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Reactive Extraction of 2-Methylidenebutanedioic Acid with *N*,*N*-Dioctyloctan-1-amine Dissolved in Six Different Diluents: Experimental and Theoretical Equilibrium Studies at (298 ± 1) K

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ABSTRACT: In this paper, the equilibrium study on the reactive extraction of 2-methylidenebutanedioic acid (five initial acid concentrations in the range of 0.05 to 0.25 $\text{mol}\cdot\text{dm}^{-3}$) from aqueous solution by *N*,*N*-dioctyloctan-1-amine (TOA, 0.115 and 0.229 $\text{mol}\cdot\text{dm}^{-3}$) as extractant dissolved in six different diluents [heptane, kerosene, methyl benzene, decane-1-ol, 4-methylpentan-2-one (MIBK), and dichloromethane (DCM)] is carried out. The extraction results are presented in terms of distribution coefficient (K_D), degree of extraction (E) and loading ratio (Z). The highest value of the K_D is found to be 32.478 at 0.05 $\text{mol}\cdot\text{dm}^{-3}$ of 2-methylidenebutanedioic acid concentration with 0.229 $\text{mol}\cdot\text{dm}^{-3}$ of TOA in DCM. The extractability of TOA in different diluents in terms of K_D is found to be in the order of DCM > MIBK ≥ decan-1-ol > methyl benzene > kerosene > heptane. The mathematical model is proposed and used to estimate the equilibrium constant (K_E) and stoichiometry (m, n) of the reactive extraction. Based on the stoichiometry, the corresponding individual equilibrium constants (K_{11}, K_{21}, and K_{12}) for the formation of (1:1), (2:1), and (1:2) acid:TOA complexes, respectively, are also determined. Further, the experimental values of K_D are correlated using the linear solvation energy relationship (LSER) model which is based on solute−solvent interaction parameters.

INTRODUCTION

2-Methylidenebutanedioic acid ($\text{p}K_{a1} = 3.65$[1] and $\text{p}K_{a2} = 5.13$[1] at 25 °C, $\log P = -0.43$, where P is the distribution coefficient of the solvent in a standard octane-1-ol and water two-phase system[2,3]) is a α-substituted propenoic acid and finds its application in the manufacture of synthetic resins, coatings, and other industrial products. Its usage as additive improves the quality of paints and makes the carpet fiber more durable. The resins of 2-methylidenebutanedioic acid with propenoic acid or 2-methylpropenoic acid or their esters are used in emulsion coating, leather coating, and coatings for cars, refrigerators, and other electrical appliances and enhance their physical properties. The polymer of 2-methylidenebutanedioic acid due to its special luster and transparency is used for making synthetic cut stone and special lens. This acid is chemically synthesized by the catalytic condensation of butanedioic acid derivatives with methanal. This process may have some disadvantages such as (i) heavy consumption of chemicals, (ii) high energy utilization, and (iii) undesired byproduct formation. Recently, fermentation technology is found to be an attractive alternative to produce 2-methylidenebutanedioic acid from renewable sources. The production of this acid using *Aspergillus terreus* by biochemical fermentation route is comparatively a clean and green technology with very low acid concentration.[4,5] Therefore, to make the fermentation route efficient and effective, there is a need to develop novel fermentation process which uses highly efficient separation technique. Several separation processes in chemical industries have been employed to recover the organic acids from aqueous solution.[6,7] Among the various alternate separation processes the reactive extraction method, which represents the interaction of acid (solute) molecule with solvent/extractant molecule and transfers solute molecule by the diffusion and solubilization mechanism of the system components, has been proposed to be an effective primary separation step for the recovery of carboxylic acid from a dilute solution.[8−11]

Many studies are available in the literature on the reactive extraction of different dicarboxylic acids from aqueous streams by different extractants [tri-n-butylphosphate (TBP), 1-dioctylphosphoryloctane (TOPO), di-2-ethylhexylphosphoric acid, *N*-methyl-*N*,*N*-dioctyloctan-1-ammonium chloride (Aliquat 336), tridodecylamine (TDDA), *N*,*N*-dioctyloctan-1-amine (TOA), Amberlite LA-2 etc.].[1,4,5,12−19] The extraction of dicarboxylic acids (2-methylidenebutanedioic, maleic, hydroxybutanedioic, oxalic, 2,3-dihydroxybutanedioic, and butanedioic acid) from aqueous solutions with TBP dissolved in dodecane was studied at different volume-phase ratios by Kyuchoukov et al.[1] They proposed the extraction mechanism based on mass action law and found the presence of two types of acid:extractant complexes namely (1:1) and (1:2) in the organic phase. Wasewar et al.[4] carried out the reactive extraction of 2-methylidenebutanedioic acid from aqueous solution using Aliquat 336 in ethyl acetate, kerosene, methylbenzene, and hexane and proposed (1:1) acid-amine complex formation in the organic phase. The maximum values of the distribution coefficient (K_D) and degree of extraction (E) were found to be 2.65 and 72.66%, respectively, with Aliquat 336 in ethyl acetate. The same group carried out the reactive extraction of 2-methylidenebutanedioic acid using two different extractants (TBP and Aliquat 336) in sunflower oil.[5] They reported the maximum values of the K_D equal to 4 with TBP and 0.95 with Aliquat 336. Asci et al.[12] used Amberlite LA-2

