Studies of Gas Chromatography with Mixed Stationary Liquids. IV. The Analysis of Aromatic Hydrocarbons from C_6 to C_{10} with a Capillary Column*

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The gas chromatographic analysis of aromatic hydrocarbon mixtures through C_{10} needs to be carried out with columns of excellent resolving powers, because these mixtures contain many groups of isomers with similar physical properties. It seems appropriate, for the analysis of such a complex mixture, to use a capillary column. Indeed, it has already been reported that fairly good separation was obtained for many types of hydrocarbon mixtures by the use of such a column,[1-3] but all of the aromatics through C_{10} have not been separated by a single column, although various types of liquids of different polarities have been investigated as stationary phases. Several authors have reported that in these cases the mixed stationary liquid is effective. By changing the composition of the mixed liquid, the selectivities for the solutes were altered widely and continuously, and a column which has a pertinent selectivity may be prepared as an aid in investigating the effects of the composition on the partition coefficients of the solutes in question.[4-6] For all the paraffins, mono-olefins, di-olefins, cycloparafins and acetylenes through C_4, an appproximate linearity was observed between the logarithm of the partition coefficient and the composition (wt.%) of the mixed phase. Accordingly, when the retention times on two stationary liquids are known, the retention time of the solute on the mixed liquid of any composition may be presumed.

The presence of similar relationships may be expected from the behaviors of aromatic hydrocarbons on some mixed liquids, and the complex mixtures of aromatic isomers might be efficiently separated by the use of the appropriate mixed liquid.

Experimental

Apparatus. — A Perkin-Elmer Model 188 vapor fractometer equipped with a flame-ionization detector was used without modification. Helium was used as the carrier, and the pressure was adjusted to a gauge pressure of 30 or 60 p. s. i. at the inlet of the column. A column consists of a 45.7 m. (or 91.4 m.) by 0.254 mm. stainless-steel capillary and is coated with squalane (SQ), dinonyl phthalate (DNP), 7, 8-benzoquinoline (BQ), polyethylene glycol 600 (PEG 600), di-*n*-propyl tetrachlorophthalate (DPTCP), 2, 4-dinitrochlorobenzene (DNCB) or a binary solution composed of these components.

Coating the Capillary.—Each of the substrates was coated in the capillary tubing as follows: a weighed amount of the refined liquid was dissolved in ether or methanol to prepare a 10—20% solution, and then this solution was injected into the capillary tubing by the aid of a 5-ml. injection cylinder. After the tubing had been completely filled with the solution, the solvent and the excess substrate were purged out in a stream of helium gas at room temperature. Consequently, the thin substrate was deposited on the inner wall of the capillary tubing. The film thickness obtained was influenced not only by the concentration of the solution, but, contrary to the reported result,[7] strongly by the speed of coating. Namely, as the rate was increased by raising the purging gas, the amount of liquid coated was increased. Therefore, this step is important in the preparation of a column which has an appropriate retention time for the sample component.

Results and Discussion

Retention Times on the Single Liquid Phase. —The relative retention times of aromatic hydrocarbons from C_6 to C_{10} and their chromatograms on the six liquid phases with different selectivities are shown in Table I and Fig. 1 respectively. The retention times in Table I have been corrected for the dead volume of the apparatus by substracting the retention time of methane. On all the liquid phases, there are several overlapping peaks: isobutylbenzene - *s*-butylbenzene and 1, 4-diethylbenzene - 1, 2-ethylbenzene on the SQ

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[1] H. Miyake and M. Mitooka, *Bull. Japan Petrol. Inst.*, **5**, 58 (1963).

[2] R. L. Martin and J. C. Winters, *Anal. Chem.*, **35**, 1930 (1963).

[3] J. A. Walker and D. L. Ahlberg, ibid., **35**, 2023 (1963).

[4] H. Miyake and M. Mitooka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **84**, 593 (1963).

[5] H. Miyake and M. Mitooka, ibid., **84**, 923 (1963).

[6] H. Miyake and M. Mitooka, ibid., **85**, 326 (1964).

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TABLE I. RELATIVE RETENTION TIMES ON VARIOUS STATIONARY LIQUIDS
(*n*-PROPYLBENZENE = 1.000)

