for the corresponding acid in the six-ring series (Fig. 2). The curve for the five-ring acid, 3-acetoxy-Δ^5-(6)-*nor*-cholestene-7-carboxylic acid (VIII)[19] parallels those of the other cyclic acids near the isosbestic points and very likely has a maximum in the vicinity of 218 mμ.

It has been observed that the acrylic acids and esters show weak fluorescence in ultraviolet light. While dimerization of the acids cannot be eliminated as a factor in the deviation from Beer's law, the deviation may be ascribed in part to "superposition of transmitted light and scattered fluorescence emission."[18]

Experimental

Materials.—The simple acrylates and methacrylates were commercial products.[20] β,β-Dimethylacrylic acid, m.p. 68–69°, was prepared according to "Organic Syntheses[21] and was purified by crystallization from petroleum ether. Its ester, b.p. 112–114° (2 mm.), was obtained in 69.5% yield from the silver salt and ethyl iodide.

3,4,5,6-Tetrahydrobenzoic Acid (II).—Cyclohexanecarboxylic acid (5 g.) heated with bromine (6.25 g.) and phosphorus trichloride (4 drops) at 60–70° for 3 hours gave 61.8% of crude bromo acid. Dehydrobromination by refluxing with 3.65 g. of collidine yielded 22.3% of pure tetrahydrobenzoic acid boiling at 131–132° (13 mm.).

2,3,4,5,6,7,8,10-Octahydro-1-naphthoic Acid (IV).[22]—Decahydro-1-naphthoic acid was converted to the 1-bromo-acid described previously.[14] Digestion and crystallization from Skellysolve F yielded one pure bromo acid, m.p. 146–148°, which on dehydrobromination with collidine gave an excellent yield of the octahydronaphthoic acid, m.p. 158–159°.

Ultraviolet Absorption Spectra.—Accurately weighed (±0.01 mg.) acrylic acids and esters were dissolved in 95% alcohol and diluted to an exact volume with the same solvent. Further dilutions were made from the same stock solution. All determinations were made in matched quartz cells of 1 cm. length with a Beckman spectrophotometer with freshly prepared solutions.

Summary

It has been shown that acrylic acids and esters exhibit maximal absorption roughly between 210 and 225 mμ. Large deviations from Beer's law are found in all these acids and an accurate comparison of similarly constituted acids can be made only at the isosbestic points.

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[19] Woodward and Clifford, THIS JOURNAL, **63**, 2727 (1941).

[20] The authors are indebted to Rohm and Haas Co., Philadelphia, for generous samples of these compounds.

[21] *Organic Syntheses*, **23**, 27 (1943).

[22] Experimental by Vernon Kerr, New Mexico Highlands University.

LAS VEGAS, NEW MEXICO RECEIVED JULY 14, 1950

[CONTRIBUTION OF THE RESEARCH AND DEVELOPMENT BRANCH, OFFICE OF SYNTHETIC LIQUID FUELS, BUREAU OF MINES]

Characterization of the Phenolic Fraction of Coal-hydrogenation Asphalt

BY RALPH HUSACK AND CALVIN GOLUMBIC

A study of the phenolic constituents of coal hydrogenation asphalt was made by the countercurrent distribution method The results of this study showed the presence of two groups of phenols. One group, which was extracted by aqueous alkali comprised alkylphenols and phenylphenols. The other group was soluble only in Claisen alkali and was probably a mixture of phenols with polynuclear structures. Close agreement between experimental and theoretical distribution curves indicated a considerable degree of homogeneity for each group with respect to partition coefficient. The oxygen content of the asphalt fraction extracted by Claisen alkali comprised about one-third of the total oxygen in the asphalt. Most of this oxygen was accounted for as hydroxyl. Only about 30% of the oxygen in the non-extracted fraction could be definitely ascribed to hydroxyl oxygen.