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as extractant in different diluents (hexane, cyclohexane, methyl benzene, 2, 2, 4-trimethylpentane, MIBK, octan-2-one, and octan-1-ol) for the reactive extraction of butanedioic acid from aqueous solution. They proposed simultaneous acid-amine complexes formation of (1:1) and (1:2) for proton-donating diluents and (1:2) and (2:3) for nonproton-donating diluents. Bayazit et al.[13] conducted the reactive extraction of 3-carboxy-3-hydroxypentanedioic acid using TDDA and Amberlite LA-2 in five different diluents such as MIBK, octan-1-ol, methyl benzene, cyclohexane, and 2,2,4-trimethylpentane. Octan-1-ol was proposed to be the most effective solvent for both TDDA ($K_{D,max}$ = 29.63) and Amberlite LA-2 ($K_{D,max}$ = 103.80). In the extraction of 3-carboxy-3-hydroxypentanedioic acid by Aliquat 336 dissolved in propan-2-ol, octan-2-ol (active solvents) and their mixture [propan-2-ol (w = 0.488) + octan-2-ol (w = 0.512)], a linear solvation energy relationship (LSER) model was proposed to explain the diluent effect on the K_D values of acid by Uslu.[14] In the reactive extraction of pentanedioic acid with various TOA concentrations in different diluents [isoamyl alcohol, octan-1-ol, nonan-1-ol, decan-1-ol, butan-2-one (MEK), 2, 6 dimethyl-4-heptanone (DIBK), hexan-2-one, methyl benzene, kerosene, and hexane], kerosene is found to be the most effective diluent ($K_{D,\ max}$ = 7.88) by Pehlivanoglu et al.,.[15] Later, they also used Aliquat 336 as extractant in various diluents (3-methyl butan-1-ol, octan-1-ol, nonan-1-ol, decan-1-ol, MEK, 2, 6-dimethyl-4-heptanone, hexan-2-one, methyl benzene, kerosene, and hexane) in the reactive extraction of pentanedioic acid.[16] Hano et al.[17] studied the extraction equilibria of different organic acids (ethanoic, 2-hydroxyethanoic, propanoic, 2-hydroxypropanoic, 2-oxopropanoic, butanoic, butanedioic, *E*-butenedioic, maleic, hydroxybutanedioic, 2-methylidenebutanedioic, 2, 3-dihydroxybutanedioic, 3-carboxy-3-hydroxypentanedioic, and 1-hydroxypropane-1, 2, 3-tricarboxylic) using TOPO in hexane. In their study, it was found that the hydrophobicity of the acid is the governing factor which decides and controls the extraction equilibrium constant. Bressler and Braun[18] conducted the selective separation of 2-methylidenebutanedioic acid by water-immiscible amine extractants and represented the experimental data in terms of loading ratios, distribution curves, FTIR, and fluorescence spectra. Matsumoto et al.[19] studied the extraction of organic acids (ethanoic, 2-hydroxyethanoic, propanoic, 2-hydroxypropanoic, butanedioic, *E*-butenedioic, L-malic, and 2-methylidenebutanedioic) with TOA and/or TBP in hexane. They correlated the extraction equilibrium constants with the hydrophobicity of the acid.

Above studies on the reactive extraction of different dicarboxylic acids suggest that amine based extractants particularly tertiary amines (TOA) are found to be most efficient extractants for the recovery of these acids from aqueous solution. The present work is aimed to intensify the recovery of 2-methylidenebutanedioic acid by reactive extraction with *N*,*N*-dioctyloctan-1-amine (TOA) in wide range of diluents such as alkane (heptane), aromatic (kerosene and methyl benzene), alcohol (decane-1-ol), ketone [4-methylpentan-2-one (MIBK)], and chloro-hydrocarbon [dichloromethane (DCM)]. Using the equilibrium experimental data and proposed mathematical model based on mass action law, the values of equilibrium constants (K_E) and stoichiometry (m: n) of reactive extraction are determined. Based on the predicted stoichiometry, the individual equilibrium constants (K_{11}, K_{21} and K_{12}), for complexes (1:1), (2:1), and (1:2), respectively, between acid and extractant are also estimated. The experimental values of K_D are used to predict LSER model equations at each initial 2-methylidenebutanedioic acid concentration.

EXPERIMENTAL SECTION

Reagents. 2-Methylidenebutanedioic acid, a white crystalline powder (a dicarboxylic acid) with a purity of mass fraction (w) = 0.995, was purchased from Himedia, India. *N*,*N*-Dioctyloctan-1-amine (molar mass 353.68 kg·kmol^{-1}) with a purity of w = 0.98 procured from Fluka, U.S.A. is used as extractant in this study. The diluents such as heptane (S. D. Fine-Chem, India; w = 0.99), kerosene (commercial-grade), methyl benzene (SISCO, India; w = 0.997), decane-1-ol (Spectrochem, India; w = 0.98), MIBK (Spectrochem, India; w = 0.998), and DCM (Fisher Scientific, India; w = 0.99) of technical grade are used to prepare the organic solutions. Sodium hydroxide used for titration is supplied by Merck, Germany, w = 0.98. 3, 3-Bis(4-hydroxyphenyl) isobenzofuran-1(3H)-one solution (pH range 8.2 to 10.0) is used as an indicator for titration and is procured from CDH, India.

Procedure. The aqueous solutions of 2-methylidenebutanedioic acid are prepared in the concentration range of 0.05 to 0.25 mol·dm^{-3} using distilled water. Two concentrations of TOA (0.115 and 0.229 mol·dm^{-3}) in the six different diluents (heptane, kerosene, methyl benzene, decane-1-ol, MIBK, and DCM) are used as the organic phase. Equal volumes of the aqueous and organic solution (20 mL) are taken in the conical flasks of 100 mL and shaken at 100 rpm for 8 h in a temperature controlled reciprocal shaker bath (HS 250 basic REMI laboratories) at constant temperature (298 ± 1) K. Based on the preliminary studies, the 8 h of mixing time is considered as the appropriate time for attaining the equilibrium. After attaining equilibrium, the mixture of aqueous and organic phase is kept for separation in the separating funnel (125 mL) for 2 h at (298 ± 1) K. After separation of both the phases, the aqueous phase is titrated to determine the concentration of 2-methylidenebutanedioic acid using fresh NaOH solution of 0.01 N and 3,3-bis (4-hydroxyphenyl) isobenzofuran-1(3H)-one as an indicator at equilibrium. The acid concentration in the organic phase is calculated by mass balance. The equilibrium pH of aqueous solution is measured using a digital pH-meter of ArmField Instruments (PCT 40, Basic Process Module, U.K.). In the present study the pH is found to be in the range of 2.50 to 3.61. The concentration of undissociated acid is a function of the pH of the aqueous phase concentration of acid at equilibrium and hence it is assumed that only undissociated acid molecules take part in the extraction process.[4,19] The uncertainty of the experimental measurements is calculated with the identification of its sources (aqueous and organic sample preparation, impurities of chemicals, tolerance of the glasswares, repeatability, and titration method) and found to be ± 4.5 %.

