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Sorption of Citric Acid from Aqueous Solutions by Macroporous Resins Containing a Tertiary Amine Equilibria

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ABSTRACT

Experiments were conducted on equilibrium distribution of citric acid between relatively concentrated aqueous solutions and macroporous resins containing tri-*n*-octylamine (TOA). The equilibrium data were well described by the Langmuir isotherm equation. Chemical model analysis of the results showed that the sorption could be also explained by the formation of an acid–amine complex with general composition $\overline{(\text{acid})(\text{TOA})_q}$ in the resin phase. The loss of amine from the impregnated resins and the effect of temperature on equilibrium distribution were also discussed.

Key Words. Citric acid; Macroporous resins; Tri-*n*-octylamine; Sorption equilibrium; Langmuir equation

INTRODUCTION

Amine extraction has been found to be a promising alternative to the conventional precipitation process for the recovery of organic acids from aqueous solutions (1–3). Much work has been done recently on the extraction equilibrium of citric acid with tertiary amines like tri-*n*-octylamine (TOA), trilaurylamine, and Alamine 336 (4–8). This process is generally considered to be economical for aqueous feeds in the organic acid concen-

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tration range of 0.1–2.0 mol/dm^3 (3). However, the solvent extraction process requires violent mixing of the phases to provide sufficient contact area for a satisfactory rate of extraction followed by gravity settling of the mixed phases (9). It requires a mixing and settling apparatus, and it must overcome the problems of reagent loss through entrainment and those of phase separation due to the formation of the third phase and the emulsion.

The use of synthetic neutral macroporous resins as polymeric adsorbents offers another choice for the recovery of organic acids from dilute aqueous solutions (10, 11). Unfortunately, the adsorption capacity for these resins decreases when the hydrophility of the acids increases. Extractant-impregnated resin (EIR) has been shown to be a novel separation medium because it can bridge the gap between solvent extraction and resin ion-exchange (or adsorption) processes (9). It combines not only the advantages of solid ion exchange for processing very dilute liquors with specific properties of the extractants, but also the high distribution and selectivity distinctive to the extractants dissolved in a liquid organic phase with the simplicity of equipment and operation distinctive to solid ion-exchange technology (9). A large amount of work on the sorption and separation of metals with EIR has been carried out (12–18). The impregnated extractants mainly include organophosphorus acids (12–16) and tertiary amines (17, 18). The possibility of the application of EIR for the recovery and separation of metals has already been justified.

The distribution equilibria of citric acid between aqueous solutions and TOA–EIR have recently been investigated at relatively low acid concentrations in the aqueous phase (<0.024 mol/dm^3) (19). The common adsorption isotherms, such as the Langmuir and Freundlich equations, are inapplicable in this case. The sorption reaction could be explained with a chemical model by considering the formation of several citric acid–TOA complexes in the EIR phase. In this work the sorption equilibria at more concentrated aqueous solutions (0.05–0.2 mol/dm^3) were studied. Experiments were performed as a function of citric acid concentration in the aqueous phase, TOA concentration in the EIR phase, and temperature.

EXPERIMENTAL

Reagents and Macroporous Resins

TOA was a product of Tokyo Chemical Industry Co., Ltd., Japan. It had a purity of about 98.5% and was used without further purification. Citric acid, *n*-hexane, and other inorganic chemicals were supplied by Merck Co. as analytical reagent grade, and all were used as received.

Deionized water produced by the Millipore Milli-Q water system was used throughout the work.

Macroporous resins Amberlite XAD-4 (styrene–divinylbenzene copolymer type) and XAD-16 (divinylbenzene type) were supplied by Rohm & Haans Co., USA. On a dry basis, they had a specific surface area of 760 and 860 m^2/g, a porosity of 0.50 and 0.61, an average pore diameter of 4.5 and 8 nm, and a mean pore volume of 0.974 and 1.404 cm^3/g, respectively (11). The particle size of both resins was 0.3–0.9 mm (20–50 mesh). These resins were washed with acetone and *n*-hexane and dried at 323 K in a vacuum for 2 hours before impregnation.

Preparation of the TOA–EIRs and Solutions

Amberlite XAD resins were impregnated by the following dry procedures (19, 20). They were first performed by dissolving TOA (0.1–0.5 g) into 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 absorbed by the resins. This step was finished within 12 hours in a drying oven at 333 K. The resins were finally evaporated to completely remove the solvent at 323 K in a vacuum for 2 hours.

