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Extraction of Benzene and Naphthalene Carboxylic Acids Using Quaternary Ammonium Salts As a Model Study for the Separation of Coal Oxidation Products

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Abstract: The ion-pair solvent extraction of benzene- and naphthalene-carboxylic acids has been investigated as a model study for the separation of coal oxidation products, which are formed by treatment with alkaline solutions at high temperatures. It was possible that benzene- and naphthalene-dicarboxylic acids are extracted into several types of organic solvents with quaternary ammonium ions. The extraction equilibrium constants (K_{ex}) for benzoic acid, 1,2-benzenedicarboxylic acid, 1,3-benzenedicarboxylic acid, 1-naphthoic acid, 2-naphthoic acid, 2,3-naphthalenedicarboxylic acid, and 2,6-naphthalenedicarboxylic acid into chloroform were determined at 20°C. The difference of K_{ex} among the aromatic acids was sufficiently large for designing a separation method for these aromatic acids. It was unexpected that the extraction of dicarboxylic acids was slower than that of monocarboxylic acids, although the ion-pair formation of aromatic carboxylate ion with quaternary ammonium ion is normally considered as a diffusion control reaction in aqueous phase. Thus, this fact suggests that the phase transfer of the ion-pair from aqueous to organic phase is the rate-determining step. Liner-free-energy relationship was observed for the monocarboxylic acids using different quaternary ammonium salts while that was ambiguous for the dicarboxylic acids. This is due to the steric influence of the counter ions for the magnitude of K_{ex}.

Keywords: Ion-pair solvent extraction, aromatic carboxylic acid, coal oxidation products, hydrothermal reaction products, quaternary ammonium salt

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INTRODUCTION

The oxidation of coal in alkaline solutions at elevated temperatures is an important process to produce coal chemicals, which are difficult to obtain from petroleum (1–5). Valuable compounds, such as oxalic acid and benzene polycarboxylic acids, are obtained from coal oxidation (3–11). In the middle of the 20th century, pilot operations of coal oxidation to produce aromatic carboxylic acid had already succeeded in sodium hydroxide solutions at high temperatures (12–14). In addition, we have demonstrated the production technique of oxalic acid using coal oxidation in sodium hydroxide solutions at high temperatures (15, 16). This was applied for producing oxamide, which is a slow-releasing nitrogen fertilizer. Besides, the oxidation behavior was investigated to produce aromatic carboxylic acids under several conditions since coal indeed involves aromatic moieties (12, 14). For instance, some aromatic dicarboxylic acids are suitable as resources for producing polyester plastics. However, industrial applications of aromatic acids formed by coal oxidation have not yet been extensively adapted. Thus, the development of separation techniques for aromatic carboxylic acids from the oxidized products of coal is important to enable practical applications of aromatic structures of coal. In the present study, the extraction behavior of benzene and naphthalene carboxylic acids was investigated on the basis of ion-pair solvent extraction using quaternary ammonium salts, since the ion-pair extraction is primarily an appropriate separation technique for ionic compounds (17–19).

EXPERIMENTAL

Chemicals

All reagents used were of analytical grade from Wako Pure Chemical Industries Ltd., Japan. Abbreviations of the aromatic carboxylic acids (Fig. 1) and quaternary ammonium salts are as follows: BE: benzoic acid, 12B: 1,2-benzenedicarboxylic acid, 13B: 1,3-benzenedicarboxylic acid, 1NA: 1-naphthoic acid, 2NA: 2-naphthoic acid, 23N: 2,3-naphthalenedicarboxylic acid, 26 N: 2,6-naphthalenedicarboxylic acid, ALQ: tri-n-octylmethylammonium chloride, ZCl: tetradecyldimethylbenzlylammonium chloride, DMABr: dilauryldimethylammonium bromide, THAI: tetrahexylammonium iodide, DTACl: dodecyltrimethylammonium chloride, HTABr: n-hexyltrimethylammonium bromide.