It has been postulated that asphalt is the primary product formed in the high-pressure hydrogenolysis of coal.[1] That portion of the coal-hydrogenation product which is soluble in benzene, but insoluble in *n*-hexane, will be referred to as asphalt for the purposes of this paper. The nature of the oxygenated constituents of asphalt has now been studied with the ultimate aim of obtaining better understanding of the type of oxygen linkages in coal. Little or no information exists on this subject, yet this knowledge is highly desirable because (a) one of the critical steps in the hydrogenolysis of coal occurs at the site of carbon–oxygen bonds,[2] and (b) the oxygen content of coal is intimately associated with its coking properties.[3]

Asphalt was separated into acidic (phenolic) and non-acidic portions by a procedure based on that described by Woolfolk, *et al.*,[4] for the recovery of phenols (tar acids) from coal-hydrogenation oils. In this procedure, alcoholic (Claisen) alkali is employed as the phenol extractant in preference to aqueous alkali because it was found to increase the phenol recovery. DeWalt and Glenn[5] have recently reported a similar observation. With asphalt, the recovery of phenolic material is increased 50% by the use of Claisen alkali. In view of these results, it may not be valid to assume, as Green and Mukherji[6] have done, that aqueous alkali alone can be used to distinguish between alcoholic and phenolic groups in coal tar resins.

To obtain some definitive indication of the molecular structures present in the phenolic fraction of coal-hydrogenation asphalt, this fraction was studied by the countercurrent distribution method,[7] which is particularly suitable for the qualitative and quantitative analysis of phenolic mixtures.[8,9] Application of this technique, together with spec

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[1] M. G. Pelipetz, E. M. Kuhn, S. Friedman and H. H. Storch, *Ind. Eng. Chem.*, **40**, 1259 (1948); S. Weller, E. L. Clark and M. G. Pelipetz, *ibid.*, **42**, 334 (1950).

[2] H. H. Storch, C. H. Fisher, C. O. Hawk and A. Eisner, Bureau of Mines Tech. Paper 654, 1943, 50 pp.

[3] Blayden, Riley and Shaw, *Fuel*, **25**, 13 (1946).

[4] Woolfolk, Golumbic, Friedel, Orchin and Storch, Bur. Mines Bull. 487, in press.

[5] DeWalt and Glenn, paper presented before the Division of Gas and Fuel Chemistry, 116th meeting, A. C. S., Atlantic City, September, 1949.

[6] Green and Mukherji, *J. Soc. Chem. Ind.*, **67**, 438 (1948).

[7] Craig, *J. Biol. Chem.*, **155**, 519 (1944).

[8] Golumbic, Orchin and Weller, THIS JOURNAL, **71**, 2624 (1949).

[9] Golumbic, *ibid.*, **71**, 2627 (1949).

tral measurements, to the acidic fraction of a coal-hydrogenation oil,[10] led to the isolation and characterization of a number of phenolic compounds. A similar approach has been taken in the examination of the phenolic fraction of coal-hydrogenation asphalt. Since the complexity of this mixture precluded any simple isolation of compounds, its analysis was confined to identification of the types of phenolic substances present.

The phenolic fraction recovered from the Claisen alkali extraction was subjected first to 53-transfer distribution in the system benzene–0.5 *M* phosphate buffer of *p*H 12.54. The benzene layers of the distribution tubes were examined for selective absorption in the ultraviolet region by means of the Cary spectrophotometer. Wherever selective absorption was noted, optical density values were measured and plotted against tube number. For tubes 48–52, optical densities only at 280 mμ were plotted since selective absorption was not observed. The distribution pattern of Fig. 1 is the result of these measurements. Band A was the only clearly defined distribution band that was obtained; its close correspondence with a theoretical curve[11] indicates a considerable degree of homogeneity (with respect to distribution coefficient) for the phenols comprising band A. The total phenolic material recovered from tubes 0–4 of band A comprised about 15% by weight of the original fraction. To obtain information on the specific structures present in this composite, its ultraviolet absorption spectrum in cyclohexane solution was determined. The results of these measurements together with similar ones for bands B and C are recorded in Table I.

