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The Solubility of Water in Hydrocarbons

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The method in which tritium oxide acts as a tracer in the determination of water solubility in hydrocarbons has been used for the measurement of the solubility of water in a number of paraffinic, olefinic, and diolefinic hydrocarbons. The effect of temperature, pressure, size of hydrocarbon molecule, and the constitutive factors have been studied. Solubilities were determined in the temperature range from 5° to 30°C at pressures from 1 to 6 atmospheres.

THE method which is based upon the use of tritium oxide as a tracer in the determination of minute amounts of water has previously been tested in the measurement of the solubility of water in benzene.¹ The same method has now been further applied to the determination of the solubility of water in a series of paraffinic, olefinic, and diolefinic hydrocarbons.

EXPERIMENTAL PROCEDURE

1. Radioactive Water

The radioactive water was from the same sample used in the preceding study:¹ it was deuterium oxide containing about 10^{-12} mole per mole of tritium oxide.

2. Hydrocarbons

The hydrocarbons were of the highest purity available. The liquid hydrocarbons were, for the most part, samples of pure compounds produced at The Ohio State University under an American Petroleum Institute project. The samples of heptene-1 and hexadiene-1,5 were kindly provided by Professor G. B. Kistiakowsky of Harvard University. The butanes, butenes, and the butadiene-1,3 were hydrocarbons from the Phillips Petroleum Company, available in cylinders, and shown by mass-spectrometer analysis to be better than 98 percent pure as used.

3. Apparatus and Technique

For the liquid hydrocarbons the apparatus described in the previous paper¹ was again used.

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¹ G. G. Joris and H. S. Taylor, *J. Chem. Phys.* **16**, 45 (1948).

For the lower hydrocarbons, a brass apparatus and a slightly different experimental technique were utilized. The all-metal system is shown in Fig. 1.

The saturator *C* was charged by cooling it with liquid air while the chamber was connected to the hydrocarbon supply cylinder, *H*. Since the sample could not be observed during saturation, it was necessary to follow carefully the proved technique employed in the glass system. The sampling device in Fig. 1 consisted of a small brass cylinder (approximately 2.5 cc in volume) connected at each end through $\frac{1}{8}$ -in. copper tubes to "Baby Hoke Valves." It was connected to chamber *C* by means of the flanged pressure connector *b*. The upper end of the sample tube was connected through a Kovar tube to the male section of a ground glass joint which provided a connection to the vacuum system. The sampling device could withstand high pressure or high vacuum without leakage.

The circulation rate of the vapors in this system was of the order of 500 cc per minute, and approximately three hours of continuous circulation was required to saturate a hydrocarbon sample with water.

The vacuum system was utilized to draw a fraction of the saturated hydrocarbon liquid from chamber *C* into the sample tube, *T*. After closing valves 4, 3, and 2, the fully charged sample tube was disconnected at *Y* and at *b* and was transferred to the analytical apparatus.

The analytical procedure was similar to that used with liquid hydrocarbons.¹ The amount of hydrocarbon was measured by vaporizing and expanding into a large evacuated system of known volume after it had been freed in the U-tube, *E*, from its water content. From pressure and tem-

