Experimental Data and Theoretical (Chemodel Using the Differential Evolution Approach and Linear Solvation Energy Relationship Model) Predictions on Reactive Extraction of Monocarboxylic Acids Using Tri-*n*-octylamine[†]

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The carboxylic acids such as ethanoic, propanoic, and butanoic acids are most widely used in pharmaceutical, agricultural, polymer, and chemical industries. The separation of acids from fermentation broth and aqueous waste stream can be intensified by reactive extraction. The reactive extraction of carboxylic acids (ethanoic, propanoic, and butanoic acids) by *N*,*N*-dioctyloctan-1-amine (TOA) with six different diluents [decane, benzene, 4-methyl-2-pentanone (MIBK), decan-1-ol, chloroform, and decane ($w = 0.725$) + decan-1-ol ($w = 0.275$)] is studied. The physical equilibria using pure diluents with the same conditions are also studied. Distribution coefficients, loading factors, and degree of extraction are calculated as a result of batch extraction experiments. In the present work, a population-based search algorithm, differential evolution (DE), is employed as an optimization routine to estimate the optimum values of equilibrium constants (K_E) and stoichiometries of reactive extraction (m:n) through proposed mathematical models. On the basis of stoichiometries, the equilibrium constants (K_{11}, K_{21}, and K_{31}) for individual complexes between acid and extractant are also estimated. In addition to these parameters, the linear solvation energy relationship (LSER) model is applied to evaluate distribution coefficients, and the LSER equation is presented for each acid. The extraction power of amine/diluent system increases in the order of chloroform ≥ decan-1-ol > MIBK > decane ($w = 0.725$) + decan-1-ol ($w = 0.275$) ≥ benzene > decane.

Introduction

The carboxylic acids (HC) such as ethanoic (HA), propanoic, (HP) and butanoic acid (HB) are most widely used in the field of food and beverages as an acidulant and also in pharmaceutical, agricultural, polymer, and chemical industries. Recently, fermentation technology is an attractive alternative to produce carboxylic acids from renewable sources. The conventional fermentation technology for the production of carboxylic acid salts such as propanoate, butanoate, and succinate, etc., is thus limited by low fermentation rate and low product concentration. To make the fermentation route economically viable, it is necessary to develop novel fermentation processes that use highly efficient bioreactors and separation techniques. Separation of monocarboxylic acids from aqueous waste streams (industrial effluents) has also been important and essential from the industrial and pollution control points of view. Many separation processes in chemical industries have been employed to recover the organic acids from aqueous solution.[1,2] Among various alternate processes for the removal of the product, extraction is often the most suitable option.[3−5] Reactive extraction is developed to intensify separation by solvent extraction and represents a connection between chemical (solute and extractant reaction) and physical phenomena (diffusion and solubilization of the system components). So, a reactive extraction method has been proposed to be an effective primary separation step for the recovery of carboxylic acid from a dilute solution.[6−9] Three major factors have been found to influence the equilibrium characteristics of extraction of carboxylic acids from aqueous solutions, i.e., the nature of acid, concentrations of acid and extractant, and the type of diluent.[10−14]

Long-chain aliphatic amines with high molecular weight, such as *N*,*N*-dioctyloctan-1-amine, also known as trioctylamine (TOA) and Alamine 336 (trioctyl/decylamine), are proposed as effective extractants for the separation of carboxylic acids from dilute aqueous solution. Due to their physical properties, they must always be used in the form of solutions in organic diluents such as ketones, alcohols, hydrocarbons, etc. to provide appropriate physical properties for use in the extraction process. For the removal and separation of organic acids, it is very important to understand the influence of different parameters on the overall distribution coefficient of each organic acid. Since the presence of hydroxyl and carboxylic groups increases the solubility of acids in the water phase, the strong interactions of solvent with solutes are necessary to extract carboxylic acids from dilute aqueous solutions.[15]

The reactive extraction of carboxylic acids has been tested by various researchers. Recently, Uslu and co-workers have studied the reactive extraction of some carboxylic acids [levulinic acid (4-oxopentanoic acid), propanoic acid, tartaric acid (2,3-dihydroxybutanedioic acid), glycolic acid (2-hydroxyethanoic acid)] with TOA, trioctyl methylammonium chloride (Aliquat 336), and Alamine 336 as extractants, and the magnitudes of distribution coefficients have been demonstrated.[16−19] Very recently, Wasewar and group also extensively studied the extraction equilibrium of carboxylic acids such as propanoic, acrylic (propenoic), methanoic, and 4-oxopentanoic acids using

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Table 1. Comparison with Literature Data on Reactive Extraction of Monocarboxylic Acids

acids	extractants	diluents	parameter studied	literature
methanoic, ethanoic, propanoic, butanoic, caproic, and lactic acids	TRPO	kerosene	1. equilibrium isotherms; 2. K_{11} evaluated by regression method	ref 26
methanoic, ethanoic, propanoic, butanoic, and lactic acids	TBP and TOA	*n*-dodecane and *n*-dodecane + decan-1-ol	acid and extractant concentrations, volume phase ratio, graphical method for equilibrium parameters	ref 15
methanoic-, ethanoic, and propanoic acids	TRPOs (Cyanex921 and Cyanex923)	toluene, octane, and Exxsol@D 220/230	effect of acid concentration, solvent, temperature, and determination of the extraction and stripping isotherms	ref 25
butanoic acid	TOA	17 different solvents	diluent effect	ref 26
propanoic acid	TBP, TOA, and Aliquat 336	octan-1-ol	type of extractant, graphical method for equilibrium parameters	ref 21
ethanoic, propanoic, and butanoic acids	TOA	decane, benzene, chloroform, MIBK, decan-1-ol, and mixture of decane (w = 0.725) + decan-1-ol (w = 0.275)	1. physical extraction with pure diluents as well as chemical extraction with TOA in different diluents; 2. differential evolution (DE) approach to determine equilibrium parameters; 3. LSER modeling to predict K_D	present study

Table 2. Reagents Used in the Study

						mol. wt.	specific gravity
S. No.	reagents	IUPAC name	CAS #	suppliers	purity, w	$kg \cdot kmol^{-1}$	$kg \cdot m^{-3}$
1.	ethanoic acid	ethanoic acid	64-19-7	HIMEDIA, India	0.99	60.05	1049
2.	propanoic acid	propanoic acid	79-09-4	Sigma-Aldrich Co., USA	0.98	74.08	990
3.	butanoic acid	butanoic acid	107-92-6	BDH Pvt. Ltd., India	0.98	88.11	960
4.	tri-*n*-octylamine	*N*,*N*-dioctyloctan-1-amine	1116-76-3	Fluka, USA	0.98	353.68	0.809
5.	*n*-decane	decane	124-18-5	Spectrochem. Pvt. Ltd., India	0.995	142.29	730
6.	benzene	benzene	71-3-2	SISCO Res. Lab. Pvt. Ltd., India	0.995	78.11	878.6
7.	chloroform	trichloromethane	67-66-3	S. D. Fine-Chem Ltd., India	0.99	119.38	1480
8.	MIBK	4-methylpentan-2-one	108-10-1	Spectrochem. Pvt. Ltd., India	0.998	100.16	801
9.	decan-1-ol	decane-1-ol	112-30-1	Spectrochem. Pvt. Ltd., India	0.98	158.28	830

organophosphorous [phosphoric acid tributyl ester, also known as tri-*n*-butyl phosphate (TBP)] and aminic [TOA, Aliquat 336, and Alamine 336] compounds.[20−24] Equilibrium parameters such as distribution coefficients, loading ratio, degree of extraction, and equilibrium complexation constants have been presented for different extractant−diluent systems. The study has been made to examine the use of the organophosphine oxides (Cyanex@921 and Cyanex@923) for the extraction of methanoic, ethanoic, and propanoic acids from aqueous solutions by Wisniewski and Piezchalska.[25] Wang et al. have used Cyanex 923 in kerosene to extract monocarboxylic acids and found that the distribution ratios increased with an increase in the 1-dialkylphosphorylalkane also known as trialkylphosphine oxide (TRPO) concentration but decreased with the carboxylic acid concentration in the aqueous phase.[26] The research work on the reactive extraction of monocarboxylic acids carried out is briefly described and compared with the present work in Table 1.

