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Separation of Aromatic Carboxylic Acids Using Quaternary Ammonium Salts on Reversed-Phase HPLC. 1. Separation Behavior of Aromatic Carboxylic Acids

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Abstract: In order to develop separation processes and analytical methods for aromatic carboxylic acids for the coal oxidation products, the separation behavior of aromatic carboxylic acids on a reversed-phase HPLC using eluent containing quaternary ammonium salt has been investigated. The retention mechanism of aromatic carboxylic acids was discussed on the basis of both ion-pair partition model and ion–exchange model. The retention behavior of aromatic carboxylic acids possessing one (or two) carboxylic acid group(s) followed the ion-pair partition model, where linear free energy relationship was observed between the capacity factor and the extraction equilibrium constants of benzoic acid and naphthalene carboxylic acid. Besides, the retention behavior followed ion-exchange model with increasing the number of carboxylic acids, where the capacity factor of benzene polycarboxylic acids is proportional to the association constants between aromatic acids and quaternary ammonium ions calculated on the basis of an electrostatic interaction model.

Keywords: High performance liquid chromatography, aromatic carboxylic acid, coal oxidation products, quaternary ammonium salt, ion-pair solvent extraction, ion-exchange

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INTRODUCTION

Oxidation of coal in aqueous solutions at high temperatures is a useful technique for the utilization of different rank of coal resources (1–5). Several kinds of coal chemicals, such as, oxalic acid, acetic acid, and benzenpolycarboxylic acids are possible to obtain from the coal oxidation in acidic and alkaline solutions (6–11). A few decades ago, a pilot operation of coal oxidation in alkaline solution and a continuous removal technique of carbon dioxide for the coal oxidation in alkaline solution at high temperatures were developed (12–14). In addition, the coal oxidation in alkaline solution at high temperatures using nitrate (15) or oxygen (16) were investigated and the optimum conditions were determined to produce oxalic acid in our group. Based on this finding, a method to produce oxamide, which is a valuable slow-releasing nitrogen fertilizer, was established (15, 16).

On the other hand, a large amount of water-soluble aromatic carboxylic acids have been obtained in the coal oxidation products, where the total yields of aromatic carboxylic acids sometimes reach to 50 wt% of the oxidation products (16). However, useful applications of the production of aromatic carboxylic acids from coal have not been adequately established. The possibility whether or not practical industrial applications are carried out is dependent on several factors, such as, the relative costs to use petroleum or coal, and the demand of aromatic polycarboxylic acids (17–19). Additionally, the efficient and practical separation methods of these aromatic carboxylic acids have not been developed since the coal oxidation products involve a fairly complicated mixture of carboxylic acid isomers. Moreover, this causes difficulty in the analysis of aromatic carboxylic acids of coal oxidation products and there are few systematic investigations for aromatic carboxylic acids (20–24). Thus, a simple and practical technique of the separation and recovery of aromatic carboxylic acids is essential to establish useful industrial applications of these aromatic carboxylic acids. Although solvent extraction and liquid chromatography would be powerful techniques for the separation of the aromatic carboxylic acids, few practical investigations were carried out.

In this study, the separation behavior of aromatic carboxylic acids in the presence of quaternary ammonium has been investigated using the reversed-phase HPLC. This is regarded as a continuous separation technique concerning ion-pair solvent extraction (25–27) of aromatic carboxylic acids (28). The separation was performed on an ion-pair and/or ion-exchange mode in the presence of quaternary ammonium salt on a reversed-phase column. The separation behavior was investigated on the basis of the relationship between the structure of aromatic carboxylic acids and their capacity factor on HPLC concerning the hydrophobic and electrostatic interactions between analytes and ion-paring reagents.

