The Effects of Stationary Liquids on the Separation of the Isomers of Aromatic Hydrocarbons in Gas Chromatography[*1]

By Takeo ARAKI[*2]

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The author has continued gas chromatographic studies of stationary liquids with regard to the separation of xylene isomers[1-4]. Such mixed stationary phases as β-naphthylamine/fluorenone (1 : 1) have been proven to be effective for the separation of xylene isomers containing ethylbenzene[3]. When the separating power of this mixed stationary liquid was compared with that of 7, 8-benzoquinoline, which was proposed by Desty et al.[5], there was no appreciable difference between these two stationary phases in the case of the xylene isomers, but when ethylbenzene was present in the isomers, the former one seemed to be rather more suitable[*3, *4].

Of the xylene isomers, the para-isomer can be regarded as the most electronically inactive, its dipole moment is zero. Therefore, *p*-xylene was chosen as the standard isomer in the estimation of the separation factors; the relation of the separation factors to the σ_p values (Jaffé[6]) of the substituents in the aromatic stationary liquids was investigated and discussed in a previous paper[4].

It was found that this relation did not coincide entirely with Hammett's rule, but it had a rather closer relationship. More interesting facts were illustrated by smooth curves, which formed what has been called a "separation diagram"[4].

In connection with the preceding works, there remains the question of whether or not the "separation diagram" of xylenes at 88°C can be applied generally to the gas chromatographic separation of other aromatic hydrocarbon isomers in the same isomeric relation. The present work was undertaken to answer this problem.

Experimental

Apparatus.—The apparatus used was constructed in this laboratory. Some glass chromatographic columns (the dimensions of a unit are 1 m.×6 mm. i. d.) were joined together with copper slender tubes (1 mm. i. d.). A thermal conductivity detector with a tungsten filament was then settled in the apparatus.

Samples. — The ethyltoluene isomers, *o*-, *m*- and *p*-ethyltoluenes and *n*-propylbenzene, were prepared in this laboratory by the preparative methods reported in the literature[7].

Stationary Liquids.—The stationary liquids used were restricted to aromatic compounds. α-Naphthylamine, α-naphthol, benzophenone, 1, 3-diphenylbenzene, DOP (dioctylphthalate), dichloronaphthalene and *m*-dinitrobenzene were used as typical of those stationary liquids which showed substituent effects in the separation diagram of a previous paper. TCP (tricresylphosphate), 7, 8-benzoquinoline fluorenone, fluorene picrate, α-naphthonitrile and 1, 4-dichloro-2-nitrobenzene were used as typical of different stationary liquids which gave results which somewhat deviated from the separation diagram. The inert solid support was coated with these compounds and then packed in glass columns.

Experimental Conditions.—Every effort was made to adjust the many conditions so as to be able to compare the results obtained with ethyltoluenes and xylenes with each other. The experimental conditions for the separation of the ethyltoluene series, together with those of the xylene series, are shown in Table I. The column temperature is setteled at 105°C in this work; it may be assumed

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[*1] This article is the fourth paper in the series, "Studies of Gas Liquid Partition Chromatography". The preceding papers are cited below.

[*2] Present address: Department of Polymer Science, Faculty of Science, Osaka University, Nakanoshima, Osaka.

1) R. Goto, T. Araki and S. Munemiya, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 1315 (1960).

2) T. Araki and R. Goto, This Bulletin, **33**, 115 (1960).

3) T. Araki, R. Goto and A. Ono, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 1318 (1960).

4) T. Araki, R. Goto and A. Ono, ibid., **82**, 1081 (1961).

[*3] Separation factors are determined as follows: $S_{E,p}$= 0.104, $S_{p,m}$=0.077 on the mixed stationary liquid of β-naphthylamine/fluorenone (1 : 1) and 0.072 and 0.075 on 7, 8-benzoquinoline respectively, with a 6 mm.×3 m. column, packed with 17 parts of stationary liquid on 100 parts (w/w) of Celite-545 (60~80 mesh), at 80°C. The separation factors are represented in this paper by the term of S_{12}. in which the suffix 1 denotes the first peak and 2, the second peak. Thus, $S_{E,p}$ is the separation factor between the ethylbenzene and *p*-xylene peaks, and $S_{p,m}$ is that between the *p*- and *m*-xylene peaks.