Although much work on the extraction equilibria of monocarboxylic acids can be found in the literature,[10,15,16,19−28] conventional optimization routines used for equilibrium parameter estimation do not guarantee the global optimum. In the present work, a population-based search algorithm, differential evolution (DE), which has been successfully applied to many industrial problems, is employed as an optimization routine to estimate the optimum values of equilibrium constants and stoichiometries of reaction. The reactive extraction of monocarboxylic acids (ethanoic, propanoic, and butanoic acids) from aqueous solutions using *N*,*N*-dioctyloctan-1-amine (TOA) in different diluents covering a wide range of categories (aliphatic hydrocarbon, chlorinated hydrocarbon, ketone, aromatic, and alcohol) is carried out to provide the extraction equilibrium data for intensification of separation of acids. The physical equilibria using pure diluents with the same conditions are studied. Distribution coefficients, loading factors, and degree of extraction are calculated as a result of batch extraction experiments. In addition to these parameters, the linear solvation energy relationship (LSER) model is applied to evaluate distribution coefficients, and a LSER equation is presented for each acid.

Experimental Section

The materials used in this study are various monocarboxylic acids (ethanoic, propanoic, and butanoic acids), extractant [*N*,*N*-dioctyloctan-1-amine (TOA)], and diluents [decane, benzene, chloroform, 4-methylpentan-2-one (MIBK), decan-1-ol, and mixture of decane (w = 0.725) + decan-1-ol (w = 0.275)], which are listed in Table 2.

Organic solutions are prepared using TOA (0.46 $kmol \cdot m^{-3}$) dissolved in different diluents. Deionized water with specific conductance of $6.2 \cdot 10^{-6}$ $S \cdot m^{-1}$ is used to prepare the aqueous solutions of various concentrations of different carboxylic acids [ethanoic acid (0.05 to 0.25) $kmol \cdot m^{-3}$, propanoic acid (0.0675 to 0.408) $kmol \cdot m^{-3}$, and butanoic acid (0.095 to 0.567) $kmol \cdot m^{-3}$]. The extraction equilibrium experiments are carried out at constant temperature (298 K) with equal volumes (16 cm^3 of each phase) of the aqueous and organic solutions shaken at 100 rpm for 8 h in conical flasks of 100 mL on a temperature-controlled reciprocal shaking machine (HS 250 basic REMI laboratories). After attaining equilibrium, the phases are brought into contact with each other for 2 h in separating funnels of 125 mL at constant temperature (298 K) and atmospheric pressure. After settling, organic and aqueous phases are separated. The concentration of acid in the aqueous phase is determined by titration with fresh sodium hydroxide solution of 0.015 $kmol \cdot m^{-3}$ concentration using 3,3-bis(4-hydroxyphenyl)isobenzofuran-1(3*H*)-one as an indicator. The acid concentration in the organic phase is calculated by mass balance. The equilibrium pH values of aqueous solutions are measured using a digital pH-meter of ArmField Instruments (PCT 40, Basic Process Module). The reproducibility is checked by carrying out the experiments twice in some selected cases. The results are found to be reproducible within ± 5 %.

The extraction process was analyzed by means of the degree of extraction and distribution coefficient. The distribution coefficient, K_D, is calculated using eq 1.

Table 3. Physical Equilibria of Ethanoic Acid Extraction Using Different Diluents

diluent	C_{in} $\mathrm{kmol \cdot m^{-3}}$	C_{HA} $\mathrm{kmol \cdot m^{-3}}$	$\bar{C}_{\mathrm{HA}}$ $\mathrm{kmol \cdot m^{-3}}$	$K_{\mathrm{D}}^{\mathrm{diluent}}$	P	D	R^2	SD
decan-1-ol	0.05	0.0370	0.0130	0.352	0.35	1.40	0.90	0.012
	0.10	0.0718	0.0282	0.392				
	0.15	0.1077	0.0423	0.392				
	0.20	0.1424	0.0576	0.404				
	0.25	0.1778	0.0722	0.406				
decane	0.05	0.0497	0.0003	0.006	0.004	4546	0.95	0.004
	0.10	0.0979	0.0021	0.022				
	0.15	0.1460	0.0040	0.027				
	0.20	0.1942	0.0058	0.03				
	0.25	0.2416	0.0084	0.035				
benzene	0.05	0.0486	0.0014	0.029	0.025	112	0.97	0.003
	0.1	0.0961	0.0039	0.04				
	0.15	0.1432	0.0068	0.047				
	0.2	0.1897	0.0103	0.054				
	0.25	0.2363	0.0137	0.058				
chloroform	0.05	0.0493	0.0007	0.014	0.002	31250	0.98	0.003
	0.10	0.0979	0.0021	0.022				
	0.15	0.1439	0.0061	0.042				
	0.20	0.1906	0.0094	0.049				
	0.25	0.2366	0.0134	0.057				
MIBK	0.05	0.0401	0.0099	0.246	0.42	0.75	0.89	0.008
	0.10	0.0697	0.0303	0.434				
	0.15	0.1030	0.0470	0.456				
	0.20	0.1369	0.0632	0.462				
	0.25	0.1704	0.0796	0.467				

Table 4. Physical Equilibria of Propanoic Acid Extraction Using Different Diluents

diluent	C_{in} $\mathrm{kmol \cdot m^{-3}}$	C_{HP} $\mathrm{kmol \cdot m^{-3}}$	$\bar{C}_{\mathrm{HP}}$ $\mathrm{kmol \cdot m^{-3}}$	$K_{\mathrm{D}}^{\mathrm{diluent}}$	P	D	R^2	SD
decan-1-ol	0.068	0.0260	0.0416	1.601	1.60	0.01	0.90	0.006
	0.135	0.0520	0.0830	1.597				
	0.203	0.0781	0.1244	1.592				
	0.270	0.1052	0.1656	1.575				
	0.338	0.1311	0.2064	1.575				
	0.408	0.1583	0.2498	1.578				
decane	0.068	0.0665	0.0011	0.016	0.03	117	0.80	0.019
	0.135	0.1261	0.0089	0.07				
	0.203	0.1872	0.0153	0.082				
	0.270	0.2501	0.0199	0.08				
	0.338	0.3107	0.0273	0.088				
	0.408	0.3749	0.03	0.089				
benzene	0.068	0.0589	0.0087	0.148	0.11	19.41	0.97	0.013
	0.135	0.1177	0.0173	0.147				
	0.203	0.1695	0.0330	0.195				
	0.27	0.2179	0.0492	0.226				
	0.338	0.2705	0.0664	0.246				
	0.408	0.3241	0.0839	0.259				
chloroform	0.068	0.0543	0.0133	0.245	0.25	2.84	0.93	0.015
	0.135	0.1040	0.0310	0.298				
	0.203	0.1547	0.0478	0.309				
	0.27	0.2077	0.0661	0.318				
	0.338	0.2562	0.0861	0.336				
	0.408	0.3043	0.1037	0.341				
MIBK	0.068	0.0283	0.0393	1.39	1.46	1.01	0.82	0.136
	0.135	0.0482	0.0868	1.803				
	0.203	0.0709	0.1316	1.856				
	0.27	0.0932	0.1778	1.908				
	0.338	0.1151	0.2228	1.936				
	0.408	0.1376	0.2704	1.965				

$$K_{\mathrm{D}} = \frac{\bar{C}_{\mathrm{HC}}}{C_{\mathrm{HC}}} \qquad (1)$$

where $\bar{C}_{\mathrm{HC}}$ is the total (analytical) concentration of carboxylic acid in organic phase and C_{HC} is the total (analytical) concentration (dissociated and undissociated) in aqueous phase at equilibrium.

