On the Possibility of Predicting the Extraction of Dicarboxylic Acids with Tributylphosphate Dissolved in a Diluent

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The extraction of dicarboxylic acids (itaconic, maleic, malic, oxalic, tartaric, and succinic acid) from aqueous solutions with tributylphosphate dissolved in dodecane was studied at different volume phase ratios. The concentration of the acids was varied in a broad range. The experimental data were interpreted by the chemical interaction mechanism. Considering the mass action law, two complexes (one molecule of dicarboxylic acid interacting with one or two molecules of extractant) were assumed to exist in the organic phase, and the corresponding extraction constants were evaluated. It was shown that the number of interacting molecules of the extractant and hence the overall extraction constant strongly depend on the composition of the extraction system. The prediction of acid extraction was possible only for a limited range of acid concentrations. The experimental results revealed that the concentration of the interaction product in the aqueous phase cannot be neglected.

Introduction

Long-chain tertiary amines and tributylphosphate are effective extractants for the removal of carboxylic acids from aqueous solutions. They are strong Lewis bases and interact chemically with the acids. In the general case, p acid (H_qA) molecules interact with n extractant (E) molecules to form complexes. The values of the corresponding overall apparent equilibrium extraction constants ($K_{p,n}$) give grounds to assume that the concentration of the interaction product in the aqueous phase may be neglected[1–11]

$$pH_qA + n\overline{E} \leftrightarrow \overline{(H_qA)_pE_n} \tag{1}$$

For practical application, the activities of the organic phase species are assumed to be proportional to the concentrations of the species and the activity of the acid is assumed to be proportional to the concentration of undissociated acid in the equilibrium aqueous phase. Thus, the constants of proportionality are included in the equilibrium constant. The apparent equilibrium constant for the overall reaction can be written as[2]

$$K_{p,n} = \frac{[\overline{(H_qA)_pE_n}]}{[H_qA]^p[\overline{E}]^n} \tag{2}$$

where molar concentrations are denoted by square brackets; species in the organic phase are marked with an overbar; and q is the number of carboxylic groups.

By neglecting the physical interactions in the system, the efficiency of the mass transfer process can be predicted on the basis of the mass action law, taking into account the apparent equilibrium constant ($K_{p,n}$) and the number of interacting molecules. These parameters are determined in a series of studies, and the obtained values are different depending on the composition of the solvent for the same extractant and organic acid.[2,3,7,10,12–15]

In our previous paper[15] dealing with the extraction of monocarboxylic acids, it was shown that the value of the apparent equilibrium extraction constant ($K_{p,n}$) and the number of interacting molecules (n) depend on both the initial acid concentration and the phase ratio when the experiments are carried out at constant initial aqueous concentration of extracted acid and different concentrations of extractant in the organic phase. More exact results were obtained when several extraction isotherms were considered. In this case, constant equilibrium acid concentration in the aqueous phase at different equilibrium extractant concentrations could be used, and the estimated values did not significantly differ depending on the equilibrium acid concentration. It was also shown that the influence of the diluent on the efficiency of extraction can be positive or negative depending on the extracted acid.

The concentration of the interaction product in the aqueous phase has been generally neglected in the models developed so far.[2,8,10,12,16,17] They take into account the physical extraction by the diluent, the dimerization of the molecules in the organic phase, and various combinations between the molecules of the extractant and the acid but are valid for the studied extraction system only.

The aim of the present study was to examine the extraction of various dicarboxylic acids with tributylphosphate (TBP) dissolved in a diluent, to determine the apparent equilibrium constants and the number of reacting extractant molecules, to elucidate whether the concentration of the interaction product in the aqueous phase could be neglected, and to ascertain whether the extraction of acid can be predicted for a broad range of acid concentrations.

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Extraction Equilibrium

When a basic extractant interacts with a dicarboxylic acid, the equilibrium can be described by different equations, depending on the type of bond formed (hydrogen bond or ion-pair).[3,18–20] Two equilibrium interactions are possible for each bond depending on the number of carboxylic groups involved in the interaction with the extractant.

In the case of ion-pair formation when the extractant interacts with:

(A) One carboxylic group

$$\overline{\mathrm{E}} + \mathrm{H}^+ + \mathrm{HA}^- \leftrightarrow \overline{\mathrm{EH}^+\mathrm{HA}^-} \tag{3}$$

the corresponding apparent extraction equilibrium constant is

$$\begin{aligned} K_{\mathrm{E}(\overline{\mathrm{EH^+HA^-}})} &= \frac{[\overline{\mathrm{EH^+HA^-}}]}{[\overline{\mathrm{E}}][\mathrm{H}^+][\mathrm{HA}^-]} \\ &= \frac{[\overline{\mathrm{EH^+HA^-}}]([\mathrm{H}^+]^2 + K_{\mathrm{a}2,1}[\mathrm{H}^+] + K_{\mathrm{a}2,1}K_{\mathrm{a}2,2})}{[\overline{\mathrm{E}}][\mathrm{H}^+]C_{\mathrm{H_2A}}K_{\mathrm{a}2,1}[\mathrm{H}^+]} \\ &= \frac{m_{(\overline{\mathrm{EH^+HA^-}})}}{[\overline{\mathrm{E}}][\mathrm{H}^+]\alpha_{(\mathrm{HA}^-)}} \\ &= \frac{m_{(\overline{\mathrm{EH^+HA^-}})}}{[\overline{\mathrm{E}}]K_{\mathrm{a}2,1}\alpha_{(\mathrm{H_2A})}} \end{aligned} \tag{4}$$

and

$$m_{(\overline{\mathrm{EH^+HA^-}})} = K_{\mathrm{E}(\overline{\mathrm{EH^+HA^-}})}K_{\mathrm{a}2,1}[\overline{\mathrm{E}}]\alpha_{(\mathrm{H_2A})} \tag{5}$$

or

$$\frac{m_{(\overline{\mathrm{EH^+HA^-}})}}{\alpha_{(\mathrm{H_2A})}} = K_{\mathrm{E}(\overline{\mathrm{EH^+HA^-}})}K_{\mathrm{a}2,1}[\overline{\mathrm{E}}] \tag{6}$$

where $K_{\mathrm{a}2,1}$ and $K_{\mathrm{a}2,2}$ are the first and second dissociation constants of the dicarboxylic acid, respectively,

$$C_{\mathrm{H_2A}} = [\mathrm{HA}^-] + [\mathrm{A}^{2-}] + [\mathrm{H_2A}]$$

is the total concentration of dicarboxylic acid in the aqueous phase,

$$m_{(\overline{\mathrm{EH^+HA^-}})} = \frac{[\overline{\mathrm{EH^+HA^-}}]}{C_{\mathrm{H_2A}}}$$

is the partial distribution coefficient referring to the interaction product ($\overline{\mathrm{EH^+HA^-}}$),

$$\alpha_{(\mathrm{HA}^-)} = \frac{[\mathrm{HA}^-]}{[C_{\mathrm{H_2A}}]} = \frac{K_{\mathrm{a}2,1}[\mathrm{H}^+]}{[\mathrm{H}^+]^2 + K_{\mathrm{a}2,1}[\mathrm{H}^+] + K_{\mathrm{a}2,1}K_{\mathrm{a}2,2}}$$

$$\alpha_{(\mathrm{A}^{2-})} = \frac{[\mathrm{A}^{2-}]}{C_{\mathrm{H_2A}}} = \frac{K_{\mathrm{a}2,1}K_{\mathrm{a}2,2}}{[\mathrm{H}^+]^2 + [\mathrm{H}^+]K_{\mathrm{a}2,1} + K_{\mathrm{a}2,1}K_{\mathrm{a}2,2}}$$

and

$$\begin{aligned} \alpha_{(\mathrm{H_2A})} &= 1 - \alpha_{(\mathrm{HA}^-)} - \alpha_{(\mathrm{A}^{2-})} \\ &= \frac{[\mathrm{H_2A}]}{C_{\mathrm{H_2A}}} \\ &= \frac{[\mathrm{H}^+]^2}{[\mathrm{H}^+]^2 + K_{\mathrm{a}2,1}[\mathrm{H}^+] + K_{\mathrm{a}2,1}K_{\mathrm{a}2,2}} \end{aligned}$$

represent the parts of (HA^-), (A^{2-}), and ($\mathrm{H_2A}$) of the total acid concentration in the aqueous phase ($C_{\mathrm{H_2A}}$), respectively.

