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Reactive Extraction of Formic Acid by Amberlite LA-2 Extractant

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The reactive extraction of formic acid by Amberlite LA-2 dissolved in five different esters (dimethyl phthalate, dimethyl adipate, dimethyl succinate, dimethyl glutarate, diethyl carbonate), five different alcohols (isoamyl alcohol, hexan-1-ol, octan-1-ol, nonan-1-ol, decan-1-ol), and two different ketones (diisobutyl ketone (DIBK), methylisobutyl ketone (MIBK)) as diluents as well as the extraction capacity of pure diluent alone have been studied at isothermal conditions. All measurements have been carried out at 298.15 K. The comparison of physical and reactive extractions has been studied. The loading factor, T_T, extraction efficiency, E, modified separation factor, S_F, and distribution coefficients, K_D, have been calculated. The isoamylalcohol has been found to be the most effective solvent with a maximum distribution value of 19.223. Furthermore, the linear solvation energy relationship (LSER) model equation has been obtained to calculate distribution coefficients for alcohols with an R square of 0.976.

1. Introduction

Formic acid is a colorless, fuming liquid that is miscible with water. In the vapor phase, it consists of dimers formed by hydrogen bonds (Figure 1 shows the formic acid dimers), but in the aqueous phase, it is in the form of single molecules.

Formic acid is an essential chemical industry material. It is widely used in the textile industry, tanning industry, rubber processing industry, and pharmaceutical industry. In addition, formic acid is used as a preservative and antibacterial agent in livestock feed, and it is used as a miticide against the Varroa mite in the beekeeping industry.[1,2] In the industrial synthesis of formic acid, for example, by the reaction of methanol and carbon monoxide and hydrolysis of the methyl formate formed, aqueous solutions containing (20 to 50) % acid are always obtained. When concentrated by distillation, these aqueous solutions give an azeotrope, so that the formic acid cannot be obtained directly in an anhydrous form. Distillation under pressure, extractive distillation, and azeotropic distillation are used to concentrate the solutions. These processes are of high-energy consumption. To reduce the cost of concentrating acid solutions, extraction can be applied as an alternative.[3] The extraction equilibria of formic acid have been studied by some researchers.[4−7] Formic acid is also found in natural gas and crude oil fields. Thus, knowledge of the liquid−liquid phase behavior of formic acid, in general, is of great importance to the chemical and petrochemical industries. A significant amount of formic acid is also produced as a byproduct in the manufacture of other chemicals, especially acetic acid.[8,9]

Long-chain, aliphatic amines dissolved in suitable organic solvents are effective extractants for carboxylic acids.[1,11] 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.[1,2,6] 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 the acid, concentrations of acid and amine, and the type of diluent.[10−13] Simultaneously, the effect of additional controlling factors, such as the swing effect of a mixed diluent and third phase formation, can also modify the reversible complexation stage.[14,15] 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.[16]

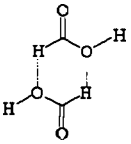

Figure 1. Structure of formic acid dimers.

Table 1. Results for Physical Extraction of Formic Acid with Pure Solvents[a]

	solvents	$pH_{aq.}$	(C^*_{FA}) (mol·L^{-1})	K_D	E
esters	dimethylphthalate	3.27	0.229	0.118	10.538
	dimethyladipate	3.39	0.356	0.196	16.383
	dimethylglutarate	3.45	0.406	0.229	18.684
	dimethylsuccinate	3.48	0.437	0.252	20.110
	diethylcarbonate	3.63	0.586	0.369	26.967
ketones	diisobutylketone	3.58	0.546	0.335	22.640
	methylisobutylketone	3.66	0.625	0.403	25.834
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

[a] C^*_{FA} is the concentration of formic acid in the organic phase; K_D is the distribution coefficient; and E is the extraction efficiency.

