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Reactive Extraction of Formic Acid by using Tri Octyl Amine (TOA)

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Abstract: Distribution of formic acid (methanoic acid) between water and tri octyl amine (TOA) dissolved in various alcohols (isoamyl alcohol, hexan-1-ol, octan-1-ol, nonan-1-ol, decan-1-ol) as diluents, as well as the extraction capacity of pure diluent alone have been studied at isothermal conditions. All measurements were carried out at 298.15 K. The difference between the physical extraction and reactive extraction was studied. The loading factor, T_T, extraction efficiency, D_E, modified separation factor, S_F, and, distribution coefficients, K_D were calculated. The isoamylalcohol was found most effective solvent with maximum distribution value of 14.521. Possible equilibrium complexation constants for (acid:amine) (5:1), (6:1), and (7:1) have been determined as values of about 21.8×10^3, 15.6×10^4, and 11.1×10^5 for K_{51}, K_{61}, and K_{71}, respectively with isoamylalcohol. Furthermore, Linear Solvation Energy Relationship (LSER) model equation has been obtained to calculate distribution coefficients for alcohols with regression coefficient of 0.981.

Keywords: Formic acid, LSER, reactive extraction, TOA

INTRODUCTION

Formic acid is a colorless, fuming liquid that is miscible with water. It consists of hydrogen bonded dimers (Fig. 1 shows the formic acid dimers) rather than individual molecules. In the gas phase, significant deviations

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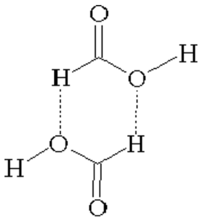

Figure 1. Formic acid dimers.

from the ideal gas law arise as a result of this hydrogen bonding. In its liquid and solid state, formic acid can be thought of as an effectively infinite network of hydrogen bonded molecules.

Long-chain, aliphatic tertiary amines (especially TOA and Alamine 336) dissolved in suitable organic solvents are effective extractants for carboxylic acids. Recently, extractive recovery of carboxylic acids by amine systems from aqueous solutions, such as fermentation broth and wastewater, including lower than 10% (w/w) acid concentrations, has received increasing interest (1,2). Three major factors have been found to influence the equilibrium characteristics of amine extraction of carboxylic acids from aqueous solutions, i.e. the nature of acid, concentrations of acid and amine, and the type of diluent (1–5). Simultaneously, the effect of additional controlling factors, such as the swing effect of a mixed diluent and the third phase formation, can also modify the reversible complexation stage (6,7). Process considerations dealing with the competition between physical extraction and chemical interaction of highly hydrophobic acids still remain a challenging problem, since such systems show extremely nonideal behavior (8).

The reactive extraction of carboxylic acids has been tested by various scientists. Yang et al. (2) studied the extraction of carboxylic acids with tertiary and quaternary amines and they showed the effect of pH on reactive extraction of carboxylic acid. Uslu worked the reactive extraction of some carboxylic acids (propionic acid, tartaric acid, glycolic acid) with trioctyl methylammonium chloride (Aliquat 336) and Alamine 336 as extractants and the magnitude of distribution coefficients have been demonstrated (9–11). Kyuchoukov et al. explained the mechanism of extraction of lactic acid by Aliquat 336 (12). Wasewar et al. (13) reported equilibria and kinetics for reactive extraction of lactic acid using Alamine 336 in decanol. Martak and Schlosser (14) studied liquid-liquid equilibria of dimethyl cyclopropane carboxylic acid in water + solvent systems with trioctylamine as an extractant.

In this study, the reactive extraction of formic acid from aqueous solutions by TOA extractant in a variety of diluents was examined in a range of amine concentration ($0.590–1.731 \cdot L^{-1}$). Distribution coefficients, loading factors, and the degree of extraction were calculated as a result of batch extraction experiments. In addition to these parameters, LSER model was applied to evaluate the distribution coefficients and a new LSER equation was presented.