The TOA content held in the EIR phase was determined from the amount of HCl adsorbed by shaking the EIR with 0.1 mol/dm^3 HCl (18, 19). In this work the concentrations of TOA and citric acid sorbed in the impregnated resins were expressed on the basis of the dry EIR. The aqueous phase was prepared by dissolving citric acid in deionized water without pH adjustment. The initial acid concentration ranged from 0.05 to 0.20 mol/dm^3. In the EIR phase, the initial TOA concentration varied from 0.653 to 1.164 mol/kg.

Experimental Procedures

In each experiment the TOA–EIR (1 g) and aqueous citric acid solution (50 cm^3) were placed in a 125-cm^3 glass-stoppered flask and shaken at 110 rpm for at least 24 hours using a thermostated shaker (Firstek Model B603, Taiwan). Preliminary experiments had shown that the sorption was complete after 12 hours. After standing for 1 hour, the aqueous phase was separated from the EIR and its equilibrium pH was measured with a pH meter (Radiometer Model PHM82). The concentration of citric acid in the aqueous phase was titrated with a known concentration of NaOH using Radiometer Autotitrator Model RTS82. The contents of citric acid sorbed and unreacted TOA in the EIR phase were calculated from the mass balance. Each experiment was duplicated under identical conditions.

RESULTS AND DISCUSSION

Preparation of the TOA–EIRs

Figure 1 shows the effect of the amount of TOA in the impregnating solution on TOA content in the prepared XAD-16/EIR. Similar results were observed in the case of XAD-4/EIR (not shown). The TOA content in the EIR phase increases with the solution concentration. The amount of TOA transferred from the organic solution to the resin was found to be more than 98% for the ranges studied. The TOA content analyzed by titration agrees well with that calculated from the changes in the weight of the resins before and after the impregnations.

It should be noted that the resulting XAD-4/EIR and XAD-16/EIR become adhesive after drying when the TOA content exceeds about 1.339 and 1.542 mol/kg, respectively. It was reported that the swelling ratio, defined as the ratio of the volume of the resin immersed in a solvent to that in the dry state, for XAD-16 is not less than that of XAD-4. For

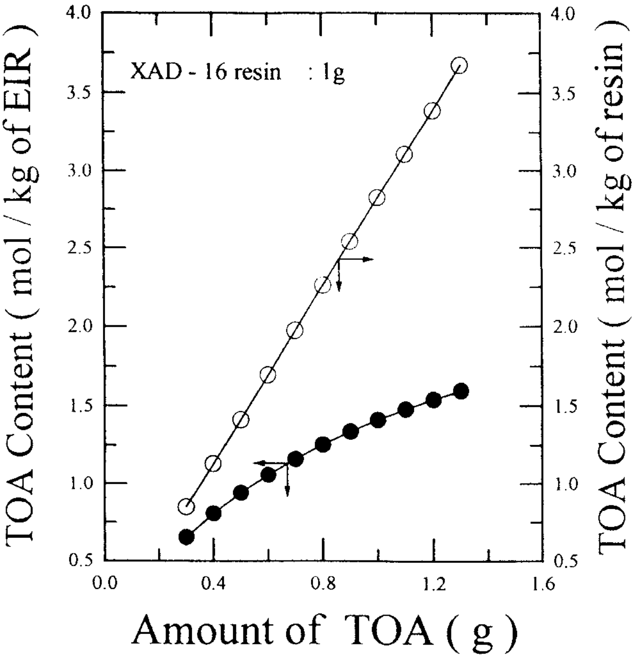

FIG. 1 Effect of the amount of TOA in the impregnating solution (*n*-hexane) on TOA content in the XAD-16/EIR.

example, in water they both are 1.02, but in toluene they are 1.21 for XAD-16 and 1.17 for XAD-4 (11). This means that swelling of these polymeric resins plays an important role in solute sorption (extractant impregnation, in this case). Hoshi et al. (21) recently studied the preconcentration of metals by Amberlite XAD resins coated with various dithiosemicarbazone compounds and they also found that the loaded amount of the reagent on the resins increases in the order of XAD-16 > XAD-7 > XAD-4. This is likely to involve such properties as the framework and polarity of the resins (21).