EXPERIMENTAL

Materials and Apparatus

All reagents used were of extra pure grade. Separation behavior of aromatic carboxylic acids was analyzed using a HPLC system consisting of UVIDEC-100V, TRIROTAR-S, and M6000 pump (JASCO, Japan) on a reversed-phase column (Merck LichroCART 125-4 RP-18) at 0.5 mL min^{-1} at 30°C. Samples were detected at 254 nm. Abbreviations are following; tetrabuthylammonium bromide: TBABr, trimethyl-n-octylammonium bromide: TMOABr, trimethyl-n-hexylammonium bromide: TMHABr, benzoic acid: 1BE, 1,2-benzenedicarboxylic acid: 12BE, 1,3-benzenedicarboxylic acid: 13BE, 1,4-benzenedicarboxylic acid: 14BE, 1,3,5-benzenetricarboxylic acid: 135BE, 1,2,4-benzenetricarboxylic acid: 124BE, 1,2,3-benzenetricarboxylic acid: 123BE, 1,2,4,5-benzenetetracarboxylic acid: 1245BE, 1,2,3,4,5-benzenepentacarboxylic acid: 12345BE, 1,2,3,4,5,6-benzenehexacarboxylic acid: 123456BE, 1-naphthoic acid: 1NA, 2-naphthoic acid: 2NA, 2,3-naphthoic acid: 23NA, 2,6-naphthoic acid: 26NA, 9-anthracene-carboxylic acid: 9AN.

RESULTS AND DISCUSSION

Linear Free Energy Relationship among the Capacity Factor of Aromatic Carboxylic Acids

Separation behavior of aromatic carboxylic acids on the reversed-phase HPLC was investigated on the basis of both ion-pair and ion-exchange mechanisms, since these are taken into account for the separation of ionic analytes. The retention times of a series of aromatic carboxylic acids were determined in the presence of TBABr, TMOABr, or TMHABr (Table 1). The retention times were less affected by pH at pH 6–8. This is due to the fact that carboxylic groups of these acids are deprotonated at the pH range, where most of the pKa values of aromatic carboxylic acids are smaller than 6–8 (Table 1) (29). For the following investigations, the pH of the eluent was adjusted at 7.6 using sodium acetate.

To evaluate the retention behavior, capacity factors of aromatic acids were determined from the retention times by using Eq. (1).

$$k' = (t_i - t_0)/t_0 \tag{1}$$

where t_i is the retention tine of an anion and t_0 is that of non-retarded component (water).

The methanol content of eluent containing TBABr, TMOABr or TMHABr affected the capacity factor differently. The capacity factor of 123456BE in the

Table 1. Retention times and capacity factor (k′) of aromatic polycarboxylic acids on reversed-phase HPLC

	QX						
	TBABr		TMOABr methanol (%)		TMHABr		
Aromatic acids	35	30	35	30	30	30^a	pKa of aromatic acids
1 (1BE)	6.02 (1.81)	8.41 (3.08)	7.25 (2.36)	11.73 (3.96)	3.62 (0.66)	5.50 (1.55)	4.01
2 (12BE)	5.16 (1.41)	8.01 (2.89)	6.86 (2.18)	12.73 (4.38)	3.09 (0.42)	4.23 (0.96)	2.76, 4.92
3 (13BE)	4.47 (1.09)	7.30 (2.54)	6.57 (2.04)	11.05 (3.67)	2.72 (0.25)	3.67 (0.70)	3.70, 4.60
4 (14BE)	4.23 (0.98)	6.41 (2.11)	5.77 (1.67)	8.82 (2.73)	2.45 (0.12)	3.05 (0.41)	3.50, 4.34
5 (123BE)	6.71 (2.14)	11.11 (4.39)	11.19 (4.18)	25.35 (9.71)	2.65 (0.20)	3.75 (0.74)	2.64, 3.82, 5.51
6 (124BE)	5.61 (1.62)	11.51 (4.59)	10.33 (3.78)	24.25 (9.25)	2.50 (0.15)	3.58 (0.66)	2.42, 3.71, 5.01
7 (135BE)	5.15 (1.41)	9.92 (3.82)	9.47 (3.38)	22.55 (8.53)	2.51 (0.15)	3.82 (0.77)	
8 (1245BE)	7.61 (2.56)	22.07 (9.71)	21.57 (8.99)		2.62 (0.20)	4.37 (1.02)	1.87, 2.72, 4.30, 5.52
9 (12345BE)	8.33 (2.89)	27.38 (12.29)	34.40 (14.93)		2.52 (0.16)	4.88 (1.26)	
10 (123456BE)	7.61 (2.56)	35.36 (16.17)	51.00 (22.61)	127.30 (52.80)	2.29 (0.05)	5.18 (1.40)	0.8, 2.26, 3.54, 5.15, 6.52, 7.71
11 (1NA)	13.51 (5.31)	26.18 (11.41)	16.77 (6.76)	35.83 (14.14)	9.39 (3.31)	13.23 (5.13)	3.597
12 (2NA)	19.53 (8.13)	42.04 (18.92)	25.21 (10.67)	66.67 (24.60)	14.48 (5.64)	21.08 (8.76)	4.141
13 (23NA)	11.00 (4.14)	25.42 (11.05)	19.21 (7.89)	51.67 (20.80)	5.77 (1.65)	8.96 (3.15)	
14 (26NA)	4.49 (1.10)	8.98 (3.26)	6.54 (2.03)	12.17 (4.14)	2.87 (0.32)	3.73 (0.73)	
15 (9AN)	40.50 (17.93)	100.53 (46.64)	51.00 (22.61)	132.67 (55.1)	30.31 (12.90)	45.20 (19.93)	