THEORETICAL SECTION

The activities of the aqueous and organic phase species are assumed to be proportional to the respective concentration of the species, where the equilibrium constant takes care of the constant of proportionality (the nonidealities). Therefore, the apparent equilibrium constant (written in terms of species concentration) is used for the development of mathematical model of the reactive extraction. To describe the reactive extraction process, the assumptions made are (i) negligible physical extraction of 2-methylidenebutanedioic acid by individual diluents, (ii) no acid dimer formation in the organic phase,

(iii) water coextraction is neglected due to strong interactions between acid and extractant molecules, and (iv) only undissociated acid molecule is extracted by the extractant.[4,5,20,21] The equilibrium extraction process can be described as a set of reactions between *m* molecules of acid (H_2A), and *n* molecules of extractant (T) to form various (*m:n*) acid:extractant complexes (eq 1), with corresponding apparent equilibrium constant (K_E) (eq 2)

$$m\mathrm{H_2A} + n\overline{\mathrm{T}} \Leftrightarrow \overline{(\mathrm{H_2A})_m(\mathrm{T})_n} \tag{1}$$

$$K_E = \frac{[\overline{(\mathrm{H_2A})_m(\mathrm{T})_n}]}{[\mathrm{H_2A}]^m[\overline{\mathrm{T}}]^n} \tag{2}$$

The extraction process is analyzed by means of experimentally determined distribution coefficient (K_D) and given by eq 3

$$K_D = \frac{\overline{C}_{\mathrm{H_2A}}}{C_{\mathrm{H_2A}}} = m\frac{[\overline{(\mathrm{H_2A})_m(\mathrm{T})_n}]}{C_{\mathrm{H_2A}}} \tag{3}$$

where $\overline{C}_{\mathrm{H_2A}}$ and $C_{\mathrm{H_2A}}$ are the total 2-methylidenebutanedioic acid concentration in the organic and aqueous phase, respectively, and $[\overline{(\mathrm{H_2A})_m(\mathrm{T})_n}]$ is the concentration of acid:amine complex in the organic phase at equilibrium.

The 2-methylidenebutanedioic acid dissociates in the aqueous phase at equilibrium and the dissociation mechanism is given by following eqs 4 and 5:

$$\mathrm{H_2A} \Leftrightarrow \mathrm{H^+} + \mathrm{HA^-} \tag{4}$$

$$\mathrm{HA^-} \Leftrightarrow \mathrm{H^+} + \mathrm{A^{2-}} \tag{5}$$

The corresponding dissociation constants (K_{a1} and K_{a2}) are given by eqs 6 and 7, respectively

$$K_{a1} = \frac{[\mathrm{H^+}][\mathrm{HA^-}]}{[\mathrm{H_2A}]} \tag{6}$$

$$K_{a2} = \frac{[\mathrm{H^+}][\mathrm{A^{2-}}]}{[\mathrm{HA^-}]} \tag{7}$$

Again, the total acid concentration in the aqueous phase ($C_{\mathrm{H_2A}}$) at equilibrium can be expressed in terms of undissociated acid concentration ([H_2A]), and dissociated acid concentration ([HA^-] and [A^{2-}])

$$C_{\mathrm{H_2A}} = [\mathrm{H_2A}] + [\mathrm{HA^-}] + [\mathrm{A^{2-}}] \tag{8}$$

The values of pK_{a1} and pK_{a2} of 2-methylidenebutanedioic acid are 3.65 and 5.13, respectively. In this study the values of pH are found to be less than pK_{a1} of acid. Considering the second dissociation of acid, the concentration of undissociated ([H_2A]), first dissociated ([HA^-]), and second dissociated ([A^{2-}]) acid are found to be (0.03972, 0.00644, and 3.45945×10^{-5}) $\mathrm{mol \cdot dm^{-3}}$, respectively, for 0.05 $\mathrm{mol \cdot dm^{-3}}$ of 2-methylidenebutanedioic acid concentration. Therefore, the second dissociation of acid is very small as compared to undissociation and first dissociation of the acid and it can be neglected. Therefore, the dissociation of second carboxylic group is neglected in the extraction process and the eq 8 is rewritten as eq 9

$$C_{\mathrm{H_2A}} = [\mathrm{H_2A}] + [\mathrm{HA^-}] \tag{9}$$

The undissociated acid concentration is given by eq 10

$$[\mathrm{H_2A}] = \frac{C_{\mathrm{H_2A}}}{\left(1 + \frac{K_{a1}}{[\mathrm{H^+}]}\right)} \tag{10}$$

The equilibrium free extractant concentration ([$\overline{T}$]) in the organic phase is written as:

$$[\overline{\mathrm{T}}] = [\overline{\mathrm{T}}]_0 - n[\overline{(\mathrm{H_2A})_m(\mathrm{T})_n}] \tag{11}$$

or

$$[\overline{\mathrm{T}}] = [\overline{\mathrm{T}}]_0 - K_D n C_{\mathrm{H_2A}}/m \tag{12}$$

Using eqs 2, 3, 10, and 12, eq 13 is derived.

$$K_D = mK_E\left([\overline{\mathrm{T}}]_o - K_D n\frac{C_{\mathrm{H_2A}}}{m}\right)^n \frac{(\mathrm{H_2A})^m}{C_{\mathrm{H_2A}}} \tag{13}$$

The values of equilibrium extraction constants (K_E) and the stoichiometry (*m, n*) of the reactive extraction of 2-methylidenebutanedioic acid are estimated by optimizing the error between the experimental and predicted values of K_D using the following objective function known as root-mean-square deviation (rmsd).

$$\mathrm{RMSD} = \left[\frac{\Sigma(K_D^{\mathrm{exp}} - K_D^{\mathrm{model}})^2}{N}\right]^{1/2} \tag{14}$$

where *N* is the number of data points.

