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# Reactive Extraction of Glycolic Acid Using Tri-*n*-Butyl Phosphate and Tri-*n*-Octylamine in Six Different Diluents: Experimental Data and Theoretical Predictions

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**ABSTRACT:** The present study deals with the equilibrium reactive extraction of glycolic acid from aqueous solution by two different extractants [tri-*n*-butyl phosphate (TBP) and tri-*n*-octylamine (TOA)] at constant concentration of 0.573 kmol·m$^{-3}$ dissolving in a wide range of diluents [*n*-hexane, decane-1-ol, *n*-hexane + decane-1-ol (1:1 v/v), 4-methylpentan-2-one (MIBK), benzene, and dichloromethane (DCM)] at isothermal conditions (298 ± 1 K). The effects of various parameters such as acid concentration (0.10−0.57 kmol·m$^{-3}$), extractant type, and type of diluent on the recovery of glycolic acid from aqueous solution are derived. The values of equilibrium constants ($K_E$), number of reacting acid molecules ($m$) per extractant molecule, and also the equilibrium constants ($K_{11}$ and $K_{21}$) for individual complexes between acid and extractant are estimated through the proposed mathematical model. Further, the experimental values of the distribution coefficients ($K_D$) are correlated using the linear solvation energy relationship (LSER) model which is based on solute−solvent interaction parameters. The extraction power of TBP and TOA in terms of $K_D$ increases in the order of DCM ≥ MIBK > decan-1-ol > *n*-hexane + decan-1-ol (1:1 v/v) ≥ benzene ≥ *n*-hexane, and DCM ≥ decan-1-ol > MIBK > *n*-hexane + decan-1-ol (1:1 v/v) > benzene > *n*-hexane, respectively.

## ■ INTRODUCTION

Glycolic acid is the simplest and smallest organic molecule of the α-hydroxy acid family of carboxylic acids with both the acid (−COOH) and alcohol (−OH) functionality. Glycolic acid occurs naturally as a trace component in sugarcane, beets, grapes, and fruits. The acid has a broad spectrum of consumer and industrial applications including use in water well rehabilitation, in the leather, oil and gas, laundry, and textile industries, and as a component in personal care products such as skin care creams. Glycolic acid can be produced by the enzymatic conversion (typically the enzyme catalyst used is nitrilase or a combination of a nitrile hydratase and an amidase) of glycolonitrile, which results in the production of an aqueous solution of ammonium glycolate. Several processes are used to recover glycolic acid from the aqueous ammonium glycolate solution including crystallization, distillation, ion exchange (cationic and/or anionic), electrodialysis, liquid−liquid extraction, and alcoholysis. However, these separation methods with limitations such as low ammonium glycolate concentrations, undesired product stream, and the use of expensive and difficult-to-handle equipment (e.g., electrodialysis) will be unattractive in the future for industrial production. In this regard, separation of glycolic acid by reactive extraction technique is proposed to be an efficient and eco-friendly process due to its high degree of extraction and low process waste. The reactive extraction process has advantages such as (i) it can use high concentrations of substrates in the extractive fermentation, (ii) the acid is re-extracted and the solvent can be reused, (iii) it can control the pH in the reactor, (iv) higher product concentration results, and (v) there is a reduction of downstream processing load and recovery cost.[1−3]

The hydrophilic nature of glycolic acid (log $P$ = −1.097)[4] makes it poorly extractable by common organic solvents; hence

reactive extraction has been considered for the separation of this acid from aqueous solution. Phosphorus bonded oxygen containing extractants such as tri-*n*-butyl phosphate (TBP), trialkyl phosphine oxide, and trioctyl phosphine oxide and long chain aliphatic amines such as tri-*n*-octylamine (TOA), trioctyl methyl ammonium chloride (Aliquat 336), and Amberlite LA-2 are effectively used for the reactive extraction of carboxylic acids.[5−11] These extractants are used with diluents to provide appropriate physical properties to use in the extraction process. The high affinity of extractant to separate out selectively the acid over other nonacidic components in the aqueous solution and the strong interaction with acid by the formation of acid−extractant complexes confirm high equilibrium distribution ratios of acid compared to conventional solvents such as alcohols, ketones, hydrocarbons, etc.[3,11]

Inci[12] studied reactive extraction of glycolic acid with TOA and Alamine 336 dissolving in heptane, cyclohexane, toluene, and 4-methylpentan-2-one (MIBK). The extraction process was analyzed by calculating the distribution coefficients and loading factors. Li et al.[13] studied the separation of glyoxylic acid, glycolic acid, acrylic acid, and benzoic acid with trialkylphosphine oxide (TRPO) in kerosene. They determined the equilibrium constants ($K_{11}$) from the experimental data, and loading ratios were calculated and compared with the experimental values. Qin et al.[14] conducted equilibrium experiments to recover glycolic acid and glyoxylic acid from aqueous solution by TRPO in MIBK and TOA in 1-octanol. They proposed an extraction mechanism

**Table 1. Reagents Used in the Present Study**

| chemical | IUPAC name | MW (kg kmol$^{-1}$) | density (kg m$^{-3}$) | viscosity (cP) | supplier | purity (wt %) |
|---|---|---|---|---|---|---|
| glycolic acid | 2-hydroxyethanoic acid | 76.05 | 1330 | 11.28 (15.6 °C) | Spectrochem, India | 98 |
| tri-n-butyl phosphate (TBP) | tri-n-butyl phosphate | 266.32 | 977 | 3.4 (25 °C) | Spectrochem, India | 99 |
| tri-n-octylamine (TOA) | N,N-dioctyloctan-1-amine | 353.67 | 810 | | Fluka, USA. | 98 |
| n-hexane | hexane | 86.18 | 650 | 0.294 (25 °C) | CDH, India | 99 |
| decane-1-ol | decane-1-ol | 158.28 | 830 | 34 (22 °C) | Spectrochem Pvt. Ltd., India | 98 |
| methyl isobutyl ketone (MIBK) | 4-methylpentan-2-one | 100.16 | 801 | 0.58 (20 °C) | Spectrochem Pvt. Ltd., India | 99.8 |
| benzene | benzene | 78.11 | 880 | 0.652 (20 °C) | SISCO Res. Lab. Pvt. Ltd., India | 99.8 |
| dichloromethane (DCM) | dichloromethane | 84.93 | 1330 | 0.406 (25 °C) | Fisher Scientific, India | 99.5 |

