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Extraction Mechanism and Behavior of Malic Acid with Tri-octylamine (TOA)

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ABSTRACT

Liquid–liquid equilibria of malic acid with tri-octylamine (TOA) as extractant and 1-octanol, methyl isobutyl ketone (MIBK) and chloroform as the diluents were investigated, and Fourier transform infrared spectrometer (FTIR) spectrum of the organic phase samples loaded with malic acid were taken to obtain the stoichiometry of complex. The extraction behavior depends on the concentration of malic acid in the equilibrium aqueous phase, species of diluent, and TOA concentrations in the organic phase. A large degree of extraction in protonated diluent appeared at low equilibrium malic acid concentration in the aqueous phase, while the sequence was as MIBK > 1-octanol > chloroform at high equilibrium malic acid concentration. It has the same sequence as the degree of extraction at overloading region. Malic acid is bonded to TOA

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in three forms of (1,2), (1,1), and (2,1), and for the complex (1,2), one carboxyl on malic acid was bonded to TOA with ion-pair association and another with hydrogen bond. By using mass action law, and taking some assumptions, an expression of extraction equilibrium was derived, and the apparent extraction equilibrium constants were evaluated. The predict equilibrium data agreed well with the experimental values.

Key Words: TOA; Malic acid; Extraction equilibrium; Ion-pair association; Hydrogen bond association.

INTRODUCTION

In recent years, reactive extraction processes have received increasing attention for recovery of carboxylic acids from dilute aqueous solutions, notably with hydrophobic tertiary amines dissolved in various organic diluents.[1–7]

It is very important for the solutes with multiple functional groups to get the stoichiometry and association forms of complex formation for setting up mathematic models and to explore the mechanism. Di-carboxylic acid is a typical solute with multiple functional groups. Tamada and King[8] studied the FTIR spectra of complexes of fumaric acid, maleic acid, and succinic acid with TOA in chloroform. Fumaric acid formed (1,2) acid–amine complexes with excess amine in chloroform, while the complexes of succinic and maleic acids showed (1,1) stoichiometry. Gusakova et al.[9] proposed that the diluent also affected the complex formation, and there was less overloading tendency with proton-donating diluent. Alcohol diluent might interfere with internal hydrogen bonding of some di-carboxylic acids allowing formation of (1,2) complex. Kirsch and Maurer[10] obtained similar results for oxalic acid in TOA with MIBK, chloroform, and toluene as the diluent.

All of the research is involved in the stoichiometry of complex formation only. It is very important to ascertain the association forms of complex with acid and TOA[3] to better understand the reactive extraction mechanism.

Malic acid (hydroxy-succinic acid, $\mathrm{p}K_{\mathrm{a1}} = 3.40$, $\mathrm{p}K_{\mathrm{a2}} = 5.11$)[11] is an important di-carboxylic acid, widely used in food, tobacco, medicine, and daily supplies industry. In the present work, extraction equilibrium of malic acid with TOA in 1-octanol, MIBK, and chloroform, were investigated, and FTIR spectrum of organic phase samples loaded with malic acid were analyzed. The primary goals were to analyze the stoichiometry and the associated forms of complex formation by batch experimental data and infrared spectrum of the organic-samples-loading solute, to propose a mathematic model describing the relationship between TOA and malic acid, to obtain model parameters by fitting equilibrium data, and to understand the reactive extraction mechanism further.

EXTRACTION EXPERIMENTS

All extraction experiments were conducted with 50-mL conical flasks at $25 \pm 0.5^{\circ}$C. The conical flasks containing mixtures of 10-mL extractant and 10-mL malic acid aqueous solution were shaken for about 3 h in a shaker bath with a vibrating rate of 220 ± 2 rpm, left to equilibrate for 0.5 h, and then separated in two phases. An aqueous phase sample was then taken from the bottom layer for pH and acid concentration analyses.

ANALYSES

The solute concentrations in equilibrium aqueous phase (x) were titrated with NaOH by using phenolphthalein as an indicator. The solute concentrations in equilibrium organic phase (y) were calculated by material balance. The pretest of stripping organic phase showed that the deviation was within 3%. The pH value of aqueous phase was determined by a pH meter, Hanna pH 201 model.