The eq 13 is used to predict the values of *m* per extractant molecule and based on these values the formation of different types of acid:amine complexes like (1:1), (2:1), and (1:2) are considered and represented by the following stoichiometric eqs 15, 16, and 17, respectively:

$$\mathrm{H_2A} + \overline{\mathrm{T}} \Leftrightarrow \overline{(\mathrm{H_2A})(\mathrm{T})} \tag{15}$$

$$\mathrm{H_2A} + \overline{(\mathrm{H_2A})(\mathrm{T})} \Leftrightarrow \overline{(\mathrm{H_2A})_2(\mathrm{T})} \tag{16}$$

$$\overline{(\mathrm{H_2A})(\mathrm{T})} + \overline{\mathrm{T}} \Leftrightarrow \overline{(\mathrm{H_2A})(\mathrm{T})_2} \tag{17}$$

The corresponding equilibrium extraction constants (K_{11}, K_{21}, and K_{12}) for individual acid:extractant complexes are obtained using eqs 18, 19, and 20, respectively:

$$K_{11} = \frac{[\overline{(\mathrm{H_2A})(\mathrm{T})}]}{[\mathrm{H_2A}][\overline{\mathrm{T}}]} \tag{18}$$

$$K_{21} = \frac{[\overline{(\mathrm{H_2A})_2(\mathrm{T})}]}{[\mathrm{H_2A}][\overline{(\mathrm{H_2A})(\mathrm{T})}]} \tag{19}$$

$$K_{12} = \frac{[\overline{(\mathrm{H_2A})(\mathrm{T})_2}]}{[\overline{(\mathrm{H_2A})(\mathrm{T})}][\overline{\mathrm{T}}]} \tag{20}$$

The equilibrium 2-methylidenebutanedioic acid and free extractant concentration in the organic phase are represented by eqs 21 and 22, respectively:

$$\begin{aligned}\overline{C}_{\mathrm{H_2A}} &= [\overline{(\mathrm{H_2A})(\mathrm{T})}] + 2[\overline{(\mathrm{H_2A})_2(\mathrm{T})}] + [\overline{(\mathrm{H_2A})(\mathrm{T})_2}] \\ &= K_{11}[\mathrm{H_2A}][\overline{\mathrm{T}}] + 2K_{11}K_{21}[\mathrm{H_2A}]^2[\overline{\mathrm{T}}] + K_{11}K_{12}[\mathrm{H_2A}][\overline{\mathrm{T}}]^2\end{aligned} \tag{21}$$

$$\begin{aligned}[\overline{\mathrm{T}}] &= [\overline{\mathrm{T}}]_o - \overline{(\mathrm{H_2A})(\mathrm{T})} - \overline{(\mathrm{H_2A})_2(\mathrm{T})} - 2\overline{(\mathrm{H_2A})(\mathrm{T})_2} \\ &= [\overline{\mathrm{T}}]_o - K_{11}[\mathrm{H_2A}][\overline{\mathrm{T}}] - K_{11}K_{21}[\mathrm{H_2A}]^2[\overline{\mathrm{T}}] \\ &\quad - 2K_{11}K_{12}[\mathrm{H_2A}][\overline{\mathrm{T}}]^2 \end{aligned} \tag{22}$$

The values of the equilibrium constants K_{11}, K_{21}, and K_{12} are estimated based on the total acid concentration in the aqueous phase at equilibrium and by optimizing the error between the experimental and predicted values of organic phase acid concentration ($\overline{C}_{\mathrm{H_2A}}$) using the following objective function:

$$\mathrm{RMSD} = \left[\frac{\Sigma(\overline{C}^{\mathrm{exp}}_{\mathrm{H_2A}} - \overline{C}^{\mathrm{model}}_{\mathrm{H_2A}})^2}{N}\right]^{1/2} \tag{23}$$

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 written as eq 24

$$E = \frac{K_D}{1 + K_D} \times 100 \tag{24}$$

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).

$$Z = \frac{\overline{C}_{\mathrm{H_2A}}}{[\overline{\mathrm{T}}]_o} \tag{25}$$

■ LSER MODEL

The experimental values of the distribution coefficients (K_D) are also used to correlate the solvent properties of the diluent system using the linear solvation energy relationship (LSER)[22,23] and is represented by eq 26

$$\log_{10} K_D = \log_{10} K_D^o + s(\pi^* + d\delta) + b\beta + a\alpha + h\delta_h \tag{26}$$

where π^*, δ, β, and α are the solvatochromic parameters of the solvent; δ_h is the Hildebrand's solubility parameter; and s, d, b, a, and h are regression coefficients depend on the properties of solute. π^* is an index of the solvent dipolarity/polarizability that is a measure of solvent's ability to stabilize a charge or a dipole by its own dielectric effect. α (scale of hydrogen-bond donor, HBD) acidities describe the ability of solvent to donate a proton in a solvent-to-solute hydrogen bond. The scale β 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 δ is a polarizability correction factor. The values of δ reflect differences in solvent polarizability are significantly greater between different classes of solvent rather than same classes of solvent. The K_D^0 represents the distribution coefficient for an ideal pure solvent. δ_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. But here, the parameter δ_h in eq 26 does not affect the values of the objective function ($\log_{10} K_D$) significantly. Thus, eq 26 results in eq 27

$$\log_{10} K_D = \log_{10} K_D^o + s(\pi^* + d\delta) + b\beta + a\alpha \tag{27}$$