THEORY

The caryboxlic acids intent to form dimers (see Fig. 1) in organic phase because they exhibit intermolecular hydrogen bonding (15). The extraction of formic acid (HA) with amine (R_3N) can be formation of a complex via the interfacial reaction and can be represented as:

$$pHA_{aq} + (R_3N)_{org} \longleftrightarrow ((HA)_p \cdot (R_3N))_{org} \tag{1}$$

Reactive extraction of carboxylic acids with amine based extractant can be described by following equations:

$$HA + \overline{R_3N} \longleftrightarrow \overline{HA - R_3N}, \qquad K_{11} = \frac{\overline{C_{HA-R_3N}}}{C_{HA} \cdot \overline{C_{R_3N}}} \tag{2}$$

$$2HA + \overline{R_3N} \longleftrightarrow \overline{(HA)_2 - R_3N}, \qquad K_{21} = \frac{\overline{C_{(HA)_2-R_3N}}}{C_{HA}^2 \cdot \overline{C_{R_3N}}} \tag{3}$$

where HA represents the nondissociated part of the acid present in the aqueous phase and organic phase species are marked with over bar($^{-}$).

The equilibrium complexation constant is defined as:

$$K_s = [(HA)_p \cdot (R_3N)]_{org}/[HA]_{aq}^p[R_3N]_{org} \tag{4}$$

K_s is expected to depend on the properties of the acid and the solvation efficiency of the diluent used. Distribution coefficients (K_D) is defined as the ratio of concentration of acid in organic phase and total concentration of acids in aqueous phase.

$$K_D = \frac{\overline{C_{HA}}}{C_{HA,total}} = \frac{\overline{C_{(HA_p \cdot R_3N)}}}{C_{HA} + C_{(A^-)}} \tag{5}$$

In equation 5, the over bar($^{-}$) shows the organic phase, $C_{HA,total}$ is the total concentration of the acid in the aqueous phase.

On the other hand, the apparent equilibrium constant K_A for acid dissociation reaction can be written in terms of species concentration for dilute solutions,

$$\mathrm{HA} \longleftrightarrow \mathrm{H}^+ + \mathrm{A}^-, \qquad K_\mathrm{A} = \frac{\mathrm{C}_{\mathrm{H}^+} \cdot \mathrm{C}_{\mathrm{A}^-}}{\mathrm{C}_\mathrm{HA}} \tag{6}$$

So, the concentration of undissociated monocarboxylic acid is given by,

$$\mathrm{C}_\mathrm{HA} = \frac{\mathrm{C}_\mathrm{HA,total}}{1 + 10^{\mathrm{pH}-\mathrm{pK_A}}} \tag{7}$$

The total equilibrium concentration of monocarboxylic acid in the organic phase is obtained by following equation:

$$\overline{\mathrm{C}}_\mathrm{HA} = \overline{\mathrm{C}}_{\mathrm{HA-R_3N}} + 2 \cdot \overline{\mathrm{C}}_{\mathrm{(HA)_2-R_3N}} = \mathrm{K}_{11} \cdot \mathrm{C}_\mathrm{HA} \cdot \overline{\mathrm{C}}_{\mathrm{R_3N}} + 2 \cdot \mathrm{K}_{21} \cdot \mathrm{C}^2_\mathrm{HA} \cdot \overline{\mathrm{C}}_{\mathrm{R_3N}} \tag{8}$$

Free trioctly amine (TOA) concentration in the organic phase can be calculated as,

$$\overline{\mathrm{C}}_{\mathrm{R_3N}} = \mathrm{C}^0_{\mathrm{R_3N}} - \overline{\mathrm{C}}_{\mathrm{HA-R_3N}} - 2\overline{\mathrm{C}}_{\mathrm{(HA)_2-R_3N}} = \mathrm{C}^0_{\mathrm{R_3N}} - \mathrm{K}_{11} \cdot \mathrm{C}_\mathrm{HA} \cdot \overline{\mathrm{C}}_{\mathrm{R_3N}} - 2\mathrm{K}_{21} \cdot \mathrm{C}^2_\mathrm{HA} \cdot \overline{\mathrm{C}}_{\mathrm{R_3N}} \tag{9}$$

The loading factor $\mathrm{T_T}$ can be written following form,

$$\mathrm{T_T} = \frac{\overline{\mathrm{C}}_\mathrm{HA}}{\overline{\mathrm{C}}^0_{\mathrm{R_3N}}} \tag{10}$$

The stoichiometric loading factor, T_s, is the ratio of the overall complexed acid to total amine in the organic phase. This factor includes a correction term, $\left(v \cdot \overline{C^s_{HA}}\right)$, for the amount of acid extracted by the modifiers in the solvent mixture.

$$\mathrm{T_s} = \frac{\left(\overline{C_{HA}} - v \cdot \overline{C^s_{HA}}\right)}{\overline{C^0_{R_3N}}} \tag{10}$$

In Eq. 14, v is the volume fraction of modifiers in mixture, and $\overline{C^s_{HA}}$ is the concentration of acid extracted by the pure solvent (not containing amine) (see Table 1).

