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Influence of pH and Diluent on the Ion-Pair Solvent Extraction of Aromatic Carboxylic Acids Using Quaternary Ammonium Salts

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Abstract: The influence of pH and diluent on the ion-pair solvent extraction of benzene polycarboxylic acids have been investigated for the separation of the coal oxidation products, which are formed by the treatment with alkaline solutions at high temperatures. Although the extent of the solvent extraction of benzoic acid (1BE) with a quaternary ammonium reagent (tri-n-octylmethylammonium chloride) into chloroform and benzene did not change at a very acidic and alkaline solutions, those of 1,2-benzenedicarboxylic acid (12BE) and trimellitic acid (124BE) somewhat decreased at very low pH and very high pH. The magnitudes of the equilibrium constants (K_{ex}) of 1BE using a different diluent decreased in the order benzene > carbontetrachloride > 1,2-dichloroethane > cyclohexane > hexane > chloroform > 1-octanol and those of 12BE decreased in the order benzene > cyclohexane > carbontetrachloride > hexane > 1,2-dichloroethane > chloroform. The inspection of the correlation between the values of K_{ex} and several parameters of the diluent implies that the magnitude of K_{ex} can be described by using the dielectric constant and the solubility parameter of diluent.

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

INTRODUCTION

The oxidation of coal in alkaline solutions at elevated temperatures is an important process to produce coal chemicals, which are sometimes difficult

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to obtain from petroleum (1–3). Since oxalic acid and benzene polycarboxylic acids are obtained from coal oxidation (3–11), pilot operations of the coal oxidation to produce aromatic carboxylic acid in sodium hydroxide solutions at high temperatures were already developed in the middle of the 20th century (12–14). It has been demonstrated that the production of oxalic acid using the coal oxidation technique in sodium hydroxide solutions at high temperatures is useful for producing oxamide which is a slow releasing nitrogen fertilizer (15, 16). Aromatic polycarboxylic acids are also attractive (12, 14). For instance, phthalic acid isomers are suitable as resources for polyester plastics. However, the industrial applications of aromatic acids formed by the coal oxidation have not yet practically succeeded, since the practical separation and recovery techniques are essential to use these aromatic acids.

The solvent extraction technique using several kinds of diluent has been applied for the recovery of carboxylic acids with tertiary amines or quaternary ammonium salts. Successful studies involve the extraction of aliphatic carboxylic acids, such as acetic acid, formic acid, proionic acid, lactic acid, using tertiary or quaternary ammonium ions in a different diluent (17–22). However, few investigations of the extraction of aromatic acids have been carried out. Recently, we have found that it is possible to extract aromatic polycarboxylic acids using quaternary ammonium salts into organic phase and this technique is useful for the separation and the recovery of aromatic polycarboxylic acids (23). Based on the previous study, the influences of pH and diluent for the extraction behavior of benzene polycarboxylic acids were investigated to develop a practical separation method.

EXPERIMENTAL

Chemicals

All reagents used were of analytical grade from Wako Pure Chemical Industries Ltd., Japan. Abbreviations of the benzene polycarboxylic acids and a quaternary ammonium salt are as follows; 1BE: benzoic acid, 12BE: 1,2-benzenedicarboxylic acid, 124BE: trimellitic acid (1,2,4-benzenetricarboxylic acid), 135BE: trimesic acid (1,3,5-benzenetricarboxylic acid), 1245BE: pyromellitic acid (1,2,4,5-benzenetricarboxylic acid), 12345BE: 1,2,3,4,5-benzenepentacarboxylic acid, 123456BE: mellitic acid (1,2,3,4,5,6-benzenehexacarboxylic acid), TOMACl: tri-n-octylmethylammonium chloride.

Extraction Procedure and Equipment

The extraction behavior was investigated using the following procedure (23). To investigate the influence of pH, solutions containing 10^{-3} M benzene polycarboxylic acid were prepared in aqueous solution at pH 0–14. In a test tube, a 20 ml of benzene polycarboxylic acid solution was placed, and to it was added a 20 ml of organic phase involving 10^{-2} M TOMACl. For the influence of the diluent, solutions containing 10^{-3} M benzene polycarboxylic acid were prepared in 0.1 M sodium hydroxide solution. The pH of the aqueous phase was controlled using HCl, $HClO_4$, or H_2SO_4 ($pH < 0$), 0.1 M phosphate buffer ($pH = 2–3$, 6–8, 11–12), 0.1 M acetate buffer ($pH = 3.5–5$), 0.1 M borate buffer (9.5), NaOH ($pH > 13$). The sample solution was shaken for 20 min at 20°C. After the centrifugation of the two-phase system, the residual concentration of aromatic polycarboxylic acids in the aqueous phase was determined on the basis of UV absorbance at 269–286 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 Hitachi-Horiba F-7ss II pH meter.