The degree of extraction 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 as given by eq 2.

$$E = \frac{K_{\mathrm{D}}}{1 + K_{\mathrm{D}}} \cdot 100 \qquad (2)$$

Results and Discussion

In this section, the results obtained on the extraction equilibrium of monocarboxylic acids [ethanoic, propanoic, and butanoic acids] from aqueous solutions with and/or without TOA in six different diluents [decan-1-ol, chloroform, MIBK, decane, benzene, and a mixture of decane ($w = 0.725$) and decan-1- ol ($w = 0.275$)] are presented. Two factors need to be accounted to show the influence of diluents on the extraction of acids: (1) partial dissociation of the acids in the aqueous phase and (2)

Table 5. Physical Equilibria of Butanoic Acid Extraction Using Different Diluents

diluent	$\frac{C_{\mathrm{in}}}{\mathrm{kmol \cdot m^{-3}}}$	$\frac{C_{\mathrm{HB}}}{\mathrm{kmol \cdot m^{-3}}}$	$\frac{\bar{C}_{\mathrm{HB}}}{\mathrm{kmol \cdot m^{-3}}}$	$K_{\mathrm{D}}^{\mathrm{diluent}}$	P	D	R^2	SD
decan-1-ol	0.0945	0.0153	0.0792	5.181	5.18	0.07	0.93	0.048
	0.189	0.0298	0.1592	5.339				
	0.2835	0.0444	0.2391	5.387				
	0.378	0.0585	0.3190	5.454				
	0.4725	0.0734	0.3991	5.441				
	0.567	0.0872	0.4798	5.506				
decane	0.0945	0.0849	0.0096	0.114	0.03	738	0.98	0.036
	0.189	0.1521	0.0369	0.242				
	0.2835	0.2089	0.0746	0.357				
	0.378	0.2635	0.1145	0.434				
	0.4725	0.3202	0.1523	0.476				
	0.567	0.3746	0.1924	0.514				
benzene	0.0945	0.0459	0.0486	1.06	0.68	8.77	0.99	0.073
	0.189	0.0841	0.1049	1.247				
	0.2835	0.1094	0.1742	1.593				
	0.378	0.1339	0.2441	1.823				
	0.4725	0.1590	0.3135	1.972				
	0.567	0.1835	0.3835	2.09				
chloroform	0.0945	0.0359	0.0586	1.63	0.99	10.06	0.99	0.112
	0.189	0.0612	0.1278	2.09				
	0.2835	0.0783	0.2052	2.619				
	0.378	0.0956	0.2824	2.954				
	0.4725	0.1125	0.3600	3.2				
	0.567	0.1292	0.4378	3.389				
MIBK	0.0945	0.0169	0.0777	4.619	4.74	0.55	0.97	0.133
	0.189	0.0298	0.1592	5.339				
	0.2835	0.0416	0.2419	5.816				
	0.378	0.0527	0.3253	6.176				
	0.4725	0.06431	0.4082	6.347				
	0.567	0.0757	0.4913	6.492				

dimerization in the organic phase. The physical extraction (with pure diluents) of carboxylic acids is described using the distribution coefficient ($K_{\mathrm{D}}^{\mathrm{diluent}}$). For the dilute concentration of acids (as used in the study), Kertes and King[7] presented a correlation of $K_{\mathrm{D}}^{\mathrm{diluent}}$ in terms of dimerization constant (D) and partition coefficient (P) as

$$K_{\mathrm{D}}^{\mathrm{diluent}} = P + 2DP^2[\mathrm{HC}]_{\mathrm{aq}} \tag{3}$$

The plots of $K_{\mathrm{D}}^{\mathrm{diluent}}$ versus $[\mathrm{HC}]_{\mathrm{aq}}$ using the linear fit program on the origin 6.0 software package yield the value of P as an intercept and $2DP^2$ as a slope. In the linear fit program of origin 6.0, the chi-square minimization or "weighted least-square" method is used to estimate the parameters. The goal is to minimize the sum of the squares of the deviations between the theoretical curve and the experimental points for a range of independent variables. After fitting, the model is evaluated using hypothesis tests and plotting of residuals. The physical extraction of ethanoic, propanoic, and butanoic acids using six different diluents was presented in Tables 3 to 5. The nature of the extracted acid [hydrophobicity ($\log P^{\mathrm{a}}$ = distribution coefficient with octan-1-ol as the extractant in log form) and acidity] is one of the most important factors affecting the degree of extraction. The extraction is found to increase with an increase in acidity and hydrophobicity of the acid [ethanoic acid ($\mathrm{p}K_{\mathrm{a}} = 4.74$, $\log P^{\mathrm{a}} = -0.313$), propanoic acid ($\mathrm{p}K_{\mathrm{a}} = 4.87$, $\log P^{\mathrm{a}} = 0.290$), butanoic acid ($\mathrm{p}K_{\mathrm{a}} = 4.81$, $\log P^{\mathrm{a}} = 0.802$)]. Except the extraction of butanoic acid, the extraction efficiency is low: (1) a maximum $K_{\mathrm{D}}^{\mathrm{diluent}}$ of 0.41 for decan-1-ol, 0.47 for MIBK, and ranging from 0.006 to 0.06 for other inert diluents such as decane, chloroform, and benzene (Table 3) in the case of ethanoic acid and (2) a maximum $K_{\mathrm{D}}^{\mathrm{diluent}}$ of 1.60 for decan-1-ol, 1.97 for MIBK, and ranging from 0.02 to 0.34 for other inert diluents such as decane, chloroform, and benzene (Table 4) in the case of propanoic acid. Due to high hydrophobicity, the butanoic acid shows the reasonably better extractability with pure diluents (Table 5: a maximum $K_{\mathrm{D}}^{\mathrm{diluent}}$ of 5.51, 6.49 for MIBK, and ranging from 0.11 to 3.4 for other diluents). Classical extractants such as aliphatic and aromatic hydrocarbons are thus not able to fulfill the basic requirements of high distribution coefficient and high selectivity. The reason for this may be the higher affinity of acid for water. The higher $K_{\mathrm{D}}^{\mathrm{diluent}}$ value for active diluents (decan-1-ol and MIBK) can be explained by their nature. Decan-1-ol, MIBK, and chloroform are active polar solvents with higher dipole moments, μ (2.62, 2.79, and 1.01 respectively), and E_{T} (47.7, 39.4, and 39.1, respectively) values than those of other inert diluents such as benzene ($\mu = 0.00$ and $E_{\mathrm{T}} = 34.3$) and decane ($\mu = 0.01$ and $E_{\mathrm{T}} = 31.1$). The E_{T} parameter is an empirical parameter that should give assessment of solvation energy of the solute and is based on the absorption spectrum of pyridinium-*N*-phenolbetaine.[29] It provides anion solvation by ion−dipole and ion-induced dipole forces. The values of partition coefficients are obtained for extraction of acids using different diluents, by fitting eq 3 to experimental data. As decan-1-ol and MIBK are active diluents involving solvation of acid by ion pair interaction, no dimerization or very small dimerization of acid is found in the organic phase. This is due to strong solute−diluent interaction in comparison to solute−solute interaction which probably results in dimer formation. These physical extraction data will be utilized to understand the effect of diluents on reactive extraction of carboxylic acids using TOA in diluents. The higher values of D may show the existence of acid in dimer form. A small error in the values of P may lead to a very high value of D such as 4546 and 31 250 in the extraction of acids with diluents such as decane and chloroform, respectively.

In general, the degree of extraction depends on the type of diluent used. A polar diluent increases the extracting ability of relatively low polar amines (TOA). These provide additional solvating power that allows higher levels of polar−amine complexes to stay in the organic phase. On the other hand, a