(B) Both carboxylic groups

$$\overline{2\mathrm{E}} + 2\mathrm{H}^+ + \mathrm{A}^{2-} \leftrightarrow \overline{(\mathrm{EH}^+)_2\mathrm{A}^{2-}} \tag{7}$$

with the corresponding apparent extraction equilibrium constant

$$\begin{aligned} K_{\mathrm{E}(\overline{(\mathrm{EH^+})_2\mathrm{A}^{2-}})} &= \frac{[\overline{(\mathrm{EH}^+)_2\mathrm{A}^{2-}}]}{[\overline{\mathrm{E}}]^2[\mathrm{H}^+]^2[\mathrm{A}^{2-}]} \\ &= \frac{[\overline{(\mathrm{EH}^+)_2\mathrm{A}^{2-}}]([\mathrm{H}^+]^2 + K_{\mathrm{a}2,1}[\mathrm{H}^+] + K_{\mathrm{a}2,1}K_{\mathrm{a}2,2})}{[\overline{\mathrm{E}}]^2[\mathrm{H}^+]^2C_{\mathrm{H_2A}}K_{\mathrm{a}2,1}K_{\mathrm{a}2,2}} \\ &= \frac{m_{(\overline{(\mathrm{EH^+})_2\mathrm{A}^{3-}})}}{[\overline{\mathrm{E}}]^2[\mathrm{H}^+]^2\alpha_{(\mathrm{A}^{2-})}} \\ &= \frac{m_{(\overline{(\mathrm{EH^+})_2\mathrm{A}^{3-}})}}{[\overline{\mathrm{E}}]^2K_{\mathrm{a}2,1}K_{\mathrm{a}2,2}\alpha_{(\mathrm{H_2A})}} \end{aligned} \tag{8}$$

and

$$m_{(\overline{(\mathrm{EH^+})_2\mathrm{A}^{3-}})} = K_{\mathrm{E}(\overline{(\mathrm{EH^+})_2\mathrm{A}^{2-}})}K_{\mathrm{a}2,1}K_{\mathrm{a}2,2}[\overline{\mathrm{E}}]^2\alpha_{(\mathrm{H_2A})} \tag{9}$$

or

$$\frac{m_{(\overline{(\mathrm{EH^+})_2\mathrm{A}^{3-}})}}{\alpha_{(\mathrm{H_2A})}} = K_{\mathrm{E}(\overline{(\mathrm{EH^+})_2\mathrm{A}^{2-}})}K_{\mathrm{a}2,1}K_{\mathrm{a}2,2}[\overline{\mathrm{E}}]^2 \tag{10}$$

In the case of hydrogen bond formation with:

(C) One carboxylic group

$$\overline{\mathrm{E}} + \mathrm{H_2A} \leftrightarrow \overline{\mathrm{E:H_2A}} \tag{11}$$

with the corresponding apparent extraction equilibrium constant:

$$\begin{aligned} K_{\mathrm{E}(\overline{\mathrm{E:H_2A}})} &= \frac{[\overline{\mathrm{E:H_2A}}]}{[\overline{\mathrm{E}}][\mathrm{H_2A}]} \\ &= \frac{[\overline{\mathrm{E:H_2A}}]([\mathrm{H}^+]^2 + K_{\mathrm{a}2,1}[\mathrm{H}^+] + K_{\mathrm{a}2,1}K_{\mathrm{a}2,2})}{[\overline{\mathrm{E}}]C_{\mathrm{H_2A}}[\mathrm{H}^+]^2} \\ &= \frac{m_{(\overline{\mathrm{E:H_2A}})}}{[\overline{\mathrm{E}}]\alpha_{(\mathrm{H_2A})}} \end{aligned} \tag{12}$$

and

$$m_{(\overline{\mathrm{E:H_2A}})} = K_{\mathrm{E}(\overline{\mathrm{E:H_2A}})}[\overline{\mathrm{E}}]\alpha_{(\mathrm{H_2A})} \tag{13}$$

or

$$\frac{m_{(\overline{\mathrm{E:H_2A}})}}{\alpha_{(\mathrm{H_2A})}} = K_{\mathrm{E}(\overline{\mathrm{E:H_2A}})}[\bar{\mathrm{E}}] \tag{14}$$

(D) Both carboxylic groups

$$2\bar{\mathrm{E}} + \mathrm{H_2A} \leftrightarrow \overline{\mathrm{(E)_2:H_2A}} \tag{15}$$

$$K_{\mathrm{E}(\overline{\mathrm{E_2:H_2A}})} = \frac{[\overline{\mathrm{E_2:H_2A}}]}{[\bar{\mathrm{E}}]^2[\mathrm{H_2A}]} = \frac{m_{(\overline{\mathrm{E_2:H_2A}})}}{[\bar{\mathrm{E}}]^2\alpha_{(\mathrm{H_3A})}} \tag{16}$$

$$m_{(\overline{\mathrm{E_2:H_2A}})} = K_{\mathrm{E}(\overline{\mathrm{E_2:H_2A}})}[\bar{\mathrm{E}}]^2\alpha_{(\mathrm{H_3A})} \tag{17}$$

$$\frac{m_{(\overline{\mathrm{E_2:H_2A}})}}{\alpha_{(\mathrm{H_3A})}} = K_{\mathrm{E}(\overline{\mathrm{E_2:H_2A}})}[\bar{\mathrm{E}}]^2 \tag{18}$$

(E) The two carboxylic groups interact with the extractant by forming different bonds

$$2\bar{\mathrm{E}} + \mathrm{H_2A} \leftrightarrow \overline{\mathrm{E:EH^+HA^-}} \tag{19}$$

$$K_{\mathrm{E}(\overline{\mathrm{E:EH^+HA^-}})} = \frac{[\overline{\mathrm{E:EH^+HA^-}}]}{[\bar{\mathrm{E}}]^2[\mathrm{H_2A}]} = \frac{m_{(\overline{\mathrm{E:EH^+HA^-}})}}{[\bar{\mathrm{E}}]^2\alpha_{(\mathrm{H_2A})}} \tag{20}$$

$$m_{(\overline{\mathrm{E:EH^+HA^-}})} = K_{\mathrm{E}(\overline{\mathrm{E:EH^+HA^-}})}[\bar{\mathrm{E}}]^2\alpha_{(\mathrm{H_2A})} \tag{21}$$

$$\frac{m_{(\overline{\mathrm{E:EH^+HA^-}})}}{\alpha_{(\mathrm{H_2A})}} = K_{\mathrm{E}(\overline{\mathrm{E:EH^+HA^-}})}[\bar{\mathrm{E}}]^2 \tag{22}$$

The above expressions (3 to 22) are valid only in the case when (i) the physical extraction and the influence of diluents on the extractant ability can be neglected, (ii) the concentration of the interaction product in the aqueous phase can be neglected, and (iii) only one acid molecule is involved in the acid−amine complex ($p = 1$).

