Solubilities of Gases in High-boiling Hydrocarbon Solvents

Low-pressure solubilities of methane, ethane, propane, *n*-butane, *iso*-butane, and hydrogen have been measured in *n*-hexadecane, *n*-eicosane, squalane, bicyclohexyl, octamethylcyclotetrasiloxane, diphenylmethane, and 1-methylnaphthalene over the temperature range 25° to 200°C. The accuracy of these measurements is better than 1%. The data for the hydrocarbon gases have been correlated with a generalized configurational entropy and a van Laar-type interaction parameter. The entropic component of that parameter is related to the free volume of the solvent as suggested by Flory's equation-of-state theory of fluid mixtures. The accuracy of the correlation is about ±15%.

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SCOPE

Solubilities of gases in liquids are often required for efficient design of industrial processes. While reliable experimental data for gas solubilities are available for some common systems (Wilhelm and Battino, 1973; Battino and Clever, 1966), many systems of industrial interest have not been studied. Experimental data are particularly scarce at advanced temperatures and for solvents whose molecular size is large.

The primary objective of this work is to provide accurate gas-solubility data for hydrocarbon gas-liquid systems in the temperature range 25° to 200°C. Using the apparatus described by Cukor (1971), new gas-solubility measurements in large-molecule solvents were made in the vicinity of 1 atm pressure. Equilibrium compositions, accurate to 1% or better, were determined from the measured total gas pressure and from a material balance.

Presently available correlations for predicting gas solubilities in liquids are of limited accuracy, especially at advanced temperatures. The second objective of this work, therefore, is to investigate new methods for prediction of solubilities of gases in liquids over wide ranges of temperature. Particular attention is given to the effect on solubility of the size and shape of the solvent molecule, and of the solvent's free volume, as indicated by its coefficient of thermal expansion.

CONCLUSIONS AND SIGNIFICANCE

Gas solubilities expressed by Henry's constants are reported for 26 binary systems. The data were obtained in the temperature range 25° to 200°C and in the vicinity of 1 atm pressure. Their accuracy is estimated as better than 1%. The systems studied contain high-boiling hydrocarbon solvents for which gas-solubility data are rare.

To correlate these and selected previously published solubility data, an expression for Henry's constant has been derived using a generalized configurational entropy (Staverman, 1950) and a residual term of the van Laar form. This residual contains both enthalpic and entropic contributions. At 300°K, the total residual term is correlated with the cohesive energy density of the solvent (corrected for molecular shape) and the entropic component of the residual term is correlated with the thermal expansion coefficient of the solvent. These correlations, coupled with an empirical assumption, give a good representation of the solubility data for hydrocarbon gases in the temperature range 25° to 200°C. Solubilities calculated from the correlation are accurate to about ±15%.

Staverman's configurational entropy is similar to that of Flory-Huggins, but unlike the latter it takes into account molecular shape as well as size.

Correlation of the partial molar residual entropy with the thermal expansion coefficient of the solvent illustrates the importance of equation-of-state or free-volume effects on the solubility of a gas in a liquid.

Solubility data for gases in high-boiling hydrocarbon solvents are useful in petroleum engineering. Further, they are of fundamental importance because gas solubilities in large-molecule solvents are qualitatively different from those in small-molecule solvents. Since the sizes and shapes of the gas and solvent molecules are significantly different, special consideration must be given to the entropy of mixing the gas with the solvent. Previous theoretical treatments for gas solubilities have been limited to systems of small molecules where the ideal entropy of mixing provides a reasonable approximation. For the solution of a gas in a large-molecule solvent, the ideal entropy of mixing is not appropriate.

The effect of temperature on gas solubilities is of practical engineering interest because of the wide ranges of temperature encountered in chemical processes. A zeroth approximation for describing the effect of temperature on gas solubilities is given by the ideal solubility (Hildebrand and Scott, 1950) which predicts that the solubility decreases monotonously with rising temperature. However,

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experimental data for several binary systems show that a plot of gas solubility versus temperature goes through a minimum (Preston et al., 1971). To increase understanding of the effect of temperature, we have studied the low-pressure solubilities of several low-molecular weight hydrocarbon gases and hydrogen in a variety of high-boiling hydrocarbon solvents whose molecules differ in both size and shape. Further, we have established a correlation, based on molecular theory, for estimating the solubilities of hydrocarbon gases in hydrocarbon solvents.

EXPERIMENT

The experimental apparatus, shown in Figure 1, is the same as that used by Cukor (1971). This apparatus consists of five sections: (1) a degassing flask, D; (2) an equilibrium cell, enclosed by the dotted box; (3) a reservoir for degassed solvent, E; (4) a precision gas burette, F; and (5) a section for pressure measurement.

Solvent is degassed in flask D by alternate freezing and thawing with liquid nitrogen while removing gases with a vacuum pump. Degassing is considered complete when no gas bubbles are observed during the thawing of the solvent. The solvent vapor pressure is measured and compared with available literature values as a final criterion for complete degassing. Normally five freezing-thawing cycles are required. The degassed solvent is then transferred to the thermostated equilibrium cell. The solvent level in bulb A is adjusted to a calibration mark b. Excess solvent is collected in flask E. This flask is removed, under vacuum, and weighed. The volume below the calibration mark b, denoted by the shaded area, was previously determined by weighing mercury which had filled flask A. The total volume of the cell was determined by adding a known amount of nitrogen to the empty cell and measuring its pressure and temperature. The volume of the vapor space, bulb B, is the difference between the two volumes. Since the liquid level is maintained at the calibration mark b, the vapor-space volume is known accurately. To calculate the mass of solvent in the cell, it is necessary to know the solvent density at the temperature at which the solvent level is adjusted.