Upper: retention time, lower: capacity factor in parentheses. QX (Quaternary ammonium salt): $3.5 \times 10^{-3}\,\mathrm{mol\,kg^{-1}}$.

[a] Quaternary ammonium salt: $8 \times 10^{-3}\,\mathrm{mol\,kg^{-1}}$.

Abbreviations, 1BE: benzoic acid, 12BE: 1,2-benzenedicarboxylic acid, 13BE: 1,3-benzenedicarboxylic acid, 14BE: 1,4-benzenedicarboxylic acid, 135BE: 1,3,5-benzenetricarboxylic acid, 124BE: 1,2,4-benzenetricarboxylic acid, 123BE: 1,2,3-benzenetricarboxylic acid, 1245BE: 1,2,4,5-benzenetetracarboxylic acid, 12345BE: 1,2,3,4,5-benzenepentacarboxylic acid, 123456BE: 1,2,3,4,5,6-benzenehexacarboxylic acid, 1NA: 1-naphthoic acid, 2NA: 2-naphthoic acid, 23NA: 2,3-naphthoic acid, 26NA: 2,6-naphthoic acid, 9AN: 9-anthracene-carboxylic acid.

presence of TMOABr was strongly affected by the methanol content. The type of ammonium salts also affected the capacity factor. According to comparisons of the logarithmic values of k′, the linear free energy relationship (LFER) was searched among these aromatic acids (29). First, LFER was observed for 1BE, 1NA, 2NA, and 9AN (Fig. 1a–1d). In addition, LFER was also found among the logarithmic values of k′ for these aromatic acids in the presence of different quaternary ammonium salts. This reflects the hydrophobicity of these monocarboxylic acids. The logarithmic values of k′ for 1BE, 1NA and 9AN were exactly proportional to the number of carbons within the aromatic rings, that is, 6 (1BE), 10 (1NA), and 14 (9AN), using different quaternary ammonium salts (Figure is not shown). This fact indicates that the hydrophobicity of the analytes is proportional to the logarithmic values of k′ in this case, since it is true that the hydrophobicity of analytes is approximately proportional to the size of the analytes. Besides, the logarithmic values of k′ decrease in the order TMOABr > TBABr > TMHABr (Fig. 1a) for the several aromatic carboxylic acids. The total number of carbon chains of these ion-paring reagents, which is a good indicator of the hydrophobicity

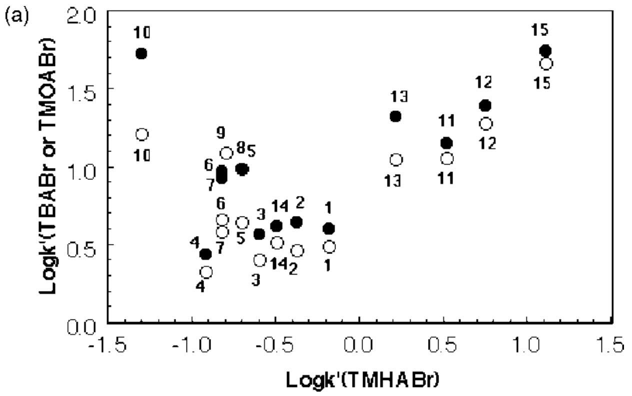


Figure 1. (a) Log k′ using TBABr or TMOABr vs. log k′ using TMHABr. Influence of the types of quaternary ammonium salts. Methanol: 30%, quaternary ammonium salt: 3.5×10^{-3} M, numbers indicate the aromatic carboxylic acids, open circles: TBABr, closed circles: TMOABr; (b) Log k′ using TMOABr vs. log k′ using TBABr. Influence of the types of quaternary ammonium salts. Methanol content: open circles: 30%, closed circles: 35%, Quaternary ammonium salt: 3.5×10^{-3} M, numbers indicate the aromatic carboxylic acids; (c) Log k′ using TBABr or TMOABr with 35% methanol vs. log k′ using TBABr or TMOABr with 30% methanol. Influence of methanol content. Quaternary ammonium salts: open circles: TBABr, closed circles: TMOABr, Quaternary ammonium salt: 3.5×10^{-3} M, numbers indicate the aromatic carboxylic acids; (d) Log k′ with 3.5 mM TMHABr vs. log k with 8 mM TMHABr. Influence of the concentration of quaternary ammonium salt. Methanol: 30%, numbers indicate the aromatic carboxylic acids.