The overall distribution coefficient ($m_{\mathrm{H_2A}}$) represents the total (analytical) concentration of all possible acid species in the organic phase vs the total concentration in the aqueous phase ($C_{\mathrm{H_2A}}$). Consequently, the overall distribution coefficient ($m_{(\mathrm{H_2A})}$) can be expressed as a sum of the partial distribution coefficients

$$\begin{aligned} m_{(\mathrm{H_2A})} &= m_{(\overline{\mathrm{EH^+HA^-}})} + m_{(\overline{\mathrm{E:H_2A}})} + \\ &\quad m_{(\overline{\mathrm{(EH^+)_2A^{3-}}})} + m_{(\overline{\mathrm{E_2:H_2A}})} + m_{(\overline{\mathrm{E:EH^+HA^-}})} \\ &= K_{\mathrm{E}(\overline{\mathrm{EH^+HA^-}})}K_{\mathrm{a2,1}}[\bar{\mathrm{E}}]\alpha_{(\mathrm{H_2A})} + \\ &\quad K_{\mathrm{E}(\overline{\mathrm{E:H_2A}})}[\bar{\mathrm{E}}]\alpha_{(\mathrm{H_2A})} + \\ &\quad K_{\mathrm{E}(\overline{\mathrm{(EH^+)_2A^{2-}}})}K_{\mathrm{a2,1}}K_{\mathrm{a2,2}}[\bar{\mathrm{E}}]^2\alpha_{(\mathrm{H_2A})} + \\ &\quad K_{\mathrm{E}(\overline{\mathrm{E_2:H_2A}})}[\bar{\mathrm{E}}]^2\alpha_{(\mathrm{H_3A})} + K_{\mathrm{E}(\overline{\mathrm{E:EH^+HA^-}})}[\bar{\mathrm{E}}]^2\alpha_{(\mathrm{H_2A})} \end{aligned} \tag{23}$$

or

$$\frac{m_{(\mathrm{H_2A})}}{\alpha_{(\mathrm{H_2A})}} = K_{R(1:1)}[\bar{\mathrm{E}}] + K_{R(1:2)}[\bar{\mathrm{E}}]^2 \tag{24}$$

or

$$\begin{aligned} \frac{m_{(\mathrm{H_2A})}}{\alpha_{(\mathrm{H_2A})}} &= [\bar{\mathrm{E}}](K_{R(1:1)} + K_{R(1:2)}[\bar{\mathrm{E}}]) \\ &= [\bar{\mathrm{E}}]^2\left(\frac{K_{R(1:1)}}{[\bar{\mathrm{E}}]} + K_{R(1:2)}\right) \\ &\approx K_{1,n}[\mathrm{E}]^n \end{aligned} \tag{24a}$$

where

$$K_{R(1:1)} = K_{\mathrm{E}(\overline{\mathrm{EH^+HA^-}})}K_{\mathrm{a2,1}} + K_{\mathrm{E}(\overline{\mathrm{E:H_2A}})}$$

and

$$K_{R(1:1)} = K_{\mathrm{E}(\overline{\mathrm{EH^+HA^-}})}K_{\mathrm{a2,1}} + K_{\mathrm{E}(\overline{\mathrm{E:H_2A}})}$$

Equations 24 and 24a determine the apparent equilibrium extraction constants $K_{R(1:1)}$ and $K_{R(1:2)}$ provided the equilibrium (free) extractant concentration is known. To this purpose, the real value of n (the number of extractant molecules interacting with one molecule of dicarboxylic acid) should be known. n may vary between 1 and 2.

For the determination of n the logarithmic form of eq 24a may be used

$$\begin{aligned} \log m_{(\mathrm{H_2A})} - \log \alpha_{(\mathrm{H_2A})} &= \log[\bar{\mathrm{E}}] + \log(K_{R(1:1)} + K_{R(1:2)}[\bar{\mathrm{E}}]) \\ &= 2\log[\bar{\mathrm{E}}] + \log\left(\frac{K_{R(1:1)}}{[\bar{\mathrm{E}}]} + K_{R(1:2)}\right) \\ &\approx n\log[\mathrm{E}] + \log K_{1,n} \end{aligned} \tag{25}$$

Equation 25 shows the logarithmic dependence of the overall distribution coefficient, corrected for the part of undissociated molecules, on the extractant concentration. It will be linear with a slope of 1 when $K_{R(1:2)} \approx 0$ and a slope of 2 when $K_{R(1:1)} \approx 0$. In the intermediate case, when both constants differ from zero, the above-mentioned dependence will be an almost straight line (slightly concave) with a slope of $1 \leq n \leq 2$. This means that n will change continuously as a function of extractant concentration. At low extractant concentrations, interaction between one molecule of extractant and one molecule of diacid will predominate, whereas at higher extractant concentrations two molecules of extractant will interact with one molecule of diacid. It is very important in which range of extractant concentrations the experiments are carried out, because n and $K_{1,n}$ depend on the equilibrium extractant concentrations and are valid only for the checked range of equilibrium extractant concentrations. As an illustration, the graphical presentation of the numerical solution of eq 25 is shown in Figure 1 for $K_{R(1:1)} = 2.0$ and $K_{R(1:2)} = 2.0$. The dependence of n and $K_{1,n}$ on the

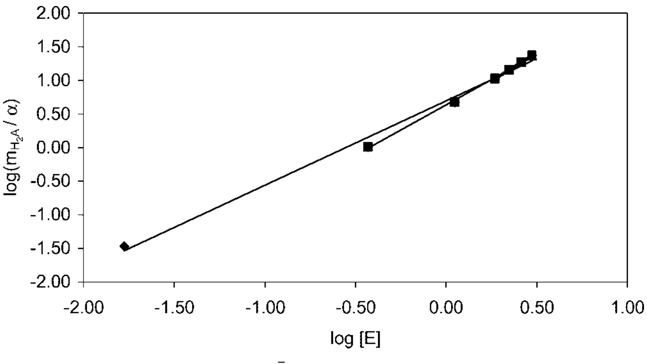

Figure 1. $\log(m_{(\mathrm{H_2A})}/\alpha)$ vs $\log[\bar{\mathrm{E}}]$. Solution of eq 25 for $K_{R(1:1)} = 2.0$ and $K_{R(1:2)} = 2.0$.

Table 1. Characteristics of the Reagents

substance	formula	purity/mass %	mol wt/g·mol^{-1}	pK_a (25 °C)
oxalic acid	HOOCCOOH	99	90.04	1.25; 4.27
maleic acid	HOOCCH=CHCOOH (cis)	99	116.07	1.87; 6.07
succinic acid	$HOOCCH_2CH_2COOH$	99	118.09	4.20; 5.64
itaconic acid	$HOOCCH_2(C{=}CH_2)COOH$	99	130.10	3.65; 5.13
malic acid	$HOOCCH_2CHOHCOOH$	99	134.09	3.22; 4.70
tartaric acid	HOOCCHOHCHOHCOOH	99	150.09	3.01; 4.38
tri-*n*-butyl phosphate	$(CH_3CH_2CH_2CH_2O)_3PO$	99	266.32	
dodecane	$CH_3(CH_2)_{10}CH_3$	99	173.30	

range of equilibrium extractant concentrations is evident. When the range of equilibrium extractant concentrations is (0.0168 to 2.97) mol·L^{-1}, the obtained values of n and $K_{1,n}$ are 1.26 and 4.96, respectively; when it is (0.372 to 2.97) mol·L^{-1}, they are 1.51 and 4.33; and when it is (1.86 to 2.97) mol·L^{-1}, they are 1.70 and 3.69. The obtained values of n and $K_{1,n}$ will also depend on the acid concentration because it influences the free extractant concentration.

The number of interacting extractant molecules should be taken into account in the calculation of the equilibrium (free) extractant concentration

$$[\overline{E}] = [\overline{E}]_{in} - n_E \overline{C}_{H_2A} \qquad (26)$$

To evaluate n, eq 25 transforms to:

$$\log m_{(H_2A)} - \log \alpha_{(H_2A)} \approx \log K_{1,n} + n \log([\overline{E}]_{in} - n_E \overline{C}_{H_2A}) \approx \log K_{1,n} + n[\overline{E}] \qquad (27)$$

supposing that $n_E = 1$ or 2. Equation 27 can also be solved by iteration supposing that $n_E = n$.

The number of extractant molecules interacting with one molecule of diacid is actually unknown. Therefore, n can be only determined when $\bar{C}_{H_2A} \ll [\bar{E}]_{in}$ and $n_{\bar{E}} C_{H_2A}$ may be neglected. Generally, different extractant concentrations are used for the determination of n at a constant initial acid concentration.[7,9,13,15,21]

It is very difficult to maintain $\bar{C}_{H_2A} \ll [\bar{E}]_{in}$ in this case, particularly when the overall distribution coefficient has a high value. Depending on the value of n_E used for calculating the free extractant concentration (1 or 2) by expression 27, different values for the slope and for n will be obtained, as shown in the Results and Discussion. Preferably, a constant low equilibrium acid concentration in the aqueous phase should be maintained. For this purpose, the extraction isotherms for different extractant concentrations should be known. This would permit the use of different acid concentrations in the organic phase at a constant equilibrium acid concentration in the aqueous phase and different extractant concentrations.