The reactive extraction of carboxylic acids has been tested by various scientists. Yang et al.[10] studied the extraction of carboxylic acids with tertiary and quaternary amines, and they showed the effect of pH on reactive extraction of carboxylic acid. Recently, Uslu and co-workers have studied the reactive extraction of some carboxylic acids (luvulinic acid, propionic acid, tartaric acid, glycolic acid) with trioctyl amine (TOA), trioctyl methylammonium chloride (Aliquat 336), and Alamine

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Table 2. Results for Extraction of Formic Acid with the Amberlite LA-2 + Alcohol System[a]

solvents	$(C^*_{\mathrm{LA-2}})$		(C^*_{FA})							
(alcohols)	$(\mathrm{mol \cdot L^{-1}})$	$\mathrm{pH_{aq}}$	$(\mathrm{mol \cdot L^{-1}})$	ν	K_D	K_D^{model}	T_T	T_s	S_f	E
isoamyl alcohol	0.371	4.95	1.907	0.083	7.169	6.774	5.154	4.957	0.9979	87,758
	0.743	5.03	1.986	0.167	10.620	9.886	2.672	2.489	0.9983	91.394
	1.115	5.07	2.028	0.250	13.986	12.998	1.818	1.635	0.9985	93.327
	1.487	5.08	2.045	0.333	15.976	16.111	1.375	1.192	0.9985	94.109
	1.859	5.11	2.069	0.417	19.894	19.223	1.112	0.929	0.9986	95.213
hexan-1-ol	0.371	4.93	1.889	0.083	6.651	6.206	5.105	4.935	0.9977	86.930
	0.743	4.99	1.952	0.167	8.832	8.751	2.627	2.471	0.9981	89.829
	1.115	5.04	1.997	0.250	11.346	11.295	1.791	1.634	0.9983	91.90
	1.487	5.05	2.011	0.333	12.413	13.839	1.352	1.196	0.9984	92.544
	1.859	5.08	2.044	0.417	15.844	16.384	1.099	0.943	0.9985	94.063
octan-1-ol	0.371	4.88	1.844	0.083	5.604	5.955	4.983	4.833	0.9974	84.859
	0.743	4.99	1.947	0.167	8.615	8.249	2.620	2.483	0.9981	89.599
	1.115	5.02	1.984	0.250	10.497	10.543	1.779	1.642	0.9982	91.302
	1.487	5.04	2.002	0.333	11.707	12.836	1.346	1.209	0.9983	92.130
	1.859	5.07	2.035	0.417	14.746	15.130	1.094	0.957	0.9985	93.649
nonan-1-ol	0.371	4.86	1.820	0.083	5.155	5.671	4.918	4.773	0.9973	83.755
	0.743	4.95	1.914	0.167	7.389	7.681	2.576	2.443	0.9979	88.080
	1.115	5.01	1.970	0.250	9.704	9.691	1.766	1.634	0.9982	90.658
	1.487	5.04	2.003	0.333	11.782	11.700	1.347	1.214	0.9983	92.176
	1.859	5.07	2.027	0.417	13.883	13.710	1.090	0.957	0.9985	93.281
decan-1-ol	0.371	4.84	1.802	0.083	4.857	5.245	4.870	4.732	0.9971	82.926
	0.743	4.92	1.876	0.167	6.316	6.829	2.524	2.399	0.9977	86.332
	1.115	4.99	1.946	0.250	8.572	8.413	1.745	1.619	0.9981	89.553
	1.487	5.03	1.989	0.333	10.809	9.997	1.337	1.212	0.9983	91.532
	1.859	5.05	2.010	0.417	12.331	11.581	1.081	0.955	0.9984	92.498

[a] $C^*_{\mathrm{LA\text{-}2}}$ is the concentration of Amberlite LA-2 in the organic phase; C^*_{FA} is the concentration of formic acid in the organic phase; K_D is the distribution coefficient; K_D^{model} is the predicted distribution coefficient; T_T is the loading factor; T_s is the stoichiometric loading factor; S_f is the separation factor; and E is the extraction efficiency.