The temperature of the bath is first raised to the highest desired temperature where the expanded solvent is again leveled to the calibration mark b. Removed solvent is collected in flask E and weighed. The mass of solvent remaining in the cell is determined from the differential weighing of flask E. Provided that the solvent is properly degassed, a known amount of gas is added to the solubility cell by using the precision gas burette F. For rapid attainment of equilibrium, the solvent is circulated through the vapor space by a magnetically-driven, glass-encased, metal plunger at C. The pressure in the cell is observed until equilibrium is reached, usually within two hours.

At equilibrium only the temperature and pressure need be measured. Knowing the mass of each component, temperature and pressure completely specify the system.

The temperature is lowered to the next desired temperature. Additional solvent is added to the solubility cell from flask E until the liquid level is again at the calibration mark b. The amount of solvent added is determined from the differential weight of flask E. Equilibrium is again attained by circulating the solvent through the vapor space; the temperature and pressure are then measured. This procedure is repeated at each desired temperature. It is an unavoidable characteristic of this procedure that solubilities can be measured only at successively decreasing temperatures. If the reverse procedure were used, maintaining the solvent level at calibration mark b, after increasing the temperature, would require removal of solvent from the cell. In addition to removal of solvent, an undetermined amount of dissolved gas would be removed, invalidating the new measurement.

Care must be taken in measuring the pressure of the hot vapors since solvent condenses at a temperature lower than that in the equilibrium cell. Cukor (1971) describes an apparatus for pressure measurement at advanced temperatures when a condensable component is present.

DATA REDUCTION

The solubility is determined by making a material balance on the gaseous solute. Let subscript 1 stand for solute and subscript 2 for solvent. The solubility (liquid-phase mole fraction of solute) x_1 is given by

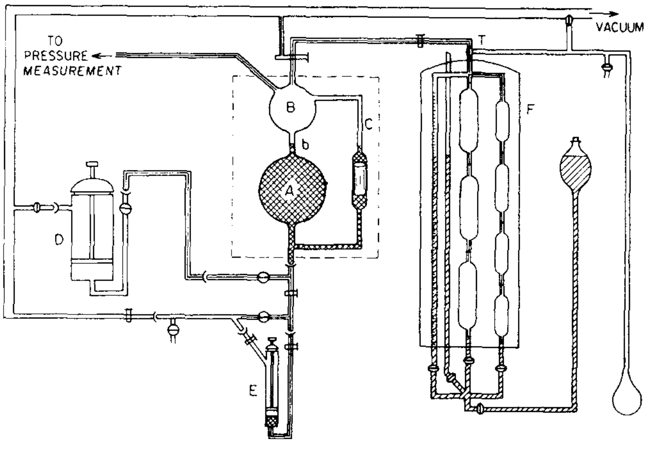

Fig. 1. Gas solubility apparatus.

$$x_1 = \frac{\Delta n_1}{\Delta n_1 + \Delta n_2} \tag{1}$$

where Δn_i is the moles of species i remaining in the liquid phase. This is the difference between the moles of i initially added to the apparatus and the moles of i remaining in the vapor phase.

Henry's constant for solute 1 in solvent 2 is defined by

$$H_{1,2} = \lim_{x_1 \to 0} \frac{f_1}{x_1} \tag{2}$$

where f is fugacity. The limit in Equation (2) is achieved in our low-pressure experiments. Additional gas may be added to the cell at any temperature to ensure that the ratio f_1/x_1 does not change.

To solve Equations (1) and (2), it is necessary to use the equations of equilibrium along with the measured total pressure, calibrated volumes, temperature, and total moles of both components. The moles of molecule i remaining in the vapor phase is $y_i\, n^v$ where y is the vapor-phase mole fraction and n^v is the total moles of gas in the vapor phase. The virial equation of state, truncated after the second term, is used to calculate n^v. Pure-component and cross-second-virial coefficients are calculated from the correlation of Pitzer and Curl (1957) with mixing rules similar to those given by Prausnitz and Chueh (1968). The equations of equilibrium are

$$\phi_1 y_1 P = H_{1,2} x_1 \tag{3}$$

$$\phi_2 y_2 P = x_2 P_2^s \tag{4}$$

where ϕ is the vapor-phase fugacity coefficient, P is the total pressure, and P_2^s is the solvent vapor pressure. Vapor-phase fugacity coefficients are calculated using the virial equation of state truncated after the second term.

Solution of Equations (3) and (4) requires an iterative trial-and-error procedure. Detailed calculation procedures and an error analysis are given elsewhere (Chappelow, 1974).

Table 1 lists Henry's constants and entropies of solution for the 26 gas-liquid systems studied. Figures 2, 3, and 4 show Henry's constant for some of these systems as a function of temperature.