Table 6. Equilibrium Results for the Extraction of Ethanoic Acid Using TOA (0.46 kmol·m^{-3}) Dissolved in Different Diluents at 298 K

diluent	C_{HA} kmol·m^{-3}	$\bar{C}_{HA}$ kmol·m^{-3}	E	$K_{D,exp}$	$K_{D,pred}$ Chemodel (eq 10)	$K_{D,pred}$ LSER (eq 24)	Z_{exp}	Z_{pred}	$K_{D,exp}^{Chem}$	$K_{D,pred}^{Chem}$	Z_{exp}^{Chem}	Z_{pred}^{Chem}
decan-1-ol	0.0056	0.0444	88.8	7.929	8.4	11.43	0.10	0.10	6.068	6.334	0.074	0.077
	0.01085	0.0892	89.2	8.217	7.59	10.47	0.19	0.18	6.140	5.549	0.145	0.131
	0.01995	0.1301	86.7	6.519	6.5	8.26	0.28	0.28	4.825	4.708	0.210	0.205
	0.03255	0.1674	83.7	5.144	5.43	6.51	0.36	0.39	3.729	3.968	0.264	0.281
	0.0455	0.2045	81.8	4.495	4.65	5.70	0.45	0.46	3.148	3.447	0.312	0.342
decane	0.049	0.001	2.0	0.02	0.03	0.059	0	0	0.015	0.022	0.002	0.002
	0.0945	0.0055	5.5	0.058	0.05	0.118	0.01	0.01	0.040	0.0351	0.008	0.007
	0.14	0.01	6.67	0.071	0.07	0.142	0.02	0.02	0.049	0.047	0.015	0.014
	0.18248	0.0175	8.76	0.096	0.08	0.156	0.03	0.03	0.053	0.057	0.021	0.023
	0.231	0.019	7.6	0.082	0.1	0.165	0.04	0.05	0.049	0.067	0.025	0.034
benzene	0.03605	0.014	27.9	0.387	0.36	0.386	0.03	0.03	0.356	0.268	0.028	0.021
	0.07	0.03	30	0.429	0.47	0.428	0.07	0.07	0.384	0.400	0.059	0.061
	0.0987	0.0513	34.2	0.52	0.53	0.519	0.11	0.11	0.465	0.485	0.100	0.104
	0.12612	0.0739	36.9	0.586	0.57	0.585	0.16	0.16	0.520	0.549	0.143	0.151
	0.154	0.096	38.4	0.623	0.6	0.622	0.21	0.2	0.549	0.601	0.184	0.202
chloroform	0.00525	0.0448	89.5	8.524	8.37	8.568	0.1	0.1	8.417	8.303	0.096	0.095
	0.0098	0.0902	90.2	9.204	9.63	9.235	0.2	0.21	9.032	9.2887	0.193	0.198
	0.01435	0.1357	90.4	9.453	10	9.484	0.3	0.31	9.114	9.503	0.285	0.297
	0.01772	0.1823	91.1	10.29	9.99	10.319	0.4	0.39	9.860	9.436	0.381	0.364
	0.021	0.229	91.6	10.91	9.87	10.946	0.5	0.45	10.322	9.283	0.472	0.425
MIBK	0.0266	0.0234	46.8	0.88	0.86	0.878	0.05	0.05	0.583	0.549	0.034	0.032
	0.04795	0.0521	52.1	1.086	1.12	1.085	0.11	0.12	0.580	0.649	0.061	0.068
	0.0665	0.0835	55.7	1.256	1.26	1.254	0.18	0.18	0.690	0.703	0.100	0.102
	0.08457	0.1154	57.7	1.365	1.36	1.363	0.25	0.25	0.767	0.738	0.141	0.136
	0.1022	0.1478	59.1	1.446	1.42	1.444	0.32	0.32	0.794	0.762	0.177	0.170
decane (w = 0.725) + decan-1-ol (w = 0.275)	0.02555	0.0245	48.9	0.957	0.94	0.226	0.05	0.05	0.732	0.707	0.041	0.039
	0.05075	0.0493	49.3	0.97	1.01	0.373	0.11	0.11	0.659	0.706	0.073	0.078
	0.0742	0.0758	50.5	1.022	1.02	0.402	0.17	0.17	0.699	0.695	0.113	0.112
	0.09856	0.1014	50.7	1.029	1.02	0.406	0.22	0.22	0.701	0.679	0.151	0.147
	0.12285	0.1272	50.9	1.04	1.00	0.408	0.28	0.27	0.685	0.662	0.183	0.177

Table 7. Equilibrium Results for the Extraction of Propanoic Acid Using TOA (0.46 kmol·m^{-3}) Dissolved in Different Diluents at 298 K

diluent	C_{HP} kmol·m^{-3}	$\bar{C}_{HP}$ kmol·m^{-3}	E	$K_{D,exp}$	$K_{D,pred}$ Chemodel (eq 10)	$K_{D,pred}$ LSER (eq 24)	Z_{exp}	Z_{pred}	$K_{D,exp}^{Chem}$	$K_{D,pred}^{Chem}$	Z_{exp}^{Chem}	Z_{pred}^{Chem}
decan-1-ol	0.005	0.063	92.79	12.87	14.05	15.50	0.14	0.15	6.039	6.515	0.064	0.069
	0.008	0.127	93.74	14.98	14.21	17.70	0.28	0.26	7.117	6.336	0.131	0.117
	0.015	0.188	92.72	12.74	13.2	14.85	0.41	0.42	5.992	5.923	0.192	0.190
	0.021	0.249	92.3	11.98	11.97	13.87	0.54	0.54	5.612	5.532	0.254	0.251
	0.029	0.309	91.34	10.55	10.41	11.83	0.67	0.66	4.905	5.051	0.313	0.322
	0.039	0.367	90.45	9.472	9	10.40	0.8	0.76	4.306	4.595	0.363	0.387
decane	0.047	0.021	30.77	0.44	0.38	0.76	0.05	0.04	0.426	0.203	0.043	0.021
	0.095	0.04	29.94	0.43	0.46	0.70	0.09	0.1	0.353	0.325	0.073	0.067
	0.14	0.063	31.07	0.45	0.51	0.71	0.14	0.15	0.363	0.412	0.11	0.125
	0.184	0.086	31.87	0.47	0.53	0.47	0.19	0.21	0.381	0.479	0.153	0.192
	0.207	0.131	38.9	0.64	0.54	0.90	0.29	0.24	0.531	0.507	0.239	0.228
	0.228	0.179	43.83	0.78	0.54	1.03	0.39	0.27	0.663	0.53	0.329	0.263
benzene	0.02	0.047	70.19	2.35	2.21	2.35	0.1	0.1	2.008	2.021	0.088	0.088
	0.034	0.101	74.48	2.92	2.98	2.91	0.22	0.22	2.518	2.547	0.189	0.191
	0.047	0.156	76.84	3.32	3.39	3.316	0.34	0.35	2.755	2.814	0.281	0.287
	0.059	0.211	78.09	3.56	3.63	2.355	0.46	0.47	2.9	2.963	0.374	0.382
	0.07	0.268	79.33	3.84	3.73	3.836	0.58	0.57	3.078	3.029	0.468	0.461
	0.081	0.327	80.18	4.05	3.77	4.047	0.71	0.66	3.21	3.052	0.561	0.534
chloroform	0.003	0.064	95.19	19.8	24.73	19.85	0.14	0.16	18.47	20.465	0.118	0.130
	0.005	0.13	96.63	28.67	26.42	28.74	0.28	0.26	23.22	21.023	0.23	0.208
	0.008	0.195	96.28	25.91	26.41	25.97	0.42	0.43	20.83	20.480	0.341	0.336
	0.01	0.26	96.15	24.96	25	24.96	0.57	0.57	19.88	19.318	0.45	0.438
	0.015	0.323	95.62	21.83	22.31	21.87	0.7	0.72	17.18	17.374	0.554	0.560
	0.019	0.387	95.27	20.12	19.82	20.15	0.84	0.83	15.79	15.611	0.66	0.652
MIBK	0.016	0.052	76.44	3.24	3.13	3.24	0.11	0.11	1.27	1.274	0.044	0.044
	0.025	0.11	81.22	4.33	4.32	4.33	0.24	0.24	1.585	1.656	0.088	0.091
	0.034	0.169	83.3	4.99	5.06	4.99	0.37	0.37	1.874	1.918	0.138	0.141
	0.042	0.228	84.59	5.49	5.5	5.49	0.5	0.5	2.071	2.106	0.188	0.191
	0.049	0.289	85.43	5.86	5.77	5.86	0.63	0.62	2.245	2.254	0.241	0.242
	0.056	0.350	86.12	6.2	5.9	6.20	0.76	0.72	2.356	2.361	0.289	0.289
decane (w = 0.725) + decan-1-ol (w = 0.275)	0.015	0.052	77.4	3.43	3.26	1.65	0.11	0.11	1.727	1.673	0.057	0.056
	0.033	0.102	75.69	3.11	3.21	1.61	0.22	0.23	1.481	1.501	0.106	0.107
	0.053	0.15	73.85	2.82	3	1.54	0.33	0.35	1.308	1.365	0.151	0.157
	0.072	0.198	73.28	2.74	2.77	1.54	0.43	0.44	1.265	1.263	0.199	0.199
	0.091	0.248	73.22	2.73	2.56	1.74	0.54	0.51	1.261	1.184	0.249	0.233
	0.111	0.297	72.84	2.68	2.37	1.86	0.64	0.57	1.216	1.111	0.291	0.266

nonpolar diluent does not affect the extraction process with low polar amines (TOA). The results obtained for the extraction of ethanoic, propanoic, and butanoic acids (Tables 6 to 8) show that the polar diluents provide a higher extraction efficiency of TOA than the others. The extraction power of amine/diluent system in terms of loading ratios (Z) or distribution coefficient (K_D) increases in the order of chloroform ≥ decan-1-ol > MIBK > decane (w = 0.725) + decan-1-ol (w = 0.275) ≥ benzene >