Table 3. Results for Extraction of Formic Acid with Amberlite LA-2 + Ester System[a]

solvents	$(C^*_{\mathrm{LA\text{-}2}})$		(C^*_{FA})					
(esters)	$(\mathrm{mol \cdot L^{-1}})$	$\mathrm{pH_{aq}}$	$(\mathrm{mol \cdot L^{-1}})$	K_D	T_T	T_s	S_f	E
diethylcarbonate	0.371	4.76	1.840	5.525	4.972	4.828	0.9966	84.675
	0.743	4.79	1.876	6.316	2.524	2.393	0.9969	86.332
	1.115	4.82	1.945	8.530	1.744	1.613	0.9972	89.507
	1.487	4.84	1.981	10.317	1.332	1.201	0.9974	91.164
	1.859	4.87	2.030	14.195	1.091	0.960	0.9976	93.419
dimethylsuccinate	0.371	4.73	1.815	5.069	4.905	4.794	0.9963	83.525
	0.743	4.76	1.844	5.604	2.481	2.383	0.9966	84.859
	1.115	4.79	1.905	7.108	1.708	1.610	0.9969	87.666
	1.487	4.80	1.981	8.6150	1.309	1.234	0.9971	89.599
	1.859	4.83	2.030	10.436	1.066	0.993	0.9974	91.256
dimethylglutarate	0.371	4.73	1.804	4.888	4.875	4.771	0.9963	83.018
	0.743	4.75	1.844	5.335	2.462	2.390	0.9965	84.215
	1.115	4.78	1.905	6.519	1.689	1.617	0.9969	86.700
	1.487	4.80	1.947	7.979	1.298	1.218	0.9971	88.863
	1.859	4.82	1.983	9.651	1.059	0.975	0.9972	90.612
dimethyladipate	0.371	4.72	1.745	4.077	4.716	4.623	0.9961	80.303
	0.743	4.75	1.772	4.418	2.384	2.304	0.9964	81.546
	1.115	4.76	1.811	5.002	1.624	1.544	0.9966	83.341
	1.487	4.79	1.864	6.032	1.253	1.173	0.9969	85.780
	1.859	4.81	1.910	7.262	1.027	0.947	0.9971	87.896
dimethylphthalate	0.371	4.70	1.713	3.723	4.629	4.566	0.9958	78.831
	0.743	4.73	1.730	3.905	2.328	2.276	0.9961	79.613
	1.115	4.76	1.776	4.473	1.592	1.541	0.9965	81.730
	1.487	4.78	1.808	4.953	1.215	1.164	0.9967	83.202
	1.859	4.80	1.866	6.078	1.003	0.952	0.9969	85.872

[a] $C^*_{\mathrm{LA\text{-}2}}$ is the concentration of Amberlite LA-2 in the organic phase; C^*_{FA} is the concentration of formic acid in the organic phase; K_D is the distribution coefficient; K_D^{model} is the predicted distribution coefficient; T_T is the loading factor; T_s is the stoichiometric loading factor; S_f is the separation factor; and E is the extraction efficiency.

336 as extractants, and the magnitudes of distribution coefficients have been demonstrated.[17−21] Kyuchoukov et al. explained the mechanism of extraction of lactic acid by Aliquat 336.[22] Wasewar et al.[23] reported equilibria and kinetics for reactive extraction of lactic acid using Alamine 336 in decanol. Martak and Schlosser[24] 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 the Amberlite LA-2 extractant in a variety of diluents was examined in a wide range of amine concentrations [(0.371 to 1.859) $\mathrm{mol \cdot L^{-1}}$]. Distribution coefficients, loading factors, and degree of extraction were calculated as a result of batch extraction experiments. In addition to these parameters, the LSER model was applied to evaluate distribution coefficients, and a new LSER equation is presented.