The present result for XAD-4/EIR is greater than that obtained earlier (1.114 mol/kg) under comparable conditions (19). This discrepancy probably results from the different sources of the resins (Rohm & Haas vs Merck). Perhaps some modifications of the resin surface or synthesis step are made by Merck Co. Preliminary experiments had generally shown that the distribution of citric acid by TOA-impregnated XAD-4 resins from Rohm & Haas was larger than about 20% compared with XAD-4 resins from Merck.

It was experimentally found that at our selected shaker speed of 110 rpm, the loss of TOA from EIR is less than 2 wt% (not shown). In addition, the concentration of TOA was kept high enough in this study, since the equilibrium distribution of citric acid is abnormally low at lower TOA concentrations (<0.47 mol/kg) in the XAD-4/EIR system (19). The loss of TOA from EIR under various TOA concentration is shown in Fig. 2, which indicates that the loss is negligibly small for both EIRs in the ranges studied.

Macroscopic Analysis of Sorption Equilibria

Figures 3 and 4 show the effect of citric acid concentration in the aqueous phase on the equilibrium distribution. It was found that the distribution of citric acid increases with the concentrations of citric acid. Moreover, the equilibrium distribution in the XAD-16/EIR system is larger about 60% than that in the XAD-4/EIR system under the same conditions. Factors leading to such a difference remain unclear. Presumably the larger porosity and mean pore volume for XAD-16 resins may be possible reasons, which could result in larger amounts of additional liquid-filled pores for sorption.

The effect of initial TOA concentration on the equilibrium distribution is shown in Figs. 5 and 6. In the XAD-16/EIR system, the equilibrium distribution increases with TOA concentration. On the other hand, a maximum uptake of citric acid is observed at $[\overline{TOA}]_0 = 0.943$ mol/kg in the XAD-4/EIR system. A possible explanation is that at this concentration

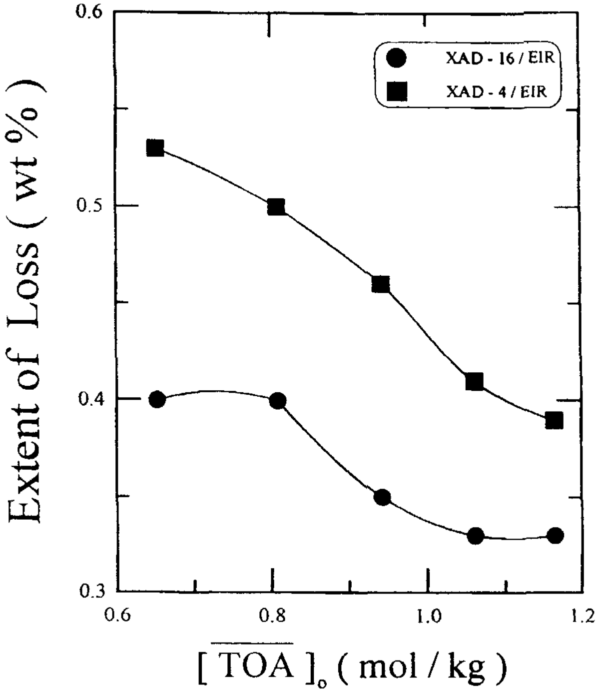

FIG. 2 Dependence of the loss of TOA from the EIRs on initial TOA concentration.

TOA is optimally and well distributed on the surface of XAD-4 resin. Beyond that value, multilayer adsorption of TOA may occur during impregnation due to the more restricted pore volumes of XAD-4 resin, reducing the effective sites for citric acid sorption. Actually, in the present work the prepared XAD-4/EIR is yellow, near the original color of TOA extractant; however, the prepared XAD-16/EIR is white, the original color of the resins.

It follows from Figs. 3 and 4 that a Langmuir-type sorption exists. The Langmuir monolayer equation is given as

$$\theta = [\overline{H_3A}]/[\overline{H_3A}]_\infty = K_L[H_3A]/\{1 + K_L[H_3A]\} \qquad (1)$$

where θ is the fractional coverage, K_L is the Langmuir constant, and the subscript ∞ indicates the equilibrium distribution corresponding to complete coverage. Rearranging Eq. (1), we have

$$1/[\overline{H_3A}] = (1/K_L[\overline{H_3A}]_\infty)(1/[H_3A]) + (1/[\overline{H_3A}]_\infty) \qquad (2)$$

