lower than the known oxygen content, while, for the original asphalt, the Grignard value is higher. No significant addition of the Grignard reagent occurred, indicating an absence of carbonyl oxygen.

From the results of the active hydrogen and methylation determinations, it appears that most of the oxygen content of the phenolic fraction can be accounted for as hydroxyl; at most, nitrogen compounds could account for about 25% of the observed active hydrogen value. As the results in Table III show, however, only about one-third of the total oxygen present in the asphalt is extractable with Claisen alkali. The remaining oxygen is presumably associated with ether, alcoholic groups and/or with phenols of such high molecular weight (or so hindered[16]) that they are insoluble in spite of the acidic hydroxyl. The relatively large amount of nitrogen in the non-extracted portion makes the active hydrogen determination unreliable for estimating hydroxyl oxygen in this fraction; the methylation–demethylation procedure indicates a minimum value of about 30% for oxygen present as hydroxyl.

Acknowledgment.—The authors wish to acknowledge the interest of Drs. Sol Weller and M. G. Pelipetz in this work. They are also indebted to Dr. Robert Friedel for the spectral interpretations and Mr. George Goldbach for technical assistance.

[16] Stillson, Sawyer and Hunt, THIS JOURNAL, **67**, 303 (1945).

BRUCETON, PENNA. RECEIVED APRIL 28, 1950

[CONTRIBUTION FROM NOYES LABORATORY, UNIVERSITY OF ILLINOIS]

The Solubility of Aromatic Hydrocarbons in Water[1]

BY ROBERT L. BOHON[2] AND W. F. CLAUSSEN

The solubilities in water of the following hydrocarbons were determined by an ultraviolet method at various temperatures between 0 and 40°: benzene, toluene, ethylbenzene, *m*-xylene, *p*-xylene, biphenyl and naphthalene. All of the liquid hydrocarbons studied exhibited a solubility minimum near 18° corresponding to a zero heat of solution. Calculated heats and entropies of solution were interpreted in terms of ice-like structures in solution and bonding between the π-electrons of the benzene ring and water. Some indication is given by the ultraviolet absorption spectra that interaction between water and aromatic hydrocarbons exists. The heat of solution of toluene in 0.4 m silver nitrate solution indicates complex formation between the cation and the hydrocarbon.

Introduction

Reliable work on the solubility of aromatic hydrocarbons in water is extremely scarce in the literature, and that which does exist is of questionable accuracy. The primary purpose of this research was to determine such solubilities and their temperature coefficients by a spectrophotometric method and interpret the results in terms of water structure and solubility mechanisms. The absorption bands near 250 mμ are of sufficient intensity to permit accurate measurements of small quantities of aromatic compounds in water.

The shape of the resulting solubility curves from 0 to 40° for the compounds studied show striking similarity to one another. All of the benzene hydrocarbons exhibit a minimum in solubility near 18° corresponding to a zero heat of solution, these solutions being similar in this respect to an ideal solution but being vastly different as exhibited by almost complete immiscibility. This same type of behavior is reported to be exhibited by the chloroethanes at 20°.[3] The change of this temperature coefficient of solubility with temperature is unusually large, this same effect also having been observed in this Laboratory with aliphatic hydrocarbons. The two multi-ring compounds studied, naphthalene and biphenyl, differ somewhat from the single-ring hydrocarbons, but they, too, have rapidly changing temperature coefficients in this temperature range.

Materials, Apparatus and Procedure

Materials.—The compounds studied included benzene, toluene, ethylbenzene, *m*-xylene, *p*-xylene, naphthalene and biphenyl. A sample of *o*-xylene did not give reproducible results and was discarded.

The benzene was obtained from Baker and Adamson and was purified by recrystallization from ethanol, washing, filtering through silica gel and distilling.[4] *p*-Xylene from Eastman Kodak Company was purified in the same fashion. Toluene was used as received from Phillips Petroleum Company, being guaranteed 99 mole % minimum. Ethylbenzene was a sample from Koppers Company which was redistilled, washed several times with water and dried by passing through silica gel. *m*-Xylene was supplied by Oronite Chemical Company and was subjected consecutively to sulfonation, hydrolysis, steam distillation, washing, drying through silica gel and distillation.[4] The index of refraction as determined with a Bausch and Lomb Dipping Refractometer was used as a criterion of purity for these liquid hydrocarbons.

Biphenyl was obtained from the Matheson Company and was recrystallized from absolute methanol.[5] Naphthalene was from the Barrett Division of the Allied Chemical and Dye Corporation and was purified by vacuum distillation.[6]

Apparatus.—A Beckman ultraviolet spectrophotometer, model DU, fitted with one cm. quartz cells was used throughout the solubility studies and a Cary recording spectrophotometer was utilized in studying the effect of solvents on the absorption spectra of these compounds.

Four water-thermostats controlled to within ±0.02° and fitted with a specially constructed shaking mechanism were used to saturate air-free conductivity water with the hydrocarbon in question. Round-bottom flasks (500 ml.) were fitted with standard taper joints and a stopcock to per-

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[1] Aided by a grant from the U. S. Public Health Service. Presented before the 118th Meeting of the American Chemical Society, September, 1950, Chicago, Illinois, before the Division of Water, Sewage, and Sanitation.

[2] Part of the work described herein was included in a thesis submitted by R. L. Bohon to the University of Illinois in partial fulfillment of the requirements for the Degree of Doctor of Philosophy. Present address: The Anderson Physical Laboratory, 609 South Sixth, Champaign, Illinois.

[3] A. E. van Arkel and S. E. Vles, *Rec. trav. chim.*, **55**, 407 (1936).

[4] B. J. Mair, D. J. Termini, C. B. Willingham and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, **37**, 229 (1946).

[5] J. Chipman and S. B. Peltier, *Ind. Eng. Chem.*, **21**, 1106 (1929).

[6] R. Kutschenreuter, *Chem. Zentr.*, **91**, II, 447 (1920).

mit out-gassing of the water used and to control the pressure above each mixture. Dow–Corning Silicone Grease was used for all joints. Blanks run on this grease showed no interference in this spectral region.