Table 4. Results for Extraction of Formic Acid with the Amberlite LA-2 + Ketone System[a]

solvents (ketones)	$(C^*_{\text{LA-2}})$ ($\text{mol}\cdot\text{L}^{-1}$)	pH_{aq}	(C^*_{FA}) ($\text{mol}\cdot\text{L}^{-1}$)	K_D	T_T	T_s	S_f	E
DIBK	0.371	4.76	1.724	3.839	4.659	4.524	0.9972	79.337
	0.743	4.80	1.758	4.236	2.366	2.243	0.9975	80.901
	1.115	4.83	1.794	4.733	1.608	1.486	0.9977	82.558
	1.487	4.89	1.847	5.665	1.242	1.119	0.9981	84.997
	1.859	4.94	1.899	6.930	1.021	0.899	0.9983	87.390
MIBK	0.371	4.90	1.857	5.876	5.018	4.865	0.9981	85.457
	0.743	4.99	1.950	8.744	2.624	2.484	0.9985	89.737
	1.115	5.03	1.991	10.939	1.785	1.645	0.9987	91.624
	1.487	5.04	2.005	11.934	1.348	1.208	0.9987	92.268
	1.859	5.08	2.037	14.977	1.095	0.955	0.9989	93.741

[a] $C_{\text{LA-2}}$ is the concentration of Amberlite LA-2 in the organic phase; C^*_{FA} is the concentration of formic acid in the organic phase; K_D is the distribution coefficient; T_T is the loading factor; T_s is the stoichiometric loading factor; S_f is the separation factor; and E is the extraction efficiency.

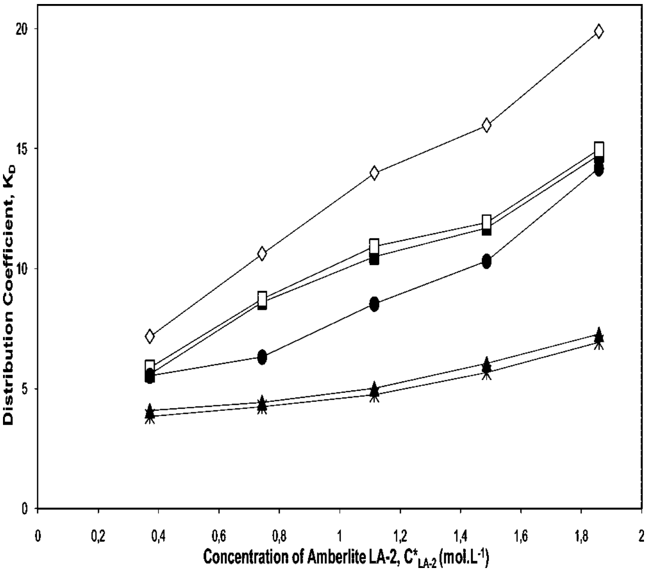

Figure 2. Plot of distribution coefficients K_D against concentration of Amberlite La-2 ($C^*_{\text{LA-2}}$). ◇, isoamyl alcohol; □, MIBK; ■, diethyl carbonate; ▲, dimethyladipate; ×, DIBK; ●, octan-1-ol.

2. Theory

The formation of a complex via an interfacial reaction can be represented by the following equation

$$\text{HA}_{\text{aq}} + pS_{\text{org}} \leftrightarrow (\text{HA}\cdot S_p)_{\text{org}} \tag{1}$$

where subscripts "aq" and "org" stand for aqueous and organic phases; HA is the undissociated acid molecule; S is the amine molecule (Amberlite LA-2); and p is solvation number of Amberlite LA-2. As the formic acid−Amberlite LA-2 complex is formed, it is rapidly extracted into the organic phase. The extraction equilibrium constant (K_S) and the number of reacting molecules of extractant are computed by applying the law of mass action that is the ratio between concentrations of reactant molecules and the concentration of the product species, according to the general equation of interaction between the extractant and the extracted species

$$K_S = \frac{[(\text{HA})\cdot(S)_p]_{\text{org}}}{[\text{HA}]_{\text{aq}}\cdot[S]^p_{\text{org}}} \tag{2}$$

K_S is expected to depend on the properties of the acid and the solvation efficiency of the diluent used. The dissociation of the acid in the aqueous phase is given as[25]

$$\text{HA} \leftrightarrow \text{H}^+ + \text{A}^-, \qquad \text{K}_{\text{HA}} = \frac{C_{\text{H}^+}\cdot C_{\text{A}^-}}{C_{\text{HA}}} \tag{3}$$