[*4] The separation of *m*- and *p*-xylene by gas chromatography has been developed recently by several investigators: a) G. M. Rouayheb, O. F. Folmer and W. C. Hamilton, *Anal. Chim. Acta*, **26**, 378 (1962); b) J. van Rysselberge and M. van der Stricht, *Nature*, **193**, 1281 (1962).

5) D. H. Desty, A. Goldup and W. T. Swanton, *Nature*, **183**, 107 (1959).

6) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

7) "Organic Syntheses", Coll. Vol. I, pp. 111, 133, 135, 136; E. Bartow and A. W. Sellards, *J. Am. Chem. Soc.*, **27**, 369 (1905); A. Claus and F. Mann, *Ber.*, **18**, 1121 (1885); H. Gilman and W. E. Catlin, "Organic Syntheses", Coll. Vol. I, p. 471.

Table I. Experimental conditions

	Xylene isomers	Et-toluene isomers
Column	3 m.×6 mm.	3 m.×6 mm.
Solid support	J. M. Sil-O-Cel C-22 Firebrick (30~50 mesh)	J. M. Sil-O-Cel C-22 Firebrick (35~50 mesh)
Ratio of stationary liquids	25 : 100~32 : 100 (w/w)	25 : 100~32 : 100 (w/w)
Column temp.	88°C	105°C
Injection temp.	90°C	110°C
Carrier gas flow	N_2, ca. 50 ml./min.	N_2, ca. 50 ml./min.
Sample size	0.02 ml.	0.02 ml.

Table II. Vapor pressures of isomeric xylenes and ethyltoluenes

Xylene	B. p. °C	Vap. press. mmHg at 88°C	Et-toluene	B. p. °C	Vap. press. mmHg at 105°C
Et-benzene	136.2	168	*n*-Pr-benzene	159.2	149
p-Xylene	138.3	157	*m*-Et-toluene	161.3	139
m-Xylene	139.1	151	*p*-Et-toluene	162.0	135
o-Xylene	144.4	128	*o*-Et-toluene	165.1	124

Table III. Relative Retention volumes (ethylbenzene=1.000) of ethyltoluene isomers at 105°C

Stationary liquid	Toluene	Et-benzene	*n*-Pr-benzene	*m*-Et-toluene	*p*-Et-toluene	*o*-Et-toluene
α-Naphthylamine	0.53_9	1.000	1.71_1	1.91_1	1.85_2	2.40_0
α-Naphthol	0.52_4	1.000	1.72_4	2.01_5	1.95_5	2.50_3
Benzophenone	0.51_5	1.000	1.80_7	1.98_4	1.97_2	2.38_1
1,3-Diphenylbenzene	0.51_5	1.000	1.86_4	2.03_1	2.03_3	2.44_1
DOP	0.51_7	1.000	1.85_9	2.01_0	2.04_9	2.36_4
Dichloronaphthalene	0.51_1	1.000	1.94_1	2.24_8	2.29_4	2.73_9
m-Dinitrobenzene	0.62_4	1.000	1.55_7	2.00_2	2.08_5	2.58_6
TCP	0.53_4	1.000	1.73_6	1.90_0	1.90_9	2.30_4
7,8-Benzoquinoline	0.51_7	1.000	1.83_7	2.08_7	2.06_2	2.58_5
Fluorenone	0.54_1	1.000	1.78_0	2.07_1	2.04_2	2.56_9
Fluorene picrate	0.61_9	1.000	1.60_7	2.00_0	2.05_1	2.64_3
α-Naphthonitrile	0.53_5	1.000	1.79_5	2.06_7	2.08_5	2.55_9
1,4-Dichloro-2-nitrobenzene	0.55_8	1.000	1.76_2	2.09_6	2.19_3	2.64_3

to be a thermal condition parallel to the previous case of the xylene series at 88°C. The vapor pressures of all these isomers are shown in Table II. The other factors are adjusted so as to be identical in both cases.

Results and Discussion

A Comparison of the Separation Power of Stationary Liquids. — By the separation factor S_{12}*, which was defined by Jones et al.[8], the separation powers of stationary liquids were compared with each other, as had been done in preceding papers. *p*-Ethyltoluene was chosen as a standard isomer for the estimation of the separation factors for the same reasons as *p*-xylene was chosen. It might be interesting to compare the experimental results of the ethyltoluene series directly with those of the xylene series. In the expression of the separation factor given by

$$S_{12}=(t_2-t_1)/t_1 \tag{1}$$

of either t_1 or t_2, the retention time of the first or the second peak respectively, is always chosen as the retention time of *p*-ethyltoluene.