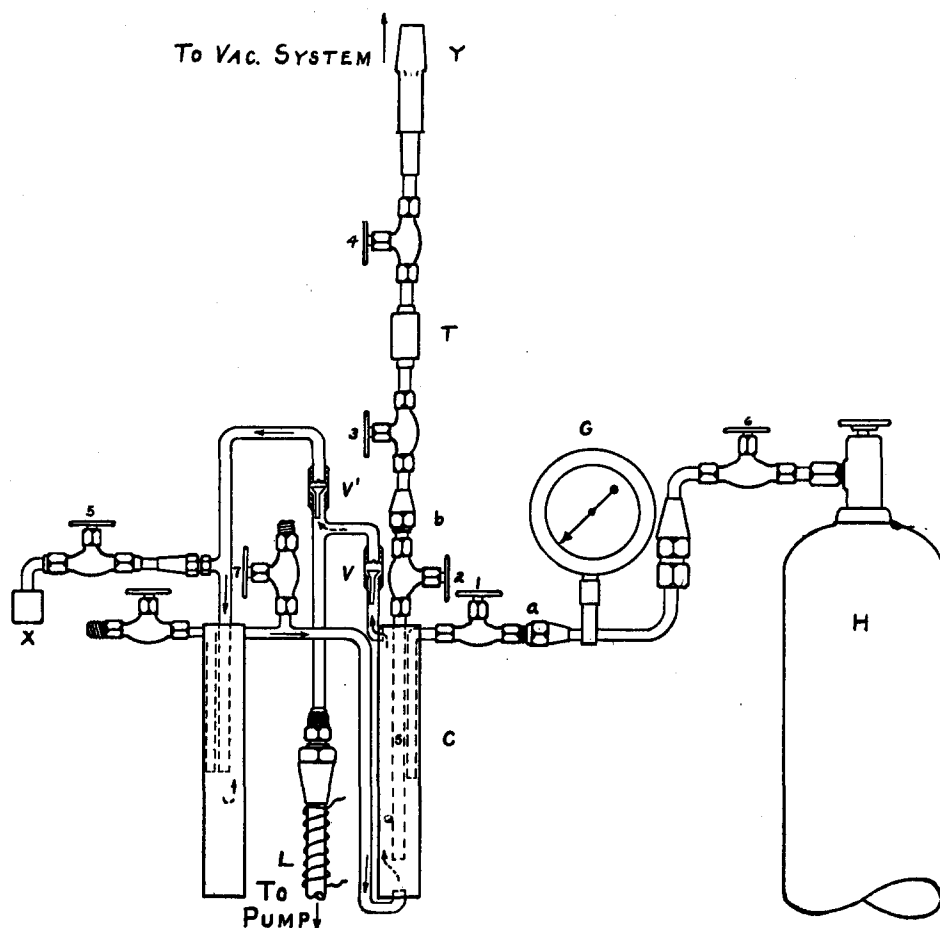


FIG. 1. Apparatus for saturating hydrocarbons with water (all-metal).

perature readings the weight of the hydrocarbon could be calculated. This indirect procedure was necessary because exact quantitative reproducibility could not always be obtained with the sampling device of the all-metal system.

The same technique of radioactivity measurement and of estimation of corrections, as described in the earlier paper, was used.

EXPERIMENTAL RESULTS

The solubility data obtained are recorded in Table I. These data are plotted in the following manner. In Fig. 2† the solubilities in mole percent

are plotted as a function of temperature. Figure 3† gives the solubility in grams water per 100 grams of hydrocarbon *versus* the temperature in degrees centigrade. The relationships in Fig. 4† are the result of plotting the logarithm of the solubility (expressed in mole percent) against the reciprocal of the absolute temperature.

The data and their plots emphasize the regularities which exist in the water solubilities of these hydrocarbons. With the normal paraffin hydrocarbons at a given temperature there is a progressive increase in the water solubility in passing from *n*-butane to *n*-octane.

The solubility of water in cyclohexane at 20°C (0.047) is of the same order of magnitude as in *n*-hexane and is in good agreement with results published by Tarassenkow and Poloshinzewa² for

- † Index of solvents given in Figs. 2, 3 and 4:
- Butadiene-1,3
 - Butene-1
 - ⊗ Butene-2
 - ⊙ Isobutylene
 - △ Cyclohexane (Data for Tarassenkow and Poloshinzewa (see reference 2.))
 - Interpolated for N-Hexane
 - N-Butane
 - Isobutane
 - N-Pentane
 - Isopentane
 - Benzene
 - N-Heptane
 - Heptene-1
 - Hexadiene-1,5

² N. D. Tarassenkow and E. N. Poloshinzewa, Zhur. Obshchei Khim. Khim. Ser. I, 71-9 (1931); Chem. Abs. 25, 4762 (1931); Ber. 65B, 184-6 (1932); C.A. 26, 2363 (1932).

TABLE I.