$[\text{H}^+]$ and $[\text{A}^-]$ are concentrations of the proton and anion of acid, and K_{HA} is the dissociation constant. The overall distribution coefficient is evaluated as the function of extraction constant and the number of reacting species as

$$K_D = \frac{[\text{HA}\cdot S_p]_{\text{org}}}{[\text{HA}]_{\text{aq}} + [\text{A}^-]_{\text{aq}}} = \frac{K_S\cdot[\text{HA}]_{\text{aq}}\cdot[S]^p_{\text{org}}}{[\text{HA}]_{\text{aq}} + K_{\text{HA}}[\text{HA}]_{\text{aq}}/[\text{H}^+]_{\text{aq}}} = \frac{K_S[S]^p_{\text{org}}}{1 + K_{\text{HA}}/[\text{H}^+]_{\text{aq}}} \tag{4}$$

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, $(v\cdot C^{*s}_{\text{FA}})$, for the amount of acid extracted by the modifiers in the solvent mixture.

$$T_s = \frac{(C^*_{\text{FA}} - v\cdot C^{*s}_{\text{FA}})}{C^*_{\text{LA2}}} \tag{5}$$

In eq 5, v is the volume fraction of modifiers in the mixture, and C^{*s}_{FA} is the concentration of acid extracted by the pure solvent alone, i.e., not containing the amine.

The degree of extraction is defined by the following equation

$$D_E = \frac{K_D\cdot 100}{1 + K_D} \tag{6}$$

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

$$s_f = \frac{C^*_{\text{FA}}}{C^*_{\text{FA}} + C^*_{\text{A}^-}} \tag{7}$$

3. Chemicals and Methods

3.1. Chemicals. Amberlite LA-2, which is also called *N*-lauryltrialkyl-methyl amine that has 24 to 28 carbon atoms (Merck Co.) > 99 %, is an anion exchange extractant and is a yellow liquid with the molecular weight of 353.67. Formic acid (pK_a: 3.75) (Merck, > 95 %), esters (dimethyl phthalate, dimethyl adipate, dimethyl succinate, dimethyl glutarate, diethyl carbonate), alcohols (isoamyl alcohol, hexan-1-ol, octan-1-ol, nonan-1-ol, decan-1-ol), and ketones (diisobutyl ketone (DIBK), methylisobutyl ketone (MIBK)) were supplied from Merck and Fluka to dilute Amberlite LA-2. All chemicals were used without further purification.

3.2. Methods. 3.2.1. Preparation. The known masses of formic acid were dissolved in distilled water to prepare the solutions with initial concentrations of acid of about 2.173 $\text{mol}\cdot\text{L}^{-1}$ which is similar to 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

Table 5. Values of the Complexation Constants of Formic Acid for Various Diluents + Amberlite LA-2[a]

solvents	K_{51} ($L^5 \cdot mol^{-5}$)	K_{61} ($L^6 \cdot mol^{-6}$)	K_{71} ($L^7 \cdot mol^{-7}$)	(C^*_{FA}) ($mol \cdot L^{-1}$)	solvents	K_{51} ($L^5 \cdot mol^{-5}$)	K_{61} ($L^6 \cdot mol^{-6}$)	K_{71} ($L^7 \cdot mol^{-7}$)
isoamyl alcohol	3870	14549	54698	0.371	diethyl carbonate	1214	3647	10952
	11689	62508	334271	0.743		1092	3678	12386
	28376	195697	1349637	1.115		2831	12417	54462
	40025	312696	2442938	1.487		5105	26592	138504
	91477	879591	8457611	1.859		18261	127702	893026
hexan-1-ol	2763	9730	34261	0.371	dimethyl succinate	834	2330	6508
	4983	22549	102034	0.743		643	1957	5948
	10605	60259	342384	1.115		1235	4611	17205
	12120	74818	461844	1.487		2220	9826	43480
	30778	238596	1849581	1.859		4307	22673	119335
octan-1-ol	1292	3929	11945	0.371	dimethyl glutarate	712	1931	5234
	4444	19666	87019	0.743		518	1512	4409
	7378	39038	206554	1.115		838	2900	10035
	9208	53848	314905	1.487		1564	6465	26715
	21872	158493	1148501	1.859		2997	14695	72036
nonan-1-ol	897	2542	7201	0.371	dimethyl adipate	328	767	1792
	2210	8534	32949	0.743		230	573	1430
	5125	25247	124370	1.115		261	721	1993
	9486	55805	328267	1.487		444	1440	4660
	16436	112579	771088	1.859		816	3104	11804
decan-1-ol	692	1867	5034	0.371	dimethyl phthalate	224	488	1062
	1092	3678	12386	0.743		136	308	695
	2895	12755	56193	1.115		161	406	1024
	6342	34468	187326	1.487		187	514	1408
	9396	57648	353674	1.859		368	1198	3905
DIBK	255	568	1266	0.371	MIBK	1592	5040	15951
	192	463	1116	0.743		4759	21341	95699
	205	542	1432	1.115		8942	49132	269958
	337	1034	3174	1.487		10075	59971	356975
	661	2414	8810	1.859		23551	173172	1273325