Table 8. Equilibrium Results for the Extraction of Butanoic Acid Using TOA (0.46 kmol·m^{-3}) Dissolved in Different Diluents at 298 K

diluent	C_{HB} kmol·m^{-3}	$\bar{C}_{HB}$ kmol·m^{-3}	E	$K_{D,exp}$	$K_{D,pred}$ Chemodel (eq 10)	$K_{D,pred}$ LSER (eq 24)	Z_{exp}	Z_{pred}	$K_{D,exp}^{Chem}$	$K_{D,pred}^{Chem}$	Z_{exp}^{Chem}	Z_{pred}^{Chem}
decan-1-ol	0.003	0.092	97.25	35.3	37.06	39.27	0.2	0.21	10.970	11.99	0.062	0.068
	0.004	0.185	97.76	43.7	39.14	48.21	0.4	0.36	13.590	11.487	0.125	0.107
	0.008	0.275	97.11	33.6	35.89	36.73	0.6	0.64	10.240	10.315	0.183	0.185
	0.012	0.366	96.82	30.4	31.06	33.07	0.8	0.81	9.217	9.403	0.241	0.246
	0.017	0.455	96.3	26	25.28	27.89	0.99	0.96	7.760	8.347	0.296	0.318
	0.023	0.544	95.99	23.9	21.17	25.47	1.19	1.05	7.049	7.537	0.349	0.373
decane	0.028	0.067	70.42	2.38	1.81	3.26	0.15	0.11	2.105	1.852	0.128	0.113
	0.052	0.137	72.66	2.66	2.93	3.55	0.3	0.33	2.087	2.326	0.235	0.261
	0.068	0.216	76.14	3.19	3.42	4.16	0.47	0.5	2.310	2.477	0.34	0.366
	0.084	0.294	77.9	3.53	3.71	4.52	0.64	0.68	2.429	2.544	0.442	0.462
	0.092	0.381	80.59	4.15	3.8	5.09	0.83	0.76	2.823	2.556	0.564	0.510
	0.1	0.467	82.41	4.68	3.85	5.64	1.02	0.84	3.141	2.556	0.683	0.556
benzene	0.009	0.085	90.37	9.38	11.97	9.37	0.19	0.23	5.336	5.766	0.102	0.111
	0.013	0.176	92.95	13.2	15.74	13.19	0.38	0.46	6.886	6.658	0.200	0.194
	0.018	0.266	93.76	15	17.72	15.01	0.58	0.68	7.148	7.148	0.276	0.275
	0.022	0.356	94.15	16.1	18.53	16.09	0.78	0.89	7.268	7.413	0.35	0.357
	0.026	0.446	94.45	17	18.55	17.01	0.97	1.06	7.455	7.509	0.426	0.429
	0.03	0.537	94.67	17.8	18.19	17.79	1.17	1.2	7.608	7.525	0.501	0.495
chloroform	0.002	0.093	98.28	57.2	54.44	57.29	0.2	0.19	28.320	28.688	0.100	0.102
	0.003	0.186	98.45	63.6	65.47	63.69	0.41	0.42	28.650	27.520	0.183	0.174
	0.004	0.279	98.51	66.2	67	66.26	0.61	0.62	27.290	25.973	0.251	0.240
	0.006	0.372	98.45	63.6	63.68	63.67	0.81	0.81	25.000	24.059	0.319	0.307
	0.008	0.464	98.27	57	56.41	57.01	1.01	1	21.630	21.662	0.384	0.386
	0.01	0.557	98.17	53.5	49.59	53.55	1.21	1.12	19.840	19.688	0.450	0.447
MIBK	0.008	0.086	91.06	10.2	11.45	10.19	0.19	0.21	2.829	3.366	0.052	0.061
	0.012	0.177	93.81	15.2	15.35	15.19	0.39	0.39	4.269	4.196	0.109	0.107
	0.015	0.269	94.74	18	18.19	17.99	0.59	0.59	5.029	4.876	0.164	0.159
	0.019	0.359	95.01	19.1	20.3	19.09	0.78	0.83	5.246	5.548	0.215	0.229
	0.022	0.451	95.41	20.8	21.05	20.78	0.98	0.99	5.729	5.939	0.271	0.281
	0.024	0.543	95.7	22.3	21.32	22.29	1.18	1.13	6.136	6.250	0.326	0.331
decane (w = 0.725) + decan-1-ol (w = 0.275)	0.009	0.085	90.37	9.38	8.51	6.16	0.19	0.17	3.160	3.134	0.063	0.063
	0.017	0.172	91.06	10.2	10.48	6.92	0.38	0.39	3.299	3.360	0.121	0.124
	0.025	0.259	91.19	10.4	10.9	7.26	0.56	0.59	3.364	3.409	0.183	0.185
	0.033	0.345	91.32	10.5	10.61	7.53	0.75	0.76	3.416	3.384	0.244	0.242
	0.042	0.431	91.18	10.3	9.98	7.87	0.94	0.91	3.359	3.316	0.305	0.301
	0.05	0.517	91.17	10.3	9.28	8.30	1.13	1.01	3.343	3.226	0.365	0.351

decane. In the case of butanoic acid extraction with TOA, benzene is found to be a better diluent than the mixture of decane (w = 0.725) + decan-1-ol (w = 0.275). The extraction power of the amine/alcohol system is remarkably higher due to the simultaneous effect of the physical extraction and chemical interaction through hydrogen bonding. Carboxylic acids are physically more easily extracted by the protic diluent (decan-1-ol) and aprotic MIBK as compared to others (Tables 3 to 5), whereas the magnitude of the acid–amine complexation is found to be larger for chlorinated hydrocarbon diluent (Tables 6 to 8). Chloroform affects the diluent–complex aggregation more readily through hydrogen bonding and dipole–dipole interaction than the amine-free diluent–acid association. This phenomenon of chloroform is confirmed by a maximum value of loading ratio. The values of Z in the range of 0.05 to 0.84 for propanoic acid and in the range of 0.15 to 1.21 for butanoic acid suggest simultaneous formation of 1:1, 2:1, and 3:1 complexes between the acid and amine. The values of Z in the range of 0.0 to 0.5 for ethanoic acid suggest the formation of 1:1 and 2:1 complexes between the acid and amine. For the estimation of equilibrium extraction constants (K_E) and the number of acid molecules (m) per extractant molecule (n) with different diluents, the following theoretical study is performed.