No.	Name of compound	Abbreviation	Relative retention time					
			SQ 90°C	DNP 70°C	BQ 90°C	PEG 600 90°C	DPTCP 90°C	DNCB 70°C
1	Benzene	B	0.109	0.087	0.132	0.217	0.128	0.143
2	Toluene	T	0.248	0.221	0.269	0.382	0.296	0.337
3	Ethylbenzene	EB	0.500	0.484	0.533	0.630	0.534	0.566
4	*p*-Xylene	*p*-X	0.559	0.536	0.582	0.658	0.666	0.863
5	*m*-Xylene	*m*-X	0.567	0.553	0.608	0.681	0.642	0.834
6	*o*-Xylene	*o*-X	0.664	0.683	0.759	0.816	0.859	1.120
7	Isopropylbenzene	*i*-PB	0.796	0.788	0.797	0.885	0.769	0.743
8	*n*-Propylbenzene	*n*-PB	1.000	1.000	1.000	1.000	1.000	1.000
9	1-Methyl-3-ethylbenzene	1-M-3-EB	1.107	1.146	1.141	1.093	1.097	1.331
10	1-Methyl-4-ethylbenzene	1-M-4-EB	1.127	1.151	1.113	1.080	1.150	1.377
11	1, 3, 5-Trimethylbenzene	1, 3, 5-TMB	1.290	1.351	1.370	1.209	1.289	2.097
12	1-Methyl-2-ethylbenzene	1-M-2-EB	1.255	1.359	1.412	1.354	1.428	1.811
13	*t*-Butylbenzene	*t*-BuB	1.340	1.357	1.221	1.171	1.234	1.234
14	1, 2, 4-Trimethylbenzene	1, 2, 4-TMB	1.485	1.603	1.618	1.508	1.813	2.857
15	Isobutylbenzene	*i*-BuB	1.510	1.495	1.337	1.190	1.425	1.251
16	*s*-Butylbenzene	*s*-BuB	1.523	1.540	1.464	1.251	1.374	1.206
17	1-Methyl-3-isopropylbenzene	1-M-3-*i*-PB	1.690	1.772	1.599	1.374	1.483	1.646
18	1, 2, 3-Trimethylbenzene	1, 2, 3-TMB	1.810	2.081	2.181	2.066	2.511	3.908
19	1-Methyl-4-isopropylbenzene	1-M-4-*i*-PB	1.789	1.868	1.639	1.400	1.576	1.748
20	1-Methyl-2-isopropylbenzene	1-M-2-*i*-PB	1.881	2.069	1.957	1.684	1.861	2.171
21	1, 3-Diethylbenzene	1, 3-DEB	2.071	2.239	2.058	1.672	1.859	2.320
22	1-Methyl-3-*n*-propylbenzene	1-M-3-*n*-PB	2.150	2.279	2.054	1.690	1.994	2.222
23	*n*-Butylbenzene	*n*-BuB	2.188	2.331	2.113	1.786	2.142	2.074
24	1-Methyl-4-*n*-propylbenzene	1-M-4-*n*-PB	2.244	2.352	2.059	1.714	2.126	2.314
25	1, 2-Diethylbenzene	1, 2-DEB	2.254	2.551	2.499	1.983	2.279	2.788
26	1, 3-Dimethyl-5-ethylbenzene	1, 3-DM-5-EB	2.422	2.675	2.452	1.894	2.090	3.126
27	1, 4-Diethylbenzene	1, 4-DEB	2.258	2.432	2.167	1.761	2.032	2.251
28	1-Methyl-2-*n*-propylbenzene	1-M-2-*n*-PB	2.370	2.618	2.426	2.038	2.513	2.926
29	1, 4-Dimethyl-2-ethylbenzene	1, 4-DM-2-EB	2.655	3.005	2.811	2.226	2.850	4.240
30	1, 3-Dimethyl-4-ethylbenzene	1, 3-DM-4-EB	2.784	3.179	2.964	2.311	2.868	4.343
31	1, 2-Dimethyl-4-ethylbenzene	1, 2-DM-4-EB	2.887	3.302	3.014	2.417	2.947	4.297
32	1, 2-Dimethyl-3-ethylbenzene	1, 2-DM-3-EB	3.287	3.966	3.853	3.069	3.871	6.145
33	1, 2, 4, 5-Tetramethylbenzene	1, 2, 4, 5-TeMB	3.809	4.532	4.376	3.280	4.740	9.542
34	1, 2, 3, 5-Tetramethylbenzene	1, 2, 3, 5-TeMB	3.976	4.806	4.612	3.477	4.830	9.811
35	1, 2, 3, 4-Tetramethylbenzene	1, 2, 3, 4-TeMB	4.813	6.086	5.989	4.617	7.154	15.059

column; *t*-butylbenzene - 1-methyl-2-ethylbenzene-1, 3, 5-trimethylbenzene and 1-methyl-2-isopropylbenzene - 1, 2, 3-trimethylbenzene on the DNP column; 1, 3-diethylbenzene - 1-methyl-3-*n*-propylbenzene - 1-methyl-4-*n*-propylbenzene, 1, 2, 3-trimethylbenzene - 1, 4-diethylbenzene and 1,3-dimethyl-5-ethylbenzene - 1,2-diethylbenzene on the BQ column; 1-methyl-2-isopropylbenzene - 1-methyl-3-*n*-propylbenzene on the PEG 600 column, and *t*-butylbenzene-isobutylbenzene and others on the DNCB column.

In the case of SQ, which is almost nonpolar and does not have a marked selectivity for solutes, the aromatic hydrocarbons are eluted approximately in order of their boiling points. DNP and PEG have weak polarities and show small selectivities. In the case of BQ, which forms inclusion complexes with aromatic hydrocarbons, the heat of mixing is small and the solute molecules adopt less random configurations.[8] It can be surmised that DPTCP and DNCB form molecular complexes with aromatic hydrocarbons.[9] The heats of the mixing of aromatic hydrocarbons for these two stationary liquids, therefore, must be negative and large; also, the change in the activity coefficients with the temperature must be large. Consequently, it may be expected that the selectivities of these liquids will change considerably with the temperature.

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[8] D. H. Desty and W. J. Swanton, *J. Phys. Chem.*, **65**, 706 (1961).

[9] S. H. Langer, C. Zahn and G. Pantazoplos, *J. Chromotog.*, **3**, 154 (1960).