(*continued*)

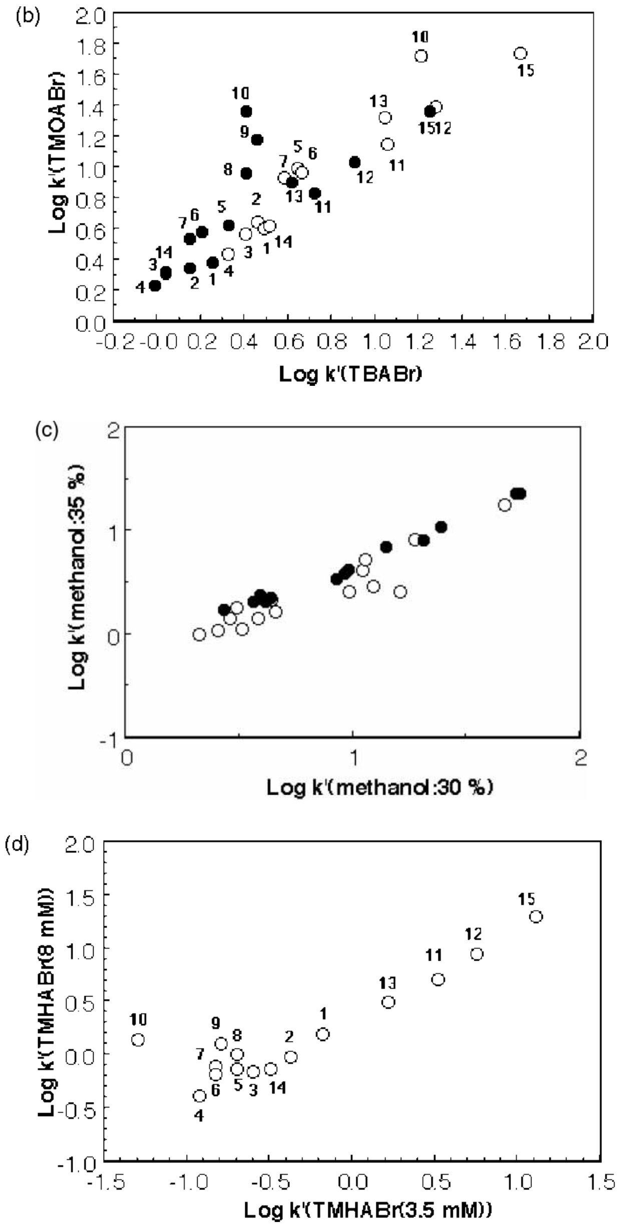


Figure 1. Continued.

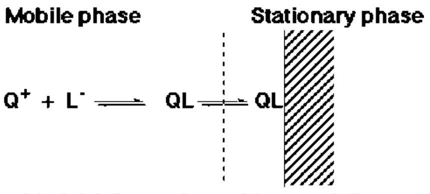
of the ion-paring reagents, is 11 for TMOABr, 16 for TBABr, and 9 for TMHABr. Thus, the order of hydrophobicity is different from that of the values of k′ and this is due to that TBA$^+$ ion is spherical compared with others.

On the other hand, the retention time of aromatic carboxylic acids deviates from LFER with increasing the number of carboxylic groups, especially for the cases of benzene polycarboxylic acids. This fact may indicate that the partition of benzene polycarboxylic acids to the stationary phase and that of aromatic monocarboxylic acids involve different mechanisms. In other words, the separation behavior of HPLC using quaternary ammonium salts seems to be classified into the separation behaviors whether showing or not showing LFER. Conclusively, the first group involves aromatic carboxylic acids possessing one or two carboxylic groups and showed LFER among HPLC conditions using different methanol contents and/or different quaternary ammonium salts. The second group involves aromatic carboxylic acids possessing a larger number of carboxylic groups and did not show LFER.