Hydrocarbon (HC)	Saturation temp. C	Total sat. press. atmos.	Sat. time hrs.	Solubility mole water per 100 moles HC.	Solubility g water per 100 g HC.
Butadiene-1,3	7.0	3.7	4.0	0.1466	0.0488
	7.5	3.7	3.0	0.1430	0.0476
	14.0	4.0	4.0	0.1706	0.0568
	15.0	3.7	3.5	0.1700	0.0566
	21.0	4.0	4.5	0.1988	0.0662
	21.0	3.7	3.5	0.1940	0.0646
Butene-1	6.0	3.0	3.0	0.0633	0.0203
	7.5	2.9	3.5	0.0764	0.0245
	14.0	3.3	3.0	0.0957	0.0307
	20.0	3.0	4.0	0.1237	0.0397
	21.5	2.9	4.0	0.1253	0.0402
Butene-2	7.0	2.8	3.0	0.0867	0.0278
	7.5	2.4	3.5	0.0876	0.0281
	14.0	2.8	3.5	0.1123	0.0360
	20.8	2.4	5.5	0.1416	0.0454
	21.0	2.8	4.5	0.1343	0.0431
Isobutylene	6.0	4.0	3.0	0.0717	0.0230
	7.0	4.4	4.0	0.0711	0.0228
	7.0	4.2	3.0	0.0671	0.0215
	14.0	4.0	3.5	0.0998	0.0320
	16.0	4.0	4.0	0.1141	0.0366
	21.0	4.4	6.0	0.1209	0.0388
	21.0	5.0	6.0	0.1200	0.0385
<i>n</i> -butane	5.0	2.7	4.0	0.00775	0.00240
	5.0	2.7	4.0	0.00775	0.00240
	5.5	2.8	2.5	0.00985	0.00305
	14.5	3.1	6.0	0.01227	0.00389
	15.0	3.4	3.8	0.01453	0.00459
	20.0	6.4	4.0	0.02002	0.00620
	20.0	3.4	2.5	0.02220	0.00688
	21.0	3.4	3.5	0.02430	0.00753

the solubility of water in cyclohexane. Two points of the Russian data are shown on the graph in Fig. 4.

There is but small variation in solubility with isomerism in the paraffin series, as evidenced by the result of the water solubilities in *n*-butane and isobutane and in *n*-pentane and isopentane. A similar conclusion can be reached for the olefin series as far as it has been investigated, butene-1, butene-2, and isobutylene having water solubilities of about the same magnitude.

The very large increase in water solubility as one passes from the paraffin to the olefin hydrocarbons is illustrated in the water solubilities of the butanes and butenes. A similar increase is noted in passing from *n*-heptane to heptene-1. This effect recalls the increased solubility of oleic acid over stearic acid in water. The attraction of the double bond to the surface with oleic acid

TABLE I.—Continued.

Hydrocarbon (HC)	Saturation temp. C	Total sat. press. atmos.	Sat. time hrs.	Solubility mole water per 100 moles HC.	Solubility g water per 100 g HC.
Isobutane	7.0	3.4	3.3	0.00898	0.00278
	18.0	3.9	4.3	0.02060	0.00638
	19.0	4.0	3.5	0.02220	0.00688
	21.8	4.0	5.0	0.02695	0.00835
<i>n</i> -pentane*	5.5	1.0		0.0144	0.0036
	15.0	1.0		0.0245	0.0061
	24.8	1.0		0.0477	0.0119
	24.8	1.0		0.0481	0.0120
Isopentane*	15.3	1.0		0.0263	0.0066
	21.3	1.0		0.0383	0.0096
	21.8	1.0		0.0390	0.0097
Isopentane	6.0	1.0	3.5	0.01777	0.00443
	6.0	1.0	4.0	0.01735	0.00433
	6.0	1.0	4.5	0.01762	0.00440
	20.0	1.0	8.0	0.03764	0.00940
	20.0	1.0	4.0	0.03613	0.00902
	20.0	1.0	4.5	0.03770	0.00942
	20.5	1.0	4.0	0.04020	0.01001
Benzene*	10	1.0		0.1305	0.030
	20	1.0		0.1846	0.0425
	20	1.0		0.1932	0.0445
	26	1.0		0.2344	0.0540
<i>n</i> -hexane*	20	1.0		0.053	0.0111
Cyclohexane*	20	1.0		0.047	0.010
<i>n</i> -heptane*	10	1.0		0.0429	0.0077
	20	1.0		0.0757	0.0136
	20	1.0		0.0701	0.0126
	25	1.0		0.0840	0.0151
Heptene-1*	10.0	1.0	6.0	0.3774	0.0692
	20.1	1.0	6.5	0.6139	0.1126
	20.5	1.0	4.5	0.5710	0.1047
	21.2	1.0	6.3	0.6310	0.1158
Hexadiene-1,5*	13.5	1.0	6.0	0.2820	0.0618
	20.2	1.0	7.5	0.4417	0.0969
<i>n</i> -octane*	20	1.0		0.090	0.0142

* Determinations made in glass apparatus.

films on water is evidence³ of the affinity of the double bond for water.