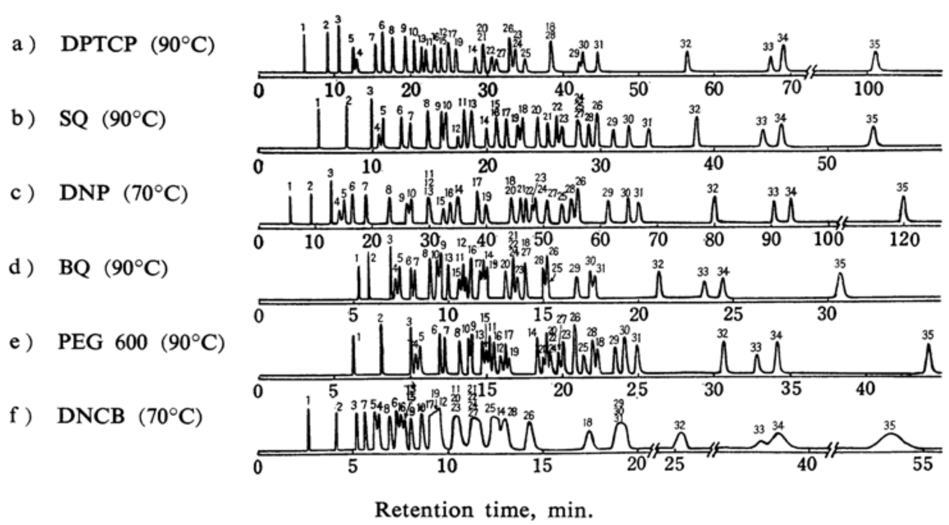


Fig. 1. Chromatograms of C_6 through C_{10} aromatic hydrocarbons on the six liquid phases.

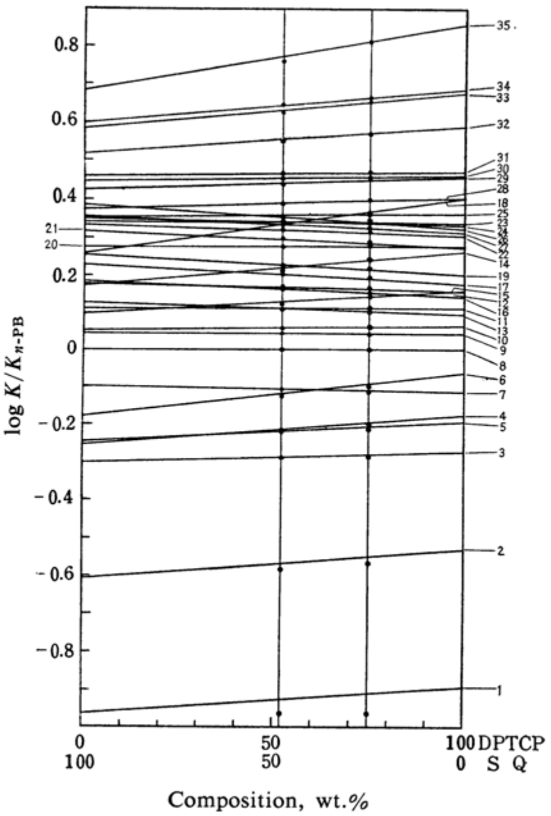


Fig. 2. The relationship between the relative retention time of solute (log $K/K_{n\text{-PB}}$) and the composition (wt.%) of the mixed stationary liquid SQ-DPTCP at 70°C.

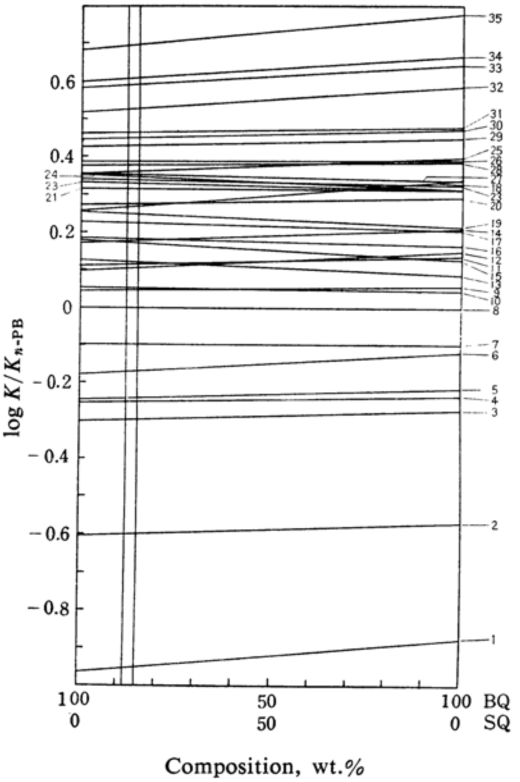


Fig. 3. The relationship between the relative retention time of solute (log $K/K_{n\text{-PB}}$) and the composition (wt.%) of the mixed stationary liquid SQ-BQ at 70°C.

The Relationship between the Relative Retention Times and the Composition of Stationary Liquids.—For each hydrocarbon, the logarithms of the relative partition coefficients on the SQ column and DPTCP column were marked on the left and right ordinates respectively, and a straight line was drawn through them, as Fig. 2 shows.

If a linear relationship of the same kind as

TABLE II. COMPARISON BETWEEN THE PRESUMED AND THE OBSERVED RELATIVE RETENTION TIMES ON THE SQ-DPTCP COLUMNS AT 90°C (*n*-PROPYLBENZENE=1.000)