In the experiments to confirm the stoichiometry of complex formation, the FTIR spectra of the organic-samples-loading solute were investigated by infrared spectrometer, Shimadzu FTIR-8201PC, and all measurements were done with a cell equipped with CaF_2 windows of 0.05 mm between two CaF_2 plates.

RESULTS AND DISCUSSION

Effect of Diluents on Extraction Equilibrium

It is known that the distribution coefficient, D, depends on the type of diluent used. A polar diluent will increase the degree of extraction of relative low polar amines by providing additional solvating power, which allows higher levels of polar-amine complexes to stay in the organic phase.

As indicated by the D values in the various diluents in Figs. 1 through 3, the degree of extraction of malic acid also depends on the acid concentration in the equilibrium aqueous phase. The sequence of the degree of extraction is 1-octanol > chloroform > MIBK at relatively low equilibrium solute concentrations, which is in agreement with the result that protic or polar

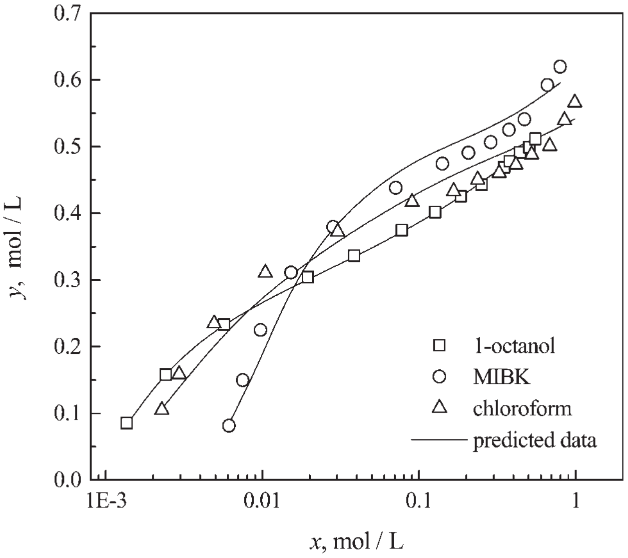

Figure 1. Dependence of extraction equilibrium on diluent for 0.50 mol/L TOA.

diluent is more favorable for extraction of polar solute.[12] Conversely, the degree of extraction shows MIBK > 1-octanol > chloroform at high equilibrium solute concentrations, which is the same sequence as the polarity of the diluent. Meanwhile, overloading also appears at this concentration region, indicating that a complex with more than one acid per amine has been formed.

Effect of TOA Concentration on the Extraction Equilibrium

TOA concentration has a strong effect on the equilibrium distribution of acid as shown in Figs. 4 and 5. Similarly, the degree of extraction for malic acid depends on the acid concentration in the equilibrium aqueous phase. The greater the TOA concentration, the less the degree of extraction at relatively low equilibrium solute concentrations, which is in agreement with the result that protic or polar diluent has a solvating effect for TOA.[2]

Moreover, malic acid is extracted into the organic phase very effectively at a higher TOA concentration at a higher equilibrium solute concentration. The malic acid concentration in organic phase approaches the initial TOA concentration S_0 at a high equilibrium solute concentration, and equivalent to S_0 in the saturation region.

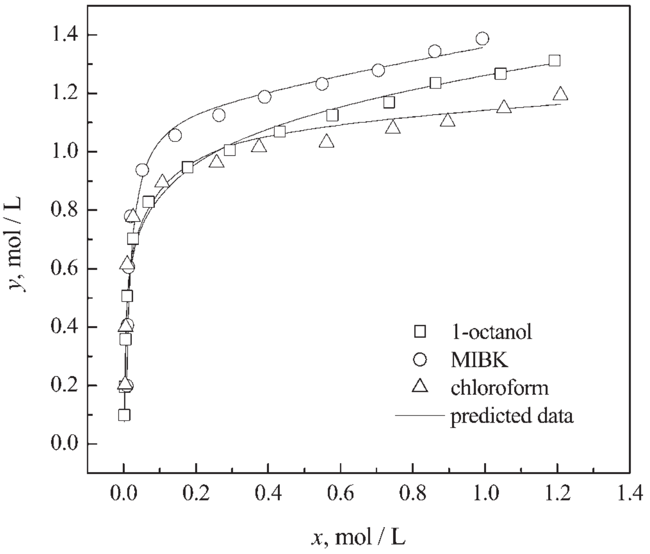

Figure 2. Dependence of extraction equilibrium on diluent for 1.10 mol/L TOA.