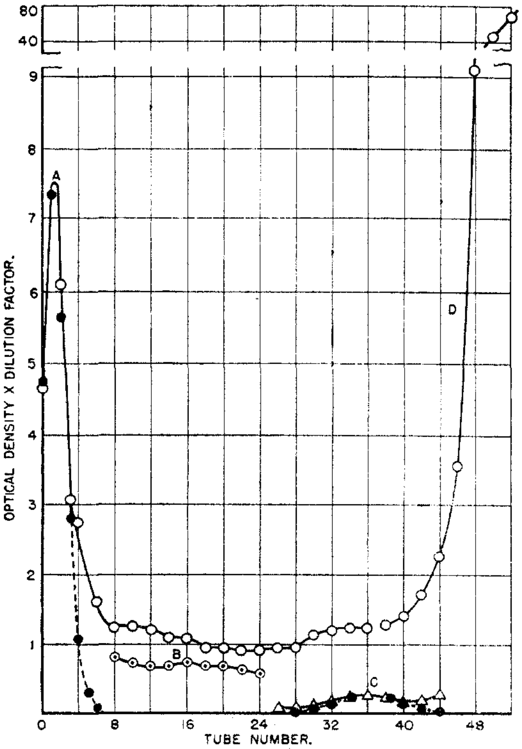

Fig. 1.—Distribution of tar acids of asphalt: ○, 280 mμ; ⊙, 290 mμ; △, 338 mμ; ●, theoretical.

Table I

Countercurrent Distribution of Asphalt Phenolic Fraction

Band	Tubes	Partition coefficient[a]	Approx., %	Ultraviolet spectrum	Interpretation
A	0–4	0.03	15	Doublet branching at 274 and 280 mμ, broad band at 250 mμ	Simple alkyl phenol plus phenol with diphenyl structure
B	12–18	0.44	2	Bands at 279 and 253 mμ, shoulders at 273 and 287 mμ	Uncertain
C	32–40	2.3	5	Bands at 248 and 338 mμ, shoulder at 279 mμ	Phenols with 3 or 4 condensed ring systems
D	48–52	>50	70	.. ..	High mol. wt. and/or partially hindered phenols[b]

[a] Defined by the ratio, concentration of solute in lighter phase/concentration of solute in heavier phase; it is calculated from the position of the maximum of a distribution band, according to Williamson and Craig.[11] [b] *Cf*. ref. 18.

The composition of the material in band A appears to be fairly simple. Its ultraviolet spectrum denotes the presence of an alkylphenol and a phenylphenol. The observed low partition coefficient is in the proper range for such structures.[8] The structures present in band B are not clearly defined. The ultraviolet spectrum of the constituents comprising band C exhibits a maximum at 338 mμ; this is an indication of the presence of phenols containing condensed ring systems.

The material comprising band D (tubes 48–52) which represents about 70% of the fraction, did not distribute in the benzene–aqueous alkali system. Since it is soluble in Claisen alkali, it was possible to distribute this material in a solvent pair composed of benzene and Claisen alkali. The results of the 53-transfer distribution of a composite of the material in tubes 48–53 are given in Fig. 2.

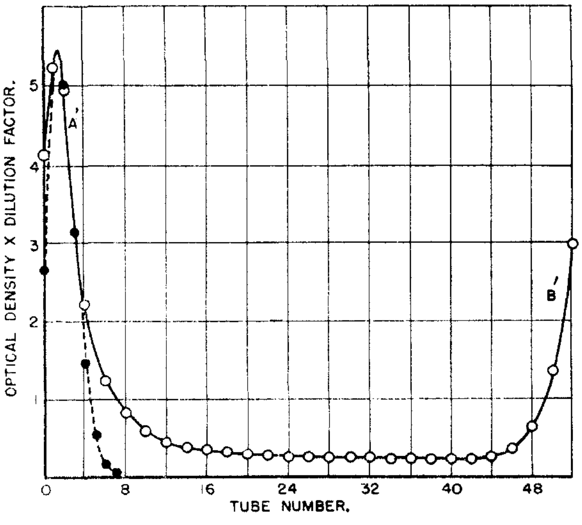

Fig. 2.—Distribution of band D (tubes 48–52): ○, 330 mμ; ●, theoretical.

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(10) Golumbic, Woolfolk, Friedel and Orchin, This Journal, **72**, 1939 (1950).

(11) Williamson and Craig, *J. Biol. Chem.*, **186**, 687 (1947).