THEORETICAL INTERPRETATION

No straightforward method for correlating gas solubilities is readily apparent when Henry's constants for differ-

Table 1. Henry's Constant and Entropy of Solution
Henry's constant, atm (first line)
Entropy of solution (multiplied by minus one), cal/mol °K (second line)†

Gas	Liquid	Temperature °K							
		300	325	350	375	400	425	450	475
Methane	*n*-Eicosane	—	170	184	196	205	210	214	216
		—	2.26	1.95	1.58	1.14	0.73	0.46	0.36
	Squalane	111	124	135	144	151	156	160	163
		3.08	2.51	2.03	1.65	1.30	1.00	0.76	0.58
	OMCTS	107	119	131	138	138	135	—	—
		2.14	2.76	2.25	0.69	−0.24	−1.80	—	—
	1-Methylnaphthalene	644	676	705	728	740	738	719	680
		1.22	1.19	1.03	0.72	0.25	−0.44	−1.41	−2.82
Ethane	*n*-Eicosane	—	35.7	47.3	59.1	71.0	83.1	95.1	107
		—	8.31	6.89	6.00	5.37	4.89	4.51	4.19
	Squalane	22.2	28.6	35.2	42.2	49.7	57.8	65.9	73.2
		6.78	5.83	5.34	5.11	5.04	4.80	4.25	3.48
	OMCTS	19.4	26.7	35.6	43.5	50.4	56.6	—	—
		6.68	8.29	6.70	5.03	4.11	3.63	—	—
	1-Methylnaphthalene	90.9	120	150	182	212	238	257	260
		7.32	6.42	5.81	5.13	4.27	3.24	1.98	−1.84
Propane	*n*-Hexadecane	8.34	12.9	18.6	25.4	33.2	41.6	50.1	58.4
		11.5	10.2	9.43	8.61	7.76	6.95	6.08	5.11
	n-Eicosane	—	12.7	18.3	25.6	34.1	43.1	52.0	60.3
		—	9.25	9.96	9.28	8.22	7.11	5.99	4.84
	Squalane	5.66	8.83	13.0	17.9	23.5	29.6	35.9	41.7
		11.1	10.8	9.81	8.82	7.92	7.11	6.39	4.13
	Bicyclohexyl	11.7	19.0	28.4	40.0	53.1	66.4	77.3	76.6
		13.6	11.2	10.3	9.33	8.02	6.66	3.18	−4.97
	OMCTS	6.09	9.72	14.5	19.9	25.2	30.0	—	—
		10.9	11.6	9.88	8.08	6.53	5.07	—	—
	Diphenylmethane	26.0	37.4	51.1	66.2	82.1	98.6	115	132
		9.30	8.74	7.89	7.02	6.29	5.71	5.23	4.81
	1-Methylnaphthalene	27.1	41.1	58.0	77.1	97.7	118	135	146
		10.8	9.76	8.71	7.77	6.71	5.47	4.07	1.00
n-Butane	*n*-Hexadecane	2.60	4.18	7.08	10.8	15.4	20.8	26.8	33.1
		6.77	14.4	13.2	11.4	10.2	9.36	8.35	7.12
	n-Eicosane	—	3.90	6.30	9.88	14.0	18.8	24.8	29.4
		—	10.1	13.8	11.7	10.0	9.57	9.54	0.59
	Squalane	2.10	2.95	5.15	8.34	12.2	16.3	20.3	24.0
		0.65	13.8	14.9	12.8	10.5	8.59	6.87	5.24
	Bicyclohexyl	4.59	7.34	11.4	17.2	24.3	31.9	39.5	46.4
		12.1	11.6	12.1	11.4	9.80	8.17	6.62	5.10
	OMCTS	2.19	3.81	6.32	9.40	12.7	16.0	—	—
		11.6	14.4	12.6	10.4	8.37	6.58	—	—
iso-Butane	*n*-Eicosane	—	5.80	9.15	13.3	18.1	23.6	29.8	36.0
		—	13.2	11.4	10.0	9.09	8.45	7.58	6.33
	Bicyclohexyl	6.43	10.5	16.3	23.0	31.3	41.4	50.6	55.7
		9.60	12.9	10.6	9.46	9.61	8.37	5.44	1.23
	OMCTS	2.98	5.05	7.96	11.4	15.4	20.3	—	—
		11.6	13.2	11.0	9.65	9.14	9.01	—	—
	1-Methylnaphthalene	12.0	19.9	30.3	42.8	57.1	72.1	86.8	92.9
		13.2	11.9	10.6	9.42	8.25	7.04	5.80	−3.34
Hydrogen	Squalane	726	650	589	538	494	455	421	391
		−2.8	−2.7	−2.6	−2.7	−2.7	−2.7	−2.7	−2.6
	OMCTS	706	622	555	490	420	338	—	—
		−3.3	−3.0	−3.2	−4.0	−5.7	−9.0	—	—

OMCTS = Octamethylcyclotetrasiloxane.

† The entropy of solution is defined by

$$\Delta \bar{s}_1 = \bar{s}_1^L (T, x_1 = 1/H_{1,2}) - s_1^G (T, f_1 = 1 \text{ atm}) = -R (\partial \ln H_{1,2}/\partial \ln T)$$

where $H_{1,2}$ is in atmospheres and where superscript G stands for ideal gas. This entropy of solution has been calculated as described elsewhere (Chappelow, 1974). The values for $\Delta \bar{s}_1$ at the lowest and highest temperature, where Henry's constant was measured, are estimates.