Extraction Procedure and Equipment

Extraction behavior was investigated using the following procedure: Solutions containing 10^{-4}–10^{-2} M benzene- or naphthalene-carboxylic

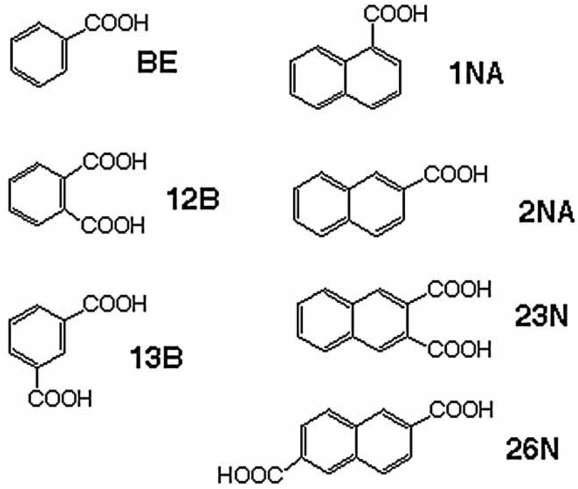

Figure 1. Structures of aromatic acids used in the study.

acid were prepared in 0.1 M sodium hydroxide solution. In a test tube, a 20 ml of carboxylic acid solution was placed, and to it was added a 20 ml of organic phase involving 10^{-2} M quaternary ammonium salt (QX). The pH of the aqueous phase was adjusted between 12–13 using 0.1 M NaOH solution. This is regarded as a typical solution obtained from coal oxidation in alkaline solutions at high temperatures. The sample solution was shaken for 20 min at 20°C. After the centrifugation of the two-phase system, the residual concentration of aromatic acids in the aqueous phase was determined on the basis of UV absorbance at 250–350 nm. A Shimadzu UV-365 double-beam spectrophotometer with 1 cm quartz cells was used. The pH of the sample solutions was measured using a Hitach-Horiba F-7ss II pH meter.

The perspective views of the association between carboxylic acid and quaternary ammonium salt were generated using a CAChe program on the basis of classical mechanics.

RESULTS AND DISCUSSION

Selection of Quaternary Ammonium Salts and Solvents

The extraction behavior of 1-NA was examined qualitatively using several types of QX and organic solvents. The results are summarized in Table 1. A trend was found that the extraction degree increased with increasing the number of the carbon atoms of QX (ALQ (25) $>$ THAI (24) $>$ DTACl

Table 1. Extraction ability of organic solvents with quaternary ammonium salts

Solvent QX	Carbon number	$CHCl_3$	n-Hexane	Benzene	n-Cyclohexane	n-Octanol
ALQ	25	S	S	S	S	S
THAI	24	S	W	M	W	W
DTACl	15	W	W	W	W	W
HTABr	9	W	W	W	W	W

Extraction ability of 1-naphthoic acid: S (strong) > M (moderate) > W (weak) $[QX]_T = 10^{-2}$ M, [1-naphthoic acid]$_T = 10^{-3}$ M, shaking time: 20 min, ALQ: tri-n-octylmethylammonium chloride, THAI: tetrahexylammonium iodide, DTACl: dodecyltrimethylammonium chloride, HTABr: n-hexyltrimethylammonium bromide.

(15) > HTABr (9)). According to this inspection, four kinds of QX and chloroform were selected for further investigations.

Effects of Shaking Time

When ALQ, ZCl, and DMABr were used as ion-pairing reagents, naphthalene-monocarboxylic acids (1NA and 2NA) were extracted within one minute (Fig. 2). Besides, it was surprising that the extraction of 13B, 23NA and 26NA with THAI required 20 min even though these were quantitatively extracted. This finding was unexpected since the ion-pair formation should follow a diffusion control reaction (20). Thus, the partition process of the ion-pair of aromatic carboxylate with quaternary ammonium ion through the interface between the aqueous and organic phases should be the rate-determining step. To the contrary, the extraction of monocarboxylic acids was indeed rapid. This fact supports that the slow extraction of dicarboxylic acids using QX is due to the slow rate of the phase transfer of the dicarboxylate-Q^+ ion-pair from aqueous to organic phase. In addition, this finding would be important since the kinetic selectivity may be applied for the separation of these carboxylic acids.

Extraction Equilibrium

Extents of extraction of the aromatic acids were determined as a function of the concentration of QX (Figs. 3a–3d). The quantitative extraction of 1NA and 2NA was possible with ALQ, ZCl, or DMABr. The extents of the extraction of other types of the aromatic acids were not really high. The selectivity of 1NA and 2NA to other aromatic carboxylic acids is sufficient to design the separation method of coal oxidation products. Based on the plots shown in Fig. 3, stoichiometry of the extraction reaction and its