[a] C^*_{LA-2} is the concentration of Amberlite LA-2 in the organic phase; K_{51}, K_{61}, and K_{71} are the complexation constants for (5 acids + 1 amine), (6 acids + 1 amine), and (7 acids + 1 amine), respectively.

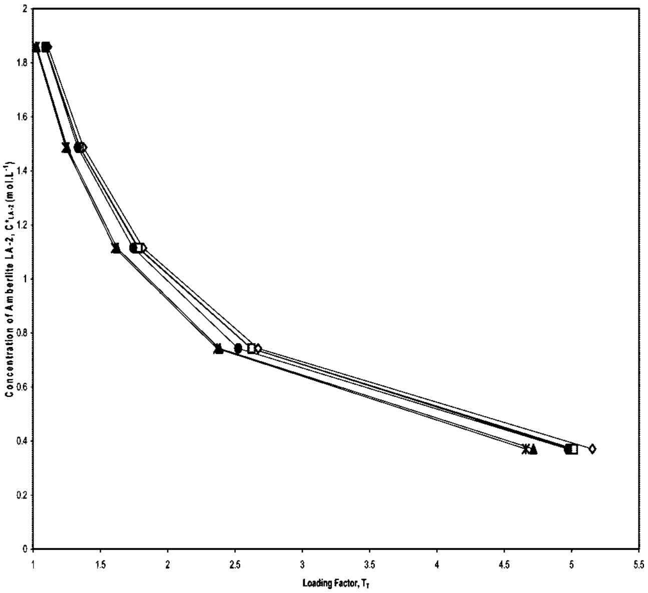

Figure 3. Plot of loading factor T_T against concentration of Amberlite La-2 (C^*_{LA-2}). ◇, isoamyl alcohol; □, MIBK; ■, diethyl carbonate; ▲, dimethyladipate; ×, DIBK; ●, octan-1-ol.

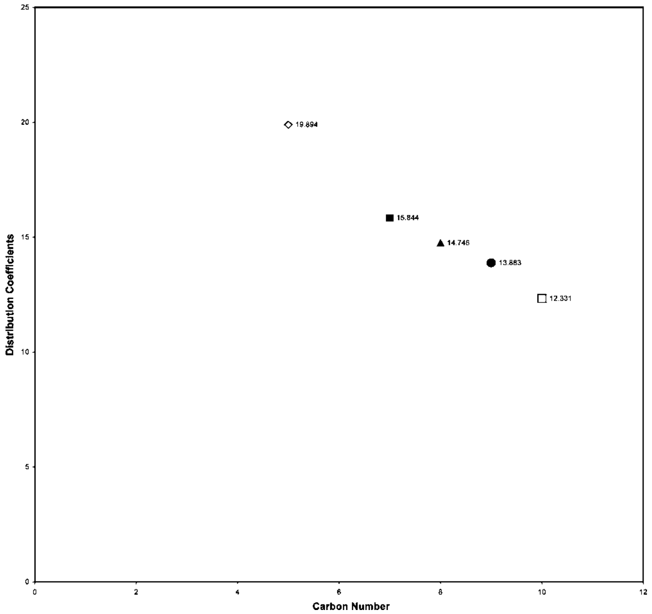

Figure 4. Distribution coefficients of extraction of formic acid according to carbon number of alcohols at 1.731 $mol \cdot L^{-1}$ of Amberlite LA-2 concentration. ◇, isoamyl alcohol; □, decan-1-ol; ■, hexan-1-ol; ▲, octan-1-ol; ●, nonan-1-ol.