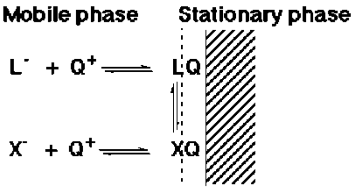
Separation Models for Aromatic Carboxylic Acids using Quaternary Ammonium Salts

The retention behavior of the aromatic carboxylic acids would reflect the difference of the retention mechanisms with increasing the number of carboxylic groups (31–34). Here, the retention mechanisms of the aromatic carboxylic acids are discussed on the basis of two different mechanisms, that is, ion-pair partition model and ion-exchange model. It is postulated that the separation of the former group is based on a model that the partition of ion-pair occurs between the mobile phase and the stationary phase (model 1 in Fig. 2). Aromatic carboxylic acids having one or two carboxylic groups follow the partition model. Besides, it is assumed that aromatic polycarboxylic acids possessing a greater number of carboxylic acid group follow the ion-exchange mechanism, where aromatic anions interact with positive charges of quaternary ammonium ions. This is regarding the anion-exchange sites which are dynamically coated on the stationary phase (model 2).

For the case of the ion-pair partition model (model 1), the values of k' should be proportional to that of partition coefficient of ion-pair to the stationary phase. This is true in many cases wherein LFER has been observed between the ion-pair partition HPLC and the ion-pair solvent extraction. Thus, the relationship between the logarithmic values of k' vs. those of the extraction coefficient (K_{ex}) for some aromatic acids was examined (Fig. 3). Simple LFER for the cases of benzene and naphthalene mono- and/or dicaboxylic acids was observed between the logarithmic values of k' and K_{ex} except for the cases of 2,3- and 2,6-naphthalendicarboxylic acids using tetra-n-hexylammonium bromide. The trend that the values of k' of these aromatic monocarboxylic acids using TMOABr or TBABr is greater than those using TMHABr supports the partition model since the hydrophobicity of the ion-pairs increases with the carbon chain length.



Model 1 (ion-pair partition model)



Model 2 (ion-exchange model)

Figure 2. Schematic models of the separation of aromatic carboxylic acids; Model 1: ion-pair partition model, model 2: ion-exchange model.

The values of pKa are also important to consider the retention behavior of the aromatic acids, while the running pH is higher than most of the pKa values of the aromatic acids (Table 1). There seems to be no systematic relationship between the pKa values and the logarithmic values of k′. However, the logarithmic values of k′ are proportional to the pKa2 (second protonation constant) values of 12BE, 13BE, and 14BE. The same trend was observed for the case of

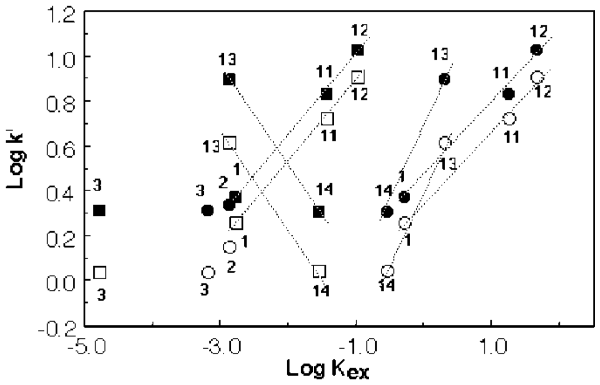


Figure 3. Log k′ vs. log K_{ex} for the aromatic carboxylic acids. Open circles: k′ (TBABr, 35°C) vs. K_{ex} (zephyramine), closed circles: k′ (TMOABr, 35°C) vs. K_{ex} (zephyramine), open squares: k′ (TBABr, 35°C) vs. K_{ex} (tetra-n-hexylammonium iodide), closed squares: k′ (TMOABr, 35°C) vs. K_{ex} (tetra-n-hexylammonium iodide). The values of K_{ex} are in reference 28.

pKa values of 1NA and 2NA. The values of pKa indicate the strength of the associate formation between aromatic carboxylate anions with protons while the logarithmic values of k′ indicate the strength of the associate formation between aromatic carboxylate anions with quaternary ammonium cations. Thus, the observation of the correlation between the pKa values and logarithmic values of k′ would reflect this trend in these particular cases.