and estimated the equilibrium constants using the experimental data. Extraction of glycolic acid from an aqueous glycolonitrile hydrolysate with TOA in diluents (1-octanol and kerosene) had been studied by Yunhai et al.[15] The effects of TOA concentration, extraction temperature, and volume ratio of organic phase to aqueous phase on the distribution coefficient of acid and loading factor of TOA were measured. The separation of glycolic acid from aqueous solutions using Aliquat 336 in the diluents such as propanol, cyclohexane, isooctane, butanol, toluene, MIBK, and ethyl acetate was performed by Inci et al.[16] The distribution coefficients, loading factors, and extraction efficiencies were used to analyze the extraction of acid. Very recently, Asci et al.[17] carried out glycolic acid extraction by Amberlite LA-2, a secondary amine mixture, dissolved in 1-octanol, cyclohexane, isooctane, toluene, 2-octanone, and MIBK. The effects of parameters such as solvent type, amine concentration, and initial acid concentration on the recovery of glycolic acid were derived.

The present work is aimed at intensifying the recovery of glycolic acid using reactive extraction with tri-n-butyl phosphate (TBP) and tri-n-octylamine (TOA) using a wide range of diluents such as an alkanes (n-hexane), alcohol (decane-1-ol), ketones (4-methylpentan-2-one, MIBK), aromatic (benzene), and chlorohydrocarbon (dichloromethane, DCM). Using the equilibrium experimental data and proposed mathematical model based on the mass action law, the values of equilibrium constants ($K_E$) and stoichiometry ($m$:$n$) of reactive extraction are determined. Based on the predicted stoichoimetry, the equilibrium constants ($K_{11}$ and $K_{21}$) for individual complexes (1:1) and (2:1), respectively, between acid and extractant are also estimated. The experimental values of $K_D$ are used to predict the linear solvation energy relationship (LSER) equation at each initial glycolic acid concentration for both extractants. A comparative analysis between the two extractants (TBP and TOA) at identical conditions is made, and the best extractant—diluent system for the glycolic acid extraction from aqueous solution is proposed.

## ■ EXPERIMENTAL SECTION

The chemicals with their physical properties used in the present equilibrium study are listed in Table 1.

The glycolic acid concentration in the aqueous solution (fermentation broth) is found to be less than 10% w/w,[12] and the values of $K_D$ are found to be decreased (from 80.25 to 3.86) with an increase in the glycolic acid concentration (from 0.34 to 1.55 kmol·m$^{-3}$).[17] Therefore, the aqueous solutions of glycolic acid are prepared in the range of 0.10—0.57 kmol·m$^{-3}$ (0.81—4.6% w/w) using deionized water for optimum extraction efficiency. The organic solutions are prepared by dissolving the extractants (TBP and TOA) in different diluents (n-hexane,

decane-1-ol, MIBK, benzene, and DCM) at a constant concentration of 0.573 kmol·m$^{-3}$. Equal volumes of the aqueous solution and the organic solution (16 mL of each phase) are taken in conical flasks of 100 mL and shaken at 100 rpm for 8 h on a temperature-controlled reciprocal shaker bath (HS 250 basic, REMI Laboratories) at constant temperature (298 ± 1 K). After attaining equilibrium, the mixture of aqueous phase and organic phase is kept for separation of phases in a separating funnel (125 mL) for 2 h at 298 ± 1 K. After separation of both phases, the aqueous phase is analyzed to determine the concentration of glycolic acid with titration using fresh NaOH solution of 0.053 N and phenolphthalein as an indicator. The acid concentration in the organic phase is calculated by mass balance. The equilibrium pH of the aqueous solution is measured using a digital pH meter from ArmField Instruments (PCT 40, Basic Process Module). For selected data points reproducibility was checked and it was found that the experimental data are reproducible within ±5% of accuracy. The conventional solvents such as n-hexane, decane-1-ol, MIBK, benzene, and DCM have poor solubility in water. It is also seen that carboxylic acids carry small amounts of water with them, and hence there is less tendency of water coextraction in the organic phase by the solvents.[18] A very small (maximum phase volume of organic phase is found to be 16.25 after reaching equilibrium) change in the organic phase volume is observed, when TBP and TOA (dissolved in different diluents) are used in the reactive extraction of glycolic acid. Therefore, in the calculation of $K_D$, it is assumed that the change in volume at equilibrium is negligible and $K_D$ value is affected by only ±1%. Hence, the solvent's solubility effect on the distribution coefficients ($K_D$) and other parameters is very small and therefore has been neglected.
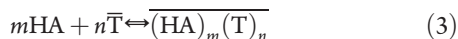
## ■ THEORY

The apparent equilibrium constant, written in terms of species concentration, is used for simplification. To describe the reactive extraction process, the following assumptions are made: (i) there is negligible physical extraction of glycolic acid; (ii) there is no acid dimer formation; (iii) water coextraction is neglected due to strong interactions between acid and extractant molecules. The interaction of glycolic acid molecule with the extractant molecule can happen in two ways: one way is through hydrogen bonding of nondissociated acid molecule, eq 1, and another is by ion pair formation, eq 2.[19]

$$HA + \overline{T} \leftrightarrow \overline{(HA)(T)} \tag{1}$$

$$H^+ + A^- + \overline{T} \leftrightarrow \overline{H^+A^-T} \tag{2}$$
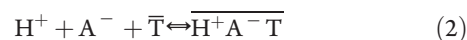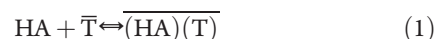
HA, H$^+$, and A$^-$ represent the nondissociated glycolic acid and its ions, respectively. The species concentrations are denoted

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by brackets, and the organic-phase species are marked with an over bar. The extraction mechanism described in eqs 1 and 2 depends on the pH and the p$K_a$ of acid, the acid and extractant concentrations, and the basicity of the extractant with respect to the acid. The extraction of glycolic acid by TBP can be described by eq 1 and that for TOA by both mechanisms (eqs 1 and 2). Now, the equilibrium extraction process can be described as a set of reactions between $m$ molecules of acid (HA) and $n$ molecules of extractant (T) to form various ($m{:}n$) complexes, with a corresponding apparent equilibrium constant ($K_E$) as given by eqs 3 and 4.

$$m\text{HA} + n\overline{\text{T}} \Longleftrightarrow \overline{(\text{HA})_m(\text{T})_n} \tag{3}$$

$$K_E = \frac{[\overline{(\text{HA})_m(\text{T})_n}]}{[\text{HA}]^m[\overline{\text{T}}]^n} \tag{4}$$

The extraction process is analyzed by means of the distribution coefficient ($K_D$) and is experimentally calculated as

$$K_D = \frac{\overline{C}_{\text{HA}}}{C_{\text{HA}}} = m\frac{[\overline{(\text{HA})_m(\text{T})_n}]}{C_{\text{HA}}} \tag{5}$$

where $\overline{C}_{\text{HA}}$ is the total concentration of glycolic acid in the organic phase and $C_{\text{HA}}$ is the total concentration (dissociated and undissociated) of glycolic acid in the aqueous phase at equilibrium.