Chemodel. The extraction mechanism of monocarboxylic acid (HC) using TOA as an extractant with various diluents is described by eq 4, showing interfacial equilibrium in the formation of complexes between acid and extractant

$$m\text{HC} + n\overline{\text{NR}_3} \Leftrightarrow \overline{(\text{NR}_3)_n(\text{HC})_m} \tag{4}$$

The equilibrium constant (K_E) is calculated using eq 5

$$K_E = \frac{[\overline{(\text{NR}_3)_n(\text{HC})_m}]}{[\text{HC}]^m[\overline{\text{NR}_3}]^n} = \frac{[\overline{(\text{NR}_3)_n(\text{HC})_m}](1 + K_a/[\text{H}^+])^m}{[\overline{\text{NR}_3}]^n C_{\text{HC}}^m} \tag{5}$$

The distribution coefficient is defined as

$$K_D = \frac{\bar{C}_{\text{HC}}}{C_{\text{HC}}} = m\frac{[\overline{(\text{NR}_3)_n(\text{HC})_m}]}{C_{\text{HC}}} \tag{6}$$

Substituting the values of $[\overline{(\text{NR}_3)_n(\text{HC})_m}]$ from eq 6 in eq 5 results in eq 7.

$$K_E = \frac{K_D(1 + K_a/[\text{H}^+])^m}{m[\overline{\text{NR}_3}]^n C_{\text{HC}}^{m-1}} \tag{7}$$

The free extractant concentration, $[\overline{\text{NR}_3}]$ in the organic phase, is represented as

$$[\overline{\text{NR}_3}] = [\overline{\text{NR}_3}]_{in} - n[\overline{(\text{NR}_3)_n(\text{HC})_m}] \tag{8}$$

$$\Rightarrow [\overline{\text{NR}_3}] = [\overline{\text{NR}_3}]_{in} - K_D n C_{\text{HC}}/m \tag{9}$$

Using eqs 7 and 9, eq 10 results in

$$K_D = mK_E\left([\overline{NR_3}]_{in} - K_D n\frac{C_{HC}}{m}\right)^n \frac{C_{HC}^{m-1}}{(1 + K_a/[H^+])^m} \tag{10}$$

The values of equilibrium extraction constant (K_E) and the number of reacting acid and extractant molecules (m and n, respectively) are estimated using eq 10 with two approaches: (1) negligible physical extraction of acid compared to extractant and (2) considering physical extraction of acid. The distribution coefficient of acid by chemical extraction with TOA (K_D^{Chem}) can be defined as

$$K_D^{Chem} = \frac{\bar{C}_{HC}^{total} - \nu\bar{C}_{HC}^{diluent}}{C_{HC}} \tag{11}$$

where ν is volume fraction of diluent and $\bar{C}_{HC}^{diluent}$ is the acid extracted into the organic phase by diluent alone.

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 to the total extractant concentration) as given by eq 12

$$Z = \frac{\bar{C}_{HC}}{[\overline{NR_3}]_{in}} \tag{12}$$

Loading of the organic phase by chemical extraction using TOA is defined as

$$Z^{chem} = \frac{\bar{C}_{HC}^{total} - \nu\bar{C}_{HC}^{diluent}}{[\overline{NR_3}]_{in}} \tag{13}$$

The different model based on the assumption of simultaneous formation of various types of complexes (m, n) between acid and amine is presented. On the basis of the estimated values of m per TOA molecule, the formation of different types of complexes, i.e., (1, 1), (2, 1), and (3, 1), is considered. The stoichiometric equations describing the extraction are given by eqs 14 to 16

$$HC + \overline{NR_3} \Leftrightarrow \overline{HCNR_3} \tag{14}$$

$$HC + \overline{HCNR_3} \Leftrightarrow \overline{(HC)_2NR_3} \tag{15}$$

$$HC + \overline{(HC)_2NR_3} \Leftrightarrow \overline{(HC)_3NR_3} \tag{16}$$

The corresponding extraction constants are calculated using eqs 17 to 19

$$K_{11} = \frac{[\overline{HCNR_3}]}{[HC][\overline{NR_3}]} = \frac{\bar{C}_{11}(1 + K_a/[H^+])}{C_{HC}C_{R_3N}} \tag{17}$$

$$K_{21} = \frac{[\overline{(HC)_2NR_3}]}{[HC][\overline{HCNR_3}]} = \frac{\bar{C}_{21}(1 + K_a/[H^+])}{C_{HC}\bar{C}_{11}} \tag{18}$$

$$K_{31} = \frac{[\overline{(HC)_3NR_3}]}{[HC][(HC)_2NR_3]} = \frac{\bar{C}_{31}(1 + K_a/[H^+])}{C_{HC}\bar{C}_{21}} \tag{19}$$

$\bar{C}_{11}$, $\bar{C}_{21}$, and $\bar{C}_{31}$ are the concentrations of the complexes of (1, 1), (2, 1), and (3, 1) respectively. The acid concentration and free amine concentration in the organic phase are given by eq 20 and eq 21, respectively.

$$\bar{C}_{HC} = \bar{C}_{11} + 2\bar{C}_{21} + 3\bar{C}_{31} = K_{11}C_{R_3N}C_{HC}/(1 + K_a/[H^+]) + 2K_{21}\bar{C}_{11}C_{HC}/(1 + K_a/[H^+]) + 3K_{31}\bar{C}_{21}C_{HC}/(1 + K_a/[H^+]) \tag{20}$$

$$C_{R_3N} = C_{R_3N_{in}} - (\bar{C}_{11} + \bar{C}_{21} + \bar{C}_{31}) = C_{R_3N_{in}} - (K_{11}C_{R_3N}C_{HC}/(1 + K_a/[H^+]) + K_{21}\bar{C}_{11}C_{HC}/(1 + K_a/[H^+]) + K_{31}\bar{C}_{21}C_{HC}/(1 + K_a/[H^+])) \tag{21}$$

The values of the equilibrium constants K_{11}, K_{21}, and K_{31} are estimated based on the total acid concentration in the aqueous phase at equilibrium and by applying the mass action law (experimental results).

LSER Model. According to Kamlet et al.,[30] the linear solvation energy relationship (LSER) that measures property *XYZ*, in terms of solvent properties, is represented by eq 22

$$XYZ = XYZ^0 + \frac{p(\delta_h)^2}{100} + s(\pi^* + d\delta) + b\beta + a\alpha \tag{22}$$

where δ_h is Hildebrand's solubility parameter; π^* and δ are the solvatochromic parameters that measure the solute + solvent, dipole + dipole, and dipole + induced dipole interactions, respectively. Solvatochromic parameter β, scale of solvent HBD (hydrogen-bond donor) acidities, describes the ability of solvent to donate a proton in a solvent-to-solute hydrogen bond. The α scale of HBA (hydrogen-bond acceptor) basicities provides a measure of the solvent's ability to accept a proton (donate an electron pair) in a solute-to-solvent hydrogen bond. The coefficients p, s, d, a, and b include the properties of solute. Rather than p, s, d, b, and a are also regression coefficients. Equation 22 can be adopted to describe the effect of diluents on the values of distribution coefficients K_D, in the form eq 23[31−33]

$$\ln K_D = \ln K_D^0 + \frac{p(\delta_h)^2}{100} + s(\pi^* + d\delta) + b\beta + a\alpha \tag{23}$$

where the parameters π^*, δ, β, and α refer to the diluents, and K_D^0 represents the distribution coefficients for an ideal inert diluent. The second term of eq 23, which contains the solubility parameter δ_h, does not affect the values of the objective function ($\ln K_D$) significantly. Thus, eq 23 results in eq 24

$$\ln K_D = \ln K_D^0 + s(\pi^* + d\delta) + b\beta + a\alpha \tag{24}$$

The solvatochromic parameters of the solvent mixtures can be calculated according to eq 25[14]

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

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 parameters of the second solvent in solvent mixtures.

Differential Evolution Approach. The graphical method for determining the number of extractant or acid molecules taking part in the formation of complexes is applicable, when only one type of complexes is formed. The model eqs (10 and 20) are solved to determine the values of equilibrium extraction constants (K_E) and the number of acid molecules (m) and reacting extractant molecules (n) in the formation of acid: extractant complexes using the optimization procedure. Most of the traditional optimization algorithms based on gradient methods have the possibility of getting trapped at local optimum depending upon the degree of nonlinearity and initial guess.[34] In the recent past, nontraditional search and optimization techniques (evolutionary computation) based on natural phenomena such as genetic algorithms (GAs), DE, etc. have been developed to overcome these problems.[34,35] An evolutionary optimization routine is also used to solve the model equations for the estimation of extraction equilibrium constants and the stoichiometry of reactive extractions. A population-based search algorithm called differential evolution (DE), which is simple and robust and has a proven successful record for various engineering applications in both single- and multiobjective optimization is employed.[34−37] The key parameters of control in DE are: NP, the population size; CR, the cross over constant; and F, the weight applied to random differential (scaling factor). These parameters are problem dependent. However, certain guidelines and heuristics are available for the choice of these parameters.[34] NP should be 5−10 times the value of D, that is, the dimension of the problem. Initially $F = 0.5$ is recommended. If this leads to premature convergence, then F needs to be increased. The range of values of F is $0 < F < 1.2$, but the optimal range is $0.4 < F < 1.0$. Values of $F < 0.4$ and $F > 1.0$ are seldom effective. CR = 0.9 is a good first guess. CR = 0.9 is tried first, and then CR = 0.1 is tried. Judging by the speed, a value of CR between 0 to 1 is chosen. On the basis of these heuristics, the values of DE key parameters for the present