Degree of extraction is defined as following equation:

$$D_E = \frac{K_D \times 100}{1 + K_D} \tag{11}$$

Table 1. Results for physical extraction of formic acid with pure solvents

Solvents	$pH_{aq.}$	$\overline{C_{HA}}$	K_D	D_E
Alcohols				
Isoamyl alcohol	3.86	0.819	0.605	37.690
Hexan-1-ol	3.73	0.696	0.471	32.029
Octan-1-ol	3.65	0.612	0.392	28.164
Nonan-1-ol	3.63	0.591	0.374	27.197
Decan-1-ol	3.60	0.560	0.347	25.771

The relative proportion between physical interaction and chemical reaction was evaluated with respect to a modified separation factor which is expressed as the ratio of the complexed acid to overall extracted acid

$$s_f = \frac{\overline{C_{HA}}}{\overline{\overline{C_{HA}}} + \overline{\overline{C_{A^-}}}} \tag{12}$$

CHEMICALS AND METHODS

Chemicals

TOA, which is a synonyms name N,N-dioctyl-1-octanamine ((Merck Co.) >99, %,), anion exchange extractant, is a colorless liquid with the molecular weight of 353.67 g/mol. Formic acid (pKa: 3.75) (Merck, >95%), Alcohols: isoamyl alcohol (Merck, >99%), (hexan-1-ol (Merck, >99%), octan-1-ol (Merck, >99), nonan-1-ol (Merck, >99), decan-1-ol (Merck, >99%)), were used without further purification.

Methods

Preparation

The known masses of formic acid were dissolved in distilled water to prepare the solutions of acid 2.173 mol · L^{-1} because of the practical case of acid recovery from fermentation broths and wastewater. The amine + alcohol mixtures were prepared as extractants. The organic phases were prepared by the dissolution of TOA in the diluents to produce solutions at five constant concentrations in the range of (0.590–1.731) mol · L^{-1}. Known volumes of aqueous (10 ml) and organic solutions (10 ml) of known concentration were added to Erlenmayer flasks of 50 ml and equilibrated in a Nuve Shaker ST402 bath at 298.15 K for 2 h, which preliminary tests demonstrated to be a sufficient time for equilibration. Thereafter the mixture was kept in a bath for another 3 h to reach full separation of phases. After equilibration, both phases were separated by a centrifuge at 1200 rpm for about 7 min for better separation.

Analysis

The aqueous phase samples were analyzed for solute concentration by using titration with sodium hydroxide (relative uncertainty: 1+ %) as a standard solution and phenolphthalein as the indicator, with each measurement being performed in duplicate. The formic acid concentration in the organic phase was calculated by material balance (1,3). Since the volume changes of the phases are so small, they can be neglected for calculation purposes. In most cases the deviation between the amount of analyzed acid and the amount of known acid by preparing the solutions by mass did not exceed 3+ %. The pH value of the aqueous phase was determined with a pH meter (Hanna pH 211 Microprocessor pH meter) with deviation ±0.01.

RESULTS AND DISCUSSION

Experimental Results

It is important to do a physical extraction of formic acid to show the effect of amine on the extraction of formic acid (reactive raction). Table 1 presents the extraction of formic acid by pure solvents not containing TOA in organic phase. The low activity of formic acid towards these diluents particularly in lower concentrations of acid i.e., its higher solubility in water than in organic solvents is the cause of the low distribution coefficient. Isoamyl alcohol gave the highest extraction degree with the help of pure isoamyl alcohol. The percentage of 37.690 formic acid in the aqueous phase was removed into the organic phase.