■ RESULTS AND DISCUSSION

The equilibrium results on the reactive extraction of 2-methylidenebutanedioic acid [in the concentration range of (0.05 to 0.25) mol·dm^{-3}] from aqueous solution using TOA [(0.115 and 0.229) mol·dm^{-3}] as extractant in six different diluents (heptane, kerosene, methyl benzene, decane-1-ol, MIBK, and DCM) are presented in Table 1. In this study, decan-1-ol, MIBK, and DCM are used as active polar solvents having higher dipole moment, μ [(8.74 × 10^{-30}, 9.31 × 10^{-30}, and 5.34 × 10^{-30}) Cm, respectively] and relative permittivity, ε_r (7.6, 13.11, and 8.93, respectively) than that of other inert diluents [heptane (μ = 0.00 Cm, ε_r = 1.88), kerosene ($\mu \approx$ 0.00 Cm, ε_r = 1.80), and methyl benzene (μ = 0.31 Cm, ε_r = 2.38)]. The active diluents (decane-1-ol, MIBK, and DCM) are found to be better solvating medium than inactive ones (heptane, kerosene, and methyl benzene) with TOA as shown in Figure 1. With the increase in the initial acid concentration, the slope of the isotherm is found to be decreased and hence the K_D value with TOA in all the diluents. Solvation of the acid:extractant complex takes place by dipole−dipole interaction of solute−solvent molecule and plays a major role in the neutralization reaction between acid and extractant. Therefore, the solvation mechanism can be promoted by increasing the polarity of the diluent. The extraction ability of TOA with six different diluent system in terms of Z or K_D values are found in the order of DCM > MIBK ≥ decan-1-ol > methyl benzene > kerosene > heptane. The active diluents take part in the extraction process mainly by solvating the acid molecules and specifically interacting with the acid:amine complex molecule by making hydrogen bond.[9] The presence of active groups such as −OH (proton donating) group, ═CO (proton accepting) group and a chlorinated (both proton accepting and donating) group in the active diluents such as decane-1-ol, MIBK, and DCM, respectively, increases the extraction potential of low polar amine (TOA) and allow higher levels of polar-extractant complexes to stay in the organic phase. MIBK being a polar diluent can promote extraction by providing a better medium for the ion pair formation. However, polarity (or polarizability) is not the only factor for solvating ability of the solvents. The capability for hydrogen bonding is also an important parameter which decides upon the extracting ability of the extractant. Therefore, DCM being both proton accepting and donating solvent has shown higher K_D values with TOA in the present study.[24,25] DCM also affects the diluent-complex aggregation more instantaneously through hydrogen bonding and ion pair formation than the acid-diluent association in the absence of extractant. On the other hand, nonpolar diluents do not affect the extraction process significantly because of providing lower distribution coefficients. In case of slightly polar aromatic diluent (methyl benzene), the K_D values are found comparatively higher than that of nonpolar diluents (heptane and kerosene) due to the solvation of the acid:amine complex with the interaction of the aromatic π-electron. The highest extraction efficiency (K_D = 32.478, E = 97.01% and Z = 1.692) is found with TOA in DCM.

The values of Z in the range of 0.017 to 0.068 for heptane and 0.046 to 0.115 for kerosene suggest no overloading of acid on

Table 1. Equilibrium Reactive Extraction Data of 2-Methylidenebutanedioic Acid using TOA in Six Different Diluents at (298 ± 1) K