Again, as in the paraffin series, the solubility of water in the olefins increases with increasing chain length, as evidenced from the data for the butenes and for heptene-1. It will be noted that the solubilities of water are not additive in the sense of there being a solubility in the hydrocarbon portion of the molecule plus one to be attributed to the attraction of the double bond for the water. Instead, the double bond acts more nearly

³ I. Langmuir, Met. Chem. Eng. 15, 469 (1916); J. Am. Chem. Soc. 1848 (1917).

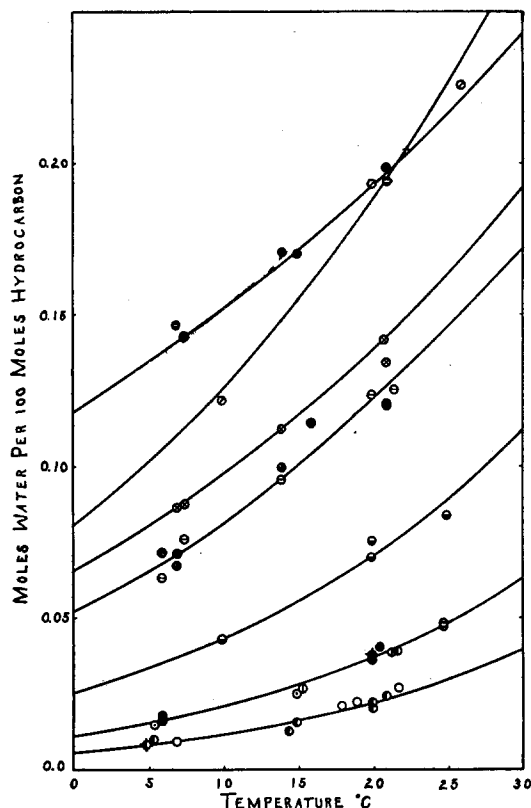


FIG. 2. Solubility of water in hydrocarbons as a function of temperature.

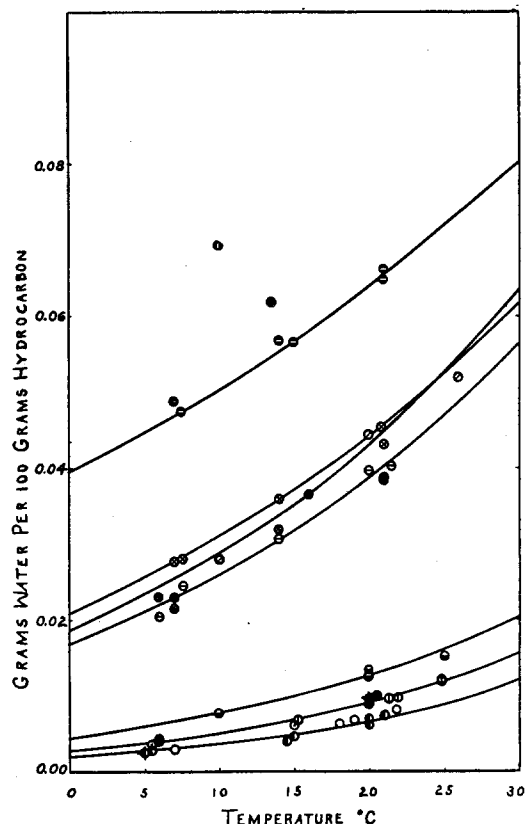


FIG. 3. Solubility of water in hydrocarbons as a function of temperature.

as though it multiplied the solubility of water in the hydrocarbon by some factor.

Butadiene, with two double bonds, shows a further increase of water solubility above that in the butenes, although the effect is not as great as that observed in going from butane to the butene solvents. This might suggest the effect of conjugation of the double bonds in butadiene-1,3. However, hexadiene-1,5 gave analogous results, indicating that conjugation was probably not responsible for this effect.

Near 20°C the molar solubilities of water in benzene and in butadiene-1,3 are of about the same order; with the benzene solvent, however, the solubility shows a steeper temperature coefficient. Qualitative measurements at 20°C indicate that cyclohexene with the single ethylenic linkage shows slightly greater water solubility than benzene with its three conjugated double bonds. Similarly, values for the solubility of water in hexene-1 (as determined by interpolating between values obtained for butene-1 and heptene-1

in Fig. 4) indicate slightly higher solubilities than for the solvent benzene.