Non-extraction Procedure.—This is the technique used for most of the data reported herein. The round-bottom flasks containing about 4 ml. of hydrocarbon (or about 0.5 g. if solid) and 400 ml. of air-free water were evacuated and suspended in the thermostats. They were then shaken gently at the rate of forty shakes per minute for a minimum of 24 hours. The flasks were then clamped in a motionless position for another period of at least 24 hours to allow the majority of small hydrocarbon droplets suspended throughout the water phase to float to the surface. A Tyndall Beam was used to determine this period, and the time stated was sufficiently long in most cases.

At the end of the 48-hour period of saturation (or longer) the ground glass joint was separated and the solution was siphoned out in the following manner. A rubber stopper in the top of the flask was fitted with a 4 mm. glass delivery tube and blow-tube. The tip of the delivery tube was bent into a hook shape with the opening pointing upward in order to minimize the amount of hydrocarbon that entered the tube when it was lowered through the organic layer. The tube was flushed and desired quantities of the water layer were forced into 6 glass-stoppered Erlenmeyer flasks by exerting gentle air pressure on the blow-tube. These 6 flasks had previously been tared, partially filled with the proper amount of diluent water, and weighed again. Care was taken throughout the operation to reduce evaporation losses to a minimum. Samples taken in glass tubes sealed at each end with stopcocks gave comparable results.

TABLE I

EXPERIMENTAL DETERMINATIONS OF D_0 BETWEEN 0 AND 40°

Dotted lines indicate phase change

t, °C.	T, °K.	D_0	Av. D_0
		(1) Benzene (m.p. 5.5°)	
42.8	316.0	3.757–0.791–0.790–0.851	3.797
34.9	308.1	3.573–96–92	3.587
30.2	303.4	3.507–0.498	3.502
25.6	298.8	3.402–0.396	3.399
21.0	294.2	3.401	3.401
14.9	288.1	3.339–377–403	3.373
10.0	283.2	3.414–31	3.422
5.2	278.4	3.440	3.440
······	······	······	······
0.4	273.6	3.326–290	3.308
		(2) Toluene	
45.3	318.5	1.749	1.749
42.8	316.0	1.732–13–19–07–00–12–690	1.710
35.2	308.4	1.606–2	1.604
30.2	303.4	1.567–4–9–4	1.566
30.0	303.2	1.562	1.562
25.6	298.8	1.541–30–20–21–20	1.526
15.9	289.1	1.515–15	1.515
14.9	288.1	1.515–30–16	1.520
11.2	284.4	1.523–23	1.523
10.0	283.2	1.533	1.533
3.6	276.8	1.570–82	1.576
0.4	273.6	1.601–11	1.606
		(3) *p*-Xylene (m.p. 13.2°)	
42.8	316.0	0.954–8	0.956
35.2	308.4	.890	.890
34.9	308.1	.895–84	.889
30.3	303.5	.878–9	.878
30.2	303.4	.869–60	.864
25.6	298.8	.863–57–50	.856
21.0	294.2	.846	.846
14.9	288.1	.844–33	.838
10.0	283.2	.843–42–56	.847
······	······	······	······
10.0	283.2	.808	.808
0.4	273.6	.672–66	.669
		(4) *m*-Xylene	
39.6	312.8	0.542–1	0.542
34.9	308.1	.506–6	.506
30.3	303.5	.497–85–97	.493
25.6	298.8	.480–6–97	.487
21.0	294.2	.487–6	.487
14.9	288.1	.476–9	.477
5.2	278.4	.504–491–505	.500
0.4	273.6	.511–19–25–25	.520
		(5) Ethylbenzene	
42.8	316.0	0.450–0	0.450
34.9	308.1	.418–39–28–35	.430
30.2	303.4	.412	.412
25.6	298.8	.405–03–13–07–07	.407
21.2	294.4	.403	.403
20.7	293.9	.403	.403
5.2	278.4	.414–17	.416
0.4	273.6	.433–23–25	.427
		(6) Naphthalene (solid)	
42.8	316.0	2.699–56–81–83–59	2.675
36.0	309.2	1.963–2.027	1.995
35.2	308.4	1.967–2.018–1.962	1.982
30.2	303.4	1.594–1.600	1.597
30.1	303.3	1.571–58	1.564
25.6	298.8	1.307–1.291–1.313	1.303
19.3	292.5	1.021	1.021
15.9	289.1	1.893–5	0.894
14.9	288.1	0.853	.853
10.0	283.2	.707	.707
9.4	282.6	.714	.714
1.9	275.1	.547	.547
0.9	274.1	.531	.531
.5	273.7	.504	.504
.4	273.6	.500	.500
.0	273.2	.496–0.504	.500
		(7) Biphenyl (solid)	
42.8	316.0	1.870–46–60–69	1.861
36.0	309.2	1.345	1.345
34.9	308.1	1.294–86	1.290
33.3	306.5	1.175–92	1.184
30.4	303.6	1.035	1.035
30.1	303.3	1.041	1.041
25.6	298.8	0.843–38	0.840
15.9	289.1	.574–69–66	.569
14.9	288.1	.552	.552
12.6	285.8	.500–487–498	.495
10.0	283.2	.441–38	.439
7.6	280.8	.391–94–94	.393
5.2	278.4	.374–61–61	.365
2.4	275.6	.319–23	.321
0.4	273.6	.305–8	.306
		(8) Toluene in 0.400 molar silver nitrate (heptane extraction)	
34.9	308.1	1.614–1.754	1.684
25.6	298.8	1.790	1.790
10.0	283.2	2.025	2.025
0.4	273.6	2.303	2.303

After a final weighing, portions of each of the samples were inserted into the spectrometer for measurement. The dilutions were adjusted so as to give an optical density as close to 0.400 as

TABLE II

SOLUBILITIES AT 25° IN WATER

m/p represents the molar solubility at the same vapor pressure for all compounds, V_M is the molar volume of the pure liquid hydrocarbon