The relative retention volumes (ethylbenzene=1.000) of the ethyltoluene series on the above-mentioned stationary liquids are tabulated in Table III, while the separation factors estimated from these data are shown in Table IV, in which the separation factors of the xylene series at 88°C on the same stationary liquids are presented for the sake of comparison.

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* The $(S_{12}+1)$ value is ordinarily used as the separation factor. In this investigation, however, S_{12} is used as the significant figure of results obtained, because the retention values of these isomers are very close.

[8] W. L. Jones and R. Kieselbach, *Anal. Chem.*, **30**, 1590 (1958).

TABLE IV. SEPARATION FACTORS OF ETHYLTOLUENE ISOMERS AT 105°C COMPARED WITH THOSE OF XYLENE ISOMERS AT 88°C

Stationary liquid	Separation factor (S_{12})[a]							
	$S_{E,p'}$	($S_{T,p}$)	$S_{Pr,p'}$	($S_{E,p}$)	$S_{m',p'}$	($S_{p,m}$)	$S_{p',o'}$	($S_{p,o}$)
α-Naphthylamine	0.85	(0.94)	0.082	(0.009)	−0.032[b]	(0.085)	0.296	(0.404)
α-Naphthol	0.96	(1.08)*	0.134	(0.049)*	−0.031[b]	(0.082)*	0.280	(0.41)*
Benzophenone	0.97	(1.10)	0.092	(0.042)	−0.006[b]	(0.056)	0.207	(0.331)
1,3-Diphenylbenzene	1.03	(1.19)	0.090	(0.089)	0.001	(0.033)	0.201	(0.282)
DOP	1.05	(1.17)	0.102	(0.074)	0.019	(0.025)	0.154	(0.253)
Dichloronaphthalene	1.29	(1.46)	0.182	(0.188)	0.021	(0.034)	0.194	(0.293)
m-Dinitrobenzene	1.09	(1.23)**	0.339	(0.364)	0.042	(0.011)	0.240	(0.325)
TCP	0.91	(1.04)	0.100	(0.057)	0.005	(0.035)	0.207	(0.304)
7,8-Benzoquinoline	1.06	(1.22)	0.123	(0.070)	−0.012[b]	(0.070)	0.253	(0.356)
Fluorenone	1.04	(1.22)	0.147	(0.170)	−0.014[b]	(0.056)	0.258	(0.329)
Fluorene picrate	1.06	(1.25)	0.279	(0.334)	0.030	(0.019)	0.288	(0.347)
α-Naphthonitrile	1.09	(1.24)	0.162	(0.147)	0.007	(0.034)	0.227	(0.323)
1,4-Dichloro-2-nitrobenzene	1.19	(1.41)	0.244	(0.290)	0.046	(−0.006)[b]	0.206	(0.281)

a) Suffix T : toluene, E : ethylbenzene, p : *p*-xylene, m : *m*-xylene, Pr : *n*-propylbenzene. p′ : *p*-ethyltoluene, m′ : *m*-ethyltoluene, o′ : *o*-ethyltoluene
For example, $S_{E,p'}$ denotes separation factor between ethylbenzene and *p*-ethyltoluene.

b) Negative sign represents that the order of emergence of two components is inverse to boiling point of these components.

* Values obtained on β-naphthol column (extrapolated from the results of mixed stationary liquid with TCP).

** This value is re-examined; the author reported incorrectly 0.98 in the preceding paper.

Separation Diagrams.—In Fig. 1 of previous paper[4] the separation factors are plotted against the σ_p values (Jaffé) of the substituents in the aromatic stationary liquids. These relationships are interesting, although they are not entirely subject to Hammett's rule. Some discussion of this has already been presented in a previous paper, where the authors pointed out that the diagram of the separation factors against the modified σ_p values of substituents in the stationary liquids was rather effective for practical application to the estimation of the separation of aromatic hydrocarbons in gas chromatography. Figure 2 of this previous paper[4] was obtained when the σ_p values of $-OH$ and $-CO_2R$ radicals were transferred moderately in a negative direction (−0.45 and 0.1 respectively), that of the $-COC_6H_5$ radical, excessively in the same direction (−0.25), and the −X (halogens) radical, in a positive direction (0.35).