DISCUSSION

The variations in the solubility of water from one hydrocarbon to another are well outside the limits of experimental error which are estimated to be of the order of a few percent. The highest molar concentration of water recorded is that in heptene-1 at 20°C; it corresponds to only one molecule of water in 160 molecules of the heptene. It is therefore apparent that, in all the examples studied, the water molecules should be exclusively surrounded by hydrocarbon molecules and should be in a constant environment in a particular hydrocarbon. The tendency of the water molecules to escape into the gaseous phase should, as a consequence, be proportional to their concentration in the hydrocarbon solvent; it will also depend on the interaction between a water molecule and the neighboring hydrocarbon mole-

cules. Since the experimental conditions were such as to maintain constant the vapor pressure of water in the gaseous phase, the variations in solubility with the different hydrocarbons reflect differences of interaction between water and the various hydrocarbon molecules. The assumption implicit in the calculation of solubilities that the Henry's law constants were identical for TDO and for H₂O, thus neglecting the isotope effect, undoubtedly introduces a systematic error into the results. Such an error is, however, obviously too small to vitiate any comparison between the calculated solubilities of water in the various hydrocarbons.

The increase with temperature of the solubilities of water in all the hydrocarbons studied indicates a positive deviation from Raoult's law. Such a deviation is, in general, observed when (a) there is a large difference in the internal pressures of the two substances, (b) the polarity is different, (c) the molecules are dissimilar, and (d) one or both of the substances are associated in the liquid state. Hildebrand, examining the case of components of unequal volumes with differences in internal pressures, obtains⁴ the following expression:

$$RT \ln \frac{\alpha_1}{N_1} = V_1 \left(\frac{N_2 V_2}{N_1 V_1 + N_2 V_2} \right)^2 \times \left[\left(\frac{\Delta E_1}{V_1} \right)^{\frac{1}{2}} - \left(\frac{\Delta E_2}{V_2} \right)^{\frac{1}{2}} \right]^2, \quad (1)$$

where $\alpha_1 = f/f_0$, f being the fugacity of the solute in the solution and f_0 the fugacity of the pure solute. N_1 and N_2 , V_1 and V_2 are, respectively, the molar concentrations and volumes of solute and solvent, ΔE_1 and ΔE_2 their heats of vaporization. Several assumptions are involved in the derivation of this relation. The repulsion potentials are neglected; the different molecular species are assumed to possess spherical symmetry and to follow the same general type of arrangement; the attraction constants are assumed to be the geometric mean of the constants of like molecules. If this equation were applicable to the present measurements a further simplification

TABLE II.

Hydrocarbon	$(\Delta E/V)^{\frac{1}{2}}$	$10^{-2} N_1$ mole %		$\frac{N_1 \text{ obs.}}{N_1 \text{ calc.}}$
		calc.	obs.	
<i>n</i> -butane	6.6	1.66	2.1	1.26
<i>n</i> -pentane	7.0	2.41	3.6	1.49
<i>n</i> -hexane	7.2	2.94	5.3	1.80
<i>n</i> -heptane	7.4	3.70	7.3	1.97
<i>n</i> -octane	7.6	4.46	9.0	2.02
iso-butane	6.15	1.04	2.4	2.3
iso-pentane	6.75	1.95	3.6	1.85
cyclohexane	7.8	5.56	4.65	0.88
toluene	8.9	15.3	22.0	1.44
benzene	9.15	19.0	19.0	1.0
1-butene	7.0	2.41	12.4	5.15
2-butene	6.9	2.29	14.0	6.10
1-heptane	7.7	6.14	57.0	9.3
butadiene	7.6	4.52	19.0	4.2
1-5 hexadiene	8.2	8.4	46.0	5.48

could be made since, because of the small solubilities of water in these hydrocarbon systems, $N_1 V_1$ is small compared with $N_2 V_2$, so that

$$RT \ln \frac{\alpha_1}{N_1} = V_1 \left[\left(\frac{\Delta E_1}{V_1} \right)^{\frac{1}{2}} - \left(\frac{\Delta E_2}{V_2} \right)^{\frac{1}{2}} \right]^2. \quad (2)$$