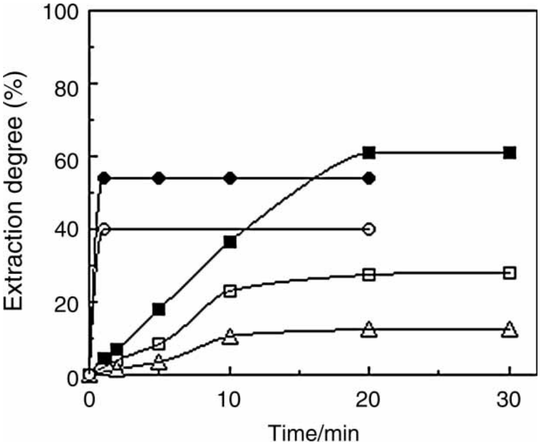

Figure 2. Reaction curves for the extraction of aromatic acids. [aromatic acid]$_T = 10^{-3}$ M, [THAI]$_T = 10^{-2}$ M, organic phase: chloroform, (volume of water phase)/(volume of organic phase) = 1, 20°C, aromatic acids: open circles: 1-naphtholic acid (1NA), closed circles: 2-naphtholic acid (2NA), open squares: 2.3-naphthalenedicarboxylic acid (23 N), closed squares: 2,6-naphthalene dicarboxylic acid (26 N), open triangles: 1,3-benzenedicarboxylic acid (13B).

equilibrium constant were examined. Eqs. (1) and (2) give the extraction reaction and the extraction equilibrium constant.

$$L^{n-} + nQX_{(o)} \overset{K_{ex}}{\rightleftharpoons} nX^- + Q_nL_{(o)} \tag{1}$$

$$K_{ex} = \frac{[X^-]^n[Q_nL_{(o)}]}{[L^{n-}][QX_{(o)}]^n} \tag{2}$$

where L^{n-} indicates aromatic carboxylate ion. The plots in Fig. 3a–d support that the extraction of a monocarboxylic acid requires one Q^+ molecule and that of a dicarboxylic acid requires two Q^+ molecules. The values of K_{ex} were determined on the basis of the following calculations. The mass valance of this system is given by Eqs. (3)–(5),

$$[Q^+]_T = [QX_{(o)}] + n[Q_nL_{(o)}] \tag{3}$$

$$[L^{n-}]_T = [L^{n-}] + [Q_nL_{(o)}] \tag{4}$$

$$[X^-]_T = [Q^+]_T = [QX_{(o)}] + [X^-] \tag{5}$$

where the carboxylic groups of the aromatic acids dissociate at pH 12–13 and the partition coefficients of QX between aqueous and organic phases are assumed to be sufficiently high (21, 22). In addition, the volumes of organic

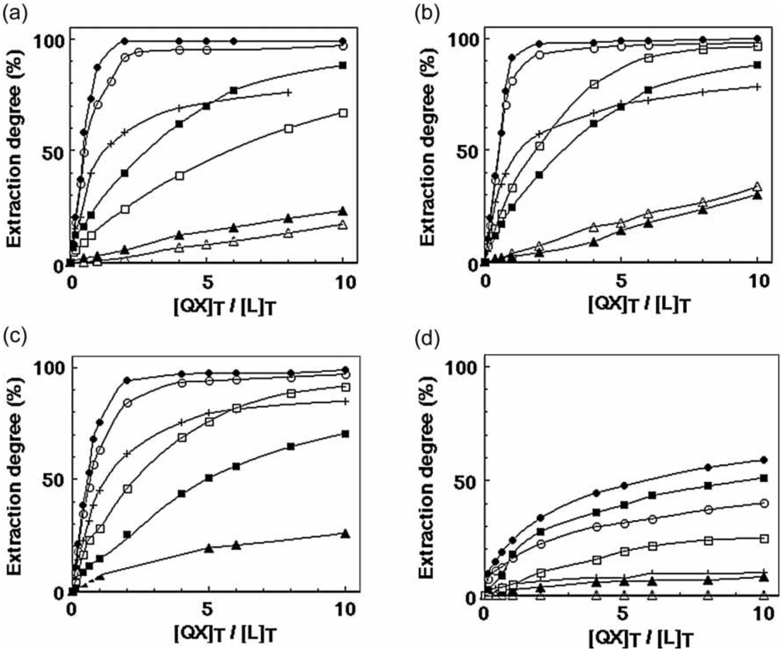

Figure 3. Molar ratio plots for the extraction of aromatic acids. $[\text{aromatic acid}]_T = 10^{-3}$ M, $[\text{THAI}]_T = 10^{-2}$ M, organic phase: chloroform, 20°C. Quaternary ammonium salts: (a) ALQ; (b) ZCl; (c) DMABr; (d) THAI, aromatic acids, +benzoic acid (BE), open circles: 1NA, closed circles: 2NA; open triangles: 1,2-benzenedicarboxylic acid (12B), closed triangles: 13B, open squares: 23 N, closed squares: 26N.