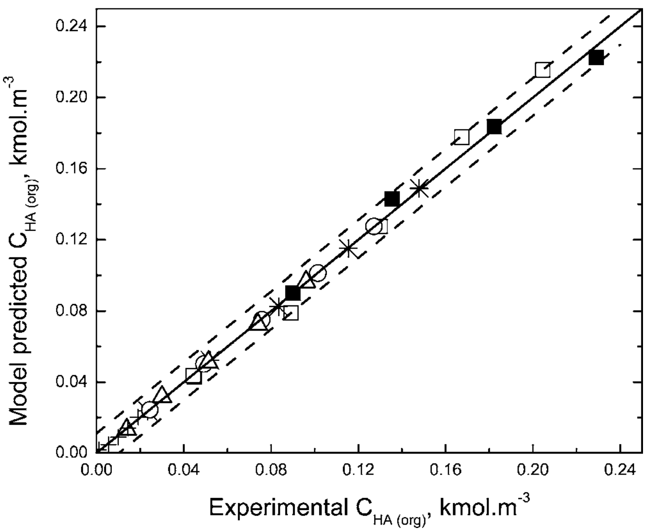

Figure 1. Equilibrium organic phase concentrations [model predicted (eq 20) and experimental data] of ethanoic acid with TOA (0.46 kmol·m^{-3}) dissolved in different diluents. Symbols: ■, chloroform; □, decan-1-ol; ∗, MIBK; ○, decane ($w = 0.725$) + decan-1-ol ($w = 0.275$); Δ, benzene; +, decane; - - -, ± 10 % error limit lines.

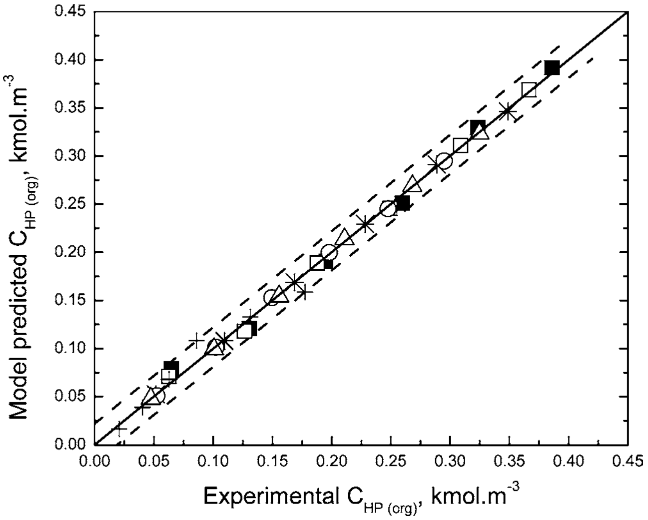

Figure 2. Equilibrium organic phase concentrations [model predicted (eq 20) and experimental data] of propanoic acid with TOA (0.46 kmol·m^{-3}) dissolved in different diluents. Symbols: ■, chloroform; □, decan-1-ol; ∗, MIBK; ○, decane ($w = 0.725$) + decan-1-ol ($w = 0.275$); Δ, benzene; +, decane; - - -, ± 20 % error limit lines.

Table 9. Values of Equilibrium Constants (K_E) and Number of Reacting Acid:TOA Molecules (m:n) with Different Diluents Using DE

acid	diluent	m	n	K_E	SE	K_{11}	K_{21}	K_{31}	SE
ethanoic acid	decan-1-ol	0.95	1	18.42	1.090	19.73	-	-	0.0025
	decane	1.77	1	0.40	0.0008	0.06	5.08	-	0.0007
	benzene	1.42	1	2.41	0.0029	0.62	5.35	-	0.0002
	chloroform	1.32	1	91.14	0.8530	16.05	32.68	-	0.0007
	MIBK	1.50	1	8.41	0.0018	1.43	9.56	-	0.00003
	decane ($w = 0.725$) + decan-1-ol ($w = 0.275$)	1.16	1	3.51	0.0023	2.09	1.84	-	0.00008
propanoic acid	decan-1-ol	1.20	1	93.14	2.660	38.47	8.06	-	0.0017
	decane	1.34	1	1.86	0.0303	0.78	0.02	454.51	0.0081
	benzene	1.67	1	46.39	0.067	3.79	13.32	3.84	0.00007
	chloroform	1.30	1	319.99	17.80	69.79	24.95	-	0.0040
	MIBK	1.82	1	131.30	0.035	3.32	45.94	2.60	0.00008
	decane ($w = 0.725$) + decan-1-ol ($w = 0.275$)	1.12	1	12.49	0.212	8.56	0.03	429.24	0.0002
butanoic acid	decan-1-ol	1.33	1	612.83	74.13	114.62	27.88	5.80	0.005
	decane	1.95	1	71.24	0.970	4.31	0.11	998.21	0.007
	benzene	1.92	1	1381.71	0.70	9.41	99.09	12.90	0.0004
	chloroform	1.52	1	3266.14	20.51	125.53	156.35	-	0.0019
	MIBK	2.15	1	3516.33	20.30	2.11	676.78	15.54	0.0027
	decane ($w = 0.725$) + decan-1-ol ($w = 0.275$)	1.56	1	208.04	2.680	21.05	14.74	9.08	0.0001

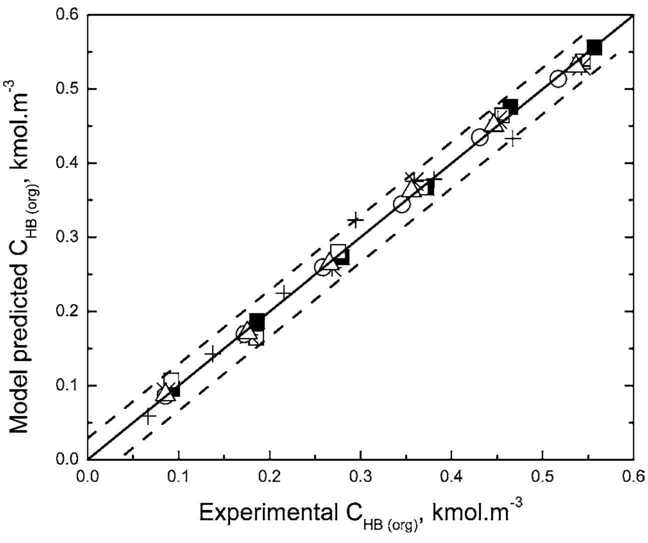

Figure 3. Equilibrium organic phase concentrations [model predicted (eq 20) and experimental data] of butanoic acid with TOA (0.46 kmol·m^{-3}) dissolved in different diluents. Symbols: ■, chloroform; □, decan-1-ol; $*$, MIBK; ○, decane ($w = 0.725$) + decan-1-ol ($w = 0.275$); Δ, benzene; +, decane; - - -, ± 10 % error limit lines.

Table 10. Solvatochromic Parameters, Hydrogen-Bond Donor Acidities ($\pi^*$and δ), and Hydrogen-Bond Acceptor Basicities (α and β) for Diluents[14,30]

component	π^*	β	α	δ
decane	0.03	0	0	0
decan-1-ol	0.40	0.45	0.33	0
benzene	0.59	0.10	0	1.0
MIBK	0.63	0.48	0	0
chloroform	0.58	0.20	0.10	0.50
decane ($w = 0.725$) + decan-1-ol ($w = 0.275$)	0.124	0.114	0.084	0.00

problem are set as NP = 20, 30; CR = 0.9; and $F = 0.5$. An objective function based on least-squares error between experimental data and the predicted value of K_{D} has been minimized. For the estimation of simultaneous equilibrium extraction constants (K_{11}, K_{21}, and K_{31}), an objective function based on the least-squares error between experimental data and the predicted value of $\bar{C}_{\mathrm{HC}}$ has been minimized.