Figure 1 illustrates a separation diagram for the ethyltoluene series obtained in a manner analogous to the case of the xylene series; data for the xylene series (88°C) are superposed in broken lines for the sake of comparison. The original points on the horizontal axis indicate the para-isomer.

A parallel relationship between the solid lines and the broken lines is well established in Fig. 1. Only a pair of curves does not show such excellent agreement; they are a solid line for *n*-propylbenzene ($S_{Pr,p'}$) and a broken line for ethylbenzene ($S_{E,p}$). Even in these cases, the inclination of two lines is similar. From the parallel relationship between two series of isomers, it is clear that the results for the xylene series illustrated in Fig. 2 of the previous paper[4] (the separation factors were plotted against the modified σ_p values of the substituents of the aromatic stationary liquids) can be applied to the ethyltoluene series; therefore, the relationship illustrated in Fig. 1 of the previous paper (the separation factors and unmodified σ_p values of the substituents in the aromatic stationary liquids were related to each other by means of Hammett's rule) can also be applied to this series.

It appears certain that the factor which controls the gas chromatographic separation is common in the two isomeric series. For the separation of isomeric aromatic hydrocarbons of *o*-, *m*-, *p*- and *n*-alkylbenzene, these points seem to be important in the selection of the suitable stationary liquids.

A Survey of the Separation Factor, ΔS_{12}.—It can be seen from Fig. 1 that the separation between individual isomers is better in the xylene series than in the ethyltoluene series. The vapor pressures of these isomers at operating column temperature are shown in Table II. The values for the ethyltoluene series (at 105°C) are lower than for the xylene

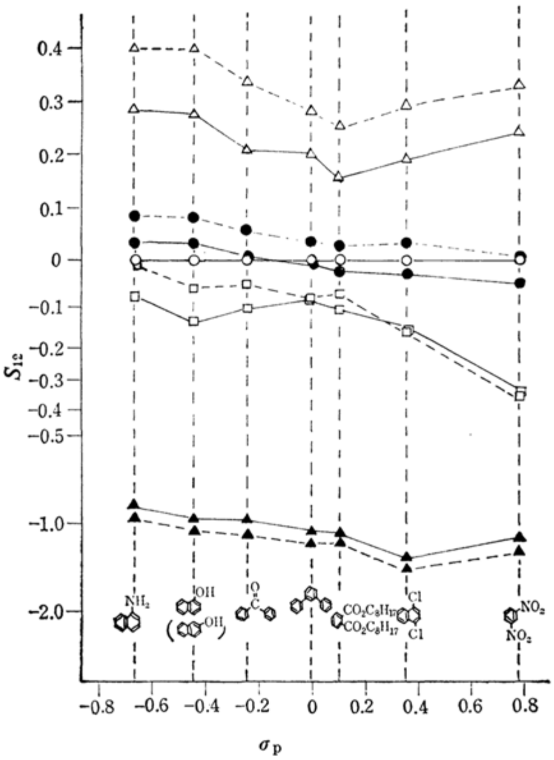

Fig. 1. Comparison of separation diagrams of ethyltoluene series and xylene series.
---- Xylene series (88°C)
—— Ethyltoluene series (105°C)
△ $S_{p,o}$ ● $S_{p,m}$
○ *p*-Xylene and *p*-ethyltoluene
□ $S_{A,p}$ ▲ $S_{A-1,p}$ (cf. Table V)

series (at 88°C). In fact, all ethyltoluenes eluted from the column more rapidly on every stationary liquid used than on corresponding xylenes. This depression of the separation factor (ΔS_{12}) in the ethyltoluene series relative to the xylene series is illustrated in Fig. 1 as roughly uniform on seven liquids, except for the values between $S_{E,p}$ and $S_{Pr,p'}$. ΔS_{12} is defined as follows:

$$\Delta S_{12}=S_{12}(\text{xylenes at } 88^\circ\text{C}) - S_{12}(\text{ethyltoluenes at } 105^\circ\text{C}) \qquad (2)$$

On the other stationary liquids, which show something of a deviation, as has been mentioned above, the ΔS_{12} values likewise fell to roughly constant values (Table V). When an average of thirteen stationary liquids is taken, the values for $\Delta S_{p,o}$, $\Delta S_{p,m}$ and $\Delta S_{A-1,p}$ are 0.094, 0.047 and 0.15 respectively. $\Delta S_{A,p}$ does not, however, show any constant value.

