated solution was transferred into the weighing bottle, immediately covered, and weighed again. All the weighings were made on an Ainsworth (Type 10) single-pen analytical balance reading to 10^{-4} grams. The sample was dried in an oven at 40°C for 12 hr and then placed in a vacuum desiccator for at least 4 hr until a constant weight was achieved. The vacuum step was used to speed up the drying process and to minimize the decomposition of urea at the higher temperatures needed for drying at atmospheric pressure. Finally, the bottle with dried crystals was weighed again, from which the solubility data were calculated. To determine the experimental error, replications of experiments were made for each temperature with three samples taken for each case, and the average values were considered to be the results. The reproducibility of the data was within ±0.5%. Recrystallization of urea in water showed no change in the solubility.

MATERIALS

Certified ACS-grade urea (minimum purity of 99.976%) from Matheson, Coleman & Bell was used as the solute. Methanol and isopropanol were also certified ACS grade from Fisher. Absolute ethanol was purchased from Commercial Solvents, and the water was doubly distilled.

DISCUSSION

The experimental solubilities are presented in Tables I–III. A General Electric Time Sharing Computer Mark 1 was used to

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