FTIR Spectra Analysis

Figure 6 shows the typical spectra of malic acid in the mixed solvent. The concentration ratios of TOA to malic acid in the sample are 2.2, 4.3, and 6.5. Two bands are observed, one at 1737.7 cm^{-1} and another at 1595.1 cm^{-1}. The band at 1737.7 cm^{-1} results from the C═O stretching vibration in a carboxyl group, which is bonded to an amine molecule with a hydrogen bond or not bonded. The band at 1595.1 cm^{-1} is caused by the (COO^-) stretching vibration in a carboxyl group of malic acid molecule bonded to an amine molecule with an ion-pair association. This band assignment is in agreement with results by Kirsch and Maurer.[10]

Furthermore, the band of the carboxylate group stays almost unchanged with an increasing concentration ratio of TOA to malic acid at a fixed TOA concentration, indicating that a carboxyl group on malic acid cannot combine the second TOA by ion-paring association.

Stoichiometry of Complex Formation with Malic Acid and TOA

Most organic acids, including malic acid, exist as dimer in the organic phase due to their strong intermolecular hydrogen-bonding, especially in

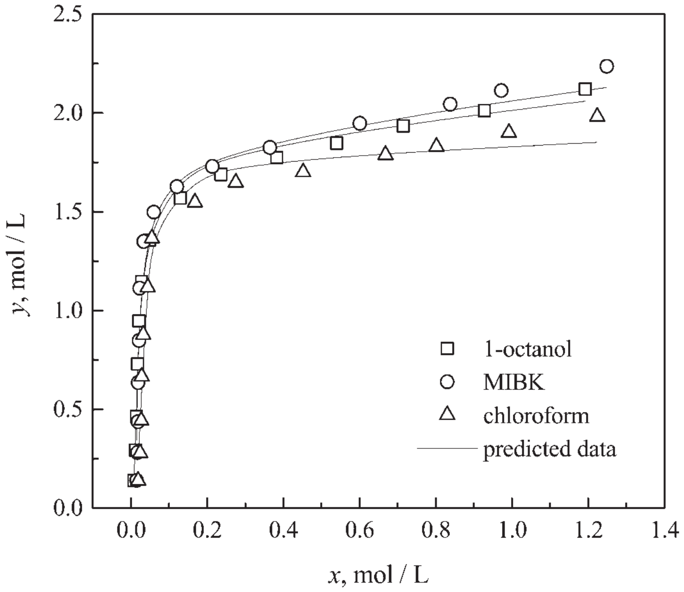

Figure 3. Dependence of extraction equilibrium on diluent for 1.76 mol/L TOA.

nonpolar solvent.[13,14] The stoichiometry of complex formation of TOA and malic acid in the organic phase is determined first by the following method as described elsewhere.[15]

Using the mass action law[13] and neglecting physical partitioning of malic acid between diluent and water due to the low distribution coefficient, the extraction equilibrium for malic acid can be written as a reaction of 1 molecule of malic acid, H_2A, and p molecules of TOA, R_3N, to form a (1, p) complex. With respect to the apparent equilibrium constants, K_{1p}:

$$H_2A + p\overline{R_3N} \overset{K_{1p}}{\longleftrightarrow} \overline{H_2A \cdot (R_3N)_p} \quad (1)$$

where the organic phase species are marked with an overbar.