Compound	$\lambda_{max.}$ (mμ)	k (l./g. cm.)	Solubility, c (g./l. satd. soln.) Exp.	Lit.[a]	m (mole/l.)	p at 25° (mm.)[b]	m/p × 10^4	V_M at 25°[c] (ml./mole)
Benzene	254.0	1.90	1.79	1.74	0.0229	94.97	2.41	89.401
Toluene	261.0	2.44	0.627	0.53	.00680	28.47	2.39	106.846
Ethylbenzene	260.0	1.95	.208	...	.00196	9.494	2.06	123.064
m-Xylene	264.0	2.49	.196	.173	.00185	8.287	2.22	123.456
p-Xylene	267.0	4.30	.198	.200	.00186	8.763	2.12	123.919
Naphthalene	275.0	36.4	.0344	.0315	2.68×10^{-4}	0.107[d]	25.0	133.2
Biphenyl	247.0	108.0	7.48×10^{-3}	5.94×10^{-3}	4.85×10^{-5}	0.0303[e]	16.0	155.5
Toluene in 0.40 *m* $AgNO_3$	261.5	1.62[f]	1.09	...	0.0118	28.47	4.14	.....

[a] From Andrews and Keefer, reference (7). [b] All values of p from A.P.I.–N.B.S. Project 44 Table 5 k unless otherwise indicated. [c] All values of V_M from Project 44 except that naphthalene was calcd. from the density at 100° in "I. C. T.," **3**, 34 (1929), and biphenyl from density at 73° in "Handbook of Chem. and Physics," 1944. [d] G. W. Sears and E. R. Hopke, THIS JOURNAL, **71**, 1632 (1949). [e] From Chipman and Peltier, reference (5). [f] Measured in *n*-heptane, $k' = 2.37$ and k = (density of heptane) × (k') = 0.684 × 2.37 = 1.62.

possible. The readings of optical density for the six samples were then corrected (D_c) for cell differences due to absorption of hydrocarbon on the walls of one of the cells during the course of a run. From the amount of diluent water, A, and the amount of saturated hydrocarbon solution added, B, one can calculate the optical density of the pure saturated hydrocarbon solution, D_0, by the relation

$$D_0 = \frac{D_c(A + B)}{B} \quad (1)$$

The values of D_0 for the 6 samples were averaged and the deviation of each D_0 from this average was calculated. The average percentage deviation from the mean rarely exceeded 0.5%.

From the Beer–Lambert law

$$D_0 = kcl \quad (2)$$

where D_0 is the optical density of the saturated solution, k is the extinction coefficient, and l is the path length, one can calculate c, the concentration of absorbing substance present. The solvent employed has very little effect on the value of k for the bands in the 250 mμ region, and the quantities used herein were determined in 95% ethanol.

Extraction Procedure.—An extraction technique was used for the few runs made on the solubility of toluene in aqueous silver nitrate solutions. This method also afforded a satisfactory check on the non-extraction procedure. The method used was almost identical with that described by L. J. Andrews and R. M. Keefer[7] except for a few details. *n*-Heptane, purified by passing slowly over silica gel,[8] was used as the extracting solvent instead of hexane because of heptane's lower vapor pressure with consequent reduction of evaporation losses. A magnetic stirrer was used to assure complete extraction of the hydrocarbon into the heptane layer.

A slightly different method of calculation must be used with this procedure since the amount of hydrocarbon per sample is now measured in a solvent of different density than water. It can be shown that the concentration of hydrocarbon, c, is given by the relation

$$c = D_cA/k'lBd = D_0'/k'ld \quad (3)$$

where D_c is the corrected optical density as read from the spectrometer on the heptane solution containing all the hydrocarbon originally present in B grams of aqueous solution. A is the weight of heptane used in the extraction. k' is the extinction coefficient determined in heptane solution, and d, the density of heptane. $D_0' = D_cA/B$.

Experimental Results

Solubility Measurements.—At least two separate runs, and generally more, were made at 5° intervals from 0 to 40° for every compound studied. Table I gives the experimental data for each compound with the average values for D_0 listed in the last column. These average values were then plotted as log D_0 *vs.* $1/T$ where T is the absolute temperature. The resulting plots were very similar in shape, each having an almost parabolic form with a minimum near 18° for the liquids. These plots were used as working curves for all subsequent calculations.

Utilizing experimentally determined values for the extinction coefficients, k, and values for D_0 as read from the working curves, Beer's law was applied to calculate the concentrations, c, of hydrocarbons dissolved in pure water at any temperature. Table II indicates the wave lengths and extinction coefficients used, the determined solubilities at 25° as compared with a different investigator, and a comparison of the molar solubilities at the same vapor pressure, m/p, with the molar volumes of the pure hydrocarbons, V_M.

Apparently, considerable differences in molar volume can have a noticeable effect upon the solubility; the larger the molecule, the less soluble it becomes in water. This would indicate that the actual volume occupied by the hydrocarbon in a water solution plays an important role in determining its solubility.

Note further, however, that the solubilities for naphthalene and biphenyl are 7 to 10 times as soluble in water as the benzene hydrocarbons in spite of the larger size of the multi-ring compounds.

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[7] L. J. Andrews and R. M. Keefer, THIS JOURNAL, **71**, 3645 (1949).

[8] M. M. Graff, R. T. O'Connor and E. L. Skau, *Ind. Eng. Chem., Anal. Ed.*, **16**, 556 (1944).