RESULTS AND DISCUSSION

Effect on pH for the Extraction of Benzene Polycarboxylic Acids

The extraction degree of 1BE, 12BE, and 124BE with TOMACl into chloroform or benzene is illustrated as a function of pH in Fig. 1a–1c and Fig. 2. The benzene polycarboxylic acids were extracted at pH 2–7 in all the cases but the extraction degree decrease in the order 1BE > 12BE > 124BE at below pH 2 and above pH 7. The extraction degree of the benzene polycarboxylic acids using benzene was constant at 100 % at pH 2–11. There was no obvious influence of the kind of pH buffer at pH 0–14 while different buffer solutions were used in this pH range. This fact indicates that the influence of anions to control pH of aqueous phase do not strongly affect the extraction degree of aromatic acids at pH 0–14. On the other hand, the extraction degree decreased with increasing the acid concentration at pH below 0 using different acids in the order $H_2SO_4 > HCl > HClO_4$. The decrease of the extraction degree at the very acidic pH is probably due to the competition between the ion-pair formation of $TOMA^+$ with benzene polycarboxylate anions and that of $TOMA^+$ with inorganic anions (SO_4^{2-}, HCl^-, ClO_4^-). This fact is consistent with previous studies (18, 24), in which competitive extractions between carboxylic and mineral acids by amines have been observed. At very low pH, the aromatic carboxylic acids exist as neutral acid forms in aqueous phase since the pKa values are 4.01 for 1BE, 2.76, 4.91 for 12BE, and 2.42, 3.71, 5.01 for 124BE (25). Thus, the ion-pair extraction degree should be reduced at low pH, while the neutral forms are extracted into organic phase as shown in the solid lines in Figs. 1a and 2. The extraction of neutral form acids is discussed later. The strength of the ion-pair formation between inorganic anions and quaternary ammonium ions decreased in the order $ClO_4^- > Cl^- > SO_4^{2-}$ (26, 27).