phase and water phase used in this study are the same. Thus, K_{ex} is given by Eqs. (6)–(8).

$$K_{ex} = \frac{n^n([L^{n-}]_T - [L^{n-}])^{n+1}}{[L^{n-}]\,\{[Q^+]_T - n([L^{n-}]_T - [L^{n-}])\}^n} \tag{6}$$

$$K_{ex} = \frac{n^n E^{n+1}}{(1 - E)\,\{[Q^+]_T/[L^{n-}]_T - nE\}^n} \tag{7}$$

$$E = [Q_nL_{(o)}]/[L^{n-}]_T \tag{8}$$

where E shown in Eq. (8) indicates the ratio between the amount of L extracted and the initial amount of L dissolved in the aqueous phase. The values of K_{ex} were determined by the least square fitting calculations (Table 2). In this analysis, the counter anion within $QX_{(o)}$ ion-pair can be replaced with OH^- since the concentration of OH^- was fairly high. The contribution of OH^- for the ion-pair extraction should be relatively smaller than that of other halogen ions, since OH^- has relatively weaker extractability than halogen

Table 2. Logarithmic values of K_{ex}

QX acids	ALQ	ZCl	DMABr	THAI
BE	-0.27 ± 0.05	-0.29 ± 0.08	-0.24 ± 0.02	-2.76 ± 0.06
12B	-4.03 ± 0.28	-2.87 ± 0.19	NA	NA
13B	-3.34 ± 0.11	-3.18 ± 0.21	-2.79 ± 0.04	-4.79 ± 0.10
1NA	0.67 ± 0.03	1.25 ± 0.03	0.56 ± 0.01	-1.42 ± 0.04
2NA	1.41 ± 0.02	1.68 ± 0.01	1.05 ± 0.01	-0.98 ± 0.02
23 N	-1.54 ± 0.04	0.30 ± 0.08	-0.19 ± 0.06	-2.86 ± 0.05
26 N	-0.48 ± 0.06	-0.53 ± 0.05	-1.26 ± 0.12	-1.54 ± 0.07

ZCl: tetradecyldimethylbenzlylammonium chloride, DMABr: dilauryldimethylammonium bromide. All other abbreviations are the same as shown in Figs. 1, 2 and Table 1.

ions (18, 23). In the present study, the concentration of OH^- was common for the determination of K_{ex} using different quaternary ammonium salts so that the comparison of the values of K_{ex} is valuable.

The maximum difference of K_{ex} among the aromatic acids using each QX reaches to 10^5. This fact indicates that this ion-pair extraction system using quaternary ammonium salt is applicable as a separation technique of the aromatic carboxylic acids. The values of K_{ex} of benzenecarboxylic acids are smaller than those of naphthalenecarboxylic acids. Moreover, the values of K_{ex} of monocarboxylic acids are greater than those of dicarboxylic acids. In addition, the values of K_{ex} using THAI are somewhat smaller than those using other QX. This fact indicates that the THA^+ ion does not possess enough ability for use as the counter cation for the extraction of the aromatic acids. The hydrophobicity of these QX is approximately equal since the molecular weight of QX is nearly the same. Thus, the reason for the weak ability of THA^+ may be that THA^+ is relatively spherical compared with Q^+ ions. In addition, the stronger affinity of I^- with THA^+ would contribute the small values of K_{ex} (18, 22).

In order to evaluate the relationship between the values of K_{ex} and the molecular structures of Q^+, the linear free energy relationship (LFER) for K_{ex} was examined (Fig. 4). LFER for BE, 1NA, and 2NA (compounds 1, 2, 3 in Fig. 4) was observed among the four types of QX. (24) This fact indicates that the extraction mechanisms for BE, 1NA, and 2NA are similar even using different types of Q^+. However, LFER for aromatic dicarboxylic acids (compounds 4, 5, 6, 7 in Fig. 4) was ambiguous, and LFER was only found between the systems using ALQ and THAI. Although the value of K_{ex} of 23 N is smaller than that of 26 N acid using ALQ or THAI, the value of K_{ex} of 23 N is greater than that of 26 N using DMABr or ZCl. The value of K_{ex} of 12B is smaller than that of 13B with ALQ, DMABr, or THAI.