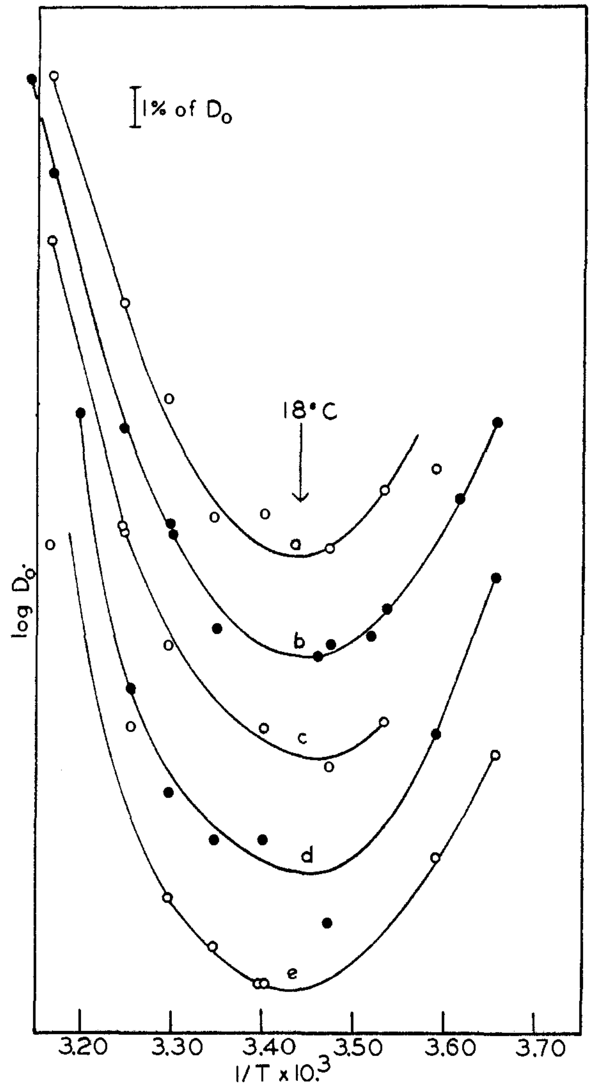

Fig. 1.—Logarithm of the optical density of saturated aqueous solutions *vs.* reciprocal absolute temperature. Ordinate values are not relative between curves: a, benzene; b, toluene; c, *p*-xylene; d, *m*-xylene; e, ethylbenzene.

This is perhaps an indication that some property of the benzene ring itself is vital to the solubility mechanism.

Solubility of Toluene in Silver Nitrate Solutions.—A few measurements were made of the solubility of toluene in various silver nitrate solutions and the results are indicated in Table III and Fig. 3. The extraction and non-extraction methods checked one another rather well although the technique used in our extraction studies was not as refined as that used in the non-extraction work.

Table III shows the pronounced effect of electrolytes upon the solubility of toluene. Whereas potassium nitrate causes a marked reduction in the solubility[7] ("salting-out effect"), silver nitrate has the opposite effect and increases the solubility almost 73% over that in pure water at 25°. This effect with silver ions has been attributed by Andrews and Keefer to the formation of π-complexes between the benzene ring and the cation. The ring acts as an electron donor (Lewis base) and the cation as an acceptor (Lewis acid). This type of complex has been observed in several other instances involving either an aromatic compound or an olefin and some electron acceptor, as BF_3-HF,[9] the halogens,[10,11,12,13] sulfur,[14] and hydrogen chloride.[15] The introduction of silver nitrate also has a profound effect on the shape of the solubility curve as evidenced in Fig. 3. No minimum occurs in this case.

TABLE III

COMPARISON OF EXTRACTION AND NON-EXTRACTION TECHNIQUES

Toluene at 25° (approx.); all extractions listed made with *n*-hexane

Method	Ag^+ (mole/l.)	K^+ (mole/l.)	*c* (g./l.)
Non-extraction	0.0	0.0	0.627
Extraction	.0	.0	0.61
Extraction	.402	.0	1.04
Extraction	.402	.0	1.07
Extraction	.400	.600	0.90
Andrews and Keefer	.0	.0	0.53
Andrews and Keefer	.400	.600	0.89
Andrews and Keefer	.0	1.00	0.40

Heats and Entropies of Solution.—It can be shown that the partial molar heat of solution, $\Delta\bar{H}_{sol}$, of a pure hydrocarbon dissolving in pure water is given by the expression

$$\Delta\bar{H}_{sol} = RT^2\left[\frac{d \ln m}{dT}\right] \quad (4)$$

where *m* is the molar solubility and *R* and *T* have their usual significance. Since *m* is proportional to D_0, our experimentally determined quantity, and since $d(1/T) = -dT/T^2$, equation 4 can be transformed into

$$\Delta\bar{H}_{sol} = -4.575\left[\frac{d \log_{10} D_0}{d(1/T)}\right] \quad (5)$$

The heat of solution is proportional to the slope of the curve formed by plotting the logarithm of the solubility *versus* the reciprocal of the ab-

TABLE IV

HEATS OF SOLUTION ($\Delta\bar{H}_{sol}$) FOR LIQUIDS IN WATER

Naphthalene and biphenyl are considered as supercooled liquids; all values in cal./mole

T, °K.	Benzene	Toluene	Ethylbenzene	*m*-Xylene	*p*-Xylene	Naphthalene	Biphenyl	Toluene in 0.4 *m* $AgNO_3$
275	...	−940	−952	−1340	−1010	990	1680	−2800
280	...	−720	−663	− 915	−1010	1380	2420	....
285	−550	−330	−390	− 380	− 320	1730	2690	....
290	− 60	0	− 82	0	123	2030	3000	−1300
295	320	230	279	272	324	2430	3210	....
300	720	770	471	476	547	3060	3590	−1300
305	1060	1060	864	938	1012	3400	4440	....
310	1400	1370	1760	2120	1760	3750	5120	....
315	...	1710	...	....	....	4480	5040	....

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(9) D. A. McCaulay, A. P. Lien and B. H. Shoemaker, "Abstracts of Papers," 117th American Chemical Society Meeting, April, 1950, page 3-0.

(10) F. Fairbrother, *J. Chem. Soc.*, 1051 (1948).

(11) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949).

(12) J. H. Hildebrand, H. A. Benesi and L. M. Mower, *ibid.*, **72**, 1017 (1950).

(13) R. S. Mulliken, *ibid.*, **72**, 600 (1950).

(14) B. Ghosh and S. P. Sinha, *J. Indian Chem. Soc.*, **22**, 15 (1945).

(15) H. C. Brown and J. Brady, THIS JOURNAL, **71**, 3573 (1949).

solute temperature. These slopes were read graphically from the curves in Figs. 1 and 2. The results are collected in Table IV and illustrated in Figs. 4 and 5. The values for the heats of solution of the solids were corrected to those for supercooled liquids by subtracting the heats of fusion for each compound from the values determined from the working curves.[16]

The heats of solution for benzene, toluene, ethylbenzene, *m*-xylene and *p*-xylene, all appear to be very similar, and this similarity is evident when the heats are plotted as a function of the temperature as in Fig. 4. The experimental accuracy does not permit one to do more than draw a straight line through these points with a slope of approximately 108 calories per degree. The rough curve for toluene in silver nitrate appears to have about the same slope from 0° to about 18°, but there is a distinct tendency to flatten out at higher temperatures. This may only be fortuitous, but the correspondence of this temperature with zero heat of solution for the pure water is striking.