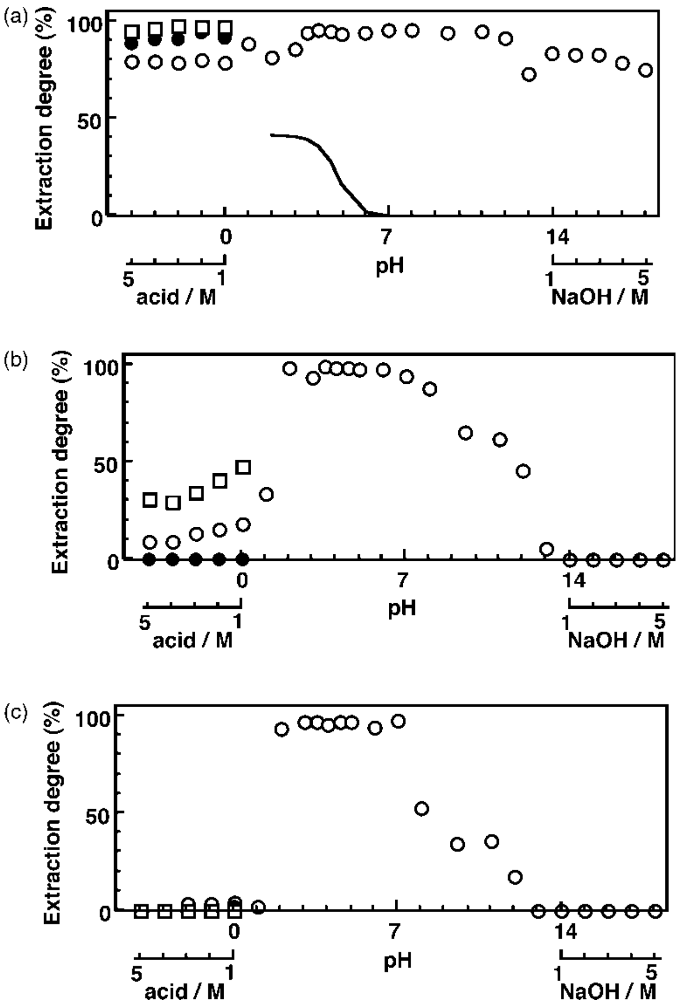

Figure 1. Influence of pH for the extraction of benzene polycarboxylic acids into chloroform. [Benzene polycarboxylic acid]$_T = 10^{-3}$ M, [TOMACl]$_T = 10^{-2}$ M, organic phase: chloroform, (volume of water phase)/(volume of organic phase) = 1, 20°C. a: 1BE, b: 12BE, c: 124BE. Mineral acids to control pH < 0 in a–c: open circles: HCl, closed circles: $HClO_4$, open squares: H_2SO_4. The solid curve in Fig. 1a indicates the extraction degrees in the absence of TOMACl.

Thus, this trend is consistent with the extraction degrees using the inorganic anions at very low pH where $TOMA^+$ are consumed to form strongly the ion-pairs with these inorganic anions rather than with benzene polycarboxylate anions. The ion-pairs of $TOMA^+$ with the inorganic anions would be extracted into the organic phase or possibly retains at the interface between the water and organic phases. On the other hand, the extraction

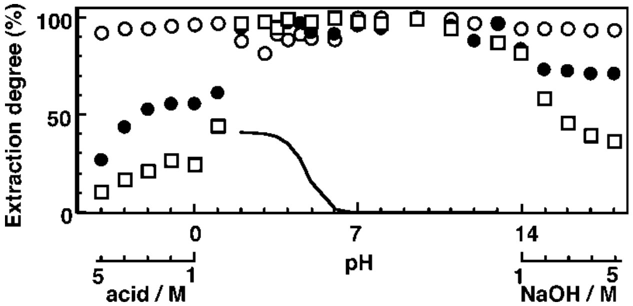

Figure 2. Influence of pH for the extraction of benzene polycarboxylic acids into benzene. [Benzene polycarboxylic acid]$_T$ = 10^{-3} M, [TOMACl]$_T$ = 10^{-2} M, organic phase: benzene, (volume of water phase)/(volume of organic phase) = 1, 20°C. Benzene polycaroboxylic acids: open circles: 1BE, closed circles: 12BE, open squares: 124BE. H_2SO_4 was used to control pH < 0. The solid curve indicates the extraction degrees in the absence of TOMACl.

degrees decreased at highly concentrated alkaline pH. This is primarily due to the competition between the ion-pair formation of $TOMA^+$ with benzene polycarboxylic acids and that with OH^-. Possibly, coextraction of acids and OH^- would have occurred at a very high concentration of alkaline solution (28), while the molar ratio plots are consistent with the stoichiometric extraction between aromatic polycarboxylic acid and $TOMA^+$ ion (Fig. 3a–3d). Besides, a trend was found that the extraction degree decreases with increasing pH is in the order 1BE > 12BE > 124BE. This would be useful for the separation of these aromatic acids. This is probably due to the following reason. The hydrophilic nature of the benzene polycarboxylic acids would increase with increasing the number of the carboxylic group. Besides, the extraction degree of 1BE, 12BE, and 124 BE into benzene using TOMACl was also investigated as a function of pH (Fig. 2). The extraction ability into benzene at alkaline pH is greater than that into chloroform. The pH dependence using benzene is basically consistent with that using chloroform.

Besides, the extraction degree of 1BE, 12BE, and 124BE in the absence of TOMACl is shown in the solid lines Figs. 1a and Fig. 2. 12BE and 124BE were not extracted into chloroform at all and the extraction degree of 1BE was much smaller than that in the presence of TOMACl. According to the values of lowest pKa for 12BE (2.76) and 124BE (2.42), 12BE and 124BE are almost deprotonated at neutral pH (25). Thus, the extraction of 12BE and 124BE at their neutral forms is obviously difficult. The slope of the plots for the logarithmic values of the extraction degree of 1BE as a function of pH was −1. This indicates that the neutral form of 1BE is extracted into chloroform. The extraction behavior in the absence of TOMACl clearly demonstrates that the quaternary ammonium salt is essential for the extraction of benzene polycarboxylic acids.