The extraction of formic acid by TOA dissolved in 5 various alcohols (isoamyl alcohol, hexan-1-ol, octan-1-ol, nonan-1-ol, and decan-1-ol) were studied. The results of the equilibrium data on the distribution of formic acid between the aqueous phase and the organic phase were presented in Table 2. The constant concentrations of TOA in various solvents were prepared in the range of 0.590 $\mathrm{mol} \cdot \mathrm{L}^{-1}$ to 1.731 $\mathrm{mol} \cdot \mathrm{L}^{-1}$. Initial formic acid concentration in the aqueous phase was prepared as $2.173 \cdot \mathrm{L}^{-1}$. Distribution coefficient increases from 1.147 to 14.521 with

Table 2. Extraction equilibrium results for the system (Formic acid (HA) + TOA (R_3N) + Alcohol)

Solvents	$\overline{C_{R_3N}}$	pH_{aq}	$\overline{C_{HA}}$	ν	K_D	K_D^{model}	T_T	T_S	S_f	D_E
Isoamyl alcohol	0.590	4.39	1.356	0.417	1.659	1.348	2.298	2.183	0.989	62.402
	0.861	4.61	1.573	0.333	2.621	2.376	1.826	1.668	0.994	72.388
	1.158	4.77	1.728	0.250	3.883	4.186	1.492	1.315	0.996	79.521
	1.431	4.94	1.896	0.167	6.844	7.375	1.324	1.134	0.997	87.252
	1.731	5.07	2.033	0.083	14.521	12.99	1.174	0.977	0.998	93.557
Hexan-1-ol	0.590	4.31	1.273	0.417	1.414	1.284	2.157	2.059	0.986	58.582
	0.861	4.49	1.456	0.333	2.031	2.155	1.691	1.556	0.992	67.004
	1.158	4.69	1.651	0.250	3.162	3.617	1.425	1.275	0.995	75.977
	1.431	4.87	1.833	0.167	5.391	6.070	1.281	1.118	0.997	84.353
	1.731	5.04	1.995	0.083	11.208	10.185	1.152	0.984	0.998	91.808
Octan-1-ol	0.590	4.27	1.226	0.417	1.294	1.218	2.077	1.991	0.984	56.419
	0.861	4.45	1.411	0.333	1.851	1.940	1.638	1.520	0.991	64.933
	1.158	4.62	1.583	0.250	2.683	3.089	1.367	1.234	0.994	72.848
	1.431	4.81	1.766	0.167	4.339	4.918	1.234	1.091	0.996	81.270
	1.731	4.99	1.948	0.083	8.657	7.831	1.125	0.977	0.998	89.645
Nonan-1-ol	0.590	4.22	1.186	0.417	1.201	1.189	2.010	3.599	0.982	54.578
	0.861	4.44	1.403	0.333	1.822	1.848	1.629	2.409	0.990	64.565
	1.158	4.61	1.573	0.250	2.621	2.872	1.358	1.748	0.994	72.388
	1.431	4.79	1.751	0.167	4.149	4.462	1.223	1.380	0.996	80.579
	1.731	4.98	1.936	0.083	8.168	6.933	1.118	1.112	0.998	89.093
Decan-1-ol	0.590	4.20	1.161	0.417	1.147	1.146	1.967	3.604	0.981	53.428
	0.861	4.42	1.381	0.333	1.743	1.718	1.603	2.415	0.990	63.552
	1.158	4.57	1.531	0.250	2.385	2.574	1.322	1.755	0.993	70.455
	1.431	4.76	1.723	0.167	3.829	3.856	1.204	1.388	0.996	79.291
	1.731	4.92	1.878	0.083	6.366	5.776	1.084	1.120	0.997	86.423

increasing the amount of TOA. It can be seen from Fig. 2 that the extraction power (efficiency) of (TOA + diluent) mixture changes with increasing initial concentration of TOA in the organic phase. According to Table 2, the distribution coefficients of formic acid in solvets + TOA were obtained the following orders:

$$\text{isoamyl alcohol} > \text{hexan-1-ol} \gg \text{octan-1-ol} > \text{nonan-1-ol} > \text{decan-1-ol}.$$

Figure 3 illustrates the loading curves for extraction of formic acid by TOA in different diluents. The loading curve is a plot of T_T vs log $[C_{HA}]$ and Table 2 shows the values of the loading factors and the ratio of the overall complexed acid to total amine in the organic phase (stoichiometric loading factor) Ts. With all of the solvents, the loading decreases, indicating that complexes include the diluents. For systems with only one