dissolution of Amberlite LA-2 in the diluents to produce solutions with approximately five constant concentrations, in the range of (0.371 to 1.859) $mol \cdot L^{-1}$. Known volumes of aqueous and organic solutions of known concentration were added to Erlenmeyer flasks (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 the phases. After equilibration, both phases were separated by centrifugation at 1200 rpm for about 7 min for better separation.

*3.2.2. **Analysis.*** The aqueous phase samples were analyzed for solute concentration by 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.[1,10,11] The volume of phases changing after the extraction is neglected so that the changing of the phase volume is very small. In most cases, the deviation between the amount of acid analyzed and

Table 6. Solvatochromic Parameters for Alcohols[a]

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

[a] π^*, δ, β, and α are the solvatochromic paremeters.[23]

Table 7. Results of the Regression Coefficient for the LSER Equation

coefficients	K_D^0	s	d	b	a	R^2	standard error
	3.662	−117.282	0	−70.047	170.357	0.976	0.632

the amount of acid known by preparing the solutions by mass did not exceed ± 3 %. The solubility of the amine salts and diluents in the aqueous phase were negligible in the range of variables investigated.

The pH value of the aqueous phase was determined with a pH meter (Hanna pH 211 Microprocessor pH meter) with a precision of ± 0.01.

4. Results and Discussion

4.1. Experimental Results. The reactive extraction of formic acid by Amberlite LA-2 dissolved in esters (dimethyl phthalate, dimethyl adipate, dimethyl succinate, dimethyl glutarate, diethyl carbonate), five different alcohols (isoamyl alcohol, hexan-1-ol, octan-1-ol, nonan-1-ol, decan-1-ol), and two different ketones (diisobutyl ketone (DIBK), methylisobutyl ketone (MIBK)) was studied. The results of the equilibrium data on the distribution of formic acid between the aqueous phase and organic phase in the presence of Amberlite LA-2 in the organic phase are presented in Tables 2 to 4. The constant concentrations of Amberlite LA-2 in various solvents were prepared in the ratio of 0.371 mol·L^{-1} to 1.859 mol·L^{-1}. The formic acid concentration in the initial aqueous phase was prepared as 2.173 mol·L^{-1}. Distribution coefficients increase from 3.723 to 19.894 with an increasing amount of Amberlite LA-2. It can be seen that the extraction power of the Amberlite LA-2 + diluent mixture changes with increasing initial concentration of Amberlite LA-2 in the organic phase. Using the data shown in Tables 2 to 4, the following order of alcohols as diluents can be obtained according to the decreasing distribution coefficient in the extraction of formic acid by Amberlite LA-2:

Alcohols: isoamyl alcohol > hexan-1-ol > octan-1-ol > nonan-1-ol > decan-1-ol.

Esters: diethyl carbonate > dimethyl succinate > dimethyl glutarate > dimethyl adipate > dimethyl phthalate.

Ketones: methyl isobutyl ketone (MIBK) > diisobutyl ketone (DIBK).

Tables 2 to 4 and Figure 2 (the figures were drawn only for six solvents not to cause any confusion) present the extraction of formic acid by pure solvents not containing Amberlite LA-2 in the organic phase in terms of physical extraction. Physical extraction of formic acid is important to show the effect of amine on formic acid extraction (reactive extraction). In physical extraction, formic acid has a low affinity toward 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. It can been seen from Table 1 that in the physical extraction, with the help of pure isoamyl alcohol, the highest extraction degree 37.690 % of formic acid in the aqueous phase was removed into the organic phase.