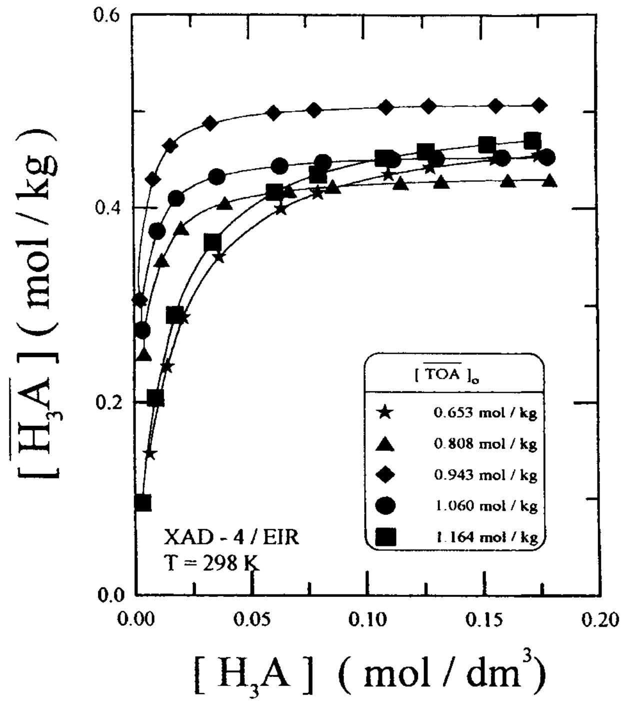

FIG. 3 Effect of citric acid concentration in the aqueous phase on equilibrium distribution in XAD-4/EIR system at 298 K.

Therefore, a plot of $(1/[\overline{H_3A}])$ vs $(1/[H_3A])$ would give a straight line. Typical plots of equilibrium data are shown in Fig. 7, revealing a good linear relationship. The values of K_L and $[\overline{H_3A}]_\infty$ are listed in Table 1. In fact, a similar analysis of adsorption data has recently been reported in the preconcentration of metals by Amberlite XAD resins coated with dithiosemicarbazone compounds (21).

Figures 8 and 9 show the effects of temperature on equilibrium distribution. It is found that the amount of citric acid sorbed increases as the temperature is increased. This is exactly opposite to those obtained previously at low citric acid concentrations (<0.024 mol/dm^3) (19). In general, the citric acid–TOA complexation reactions involve proton transfer or hydrogen-bond formation and are thus expected to be exothermic. Also, the formation of a complex makes the system more ordered and therefore decreases the entropy (6, 7).

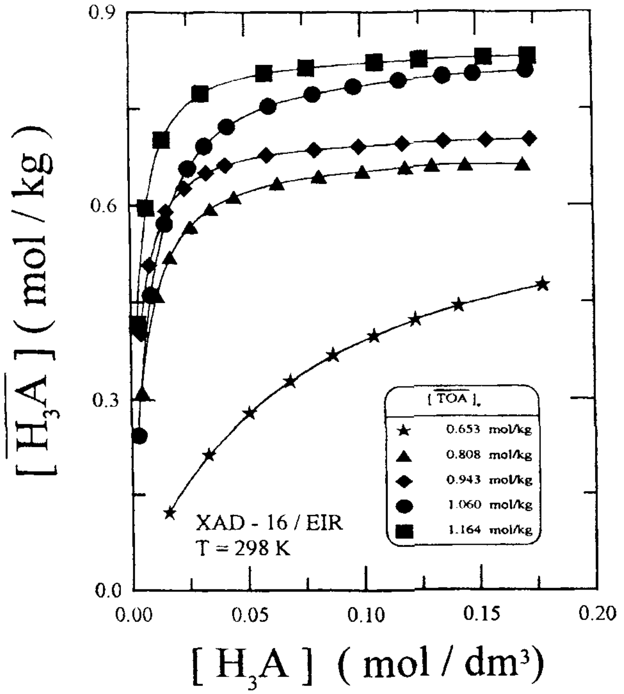

FIG. 4 Effect of citric acid concentration in the aqueous phase on equilibrium distribution in XAD-16/EIR system at 298 K.

It should be noted that the sorption isotherms obtained at different temperatures are also well fit by the Langmuir equation. The temperature dependence of K_L can be used to determine the isosteric enthalpy of sorption, ΔH, the enthalpy of sorption at a fixed surface coverage (22, 23):

$$(\partial \ln K_L/\partial T)_\theta = -(\partial \ln[H_3A]/\partial T)_\theta = \Delta H/RT^2 \qquad (3)$$

Therefore, a plot of ln K_L against $1/T$ should be a straight line with a slope of $\Delta H/R$. Figure 10 shows the results. The values of ΔH obtained are -43.35 and -38.12 kJ/mol in XAD-4/EIR and XAD-16/EIR systems, respectively. In general, the enthalpy change due to chemical adsorption (40–120 kJ/mol) is considerably larger than that due to physical adsorption (below 40 kJ/mol) (22). Hence, the adsorption of citric acid on these TOA–EIRs is probably due to weak chemical adsorption.