Wilhelm and Battino (1973) report the entropy of solution defined as

$$\Delta \bar{s}_1^{WB} = \bar{s}_1^L (T, x_1 = 1) - s_1^G (T, f_1 = 1 \text{ atm})$$

where $\bar{s}_1^L$ is the entropy of component 1 in the liquid phase which would exist if Henry's law held up to $x_1 = 1$. Their definition is related to that reported here by

$$\Delta \bar{s}_1^{WB} = \Delta \bar{s}_1 - R \ln H_{1,2}.$$

Hildebrand often reports the entropy of solution defined as

$$\Delta \bar{s}_1^H = \bar{s}_1^L (T, x_1 = 10^{-4}) - s_1^G (T, f_1 = 1 \text{ atm}).$$

This definition is related to that reported here by

$$\Delta \bar{s}_1^H = \Delta \bar{s}_1 - R \ln H_{1,2}/10^4.$$

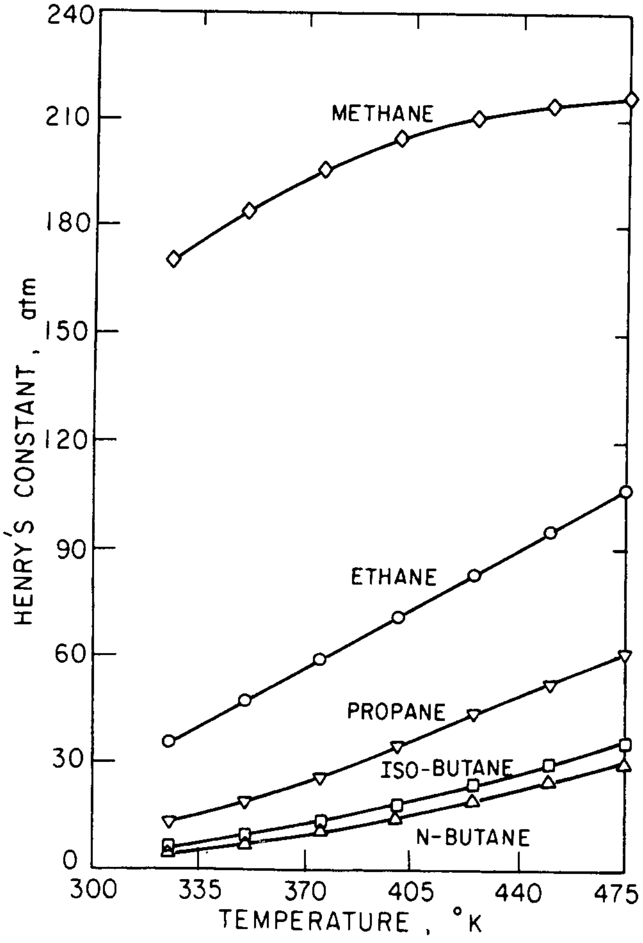

Fig. 2. Henry's constants in *n*-eicosane.

ent gases and liquids are examined. Previous attempts to correlate gas solubilities have been limited to solutions of gases in small-molecule solvents. For this reason, it is not surprising to find poor agreement between predicted and experimental Henry's constants for gases in large-molecule solvents.

We consider the isothermal solution of a gas 1 at unit fugacity in a liquid 2 as a two-step process: (I) condensation of pure gas to a pure liquid followed by (II) dissolution of pure liquid 1 in solvent 2. The chemical potential change of the gas for Step I is

$$\Delta\mu_1^I = RT \ln f_1^{0L} \tag{5}$$

where f_1^{0L} is the fugacity of pure liquid 1.

For a supercritical fluid, such as methane above 190.7°K, no liquid phase exists. Thus a hypothetical liquid must be postulated to obtain f_1^{0L}. Prausnitz and Chueh (1968) give equations for f_1^{0L} for several fluids which apply from the triple point to a reduced temperature of 0.95. These equations were extrapolated graphically to a reduced temperature of 2.5 to obtain reasonable f_1^{0L} values in the supercritical region. The extrapolations are represented by

$$\ln \frac{f_1^{0L}}{P_{c1}} = C_1 + \frac{C_2}{T_R} + \frac{C_3}{T_R^2} + \frac{C_4}{T_R^3} \tag{6}$$

where P_{c1} is the critical pressure and $T_R = T/T_{c1}$ is the reduced temperature. Table 2 presents the coefficients in Equation (6) for several hydrocarbon gases. Because of the very large extrapolation required, we do not present coefficients for hydrogen.

The chemical potential change for Step II is

$$\Delta\mu_1^{II} = \mu_1^L - \mu_1^{0L} = RT \ln \gamma_1 x_1 = \Delta\mu_1^c + \Delta\mu_1^R \tag{7}$$

where γ_1 is the activity coefficient and $\gamma_1 x_1$ is the activity of the solute; $\Delta\mu_1^c$ is the contribution from the configurational entropy of mixing and $\Delta\mu_1^R$ is a residual term which accounts for all other contributions.

CONFIGURATIONAL ENTROPY

The configurational chemical potential change for the solute is the negative of the product of the partial molar configurational entropy of mixing and the temperature. Hildebrand (1947) has shown that the true configurational entropy of mixing is bounded above by the Flory-Huggins entropy of mixing and below by the ideal entropy of mixing. The ideal and Flory-Huggins expressions for $\Delta\mu_1^c$ are respectively

$$\left(\frac{\Delta\mu_1^c}{RT}\right)_{\text{Ideal}} = \ln x_1 \tag{8}$$

$$\left(\frac{\Delta\mu_1^c}{RT}\right)_{\text{Flory-Huggins}} = \ln \Phi_1 + \left(1 - \frac{1}{m}\right)\Phi_2 \tag{9}$$

where Φ is the volume fraction and m is the ratio of the solvent-to-solute molar volumes.