Glycolic acid dissociation reaction at equilibrium in the aqueous phase is written as eq 6.

$$\text{HA} \Longleftrightarrow \text{H}^+ + \text{A}^- \tag{6}$$

The dissociation constant ($K_a$) is given by eq 7.

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \tag{7}$$

Therefore, the total glycolic acid concentration in the aqueous phase, $C_{\text{HA}}$, can be expressed in terms of undissociated acid concentration ([HA]), $K_a$, and proton concentration ([H$^+$]).

$$C_{\text{HA}} = [\text{HA}] + [\text{A}^-] \tag{8}$$

$$C_{\text{HA}} = [\text{HA}]\left(1 + \frac{K_a}{[\text{H}^+]}\right) \tag{9}$$

Substituting the values of $[\overline{(\text{HA})_m(\text{T}_n)}]$ and [HA] from eqs 5 and 9, respectively, in eq 4 results in eq 10.

$$K_E = \frac{K_D(1 + K_a/[\text{H}^+])^m}{mC_{\text{HA}}^{m-1}[\overline{\text{T}}]^n} \tag{10}$$

The equilibrium free extractant concentration, [T], in the organic phase, is represented as

$$[\overline{\text{T}}] = [\overline{\text{T}}]_0 - n[\overline{(\text{HA})_m(\text{T})_n}] \tag{11}$$

or

$$[\overline{\text{T}}] = [\overline{\text{T}}]_0 - K_D n C_{\text{HA}}/m \tag{12}$$

Putting the values of [T] from eq 12 in eq 10 results in eq 13.

$$K_D = mK_E\left([\overline{\text{T}}]_0 - K_D n\frac{C_{\text{HA}}}{m}\right)^n \frac{C_{\text{HA}}^{m-1}}{(1 + K_a/[\text{H}^+])^m} \tag{13}$$

The values of the equilibrium extraction constant ($K_E$) and the stoichoimetry ($m, n$) of the reactive extraction of glycolic acid are

estimated by optimizing the error between the experimental and predicted values of $K_D$ using the following objective function known as the root-mean-square deviation (rmsd).

$$\text{rmsd} = \left[\frac{\sum (K_D^{\text{exp}} - K_D^{\text{model}})^2}{N}\right]^{1/2} \tag{14}$$

where $N$ is the number of data points.

The degree of extraction ($E$) is defined as the ratio of acid concentration in the extracted phase to the initial acid concentration in aqueous solution by assuming no change in volume at equilibrium and is written as eq 15.

$$E = \frac{K_D}{1 + K_D} \times 100 \tag{15}$$

The extent to which the organic phase (extractant and diluents) may be loaded with acid is expressed by the loading ratio, $Z$ (ratio of total acid concentration in the organic phase at equilibrium to the total initial extractant concentration in the extract phase).

$$Z = \frac{\overline{C}_{\text{HA}}}{[\overline{\text{T}}]_0} \tag{16}$$

Based on the predicted values of $m$ per extractant molecule, the formation of different types of complexes such as (1:1) and (2:1) can be considered and represented by the following stoichiometric eqs 17 and 18, respectively.

$$\text{HA} + \overline{\text{T}} \Longleftrightarrow \overline{(\text{HA})(\text{T})} \tag{17}$$
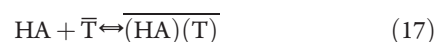
$$\text{HA} + \overline{(\text{HA})(\text{T})} \Longleftrightarrow \overline{(\text{HA})_2(\text{T})} \tag{18}$$

The corresponding equilibrium extraction constants ($K_{11}$ and $K_{21}$) for individual acid–extractant complexes are obtained using eqs 19 and 20.

$$K_{11} = \frac{[\overline{(\text{HA})(\text{T})}]}{[\text{HA}][\overline{\text{T}}]} = \frac{\overline{C}_{11}(1 + K_a/[\text{H}^+])}{C_{\text{HA}}[\overline{\text{T}}]} \tag{19}$$

$$K_{21} = \frac{[\overline{(\text{HA})_2(\text{T})}]}{[\text{HA}][\overline{(\text{HA})(\text{T})}]} = \frac{\overline{C}_{21}(1 + K_a/[\text{H}^+])}{C_{\text{HA}}\overline{C}_{11}} \tag{20}$$

$\overline{C}_{11}$ and $\overline{C}_{21}$ are the concentrations of the complexes (1:1) and (2:1) formed in the organic phase at equilibrium, respectively. The glycolic acid concentration and free extractant concentration in the organic phase are represented by eqs 21 and 22, respectively.

$$\overline{C}_{\text{HA}} = \overline{C}_{11} + 2\overline{C}_{21} = \frac{K_{11}[\overline{\text{T}}]C_{\text{HA}}}{1 + K_a/[\text{H}^+]} + \frac{2K_{21}\overline{C}_{11}C_{\text{HA}}}{1 + K_a/[\text{H}^+]} \tag{21}$$

$$[\overline{\text{T}}] = [\overline{\text{T}}]_0 - (\overline{C}_{11} + \overline{C}_{21})$$

$$= [\overline{\text{T}}]_0 - \left(\frac{K_{11}[\overline{\text{T}}]C_{\text{HA}}}{1 + K_a/[\text{H}^+]} + \frac{K_{21}\overline{C}_{11}C_{\text{HA}}}{1 + K_a/[\text{H}^+]}\right) \tag{22}$$