The problem becomes more complicated when the diluent significantly influences the extractant ability and the concentration of the interaction product in the aqueous phase cannot be neglected. These phenomena were observed for some dicarboxylic acids in our experimental work.

Experimental

Reagents. (a) Extractants. Tributylphosphate (TBP) with 99 mass % purity was supplied by Acros Organics. It was used as extractant without any further purification.

(b) Diluents. Dodecane from Acros Organics with 99 mass % purity was utilized as inactive diluent.

(c) Dicarboxylic Acids. Oxalic acid (99 mass %), maleic acid (99 mass %), succinic acid (99 mass %), itaconic acid (99 mass %), malic acid (99 mass %), and tartaric acid (99 mass %) were provided by Sigma Aldrich Co.

Aqueous solutions were prepared by dissolving different quantities of the organic acid in deionized water (Millipore Milli-Q Water System) without pH adjustment. The acid concentrations were between (0.0721 and 0.250) mol·L^{-1} with an accuracy of ± 1 %.

The characteristics of the reagents used in this study are shown in Table 1.

Experimental Procedure

The experiments were carried out in 125 mL separatory funnels. The organic and the aqueous phases were shaken on a shaking machine AGITELEC at a frequency of 280 rpm at ambient temperature (20 ± 1) °C for 30 min. This mixing time was sufficient for the liquid–liquid equilibrium to be reached in all studied systems.

The pH of the aqueous phase before extraction and after phase separation was measured with a WTW microprocessor pH-meter equipped with a temperature compensating probe. The volume

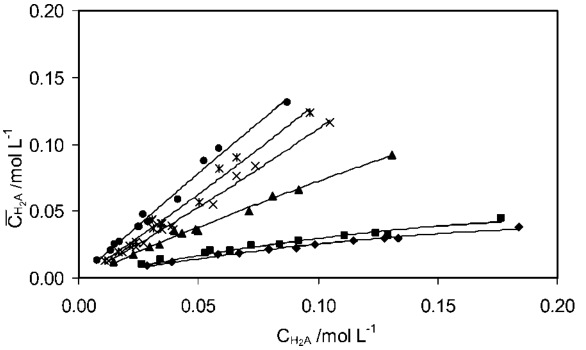

Figure 2. Equilibrium isotherms of oxalic acid for TBP dissolved in dodecane. Symbols: ♦, 10; ■, 30; ▲, 50; ×, 60; *, 70; •, 80 % vol.

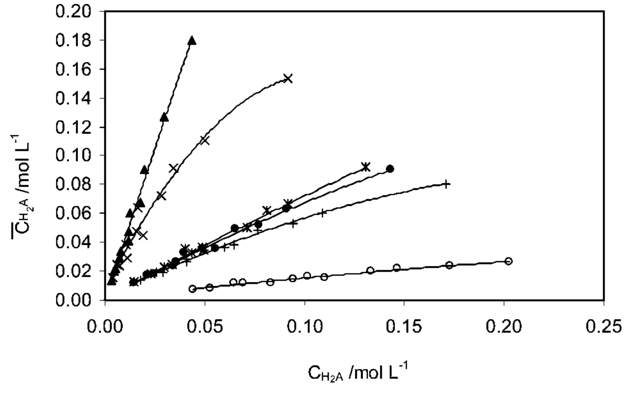

Figure 3. Equilibrium isotherms for the extraction of the studied acids with TBP and dodecane (1:1 volume ratio). Symbols: ▲, succinic acid; ×, itaconic acid; *, oxalic acid; •, malic acid; +, maleic acid; ○, tartaric acid.

Table 2a. Values of the Overall Apparent Extraction Coefficient ($K_{1,n}$) and the Apparent Number of Interacting Extractant Molecules (n) Determined from the Dependence $\log(m_{(H_2A)}/\alpha)$ vs $\log[\bar{E}]$ at a Constant Initial Acid Concentration in the Aqueous Phase (First Method)

acid	$[E]_{in}$ (from/to)	$(C_{H_2A})_{in}$	n when $n_E = 1$	n when $n_E = 2$	n when $n_E = n$	$K_{1,n}$ when $n_E = 1$	$K_{1,n}$ when $n_E = 2$	$K_{1,n}$ when $n_E = n$
SA	0.361 to 2.88	0.0729	1.47	1.44	1.46	2.15	2.30	2.22
SA	0.361 to 2.88	0.110	1.42	1.38	1.40	2.28	2.53	2.38
SA	0.361 to 2.88	0.156	1.36	1.29	1.34	2.45	2.85	2.58
SA	0.361 to 2.88	0.224	1.28	1.15	1.25	2.72	3.38	2.87
MA	0.361 to 2.88	0.0839	1.94	1.95	1.95	0.329	0.337	0.337
MA	0.361 to 2.88	0.125	1.95	1.97	1.97	0.283	0.294	0.293
MA	0.361 to 2.88	0.169	1.99	2.01	2.01	0.246	0.253	0.253
MA	0.361 to 2.88	0.250	2.08	2.12	2.12	0.187	0.201	0.203
TA	1.08 to 2.88	0.0752	2.05	2.06	2.06	0.0932	0.0940	0.0940
TA	1.08 to 2.88	0.115	2.06	2.08	2.08	0.0664	0.0671	0.0672
TA	1.08 to 2.88	0.149	2.11	2.13	2.13	0.0548	0.0556	0.0557
TA	1.08 to 2.88	0.229	2.31	2.36	2.37	0.0379	0.0384	0.0386
IA	0.361 to 2.88	0.0821	2.09	2.09	2.09	1.07	1.14	1.15
IA	0.361 to 2.88	0.127	2.10	2.11	2.11	0.879	1.09	1.10
IA	0.361 to 2.88	0.162	2.11	2.12	2.12	0.923	1.04	1.06
IA	0.361 to 2.88	0.248	2.09	2.12	2.12	0.702	0.835	0.853
MLA	0.361 to 2.88	0.0721	1.19	1.18	1.19	0.394	0.403	0.396
MLA	0.361 to 2.88	0.114	1.17	1.17	1.17	0.375	0.388	0.377
MLA	0.361 to 2.88	0.153	1.15	1.15	1.15	0.358	0.374	0.360
MLA	0.361 to 2.88	0.231	1.10	1.09	1.10	0.322	0.341	0.324
OA	1.08 to 2.88	0.0759	2.75	2.75	2.74	3.13	3.30	3.32
OA	1.08 to 2.88	0.142	2.98	2.99	2.99	1.02	1.13	1.24
OA	1.08 to 2.88	0.158	3.04	3.05	3.06	0.850	0.946	1.06
OA	1.08 to 2.88	0.222	3.27	3.30	3.13	0.473	0.548	0.681

of the aqueous and of the organic phase was measured before and after extraction with an error of ± 0.1 mL.

Four synthetic aqueous solutions containing different concentrations of the organic acid were prepared for the batch experiment. Three volume ratios between the organic and the aqueous phase ($\bar{V}/V$) equal to 1, 3, and 5 were examined at a constant volume of the aqueous phase equal to 15 mL. Six concentrations of the extractant were used.

The concentration of the organic acid in the aqueous phase was determined by high-performance liquid chromatography (HPLC) using a column for organic acids analyses, Aminex HPX-87H (Bio-Rad), 0.005 M H_2SO_4 as a mobile phase, and a Spectra 100-UV–vis detector (Spectra-Physics) at 210 nm wavelength. Each sample was analyzed in triplicate under identical conditions, and the average values were reported. The concentration of organic acid in the organic phase was calculated from the mass balance with an error of ≤ 3 % according to $V_{in}C_{(H_2A)in} - VC_{H_2A} = \bar{V}\bar{C}_{H_2A}$ where V is the phase volume and in refers to the initial solution.

The distribution coefficient ($m_{(H_2A)}$) was calculated with an uncertainty lower than ± 4 %.

Results and Discussion

In the present study, the equilibrium of the liquid–liquid extraction of dicarboxylic acids with the organic extractant TBP was investigated under various experimental conditions.

To determine the extraction isotherms for each acid, four acid concentrations in the aqueous phase were used at different volume ratios to the organic phase (1, 3, and 5) for six concentrations of the extractant. The tabulated results of this study can be found as Supporting Information.