No.	Compound	SQ 48%-DPTCP 52% column		SQ 25%-DPTCP 75% column	
		Presumed	Observed	Presumed	Observed
1	B	0.118	0.108	0.121	0.108
2	T	0.269	0.262	0.279	0.271
3	EB	0.517	0.514	0.525	0.517
4	*p*-X	0.610	0.610	0.635	0.630
5	*m*-X	0.604	0.605	0.622	0.613
6	*o*-X	0.759	0.750	0.803	0.795
7	*i*-PB	0.785	0.782	0.778	0.770
8	*n*-PB	1.000	1.000	1.000	1.000
9	1-M-3-EB	1.100	1.104	1.097	1.103
10	1-M-4-EB	1.140	1.139	1.148	1.145
11	1,3,5-TMB	1.291	1.277	1.289	1.294
12	1-M-2-EB	1.340	1.320	1.385	1.386
13	*t*-BuB	1.286	1.281	1.259	1.260
14	1,2,4-TMB	1.641	1.613	1.718	1.732
15	*i*-BuB	1.462	1.476	1.449	1.464
16	*s*-BuB	1.442	1.444	1.409	1.414
17	1-M-3-*i*-PB	1.578	1.590	1.531	1.548
18	1,2,3-TMB	2.143	2.165	2.312	2.303
19	1-M-4-*i*-PB	1.675	1.670	1.626	1.678
20	1-M-2-*i*-PB	1.866	1.863	1.862	1.870
21	1,3-DEB	1.954	1.968	1.910	1.927
22	1-M-3-*n*-PB	2.089	2.085	2.033	2.059
23	*n*-BuB	2.163	2.170	2.158	2.171
24	1-M-4-*n*-PB	2.183	2.192	2.160	2.180
25	1,2-DEB	2.270	2.252	2.270	2.278
26	1,3-DM-5-EB	2.244	2.236	2.168	2.194
27	1,4-DEB	2.138	2.138	2.085	2.099
28	1-M-2-*n*-PB	2.438	2.436	2.477	2.490
29	1,4-DM-2-EB	2.748	2.734	2.793	2.818
30	1,3-DM-4-EB	2.825	2.809	2.851	2.861
31	1,2-DM-4-EB	2.917	2.900	2.925	2.948
32	1,2-DM-3-EB	3.581	3.53	3.716	3.710
33	1,2,4,5-TeMB	4.265	4.20	4.509	4.501
34	1,2,3,5-TeMB	4.406	4.42	4.592	4.601
35	1,2,3,4-TeMB	5.889	5.76	6.482	6.453

that for C_1 to C_4 hydrocarbons exists for aromatic hydrocarbons, it is possible to deduce the relative retention times on the mixed phases of any composition from Fig. 2. Table II shows the observed values on the mixed phases as compared with the presumed values from the figure. The points in Fig. 2 represent the observed values. These results show that the presumed values are in fair agreement with the observed values. The considerably large differences between the presumed and the observed values of benzene may be due to errors in the measurement of its small retention times. It may be expected that similar linearities also exist in the other sets of liquids.

TABLE III. SETS OF STATIONARY LIQUIDS

	DNCB	DPTCP	PEG 600	BQ	DNP
SQ	not miscible	×	not miscible	●	×
DNP	○	×	not miscible	×	
BQ	×	●	×		
PEG 600	×	×			
DPTCP	×				
DNCB					

×: There is no possibility of the separation of all hydrocarbons on the presuming diagram.

●: There are same possibilities of the separation on the presuming diagram, however, all hydrocarbons cannot be experimentally separated.

○: All hydrocarbons can be separated.

Table III shows the sets of the six liquids.

To constitute a mixed phase for a capillary column, the two liquids must be soluble in each other. Using the presumed diagrams of retention times in Fig. 2 on each set of two liquids, a mixed phase which gives a separation of all the aromatic hydrocarbons from C_6 to C_{10} has been sought.

SQ-BQ System. — As may be observed in Fig. 3, there are possibilities of the separation of all solutes in the 10—15% range of BQ. Experiments show, however, that isobutylbenzene overlapped with 1, 2, 4-trimethylbenzene on the BQ 12% column. On the BQ 15% column, these components could be separated, but 1, 2, 4-trimethylbenzene overlapped with *s*-butylbenzene. All the other solutes were separated in both cases.

BQ-DPTCP System.—As may be observed in Fig. 4, there are possibilities of the separation in the 20—25% range of BQ. However, the mixture of BQ and DPTCP, when allowed to stand, gave a white crystalline material which seems to be a molecular complex of these compounds. In the case of two liquids which constitute a mixed phase interacting strongly with each other, it was doubtful that the linear relationship described above would be present. However, the observed values on the BQ 21% column agreed well with the presumed values. On this column, *n*-butylbenzene and 1-methyl-4-*n*-propylbenzene are unseparated. On a BQ-enriched column, these were separated, while isobutylbenzene and *s*-butylbenzene became inseparable from each other.

DNP-DNCB System.—As is described above, the separation on this system might be influenced by the charge transfer interaction between DNCB and the aromatic hydrocarbons to be separated. In these cases, the temperature effect on selectivity seems to be more remarkable. Therefore, retention times were measured at three different temperatures; 70, 80 and 90°C.

Figure 5 is the presumed diagram for retention times at 70°C. In this diagram, there are possibilities of the separation of all the solutes on the mixed phase of DNCB concentration near 10%. As a result of the retention time measurement with three mixed phases, DNCB 9%, 10% and 11%, all the aromatics from C_6 to C_{10} (except for 1, 3-dimethyl-2-ethylbenzene) were successfully separated on the DNP 90% - DNCB 10% column. As no standard sample of 1, 3-dimethyl-2-ethylbenzene could be obtained, the retention time of the compound will be presumed afterwards by the use of another relationship. The chromatogram is shown in Fig. 6. The observed