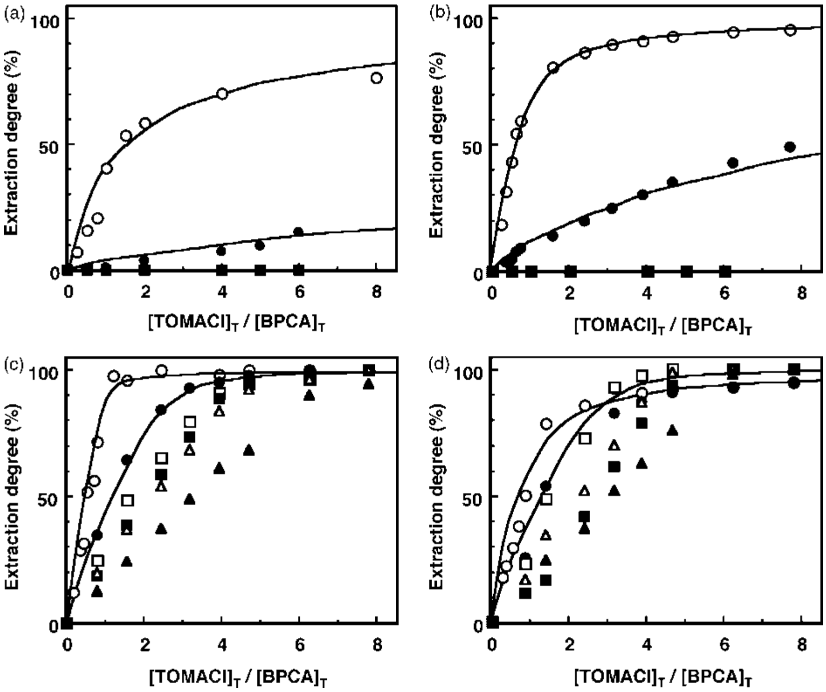

Figure 3. Molar ratio plots for the extraction of aromatic polycarboxylic acids into different diluent. [Benzene polycarboxylic acid]$_T$ = 10^{-3} M, quaternary ammonium salt: TOMACl, 20°C, diluent: a; chloroform, b: 1,2-dichloroethane, c: benzene, d: cyclohexane; open circles: 1BE, closed circles: 12BE; open squares: 135BE, closed squares: 1234BE, open triangles: 12345BE, closed triangles: 123456BE. BPCA: benzene polycaroboxylic acid. The lines drawn through the experimental points were fit on the basis of the reaction model shown in Eq. (1) and (2).

Influence of Diluent

The extent of extraction of benzene polycarboxylic acids (1BE, 12BE, 123BE, 1245BE, 12345BE, 123456BE) with TOMACl into several diluents was determined as a function of the molar ratio of TOMACl to the benzene polycarboxylic acids (Fig. 3a–3d, Fig. 4a, 4b). Based on the plots shown in Fig. 3a–3d, Fig. 4a, 4b, the stoichiometry of the extraction and its equilibrium constant are expressed as Eq. (1) and (2) give the extraction equilibrium constant,

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

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

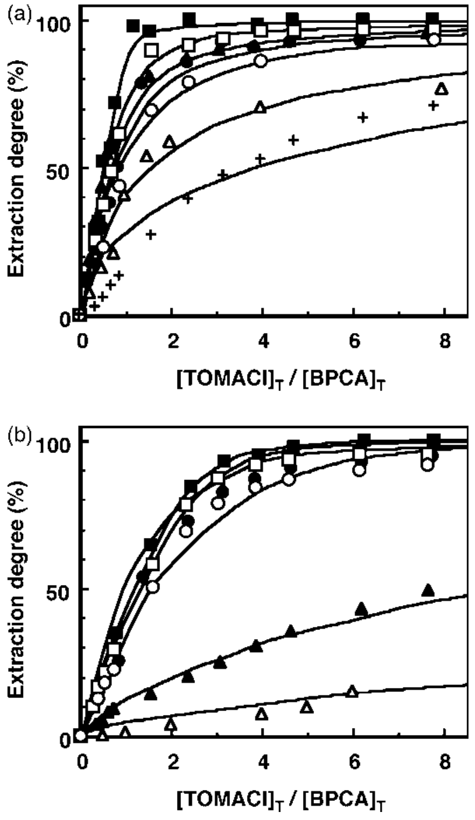

Figure 4. Molar ratio plots for the extraction of benzoic acid (1BE) and 1,2-benzenedicarboxylic acid (12BE) into different diluent. [Benzene polycarboxylic acid]$_T$ = 10^{-3} M, 20°C, quaternary ammonium salt: TOMACl. a: 1BE, b: 12BE; diluent: open circles: hexane, closed circles: cyclohexane; open squares: carbontetrachloride, closed squares: benzene, open triangles: chloroform, closed triangles: 1,2-dichloroethane; plus: 1-octanol. BPCA: benzene polycaroboxylic acid. The lines drawn through the experimental points were fit on the basis of the reaction model shown in Eq. (1) and (2).

