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Column Sorption of Citric Acid from Aqueous Solutions Using Tri-*n*-octylamine-Impregnated Macroporous Resins

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ABSTRACT

Column sorption of citric acid from aqueous solutions using tri-*n*-octylamine (TOA)-impregnated macroporous resins was studied at 298 K. The breakthrough curves were measured as a function of the feed flow rate, citric acid concentration in the feed solution, TOA concentration in the resin phase, and type of resin. It was found that the type of resin played a most important role in determining the saturated capacity under comparable conditions. The desorption of citric acid from loaded resins was also evaluated with various eluants, including HCl, HNO_3, H_2SO_4, and Na_2CO_3

INTRODUCTION

Due to the difficulty and low yield of acid crystallization, as well as the extra consumption of chemicals and the damage to the environment, amine extraction has been found to be a promising alternative to the conventional precipitation process for the recovery of citric acid from aqueous solutions (1–5). A large amount of work has been done on the extraction equilibrium of citric acid with tertiary amines like tri-*n*-octylamine (TOA), trilaurylamine, and Alamine 336 (4–6).

However, the solvent extraction process requires violent mixing of the phases to provide sufficient contact area for a satisfactory rate of extrac-

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tion followed by gravity settling of the mixed phases. It needs mixing and settling apparatuses and must overcome the problems of reagent loss through entrainment and those of phase separation due to the formation of a third phase and emulsion. Also, the solvent extraction process is, in general, considered to be economical for aqueous feed in the acid concentration range of 0.1–2 mol/dm^3 (2).

The use of synthetic neutral macroporous resins as polymeric adsorbents offers another choice for the recovery of carboxylic acids from dilute aqueous solutions, because the resins have the necessary physical and chemical strengths, a high surface area/volume ratio, and an easy regeneration nature through the use of appropriate organic solvents (7–9). Nevertheless, the adsorption capacity of carboxylic acids by these resins is largely reduced when the hydrophilicity of the acids is increased (7, 8). For example, the adsorption of citric acid is considerable only when the acid concentration in the aqueous phase is relatively high (9).

Extractant-impregnated resin (EIR) is a kind of novel separation medium and can bridge the gap between solvent extraction and resin ion-exchange (or adsorption) processes. It combines the advantages of ion exchange for processing very dilute liquors with the specific properties of extractants. It also combines the high distribution and selectivity distinctive of extractants dissolved in a liquid organic phase with a simplicity of equipment and an operation distinctive to solid ion-exchange technology (10, 11). Hence, EIR is very suitable for recovering a specific solute with high selectivity over other species.

Much work on the sorption and separation of metals with EIRs has been carried out (12–19). The impregnated extractants commonly include organophosphorus acids (12–17) and TOA (18, 19). It has been recognized that the impregnated extractant will exhibit a strong affinity for the polymeric matrix and may behave as if it were in the liquid state (10–12). The possibility of the application of EIR for the recovery and separation of metals has been justified. To our knowledge, however, little attention has been paid to studying the sorption of organic solutes. In this study, column sorption of citric acid from aqueous solutions with TOA-impregnated resins (TOA–EIR) was studied by changing such variables as the linear flow rate, the citric acid concentration in the feed phase, and the TOA concentration in the EIR phase. The desorption ability of citric acid from loaded TOA–EIR by various eluants was also evaluated.

EXPERIMENTAL

Reagents and Macroporous Resins

TOA was the product of Tokyo Chemical Industry Co., Ltd., Japan. It had a purity of about 98.5% and was used as received. Citric acid, *n*-

hexane, and the other inorganic chemicals were supplied by Merck Co. as analytical reagent grade and all were used without further purification. Deionized water produced by the Millipore Milli-Q water system was used throughout.

Amberlite XAD-2 and XAD-4, supplied by Rohm & Haas Co., USA, are macroporous resins made of styrene–divinylbenzene copolymer with a highly aromatic structure. On a dry basis, they have specific surface areas of 330–350 and 750–780 m^2/g, porosities of 0.42 and 0.51, and average pore diameters of 9 and 5 nm, respectively (20). The particle size of both resins is 0.3–0.9 mm (20–50 mesh). These resins were washed by acetone and *n*-hexane and dried at 323 K in a vacuum for 2 hours before impregnation.