Figure 3 illustrates the loading curves for extraction of formic acid by Ambetlite LA-2 in different diluents. The loading curve is a plot of T_T vs $C^*_{LA\text{-}2}$, and Tables 2 to 4 show all values of the loading factors and the ratio of the overall complexes acid to total amine in the organic phase (stoichiometric loading factor) T_s.

The complex formations which are resulting from acid amine interactions are reported as acid + amine (5:1), (6:1), and (7:1). Overloading has been observed for each concentration of the amine, and the value of the loading factors exceeds $T_T > 4$ for some points. This situation can be explained by high complex formation. The values of the overall extraction constants, K_{51}, K_{61}, and K_{71}, for each solvent are given in Table 5. With all of the solvents, the loading decreases, indicating that complexes include the diluents specifically. For systems with only one 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 the acid.

The resulting acid + amine complexes were supposed to be stabilized due to hydrogen bonding with the modifiers.[2,16] The values K_{61} and K_{71} for the most effective three diluents at 1.859 mol·L^{-1} of Amberlite LA-2 increase in the following trend.

Amberlite LA-2 + isoamyl alcohol (879591, 8457611) > Amberlite LA-2 + hexan-1-ol (238596, 1849581) > Amberlite LA-2 + octan-1-ol (158493, 1148501), respectively. The large difference among complexation constant values for the extraction of formic acid by Amberlite LA-2 + different diluents indicates that solvation of the complex in different diluents is a critical factor in acid extraction.

For all the results mentioned above, the polarity is the most important factor. Among the diluents, isoamyl alcohol has the highest dipole moment. Polarity is a function of transition energy, E_T, or Z. Kosower[26,27] defined the polarity parameter, Z, as the molar transition energy, E_T, which is expressed in kJ·mol^{-1}, for the CT (charge-transfer) absorption band of 1-ethyl-4-(methoxycarbonyl) pyridinium iodide in the appropriate solvent. The stronger the stabilizing effect of the solvent on the ground-state ion pair as compared with the less dipolar radical pair in the excited state, the higher this transition energy and, thus, the Z value. A high Z value corresponds to high solvent polarity.

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

4.2. Model Results. 4.2.1. LSER Model Equation. 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 multiscale association, as well as by applying a generalized solvatochromic approach with a linear solvation energy relationship (LSER).[28] A modified version of LSER for predicting the extraction equilibria of an amine/diluent/acid system is given by Bizek et al.[12]

In this study, an LSER model was applied to predict the distribution coefficient for Amberlite LA-2 + alcohol systems on the extraction of formic acid. The LSER model has been done for only alcholos because there are no adequate available solvatochromic parameters of other solvents used in this study in the literature. Calculation of distribution coefficients of solvents in amine with an LSER model equation was described in Uslu's earlier work.[29] Briefly, the following equation can be used to describe the effect of diluents on the values of distribution coefficients (K_D)

$$\ln K_D = \ln K_D^0 + s(\pi^* + d\delta) + b\beta + a\alpha \qquad (8)$$

In eq 8, 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 donate 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 solute and come from regression.[30]

The values of the distribution coefficients can be regressed with the solvatochromic parameters of the solvents from Table 6[31] according to eq 19. Distribution coefficients obtained for each alcohol were regressed by the computer program SPSS v14.0. The results of K_D^{model} and mutual comparison are presented in Table 2. The LSER model values showed a good regression to the experimental data. The estimated values of parameters of the model are presented in Table 7. It was concluded that by using this model distribution coefficients of formic acid between water and amine + solvent systems can be described. As a result of the regression, eq 9 was found to describe the distribution coefficients (K_D).

$$K_D = (3.662) + (-117.282)\cdot(v\pi^* + 0\cdot v\delta) + (-70.047)(v\beta) + 170/357(v\alpha) \qquad (9)$$

5. Conclusion

Investigation of the extractability of formic acid by using Amberlite LA-2 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 when using Amberlite LA-2 are very effective since $K_D \gg 1$. Isoamyl alcohol was found to be the most effective solvent with a maximum distribution value of 19.894. The complexation constants 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. The LSER model results gave very close values to the experimental values with an $R^2 = 0.976$.

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