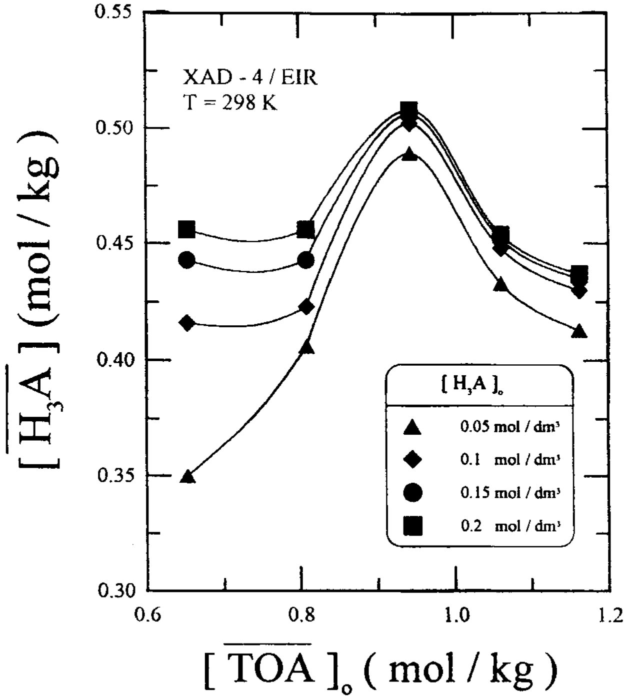

FIG. 5 Effect of TOA concentration on equilibrium distribution in XAD-4/EIR system at 298 K.

Other thermodynamic parameters, such as the apparent free energy (ΔG) and the entropy (ΔS), can be calculated by Eqs. (4) and (5), respectively (23):

$$\Delta G = -RT \ln K_L \tag{4}$$

$$\Delta S = (\Delta H - \Delta G)/T \tag{5}$$

The values of ΔS obtained in this work are -94.56 and -81.21 J/(mol·K) in XAD-4/EIR and XAD-16/EIR systems, respectively, at 298 K. The negative value of ΔS confirms that the sorption of citric acid on EIRs involves a loss of entropy due to the formation of the complexes from more than one species. In contrast to the XAD-16/EIR system, the slightly more negative ΔS in the XAD-4/EIR system could be a result of the steric

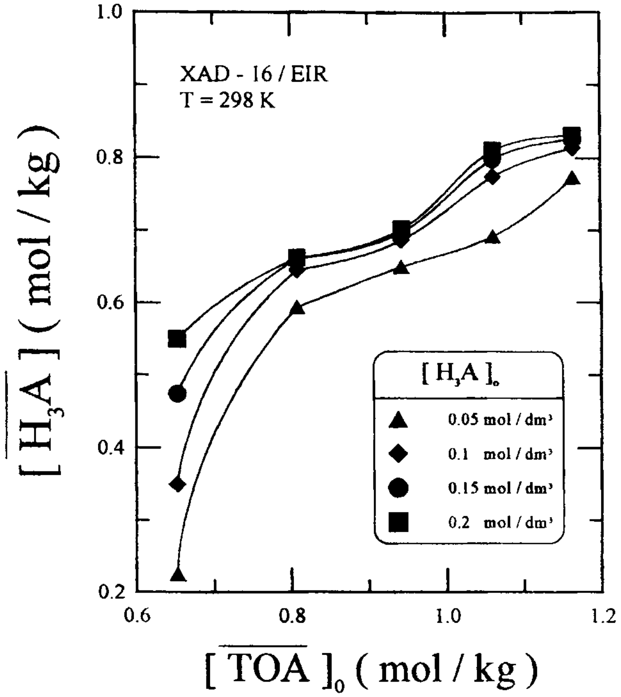

FIG. 6 Effect of TOA concentration on equilibrium distribution in XAD-16/EIR system at 298 K.

effect on the EIR surface or within the polymeric network, that is, the more restricted reaction environment (19).