The values of the equilibrium constants $K_{11}$ and $K_{21}$ are estimated based on the total acid concentration in the aqueous phase at equilibrium.
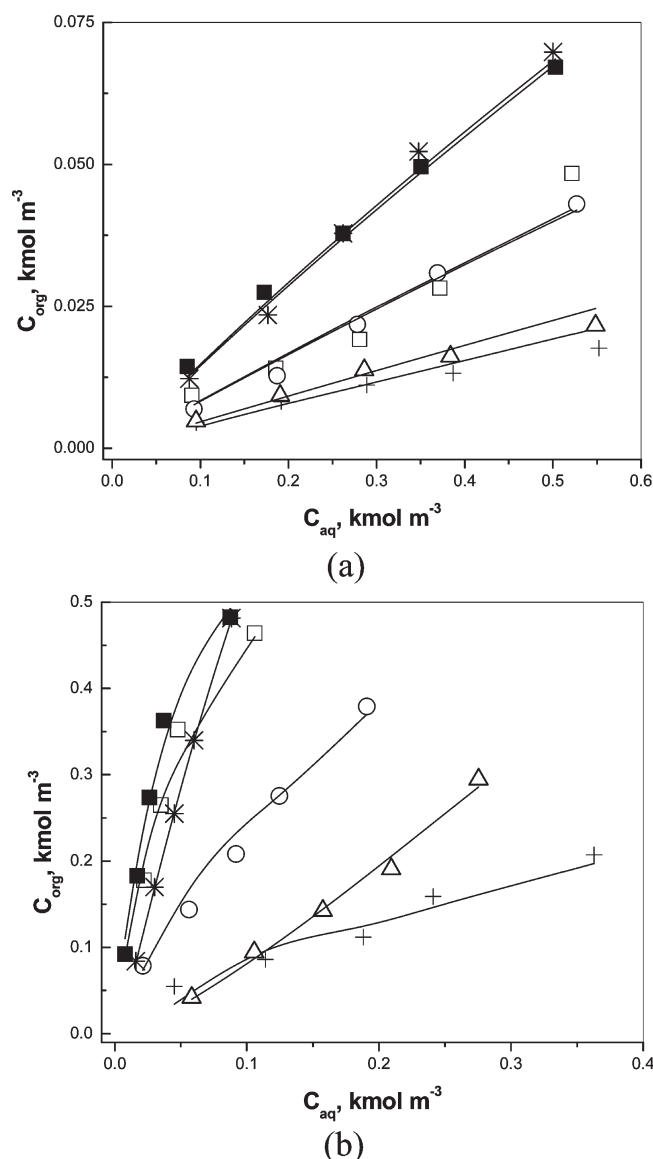
**Figure 1.** Equilibrium isotherm between organic phase concentration ($C_{org}$) and aqueous phase concentration ($C_{aq}$) of glycolic acid with (a) TBP ($0.573$ kmol·m$^{-3}$) and (b) TOA ($0.573$ kmol·m$^{-3}$) dissolved in different diluents at $298 \pm 1$ K. Symbols: +, *n*-hexane; □, decan-1-ol; ○, *n*-hexane + decan-1-ol (1:1 v/v); ∗, MIBK; △, benzene; ■, DCM; —, solid line for model predicted values [eqs 21 and 22].



**Figure 2.** Distribution coefficients ($K_D$) at 0.1 kmol·m$^{-3}$ of glycolic acid with (a) TBP ($0.573$ kmol·m$^{-3}$) and (b) TOA ($0.573$ kmol·m$^{-3}$) in different diluents at $298 \pm 1$ K.

## ■ LSER MODEL

The experimental data are also used to predict the values of distribution coefficient ($K_D$) using the linear solvation energy relationship (LSER)[20] that measures $K_D$ by taking into account the solvent properties of the system and is represented by eq 23.

$$\log K_D = \log K_D^{\circ} + s(\pi^* + d\delta) + b\beta + a\alpha + h\delta_h \qquad (23)$$

where $\pi^*$, $\delta$, $\beta$, and $\alpha$ are the solvatochromic parameters of the solvent; $\delta_h$ is the Hildebrand's solubility parameter; and $s$, $d$, $b$, $a$, and $h$ are regression coefficients dependent on the properties of the solute. $\pi^*$ is an index of the solvent dipolarity/polarizability that is a measure of the solvent's ability to stabilize a charge or a dipole by its own dielectric effect. $\alpha$ (scale of hydrogen bond donor, HBD) acidities describe the ability of the solvent to
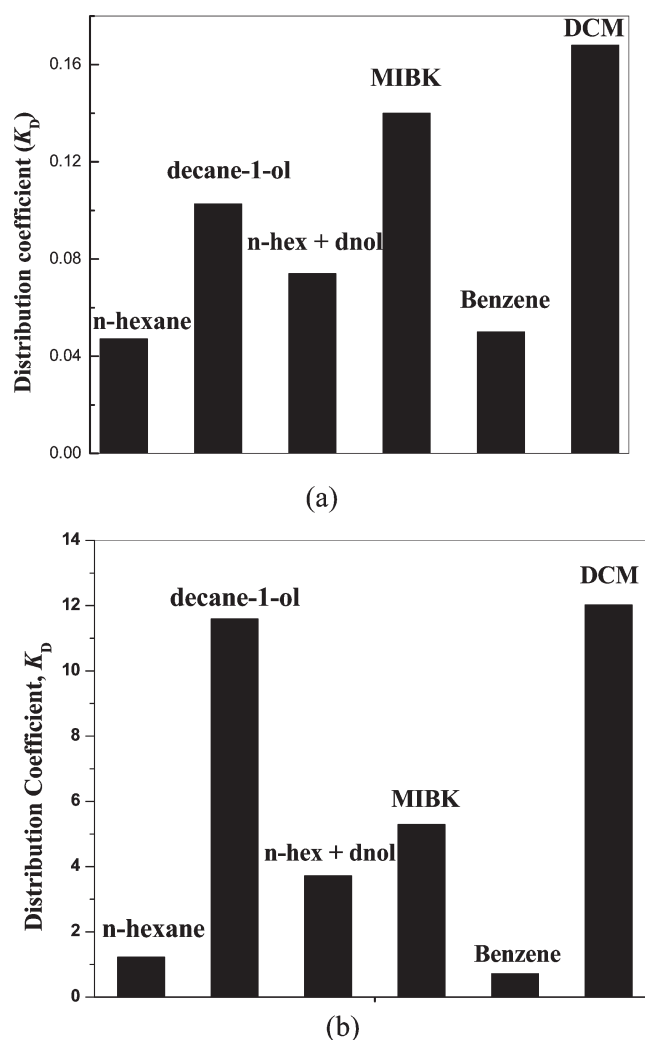
donate a proton in a solvent-to-solute hydrogen bond. The scale $\beta$ of hydrogen bond acceptor (HBA) basicities provides a measure of the solvent's ability to accept a proton or donate an electron pair in a solute-to-solvent hydrogen bond. The parameter, $\delta$ is a polarizability correction factor. The values of $\delta$ reflect that differences in solvent polarizability are significantly greater between different classes of solvent rather than the same classes of solvent. $K_D^{\circ}$ represents the distribution coefficient for an ideal pure solvent. $\delta_h$ is a measure of solvent/solvent interactions that are interrupted in creating a cavity for the solute and is important when dealing with enthalpies or free energies of solution or transfer between solvents, or with gas−liquid chromatographic partition coefficients. Here, the parameter $\delta_h$ in eq 23 does not affect the values of the objective function ($\log K_D$) significantly. Thus, eq 23 results in eq 24.