If one makes the further assumption that α_1 is

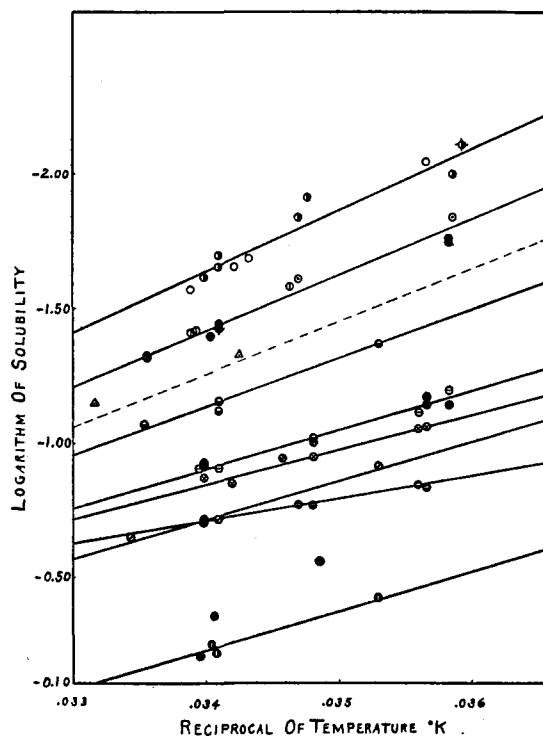


FIG. 4. Logarithm of solubility in mole percent as a function of the reciprocal temperature in degrees Kelvin.

⁴ J. H. Hildebrand, *Solubility* (Reinhold Publishing Corporation, Inc., New York, 1936), Chapter 3, p. 73.

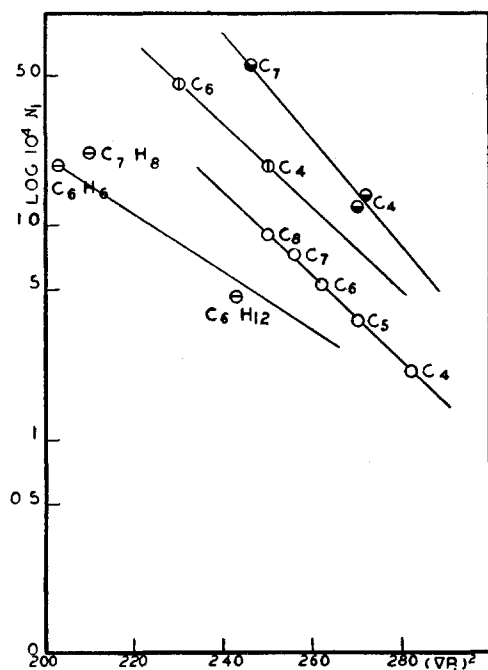


FIG. 5. Logarithm of molar solubilities (10^4) plotted against $[(\Delta E_1/V_1)^{1/2} - (\Delta E_2/V_2)^{1/2}]^2$. \circ : *n*-paraffinic hydrocarbons; \bullet : olefins; \odot : diolefins; \ominus : aromatics.

unity, one obtains

$$-RT \ln N_1 = V_1 \left[\left(\frac{\Delta E_1}{V_1} \right)^{1/2} - \left(\frac{\Delta E_2}{V_2} \right)^{1/2} \right]^2. \quad (3)$$

From Eq. (3), at a given temperature, the logarithm of the solubility should be proportional to the square of the difference of the square roots of the internal pressures of solute and solvent.

The calculated and observed values of N_1 at 20°C , obtained when necessary by interpolation from the observations, are recorded in Table II. The ratios, $N_{1 \text{ obs.}}/N_{1 \text{ calc.}}$, are also recorded in the table. The observed values of $\ln N_1$ are plotted in Fig. 5 as a function of $[(\Delta E_1/V_1)^{1/2} - (\Delta E_2/V_2)^{1/2}]^2$. Examination of Table II and Fig. 5 indicates that by use of Eq. (3) it is possible to group the solubilities of water according to the class of hydrocarbons studied, whether paraffins, olefins, diolefins, and aromatics. Only in the case of benzene do experimental and calculated values coincide, while in cyclohexane and toluene the Hildebrand function gives a fair approximation. The solubilities of water in the paraffin hydrocarbons increase linearly as the internal pressure