TABLE II

COUNTERCURRENT DISTRIBUTION OF MATERIAL IN DISTRIBUTION BAND D

Band	Tubes	Partition coefficient[a]	Approx. %	Ultraviolet spectrum	Infrared spectrum	Interpretation
A′	0–4	0.037	60	Sharp band at 338 mμ, broad band at 252 mμ	Strong OH band; spectrum shows some resemblance to original fraction but large changes in intensity have occurred	Phenols with 3 or 4 condensed ring systems
B′	50–53	>50	20	Band at 335 mμ, shoulders at 302, 290 and 273 mμ	Very few OH bonds are present	Neutral polynuclear compounds

[a] See Table I, footnote (*a*).

Most of the material concentrated at the left of the pattern in the form of a sharp band (A′) as would be expected for a phenolic substance. Interpretation of spectral measurements of this band, summarized in Table II, indicates that its constituents are probably polynuclear phenols similar to those of band C (Table I). The material concentrated at the right of the distribution pattern (band B′) appears to consist of neutral substances entrained during the original extraction of the phenolic fraction.

These results of the distribution study show that the phenolic fraction of asphalt can readily be segregated into two groups of phenolic compounds by partition in systems containing benzene as one phase and aqueous alkali or alcoholic alkali as the other. The phenolic group which favors the aqueous alkali phase comprises simple alkyl and phenyl phenols, whereas the group which is soluble only in Claisen alkali is probably a mixture of phenols containing several fused aromatic rings. Both groups exhibit sharp distribution patterns. This is evidence that each is composed of compounds which do not differ widely in molecular weight.

Experimental

Asphalt.—The source material for asphalt was the total liquid product obtained from the hydrogenation of Pittsburgh-bed (Bruceton) coal at 440° with 1% MoO_3 as catalyst, in the Bureau of Mines experimental hydrogenation plant. This liquid product represents nearly 80% of the original coal on a moisture and ash-free basis. The particular sample of product oil used was obtained from the last two batches of test 17, operation 182 of the experimental plant. A detailed description of this plant run is given by Elliott, *et al.*[12] Asphalt was separated from product oil as follows: Twenty-five pounds (11.4 kg.) of product oil was added slowly, with efficient stirring, to 8 times its weight of *n*-hexane, which was kept below 10°. After being stirred for several hours, the mixture was allowed to settle overnight and then was filtered. The residue, consisting of material insoluble in *n*-hexane, was air-dried and crushed. It was then added slowly, with efficient stirring, to 1.5 times its weight of benzene. After being stirred for several hours, the mixture was allowed to settle overnight and then was filtered. Asphalt was recovered from the filtrate by distilling off the solvent at atmospheric pressure. The last traces of solvent were removed by heating and stirring *in vacuo*. The yield of asphalt was 5.4 pounds (2.45 kg.).

Extraction Procedures. 1. **Aqueous Alkali or Claisen Alkali.**—Fifty grams of asphalt was dissolved in 100 ml. of benzene and the solution was filtered. The filtrate was extracted several times with successive 100-ml. portions of alkali solution (10% aqueous potassium hydroxide, or Claisen alkali which was prepared as follows: 300 g. of potassium hydroxide was dissolved in 250 ml. of water and made up to a total volume of 1000 ml. with absolute methanol). The precipitate which formed at the interface of the benzene-alkali phase was removed by filtration during each extraction step. The combined precipitate was washed with water until neutral, dried, and then extracted with benzene. The benzene-insoluble precipitate was removed by filtration and dried to constant weight. The filtrate (benzene solution) was extracted three times with alkali. The benzene residue from the extraction of the precipitate was combined with the previous benzene-soluble fraction and the combined solution was washed with water. The solvent was evaporated and the residue was dried to constant weight. The alkali extract was combined with the previous alkali extract (aqueous KOH or Claisen) and acidified with carbon dioxide. The liberated phenolic material was extracted with benzene, which was removed by evaporation, and the phenols were dried to constant weight. A schematic representation of this fractionation scheme is given in Fig. 3.