$$\log K_D = \log K_D^{\circ} + s(\pi^* + d\delta) + b\beta + a\alpha \qquad (24)$$

The solvatochromic parameters of the solvent mixture[11,21] can be calculated according to eq 25.

$$SP_{12} = X_1 SP_1 + (1 - X_1)SP_2 \qquad (25)$$

**Table 2. Values of Number of Reacting Acid and Extractant Molecules ($m$, $n$), Equilibrium Constants ($K_E$, $K_{11}$, $K_{21}$), and rmsd with Different Diluents**

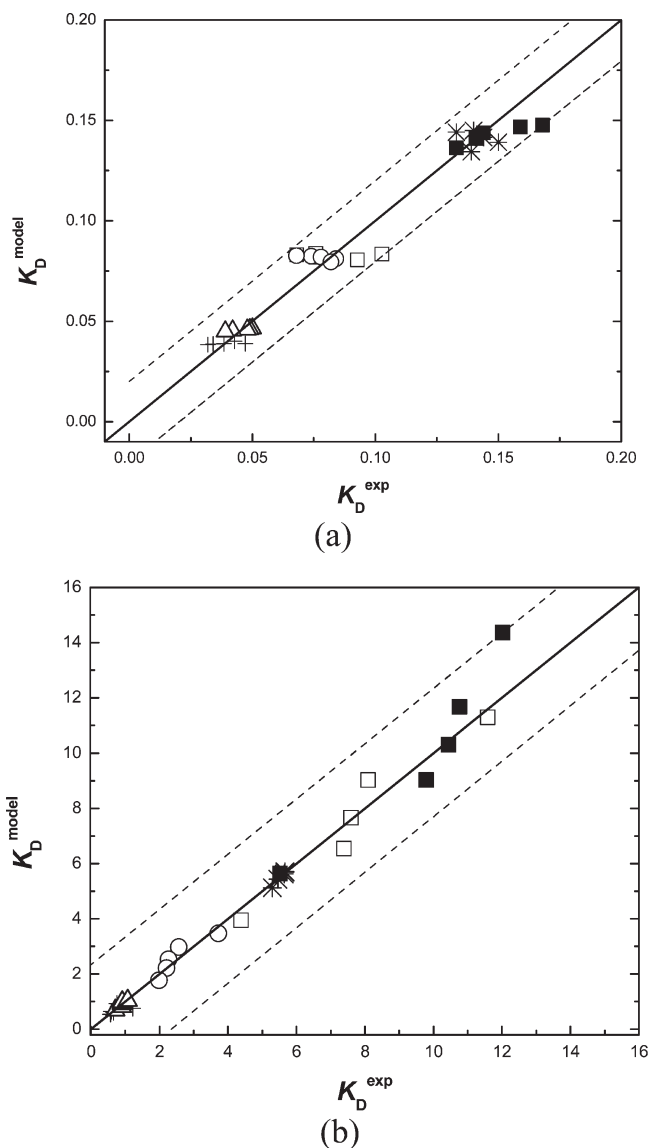| | TBP (0.573 kmol·m$^{-3}$) | | | | TOA (0.573 kmol·m$^{-3}$) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| diluents | $m$ | $n$ | $K_E$ | rmsd | $m$ | $n$ | $K_E$ | rmsd | $K_{11}$ | $K_{21}$ | rmsd |
| $n$-hexane | 0.80 | 1 | 0.07 | 0.001 | 0.75 | 1 | 1.49 | 0.073 | 1.47 | − | 0.224 |
| decane-1-ol | 0.92 | 1 | 0.15 | 0.012 | 1.01 | 1 | 27.20 | 0.611 | 26.52 | − | 0.613 |
| $n$-hexane + decane-1-ol (1:1 v/v) | 1.11 | 1 | 0.15 | 0.004 | 0.94 | 1 | 6.79 | 0.236 | 7.75 | − | 0.263 |
| MIBK | 1.06 | 1 | 0.28 | 0.005 | 1.37 | 1 | 38.84 | 0.255 | 9.67 | 8.44 | 0.047 |
| benzene | 0.89 | 1 | 0.08 | 0.002 | 1.42 | 1 | 3.23 | 0.055 | 0.98 | 3.47 | 0.052 |
| DCM | 0.91 | 1 | 0.28 | 0.002 | 1.19 | 1 | 56.01 | 0.272 | 33.15 | 1.75 | 1.178 |
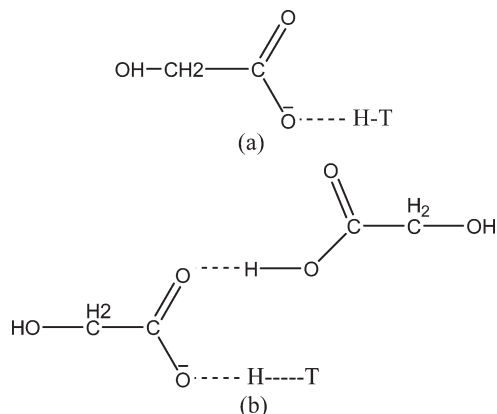


**Figure 3.** Representation of formation of (a) 1:1 and (b) 2:1 acid−extractant complexes in the organic phase.

where $X_1$ is the mole fraction of the first solvent and $X_2 = 1 - X_1$ is the mole fraction of the second solvent. $SP_1$ is the solvatochromic parameter of the first solvent, and $SP_2$ is the solvatochromic parameter of the second solvent in the solvent mixture.