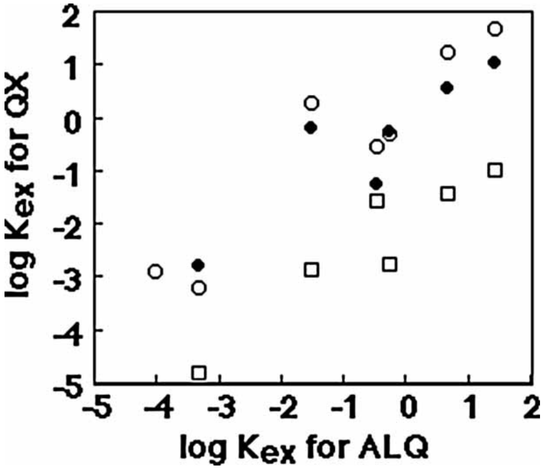

Figure 4. Linear free energy relationship on the values of K_{ex} using ZCl, DMABr, and THAI vs. those using ALQ. Abbreviation for QX and aromatic acids: QX, open circle; ZCl, closed circle; DMABr, open square; THAI, aromatic acids, 1: 2NA, 2: 1NA, 3: BE, 4: 26 N, 5: 23 N, 6: 13B, 7: 12B.

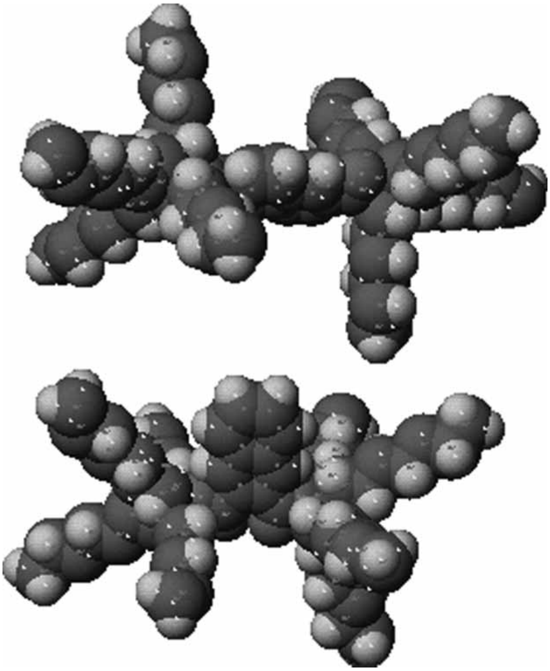

Figure 5. The perspective view of the ion-pairs of 2,3- (bottom) and 2,6-naphthalene (top) carboxylic acids with THA^+ ions. The structures were generated using a CAChe program on the basis of classical mechanics.

These results may indicate a trend that the values of K_{ex} for dicarboxylic acid isomers decrease with decreasing the distance between two carboxyl groups. The fact that ALQ has 3 long alkyl chains (C_8), DMABr has 2 long alkyl chains (C_{12}), THAI has 4 alkyl chains (C_6), and ZCl has phenyl group with a long alkyl chain (C_{14}) would be related with this trend. In the systems using ALQ and THAI, the trend is more ambiguous than that using ZCl and DMABr. This is because ALQ and THAI have relatively spherical shapes compared with ZCl and DMABr. Actually, LFER was observed much more clearly between the systems using ZCl and DMABr than between other systems. For the cases of THAI, two counter ions (Q^+) would result in steric hindrance when these counter ions approach carboxyrate charges as shown in Fig. 5. The LFER shown for monocarboxylic acids supports this assumption, since the steric hindrance and the influence of the shape of Q^+ would not be important for the extraction systems of monocarboxylic acids. The magnitude of K_{ex} using ZCl is somewhat large even though the carbon number is slightly smaller than that using other QX. This trend may reflect the influence of the aromatic group of ZCl, in which the aromatic groups of ZCl may associate with the aromatic carboxylic acids by the $\pi - \pi$ interaction.

CONCLUSIONS

By this study, it was confirmed that benzene and naphthalene mono- and dicarboxylic acids were able to be extracted with quaternary ammonium ion into organic solvents. It was unexpected that the extraction of dicarboxylic acids was slower than that of monocarboxylic acids. The equilibrium constants for the extraction of dicarboxylic acids were smaller than those of monocarboxylic acids. Linear free energy relationship for monocarboxylic acids was observed using different quaternary ammonium ions, while that for dicarboxylic acids was not clearly observed.

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