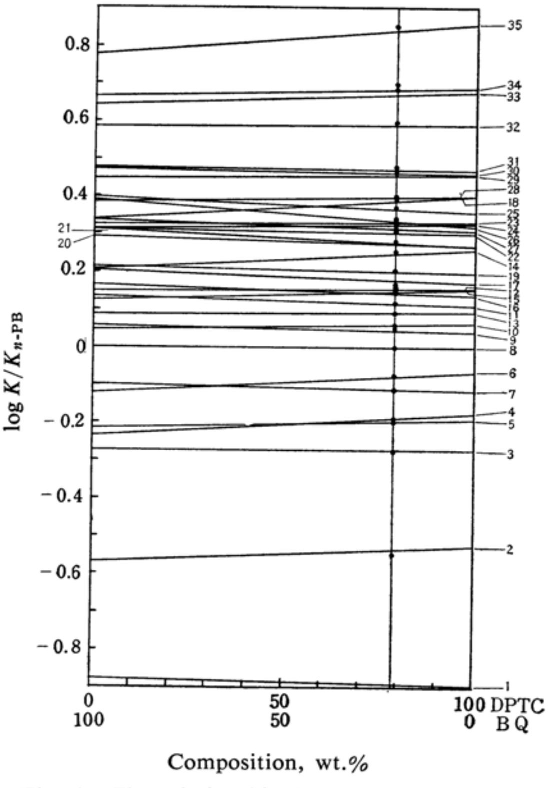


Fig. 4. The relationship between the relative retention time of the solute (log $K/K_{n\text{-PB}}$) and the composition (wt.%) of the mixed stationary liquid DPTCP-BQ at 70°C.

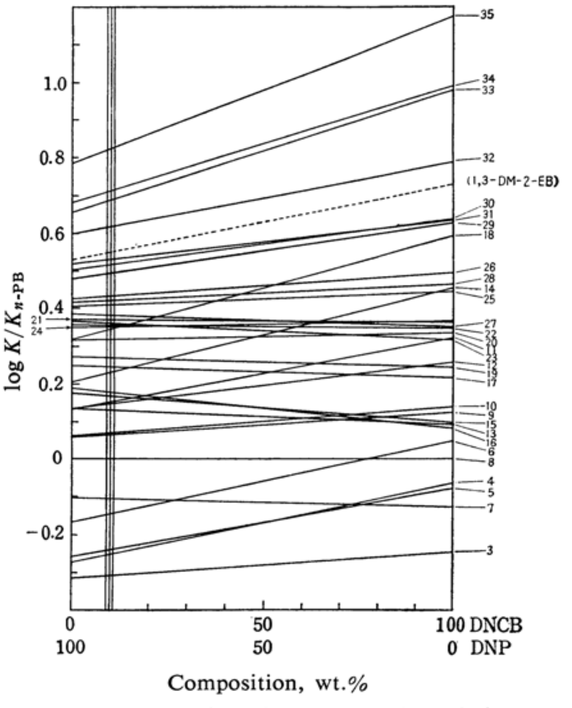
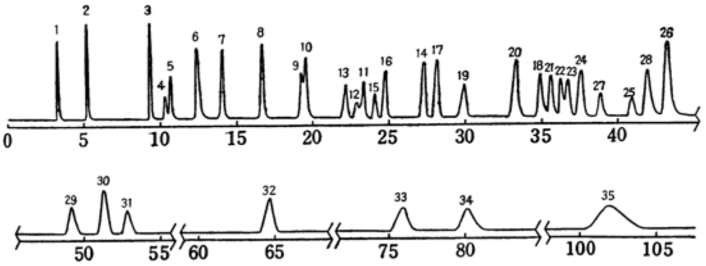


Fig. 5. The relationship between the relative retention time of the solute (log $K/K_{n\text{-PB}}$) and the composition (wt.%) of the mixed stationary liquid DNCB-DNP at 70°C.



Retention time, min.

Fig. 6. The separation of all aromatic hydrocarbons through C_{10} on the DNP 90%-DNCB 10% column.
Column length: 45 m. (I. D. 0.25 mm.), Temp.: 70°C
Carrier gas: He, Inlet pressure 60 p.s.i.g.

TABLE IV. RELATIVE RETENTION TIMES ON DNP 90% - DNCB 10% COLUMN (70°C)

No.	Compound	Presumed	Observed
1	B		0.093
2	T		0.229
3	EB	0.491	0.488
4	*p*-X	0.559	0.553
5	*m*-X	0.576	0.570
6	*o*-X	0.708	0.708
7	*i*-PB	0.784	0.787
8	*n*-PB	1.000	1.000
9	1-M-3-EB	1.159	1.159
10	1-M-4-EB	1.175	1.172
11	1,3,5-TMB	1.413	1.410
12	1-M-2-EB	1.396	1.392
13	*t*-BuB	1.346	1.352
14	1,2,4-TMB	1.698	1.688
15	*i*-BuB	1.472	1.486
16	*s*-BuB	1.500	1.522
17	1-M-3-*i*-PB	1.742	1.776
18	1,2,3-TMB	2.213	2.204
19	1-M-4-*i*-PB	1.854	1.874
20	1-M-2-*i*-PB	2.089	2.096
21	1,3-DEB	2.244	2.252
22	1-M-3-*n*-PB	2.270	2.301
23	*n*-BuB	2.302	2.330
24	1-M-4-*n*-PB	2.339	2.383
25	1,2-DEB	2.582	2.598
26	1,3-DM-5-EB	2.717	2.757
27	1,4-DEB	2.404	2.446
28	1-M-2-*n*-PB	2.649	2.677
29	1,4-DM-2-EB	3.098	3.138
30	1,3-DM-4-EB	3.281	3.314
31	1,2-DM-4-EB	3.389	3.426
32	1,2-DM-3-EB	4.131	4.163
33	1,2,4,5-TeMB	4.853	4.951
34	1,2,3,5-TeMB	5.200	5.235
35	1,2,3,4-TeMB	6.669	6.697

and the presumed values of the relative retention times are shown in Table IV. *t*-Butylbenzene - 1 - methyl - 2 - ethylbenzene - 1, 3, 5-trimethylbenzene and 1-methyl-2-isopropylbenzene - 1, 2, 3-trimethylbenzene, which were unresolved on the DNP column, were separated and eluted in the order of the supposed stabilities of the complexes with DNCB.