With appropriate material balances, the molar concentration of malic acid in the organic phase y can be expressed as:

$$y = K_{1p}[H_2A][\overline{R_3N}]^p = K_{1p}[H_2A](S_0 - py)^p \quad (2)$$

where the species concentrations are denoted by square brackets and are expressed in molar terms. S_0 is the initial molar concentration of TOA in the organic phase.

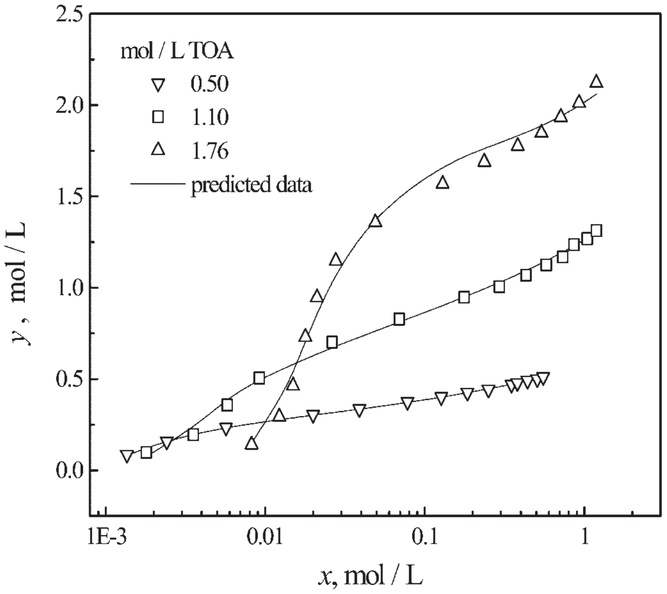

Figure 4. Dependence of extraction equilibrium on TOA concentration with 1-octanol as diluent.

Equation (2) can be rearranged to:

$$\log\frac{y}{[\mathrm{H_2A}]} = \log K_{1p} + p\log(S_0 - py) \qquad (3)$$

According to Eq. (3), the p value for a certain malic acid concentration in the organic phase can be evaluated by simple linear regression and trial-and-error calculation for three of the experimental data closed.

As shown in Fig. 7, the p values increase from 0.6 to 2.1 with decreasing malic acid concentration in organic phase. The p values between 0.6 and 1.05 with MIBK as the diluent, 1.76 mol/L TOA in chloroform as well as in 1-octanol, reveals that the stoichiometry of complex formation with malic acid and TOA are (1,1) and (2,1), while those are (1,1), (1,2), and (2,1) for 0.5, 1.00 mol/L TOA in chloroform or in 1-octanol as indicated by the p value from 0.6 to 2.1.

Obviously, the second carboxyl group on malic acid is bonded to TOA with a hydrogen bond based on the infrared spectra result and the stoichiometry of complex formation with malic acid and TOA in this article. The (1,2) complex can be expressed as follows:

$$\mathrm{R_3NH^{+-}OOC{-}CH(OH){-}CH_2{-}COOH \cdots NR_3}$$

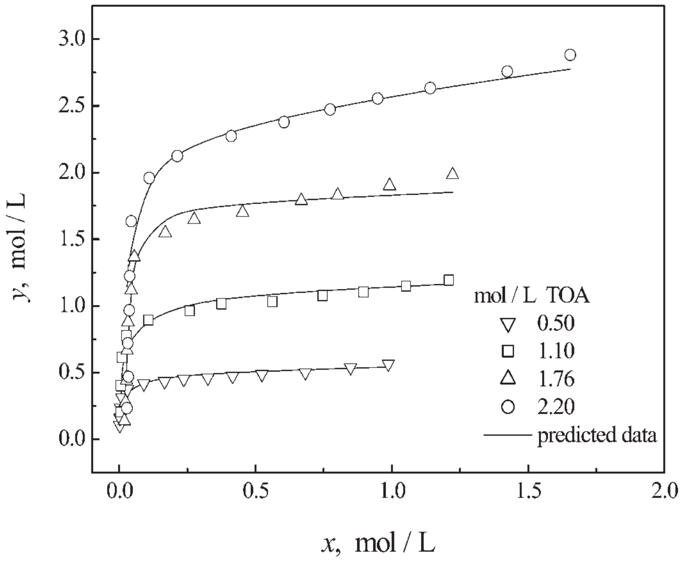

Figure 5. Dependence of extraction equilibrium on TOA concentration with chloroform as diluent.