where L^{n-} indicates aromatic carboxylate ion. The plots in Fig. 3c support the extraction of benzene polycarboxylic acid requires n Q^+ molecules but the stoichiometry is not clear when other diluent was used (Figs. 3a, b, and d). The extraction degree decreased in the order 1BE > 12BE > 123BE > 1245 BE > 12345BE > 123456BE. This coincides with the number of negative charges of the benzene polycarboxylic acids. The quantitative extraction of all types of benzene polycarboxylic acids was possible at a high concentration of TOMACl when benzene or cyclohexane was used (Figs. 3c, d). However, the extraction abilities of chloroform and 1,2-dichloroethane were weak and no other benzene polycarboxylic acids were extracted. This fact indicates that chloroform and 1,2-dichloroethane are suitable for the separation of 1BE and 12BE from others. The values of K_{ex} were determined on the basis of the following calculations for the cases of 1BE and 12BE on the basis of a previous study (23). The values of K_{ex} are summarized in Table 1. 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 for the cases of 1BE and 12BE as shown in Fig. 1 (26, 29). 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 magnitude of K_{ex} for 1BE using different diluents decreased in the order benzene > carbontetrachloride > 1,2-dichloroethane > cyclohexane > hexane > chloroform > 1-octanol and that for 12BE decreased in the order benzene > cyclohexane > carbontetrachloride > hexane > 1,2-dichloroethane > chloroform. While there seems to be no obvious relationship between the magnitude of K_{ex} and the nature of the diluent, the correlation between the logarithmic values of K_{ex} with dielectric constant (ε), solubility parameter (δs) (30), and acceptor number (AN) (31) was inspected (Fig. 5a–c). Additionally, the relationship between the logarithmic values of K_{ex} for 1BE and those for 12BE is shown in Fig. 5d. There was no obvious linear free energy relationship between the extractions of 1BE and 12BE. The difference between the values of K_{ex} for 1BE and 12BE is relatively small when the values of ε is lower than 4, while the unit of K_{ex} is different between 1BE and 12BE. This may be due to the fact that ion-pairs in a diluent possessing higher ε tends to dissociate but those in a diluent possessing lower ε does not readily dissociate. Besides, there seems

Table 1. Logarithmic values of K_{ex} and physico-chemical parameters of diluent

Diluent	1BE	12BE	ε	δs	δs(δw-δs)	AN
Hexane	0.10 ± 0.06	0.41 ± 0.10	1.19	7.27	118.21	0.0
Cyclohexane	0.42 ± 0.06	1.11 ± 0.10	2.20	8.20	125.71	–
CCl_4	0.87 ± 0.04	0.81 ± 0.1	2.23	8.55	128.08	8.6
Benzene	1.62 ± 0.04	1.35 ± 0.05	2.28	9.16	131.63	8.2
$CHCl_3$	−0.27 ± 0.05	−4.03 ± 0.28	4.72	9.16	131.63	23.1
1,2-dichloroethane	0.56 ± 0.02	−1.86 ± 0.09	10.13	9.86	134.79	16.7
1-octanol	−0.81 ± 0.28	–	10.34	8.71[a]	129.08	–

ε: dielectric constant (25°C), δw: solubility parameter (25°C), AN: acceptor number.
[a] The value was calculated from the following equations. $\delta = (\Delta E^V/V)^{1/2}$, $\Delta E^V 298 = -3542 + 23.7\ T_b + T_b^2$ (V: the mol volume of diluent, T_b: the boiling point of diluent)