Preparation of the TOA–EIR and Solutions

TOA-impregnated XAD resins were prepared by the following dry procedure (16, 19). First, TOA (0.1–0.5 g) was diluted in a precalculated amount of *n*-hexane (3 cm^3). The resulting *n*-hexane solution was then contacted with fresh resins (1–5 g) until all the organic solution was completely absorbed by the resins. In general, this step was accomplished within 12 hours in a drying oven at 333 K. These resins were finally evaporated to completely remove the solvent at 323 K in a vacuum for 2 hours.

The content of TOA held in the EIR was determined from the amount of HCl adsorbed by shaking the EIR with 0.1 mol/dm^3 HCl (18). The concentrations of TOA and citric acid sorbed in the impregnated resin are expressed on the basis of dry EIR in this study. The feed solution was prepared by dissolved citric acid in deionized water without pH adjustment, and the acid concentration in the feed solution was either 9.5×10^{-3} or 9.5×10^{-2} mol/dm^3. In the EIR phase, the initial TOA concentrations were 0.653 and 0.945 mol/kg.

Experimental Procedures

A column was packed with known amounts of the TOA–EIR (2.5 g), supported between glass wool beds, in a glass tube. The column used had a diameter of 10 mm and a length of 80 mm. The bed volume for the column was 4.8 cm^3. In the sorption run (11), a citric acid solution was fed to the bottom of the column by a Masterflex L/S digital drive (Cole-Parmer Model 7524-10) and an easy-load pump head (upflow). The linear flow rate ranged from 20.9 to 76.4 cm/h. Fresh TOA–EIR was used for the determination of the breakthrough curve, and the acid-sorbed EIR was used to follow the elution history. The effluent samples were collected at appropriate time intervals, and the concentration of citric acid was titrated with a known NaOH solution using a Radiometer Autotitrator Model RTS82.

In some runs the concentration of citric acid was too low to be analyzed by titration ($<10^{-3}$ mol/dm^3). In this instance it was determined by HPLC (Waters Model 501, Millipore Co.). The HPLC consists of a solvent delivery pump (Model 510), an injector (Model U6K), a UV/Vis detector (Model 484), and an integrator (Model 746). A Hamilton ion-exclusion column PRP-X300, a 7-μm, spherical poly(styrene–divinylbenzene)sulfonate column, was used for organic acid analysis. It had a pore size of 10 nm and an exchange capacity of 0.17 meq/g. The mobile phase was 10^{-3} N H_2SO_4. The saturated capacity of the TOA–EIR column, Q, was calculated based on the total amount of the acid sorbed until the effluent concentration reached the feed concentration.

RESULTS AND DISCUSSION

Preparation of the TOA–EIR

Figure 1 shows the effect of the amount of TOA in the impregnating solution on the TOA content in the XAD-2/EIR. Similar results were observed in the case of XAD-4/EIR (not shown). The content of TOA in the

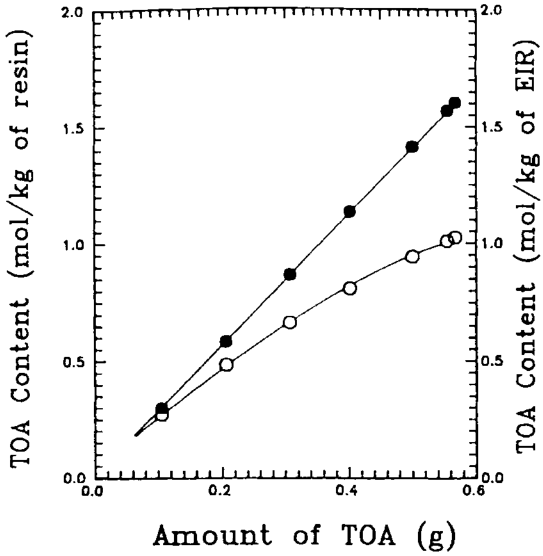

FIG. 1 Effect of the amount of TOA in the impregnating solution (n-hexane) on TOA content in the XAD-2/EIR. Fresh resin = 1 g.