As an example, the extraction isotherms of oxalic acid at different concentrations of TBP dissolved in dodecane are shown (Figure 2).

Figure 3 illustrates the extractability of the studied acids with 50 (v/v) % TBP in dodecane, which follows the order: succinic acid (SA) > itaconic acid (IA) > oxalic acid (OA) > malic acid (MLA) > maleic acid (MA) > tartaric acid (TA). This order permits us to predict which acids may be separated from one another by solvent extraction with TBP; e.g., SA may be separated from TA. The order is valid only for extraction with TBP in dodecane.

The extraction isotherms, obtained from the experimental data, were used for determining the overall apparent extraction coefficient ($K_{1,n}$), the apparent extraction constants ($K_{R(1:1)}$ and

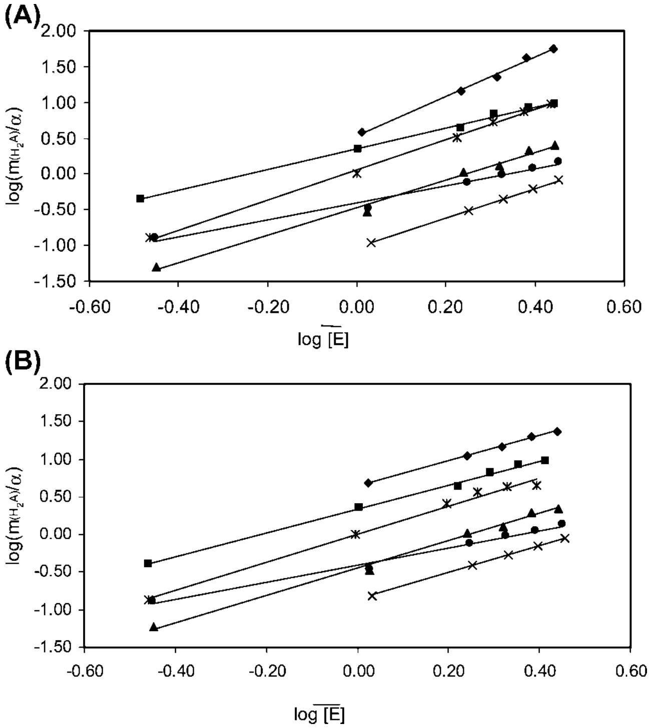

Figure 4. (a) $\log(m_{(H_2A)}/\alpha)$ vs $\log[\bar{E}]$ for the studied acids using the first method. Symbols: ◆, oxalic acid ($(C_{H_2A})_{in} = 0.0759$ M); ■, succinic acid ($(C_{H2A})_{in} = 0.0729$ M); ▲, maleic acid ($(C_{H_2A})_{in} = 0.0839$ M); ×, tartaric acid ($(C_{H_2A})_{in} = 0.0752$ M); *, itaconic acid ($(C_{H_2A})_{in} = 0.0821$ M); •, malic acid ($(C_{H_2A})_{in} = 0.0721$ M). (b) $\log(m_{(H_2A)}/\alpha)$ vs $\log[\bar{E}]$ for the studied acids using the second method. Symbols: ◆, oxalic acid ($C_{H_2A} = 0.05$ M); ■, succinic acid ($C_{H_2A} = 0.02$ M); ▲, maleic acid ($C_{H_2A} = 0.05$ M); ×, tartaric acid ($C_{H_2A} = 0.05$ M); *, itaconic acid ($C_{H_2A} = 0.05$ M).

Table 2b. Values of the Overall Apparent Extraction Coefficient ($K_{1,n}$) and the Apparent Number of Interacting Extractant Molecules (n) Determined from the Dependence $\log(m_{(H_2A)}/\alpha)$ vs $\log[\bar{E}]$ at a Constant Equilibrium Acid Concentration in the Aqueous Phase (Second Method)

acid	$[E]_{in}$ (from/to)	C_{H_2A}	n when $n_E = 1$	n when $n_E = 2$	n when $n_E = n$	$K_{1,n}$ when $n_E = 1$	$K_{1,n}$ when $n_E = 2$	$K_{1,n}$ when $n_E = n$
SA	0.361 to 2.88	0.0002	1.56	1.56	1.56	2.27	2.27	2.27
SA	0.361 to 2.88	0.002	1.56	1.56	1.56	2.00	2.02	2.01
SA	0.361 to 2.88	0.006	1.56	1.57	1.57	1.98	2.02	2.00
SA	0.361 to 2.88	0.02	1.56	1.60	1.58	2.08	2.23	2.17
MA	0.361 to 2.88	0.01	1.78	1.78	1.78	0.620	0.623	0.622
MA	0.361 to 2.88	0.05	1.80	1.82	1.81	0.351	0.360	0.358
MA	0.361 to 2.88	0.08	1.82	1.84	1.84	0.300	0.312	0.310
MA	0.361 to 2.88	0.125	1.84	1.88	1.88	0.252	0.268	0.265
TA	1.08 to 2.88	0.05	1.79	1.80	1.80	0.136	0.137	0.137
TA	1.08 to 2.88	0.1	1.90	1.91	1.91	0.0722	0.0729	0.0729
TA	1.08 to 2.88	0.15	2.02	2.05	2.05	0.0533	0.0539	0.0539
TA	1.08 to 2.88	0.20	2.17	2.21	2.22	0.0418	0.0424	0.0425
IA	0.361 to 2.88	0.005	2.00	2.01	2.01	1.30	1.32	1.32
IA	0.361 to 2.88	0.01	1.99	2.01	2.01	1.20	1.23	1.23
IA	0.361 to 2.52	0.03	1.94	2.00	2.00	0.950	1.14	1.14
IA	0.361 to 2.52	0.05	1.87	1.94	1.94	0.950	1.06	1.05
MLA	0.361 to 2.88	0.01	1.18	1.18	1.18	0.440	0.442	0.441
MLA	0.361 to 2.88	0.025	1.17	1.17	1.17	0.414	0.418	0.414
MLA	0.361 to 2.88	0.05	1.15	1.15	1.15	0.391	0.399	0.392
MLA	0.361 to 2.88	0.1	1.09	1.09	1.09	0.357	0.370	0.358
OA	1.08 to 2.88	0.008	1.42	1.42	1.42	155	156	156
OA	1.08 to 2.88	0.01	1.43	1.43	1.43	95.6	96.0	95.8
OA	1.08 to 2.88	0.05	1.65	1.67	1.67	4.36	4.47	4.43
OA	1.08 to 2.88	0.08	1.83	1.89	1.88	1.90	1.97	1.96

$K_{R(1:2)}$) and the apparent number of interacting extractant molecules (n) in two ways.

Table 2a shows the results for the overall apparent extraction coefficient ($K_{1,n}$) and the apparent number of interacting extractant molecules (n) determined in the classical way (further called first method) from the dependence $\log(m_{(H_2A)}/\alpha)$ vs $\log[\bar{E}]$ at constant initial acid concentration in the aqueous phase. As an example, Figure 4a shows the dependence of $\log(m_{(H_2A)}/\alpha)$ vs $\log[\bar{E}]$ according to eq 27 for all studied acids at constant initial acid concentration by the first method. Figure 4b shows the same dependence obtained by the second method where the equilibrium acid concentration is constant. The whole range of initial extractant concentrations was used except for oxalic and tartaric acid, for which strong deviations from the straight line at the lowest extractant concentration ($[E]_{in} = 0.361\ \mathrm{mol \cdot L^{-1}}$) were observed.

Table 2b shows the results obtained with fixed equilibrium acid concentration in the aqueous phase (further called second method). In this case, the fixed equilibrium acid concentrations were chosen in a concentration range where information about the distribution coefficient (m_{H_2A}) was available. The tables contain data about: (i) the range of initial extractant concentrations used; (ii) the concentration of the corresponding acid; (iii) the value of n when n_E is equal to 1, 2, or n according to eq 27; and (iv) the value of $K_{1,n}$ corresponding to each n.