While both size and shape of the molecules determine the configurational entropy, the Flory-Huggins formula considers only molecular size; the ideal case considers neither size nor shape. To account for differences in both size and shape, we use an expression for the configurational entropy of mixing derived by Staverman (1950):

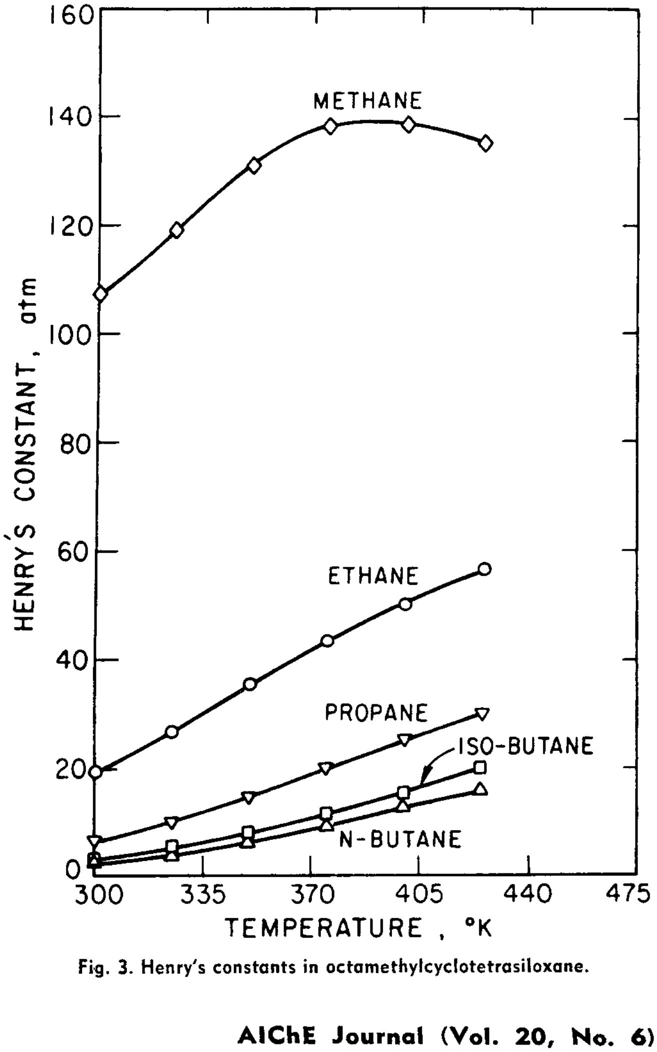

Fig. 3. Henry's constants in octamethylcyclotetrasiloxane.

TABLE 2. COEFFICIENTS FOR FUGACITY OF PURE LIQUID

$$\ln\frac{f^{0L}}{P_c} = C_1 + \frac{C_2}{T_R} + \frac{C_3}{T_R^2} + \frac{C_4}{T_R^3}$$

Gas	C_1	C_2	C_3	C_4
Methane	2.3010716	−1.7054560	−1.2222149	0.070947378
Ethane	2.7885207	−2.3240841	−0.9542893	−0.047399071
Propane	3.3902259	−3.3254962	−0.3789198	−0.205884370
n-Butane	4.1173650	−4.8437040	0.8154529	−0.655036710
iso-Butane	3.8609043	−4.3693021	0.3902093	−0.420003080

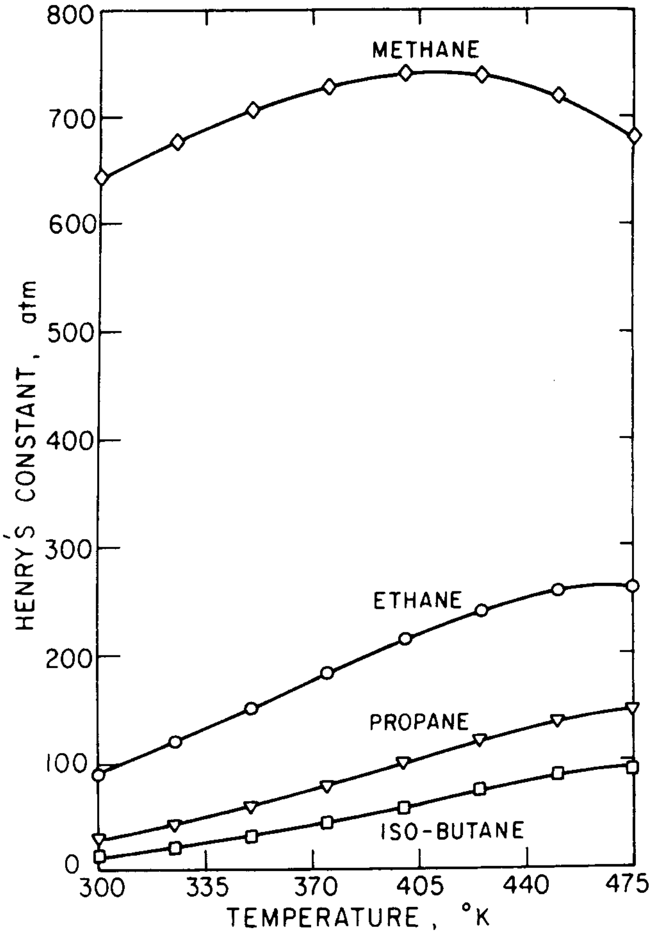

Fig. 4. Henry's constants in 1-methylnaphthalene.

