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Reactive Extraction of Benzoic Acid and Pyridine-3-Carboxylic Acid Using Organophosphoric and Aminic Extractant Dissolved in Binary Diluent Mixtures

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ABSTRACT: The reactive extraction of benzoic acid (BA) and pyridine-3-carboxylic acid (NA) using diluent mixtures, decane-1-ol ($w = 0.36$) + cyclohexane ($w = 0.64$) and 4-methylpentan-2-one ($w = 0.63$) + kerosene ($w = 0.37$) with and without reactive extractants such as tri-*n*-butylphosphate (TBP) and *N*,*N*-dioctyloctan-1-amine (TOA), is carried out. The effect of various parameters such as the type of acid, type of diluent mixture, type of extractant, and composition of aqueous and organic phases are studied to analyze the performance of reactive extraction. The maximum values of the distribution coefficient (K_D) are found to be 38.1 for BA and 7.4 for NA with TOA ($0.229\ \mathrm{mol \cdot dm^{-3}}$) in decane-1-ol ($w = 0.36$) + cyclohexane ($w = 0.64$). A mathematical model based on mass action law is proposed to estimate the values of partition coefficient (P) and dimerization constant (D) in physical extraction and equilibrium constants (K_E) and number of reacting extractant molecules per acid molecule in chemical extraction. The values of the loading ratio, Z (between 0.005 and 0.566), for the extraction of both acids using TBP and TOA in both diluent mixtures indicate a formation of a 1:1 acid/extractant complex in the organic phase. For the reactive extraction of both acids, the highest values of K_E are found with TOA in decane-1-ol ($w = 0.36$) + cyclohexane ($w = 0.64$).

INTRODUCTION

Benzoic acid (BA) is a white crystalline solid and the simplest aromatic carboxylic acid with an acid strength ($\mathrm{p}K_a$) of 4.204[1] and hydrophobicity (log P, where P is the distribution coefficient of the solvent in a standard octane-1-ol and water two-phase system) of 1.87.[2] BA and sodium benzoate are used as preservatives in beverages, fruit products, chemically leavened baked goods, and condiments. BA and its salts/esters are also used in toothpastes, mouthwashes, dentifrices, cosmetics, deodorants, and so forth and the production of other chemicals (phenol and caprolactam).[3] The enzymatic activity of *Nectria galligena* produces this acid in apples. Pyridine-3-carboxylic acid (NA, also known as niacin, nicotinic acid, vitamin B3) with a $\mathrm{p}K_a$ of 4.75[1] and log P of −0.65[2] is a water-soluble vitamin and precursor to coenzymes (NADH, $\mathrm{NAD^+}$, $\mathrm{NADP^+}$, and NADPH) which serves an important role in the redox reactions taking place inside the human living cells for the metabolism activity. Niacin helps in both DNA repair and formation of steroid hormones in the adrenal gland. A deficiency of NA can cause pellagra, a serious disease that has paralyzed mankind for centuries. Also, a mild deficiency slows down the metabolism of the body, causing decreased tolerance to cold.[4−8]

Recently, fermentation technology is found to be an attractive process to produce carboxylic acids from renewable sources due to the limitations of chemical synthesis route. Some of the disadvantages of chemical synthesis are: (i) heavy consumption of chemicals, (ii) high energy utilization, and (iii) undesired byproduct formation. The production of these acids by biochemical fermentation route is comparatively a clean and green technology. The biosynthesis process produces these acids at a lower rate, and also the concentration of the acid in the fermentation broth is found to be very low. Therefore, to make the fermentation route efficient and effective, there is a need to develop novel fermentation processes and efficient separation techniques. Several separation processes such as crystallization, distillation, ion exchange, reverse osmosis, electrodialysis, liquid−liquid extraction, and precipitation (conventional technique) are employed to recover carboxylic acids from the aqueous solution.[9,10] The reactive extraction with a higher distribution coefficient is proposed to be an efficient and eco-friendly primary separation process.[11−14] The reactive extraction process has advantages: (i) effective at high concentrations of substrate in the extractive fermentation, (ii) the acid can be re-extracted and the solvent can be reused, (iii) it can control the pH in the bioreactor, (iv) better recovery of acid with higher concentration, and (v) reduction of downstream processing load and recovery cost. The reactive extraction represents the interaction of acid (solute) molecule with solvent/extractant molecule and transfers solute molecule by the diffusion and solubilization mechanism of the system components.