EIR phase increases with the solution concentration. The amount of TOA transferred from organic solution to the resin was found to be more than 96% for the ranges studied. It should be noted that the resulting XAD-2/EIR and XAD-4/EIR become adhesive after drying when the TOA content exceeds about 1.023 and 1.114 mol/kg, respectively. The above result for XAD-2/EIR is similar to that obtained by Akita and Takeuchi (19) for 1.02 mol/kg under comparable conditions. Also, the content of TOA analyzed by titration agrees well with that calculated from the changes in the weight of the resins before and after the impregnations.

The extractant loss from EIR for various TOA concentrations was also examined (not shown). The equilibrium distribution of citric acid was found to be abnormally low at lower TOA concentrations (<0.470 mol/kg). In practice, Cortina et al. (13) also found that the extractant concentration is 0.8 mol/kg at zero water content of EIR in the preparation of Cyanex 272 (an organophosphinic acid)-impregnated XAD-2 resins. Beyond that concentration, the extractant is partially adsorbed into the macroporous resin and partially retained by the capillary forces inside the

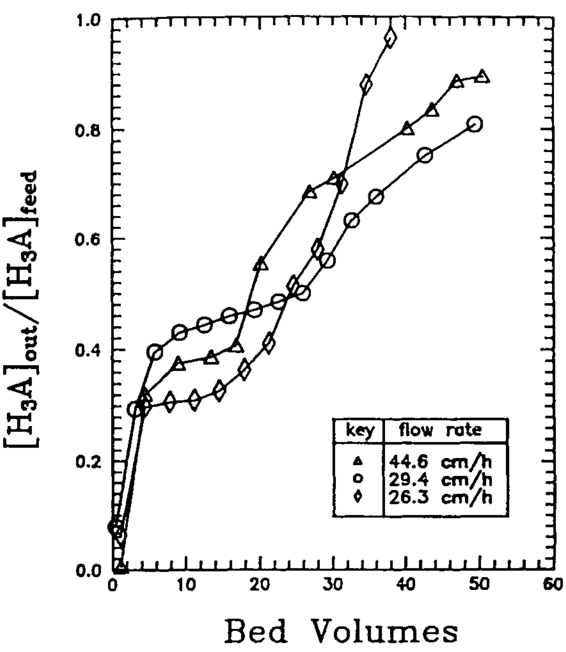

FIG. 2 Breakthrough curves of citric acid at different feed flow rates in XAD-2/EIR system. $[H_3A]_{feed} = 9.5 \times 10^{-3}$ mol/dm^3, $[TOA]_0 = 0.903$ mol/kg.

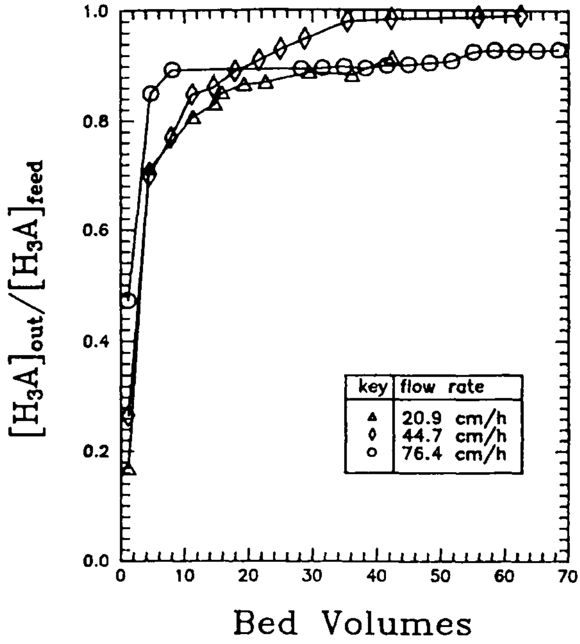

FIG. 3 Breakthrough curves of citric acid at different feed flow rates in XAD-4/EIR system. $[H_3A]_{feed} = 9.5 \times 10^{-3}$ mol/dm^3, $[TOA]_0 = 0.777$ mol/kg.

pores; i.e., the EIR is more stable. Therefore, in this study the TOA concentration in the EIR phase was kept high enough (greater than 0.47 mol/kg) based on what was observed in the work of Akita et al. (18).