Extraction Equilibrium Description

The reactive extraction equilibrium for polar dilute solution of organic solutes could be described by the mass action law in which the equilibrium behavior can be modeled by postulating the formation of various stoichiometric complexes of acid and amine.[16] A reactive equilibrium description of the system can be written as a set of equilibria involving the dissociation equilibrium of the acid in water, and the formation of a complex with acid and TOA. It is assumed that the complexation reaction between malic acid and TOA took place at the organic-aqueous interface and three types complex (1,2), (1,1), (2,1) were formed in a step-wise manner:

$$\overline{R_3N} + H_2A \overset{K_{11}}{\longleftrightarrow} \overline{R_3N{\cdot}H_2A}, \quad K_{11} = \frac{[\overline{R_3N \cdot H_2A}]}{[\overline{R_3N}][H_2A]} \tag{4}$$

$$\overline{R_3N \cdot H_2A} + \overline{R_3N} \overset{K_{12}}{\longleftrightarrow} \overline{(R_3N)_2 \cdot H_2A}, \quad K_{12} = \frac{[\overline{(R_3N)_2 \cdot H_2A}]}{[\overline{R_3N}][\overline{R_3N \cdot H_2A}]} \tag{5}$$

$$\overline{R_3N \cdot H_2A} + H_2A \overset{K_{21}}{\longleftrightarrow} \overline{R_3N \cdot (H_2A)_2}, \quad K_{21} = \frac{[\overline{R_3N \cdot (H_2A)_2}]}{[HA][\overline{R_3N \cdot H_2A}]} \tag{6}$$

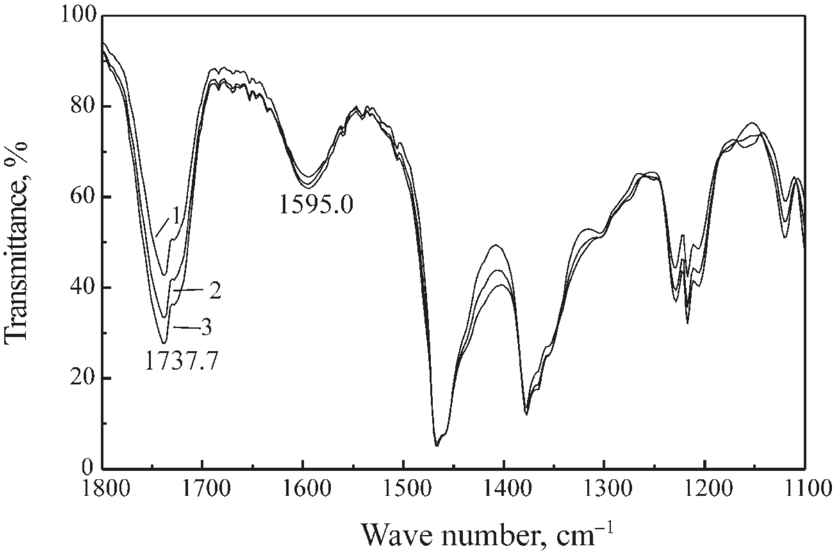

Figure 6. FTIR spectrum for various concentration ratio of TOA to malic acid with 1-octanol as diluent: 1,$N_{TOA/acid} = 2.2$; 2,$N_{TOA/acid} = 4.3$; 3,$N_{TOA/acid} = 6.5$.