diluents	$[\overline{T}]_o$ mol·dm^{-3}	C_{H_2A} mol·dm^{-3}	$\overline{C}_{H_2A}$ mol·dm^{-3}	K_D^{exp}	K_D^{model}	E	Z^{exp}	Z^{model}	pH_{eq}
heptane	0.115	0.047	0.003	0.057	0.062	5.43	0.024	0.017	2.86
		0.096	0.004	0.042	0.045	4.04	0.035	0.033	2.70
		0.145	0.005	0.036	0.038	3.45	0.045	0.047	2.61
		0.193	0.007	0.036	0.033	3.44	0.060	0.059	2.55
		0.242	0.008	0.032	0.030	3.13	0.068	0.071	2.50
	0.229	0.046	0.004	0.082	0.086	7.61	0.017	0.011	2.86
		0.094	0.006	0.062	0.064	5.80	0.025	0.021	2.71
		0.143	0.007	0.047	0.053	4.49	0.029	0.031	2.62
		0.191	0.009	0.046	0.047	4.38	0.038	0.039	2.55
		0.239	0.011	0.044	0.042	4.23	0.046	0.048	2.51
kerosene	0.115	0.045	0.005	0.117	0.115	10.51	0.046	0.035	2.87
		0.091	0.009	0.103	0.088	9.33	0.081	0.063	2.72
		0.140	0.010	0.073	0.074	6.85	0.090	0.087	2.62
		0.188	0.012	0.062	0.065	5.80	0.101	0.106	2.56
		0.237	0.013	0.053	0.059	5.02	0.109	0.123	2.51
	0.229	0.038	0.012	0.313	0.332	23.86	0.052	0.038	2.90
		0.079	0.022	0.274	0.235	21.50	0.094	0.068	2.75
		0.124	0.026	0.213	0.188	17.55	0.115	0.095	2.65
		0.175	0.025	0.145	0.157	12.70	0.111	0.119	2.57
		0.226	0.024	0.109	0.137	9.79	0.107	0.138	2.52
methyl benzene	0.115	0.023	0.027	1.160	1.149	53.70	0.234	0.175	3.01
		0.051	0.049	0.969	1.032	49.22	0.429	0.462	2.84
		0.078	0.072	0.922	0.896	47.98	0.628	0.552	2.75
		0.112	0.088	0.786	0.755	43.99	0.767	0.739	2.67
		0.153	0.097	0.633	0.629	38.77	0.845	0.921	2.60
	0.229	0.022	0.028	1.309	1.537	56.69	0.124	0.186	3.03
		0.033	0.067	2.009	1.813	66.77	0.291	0.284	2.93
		0.047	0.103	2.188	1.999	68.64	0.449	0.411	2.86
		0.067	0.133	1.976	2.073	66.40	0.579	0.580	2.78
		0.086	0.164	1.899	2.033	65.50	0.714	0.724	2.73
decane-1-ol	0.115	0.006	0.044	7.370	7.287	88.05	0.384	0.307	3.31
		0.013	0.087	6.652	6.728	86.93	0.758	0.773	3.14
		0.028	0.122	4.357	4.610	81.33	1.064	1.077	2.97
		0.045	0.155	3.464	3.242	77.60	1.354	1.354	2.87
		0.071	0.179	2.524	2.194	71.62	1.562	1.569	2.77
	0.229	0.003	0.047	16.855	15.357	94.40	0.206	0.152	3.47
		0.007	0.093	13.477	13.872	93.09	0.406	0.443	3.28
		0.012	0.138	11.174	11.604	91.79	0.600	0.537	3.15
		0.019	0.181	9.713	9.207	90.67	0.791	0.762	3.06
		0.030	0.220	7.266	6.844	87.90	0.958	1.017	2.95
MIBK	0.115	0.005	0.045	8.565	8.981	89.55	0.391	0.302	3.34
		0.011	0.089	7.928	8.066	88.80	0.775	0.788	3.17
		0.026	0.124	4.739	5.084	82.58	1.080	1.089	2.99
		0.047	0.153	3.251	3.177	76.48	1.334	1.416	2.86
		0.063	0.187	2.939	2.452	74.61	1.627	1.551	2.79
	0.229	0.003	0.047	15.739	15.267	94.03	0.205	0.143	3.46
		0.008	0.092	11.754	13.971	92.16	0.402	0.431	3.25
		0.012	0.138	11.959	11.753	92.28	0.604	0.541	3.16
		0.019	0.181	9.713	9.351	90.67	0.791	0.801	3.06
		0.026	0.224	8.565	7.684	89.55	0.976	1.008	2.99
DCM	0.115	0.004	0.046	12.391	11.450	92.53	0.404	0.272	3.41

Table 1. Continued

	$\overline{[T]}_o$	C_{H_2A}	$\overline{C}_{H_2A}$						
diluents	$mol \cdot dm^{-3}$	$mol \cdot dm^{-3}$	$mol \cdot dm^{-3}$	K_D^{exp}	K_D^{model}	E	Z^{exp}	Z^{model}	pH_{eq}
		0.009	0.091	9.713	10.154	90.67	0.791	0.809	3.21
		0.022	0.128	5.696	6.154	85.07	1.113	1.141	3.02
		0.041	0.159	3.870	3.704	79.46	1.386	1.469	2.89
		0.056	0.194	3.464	2.797	77.60	1.692	1.600	2.82
	0.229	0.001	0.049	32.478	48.508	97.01	0.212	0.154	3.61
		0.004	0.096	25.783	26.666	96.27	0.420	0.596	3.41
		0.007	0.143	21.319	18.836	95.52	0.625	0.450	3.28
		0.015	0.185	12.391	10.706	92.53	0.807	0.644	3.11
		0.028	0.222	7.928	6.338	88.80	0.968	0.772	2.97

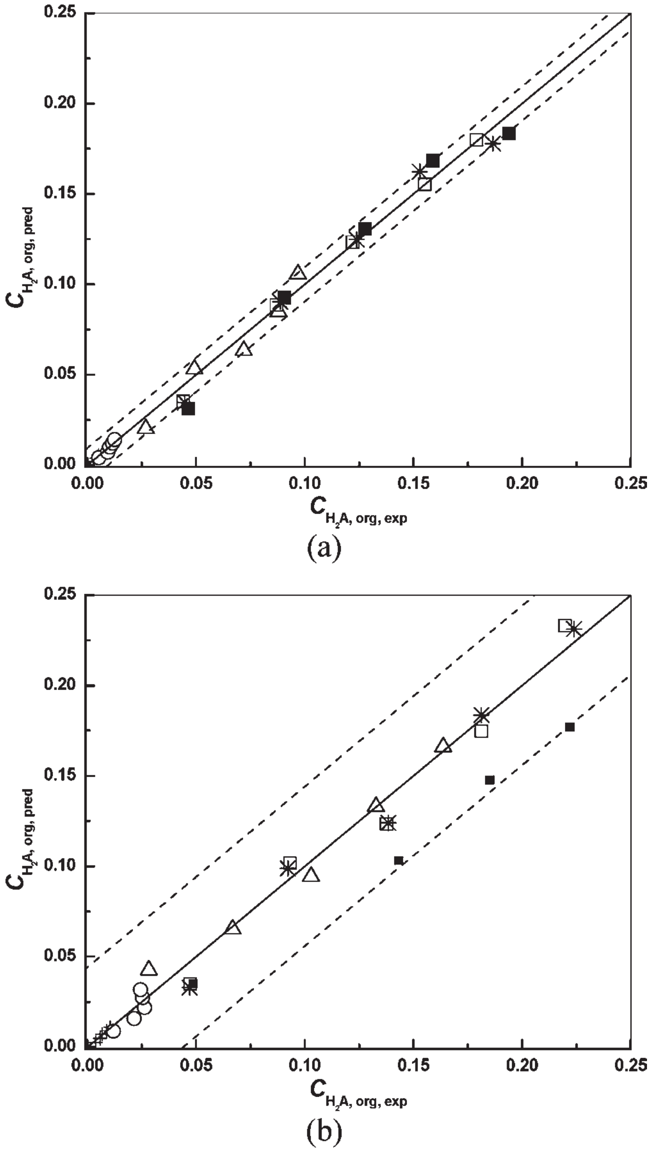

Figure 1. Model predicted (eq 21) versus experimental values of organic phase 2-methylidenebutanedioic acid concentration with TOA (a) 0.115 mol·dm^{-3}, --- ± 6 % maximum error limit lines, and (b) 0.229 mol·dm^{-3}, --- ± 20 % maximum error limit lines, dissolved in six different diluents at (298 ± 1) K. Symbols: + heptane; ○ kerosene; Δ methyl benzene; □ decan-1-ol; * MIBK; ■ DCM.