On the other hand, LFER was not clearly observed for the cases of benzene polycarboxylic acids using different methanol content and different quaternary ammonium salts. However, there is a trend that the value of k′ of benzenepolycarboxlyic acid using TMOABr decreases in the order hexa- > penta- > tetracarboxylic, while the trend is weak for the cases using TBABr and TMHABr. Thus, the retention behavior of ion-exchange HPLC model is discussed on the basis of the strength of electrostatic interaction between cation and anion. $TMOA^+$ has one octyl group and three methyl groups so that $TMOA^+$ would adsorb strongly on the stationary phase. TBA^+ is of spherical shape and $TMHA^+$ is smaller than $TMOA^+$ so that these do not strongly act as the dynamically coating reagent for cation-exchange stationary phase. If the retention mechanism of aromatic polycarboxylic acids possessing a large number of carboxylic groups follows ion-exchange model, the retention behavior would depend on the strength of the electrostatic interaction between analytes and counter ions. To examine the ion-exchange model, the strength of electrostatic interaction was estimated on the basis of a conventional theory by Fuoss (35). The association constants in aqueous solution (K_{ass}) of anion and cation were estimated (Table 2). The relationship between the logarithmic values of k′ and those of K_{ass} was examined as shown in Fig. 4. The relationship showed that the logarithmic values of k′ are clearly proportional to those of K_{ass} for the cases of benzene polycarboxylic acids using $TMOA^+$, where the logarithmic values of k′ increase with increasing of the logarithmic values K_{ass}, while this was unclear for the case using TMHABr. This fact supports the retention mechanism of benzene polycarboxylic acids using TMOABr, which is mainly based on the ion-exchange model. The trend based on the ion-exchange model is weakly observed for benzene polycarboxylic acids using TMHABr or TBABr.

It should be noted that the values of k′ for 2,6-napththalendicarboxylic acid are much smaller than those for 2,3-napththalendicarboxylic acid using

Table 2. Associate constants calculated by Fuoss equation

Log (K_{ass}/M) number of charges of aromatic polycarboxylic acids (L^{n-})						
Q^+	1	2	3	4	5	6
$TMOA^+$	0.068	1.540	3.012	4.484	5.956	7.428
TBA^+	0.135	0.908	1.681	2.454	3.227	4.001

Dielectric constant: 60.3, ionic strength: 7×10^{-3}, $T = 303.16\,K$, the distance between the center of charges of Q^+ and L^-: $TMOA^+$: 2.5×10^{-8} cm, TBA^+: 4.5×10^{-8} cm.

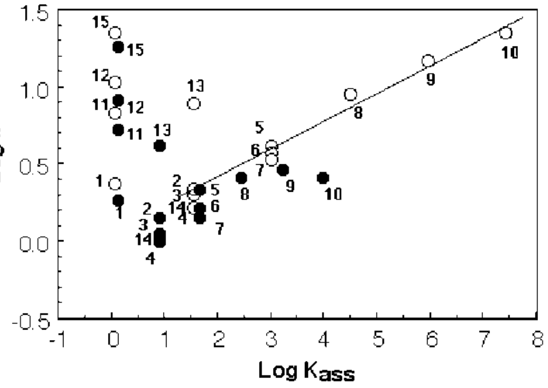


Figure 4. Log k′ vs. log K_{ass} for the aromatic carboxylic acids; Open circles: k′ (TMOABr, 35°C) vs. K_{ass} (for $TMOA^+$), closed circles: k′ (TBABr, 35°C) vs. K_{ass} (for TBA^+). The values of K_{ass} are shown in Table 2.

different methanol contents and different ammonium salts. However, the relationship of the magnitude of K_{ass} for 2,6-napththalendicarboxylic acid is greater than the magnitude of K_{ass} for 2,3-napththalendicarboxylic acid. This may be due to the shape of these naphthalenecarboxylic acids. Only one carboxylic acid group of 2,6-napththalendicarboxylic acid may interact with the cationic stationary phase and another carboxylic group may face to mobile phase. This would cause the weak retention of 2,6-napththalendicarboxylic acid.

CONCLUSIONS

The separation behavior of the aromatic carboxylic acids were discussed from both the ion-pair partition model and the ion-exchange model since the separation behavior was classified into two different groups. Aromatic acids possessing single carboxylic group followed mainly ion-pair partition model and aromatic acids having multiple carboxylic groups followed mainly ion-exchange mechanism. The analysis of the separation behavior will be important to design the separation processes of aromatic polycarboxylic acids produced by the coal oxidation.

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