With the material balances for the malic acid concentration in the organic phase and TOA concentration,

$$\begin{aligned} y &= [\overline{H_2A}] + [\overline{R_3N \cdot H_2A}] + [\overline{(R_3N)_2 \cdot H_2A}] + 2[\overline{R_3N \cdot (H_2A)_2}] \\ &= [\overline{H_2A}] + K_{11}[\overline{R_3N}][H_2A] + K_{11}K_{12}[\overline{R_3N}]^2[H_2A] \\ &\quad + 2K_{11}K_{21}[\overline{R_3N}][H_2A]^2 \end{aligned} \tag{7}$$

$$\begin{aligned} S_0 &= [\overline{R_3N}] + [\overline{R_3N \cdot H_2A}] + 2[\overline{(R_3N)_2 \cdot H_2A}] + [\overline{R_3N \cdot (H_2A)_2}] \\ &= [\overline{R_3N}] + K_{11}[\overline{R_3N}][H_2A] + 2K_{11}K_{12}[\overline{R_3N}]^2[H_2A] \\ &\quad + K_{11}K_{21}[\overline{R_3N}][H_2A]^2 \end{aligned} \tag{8}$$

and

$$H_2A = \frac{x}{1 + 10^{pH - pK_{a1}} + 10^{2pH - pK_{a1} - pK_{a2}}} \tag{9}$$

where K_{a1} and K_{a2} are the primary and the second dissociation constant of malic acid in water, respectively.

The apparent extraction equilibrium constants K_{11}, K_{12}, and K_{21} were determined by fitting the equilibria data to Eqs. (7)–(9) using computer nonlinear regressions by the Marquadt method, and are shown in Table 1. The

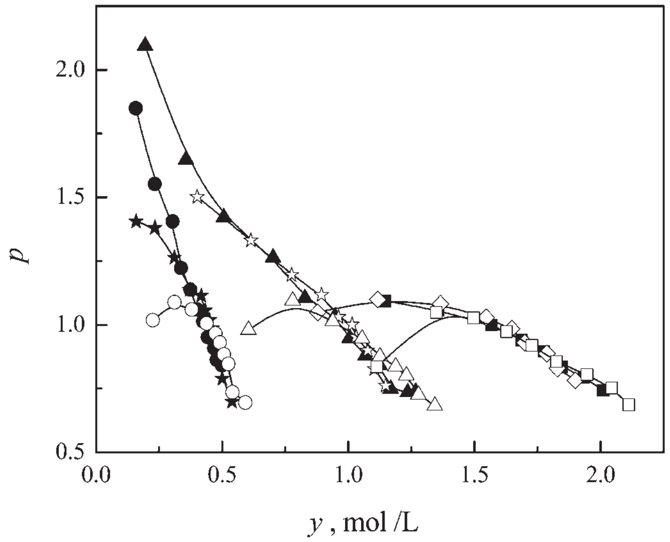

Figure 7. Dependence of the p values on the concentration of malic acid in the organic phase: ●, 0.50 mol/L TOA/1-octanol; ★, 1.10 mol/L TOA/1-octanol; ○, 1.76 mol/L TOA/1-octanol; ▲, 0.50 mol/L TOA/chloroform; ☆, 1.10 mol/L TOA/chloroform; △, 1.76 mol/L TOA/chloroform; ■, 0.50 mol/L TOA/MIBK; ◇, 1.10 mol/L TOA/MIBK; □, 1.76 mol/L TOA/MIBK.

Table 1. Modeling parameters fitted.

Diluent	S_0 (mol/L)	K_{12} (L/mol)	K_{11} (L/mol)	K_{21} (L/mol)	$pH_{a,B}$
1-Octanol	0.500	59.0	390	0.256	4.66
	1.101	14.2	280	0.250	4.45
	1.762	—	120	0.183	3.86
Chloroform	0.500	13.6	330	0.121	4.35
	1.101	8.8	330	0.076	4.40
	1.762	—	115	0.052	4.04
MIBK	0.500	—	165	0.331	3.33
	1.101	—	180	0.317	3.54
	1.762	—	120	0.225	3.53
TOA	2.203	—	85	0.224	3.32

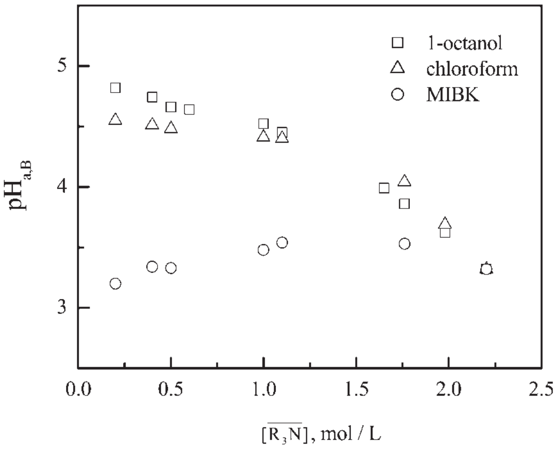

Figure 8. Specific basicity of TOA in different diluents.