From the other point of view, it is interesting to note that it is possible to predict the separation of these isomeric dialkylbenzenes from the ΔS values, since they do not depend upon sorts of stationary liquids and their polarity character, but rather seem to be dependent only upon the number of carbon atoms in the alkyl groups.

As the S_{12} values of the xylene series are known on many stationary liquids (cf. the literature), if only one set of S_{12} values of given ethyltoluenes is determined on one of these stationary liquids, then the ΔS_{12} value can be readily calculated. It will then be easy to find the suitable stationary liquid by simple

TABLE V. DISCREPANCY OF SEPARATION FACTORS BETWEEN XYLENE ISOMERS AND ETHYLTOLUENE ISOMERS (ΔS_{12})

Stationary liquid	$\Delta S_{A-1,p}$*	$\Delta S_{A,p}$*	$\Delta S_{p,m}$*	$\Delta S_{p,o}$*
α-Naphthylamine	0.086[a]	−0.073	0.053	0.11
α-Naphthol	0.12	−0.085	0.051	0.13
Benzophenone	0.13	−0.050	0.050	0.12
1,3-Diphenylbenzene	0.16	−0.001	0.034[a]	0.081
DOP	0.12	−0.028	0.044	0.099
Dichloronaphthalene	0.17	0.006	0.055	0.099
m-Dinitrobenzene	0.15	0.025	0.053	0.085
TCP	0.13	−0.043	0.040	0.097
7,8-Benzoquinoline	0.16	−0.053	0.058	0.10
Fluorenone	0.18	0.023	0.042	0.071
Fluorene picrate	0.19	0.055	0.049	0.059[a]
α-Naphthonitrile	0.16	−0.015	0.041	0.095
1,4-Dichloro-2-nitrobenzene	0.22	0.046	0.040	0.075
Average value	0.15	—	0.047	0.094

a) The value is seriously deviated from the average.

Suffix p: para-isomers, m: meta-isomers, o: ortho-isomers, A: isomeric *n*-alkylbenzenes,
A−1: *n*-alkylbenzenes of lower members than A by one carbon atom.
For example,

$$\Delta S_{A,p}=S_{E,p}(88^\circ\text{C})-S_{Pr,p'}(105^\circ\text{C}) \qquad \Delta S_{A-1,p}=S_{T,p}(88^\circ\text{C})-S_{E,p'}(105^\circ\text{C})$$

arithmetic addition or subtraction of the S_{12} value of the xylene series and of the ΔS_{12} values. For example, to separate *m*- and *p*-ethyltoluene isomers, one of the best stationary liquids may be tetrahalogenophthalate, which has been tested for the separation of xylene series by Langer et al.[9] On this stationary liquid, $S_{\mathrm{p,m}}$ (xylene) was given as -0.045; therefore, $S_{\mathrm{p',m'}}$ (ethyltoluene) will be -0.092 $(-0.045-0.047)$ or in that neighborhood[*1].

The Interaction which Controls the Separation Factor Affecting the Gas Chromatographic Separation of Xylene and Ethyltoluene Isomers.—This problem has been considered, but unfortunately, experimental proofs are not satisfactory at present.

In a gas chromatographic column, separation is affected by two sorts of factors. One of these is the vapor pressure of solutes (hydrocarbons), and the other is the solute-solvent interaction of the stationary liquid. This solute-solvent interaction may be represented approximately in the following Eq. 3[*2]. Because

$$S_{12}(\text{solute-solvent interaction}) = S_{12}(\text{observed}) - S_{12}(\text{vap. press.}) \qquad (3)$$

the separation factors of the two series are compared with each other at approximately the same vapor pressures (cf. Table II), and because, furthermore, the operating temperature of each series is kept constant, the inclination of the curves in Fig. 1 may be accepted as the measure of the solute-solvent interaction of the stationary liquids. The absolute value of S_{12} (vap. press.) was calculated from the table of vapor pressures as: $S_{\mathrm{p',o'}}$(vap. press. at 105°C) $=0.089$; $S_{\mathrm{m',p'}}$(vap. press. at 105°C)$=0.030$; $S_{\mathrm{Pr,p'}}$(vap. press. at 105°C)$=0.104$, and $S_{\mathrm{E,p'}}$(vap. press. at 105°C)$=1.03$.