$$\left(\frac{\Delta\mu_1^c}{RT}\right)_{\text{Staverman}} = \ln\Psi_1 + \Psi_2\left[\frac{z}{2}(r_1-q_1) - (r_1-1)\right] - \frac{r_1}{r_2}\Psi_2\left[\frac{z}{2}(r_2-q_2) - (r_2-1)\right] + \frac{z}{2}q\ln\frac{\theta_1}{\Psi_1} \quad (10)$$

where r is the number of segments in a molecule, z is the coordination number of the liquid ($z = 10$ in this work), and qz is the number of contact pairs made between a molecule and its neighboring molecules. The derivation of Equation (10) is given elsewhere (Chappelow, 1974). The segment fraction Ψ and surface site fraction θ are defined by

$$\Psi_i = \frac{r_iN_i}{N_r} \quad (11)$$

and

TABLE 3. VAN DER WAALS AREAS AND VOLUMES

Molecule	V_w (cc/mol)	A_w (10^9 cm^2/mol)
Standard segment	15.20	2.50
Methane	17.13	2.81
Ethane	27.34	4.24
Propane	37.57	5.59
n-Butane	47.79	6.94
iso-Butane	47.79	6.93
n-Hexadecane	170.56	23.14
n-Eicosane	211.48	28.54
Squalane	309.86	41.46
Bicyclohexyl	113.60	15.50
OMCTS*	166.96	20.40
Diphenylmethane	101.91	15.30
1-Methylnaphthalene	85.12	12.42
n-Hexane	68.26	9.64
n-Heptane	78.49	10.99
Cyclohexane	58.70	8.01
Methylcyclohexane	70.47	9.88
Benzene	48.40	7.39
Toluene	59.51	9.33
2,2,4-Trimethylpentane	85.36	12.52

* OMCTS = Octamethylcyclotetrasiloxane.

$$\theta_i = \frac{q_iN_i}{N_q} \quad (12)$$

The total number of segments N_r is given by $(N_1r_1 + N_2r_2)$. Similarly, N_q, proportional to the total number of contact pairs, is given by $(N_1q_1 + N_2q_2)$.

The number of segments in a molecule, which is a measure of molecular size, is taken as the ratio of that molecule's van der Waals volume to that of a standard segment. Similarly, the value for q, which is a measure of the molecular surface area, is taken as the ratio of that molecule's van der Waals area to that of the standard segment. A group-contribution method for estimating van der Waals areas and volumes is given by Bondi (1968) and additional group-contribution parameters are given by Lichtenthaler et al. (1973). Table 3 lists van der Waals areas and volumes for the gases and liquids in this study. The choice of the standard segment is discussed elsewhere (Chappelow, 1974).

The Staverman configurational entropy reduces to the ideal configurational entropy when both solute and solvent have the same q and the same r, and to the Flory-Huggins configurational entropy when for each molecule i, $q_i = r_i$. For the latter case the segment and volume fractions are equal and m is r_2/r_1.

RESIDUAL CHEMICAL POTENTIAL

Following Flory (1970), we assume that the residual chemical potential is of the van Laar form

$$\Delta\mu_1^R = RT\,\chi\,\Psi_2^2 \quad (13)$$

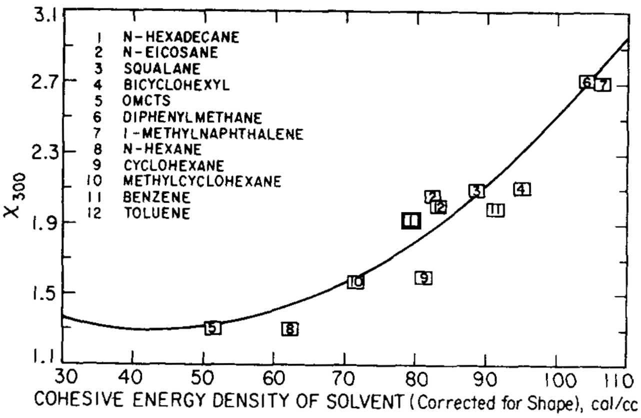

Fig. 5. Generalized methane-solvent Flory parameters at 300°K.

TABLE 4. COEFFICIENTS FOR FLORY-PARAMETER CORRELATION

$$\chi_{300} = d_1 + d_2\xi + d_3\xi^2$$

Gas	d_1	$-d_2 \times 10^2$	$d_3 \times 10^4$
Methane	1.623	1.706	2.584
Ethane	0.8205	2.087	2.756
Propane	1.055	3.349	3.568
n-Butane	1.076	2.582	2.595
iso-Butane	1.028	3.235	3.403

where χ is the Flory parameter.

Combining Equations (7), (10), and (13) and taking the limit $x_1 \to 0$ gives

$$\ln \gamma_1^\infty = \ln \frac{r_1}{r_2} + \frac{z}{2} q_1 \ln \left[\frac{q_1 r_2}{q_2 r_1} \right] + \frac{z}{2}(r_1 - q_1) - (r_1 - 1) - \frac{r_1}{r_2}\left[\frac{z}{2}(r_2 - q_2) - (r_2 - 1) \right] + \chi \tag{14}$$

The superscript ∞ represents infinite dilution. Henry's constant is related to γ_1^∞ and f_1^{0L} by

$$H_{1,2} = \gamma_1^\infty f_1^{0L} \tag{15}$$

In Equation (14), χ is the only term which characterizes binary interactions. Using new experimental Henry's constants and those of Cukor (1972), the effect of temperature on χ can be studied. We find empirically that to a good approximation, χ is a linear function of temperature:

$$\chi(T) = \chi_{300} + \left(\frac{\partial \chi}{\partial T}\right)_{300} (T - 300) \tag{16}$$

In the following we propose correlations which, for a given gas, relate χ_{300} and $(\partial\chi/\partial T)_{300}$ to pure-component properties of the solvent. These give a general method for predicting the solubilities of hydrocarbon gases in hydrocarbon solvents over wide ranges of temperature.