Microscopic Analysis of Sorption Equilibria

It was reported that the extractants can exhibit a strong affinity to the polymeric matrix and behave as in the liquid state (12, 14, 15). Although the extracted species in the EIR system may be less solvated than in an organic solvent (13), the mechanism of metal extraction with EIR is generally similar to that of solvent extraction, provided that the extractants are not chemically bonded to the polymeric matrix (13–18).

In this regard, the sorption of citric acid with TOA–EIR can be expressed by the following stoichiometric relation (4–8):

$$pH_3A + q\overline{TOA} \Leftrightarrow \overline{(H_3A)_p(TOA)_q}; \quad K_{pq} \tag{6}$$

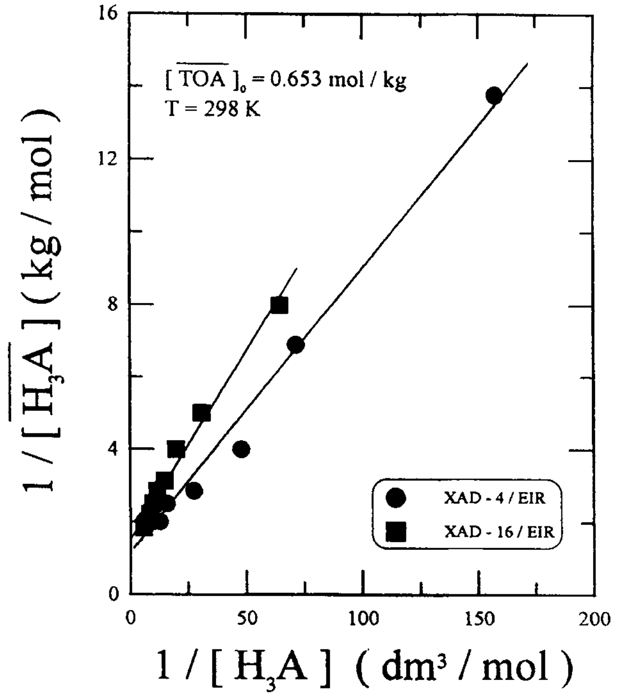

FIG. 7 Typical Langmuir plot of sorption equilibrium data at 298 K.

TABLE 1
Parameters of Langmuir Equation Obtained under Various Temperatures and TOA Concentrations

$\overline{[TOA]}_0$ (mol/kg)	T (K)	XAD-4/EIR		XAD-16/EIR	
		K_L (dm^3/mol)	$\overline{[H_3A]}_\infty$ (mol/kg)	K_L (dm^3/mol)	$\overline{[H_3A]}_\infty$ (mol/kg)
0.653	298	65.94	0.440	14.48	0.660
0.808	298	319.8	0.435	160.3	0.691
0.943	298	426.4	0.512	275.5	0.720
1.060	298	439.5	0.438	320.9	0.843
1.164	298	420.2	0.456	345.9	0.847
0.943	288	630.4	0.444	359.9	0.671
0.943	293	532.5	0.498	322.7	0.699
0.943	303	292.2	0.601	180.1	0.757
0.943	308	233.0	0.638	115.6	0.761

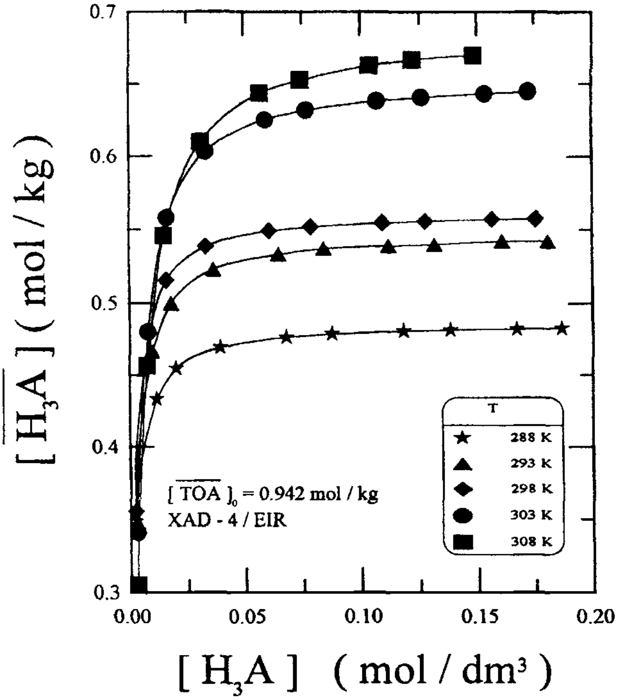

FIG. 8 Temperature dependence of equilibrium distribution in XAD-4/EIR system.