In the preceding section, it was shown that the factor which controls the separation is common in both the xylene and the ethyltoluene series. As will be seen in Fig. 1 of a preceding paper[4)], $S_{\mathrm{p,m}}$ and $S_{\mathrm{A,p}}$ curves vary monotonously, while the $S_{\mathrm{p,o}}$ curves has a minimum and the $S_{\mathrm{A-1,p}}$ curve, a maximum. From the inclination of the $S_{\mathrm{p,m}}$ and $S_{\mathrm{A,p}}$ curves, the meta-isomer and its isomeric *n*-alkylbenzene (ethylbenzene in the xylene series and *n*-propylbenzene in the ethyltoluene series) appear to interact more weakly with liquids containing electron-withdrawing groups (π-acids) and more strongly with those containing electron-releasing groups (π-bases) than the para-isomer does. The ortho-isomer seems to be independent of the sign of the σ_{p} values.

The acid strength of the π-acidic stationary liquids will decrease with the σ_{p} values. Of the stationary liquids used in this study, *m*-dinitrobenzene and 1,4-dichloro-2-nitrobenzene are extremely strong π-acids. These compounds are known as complexing agents, as are picric acid, tetracyanoethylene (TCNE)[10)], pyromellitic dianhydride (PMDA)[11)] and so on[12)], all of which make stable π-complexes (π-π) with xylene isomers.

The order of the relative basicities of the xylene isomers determined from the stabilities of the π-complexes formed with PMDA, for example, was *o*-xylene>*p*-xylene>*m*-xylene⟩⟩⟩ ethylbenzene. On gas chromatography, the solute-solvent interaction of *m*-dinitrobenzene was determined at 88°C as follows:

o-Xylene:

$$S_{\mathrm{p,o}}(\text{on } m\text{-dinitrobenzene}) - S_{\mathrm{p,o}}(\text{vap. press. at } 88^\circ\mathrm{C})^{\mathrm{a)}} = 0.33-0.23=0.10$$

m-Xylene:

$$S_{\mathrm{p,m}}(\text{on } m\text{-dinitrobenzene}) - S_{\mathrm{p,m}}(\text{vap. press. at } 88^\circ\mathrm{C}) = 0.011-0.040=-0.029$$

p-Xylene: 0.000

Ethylbenzene:

$$S_{\mathrm{p,E}}{}^{\mathrm{b)}}(\text{on } m\text{-dinitrobenzene}) - S_{\mathrm{p,E}}(\text{vap. press. at } 88^\circ\mathrm{C}) = -0.36-(-0.07)=-0.29$$

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9) S. H. Langer, C. Zahn and G. Pantazoplos, *Chem. & Ind.*, **1958**, 1145.

[*1] Stronger π-acids appear to be more effective for the separation of these isomers, inverse to the corresponding xylene isomers. The order of boiling points of this pair is opposite to that of the latter; therefore, the stationary liquid of the opposite polarity character will be more effective in this case.

[*2] The S_{12} value is represented as follows:

$$S_{12} = V_{\mathrm{R2}}/V_{\mathrm{R1}} - 1 = K_2/K_1 - 1 = \gamma_1^\circ p_1^\circ/\gamma_2^\circ p_2^\circ - 1$$

while S_{12}(vap. press.) and S_{12} (solute-solvent interaction) are:

$$S_{12}(\text{vap. press.}) \text{ or } S_{12}\ (\text{vap.}) = p_1^\circ/p_2^\circ - 1$$

$$S_{12}(\text{solute-solvent interaction}) \text{ or } S_{12}\ (\text{int.}) = \gamma_1^\circ/\gamma_2^\circ - 1$$

Therefore,

$$S_{12} = S_{12}(\text{int.})\cdot S_{12}(\text{vap.}) + S_{12}(\text{vap.}) + S_{12}(\text{int.})$$

In this case, the term $S_{12}(\text{int.})\cdot S_{12}(\text{vap.})$ is negligibly small and the following approximation is obtained:

$$S_{12} \fallingdotseq S_{12}(\text{vap.}) + S_{12}(\text{int.})$$

V_{R}: retention volume corrected by the dead volume of the column; K: partition coefficient; γ°: activity coefficient; p°: vapor pressure of solute at column temperature.

10) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

11) L. L. Ferstanding, W. G. Toland and C. D. Heaton, ibid., **83**, 1151, 5049 (1961).

12) See, for instance, L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954); R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952); S. P. McGlynn, *Chem. Revs.*, **58**, 1113 (1958).

a) S_{12}(vap. press. at 88°C) is determined from the vapor pressure difference of two isomers at 88°C:

$$S_{12}(\text{vap. press.}) = (p_1 - p_2)/p_2$$

p_{i} denotes a vapor pressure of isomer (i).

b) $S_{\mathrm{p,E}} \fallingdotseq -S_{\mathrm{E,p}}$

Thus, xylenes are absorbed in *m*-dinitrobenzene in the order of decreasing strength: *o*-xylene >*p*-xylene>*m*-xylene≫ethylbenzene, as in the order of the relative basicities in PMDA. This fact suggests a π-complex formation, on gas chromatography, between the aromatic hydrocarbon eluent and π-acidic stationary liquids as Langer et al. and Case have described.

On the other hand, the interaction on the π-basic stationary liquids is ambiguous. Case[13] explained this as dependent upon π-π repulsion between two phases. His interpretation seems to be reasonable, but other theories also appear possible.

When α-naphthylamine was used at 88°C as the stationary liquid of gas chromatographic separation, the following results were obtained:

o-Xylene:

$$S_{\mathrm{o,p}}(\text{on } \alpha\text{-naphthylamine}) - S_{\mathrm{p,o}}(\text{vap. press. at } 88^\circ\text{C}) = 0.40 - 0.23 = 0.17$$

m-Xylene:

$$S_{\mathrm{p,m}}(\text{on } \alpha\text{-naphthylamine}) - S_{\mathrm{p,m}}(\text{vap. press. at } 88^\circ\text{C}) = 0.085 - 0.040 = 0.045$$

p-Xylene: 0.000

Ethylbenzene:

$$S_{\mathrm{p,E}}(\text{on } \alpha\text{-naphthylamine}) - S_{\mathrm{p,E}}(\text{vap. press. at } 88^\circ\text{C}) = -0.011 - (-0.071) = 0.060$$

Thus, the α-naphthylamine absorbs xylenes in the order of decreasing strength: *o*-xylene> ethylbenzene>*m*-xylene>*p*-xylene.

By means of their solubility experiment with hydrogen chloride, Brown and Brady[14] determined the relative basicities of xylenes as follows; *m*-xylene: 1.26; *o*-xylene: 1.13; ethylbenzene: 1.06, and *p*-xylene: 1.00. They concluded that π-complexes were also formed between hydrogen chloride and xylenes. It is generally appreciated that the π-complex formed in this hydrogen chloride system is essentially different from that formed in the π-acid-xylene system, because the orders of the relative basicities of xylenes differ. It may be considered that the π-complex of the former case seems to be largely of the *n*-π type.

Between the results of our gas chromatographic separation and those obtained by Brown and Brady, no accurate agreement could be observed. However, these two sets of results seem to be essentially identical (*p*-xylene acts as the most acidic compound), and both of them are much different from those of the π-acid system. If π-π repulsion is an effective factor, *o*-xylene should be repulsed most strongly in the π-base system and $S_{\mathrm{p,o}}$ curve in Fig. 1 should decline monotonously as the σ_{p} value decreases.

For the above reason, we may derive a hypothesis that the separation of aromatic hydrocarbons may be affected by π-complex formation with stationary liquids of a π-base as well as of π-acid. In the ethyltoluene series, however, these complex formations will be much weaker than in the xylene series because of the steric effects of the ethyl groups.

Summary

1) The gas chromatographic separation of the isomer of aromatic hydrocarbons has been investigated on the aromatic stationary liquids.

2) It has been established from the experimental results on the xylene series that the $S_{12}-\sigma_{\mathrm{p}}$ diagram of Fig. 1 of the previous paper[4] is applicable to the separation of the ethyltoluene series.

3) ΔS_{12} has been defined, and it has been proven that this value was roughly constant between two series of dialkylbenzenes. Moreover, this value seems to throw a light on the prediction of the separation of the isomers of aromatic hydrocarbons.

4) This separation seems to be affected by π-complex formation between aromatic hydrocarbons and aromatic stationary liquids of both the π-acidic and π-basic types.

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Department of Chemistry
Faculty of Science
Kyoto University
Sakyo-ku, Kyoto

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