Sorption for a Fixed-Bed Column

Figures 2 and 3 show the effect of feed flow rate on the sorption of citric acid in XAD-2/EIR and XAD-4/EIR systems, respectively. It was found that in both EIR systems the acid concentration in the effluent is monotonously increased and finally reaches the feed concentration. However, in the XAD-2/EIR system the sorption curve reaches a plateau region after about 5 bed volumes, as shown in Fig. 2. Also, it seem that the lower the flow rate, the wider that region. These phenomena may be because XAD-2 resin has a larger pore diameter than XAD-4 resin since a similar behavior has also been reported for the removal of bisphenol A

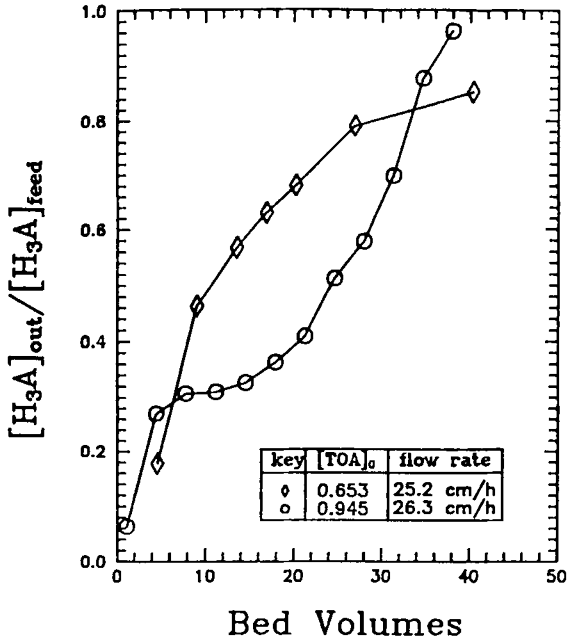

FIG. 4 Breakthrough curves of citric acid at different TOA concentrations in the EIR phase in XAD-2/EIR system. $[H_3A]_{feed} = 9.5 \times 10^{-3}$ mol/dm^3.

from wastewater at pH 10.0 using Amberlite XAD-7 resin which has the same average pore diameter as XAD-2 (20).

It is evident that the breakthrough curve obtained for the XAD-4/EIR system is nearly unaffected by the flow rate. In the XAD-2/EIR system, on the other hand, the flow rate has a greater effect on the sorption curve. Under the conditions studied, it is deduced that the dispersion effect due to high flow rate can be ignored within the column. In contrast to the XAD-2/EIR system, the steeper curve obtained in the XAD-4/EIR system perhaps represents the larger resistance of intraparticle diffusion (21). Furthermore, no breakpoint appears in either EIR system for the ranges studied. This may be due to the slow sorption rate of citric acid. Research on the sorption kinetics on this subject is necessary and is now being undertaken to analyze the sorption curves.

Figures 4 and 5 show the effect of TOA concentration in the EIR phase on the sorption of citric acid in XAD-2/EIR and XAD-4/EIR systems,

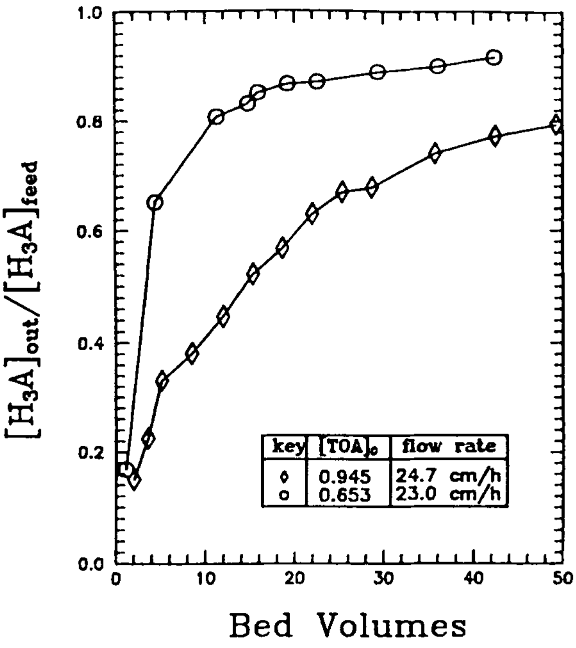

FIG. 5 Breakthrough curves of citric acid at different TOA concentrations in the EIR phase in XAD-4/EIR system. $[H_3A]_{feed} = 9.5 \times 10^{-3}$ mol/dm^3.