K_{11} value is much larger than the K_{12} and K_{21}, which are in accord with other work,[6] that is, the apparent equilibrium constant is inversely proportional to the pK_a.

The specific basicity of TOA, p$H_{a,B}$, stands for the basicity strength of TOA in various diluents, and it is another key factor that determines the extraction equilibrium behavior. The values of p$H_{a,B}$ in MIBK, 1-octanol, and chloroform were measured by the method put forward in previous work,[3] and the results are shown in Fig. 8. It is obvious that log K_{11} increases with increasing p$H_{a,B}$, as shown in Fig. 9, which can be explained as the degree of extraction of TOA increasing with the specific basicity of TOA.

As shown in Figs. 1 through 5, the predicted curves superimpose on the data very well, and deviation between the calculated data and the experimental data are within $\pm 20\%$. Thus, the model is valid in representing equilibrium behavior of malic acid with TOA.

CONCLUSION

The extraction behavior depends on the concentration of malic acid in the equilibrium aqueous phase, diluent type, and TOA concentrations in the organic phase. Protic diluent and low TOA concentration are more effective than others at low equilibrium solute concentrations.

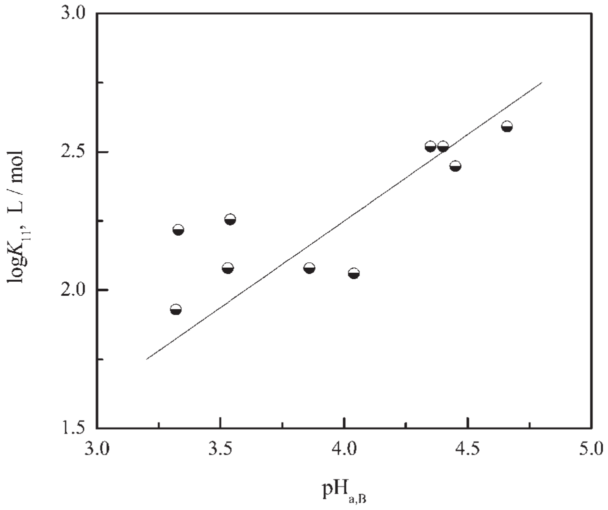

Figure 9. K_{11} vs. $pH_{a,B}$.

Malic acid is bonded to TOA in three forms of (1,2), (1,1), and (2,1), and for the complex (1,2), 1 carboxyl on malic acid was bonded to TOA with ion-pair association and another with a hydrogen bond.

By using mass action law, and some assumptions, an expression of extraction equilibrium was derived, and the apparent extraction equilibrium constants, K_{11}, K_{12}, and K_{21}, were evaluated. The predict equilibrium data agreed well with the experimental values.

NOMENCLATURE

$[H_2A]$ = concentration of undissociated malic acid, mol/L.
$[\overline{R_3N}]$ = concentration of TOA in the organic phase, mol/L.
S_0 = initial concentration of TOA, mol/L.
x = total concentration of malic acid in the aqueous phase, mol/L.
y = total concentration of malic acid in the organic phase, mol/L.
p = the average stoichiometry of complex formation for malic acid to TOA.
K_{11} = apparent chemical association constant of complex (1,1), L/mol.
K_{12} = apparent successive chemical association constant of complex (1,2), L/mol.

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K_{21} = apparent successive chemical association constant of complex (2,1), L/mol.
K_a = dissociation constant of acid, mol/L.
$pH_{a,B}$ = the specific basicity of TOA.

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