The absolute values for the heats of solution in pure water vary for the benzene hydrocarbons from about −1 kcal. per mole near 0° through zero heats at 18° and up to positive heats of about 1.4 to 2.1 kcal. near 35°. When silver nitrate is added, however, the heats for toluene decrease to between −1.3 and −2.8 kcal. over this range of temperature and are never positive. The heats of solution for naphthalene and biphenyl, when considered as supercooled liquids, never pass through zero but are always positive, the values for biphenyl being higher than those for naphthalene.

Table V summarizes the temperature coefficients of the heats of solution for the compounds studied. They are all abnormally large indicating a considerable difference in the heat capacity of the solution complex and the original reactants of pure water and hydrocarbon, (*i.e.*, $[d\Delta H/dT]_p = \Delta C_p$).

TABLE V

TEMPERATURE COEFFICIENTS FOR HEATS OF SOLUTION IN WATER

Compound	Temperature interval, °C.	$[d\Delta H/dT]$ cal./mole/°C.
Benzene	2–42	108
Toluene	2–42	108
Ethylbenzene	2–42	108
m-Xylene	2–42	108
p-Xylene	2–42	108
Naphthalene	2–22	77
	22–42	146
Biphenyl	7–22	56
	22–37	148
Toluene in 0.4 *m* $AgNO_3$	2–17	~100
	17–27	<100

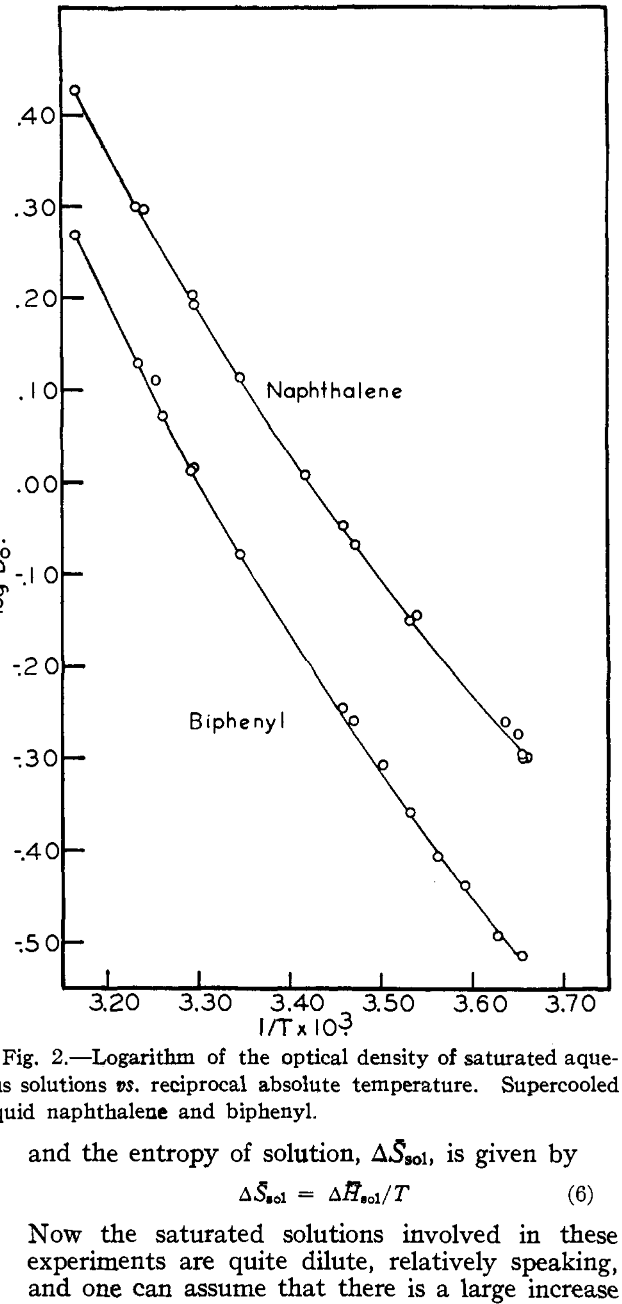

Fig. 2.—Logarithm of the optical density of saturated aqueous solutions *vs.* reciprocal absolute temperature. Supercooled liquid naphthalene and biphenyl.

Since the process of solution of the hydrocarbon into water can be considered an isothermal equilibrium reaction, the free energy change is zero and the entropy of solution, $\Delta \bar{S}_{sol}$, is given by

$$\Delta \bar{S}_{sol} = \Delta \bar{H}_{sol}/T \qquad (6)$$

Now the saturated solutions involved in these experiments are quite dilute, relatively speaking, and one can assume that there is a large increase in entropy due to dilution alone when one mole of hydrocarbon dissolves in water to form a saturated solution. This type of "volume" or "expansion" entropy, ΔS_v, can be calculated[17] from the expression

$$\Delta S_v = R \ln V_w/V_M \qquad (7)$$

where R is the gas constant per mole, V_w is the volume of solution containing one mole of dissolved hydrocarbon, and V_M is the molar volume of pure hydrocarbon.

From the experimental results, the over-all entropy change is found to be much less than the large positive value expected from equation (7). In order to rationalize this rather unusual situation one might assume that the process of solution involves more than an "expansion" of the hydro-

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(16) Calorimetric heats of fusion for naphthalene were obtained by H. L. Ward, *J. Phys. Chem.*, **38**, 761 (1934), and those for biphenyl were calculated from the heat capacities given by M. E. Spaght, S. B. Thomas and G. S. Parks, *J. Phys. Chem.*, **36**, 882 (1932).

(17) J. H. Hildebrand, *J. Chem. Phys.*, **15**, 225 (1947); *Chem. Revs.*, **44**, 37 (1949).