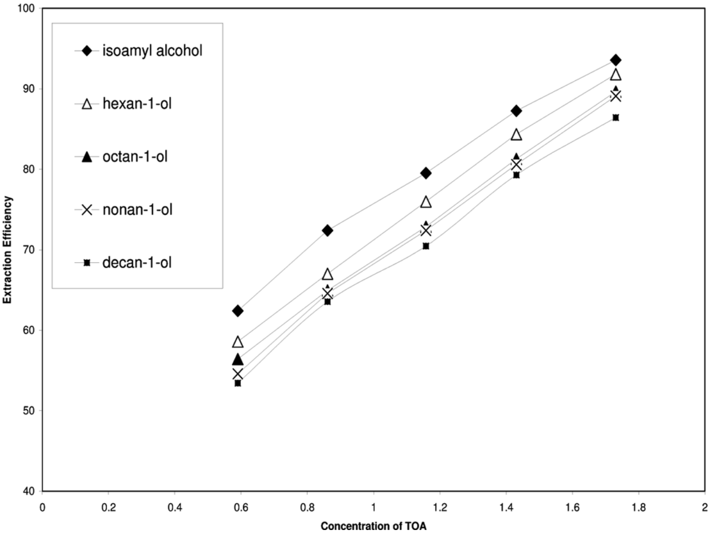

Figure 2. Plot of TOA concentration against extraction efficiency.

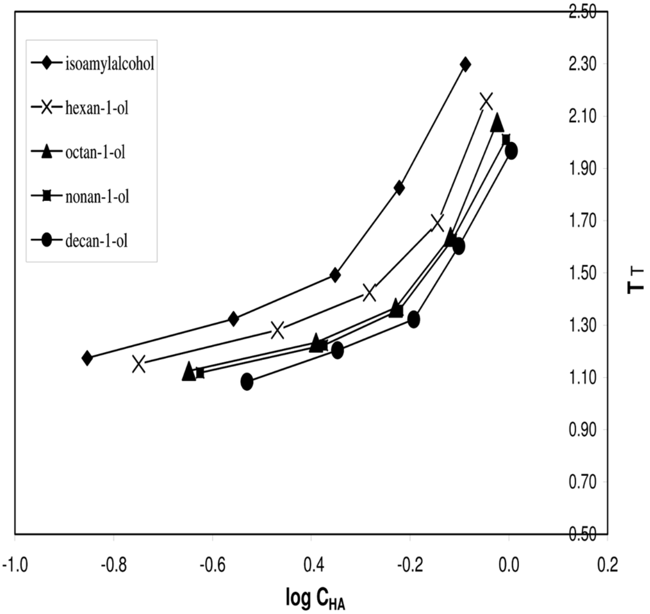

Figure 3. Plot of loading curves for extraction of formic acid by TOA in different diluents.

amine per complex, there is no effect of total amine concentration on the loading. If there is more than one amine per complex, the loadings increase with increasing amine concentration. Systems that exhibit aggregation and formation of complexes with large numbers of acid and amine molecules exhibit an increase in loading. Solvation of the complex by the diluent is a critical factor in the extraction of acid.

The complex formations which are resulting from acid amine interactions supposed as acid + amine (5:1), (6:1), and (7:1), because overloadings in each concentration of amine has been observed. Especially, the values of the loading factor exceed 2 ($Z > 2$) in experiments. This situation can be explained by high complex formations as mentioned above. The values of the overall extraction constants, K_{51}, K_{61}, and K_{71} for each solvent were given in Table 3. The resulting acid + amine complexes were

Table 3. Values of the overall complexation constants of formic acid (HA) for various diluents + TOA(R_3N)