respectively. It was found that in both EIR systems the breakthrough curve is more gentle at a higher TOA concentration, that is, with a larger saturated capacity. These observations can be explained by the reaction rate for the complex formation of citric acid and TOA. In fact, the kinetics of solvent extraction of citric acid from aqueous solutions with TOA in xylene has recently been studied using a membrane-based permeation cell (22). The intrinsic rate of complexation reactions between citric acid and TOA at the aqueous–organic interface, R, is given by

$$R = k_f [H_3A] [\overline{TOA}]^2 - k_b [H_3A] [\overline{H_3A}] [\overline{TOA}]^{-1} \quad (1)$$

where k_f and k_b are the forward and backward rate constants, respectively. The overbar refers to the organic (EIR) phase. The rate constants were determined to be 1.54×10^{-11} (m^7/mol^2·s) and 2.12×10^{-6} (mol^2/m^5·s), respectively, at 298 K (22).

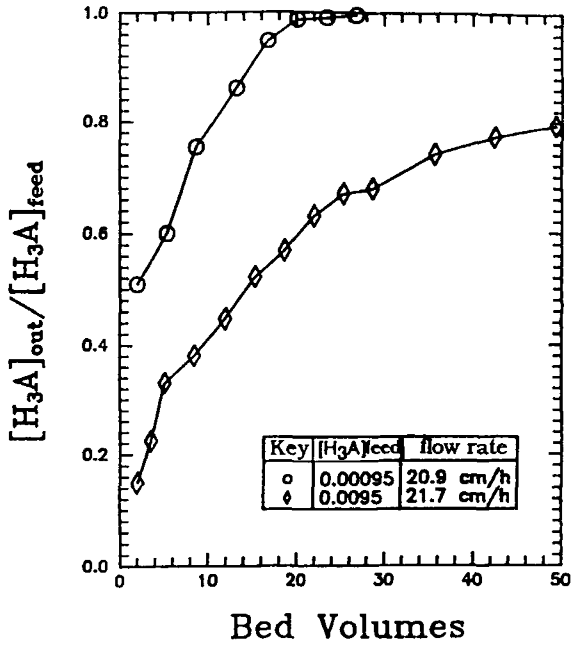

FIG. 6 Breakthrough curves of citric acid at different citric acid concentrations in the feed solution in XAD-4/EIR system. $[TOA]_0$ = 0.945 mol/kg.

As clearly indicated in Eq. (1), with increasing TOA concentration the rate of complex formation increases and that of complex destruction decreases. This leads to a more gentle sorption curve and a larger saturated capacity. *It is worth noting that the plateau region exists only in the XAD-2/EIR* system and at a higher TOA concentration ($[TOA]_0$ = 0.945 mol/kg), as seen in Figs. 4 and 5. Apart from the nature of XAD-2 resin as discussed above, the rate of complexation reactions is believed to play some role in determining the shape of a sorption curve (12).

Figure 6 shows the effect of citric acid concentration in the feed solution on the sorption of citric acid in the XAD-4/EIR system. It is found that the breakthrough curve is steeper at a lower feed acid concentration. These findings can similarly be explained by the rate of complexation reaction between citric acid and TOA.

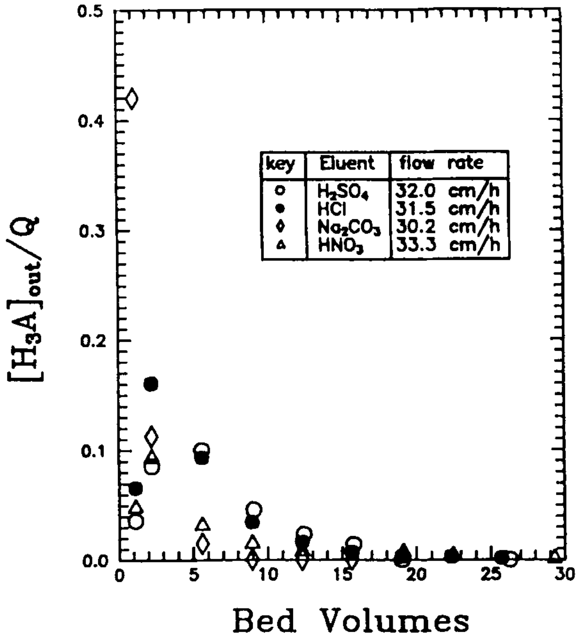

FIG. 7 Desorption curves of citric acid with various eluants (0.1 N) in XAD-2/EIR system. $[H_3A]_{feed} = 9.5 \times 10^{-3}$ mol/dm³, $[TOA]_0 = 0.945$ mol/kg; $Q = 0.332$ (○), 0.306 (●), 0.227 (◊), and 0.301 mol/kg (△).