While the Staverman entropy of mixing characterizes configurational effects upon mixing, the residual term (Flory parameter) reflects primarily energetic effects upon mixing. Hildebrand and Scott (1962) show that for a given solute, the energy of mixing is related to the cohesive energy density of the solvent. The cohesive energy density C is the energy of vaporization of a liquid to the ideal-gas state divided by the liquid's molar volume. Since molecules interact through their surface area, we modify the cohesive energy density by dividing C by the q-to-r ratio. Recalling that q is a dimensionless measure of molecular surface area and that r is a dimensionless measure of molecular volume, the modified cohesive energy density $C\ r/q$ characterizes the cohesive energy of a solvent molecule per unit molecular area. Figure 5 shows the value of χ_{300} versus the cohesive energy density at 300°K (corrected for shape) for methane-solvent systems.

The curve in Figure 5 and those for other gases have been fit to the empirical equation:

$$\chi_{300} = d_1 + d_2\xi + d_3\xi^2 \tag{17}$$

where $\xi = C/(q/r)$ and C is the cohesive energy density of the solvent at 300°K. Table 4 lists the coefficients for Equation (17) for several gases.

The Flory parameter χ contains enthalpic and entropic contributions:

$$\chi = \chi_H + \chi_S \tag{18}$$

Application of the Gibbs-Helmholtz equation gives

$$\chi_H = \frac{\Delta \bar{h}_1}{RT} = -T\left(\frac{\partial \chi}{\partial T}\right) \tag{19}$$

$$\chi_S = -\frac{\Delta \bar{s}_1^R}{R} = \frac{\partial(\chi T)}{\partial T} \tag{20}$$

A correlation for either χ_H or χ_S at 300°K would serve to establish the value for $(\partial\chi/\partial T)_{300}$, thus completing the correlating scheme. We chose to correlate χ_S based on the following consideration. The entropy of mixing is composed of two parts: (1) configurational and (2) residual. The configurational part is calculated from lattice-type arguments which account for differences in molecular size and shape, but which neglect differences in free volume between solute and solvent. Eichinger and Flory (1968) and Patterson (1969) have shown that the partial molar enentropy of mixing is sensitive to free-volume differences. This effect is dominant in $\Delta\bar{s}_1^R$. We find that for a given gas, χ_S at 300°K, correlates with the thermal expansion coefficient of the solvent since this coefficient is a measure of free volume (Eichinger and Flory, 1968; Flory, 1970).

Figure 6 shows χ_S at 300°K $= -\Delta\bar{s}_1^R(300°\text{K})/R$ plotted against the thermal expansion coefficient of the solvent at 300°K. Figure 6 shows that the partial molar entropy of mixing for the solute is more positive for a solvent with a large thermal expansion coefficient than for one with a small thermal expansion coefficient. A solvent with a large free volume provides more accessible sites for the dissolved gas than does a solvent with a small free volume. The trend shown in Figure 6, therefore, is reasonable.

Equations (18), (19), and (20) give

$$-\left(\frac{\partial \chi}{\partial T}\right)_{300} = \frac{\chi_{300} - \chi_S(300)}{300} \tag{21}$$

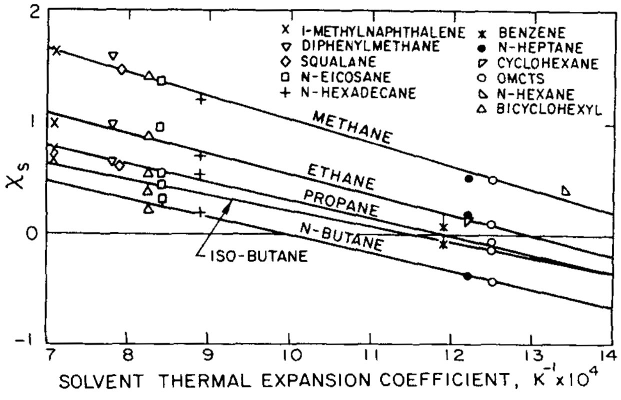

Fig. 6. Correlation of χ_S with thermal expansion coefficient of solvent at 300°K.

TABLE 5. CONFIGURATIONAL ENTROPIES AND χ_S FOR METHANE IN TWO SOLVENTS WHOSE MOLECULES ARE SIMILAR IN SIZE BUT NOT IN SHAPE

	$-\Delta s_1{}^{-c}/R$		χ_S	
	(a)	(b)	(a)	(b)
n-Hexadecane	1.40	1.30	1.32	1.22
Octamethylcyclotetrasiloxane	1.39	1.15	0.74	0.50

(a) Based on Flory-Huggins formula.
(b) Based on Staverman formula.

Equations (16) and (21), coupled with the correlating Equation (17) and Figure 6, provide good estimates of χ for hydrocarbon systems. This correlation for hydrocarbon systems yields Henry's constants accurate to about ±15%.

The development presented here is similar to that of Flory-Huggins for polymer-solvent solutions (Flory, 1953). We have modified the Flory-Huggins equation by our choice of the Staverman configurational entropy of mixing.