Solvents	$\overline{C_{R_3N}}$	$K_{51}(L^5 \cdot mol^{-5})$	$K_{61}(L^6 \cdot mol^{-6})$	$K_{71}(L^7 \cdot mol^{-7})$
Isoamyl alcohol	0.590	6	8	9.45
	0.861	23	39	65
	1.158	85	192	431
	1.431	812	2933	10588
	1.731	21837	155981	111415
Hexan-1-ol	0.590	3.65	4	4.51
	0.861	8	12	17
	1.158	36	70	135
	1.431	281	829	2438
	1.731	6449	36234	203566
Octan-1-ol	0.590	2.72	2.88	3
	0.861	6	8	11
	1.158	19	32	55
	1.431	110	271	667
	1.731	1951	8673	38549
Nonan-1-ol	0.590	2.14	2.17	2.20
	0.861	6	8	10
	1.158	17	29	48
	1.431	91	216	513
	1.731	1495	6311	26629
Decan-1-ol	0.590	1.85	1.83	1.81
	0.861	5	6	8
	1.158	12	18	29
	1.431	65	145	32
	1.731	485	1646	5580

supposed to be stabilized due to the hydrogen bonding with the modifiers (2,16). The values K_{51}, K_{61}, and K_{71} for the most effective three diluents at $1.731 \cdot L^{-1}$ of TOA increase in following trend;

TOA + isoamly alcohol (21.8×10^3, 15.6×10^4, and 11.1×10^5) > TOA 336 + hexan-1-ol (64.5×10^2, 36.2×10^3, and 20.3×10^4) > TOA+ octan-1-ol(19.51×10^2, 86.7×10^2, and 38.5×10^3), respectively. The large difference among complexation constants values for the extraction of formic acid by TOA + different diluents indicates that the solvation of the complex in different diluents is a critical factor in acid extraction.

A plot of the distribution coefficient of formic acid against the carbon number of alcohols used in this study was shown in Fig. 4. It can be seen that with increasing carbon number of alcohol, which is depending on its molecular weight the distribution coefficient of formic acid decreases.

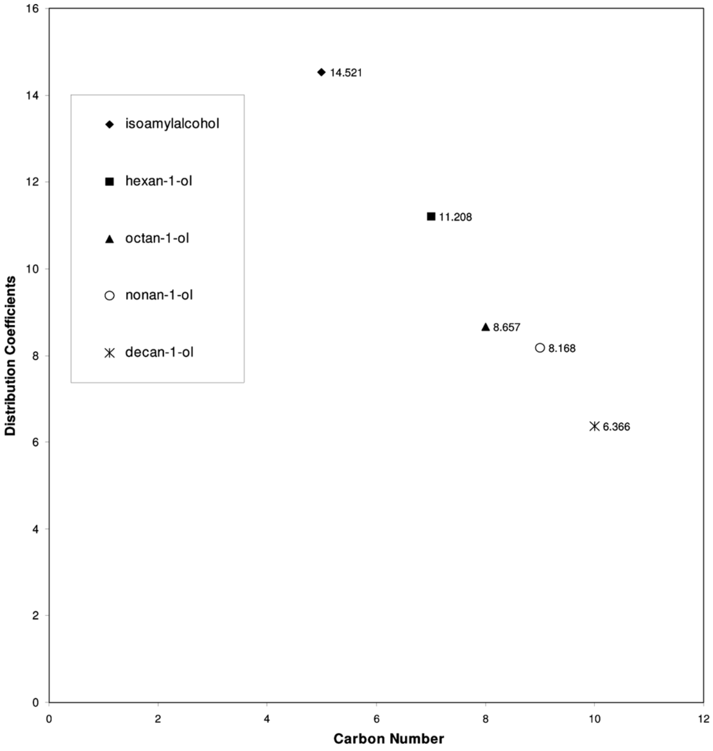

Figure 4. Distribution Coefficients of Extraction of Formic Acid according to carbon number of alcohols at $1.731\,mol \cdot L^{-1}$ of TOA Concentration.

LSER Model Results

The properties of an acid/amine system of hydrogen bond formation can be estimated through theoretically based models of the mass action law including the physical interaction terms, or by using the concept of multi-scale association, as well as by applying a generalized solvatochromic approach with linear solvation energy relationship (LSER) (17). A modified version of LSER for predicting the extraction equilibria of an amine/diluent/acid system is given by Bizek et al. (18).

In this study, the LSER model was applied to predict the distribution coefficient for TOA + alcohol systems on extraction of formic acid. Calculation of distribution coefficients of solvents in amine with LSER model equation was described in Uslu's earlier work (19). Briefly, the following equation can be used to describe the effect of diluents on the values of distribution coefficients (K_D);

$$\ln K_D = \ln K_D^0 + s(\pi^* + d\delta) + b\beta + a\alpha \tag{13}$$

In Eq. 13, π^* and δ are the solvatochromic parameters that measure solute + solvent, dipole + dipole, and dipole + induced dipole interactions, respectively. The solvatochromic parameter α scale of solvent HBD (hydrogen-bond donor) acidities describes the ability of the solvent to denote a proton in a solvent to solute hydrogen bond. The β 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, respectively. The coefficients *s*, *d*, *a*, and *b* include the properties of the solute that come from regression (20).