Desorption for a Fixed-Bed Column

The desorption of citric acid with various eluants in XAD-2/EIR and XAD-4/EIR systems is plotted in Figs. 7 and 8, respectively. In both EIR systems the desorption of the acid with all the eluants considered (0.1 N) is rapid and complete (more than 98.5%). It was found that the desorption curve rises earlier and descends about 8 bed volumes in the XAD-4/EIR system than in the XAD-2/EIR system (about 10–15 bed volumes), probably because the bed voidage of XAD-4/EIR is smaller than that of XAD-2/EIR (21), that is, 0.342 vs 0.375. Moreover, as shown in Fig. 7, the desorption curve with Na_2CO_3 is narrower and the peak concentration is higher compared to the cases of HCl, HNO_3, and H_2SO_4. Because the polymeric matrix is identical (XAD-2), it is deduced that the rate for destruction of the acid–TOA complex will decrease in the order $Na_2CO_3 >$

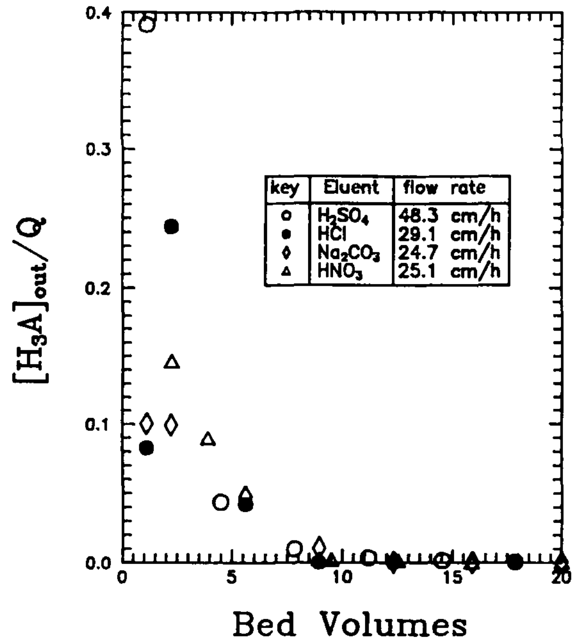

FIG. 8 Desorption curves of citric acid with various eluants (0.1 N) in XAD-4/EIR system. $[H_3A]_{feed}$ = 9.5 × 10^{-3} mol/dm^3, $[TOA]_0$ = 0.653 mol/kg; Q = 0.123 (○), 0.282 (●), 0.357 (◇), and 0.152 mol/kg (△).

HCl ≥ HNO_3 > H_2SO_4 (21). However, such an order is not valid for the XAD-4/EIR system (Fig. 8). No satisfactory explanation can be given to account for these discrepancies.

Cyclic Sorption for a Fixed-Bed Column

Figure 9 shows the breakthrough curves of citric acid before and after elutions with H_2SO_4 in the XAD-2/EIR system. Interestingly, it is found that in the second run a "whole" breakthrough curve is obtained, and hence the saturated capacity is significantly increased. It should be noted that such a behavior is not observed following regeneration with HCl, HNO_3, and Na_2CO_3. It is accordingly observed that in cyclic operations the breakthrough curve for the second run is in good agreement with that for the first run when either HCl, HNO_3, or Na_2CO_3 is used as an eluant