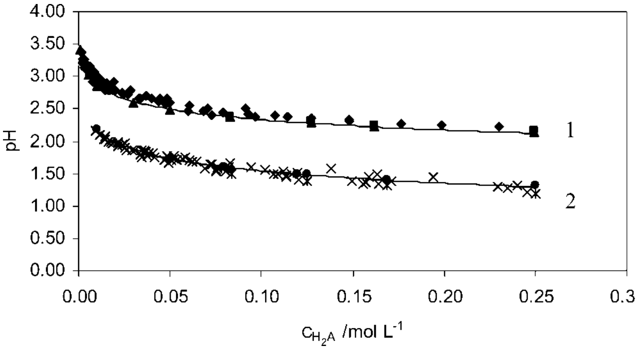

Figure 5. Influence of the equilibrium acid concentration in the aqueous phase (C_{H_2A}) on the value of pH for itaconic acid (curve 1: theoretical; ▲, theoretical values; ■, measured values of initial solution; ♦, measured values after extraction) and maleic acid (curve 2: -, theoretical; •, theoretical values; *, measured values of initial solution; ×, measured values after extraction).

It cannot be concluded from the values of n and $K_{1,n}$ obtained by the first or by the second method which method is more suitable. Applying the second method at a low equilibrium acid concentration (C_{H_2A}), irrespective of the value of n_E (1, 2, or n) put in eq 27, n remains constant even for higher C_{H_2A} values. This does not apply to$K_{1,n}$. At a constant n, changes in C_{H_2A} lead to changes in $m_{(H_2A)}$ and α because α depends on the equilibrium acid concentration and the corresponding dissociation constants ($K_{a2,1}$ and $K_{a2,2}$). As was mentioned in the theoretical part, the values of $K_{1,n}$ and n depend on the acid concentration used, but for some acids there are big differences between the calculated values of $K_{1,n}$ and n for the same acid, depending on the method used. Although all acids are dicarboxylic, for malic acid, n is close to 1; for maleic and itaconic acid, it is close to 2; for succinic acid, it is between 1 and 2. For oxalic acid, n determined by the first method (Table 2a) is close to 3 (2.74 to 3.13), and by the second method (Table 2b) it varies from 1.42 to 1.88. What are the reasons for the change in the values of $K_{1,n}$ and n?

If the diluent affects the extraction ability of the extractant, the apparent extraction constants ($K_{R(1:1)}$ and $K_{R(1:2)}$) are valid only for a fixed composition of organic phase and acid, and they will change with extractant concentration. Another reason could be the concentration of the interaction product. If this concentration cannot be neglected, the measured pH does not correspond to the total acid concentration, and the concentration of the interaction product in the aqueous phase influences in this way the part of undissociated molecules (α). Is the concentration of the interaction product in the aqueous phase very low, and can it be neglected?

If this concentration is negligible, the measured pH should correspond to the theoretical one for the measured acid concentration in the aqueous phase. Depending on the number of extractant molecules which interact with the dicarboxylic acid according to

$$\mathrm{E} + \mathrm{HOOCRCOOH} \leftrightarrow \mathrm{EHOOCRCOOH} \qquad (28)$$

or

$$2\mathrm{E} + \mathrm{HOOCRCOOH} \leftrightarrow \mathrm{EHOOCRCOOHE} \qquad (29)$$

several cases are possible:

The measured pH corresponds to the theoretical one. This means that the concentration of the interaction product according to eq 29 ($n \approx 2$) is negligible or the interaction product corresponding to eq 28 ($n \approx 1$) liberates a number of protons equal to that liberated by the free dicarboxylic acid.

The measured pH is higher than the theoretical one. This means that the concentration of the interaction product cannot be neglected and the dissociation constant of the species EHOOCRCOOH (which liberates less protons than the free acid) is lower than the first dissociation constant of the free acid.

The measured pH is lower than the theoretical one. This means that the concentration of the interaction product cannot be neglected and the dissociation constant of the species EHOOCRCOOH (which liberates more protons than the free acid) is higher than the first dissociation constant of the free acid.

The coincidence between the measured value of pH in the initial solution (before extraction) and the calculated (theoretical) one according to the first and the second constants was acceptable for all acids. After extraction (in the equilibrium), all cases discussed above were observed. To the first case belonged itaconic acid and maleic acid.

Figure 5 shows the dependence of pH on the molar concentration of the acid. Curve 1 and curve 2 illustrate the theoretical values of pH for maleic and itaconic acids, respectively. There is very good coincidence between the measured values of pH in the initial solution and the theoretical ones for both acids (*, MA; ■, IA). The experimental points for maleic acid are situated around the theoretical curve (curve 1), while those for itaconic acids are slightly higher, the deviation ($\mathrm{pH}_{\mathrm{meas}} - \mathrm{pH}$) not exceeding 0.15 pH units. The values of n determined by the two methods vary in a limited range. For IA, n varies from 2.09 to 2.12 (first method) and from 1.94 to 2.01 (second method). For MA, the variation is from 1.95 to 2.12 and from 1.78 to 1.88, respectively. The value of the overall apparent equilibrium extraction coefficient ($K_{1,n}$) for IA varies from 0.853 to 1.15 (first method) and from 1.05 to 1.32 (second method). For MA, the variation is from 0.203 to 0.337 and from 0.265 to 0.622, respectively (see Tables 2a and 2b).

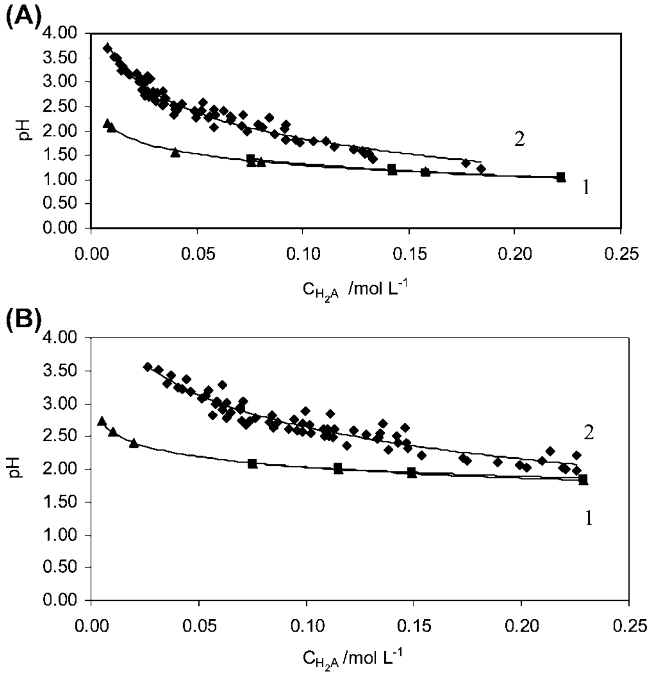

Figure 6. (a) Influence of the equilibrium acid concentration in the aqueous phase ($C_{\mathrm{H_2A}}$) on the value of pH for oxalic acid (curve 1: theoretical; curve 2: experimental; ▲, theoretical values; ■, measured values of initial solution; ♦, measured values after extraction). (b) Influence of the equilibrium acid concentration in the aqueous phase ($C_{\mathrm{H_2A}}$) on the value of pH for tartaric acid (curve 1: theoretical; curve 2: experimental; ▲, theoretical values; ■, measured values of initial solution; ♦, measured values after extraction).

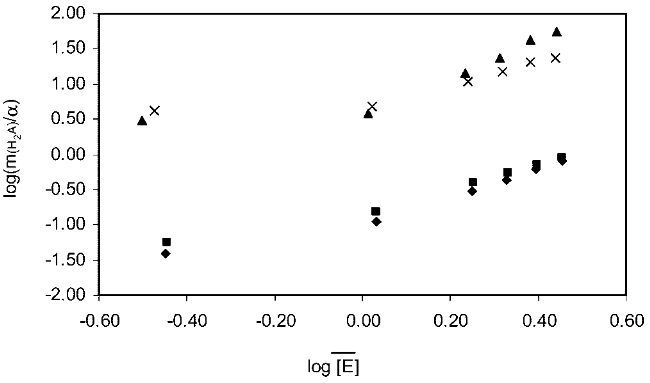

Figure 7. log($m_{(\mathrm{H_2A})}/\alpha$) vs log[$\bar{\mathrm{E}}$] using the whole studied range of extractant concentrations for oxalic acid (▲, $(C_{\mathrm{H_2A}})_{\mathrm{in}} = 0.0759$ M; ×, $C_{\mathrm{H_2A}} = 0.05$ M) and tartaric acid (♦, $(C_{\mathrm{H_2A}})_{\mathrm{in}} = 0.0752$ M; ■, $C_{\mathrm{H_2A}} = 0.05$ M).