Since the partial molar residual entropy of mixing is influenced by the choice of the configurational entropy of mixing, a good estimate for the latter is required to obtain a good correlation for the former (Lichtenthaler et al., 1973). The Staverman configurational entropy of mixing considers sizes as well as shapes of the molecules in the mixture. The choice of Staverman's formula is responsible for the good correlation shown in Figure 6, especially for octamethylcyclotetrasiloxane (OMCTS). If the partial molar residual entropy for solutes had been based on the Flory-Huggins formula, the data for OMCTS-solute systems would not have correlated as well.

The importance of the configurational entropy of mixing is best illustrated by considering two molecules of similar size but different shape. Two such molecules are n-hexadecane ($r = 11.22$, $q = 9.25$) and OMCTS ($r = 10.98$, $q = 8.16$). Table 5 shows configurational entropies and χ_S based on Flory-Huggins and on Staverman for methane in these solvents. Values of χ_S based on Flory-Huggins are larger than those based on Staverman. Also, the change in χ_S is larger for OMCTS than for n-hexadecane. The changes in χ_S for other solvents shown in Figure 6 are similar to those for n-hexadecane; however, the change is particularly large for globular-shaped OMCTS. If the correlation shown in Figure 6 had been based on the Flory-Huggins formula, the value for χ_S for OMCTS would have been well above the correlation line.

The advantage of the Staverman entropy of mixing is best realized when the solvent molecules are large and bulky; when the solvent molecules are long chains, there is little difference between the Staverman formula and the Flory-Huggins formula.

Two factors which influence the solubility of a gas in a liquid are represented by our correlations. The effect of intermolecular forces is represented by the χ_{300} correlation with the modified cohesive energy density of the solvent. The equation-of-state, or free-volume, effects are represented by the correlation of $\chi_S(300)$ with the thermal expansion coefficient of the solvent. These correlations are useful for estimating gas solubilities in hydrocarbon systems over a wide range of temperature.

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NOTATION

A = molecular area
C = cohesive energy density
f = fugacity
h = enthalpy
$H_{1,2}$ = Henry's constant
m = solvent-to-solute molar volume ratio
n = moles
P = pressure
q = molecular contact area
r = number of molecular segments
R = gas constant
s = entropy
T = temperature
V = molecular volume
x = liquid-phase mole fraction
y = vapor-phase mole fraction
z = coordination number

Greek Letters

γ = liquid-phase activity coefficient
Δ = change in a property
ξ = $C/(q/r)$
θ = surface-site fraction
μ = chemical potential
Ψ = segment fraction
Φ = volume fraction
ϕ = vapor-phase fugacity coefficient
χ = Flory parameter

Subscripts

1 = gas or solute
2 = liquid or solvent
c = critical property
H = enthalpic contribution
q = summation of molecular contact area
r = summation of molecular segments
R = reduced property
S = entropic contribution
w = van der Waals

Superscripts

0 = pure component
c = configurational
L = liquid
R = residual
s = saturation
v = vapor
∞ = infinite dilution

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Separations with Protein Liquid Crystals

A lyotropic protein liquid crystal was studied experimentally to evaluate its potential as a selective liquid membrane. Concentrated solutions of fibrinogen had nematic like properties under shear and exhibited graded selectivities toward solutes of widely differing sizes when subjected to a two-dimensional velocity field. The magnitude of the selectivity differences was found to depend on the shear orientated direction of the liquid crystal layer. The selectivity seems to be both a solubility phenomena and a relative diffusion phenomena. These anisotropic layers may have potential as controlled variable selectivity membranes.

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SCOPE

Many biological materials, particularly enzymes, cannot be purified by conventional methods which employ large gradients of temperature, pressure, *p*H, or shear. Such harsh treatments can cause protein denaturation and the consequent loss of biological activity. Therefore, milder means of purification are needed. The development of artificial membranes was hoped to provide a new selective separation technique for liquid solutions. However, in practice the thin synthetic membrane has become most useful as a concentrating tool—separating solutes from solvent. The fixed and rather wide selectivity cutoff has made it ineffective for many solute-solute separations.

Developments with liquid membranes have shown more selective solute-solute separations, although not in commercially useful systems. For example, Bangham (1967) has shown selective separation of K^+ and Na^+ with phospholipid vesicles. Bangham's work was part of a recent large effort to duplicate with phospholipid bilayers the highly selective separations performed by natural membranes. Green (1970), however, has pointed out that these highly charged bilayers do not have sufficient diversity of characteristics to be wholly satisfactory models for natural membranes. More specifically, the selectivity of these phospholipid bilayers does not respond in a controlled manner to changes in environment.

These phospholipids, however, are members of a larger class of materials called *liquid crystals*, some members of which potentially have the properties necessary to overcome the limitations of fixed membranes and phospholipid bilayers. The liquid crystal is a phase of matter which exhibits the long-range order of a solid, but has the response of a fluid to shear. For many liquid crystals, whether charged or uncharged, the structure is very sensitive to perturbations in the environment, particularly force fields. The long-range structure of a liquid crystal results in physical properties which are directionally dependent. The orientation of phase structure and, thus, the properties of the phase can be changed relative to a fixed reference by applying force fields on the phase.

This study used the liquid crystal formed from concentrated solutions of the protein fibrinogen to determine the potential of protein liquid crystals for selective solute-solute separations and to determine if control of this selectivity could be exercised by manipulating the orientation of the phase. The study also provides new information on the role of structure in protein liquid crystals for use in developing better natural membrane models.

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