the TOA. The values of Z greater than 0.5 for all other diluents (0.124 to 0.845 for methyl benzene, 0.206 to 1.562 for decane-1-ol, 0.205 to 1.627 for MIBK, and 0.212 to 1.692 for DCM) indicate that the TOA molecules are overloaded with the acid molecules and there may be the simultaneous formation of (1:1) and (2:1) complexes between 2-methylidenebutanedioic acid and TOA.[4,21] In the extraction of 2-methylidenebutanedioic 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.[25] In this study, loading factors of all diluents decrease with increasing amine concentration at fixed acid concentration and increase with increasing acid concentration at fixed amine concentration, indicate presence of more than one acid molecule per complex.

The values of number of reacting acid molecule/s (m) per extractant molecule and the equilibrium constants (K_E) are predicted by optimizing the error between experimental and estimated values of K_D using eq 11 and presented in Table 2. The predicted values of m less than one for heptane and kerosene indicate the association of two amine molecules with one acid molecule promoting the formation of (1:1) and (1:2) acid:TOA complexes in the organic phase. The m values greater than one for methyl benzene, decane-1-ol, MIBK and DCM with TOA suggest the simultaneous formation of both types of (1:1) and (2:1) complexes between acid and TOA in the organic phase and stabilize because of the hydrogen bond. The association of acid molecule with the extractant molecule in different acid:amine complexes was also determined by Barrow and Yerger.[26] 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 [$HOOC(CH_2{=})CCH_2COO^- \cdots H{-}T$, Figure 2a] and form (1:1) complex. The $-COOH$ group of the second 2-methylidenebutanedioic acid molecule combines with the conjugated =CO to form hydrogen bond which results in (2:1) acid-extractant complex. [$={CO}\cdots H{-}OOCCH_2C(=CH_2)COOH$, Figure 2b]. The 2-methylidenebutanedioic acid is a dicarboxylic acid and hence the extractant molecule can attach to the remaining $-COOH$ group in (1:1) complex by ion pair formation [Figure 2c] giving rise to (1:2) complex in the organic phase. An increase in the concentration of TOA may lead to more formation of (1:1) complexes in case of active diluents (Table 2).

On the basis of calculated values of m, the corresponding equilibrium constants (K_{11}, K_{21} ,and K_{12}) for (1:1), (2:1), and

Table 2. Values of Number of Reacting Acid:Extractant Molecules (m, n), Equilibrium Constants (K_E, K_{11}, K_{21}, and K_{12}) and RMSD with Six Different Diluents at (298 ± 1) K

	TOA (0.115 mol·dm^{-3})								TOA (0.229 mol·dm^{-3})							
diluents	m	n	K_E	rmsd	K_{11}	K_{21}	K_{12}	rmsd	m	n	K_E	rmsd	K_{11}	K_{21}	K_{12}	rmsd
heptane	0.60	1	0.28	0.003	0.002		1957.10	0.0004	0.60	1	0.19	0.003	0.002		703.00	0.001
kerosene	0.67	1	0.58	0.006	0.003		2536.65	0.001	0.59	1	0.71	0.024	0.001		3766.56	0.005
methyl benzene	1.20	1	21.9	0.038	7.51	4.33		0.006	1.61	1	46.7	0.188	7.55	7.68		0.008
decane-1-ol	1.46	1	615	0.207	49.68	32.62		0.004	1.18	1	198	0.398	52.15	22.69		0.011
MIBK	1.44	1	758	0.273	57.84	33.65		0.007	1.20	1	212	0.564	46.40	32.55		0.010
DCM	1.44	1	1092	0.344	71.80	43.70		0.009	0.90	1	155	1.736	121.80			0.037

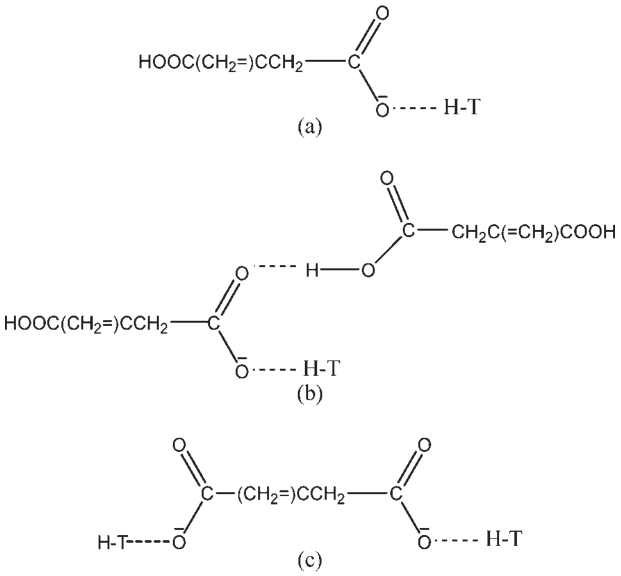

Figure 2. Representation of formation of (a) 1:1, (b) 2:1, and (c) 1:2 acid-extractant complexes in the organic phase.