## ■ RESULTS AND DISCUSSION

The equilibrium study of the reactive extraction of glycolic acid (0.10−0.57 kmol·m$^{-3}$) from aqueous solution using extractants (TBP and TOA with a constant concentration of 0.573 kmol·m$^{-3}$) dissolved in different diluents [$n$-hexane, decane-1-ol, $n$-hexane + decane-1-ol (1:1 v/v), MIBK, benzene, and DCM] was carried out. In the extraction of glycolic acid by amine extractant, the total amine concentration has no effect on the loading for the systems having only one amine molecule per acid−amine complex. If there is more than one amine molecule per complex, loading increases with increasing amine concentration.[12] Generally, the extraction efficiency is found to be increased with an increase in the concentration of amine extractant and reaches a plateau.[14,17] In the reactive extraction of glycolic acid (0.10−0.57 kmol·m$^{-3}$), TOA concentration of 0.573 kmol·m$^{-3}$ in the organic phase may not be a limiting factor for the formation of complexes between acid and amine.

The isotherms at equilibrium are drawn between the experimental organic phase concentration of glycolic acid and the aqueous phase concentration of glycolic acid at 298 ± 1 K (Figure 1a for TBP and Figure 1b for TOA). In this study, decan-1-ol, MIBK, and DCM are used as active polar solvents with higher values of the dipole moment, $\mu$ (2.62, 2.79, and 1.60, respectively), than those of other inert diluents [$n$-hexane ($\mu = 0.00$) and benzene ($\mu = 0.00$)]. The active diluents (decane-1-ol,



(a)



(b)

**Figure 4.** Model predicted, eq 13, values, versus experimental values of $K_D$ of glycolic acid (a) with TBP (0.573 kmol·m$^{-3}$) and (b) with TOA (0.573 kmol·m$^{-3}$), dissolved in different diluents at 298 ± 1 K. ---, ±8% maximum error limit lines. Symbols: +, $n$-hexane; □, decan-1-ol; ○, $n$-hexane + decan-1-ol (1:1 v/v); ∗, MIBK; △, benzene; ■, DCM.

MIBK, and DCM) are found to be better solvents than inactive ones ($n$-hexane and benzene) with both extractants (TBP and TOA) as shown in Figure 1 (slope of the isotherm for active

diluent is higher than that of inactive diluent). Figure 2 represents the comparison of the distribution coefficient ($K_D$) values of different diluents with the extractant [TBP (Figure 2a) and TOA (Figure 2b)] at constant concentration of glycolic acid (0.1 kmol·m$^{-3}$). The extraction power of TBP/diluent and TOA/diluent systems in terms of loading ratios ($Z$) and $K_D$ increases in the order DCM ≥ MIBK > decan-1-ol > $n$-hexane + decan-1-ol (1:1 v/v) ≥ benzene ≥ $n$-hexane and DCM ≥ decan-1-ol > MIBK > $n$-hexane + decan-1-ol (1:1 v/v) > benzene > $n$-hexane, respectively. The active diluents facilitate the extraction process mainly in two different ways: (i) solvation of the acid molecules with an effective competition with the water molecules that attracts the acid molecules at the interface of aqueous and organic phases and (ii) the specific interactions of the diluent with the complex by making hydrogen bonds.[3] The active diluents (decane-1-ol, MIBK, and DCM) have active groups such as the −OH (proton donor) group, the =CO (proton acceptor) group, and a chlorinated (both proton acceptor and donor) group, which enhance the extracting capability of extractant (TOA) having comparatively low polarity and allow higher levels of polar extractant complexes to stay in the organic phase. On the other hand, nonpolar diluents do not affect the extraction process significantly. Glycolic acid can be extracted by the protic (decan-1-ol) and aprotic (MIBK) diluents compared to others, whereas the degree of the acid−extractant complexation is found higher for DCM. This is because DCM affects the diluent−complex aggregation more instantaneously through hydrogen bonding and ion pair formation than the diluent−acid association in the absence of extractant. This occurrence of DCM is confirmed by the maximum value of loading ratios in the case of TOA. Therefore, the maximum values of $K_D$ and $E$ are found with

TOA in DCM (12.02 and 92.32%, respectively) for the extraction of glycolic acid.

The values of $Z$ in the range of 0.096−0.361 for $n$-hexane suggest no overloading of acid on TOA. The values of $Z$ greater than 0.5 for all other diluents (0.161−0.81 for decane-1-ol, 0.137−0.662 for $n$-hexane + decan-1-ol (1:1 v/v), 0.147−0.84 for MIBK, 0.073−0.514 for benzene, and 0.161−0.842 for DCM) suggest the overloading of acid on TOA and it may be possible to form (1:1) and (2:1) complexes between the glycolic acid and TOA, simultaneously. In the reactive extraction of glycolic acid using TBP, the values of $Z$ are found to be much less than 0.5 (0.008−0.031 for $n$-hexane, 0.016−0.084 for decan-1-ol, 0.012−0.075 for $n$-hexane + decan-1-ol (1:1 v/v), 0.021−0.122 for MIBK, 0.008−0.038 for benzene, and 0.025−0.117 for DCM) with all the diluents, implying the formation of (1:1) acid:TBP solvates in the extract phase. The reactive extraction of glycolic acid occurs by solvating alkoxy groups in TBP by competing against water molecules at the interface between the aqueous and organic phases. The studies also reported that the solvation number of the aliphatic carboxylic acids is same as the number(s) of carboxyl groups present on the acid. Since TBP extracts the acid molecules mostly by solvation, the solvation number in the reactive extraction of glycolic acid using TBP can be considered to be 1.[8,22] This fact also confirms a stoichiometric (1:1) association between the individual phosphoryl group and individual acid group. The stabilities of complexes in the organic phase are decided by the ammonium salt formation of acid by the ion pair association of alkylammonium cation and the acid radical which is a acid−base-type reaction in the case of extraction by TOA. The power of associating the proton is comparatively higher for TOA and depends on the characteristics of the diluent used other than the extraction systems. The TOA extracted the glycolic acid molecules from the aqueous solution forming two types of complexes such as (1:1) and (2:1), whereas there is formation of only (1:1) complexes in the extraction process with TBP. Therefore, the extraction of acid using TOA in different diluents is found to be much better than that of using TBP in different diluents.

The predicted values of the number of reacting acid molecules ($m$) per extractant molecule, the equilibrium constants ($K_E$) using eq 13, and the equilibrium constants ($K_{11}$ and $K_{21}$) for individual complexes using eqs 21 and 22 are given in Table 2.