The values of the distributions coefficients can be regressed with the solvatochromic parameters of the solvents from Table 4 (21) according to Eq. 13. The obtained data (distribution coefficients) for each of the alcohols were regressed by computer program SPSS v14.0. The results of K_D^{model} and mutual comparison of K_D were presented in Table 2. The

Table 4. Solvatochromic parameters for alcohols (23)

Solvents	π^*	δ	β	α
Isoamyl alcohol	0.40	0	0.84	0.84
Hexan-1-ol	0.40	0	0.84	0.80
Octan-1-ol	0.40	0	0.81	0.77
Nonan-1-ol	0.40	0	0.81	0.75
Decan-1-ol	0.40	0	0.81	0.72

Table 5. Results of regression coefficient for LSER equation

Coefficients	Log K_D^0	s	d	B	a	R^2	Standard error
	−0.116	−11.801	0	2.790	6.343	0.981	0.0462

LSER model values showed a good regression to the experimental data. The estimated values of parameters of the model were presented in Table 5. It was concluded that by using this model, distribution coefficients of formic acid between water and amine + solvent system can be described. As a result of regression Eq. 14 was found to ascertain distribution coefficients (K_D).

$$\ln K_D = (-0.116) + (-11.801) \cdot (v\pi + 0 \cdot v\delta) + 2.790(v\beta) + 6.343\ (v \cdot \alpha) \tag{14}$$

For the suitability of the data, the Root Main Square Deviation (RMSD) are calculated from the difference between the experimental data and the predictions of the LSER model according to the following equation:

$$RMSD = \sqrt{\frac{1}{N}\sum_{i=1}^{n}(K_D - K_D^{\mathrm{model}})} \tag{15}$$

where K_D is the experimental distribution coefficient, and K_D^{model} is the calculated distribution coefficient. *N* is the number of experimental data. The RMSD value of LSER model is found to be 0.95.

The RMSD value shows that all predicted distribution coefficients agree well with each other, and also the agreement between predictions and measurements is acceptable considering experimental uncertainty.

CONCLUSION

Investigation of extractability of formic acid by using TOA dissolved in several alcohols was studied. Physical and reactive extraction were compared. It was concluded that conventional solvents (modifiers) are not suitable for extraction of formic acids ($K_D < 1$). Besides, these solvents using with TOA is to be very effective ($Kd \gg 1$). The isoamyl alcohol was found most effective solvent with maximum distribution value 2.588. The complexation constants K_{51}, K_{61}, and K_{71} for each alcohol used in this study were determined. The results of the liquid-liquid equilibrium measurements for alcohols were regressed by a linear solvation energy relationship-LSER model which takes into account physical interactions. LSER model results gave very close values to experimental values with $R^2 = 0.981$.

NOMENCLATURES

$\overline{C}_{HA}$	Concentration of the formic acid in the organic phase.
$C^0_{R_3N}$	Initial concentration of the trioctyl amine in the organic phase.
$\overline{C}_{R_3N}$	Concentration of the trioctyl amine in the organic pahse.
D_E	Degree of extraction
HA	Monocarboxylic acid (Formic Acid)
$HA - R_3N$	One acid + one amine complex
$(HA)_2 - R_3N$	Two acid + one amine complex
K_{11}	Complexation constant for (Acid + amine) complex ratio 1:1
K_{21}	Complexation constant for (Acid + amine) complex ratio 2:1
K_D	Distribution Coefficients
LSER	Linear solvation energy relationship
RMSD	Root Main Square Deviation
R_3N	Tertiary Amine (Trioctyl amine)
S_f	Separation factor
T_S	Stoichiometric loading factor
T_T	Loading factor
ν	Volume fraction of the solvent
π	Solvatochromic parameter
δ	Solvatochromic parameter
β	Solvatochromic parameter
α	Solvatochromic parameter
over bar($^-$)	refer to organic phase

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