The estimated values of stoichiometries of reactive extraction, overall equilibrium constants (K_{E}), and individual equilibrium constants (K_{11}, K_{21}, and K_{31}) by this computational procedure are given in Table 9. The predicted values of K_{D} and Z for each carboxylic acid with TOA in different diluents using this model with the DE approach are comparable with the experimental values of K_{D} and Z (Tables 6 to 8). In the extraction of monocarboxylic acids (ethanoic, propanoic, and butanoic acids) with TOA, the predicted values of K_{D} show little deviation from experimental values K_{D} at much lower acid concentrations. When equilibrium extraction is carried out with very low concentration of acids, minor errors in the experimental concentration of the aqueous phase may lead to a high error in the experimental values of K_{D} ($\bar{C}_{\mathrm{HC}}/C_{\mathrm{HC}}$). Therefore, the experimental and predicted values of loading ratio ($Z = \bar{C}_{\mathrm{HC}}/[\mathrm{NR}_3]_{in}$) are found to be more close for all the acid/TOA/diluent systems. In the extraction of monocarboxylic acids using TOA, the higher strength of the complex solvation is found for chlorinated hydrocarbons (chloroform) promoting probably a (1:1) acid−amine complex formation (higher values of K_{E} and lower values of m). The formation of acid:amine complexes also depends on the nature of diluents, which affect the basicity of the amine and the stability of the ion pair formed in the extract phase. The synergistic extraction power of the TOA/decan-1-ol system is remarkably larger due to the simultaneous effect of the physical extraction and chemical interaction through hydrogen bonding. Carboxylic acids are physically more easily extracted by the oxygen-bonded carbon diluents alone (decan-1-ol and MIBK) as compared to others (Tables 3 to 5), whereas the magnitude of the acid−amine complexation is found to be larger for chlorinated hydrocarbon diluent. Chloroform affects the diluent complex aggregation more readily through hydrogen bonding and dipole−dipole interaction than the amine-free diluent−acid association. These results show that the diluents not only are involved in the physical extraction but also enhance the polarity of extractant (TOA). It is better to assume the negligible physical extraction rather than considering complete involvement of diluents in physical extraction, as the values of $K_{\mathrm{D}}^{\mathrm{Chem}}$(chemical extraction) with TOA in the polar diluents (decan-1-ol and MIBK) are found to be much less as compared to those of overall K_{D}. The values of equilibrium constants (K_{11}, K_{21}, and K_{31}) for individual complexes between acid and amine are estimated with the assumption of negligible physical extraction (Table 9). The diluents such as decan-1-ol and chloroform with TOA may lead to more extraction of acids with promoting 1:1 complexes between acid and extractant (TOA). Overloading of acid is found to be the maximum with

Table 11. Values of the LSER Model Parameters (s, d, b, a) and the Coefficient of Linear Regression (R^2)

	$C_{(\mathrm{HA})in}$		LSER model parameters					
type of acid	kmol·m^{-3}	ln K_{D}^0	a	b	s	d	R^2	SE
ethanoic acid	0.05	−1.4502	7.8578	−6.677	7.2997	−0.3565	0.8648	0.7983
	0.10	−1.1387	7.2903	−6.8334	7.07	−0.3844	0.9181	0.5289
	0.15	−1.0558	6.724	−6.7421	6.969	−0.3826	0.9111	0.5154
	0.20	−1.0229	6.4426	−7.0534	7.2113	−0.3826	0.9050	0.5143
	0.25	−1.0051	6.296	−7.2742	7.391	−0.3835	0.9009	0.5169
propanoic acid	0.0675	−0.28	5.3172	−5.4121	5.3778	−0.3684	0.9043	0.4059
	0.135	−0.3349	5.5471	−5.9496	6.0743	−0.3604	0.934	0.3650
	0.2025	−0.3223	4.9299	−5.3731	5.7129	−0.3484	0.9393	0.3343
	0.27	−0.3071	4.6152	−5.0833	5.5339	−0.3431	0.9423	0.3188
	0.338	−0.1981	4.0154	−4.5929	5.0324	−0.3433	0.9549	0.2503
	0.405	−0.1312	3.596	−4.3025	4.7438	−0.3437	0.965	0.2031
butanoic acid	0.095	0.3691	4.6603	−4.9496	4.7858	−0.3606	0.9549	0.2323
	0.189	0.4211	4.1556	−4.0772	4.3137	−0.3334	0.9618	0.2143
	0.284	0.4868	3.6231	−4.1673	4.3946	−0.3383	0.9621	0.1960
	0.378	0.5291	3.2992	−3.9636	4.2132	−0.3351	0.9627	0.1838
	0.4725	0.5903	2.7642	−3.5731	3.8770	−0.3326	0.9691	0.1511
	0.567	0.6424	2.4114	−3.3065	3.6395	−0.3321	0.9698	0.1388

completely inert diluent (decane). The deviation of predicted values of acid concentrations using a model for individual complexes (eqs 20 and 21) from those of experimental values is shown in Figures 1 to 3. It can be seen that the model values correctly represent the acid extraction using the DE approach for predicting equilibrium parameters.

LSER Model Results. In this study, an LSER model is applied to predict the distribution coefficient for various TOA + diluent systems in the extraction of monocarboxylic acids (ethanoic, propanoic, and butanoic acids). The values of the solvatochromic parameters of the diluents used in this study are given in Table 10.[14,30] The solvatochromic parameters for the mixture of decane and decan-1-ol determined by eq 25 are also given in Table 10. These parameters for different diluents are fitted to the experimental results of K_D. For the estimation of optimum model parameters, a regression-technique-assisted computer program (least-squares linear regression) is used to minimize the deviation between model predicted and the experimental values of $\ln K_D$. The estimated values of parameters of the model are presented in Table 11. The experimental data for the distribution coefficients show a good correlation to the calculated values with the values of coefficient of determination ($R^2 > 0.90$). On the basis of the satisfactory results obtained, it is inferred that the distribution coefficients of acids between water and the TOA + diluent system can be better described using the LSER model. The predicted values of K_D using the LSER model for the systems of TOA + MIBK, TOA + benzene, TOA + chloroform, and TOA + decan-1-ol are found to be better for the description of distribution coefficients of acids between water and TOA + diluent system (Tables 6 to 8). The solute hydrogen acidity and basicity (a and b) show a significant correlation with the partition coefficient. This confirms that the organic solvent serves as both a hydrogen donor and a hydrogen acceptor. The relative size of the standardized system constants (β), which are the regression coefficients derived from standardized dependent variables, relays information pertaining to the relative importance of different types of solute/solvent interactions. With this concept, the strength of the interaction decreases from dispersive interactions, hydrogen bonding, solute/solvent$-\sigma/\pi$ electron pair interactions, to solute/solvent dipolarity/polarizability interactions.

Conclusions

From the equilibrium results as presented for different monocarboxylic acids using TOA in six different diluents, the extraction power of the amine and diluent system—in terms of either loading ratio or distribution coefficient (K_D)—increases in the order of chloroform ≥ decan-1-ol > methyl isobutyl ketone > decane ($w = 0.725$) + decan-1-ol ($w = 0.275$) > benzene > decane. The values of K_D of acids between water and the TOA + diluent system are also described by the LSER model. The experimental data for the distribution coefficients show a good correlation to the calculated values using the LSER model with the values of coefficient of determination ($R^2 > 0.90$). The solute hydrogen acidity and basicity (a and b) show a significant correlation with the partition coefficient. The values of Z in the range of 0.0 to 0.5 for ethanoic acid, 0.05 to 0.84 for propanoic acid, and 0.15 to 1.21 for butanoic acid suggest simultaneous formation of different type of complexes (1:1, 2:1, and 3:1) between acid and amine. The values of K_D and Z for each acid with different TOA/diluent systems, predicted using the model with DE approach, are comparable with experimental values of K_D and Z. The diluents such as decan-1-ol and chloroform with TOA may lead to more extraction with promoting 1:1 complexes between acid and extractant (TOA). Overloading of acid is found to be the maximum with completely inert diluent (decane). It is found that the model values correctly represent the reactive extraction of different carboxylic acids (ethanoic, propanoic, and butanoic acids) using the DE approach for predicting equilibrium parameters.

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