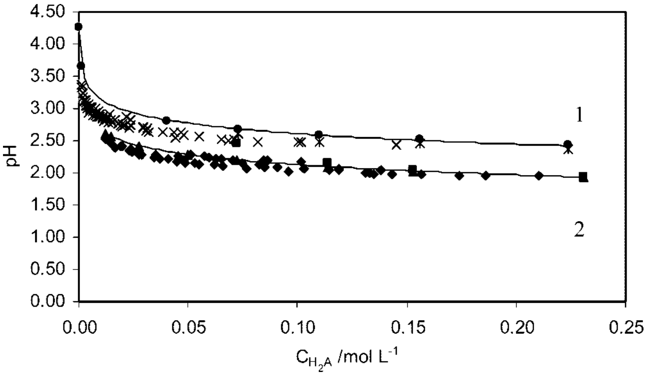

Figure 8. Influence of the equilibrium acid concentration in the aqueous phase ($C_{\mathrm{H_2A}}$) on the value of pH for succinic acid (curve 1: theoretical; •, theoretical values; *, measured values of initial solution; ×, measured values after extraction) and maleic acid (curve 2: theoretical; ▲, theoretical values; ■, measured values of initial solution; ♦, measured values after extraction).

Figure 6 illustrates the second case when pH measured at the equilibrium is significantly higher than the theoretical one. Two of the acids may be referred to this case: oxalic acid (Figure 6a) and tartaric acid (Figure 6b). The measured values of pH of the initial aqueous solution are on the theoretical curve, but those measured after extraction are above the theoretical curve (curve 1 in Figures 6a and 6b). The difference $\mathrm{pH}_{\mathrm{meas}} - \mathrm{pH}_{\mathrm{th}}$ is 1.65 for oxalic acid and 1.20 for tartaric acid at lower acid concentrations. This difference decreases on increasing the aqueous acid concentration.

For both acids, the values of n vary in a broad range and strongly depend on the method used. The values of n for OA are from 2.74 to 3.13 (first method) and from 1.42 to 1.88 (second method). For TA, they are from 2.06 to 2.37 (first method) and from 1.80 to 2.22 (second method). The value of the overall apparent equilibrium extraction coefficient ($K_{1,n}$) also depends on the method used and the acid concentration. For OA, this change is from 0.681 to 3.32 (first method) and from 1.96 to 156 (second method). For TA, the values are from 0.0386 to 0.0940 and from 0.0425 to 0.137, respectively.

Table 3a. Values of the Apparent Equilibrium Extraction Constants ($K_{R(1:1)}$ and $K_{R(1:2)}$) Determined from the Dependence $m_{(H_2A)}/\alpha$ vs [$\bar{E}$] at a Constant Initial Acid Concentration in the Aqueous Phase (First Method)

acid	$[E]_{in}$ (from/to)	$(C_{H_2A})_{in}$	$n = n_E$	$K_{R(1:1)}$	$K_{R(1:2)}$
SA	0.361 to 2.88	0.0729	1.46	1.58	0.726
SA	0.361 to 2.88	0.110	1.40	1.79	0.667
SA	0.361 to 2.88	0.156	1.34	2.06	0.596
SA	0.361 to 2.88	0.224	1.25	2.43	0.489
MA	0.361 to 2.88	0.0839	1.95	−0.0231	0.341
MA	0.361 to 2.88	0.125	1.97	−0.0537	0.322
MA	0.361 to 2.88	0.169	2.01	−0.0962	0.321
MA	0.361 to 2.88	0.250	2.12	−0.197	0.343
TA	1.08 to 2.88	0.0752	2.06	−0.0212	0.108
TA	1.08 to 2.88	0.115	2.08	−0.0113	0.0767
TA	1.08 to 2.88	0.149	2.13	−0.0120	0.0675
TA	1.08 to 2.88	0.229	2.37	−0.0230	0.0626
IA	0.361 to 2.88	0.0821	2.09	−0.362	1.43
IA	0.361 to 2.88	0.127	2.11	−0.240	1.33
IA	0.361 to 2.88	0.162	2.12	−0.178	1.26
IA	0.361 to 2.88	0.248	2.12	−0.0711	0.971
MLA	0.361 to 2.88	0.0721	1.19	0.262	0.0916
MLA	0.361 to 2.88	0.114	1.17	0.274	0.0741
MLA	0.361 to 2.88	0.153	1.15	0.289	0.0562
MLA	0.361 to 2.88	0.231	1.10	0.333	0.0100
OA	1.08 to 2.88	0.0759	2.74	−9.48	10.7
OA	1.08 to 2.88	0.142	2.99	−4.08	4.70
OA	1.08 to 2.88	0.158	3.06	−3.62	4.19
OA	1.08 to 2.88	0.222	3.36	−2.67	3.19

Table 3b. Values of the Apparent Equilibrium Extraction Constants ($K_{R(1:1)}$ and $K_{R(1:2)}$) Determined from the Dependence $m_{(H_2A)}/\alpha$ vs [$\bar{E}$] at a Constant Equilibrium Acid Concentration in the Aqueous Phase (Second Method)

acid	$[E]_{in}$ (from/to)	C_{H_2A}	$n = n_E$	$K_{R(1:1)}$	$K_{R(1:2)}$
SA	0.361 to 2.88	0.0002	1.56	1.47	0.930
SA	0.361 to 2.88	0.002	1.56	1.29	0.830
SA	0.361 to 2.88	0.006	1.57	1.25	0.843
SA	0.361 to 2.88	0.02	1.58	1.25	0.991
MA	0.361 to 2.88	0.01	1.78	0.272	0.402
MA	0.361 to 2.88	0.05	1.81	0.0994	0.268
MA	0.361 to 2.88	0.08	1.84	0.045	0.259
MA	0.361 to 2.88	0.125	1.88	0.0181	0.261
TA	1.08 to 2.88	0.05	1.80	0.0509	0.0931
TA	1.08 to 2.88	0.1	1.91	0.0165	0.0602
TA	1.08 to 2.88	0.15	2.05	0.0015	0.0553
TA	1.08 to 2.88	0.20	2.22	−0.0112	0.0557
IA	0.361 to 2.88	0.005	2.01	−0.24	1.47
IA	0.361 to 2.88	0.01	2.01	−0.186	1.36
IA	0.361 to 2.52	0.03	2.00	−0.244	1.29
IA	0.361 to 2.52	0.05	1.94	0.188	0.907
MLA	0.361 to 2.88	0.01	1.18	0.279	0.106
MLA	0.361 to 2.88	0.025	1.17	0.281	0.0894
MLA	0.361 to 2.88	0.05	1.15	0.300	0.0659
MLA	0.361 to 2.88	0.1	1.09	0.349	0.0177
OA	1.08 to 2.88	0.008	1.42	121	42.6
OA	1.08 to 2.88	0.01	1.43	73.5	27.1
OA	1.08 to 2.88	0.05	1.67	4.01	2.99
OA	1.08 to 2.88	0.08	1.88	0.511	1.55

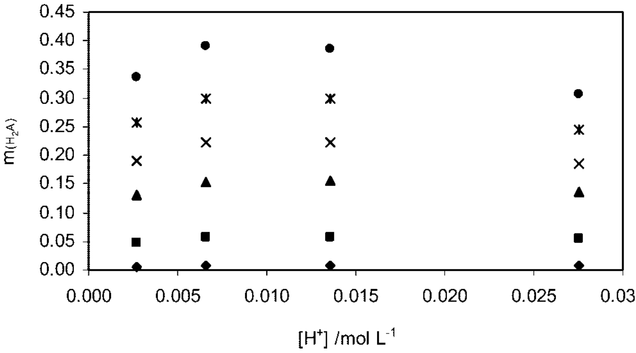

Figure 9. Theoretical dependence of $m_{(H_2A)}$ on [H$^+$] according to eq 24 supposing $n = 2$ and $K_{R(1:2)} = 0.0555$ for tartaric acid. Symbols: ◆, 10; ■, 30; ▲, 50; ×, 60; *, 70; •, 80 % vol. of TBP dissolved in dodecane.