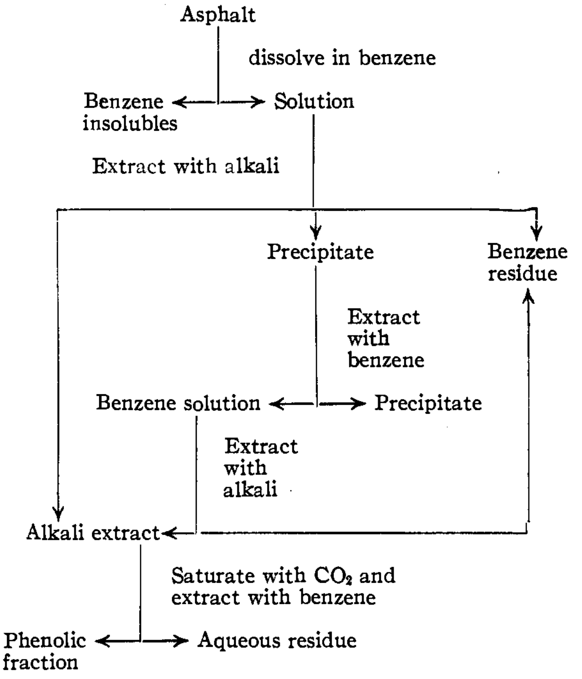

Fig. 3.—Schematic representation of extraction of phenols from coal hydrogenation asphalt.

2. **Methanol-Water "Blank."**—Fifty grams of asphalt was dissolved in 100 ml. of benzene, and the solution was filtered. The filtrate was extracted several times with successive 100-ml. portions of methanol-water solution (3 parts methanol per 1 part water). Except for the absence of a precipitate at the interface, the "blank" procedure was identical with that for the alkali extractions.

Material and Elemental Balances.—Table III lists the products recovered (based on 100 g. of asphalt) and the results of ultimate analyses and elemental balances. All analyses are reported on the moisture-free basis. The material recovery was greater than 90% in each case. The precipitate obtained during the extraction of asphalt with aqueous potassium hydroxide was not analyzed; the values shown for the precipitate plus losses in this case were calculated from the elemental balances. The formation of insoluble precipitates during the extraction procedure appears to be the same phenomenon noted by Green and Mukherji[6] in the extraction of coal tar resins. The high ash content of the precipitate in the Claisen alkali extraction

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[12] Elliott, Kandiner, Kallenberger, Hiteshue and Storch, *Ind. Eng. Chem.*, **42**, 83 (1950).

TABLE III

EXTRACTION OF COAL-HYDROGENATION ASPHALT; ANALYSES AND ELEMENTAL BALANCES

		Ash,	Hydrogen		Carbon		Nitrogen		Sulfur		Oxygen[b]	
	G.	%	%	G.	%	G.	%	G.	%	G.	%	G.
Aqueous alkali												
Orig. asphalt	100.0	0.05	6.31	6.31	88.59	88.59	1.66	1.66	0.14	0.14	3.25	3.25
Phenolic fraction	6.4	.00	7.22	0.46	81.21	5.20	1.33	0.09	.10	.01	10.14	0.65
Benzene residue	74.3	.56	6.17	4.58	89.24	66.30	1.85	1.37	.11	.08	2.07	1.54
Precipitate	12.0	..	6.58	1.27	88.55	17.09	1.04	0.20	.27	.05	3.56	1.06
Loss[a]	7.3											
Methanol–water mixture												
Orig. asphalt	100.0	0.05	6.31	6.31	88.59	88.59	1.66	1.66	0.14	0.14	3.25	3.25
Extract	3.6	Trace	6.63	0.25	81.48	3.08	2.07	0.08	.15	.01	9.67	0.37
Benzene residue	86.6	0.10	6.32	5.47	89.64	77.64	1.81	1.56	.19	.16	1.94	1.68
Loss[a]	9.8	..	5.95	0.59	79.60	7.88	0.20	0.02	..	..	12.2	1.20
Claisen alkali												
Orig. asphalt	100.0	0.00	6.37	6.37	88.55	88.55	1.85	1.85	0.12	0.12	3.11	3.11
Phenolic fraction	13.3	.24	7.36	0.98	83.41	11.09	1.01	0.13	.14	.02	7.84	1.04
Benzene residue	63.6	.00	6.20	3.94	89.73	57.07	1.94	1.23	.13	.08	2.00	1.27
Precipitate	14.2	2.80	5.35	0.76	82.46	11.71	1.94	0.28	.14	.02	7.31	1.04
Loss[a]	8.9	...	..	0.69	...	8.69	..	.21	..	.00	...	(−0.24)