Table V shows the gradients of the lines which are calculated from the logarithm of the observed relative retention times of the hydrocarbons on the DNP 100% column and the DNP 90% - DNCB 10% column. These values seem to represent roughly the relative stabilities of the complexes. Hydrocarbons of the same type have close values. Tetramethylbenzenes, the nucleous basicities of which are the highest, have the highest values, while trimethylbenzenes are the next in values. The relatively low values of dimethylethylbenzenes may be due to the steric effects of alkyl groups. It may also stem from the same reason that methylethylbenzenes have higher values than diethylbenzenes, and xylenes have still higher values. Generally, as the alkyl groups of the side chain become longer, the values become higher. In the di-substituted isomers, the values decrease in the order of *o*-(1, 2), *p*-(1, 4) and *m*-(1, 3). These tendencies agree well with that of the interactions of picric acid in chloroform with these aromatic hydrocarbons.[10]

The Presumption of the Retention Time of 1, 3-Dimethyl-2-ethylbenzene.—The elution time of 1, 3-dimethyl-2-ethylbenzene on the DNP 90% - DNCB 10% column has been presumed, for its standard sample alone could not be obtained.

For a homologous series of compounds the ratios of the heat of solution and the heat of vaporization of which are constant, a linear relationship between the logarithm of the retention times obtained on the same column and the logarithm of vapor pressures has been

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[10] H. D. Anderson and O. L. Hammick, *J. Chem. Soc.*, **1950**, 1089.

TABLE VI. RESULTS OF QUANTITATIVE ANALYSES OF AROMATIC HYDROCARBONS IN VARIOUS CRUDE OILS

No.		Kuwait	Seria	Khafji	North Sumatra	Bunju
	45—200°C fraction (vol.%)	23.1	34.5	21.6	59.2	30.7
	Aromatic hydrocarbons (vol.%)	13.9	18.9	9.6	17.4	33.1
1	B	3.6	1.4	0.8	1.2	5.2
2	T	12.3	12.6	7.2	19.2	15.2
3	EB	6.6	2.0	6.6	3.4	5.2
4	*p*-X	3.6	4.1	4.1	5.4	4.8
5	*m*-X	12.0	36.5	10.4	21.3	19.1
6	*o*-X	7.7	6.0	7.0	10.2	8.3
7	*i*-PB	1.1	0.4	0.8	0.8	1.7
8	*n*-PB	1.5	0.7	2.2	0.8	2.4
9	1-M-3-EB	3.9	2.9	3.2	2.4	3.0
10	1-M-4-EB	5.6	2.3	9.5	3.6	3.9
11	1,3,5-TMB	4.0	6.0	3.6	7.0	3.6
12	1-M-2-EB	4.3	1.0	6.1	0.6	1.6
13	*t*-BuB	0.02	0	0	0	0.4
14	1,2,4-TMB	10.2	9.2	11.1	11.5	8.7
15	*i*-BuB	0.3	0.2	0.2	0.4	0.3
16	*s*-BuB	0.5	0.3	0.3	0.4	1.1
17	1-M-3-*i*-PB	0.9	0.6	0.4	0.8	0.9
18	1,2,3-TMB	1.9	1.9	2.1	2.3	2.4
19	1-M-4-*i*-PB	0.6	0.7	0.4	0.3	0.6
20	1-M-2-*i*-PB	1.1	0.2	0.1	0.03	0.6
21	1,3-DEB	0.8	0.3	1.2	0.3	0.4
22	1-M-3-*n*-PB	1.4	1.1	1.5	0.1	1.5
23	*n*-BuB	0.6	0.3	1.2	0.4	0.9
24	1-M-4-*n*-PB	0.8	0.6	1.6	0.6	0.7
25	1,2-DEB	0.5	0	1.1	0.02	0
26	1,3-DM-5-EB	1.5	1.7	2.5	1.7	1.2
27	1,4-DEB	0.5	0.3	1.2	0.2	0.3
28	1-M-2-*n*-PB	1.6	0.2	3.2	0.4	0.5
29	1,4-DM-2-EB	1.8	1.0	1.5	0.8	1.3
30	1,3-DM-4-EB	2.9	1.5	4.4	1.1	1.8
31	1,2-DM-4-EB	1.6	1.2	1.9	1.2	1.1
	1,3-DM-2-EB (presumed)	0	0.2	0.3	0	0.1
32	1,2-DM-3-EB	0.7	0.2	1.2	0	0.1
33	1,2,4,5-TeMB	0.6	0.6	0.2	0.9	0.3
34	1,2,3,5-TeMB	0.8	1.3	0.6	0.6	0.4
35	1,2,3,4-TeMB	0.9	0.2	0.3	0	0.1
	C_{11}	1.2	0.6	0	0	0.3

shown by Hoare and Purnell.[11] This relation is mathematically induced as follows. The gas-liquid partition coefficient (K) is given by:

$$K=\frac{\rho \boldsymbol{RT}}{M\gamma^0P^0} \tag{1}$$

where ρ is the specific gravity of the solvent at the column temperature, T (°C); M is the molecular weight of the solvent; γ^0 is the activity coefficient of the solute at an infinite dilution, and P^0 is the saturation vapor pressure of the solute. If the excess free energy of the mixing of the solute is designated as $\varDelta G_m$, the heat of mixing, as $\varDelta H_m$, and the entropy of mixing, as $\varDelta S_m$, thermodynamics gives the following equations;

$$\varDelta G_m=\varDelta H_m-T\varDelta S_m$$

and $\varDelta G_m=\boldsymbol{RT}\ln\gamma^0$

If $\gamma^0=\gamma_t\gamma_a$, it can be written:

$$\ln\gamma_t=\frac{\varDelta H_m}{\boldsymbol{RT}},\quad \ln\gamma_a=-\frac{\varDelta S_m}{\boldsymbol{R}} \tag{2}$$

where γ_a is the athermal activity coefficient. The heat of the vaporization ($\varDelta H_v$) of the solute is given by the Clapeyron-Clausius equation as follows:

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[11] M. R. Hoare and J. H. Purnell, *Trans. Faraday Soc.*, 52, 222 (1956).

$$\ln P^0 = -\frac{\Delta H_v}{RT} + C_1 \qquad (3)$$

while the heat of solution (ΔH_s) is:

$$\Delta H_s = \Delta H_m - \Delta H_v \qquad (4)$$

From Eq. 1, the logarithm of the relative partition coefficient is given by:

$$\ln K/K_{n\text{-PB}} = \ln \frac{(\gamma_t \gamma_a P^0)_{n\text{-PB}}}{\gamma_t \gamma_a P^0}$$

or $\qquad \ln K/K_{n\text{-PB}} = -\ln \gamma_t - \ln P^0 - \ln \gamma_a + \ln A$

where $\quad A = (\gamma_t \gamma_a P^0)_{n\text{-PB}}$

The insertion of Eqs. 2 and 3 in this equation then gives:

$$\ln K/K_{n\text{-PB}} = -\frac{\Delta H_s}{RT} - \ln \gamma_a - C_1 + \ln A \qquad (5)$$

The rearrangement of Eq. 3 becomes:

$$\Delta H_v = -RT \ln P^0 + C_1 RT \qquad (6)$$

and if a constant a is defined as follows:

$$a = -\frac{\Delta H_s}{\Delta H_v}$$

then Eq. 6 will become:

$$-\Delta H_s = -aRT \ln P^0 + C_1 aRT \qquad (7)$$

If this is substituted into Eq. 5, the result is:

$$\ln K/K_{n\text{-PB}} = -a \ln P^0 + C_1(a-1) - \ln \gamma_a + \ln A \qquad (8)$$

Therefore, it may be recognized from this equation that the plots of $\log K/K_{n\text{-PB}}$ against $\log P^0$ yield a straight line if γ_a, which is related to the magnitude of the solute and the solvent molecules, changes little and if a is constant for a homologous series of solutes.

Figure 7 illustrates the plots of $\log K/K_{n\text{-PB}}$ obtained on the DNP column against $\log P^0$ for C_7 to C_{10} aromatic hydrocarbons. These plots fall on a nearly straight line. It may be considered that the separation of aromatic hydrocarbons on the DNP column does not deviate much from the distillation with an ideal degree of separation because the slope of this straight line is almost unity ($a=0.95$).

For a homologous series of mono-substituted compounds, viz., toluene, ethylbenzene, *n*-propylbenzene and *n*-butylbenzene, a more strict linear relationship is observed. Moreover, since five dimethylethylbenzenes fall on a nearly straight line, it may possibly be thought that 1,3-dimethyl-2-ethylbenzene will also fall on this line; that is to say, the elution time of 1,3-dimethyl-2-ethylbenzene on the DNP column may be given by the intersecting point of this line with the dotted line corresponding to $\log P^0$ of 1,3-dimethyl-2-ethylbenzene, as is shown in Fig. 7.

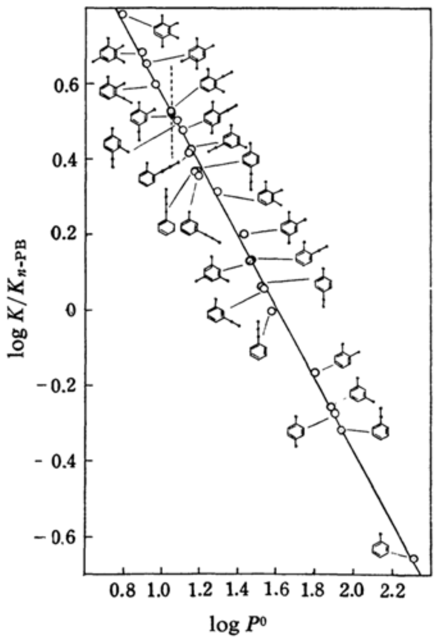

Fig. 7. The relation between the partition coefficient and vapor pressure on the DNP column (70°C).

On the other hand, as is shown clearly in Fig. 8, such plots for the data obtained on the DNCB column do not fall on a straight line. As the number of substituents increases within the compounds of the same carbon number, the plots of the $\log K/K_{n\text{-PB}}$ fall in the upper part of the figure. In C_9 aromatic hydrocarbons, for example, the value becomes higher in the order of propylbenzenes, methylethylbenzene and trimethylbenzenes. For xylenes and methylethylbenzenes, it becomes higher in the order of *m*-(1,3), *p*-(1,4) and *o*-(1,2)-substituted.

As Fig. 8 shows, all of the lines connecting the points of a homologous series of compounds are almost linear, and they are parallel to each other.