where the overbar refers to the EIR phase. The sorption equilibrium constant, K_{pq}, is given by

$$K_{pq} = [\overline{(H_3A)_p(TOA)_q}]/\{[H_3A]^p[\overline{TOA}]^q\} \qquad (7)$$

The total concentration of citric acid in the EIR phase is

$$[\overline{H_3A}]_t = \sum_p \sum_q p[\overline{(H_3A)_p(TOA)_q}] = \sum_p \sum_q pK_{pq}[H_3A]^p[\overline{TOA}]^q \qquad (8)$$

In Eq. (3), the contribution of the "physical" sorption of citric acid with TOA–EIR is ignored because the adsorption of citric acid with the unimpregnated resins is found to be only 8.07 × 10^{-3} mol/kg for XAD-4 at 298 K (19).

The term [$\overline{TOA}$] in Eqs. (8) and (9) is calculated by the following mass balance equation since the solubility of TOA in acidic aqueous solution is negligibly small.

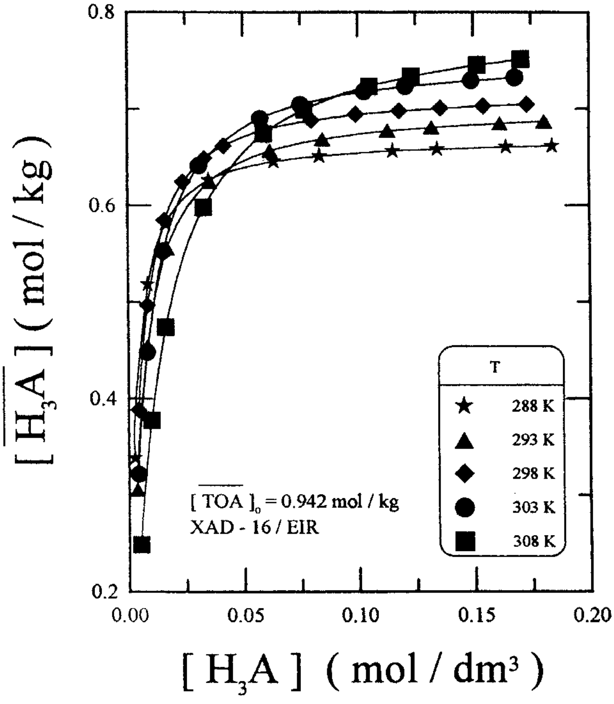

FIG. 9 Temperature dependence of equilibrium distribution in XAD-16/EIR system.

$$
\begin{aligned}
[\overline{TOA}]_0 &= [\overline{TOA}] + \sum_p \sum_q q[\overline{(H_3A)_p(TOA)_q}] \\
&= [\overline{TOA}] + \sum_p \sum_q qK_{pq}[H_3A]^p[\overline{TOA}]^q
\end{aligned}
\tag{9}
$$

The computer program LETAGROP-DISTR was originally developed to analyze the distribution data of a component between two phases using the least-squares error method (24). The "best" equilibrium constants for the formation of a set of complexes with up to four components can be calculated. This program has been extended to five-component systems and successfully used to treat equilibrium data in the extraction of metals with some organophosphoric acids (25–27). In this work we further modify this program to determine the equilibrium constants for the formation of various complexes between organic acid and TOA.

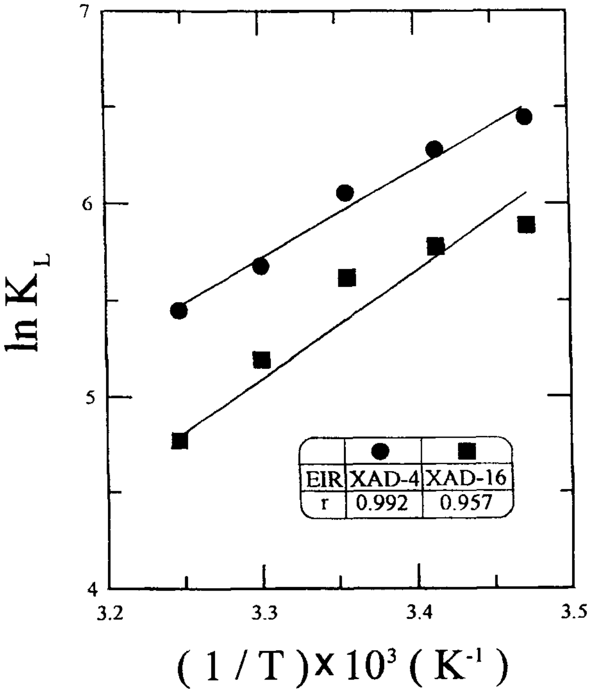

FIG. 10 Effect of temperature on Langmuir constant.