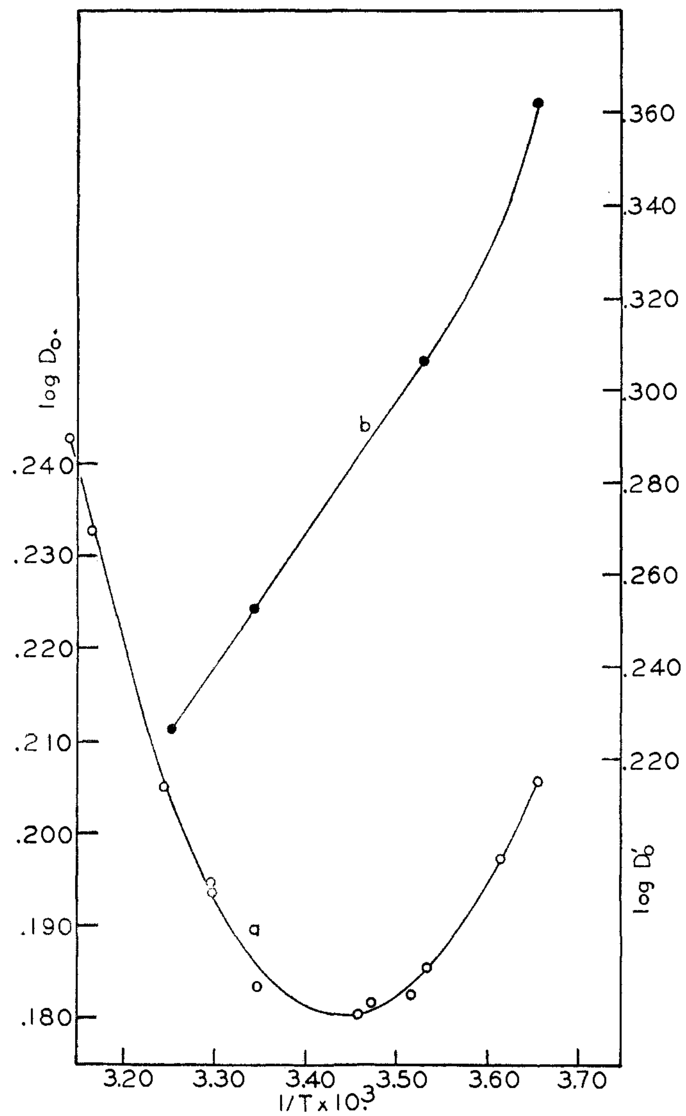

Fig. 3.—Effect of silver nitrate on the solubility of toluene in water: a, in pure water; b, in 0.400 molar silver nitrate.

carbon into the water phase. For example, suppose the solution process in some way allowed the water molecules in the vicinity of a dissolved hydrocarbon molecule to lose some of their disorder, as, for instance, becoming "ice-like." This loss of disorder would correspond to a decrease in entropy of the system, ΔS_F, which we may call the "entropy of freezing." The observed entropy of solution is then expressed as a sum of the entropy of expansion and the entropy of freezing

$$\Delta \bar{S}_{sol} = \Delta S_v + \Delta S_F = 4.575 \log (V_w/V_M) + \Delta S_F \quad (8)$$

If one knows the entropy of solution, the solubility, and the molar volume, the "entropy of freezing" can be calculated. This has been done in Table VI. The relatively small variation with temperature of V_w and V_M for the liquids causes only a 1.5% variation in the quantity ΔS_V (see benzene), and hence they may be considered constant. In comparison, $\Delta \bar{S}_{sol}$ changes by more than threefold over this temperature range. For the two solids, however, one cannot neglect the temperature coefficient of V_w and this factor has been included in the calculations for naphthalene and biphenyl.

The numerical values for the entropy of freezing can be given, perhaps, more physical significance by noting that the actual entropy of freezing to the common form of ice, ice-I,[18] is −5.26 e.u. at 0° and is comparatively independent of the temperature.[19] Dividing ΔS_F by this quantity, one obtains the number of ice-I molecules which would have to form per molecule of hydrocarbon dissolved. This number is designated by N and is plotted in Fig. 6 as a function of temperature. The lines all are seen to be relatively straight. Note that only from one to four molecules of water would have to "freeze" per hydrocarbon molecule to account for the rapidly changing heat of solution with temperature.

Spectral Shifts with Change of Solvent.—Spectra were run with a Cary recording spectrophotometer from 300 to 200 mμ on three hydrocarbons dissolved in three different solvents: *n*-heptane, alcohol and water. 100% methanol was used for naphthalene and biphenyl, and 95% ethanol was used for toluene. Several interesting facts were evident from these curves.

For all three compounds, naphthalene, biphenyl and toluene, λ_{max} in the 200 mμ region shifts to shorter wave lengths in going from heptane to alcohol to water. The effect is most pronounced for biphenyl. These same absorption maxima become broader as the solvent becomes more polar.

The maxima in the 250 mμ region are not nearly as dependent upon the solvent, and only slight shifts are observed. Water does tend to smear out these bands, however. The experimental data are summarized in Table VII.

Discussion

In order to interpret the experimental results discussed above the authors suggest a combination of two mechanisms acting against one another, one with a positive heat of solution and the other with a negative heat of solution. The positive heat is probably the heat of cavity formation and the negative heat could be due to (a) formation of a more "ice-like" structure (*i.e.*, a more ordered and more highly hydrogen-bonded cage of water) around the dissolved hydrocarbon molecules and/or (b) a complex formation of the type involving the labile π-electrons of the aromatic nucleus. The "ice-formation" picture is similar to that of the clathrate type of compound which forms, not because of any affinity between solvent and solute, but because the solvent itself is capable of forming an associated cage around a solute molecule thereby retaining it in solution.[20] Possibility (b) might actually involve complex-compound formation between hydrogen ions and the ring, or it may be a more general and weaker type affecting many

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[18] N. E. Dorsey, "Properties of Ordinary Water Substance," Reinhold Publ. Corp., New York, N. Y., 1940, p. 617.