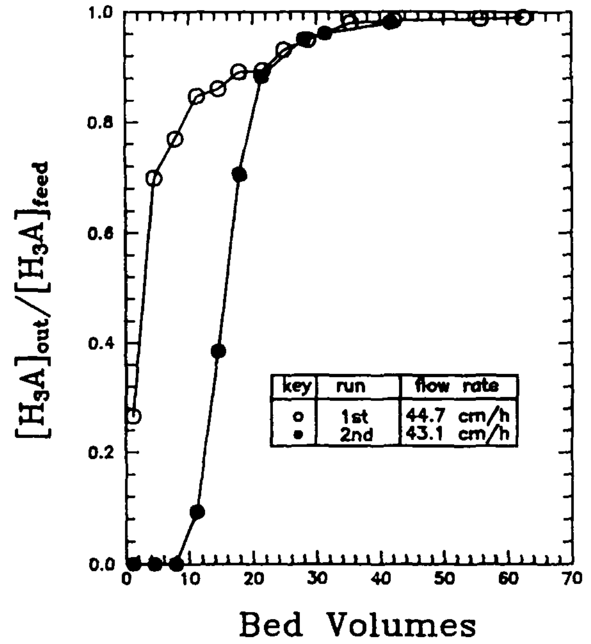

FIG. 9 Breakthrough curves of citric acid before and after the elutions with H_2SO_4 in XAD-2/EIR system. $[H_3A]_{feed} = 9.5 \times 10^{-3}$ mol/dm^3, $[TOA]_0 = 0.653$ mol/kg.

(not shown). This reveals that the loss of TOA from EIR is negligibly small.

The results shown in Fig. 9 can be explained by the fact that TOA has been converted to its sulfuric acid salt, a quaternary amine, after regeneration with H_2SO_4. The stoichiometric relation for a 1 : 1 complexation reaction, for example, before regeneration is given by (NR_3 = TOA)

$$H_3A + \overline{NR_3} \Leftrightarrow \overline{(H_3A)(NR_3)} \qquad (2)$$

After elution with H_2SO_4, the sorption reactions become

$$H_2SO_4 + 2\overline{NR_3} \Leftrightarrow \overline{(NR_3H)_2^+(SO_4)^{2-}} \qquad (3)$$

$$2H_3A + \overline{(NR_3H)_2^+(SO_4)^{2-}} \Leftrightarrow 2\overline{(H_3A)(NR_3)} + H_2SO_4 \qquad (4)$$

Actually, Wang and Hu (23, 24) recently investigated the equilibrium and kinetics of phenol extraction with the sulfuric acid salt of TOA. They found that the extractability of phenol is largely increased as compared to the case of TOA extraction. But the rates of complexation reactions in these two extraction systems are not compared in their work. It is deduced from Fig. 9 that the reaction would be faster in the case of the sulfuric acid salt of TOA. Efforts should be made to clarify the difference between the sorption of citric acid using the resins impregnating with TOA and its sulfuric acid salt.

In conclusion, although the equilibrium distribution of citric acid for both EIR systems is equivalent under the same conditions (6) and the XAD-4 resin has a larger specific surface area, as demonstrated above, XAD-2 resin is a better support for impregnation because the resulting EIR has a larger saturated capacity.

CONCLUSIONS

Column sorption of citric acid from aqueous solutions with TOA–EIR has been studied at 298 K. The following results were obtained.

1. The impregnation of TOA on Amberlite XAD-2 and XAD-4 resins can be achieved by a dry method to about 96%, and to a content below 1.203 and 1.114 mol/kg, respectively. The loss of TOA from EIR was found to be negligibly small.
2. The rates of citric acid sorption with both TOA–EIRs are relatively slow, but they can be largely enhanced following regeneration with H_2SO_4.
3. The desorption of citric acid from loaded TOA–EIR is completely and rapidly achieved with either HCl, HNO_3, H_2SO_4, or Na_2CO_3 (0.1 N).
4. In contrast to the XAD-4/EIR system, the XAD-2/EIR system has a larger saturated capacity for the sorption of citric acid under comparable conditions.

NOMENCLATURE

EIR	extractant-impregnated resin
H_3A	citric acid
k_b	backward reaction rate constant defined in Eq. (1) [$mol^2/(m^5 \cdot s)$]
k_f	forward reaction rate constant defined in Eq. (1) [$m^7/(mol^2 \cdot s)$]

R	intrinsic reaction rate between citric acid and TOA per unit area [mol/(m^2·s)]
Q	saturated capacity of the TOA–EIR (mol/kg)
TOA	tri-*n*-octylamine (NR_3)
[ ]	molar concentration of species in the brackets (mol/dm^3 or mol/kg)

Subscripts

feed	aqueous feed phase
out	effluent
0	initial

Superscript

$\overline{\text{(overbar)}}$	species in the EIR (or organic) phase

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