In this calculation the computer searches for the best set of equilibrium constants for a given model that would minimize the error squares sum defined by (24):

$$U_{\min} = \sum (\log D_{\text{expt}} - \log D_{\text{calc}})^2 \qquad (10)$$

where D_{expt} is the measured distribution ratio of the acid and D_{calc} is the corresponding value calculated by the program considering the above mass-balance equations. This program also calculates the standard deviation $\sigma(\log D)$, defined by

$$\sigma(\log D) = \sqrt{(U_{\min}/N_p)} \qquad (11)$$

where N_p is the degree of freedom, that is, the difference between the total number of experimental data points and the total number of equilibrium constants calculated.

The best-fit formulations for the complex (p,q) are found to be (1,1) in the XAD-4/EIR system and (1,2) in the XAD-16/EIR system. The corresponding values of K_{pq} and $\sigma(\log D)$ are calculated to be 0.11 dm^3/mol and 0.468, and 0.15 (kg/mol)(dm^3/mol) and 0.418, respectively. The present results for the XAD-4/EIR system are different from those obtained in the case of comparatively low acid concentrations (19). Such discrepancies may be partly due to different sources of the resins, as mentioned above. In the case of liquid–liquid extraction of citric acid with TOA in xylene, however, the equilibrium constants were found to be $K_{11} = 0.68$ dm^3/mol, $K_{12} = 1.68$ (dm^3/mol)^2, and $K_{23} = 4.15 \times 10^2$ (dm^3/mol)^4, respectively, at 298 K (7).

The different citric acid–TOA complexes which exist in the XAD-4/EIR and XAD-16/EIR systems may be caused by the different pore volumes of the two resins. The mean pore volume of XAD-16 (1.404 cm^3/g) is greater by about 40% than that of XAD-4 (0.974 cm^3/g), which means that the larger and the more steric complex would probably form in the XAD-16/EIR system.

CONCLUSIONS

The sorption equilibria of citric acid from concentrated aqueous solutions with TOA-impregnated resins have been studied in the temperature range 288–318 K. The impregnation of TOA on XAD-4 and XAD-16 resins can be achieved by the dry method to about 98%, and to a content below 1.339 and 1.542 mol/kg, respectively. The equilibrium distribution of citric acid in the XAD-16/EIR system is larger by about 60% compared to the XAD-4/EIR system under the same conditions. This is probably due to the different pore volumes and swellings of the two resins. The distribution data can be well described by the Langmuir equation. The values of ΔH obtained are -43.35 and -38.12 kJ/mol in the XAD-4/EIR and XAD-16/EIR systems, respectively. Also, the values of ΔS are -94.56 and -81.21 J/(mol·K), respectively, at 298 K. The sorption of citric acid on TOA–EIRs is due to weak chemical adsorption, and all sorption reactions are favored by entropy change and unfavored by enthalpy change. From numerical analysis of the chemical reaction model, the acid–TOA complexes $\overline{(H_3A)(TOA)}$ and $\overline{(H_3A)(TOA)_2}$ form in the XAD-4/EIR and XAD-16/EIR phases, respectively.

ACKNOWLEDGMENT

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NOMENCLATURE

EIR	extractant-impregnated resin
H_3A	citric acid
K_{pq}	sorption equilibrium constant defined in Eq. (7) [mol/kg)$^{1-q}$(dm^3/mol)^p]
p	number of citric acid molecules involved in the complex
q	number of TOA molecules involved in the complex
r	correlation coefficient
T	temperature, K
TOA	tri-*n*-octylamine
[ ]	concentration of species in the brackets (mol/kg or mol/dm^3)
ΔG	apparent Gibbs free energy change for sorption reaction (kJ/mol)
ΔH	apparent enthalpy change for sorption reaction (kJ/mol)
ΔS	apparent entropy change for sorption reaction [J/(mol·K)]

Subscript

0	initial

Superscript

overbar	EIR phase

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