[19] "International Critical Tables," 5, 131 (1929).

[20] H. M. Powell, *J. Chem. Soc.*, 61 (1948).

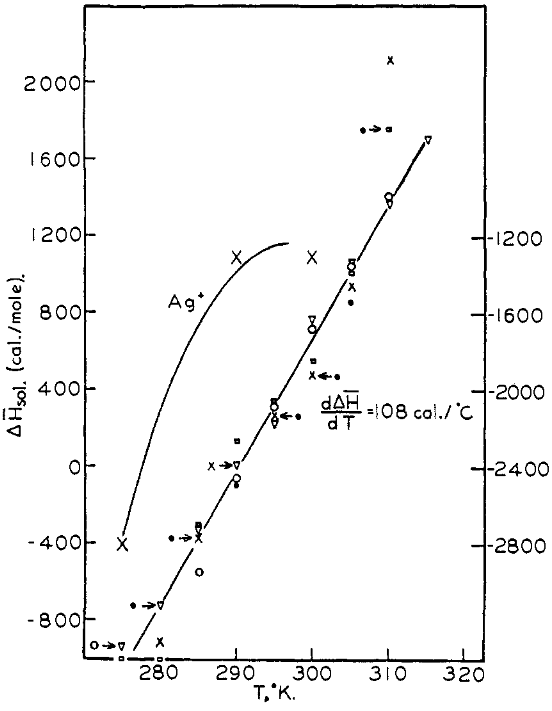

Fig. 4.—Heats of solution for liquids *vs.* °K.: O, benzene; ●, ethylbenzene; ▽, toluene; ×, *m*-xylene; □, *p*-xylene; ×, toluene in 0.400 *m* silver nitrate.

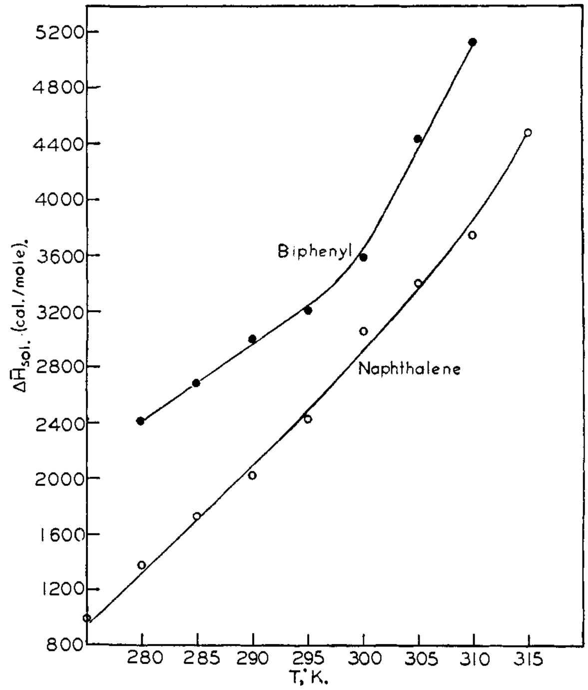

Fig. 5.—Heats of solution for supercooled liquid naphthalene and biphenyl *vs.* absolute temperature.

of the neighboring water molecules, rather than just one. In either case, the π-electrons would be functioning as a base and the water as an acid.

Above 18° the heat of cavitation would predominate for the liquid hydrocarbons, at 18° it would exactly cancel the negative heat reaction (whether "freezing" or complex formation), and below this temperature the negative heat would be the larger. In terms of ice-formation, at 18° just enough "freezing" occurs within the water to exactly cancel the energy necessary to make a hole for the hydrocarbon molecule.

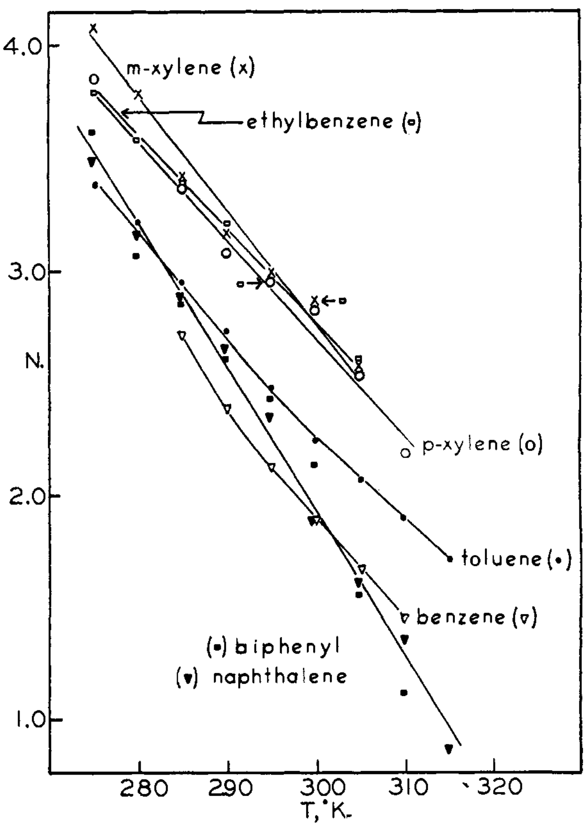

Fig. 6.—Number of "ice molecules" forming per hydrocarbon molecule.

The large change in the heats of solution with temperature for the aromatic hydrocarbons may be due to an abnormally high partial molal heat capacity of the hydrocarbon in water. This may represent the work of stretching the hydrogen bonds in the ice shell surrounding the hydrocarbon. Plans have been made to check this concept by measurement of partial molal volumes of solution at various temperatures and pressures.

A perfect correlation between the solubility at constant vapor pressure and either the molecular volume or the molecular weight is not present in the data. This fact may indicate that the shapes as well as the total volume size of the molecules may enter into the ease of solubility. The large increase in solubility (m/p) of the two polynuclear aromatics, biphenyl and naphthalene, over the substituted benzene compounds may be primarily an effect of molecular weight and size, which would permit a greater play of the van der Waals forces; however, actual association or complex formation between a benzene ring and water molecules may also play a role in increasing the solubility. This phenomenon might be expected to be at least twice as important in the case of the two binuclear aromatic compounds in comparison to alkyl benzenes. The perturbation of the 210 mμ absorption by water as a solvent may also be interpreted in terms of greater interaction between water and the binuclear aromatics.