**Table 3. Solvatochromic Parameters ($\pi^*$, $\beta$, $\alpha$, and $\delta$) for Individual Diluents[11,20]**

| no. | component | $\pi^*$ | $\beta$ | $\alpha$ | $\delta$ |
|---|---|---|---|---|---|
| 1 | $n$-hexane | −0.080 | 0.000 | 0.000 | 0.00 |
| 2 | decane-1-ol | 0.400 | 0.450 | 0.330 | 0.00 |
| 3 | benzene | 0.590 | 0.100 | 0.000 | 1.00 |
| 4 | MIBK | 0.630 | 0.480 | 0.000 | 0.00 |
| 5 | DCM | 0.820 | 0.100 | 0.300 | 0.50 |

**Table 4. Values of LSER Model Parameters ($s$, $d$, $b$, $a$) with Coefficient of Linear Regression ($R^2$) and Standard Error (SE)**

| $C_{HA}^{\circ}$ (kmol·m$^{-3}$) | log $K_D^{\circ}$ | LSER model parameters | | | | $R^2$ | SE |
|---|---|---|---|---|---|---|---|
| | | $a$ | $b$ | $s$ | $d$ | | |
| | | | TBP (0.573 kmol·m$^{-3}$) | | | | |
| 0.10 | −1.261 32 | 0.300 222 | −0.219 65 | 0.814 096 | −0.611 797 1 | 0.99 | 0.0002 |
| 0.20 | −1.302 91 | 0.282 912 | −0.192 13 | 0.823 787 | −0.575 043 5 | 0.99 | 0.0002 |
| 0.30 | −1.304 49 | 0.080 706 | −0.171 62 | 0.865 436 | −0.586 662 2 | 0.96 | 0.1022 |
| 0.40 | −1.316 33 | −0.0167 | −0.258 34 | 0.978 456 | −0.625 343 7 | 0.91 | 0.1775 |
| 0.57 | −1.330 32 | −0.068 24 | −0.341 45 | 1.011 467 | −0.633 970 7 | 0.88 | 0.2087 |
| | | | TOA (0.573 kmol·m$^{-3}$) | | | | |
| 0.10 | 0.169 866 | 1.743 537 | −0.236 93 | 1.059 619 | −0.864 87 | 0.99 | 0.0040 |
| 0.20 | −0.016 42 | 1.360 802 | −0.046 52 | 1.254 012 | −0.611 23 | 0.99 | 0.0130 |
| 0.30 | −0.111 4 | 1.338 625 | 0.073 493 | 1.316 626 | −0.543 9 | 0.99 | 0.0232 |
| 0.40 | −0.077 68 | 1.248 494 | 0.049 383 | 1.280 99 | −0.564 44 | 0.99 | 0.0007 |
| 0.57 | −0.120 84 | 0.618 998 | 0.321 235 | 1.116 693 | −0.484 61 | 0.99 | 0.0813 |

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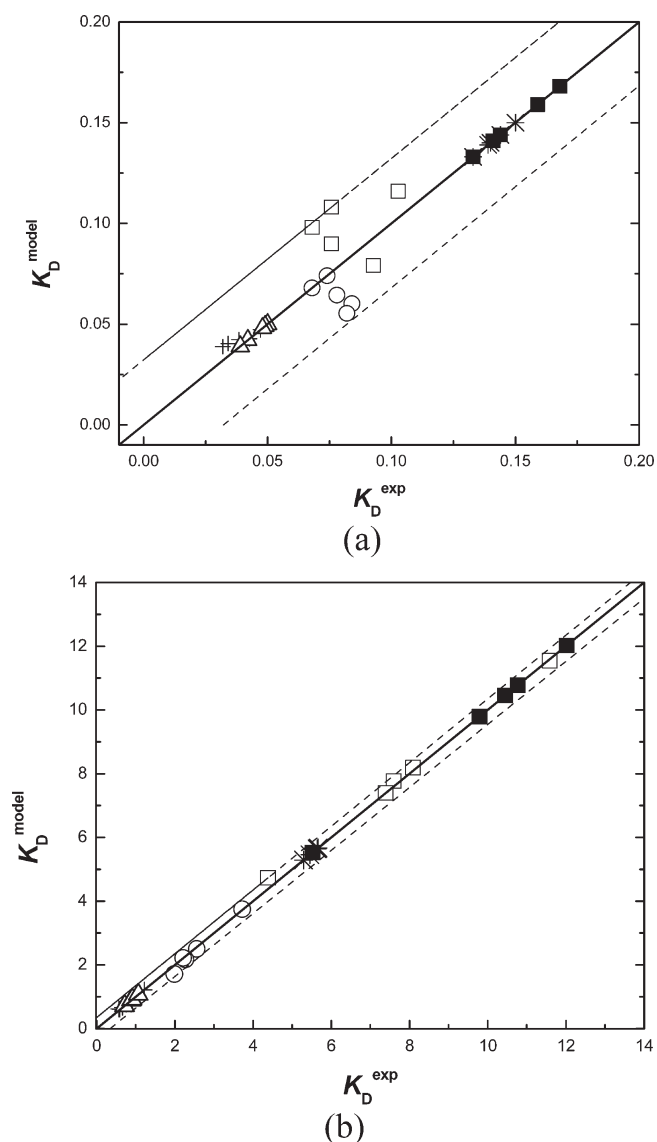dx.doi.org/10.1021/ie102024u |*Ind. Eng. Chem. Res.* 2011, 50, 3041–3048

**Figure 5.** LSER model predicted, eq 24, versus experimental values of $K_D$ of glycolic acid (a) with TBP (0.573 kmol·m$^{-3}$) (---, ±18% maximum error limit lines) and (b) with TOA (0.573 kmol·m$^{-3}$) (---, ±5% maximum error limit lines) dissolved in different diluents at 298 ± 1 K. Symbols: +, n-hexane; □, decan-1-ol; ○, n-hexane + decan-1-ol (1:1 v/v); ∗, MIBK; △, benzene; ■, DCM.