(1:2) complexes are determined (Table 2). The formation of acid: extractant complexes depend on the nature of diluents, which affect the basicity of the extractant and the stability of the ion pair formed in the extract phase. From the values of individual equilibrium constants it is seen that higher values of K_{12} for inactive diluents (heptane and kerosene) and higher values of K_{11} for active diluents (methyl benzene, decane-1-ol, MIBK and DCM) emphasize on the fact that inactive and active diluents favor the extraction process by forming mostly (1:2) and (1:1) acid:extractant complex in the organic phase, respectively. The predicted values of K_D using model eq 13 are presented in Table 1 with maximum rmsd = 1.736. The values of $\overline{C}_{H_2A}$ are estimated using model eq 21 for the extraction of 2-methylidenebutanedioic acid with TOA in different diluents and plotted in Figure 1 with the experimentally determined values of $\overline{C}_{H_2A}$. The results show that the active diluents are not only involved in the physical extraction but also enhance the polarity of low polar extractant (TOA). The highest values of individual equilibrium constants in case of DCM with TOA dictate it to be the best diluent-extractant system for the extraction of 2-methylidenebutanedioic acid from aqueous solution.

The LSER model described by eq 27 is also applied to predict the values of K_D for extractant–diluent systems in the reactive extraction of 2-methylidenebutanedioic acid from aqueous solution. Since the values of K_D of acid are found to be much better with TOA concentration of 0.229 mol·dm^{-3}, this concentration of TOA at different concentrations of acid is used to estimate model parameters. The values of the solvatochromic parameters (π^*,δ, β, and α) of the diluents used in this study are given in Table 3. 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 $\log_{10} K_D$. The estimated values of LSER model parameters ($\log_{10} K_D^0$, a, b, s, and d) are presented in Table 4 at each initial 2-methylidenebutanedioic acid concentration for 0.229 mol·dm^{-3} of TOA and the experimental values of K_D are showing good correlation to the LSER model predicted values of K_D. Based on 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.

Table 3. Solvatochromic Parameters (π^*, β, α, and δ) for Individual Diluent[21,22]

component	π^*	β	α	δ
heptane	−0.080	0.000	0.000	0.00
methyl benzene	0.540	0.110	0.000	1.00
decane-1-ol	0.400	0.450	0.330	0.00
MIBK	0.630	0.480	0.000	0.00
DCM	0.820	0.100	0.300	0.50

Table 4. Values of the LSER Model Parameters (s, d, b, and a) at 0.229 mol·dm^{-3} of TOA

		LSER model parameters			
$C_{H_2A}^o$ mol·dm^{-3}	$\log_{10} K_D^0$	a	b	s	d
0.05	−0.89833	1.843436	1.283213	2.348199	−0.16775
0.10	−1.03810	1.803306	1.611195	2.118902	0.009268
0.15	−1.15601	1.574889	1.833396	2.148686	0.062406
0.20	−1.19117	1.467299	2.142185	1.825840	0.145340
0.25	−1.22266	1.158495	2.293840	1.673565	0.206230

The higher values of K_D in case of DCM, MIBK and decane-1-ol as active diluent with TOA can be explained on the basis of the solvatochromic parameter values (Table 3). The solvent dipolarity/polarizability (π^*) value is lower for heptane (−0.08) and highest for DCM (0.82), which emphasizes on the fact that DCM has greater ability to stabilize a charge or a dipole by its own dielectric effect. α (scale of solvent hydrogen-bond donor, HBD) acidity value is higher for decane-1-ol (α = 0.33) and DCM (α = 0.30) than that of 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 TOA. The highest value ($\beta = 0.52$) of hydrogen-bond acceptor (HBA) basicity for MIBK shows its greater ability to accept a proton or donate an electron pair in a solute-to-solvent hydrogen bond. The parameter, δ is a polarizability correction factor which is 0.0 for nonchlorinated aliphatic solvents (heptane, decane-1-ol, MIBK), 0.5 for polychlorinated aliphatic solvents (DCM), and 1.0 for aromatic solvents (methyl benzene). All of these facts emphasize that the solute hydrogen acidity (α) and basicity (β) show a significant correlation with the distribution of the acid between water and extractant−diluent system. Due to the different kind of physical interactions of the solvents with the solute, the polar diluents such as decane-1-ol, MIBK, and DCM serve as hydrogen donor (HBD) and/or hydrogen acceptor (HBA) with different stabilizing power of proton bond formed.

CONCLUSIONS

The equilibrium study on the reactive extraction of 2-methylidenebutanedioic acid using TOA as extractant in six different diluents is performed. The extractability of 2-methylidenebutanedioic acid using TOA is found to be higher with the polar diluents (DCM, MIBK, decane-1-ol, and methyl benzene). The extraction efficiencies of TOA in the diluents used, are found to be in the order of DCM > MIBK ≥ decan-1-ol > methyl benzene > kerosene > heptane, respectively. The maximum values of K_D for the reactive extraction of 2-methylidenebutanedioic acid with TOA ($0.229\ \mathrm{mol \cdot dm^{-3}}$) are found to be 0.082 for heptane, 0.313 for kerosene, 1.309 for methyl benzene,16.855 for decane-1-ol, 15.739 for MIBK and 32.478 for DCM at $0.05\ \mathrm{mol \cdot dm^{-3}}$ initial acid concentration. The K_E and m are determined through proposed mathematical model (based on mass action law). The values of m less than one in case of heptane and kerosene indicate mainly (1:1) and (1:2) stoichiometric association of acid:TOA and greater than one for methyl benzene, decane-1-ol, MIBK and DCM suggest mainly (1:1) and (2:1) acid:TOA complex formation in the organic phase. The highest values of K_E with TOA in DCM also suggest it to be the best extractant-diluent system. Based on the predicted stoichiometry (m), the individual equilibrium constants (K_{11} K_{21}, and K_{12}) for the formation of (1:1), (2:1), and (1:2) acid:TOA complexes, respectively, are determined. The K_D values of acid between water and TOA system are also described by the LSER model equations and are found good correlation with the experimental values of K_D.

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