TABLE VI

ENTROPIES OF "FREEZING," ΔS_F

In this table $\Delta\bar{S}_{sol}$ is the observed entropy of solution, ΔS_v the entropy of expansion calculated from observed solubilities, ΔS_F the difference between these two values, and $N = \Delta S_F/-5.26$ where -5.26 e.u. is the true entropy of freezing to form ice-I; entropies in cal./deg./mole

Compound	T, °K.	$\Delta\bar{S}_{sol}$	$\Delta S_v{}^a$	ΔS_F	N
(1) Benzene	285	−1.93	12.31	−14.24	2.71
	290	−0.21	12.31	−12.52	2.38
	295	1.10	12.30	−11.20	2.12
	300	2.40	12.28	− 9.88	1.88
	305	3.46	12.20	− 8.74	1.66
	310	4.55	12.12	− 7.57	1.44
(2) Toluene	275	−3.43	14.36	−17.79	3.38
	280	−2.58		−16.94	3.22
	285	−1.15		−15.51	2.95
	290	0		−14.36	2.73
	295	0.79		−13.57	2.58
	300	2.56		−11.80	2.24
	305	3.48		−10.88	2.07
	310	4.42		− 9.94	1.89
	315	5.43		− 8.93	1.70
(3) *p*-Xylene	285	−1.12	16.63	−17.75	3.38
	290	0.42		−16.21	3.08
	295	1.10		−15.53	2.95
	300	1.82		−14.81	2.82
	305	3.32		−13.31	2.53
	310	5.68		−10.95	2.08
(4) *m*-Xylene	275	−4.88	16.65	−21.53	4.09
	280	−3.26		−19.91	3.79
	285	−1.33		−17.98	3.42
	290	0		−16.65	3.17
	295	0.92		−15.73	2.99
	300	1.59		−15.06	2.86
	305	3.08		−13.57	2.58
	310	6.85		− 9.80	1.86
(5) Ethylbenzene	275	−3.46	16.52	−19.98	3.80
	280	−2.37		−18.89	3.59
	285	−1.37		−17.89	3.40
	290	−0.28		−16.80	3.20
	295	0.95		−15.57	2.96
	300	1.57		−14.95	2.84
	305	2.83		−13.69	2.60
	310	5.68		−10.84	2.06
(6) Naphthalene (liquid)	275	3.60	22.0	−18.4	3.50
	280	4.93	21.6	−16.7	3.18
	285	6.07	21.3	−15.2	2.89
	290	7.00	21.0	−14.0	2.66
	295	8.24	20.6	−12.4	2.36
	300	10.20	20.2	−10.0	1.90
	305	11.15	19.7	− 8.5	1.62
	310	12.10	19.3	− 7.2	1.37
	315	14.25	18.9	− 4.6	0.87
(7) Biphenyl (liquid)	275	6.10	25.2	−19.1	3.63
	280	8.65	24.8	−16.2	3.08
	285	9.44	24.5	−15.1	2.87
	290	10.35	24.1	−13.7	2.61
	295	10.89	23.7	−12.8	2.44
	300	11.98	23.3	−11.3	2.15
	305	14.55	22.8	− 8.2	1.56
	310	16.51	22.4	− 5.9	1.12
	315	16.00	21.9	− 5.9	1.12

^{a} $\Delta S_v = R \ln V_w/V_M$ where V_w is the volume occupied by 1 mole of hydrocarbon in a saturated aqueous solution and V_M is the molar volume of the pure hydrocarbon. ΔS_v is practically constant for the benzene compounds (see benzene) and was used as such where indicated.

TABLE VII

EFFECT OF SOLVENT ON ABSORPTION MAXIMA

These spectra were run on a recording Cary instrument; all values in mμ. Parentheses indicate shoulders, brackets the concentration in g./l. Not all maxima are listed

Toluene in		
Water	95% EtOH	*n*-Heptane
[~0.038]	[0.01724]	[0.01724]
207.0	208.2	...
(211.8)	(211.5)	211.8
...	(215.5)	(215.5)
[~0.176]	[0.1724]	[0.1724]
261.3	261.9	261.8
268.0	268.7	268.7
(264.3)	(264.9)	(264.9)

Naphthalene in		
Water	100% MeOH	*n*-Heptane
[~0.0020]	[0.00107]	[0.0015]
219.5	220.4	221.0
(216.5)	(217.0)	(218.0)
(214.5)	(214.6)	(215.5)
[0.015]	[0.01068]	[0.015]
266.0	266.0	265.0
276.0	275.0	275.0
(273.0)	(272.0)	(273.0)

Biphenyl in		
Water	100% MeOH	*n*-Heptane
[~0.0037]	[0.00333]	[~0.0020]
199.0	204.0	209.0
(No apparent shoulders)		
[~0.0037]	[~0.00333]	[~0.0020]
247.0	247.0	247.0
(Very broad band)		

A recent paper by T. M. Cromwell and R. L. Scott[21] reports that the heat of formation of the benzene–iodine complex is around −1.3 to −1.4 kcal./mole at 25°. This is very nearly the same as the heat of solution of toluene in 0.4 *m* silver nitrate at 20° and also for the benzene hydrocarbons in pure water near 0°.

There remains one observed experimental fact which does not appear to fit in with the above theory. This is the observation that the heats of solution of naphthalene and biphenyl (when considered as supercooled liquids) never pass through zero, but always remain positive. The change in the heat of solution with temperature is of the correct order of magnitude, but one would expect these binuclear compounds to form complexes with water more readily than any of the benzene compounds and they should exhibit, therefore, even larger negative heats of solution. One might attempt to explain this on the basis of molar volumes, realizing that perhaps there exists an upper limit to the size of the molecule which can dissolve in water and still maintain a negative heat of solution.

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CHAMPAIGN, ILL. RECEIVED SEPTEMBER 25, 1950

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[21] T. M. Cromwell and R. L. Scott, THIS JOURNAL, **72**, 3825 (1950).