[a] The sums of the distributed losses do not exactly check the indicated total loss. The discrepancies are believed to be due to small errors in the chemical analyses. [b] By difference.

may be due to entrained alkali. The alkali-insoluble, benzene-soluble residues have about the same ultimate analyses in both the aqueous and alcoholic alkali extractions. The oxygen content is, of course, lower than that of the original asphalt. There does not seem to be much preferential distribution of the sulfur between the alkali-soluble and the alkali-insoluble fractions; however, the former fractions are poorer in nitrogen than the latter.

The calculated composition of the material lost in the Claisen alkali extraction is very similar to that of benzene, with the exception of the nitrogen content. It is possible that the original asphalt contained 8–9% of benzene which was not removed by the drying procedure used; the almost constant loss observed in each experiment is consistent with this idea. The ultimate analysis of the benzene-insoluble precipitate which formed during this experiment is similar to that of Bruceton coal. It is possible that this insoluble material is present in the original asphalt, that it is normally peptized by the rest of the asphalt in benzene solution, but that it is precipitated by the presence of aqueous or alcoholic alkali.

If the material removed by the methanol–water extraction is used as a "blank" for the neutral compounds extracted by Claisen alkali, it is clear that the net quantity of phenols extractable by Claisen alkali from a typical coal-hydrogenation asphalt is much greater than that extractable by aqueous alkali (9.7% *versus* 6.4%). The value of 9.7% for the Claisen alkali extraction is a minimum figure because the methanol–water "blank" would be expected to remove some phenolic[13] material as well as neutral material.

Countercurrent Distribution.—The distributions were carried out on a 100-mg. sample of the phenolic fraction in the 54-tube Craig instrument[14] by the standard procedure described elsewhere.[9] Analysis of the distributed samples was made by optical density measurements on a Cary recording ultraviolet spectrophotometer. Calculation of approximate composition of distributed samples has been described previously.[4]

Nature of Oxygen Linkages.—The reactive hydroxyl content of asphalt and of the various fractions of the Claisen alkali extraction was estimated by a methylation–demethylation procedure[4] and also by Zerewitinoff's active hydrogen method carried out at room temperature.[15] In order to utilize the active hydrogen method for this purpose, the assumption was made that all active hydrogen occurred as hydroxyl. Since certain possible constituent groups such as pyrrole and amino nitrogen also react with the Grignard reagent, it is evident that results obtained by the active hydrogen method would tend to be high, particularly in the fractions containing the largest amounts of nitrogen. Methylation, on the other hand, would tend to give low results because the methylation procedure is not quantitative.[4]

In Table IV, the oxygen contents of the various fractions, calculated from the "hydroxyl" determinations, are compared with the oxygen content determined by difference from the ultimate analyses. For all the materials, methylation–demethylation indicates a lower oxygen content than that deduced from the ultimate analysis. (The original methoxyl content of all materials was found to be negligible.) Oxygen contents deduced from the Grignard determinations are higher in every case than the values from the methoxyl determinations and, for the alkaline extract and the residue, they are in close agreement with those found by ultimate analysis. The Grignard value for the precipitate is

TABLE IV

OXYGEN CONTENT OF ASPHALT AND FRACTIONS (CLAISEN ALKALI EXTRACTION)

	Oxygen content, weight, %		
	Ultimate analysis	Methylation–demethylation	Grignard
Asphalt	3.1	1.7	4.3
Phenolic fraction	7.8	5.5	7.7
Benzene residue	2.0	0.6	2.3
Precipitate	7.3	2.5	5.5

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(13) Prutton, Walsh and Sesai, *Ind. Eng. Chem.*, **42**, 1210 (1950).

(14) Craig and Post, *Anal. Chem.*, **21**, 500 (1949).

(15) Orchin and Wender, *ibid.*, **21**, 875 (1949).

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.

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[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).