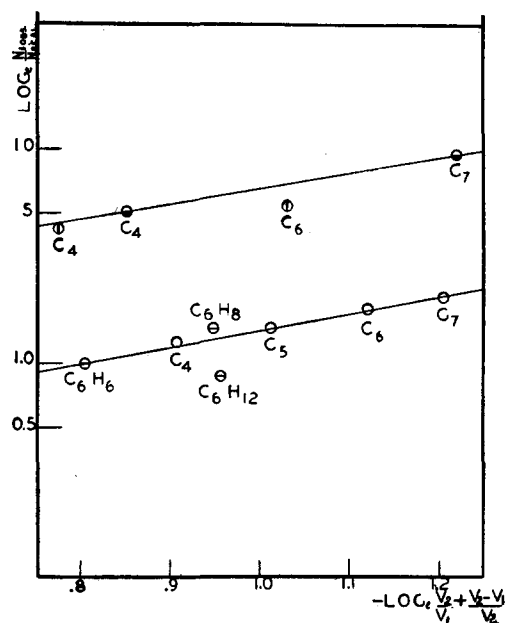


FIG. 6. Logarithm of ratio $N_{1 \text{ obs.}}/N_{1 \text{ calc.}}$ plotted against $-\ln(V_2/V_1) + (V_2 - V_1)/V_2$. \circ : *n*-paraffinic hydrocarbons; \bullet : olefins; \odot : diolefins; \ominus : aromatics.

of the hydrocarbon increases, but the curve falls markedly above the theoretical curve, with the deviations increasing with increasing molecular weight of the solvent. The solubility in the olefins and the diolefins is considerably higher than that calculated from the Hildebrand equation. What is more surprising is that the data for the diolefins lie on a plot intermediate to those of the paraffin and olefine solubilities.

In a recent communication⁵ on the entropy of solution of molecules of different size, Hildebrand has related the entropy of mixing and hence the activity to the molal volumes of the two constituents. Hildebrand's expression takes the form

$$\frac{\bar{S}_1}{R} = \ln \frac{N_1(V_1 - b_1) + N_2(V_2 - b_2)}{N_1(V_1 - b_1)} + \frac{N_2[(V_1 - b_1) - (V_2 - b_2)]}{N_1(V_1 - b_1) + N_2(V_2 - b_2)}. \quad (4)$$

If the free volumes are proportional to the molal volumes and if we can neglect $N_1 V_1$ in comparison with $N_2 V_2$ by reason of the low solubility, the expression for the activity a_1 becomes, since

⁵ J. H. Hildebrand, *J. Chem. Phys.* **15**, 225 (1947).

$$\bar{S}_1 = -R \ln a_1,$$

$$\ln a_1 = -\ln \frac{N_2 V_2}{N_1 V_1} + \frac{V_2 - V_1}{V_2}, \quad (5)$$

and the solubility N_1 per mole of solvent with unit activity becomes

$$\ln N_1 = -\ln \frac{V_2}{V_1} + \frac{V_2 - V_1}{V_2}. \quad (6)$$

In Fig. 6 we have plotted the value of the logarithm of the ratio $\ln(N_{1 \text{ obs.}}/N_{1 \text{ calc.}})$ against the function on the right of Eq. (6). It is evident that the hydrocarbons now fall into two classes, the paraffinic and aromatic in one class and the olefinic and diolefinic in the other. The linear relationship is quite satisfactory if one considers the sensitivity of $N_{1 \text{ obs.}}/N_{1 \text{ calc.}}$ to small errors in $N_{1 \text{ calc.}}$ caused by uncertainties in the heats of vaporization used in certain of the calculations, and to the experimental errors in $N_{1 \text{ obs.}}$. The slopes of the two curves are practically the same for the two classes. The net effect of the double bond is constant for the whole range of internal

pressures and molar volumes. The presence of the double bonds in the hydrocarbon chain appears to cause a fivefold increase in solubility of water over that obtained with the saturated hydrocarbon.

The data indicate that the deviation from theory becomes progressively greater with both olefinic and non-olefinic hydrocarbons the greater the length of the hydrocarbon chain, even when the Hildebrand expression in terms of the molal volumes has been applied. It must, however, be observed that in the calculations we have made use of the oversimplified assumption that the co-volumes of the liquids are proportional to the molal volumes which we have used. Data which would enable us to test the effect of such a simplification are not sufficiently reliable to justify further examination of this point.

ACKNOWLEDGMENT

We again wish to express our indebtedness to the Texaco Company for the grant-in-aid and fellowship which made this work possible, and also to Professor Ernest O. Lawrence who made available to us the supply of tritium water.