The estimated values of $m$ are found to be about 1 [0.80 for n-hexane, 0.92 for decan-1-ol, 1.11 for decan-1-ol + n-hexane (1:1 v/v), 1.06 for MIBK, 0.89 for benzene, 0.91 for DCM] with TBP and imply that there is mainly formation of (1:1) acid—TBP complex in the organic phase. However, the values of $m$ for inactive diluents (0.80 for n-hexane, 0.89 for benzene) indicate more than one solvation number of TBP may also possible. The value of $m$ (0.75) with TOA in n-hexane also suggests that there may be the possibility of a few (1:2) complexes formed between acid and TOA. The estimated stoichiometry coefficients (1.19, 1.37, and 1.42 for DCM, MIBK, and benzene, respectively) with TOA lead to the conclusion that there are simultaneous formations of both types of (1:1) and (2:1) complexes of acid—TOA in the extract phase. The formation of acid—extractant complexes can be due to the stabilization of a hydrogen bond of acid with the extractant. The structures of acid—extractant complexes in

diluents were determined by Barrow and Yerger.[23] They proposed that the proton (H$^+$) in the −COOH group of the first carboxylic acid molecule interacts directly with the extractant to form an ion pair (OHCH$_2$COO$^-$···H−T, Figure 3a) and hence the (1:1) complex. Then the −COOH group of the second glycolic acid molecule combines with the conjugated =CO to form a hydrogen bond which results in the (2:1) acid—extractant complex (=CO···H−OOCCH$_2$OH, Figure 3b).

The highest value of $K_E$ (56.01) in the case of DCM with TOA dictates it to be the best diluent—extractant system for the extraction of glycolic acid from aqueous solution. On the basis of estimated values of $m$, the equilibrium constants ($K_{11}$ and $K_{21}$) for (1:1) and (2:1) complexes, respectively, are determined. The predicted values of $K_D$ using the model eq 13 for the extraction of glycolic acid with TBP/TOA in different diluents are calculated and are comparable with the experimentally determined values of $K_D$ (Figure 4). The formation of acid:extractant complexes depends on the nature of the diluents, which affect the basicity of the extractant and the stability of the ion pair formed in the extract phase. The results show that the active diluents are not only involved in the physical extraction but also enhance the polarity of low-polarity extractant (TOA).

The LSER model is applied to predict the values of $K_D$ for extractant—diluent systems in the reactive extraction of glycolic acid from aqueous solution. The values of the solvatochromic parameters ($\pi^*$, $\delta$, $\beta$, and $\alpha$) of the diluents used in this study are given in Table 3.[20,21] For the estimation of optimum model parameters, least-squares linear regression is used to minimize the deviation between the experimental and the model predicted values of log $K_D$. The estimated values of LSER model parameters are presented in Table 4 with the values of the coefficient of determination ($R^2$) and standard error (SE). The experimental values of $K_D$ show good correlation with the LSER model predicted values of $K_D$ with $R^2 > 0.9$ and a maximum value of SE = 0.21. On the basis of the satisfactory results obtained, it is inferred that the distribution of the acid between water and extractant—diluent system can be well described using the LSER model.

The predicted values of $K_D$ using the LSER model for the system of extractants (TBP and TOA) with diluents [n-hexane, decan-1-ol, n-hexane + decane-1-ol (1:1 v/v), MIBK, benzene, and DCM] are found to be better for the description of distribution coefficients of acid between water and extractant + diluent system as shown in Figure 5. The higher $K_D$ values in the case of decane-1-ol, MIBK, and DCM as diluent with extractants can be explained on the basis of the solvatochromic parameter values (Table 3). The solvent dipolarity/polarizability ($\pi^*$) value is lowest for n-hexane (−0.08) and highest for DCM (0.82), which emphasizes the fact that DCM has a greater ability to stabilize a charge or a dipole by its own dielectric effect. The $\alpha$ (scale of solvent hydrogen bond donor, HBD) acidity value is higher for decane-1-ol ($\alpha = 0.33$) and DCM ($\alpha = 0.30$) than for other diluents, which means the ability of decane-1-ol and DCM to donate a proton in a solvent-to-solute hydrogen bond is higher. Therefore, decane-1-ol and DCM can promote more (1:1) complex formations between acid and extractant. The hydrogen bond acceptor (HBA) basicity ($\beta$) values for MIBK and decane-1-ol are 0.52 and 0.45, respectively, and show their greater ability to accept a proton or donate an electron pair in a solute-to-solvent hydrogen bond. The parameter $\delta$ is a polarizability correction factor which is 0.0 for nonchlorinated aliphatic solvents (n-hexane, decane-1-ol, MIBK), 0.5 for polychlorinated

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aliphatic solvents (DCM), and 1.0 for aromatic solvents (benzene). All these facts emphasize that the solute hydrogen acidity ($\alpha$) and basicity ($\beta$) show a significant correlation with the distribution of the acid between water and extractant−diluent system. Due to the different kinds of physical interactions of the solvents with the solute, the polar diluents such as decane-1-ol, MIBK, and DCM serve as hydrogen donors (HBD) and/or hydrogen acceptors (HBA) with different stabilizing powers of proton bonds formed.

## ■ CONCLUSIONS

An equilibrium study on the reactive extraction of glycolic acid using TBP and TOA as extractants dissolved in different diluents has been performed. The extractability of glycolic acid using TBP/TOA is found to be higher with the polar diluents (decane-1-ol, MIBK, and DCM). The extraction efficiency for the diluents used is found to be in the order DCM ≥ MIBK > decan-1-ol > n-hexane + decan-1-ol (1:1 v/v) ≥ benzene ≥ n-hexane with TBP and DCM ≥ decan-1-ol > MIBK > n-hexane + decan-1-ol (1:1 v/v) > benzene > n-hexane with TOA. Among the two extractants (TBP and TOA), TOA with higher hydrogen bonding ability is found to be the better extractant. The maximum values of $K_D$ and $E$ for reactive extraction of glycolic acid are found to be 12.02 and 92.32%, respectively, with TOA in DCM at 0.10 kmol·m$^{-3}$ of initial acid concentration. In the reactive extraction of glycolic acid with TBP in all the diluents, mainly (1:1) complexes between acid and TBP are formed, but both types of complexes (1:1) and (2:1) are formed among acid and TOA when DCM, MIBK, and benzene are used as diluent. The highest value of $K_E$ (56.01) with TOA in DCM mostly promotes (1:1) acid−TOA complex. The $K_E$ and $m$ values are determined through a proposed mathematical model (Chemodel), and based on the predicted stoichiometry ($m$), the individual equilibrium constants, $K_{11}$ and $K_{21}$, for (1:1) and (2:1) acid−extractant complexes, respectively, are estimated. The values of $K_D$ of acid between water and extractant system is also described by the LSER model, and the LSER equations for determining the $K_D$ values are also presented. The predicted values of $K_D$ using Chemodel (mass action law) and LSER model are found to be comparable with the experimental values of $K_D$.

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