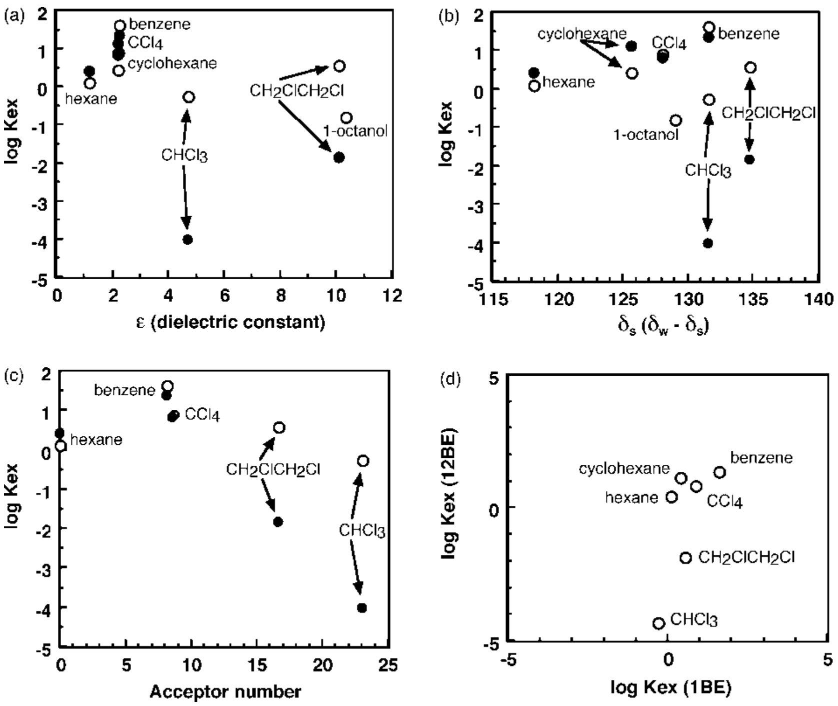

Figure 5. The logarithmic values of K_{ex} as a function of several parameters concerning the diluents. (A) log K_{ex} vs. ε (dielectric constant), (B) log K_{ex} vs. δs(δw−δs), (C) log K_{ex} vs. AN(acceptor number), (D) Log K_{ex} (12BE) vs. log K_{ex} (1BE). (A – C) open circles: 1BE, closed circles: 12BE.

to be a correlation that the logarithmic values of K_{ex} is proportional to the values of δs(δw−δs) (δw: the solubility parameter of water), where 2 lines seem to exist for the cases of 1BE and 12BE. In other words, the nature of the diluents seem to be classified into the group involving n-hexane, cyclohexane, carbontetrachloride, and benzene and the other group involving chloroform, 1,2-dichloroethane, and 1-octanol. According to the theory of regular solution, it is expected that the logarithmic value of the partition coefficient of solute is proportional to the values of δs(δw−δs). In the present system, the equilibrium constant (K_{ex}) is expressed by the product of the association formation constant of ion-pair in diluent (K_{ass}) and the partition coefficient of the ion-pair (P_{ip}) (Eq (3).

$$K_{ex} = K_{ass}P_{ip} \qquad (3)$$

For the cases of n-hexane, cyclohexane, CCl_4, and benzene, the dielectric constants are small so that the ion-pairs in the diluent would hardly dissociate L^{n-} and Q^{+}. Besides, the ion-pairs in chloroform, 1,2-dichloroethane, and 1-octanol would dissociate since the dielectric constants are greater than the former group. This could result in the correlation between the logarithmic values of K_{ex} and $\delta s(\delta w - \delta s)$ within these two groups. This trend is coincidental with the correlation between the logarithmic values of K_{ex} for 1BE and 12BE where two different LFER can be observed. Moreover, there is a correlation between the logarithmic values of K_{ass} and the values of AN. The values of AN may be a good indictor that expresses the electrostatic nature of the diluent and the nature of the regular solution.

CONCLUSIONS

By this study, it was confirmed that it was possible to extract benzene polycarboxylic acids with quaternary ammonium ion into several types of diluents. The extraction degrees of benzene polycarboxylic acids using TOMACl into chloroform or benzene decreased in the order 1BE $>$ 12BE $>$ 123BE at strong acidic or (strong) alkaline. The extraction degrees of benzene polycarboxylic acids are fairly dependent on the types of diluent and this fact is useful for designing the separation method of each component of benzene polycarboxylic acid mixtures formed by the coal oxidation. It was found that the diluents for the ion-pair solvent extraction system can be classified into two groups using dielectric constant and solubility parameter.

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