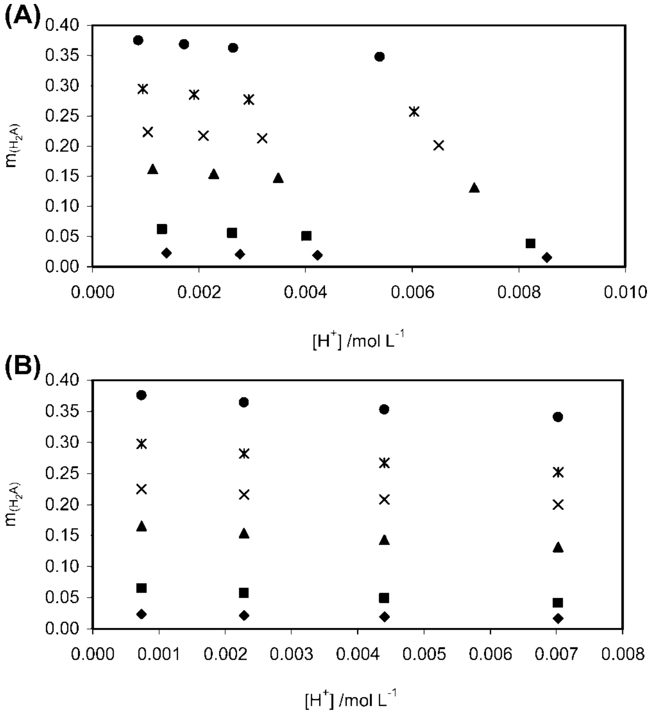

Figure 10. (a) Values of $m_{(H_2A)}$ and [H$^+$] evaluated by treating the experimental results by the first method for (0.0752, 0.115, 0.149, and 0.229) mol·L^{-1} initial concentration of tartaric acid. Symbols: ◆, 10; ■, 30; ▲, 50; ×, 60; *, 70; •, 80 % vol. of TBP dissolved in dodecane. (b) Values of $m_{(H_2A)}$ and [H$^+$] evaluated by treating the experimental results by the second method for (0.05, 0.1, 0.15, and 0.2) mol·L^{-1} equilibrium concentration of tartaric acid. Symbols: ◆, 10; ■, 30; ▲, 50; ×, 60; *, 70; •, 80 % vol. of TBP dissolved in dodecane.

It should be noted that the values of n and $K_{1,n}$ for these two acids are determined in the range of extractant concentrations from (1.08 to 2.88) mol·L^{-1} (from 30 to 80 (v/v) %) because, as Figure 7 shows, the point at 10 (v/v) % (0.366 mol·L^{-1}) cannot be satisfactorily aligned to the evaluated log($m_{(H_2A)}/\alpha$) vs log[$\bar{E}$].

The third case is illustrated in Figure 8. The difference between the experimental points and the theoretical ones is 0.45 pH units for succinic acid and 0.2 for malic acid. The obtained results of n and $K_{1,n}$ for SA do not essentially depend on the concentration of acid but depend on the method used. They vary from 1.25 to 1.46 (n) and from 2.22 to 2.87 ($K_{1,n}$) and from 1.56 to 1.58 (n) and from 2.00 to 2.27 ($K_{1,n}$), according to the first or second method, respectively. The results for MLA did not depend on the method used or the acid concentration. The value of n is 1.14 ± 0.05, and the value of $K_{1,n}$ varies from 0.324 to 0.396 (first method) and from 0.358 to 0.441 (second method). Only for maleic acid, it may be concluded that the main interaction is between one molecule of extractant and one molecule of acid according to eq 27.

If the acids are ordered according to the values of their overall apparent equilibrium extraction coefficients ($K_{1,n}$), the order is (see Table 3a and 3b): oxalic acid (OA) > succinic acid (SA) > itaconic acid (IA) > malic acid (MLA) > maleic acid (MA) > tartaric acid (TA). The comparison with the order of extractability of these acids reveals only one difference (see Figure 3): oxalic acid occupies the first place in the $K_{1,n}$ order.

The next step was to determine the apparent equilibrium extraction constants when the extractant interacts with one ($K_{R(1:1)}$) or two ($K_{R(1:2)}$) carboxylic groups. As was mentioned in the theoretical part, this is possible when the number of extractant molecules interacting with one molecule of diacid (n) is known. The values of $K_{R(1:1)}$ and $K_{R(1:2)}$ calculated by the first method are shown in Table 3a and those by the second method are shown in Table 3b. When the values of n are close to or higher than 2 (first method) or higher than 2 (second method), the apparent equilibrium extraction constants ($K_{R(1:1)}$) have a negative value because, as assumed in the theoretical part (eq 25), n cannot exceed 2. The ratio between $K_{R(1:2)}$ and $K_{R(1:1)}$ depends on n and increases upon increasing n. When n is close to 1, $K_{R(1:1)} \ll K_{R(1:2)}$ (malic acid). When $1 < n < 2$, both constants differ from zero (succinic acid), and when n is close to 2, $K_{R(1:2)} >> K_{R(1:1)}$.

Of interest was also the dependence of the overall distribution coefficient ($m_{(H_2A)}$) on the acidity of the aqueous solution due to acid dissociation only. It is well-known[10,20,22,23] that the decrease in acidity due to base addition leads to a decrease in $m_{(H_2A)}$ as well. This may be related to the fact that the acidic salt cannot interact with the basic extractant according to eq 1, while it contributes to the total acid concentration. Our experiments, carried out without base addition, showed that the overall distribution coefficient ($m_{(H_2A)}$) decreases upon increasing [H$^+$] for most of the acids. For oxalic acid at a low extractant concentration, $m_{(H_2A)}$ increases upon increasing [H$^+$]. The relation between $m_{(H_2A)}$ and [H$^+$] is not evident from eq 24. The value of [H$^+$] is related to the acid concentration and the corresponding dissociation constants. On the one hand, [H$^+$], i.e., the part of the undissociated acid (α), is proportional to the acid concentration; on the other, with the increase in acid concentration, the concentration of free extractant ([$\bar{E}$]) will decrease. For this reason, the theoretical dependence of $m_{(H_2A)}$ on [H$^+$] according to eq 24 was followed for tartaric acid, supposing $n = 2$ and $K_{R(1:2)} = 0.0555$. Figure 9 illustrates this case. There is a maximum on the curve depicting the influence of [H$^+$] on $m_{(H_2A)}$, i.e., $m_{(H_2A)}$ vs $C_{(H_2A)}$, because [H$^+$] is proportional to $C_{(H_2A)}$. This shape of the curve has been also observed by Schlosser et al.[8] for the extraction of butyric acid with trioctylamine.

The values of $m_{(H_2A)}$ and [H$^+$] obtained by treating the experimental results by the first and the second method are shown in Figures 10a and 10b, respectively. In both cases the overall distribution coefficient (m(H$_2$A)) decreases with the increase in [H$^+$] or total acid concentration ($C_{(H_2A)}$), respectively.

Conclusions

The results of the present study reveal that the number of extractant molecules interacting with one molecule of dicarboxylic acid (n) and the value of the apparent equilibrium extraction constant ($K_{1,n}$) strongly depend on the concentrations of both extractant and acid when chemical interaction only between the extractant and the solute is assumed and the mass action law is obeyed. Consequently, the values of (n) and ($K_{1,n}$) are valid for the examined extraction system only. It is also shown that the concentration of the interaction product in the aqueous phase cannot be neglected. It has a significant influence on the concentration of free acid and consequently on the acidity of the aqueous solution and on the extent of acid dissociation.

Supporting Information Available:

Table of experimental results, coefficients of distribution, pH, initial concentration, and equilibrium aqueous and organic concentrations of the liquid−liquid equilibrium for oxalic, maleic, succinic, itaconic, malic, and tartaric acids using TBP in dodecane. This information is available free of charge via Internet at http://pubs.acs.org.

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