The elution time of 1,3-dimethyl-2-ethylbenzene (0.73) was presumed by finding the point corresponding to the vapor pressure (P^0) of 1,3-dimethyl-2-ethylbenzene at the column temperature on the line drawn from the point of 1,2,3-trimethylbenzene parallel with the line connecting the points of 1,2,4-trimethylbenzene and its homologues. By inserting the presumed values of $\log K_{1,3\text{-DM-2-EB}}/K_{n\text{-PB}}$ on the DNP (0.53) and DNCB (0.73) column into Fig. 5, the presumed relative retention time of 1,3-dimethyl-2-ethylbenzene on the DNP 90% - DNCB 10% column was found to be 3.55. This shows that 1,3-dimethyl-2-ethylbenzene will be eluted in the middle

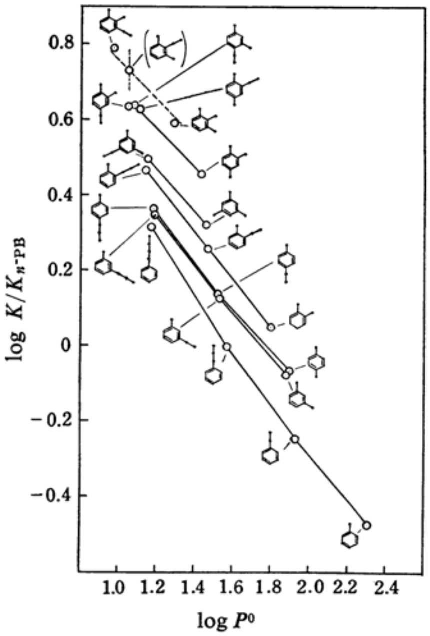

Fig. 8. The relation between the partition coefficient and vapor pressure on the DNCB column (70°C).

of 1,2-dimethyl-4-ethylbenzene and 1,2-dimethyl-3-ethylbenzene and will be overlapped by neither of them.

The Analysis of Aromatic Hydrocarbons in Crude Oil.—Aromatic hydrocarbons through C_{10} in several crude oils were analyzed using a capillary column coated with a DNCB 10%-DNP 90% mixed stationary liquid, thus making possible the effective separation of all these compounds. In the beginning, a 45—250°C fraction of each crude oil was collected by distillation, and then aromatic fractions were separated from the distillate by silica-gel chromatography.

On the chromatograms of these samples, several small peaks which do not correspond to any of the components studied in this paper were observed. It might be thought from their relatively longer elution time that all of these peaks except one correspond to the C_{11} aromatic hydrocarbons. Figure 9 shows a part of the chromatogram obtained with the aromatic fraction of Bunju Crude Oil. In this figure, the position corresponding to the presumed retention time of 1,3-dimethyl-2-ethylbenzene is shown by an arrow. It seems that peak A (relative retention time=3.52)

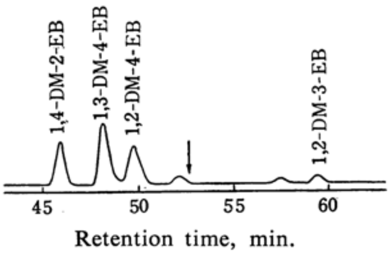

Fig. 9. A part of the chromatogram of the aromatic hydrocarbon fraction in Bunju crude oil.
Stationary liquid: DNP 90%-DNCB 10% mixture.
Column length: 45 m. (I. D. 0.25 mm.)
Temp.: 70°C
Carrier gas: He, Inlet pressure 60 p.s.i.g.

TABLE V. THE GRADIENTS OF LINES CALCULATED FROM THE LOGARITHM OF THE OBSERVED RELATIVE RETENTION TIME ON THE DNP 100% AND DNP 90%-DNCB 10% COLUMNS

Mono-substituted		Di-substituted		Tri-substituted		Tetra-substituted	
EB	0.03	*o*-X	0.16	1,2,3-TMB	0.25	1,2,3,4-TeMB	0.42
		m-X	0.13	1,2,4-TMB	0.24	1,2,3,5-TeMB	0.37
i-PB	−0.01	*p*-X	0.14	1,3,5-TMB	0.18	1,2,4,5-TeMB	0.39
n-PB	0.00						
		1-M-2-EB	0.11	1,2-DM-3-EB	0.21		
n-BuB	−0.01	1-M-3-EB	0.05	1,2-DM-4-EB	0.16		
i-BuB	−0.03	1-M-4-EB	0.08	1,3-DM-2-EB	0.18		
s-BuB	−0.06			1,4-DM-2-EB	0.19		
t-BuB	−0.02	1-M-2-*n*-PB	0.10	1,3-DM-5-EB	0.13		
		1-M-3-*n*-PB	0.04				
		1-M-4-*n*-PB	0.06				
		1-M-2-*i*-PB	0.05				
		1-M-3-*i*-PB	0.01				
		1-M-4-*i*-PB	0.02				
		1,2-DEB	0.08				
		1,3-DEB	0.03				
		1,4-DEB	0.02				

possibly corresponds to 1, 3-dimethyl-2-ethylbenzene and that pear B (4.01) corresponds to any of the C_{11} aromatic hydrocarbon isomers.

The volume fractions of the distillates of several crude oils and the results of the quantitative analyses of aromatic hydrocarbons in these fractions are shown in Table VI. The 1, 3-dimethyl-2-ethylbenzene content is calculated from peak A. In addition to some main components, such as benzene, toluene, xylenes, methylethylbenzenes and trimethylbenzenes, these crude oils contain almost all of the components discussed above, although only small quantities of each.

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