The equilibrium reactive extraction studies have been carried out for the recovery of different carboxylic acids by various researchers. Phosphorus-bonded oxygen-containing extractants such as tri-*n*-butyl phosphate (TBP)[15−20] and 1-dioctylphosphoryloctane (TOPO)[19,21,22] and long-chain aliphatic amines such as *N*,*N*-dioctyloctan-1-amine (TOA),[15,17,23−27] Alamine 336 (a $\mathrm{C_8{-}C_{10}}$ saturated straight-chain tertiary amine mixture),[28−31] *N*-methyl-*N*,*N*-dioctyloctan-1-ammonium chloride (Aliquat 336),[17,26,28,32] *N*-lauryltrialkyl-methyl amine (Amberlite LA-2),[24,33,34] and tridodecylamine (TDDA)[35] are used for the separation of carboxylic acids

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Table 1. Reagents Used in the Equilibrium Study

				mol. wt	specific gravity	viscosity
s. no.	reagent name	supplier	purity, *w*	$kg \cdot mol^{-1}$	$kg \cdot m^{-3}$	$mPa \cdot s$
1	BA	CDH, India	0.99	122.12		
2	NA	HIMEDIA, India	0.995	123.11		
3	TOA	Fluka, USA	0.98	353.68	809	8.325 (298 K)
4	TBP	Spectrochem. Pvt. Ltd., India	0.98	266.32	973	3.41 (298 K)
5	decane-1-ol	Spectrochem. Pvt. Ltd., India	0.98	158.28	830	10.974 (298 K)
6	4-methylpentan-2-one	Spectrochem. Pvt. Ltd., India	0.998	100.16	801	0.58 (293 K)
7	cyclohexane	S. D. Fine-Chem Ltd., India	0.99	84.16	779	0.98 (298 K)
8	kerosene	commercial		170	780 to 810	2.1 to 2.2 (288.6 K)

from aqueous solution. These extractants are dissolved in organic diluents (ketones, alcohols, hydrocarbons) to provide appropriate physical properties (density, viscosity, etc.) to the extractant−diluent system. Since the presence of hydroxyl and carboxylic groups increases the solubility of acid in the water phase, the strong interaction of a solvent molecule with a solute molecule is necessary to extract carboxylic acid from dilute aqueous solution. The diluents are categorized in two groups based on their activity: (i) inactive (inert) diluents, and (ii) active diluents (modifiers). The presence of polar functional groups in the modifiers enables them to act as better solvation medium for the acid−extractant complex by the formation of hydrogen bond. Also, a modifier enhances the extracting power of organophosphoric and aminic extractant as compared to an inert diluent in the extraction of organic acids.[36,37]

The present work is aimed to intensify the recovery of BA and NA using reactive extraction with TBP and TOA in a diluent mixture consisting of an active and an inactive diluent [decane-1-ol ($w = 0.36$) + cyclohexane ($w = 0.64$) and 4-methylpentan-2-one ($w = 0.63$) + kerosene ($w = 0.37$)]. The experimental data are analyzed by calculating distribution coefficients, degrees of extraction, and loading ratios. The effect of various parameters such as type of acid, type of diluent mixture, type of extractant, and compositions of aqueous and organic phase on the extraction efficiency is studied. A mathematical model based on mass action law is proposed to estimate the values of partition coefficient (P) and dimerization constant (D) in physical extraction (diluent mixtures only) and equilibrium constants (K_E) and number of reacting extractant molecules per acid molecule in chemical extraction (extractants in diluent mixtures).

EXPERIMENTAL SECTION

The reagents used in this equilibrium study are the carboxylic acids BA and NA, the extractants TBP and TOA, and the diluents decan-1-ol, 4-methylpentan-2-one, cyclohexane, and kerosene as listed in Table 1 with their physical properties.

The aqueous solutions of BA and NA are prepared in the concentration ranges of (0.003 to 0.023) $mol \cdot dm^{-3}$ and (0.02 to 0.12) $mol \cdot dm^{-3}$, respectively, using distilled water. Two concentrations of TBP [(0.183 and 0.365) $mol \cdot dm^{-3}$] and TOA [(0.115 and 0.229) $mol \cdot dm^{-3}$] in the mixtures of decane-1-ol ($w = 0.36$) + cyclohexane ($w = 0.64$) and 4-methylpentan-2-one ($w = 0.63$) + kerosene ($w = 0.37$) are used as the organic solutions. The decane-1-ol and 4-methylpentan-2-one are used as the active diluents (modifiers). Cyclohexane and kerosene are used as inactive diluents to control the density and viscosity of the organic phase. The extraction equilibrium experiments are carried out with equal volumes (0.02 dm^3) of the aqueous and organic solutions in conical flasks of 0.1 dm^3 and shaken at 100 rpm for 6 h in a temperature-controlled reciprocal shaker bath (HS 250 Basic REMI Laboratories) at a constant temperature (298 ± 1 K). After attaining equilibrium, the mixture of aqueous and organic phases is kept for separation in a separating funnel (0.125 dm^3) for 2 h at 298 ± 1 K. After the separation of both phases, the aqueous phase acid concentration is analyzed by titration using NaOH solution of 0.01 N with 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 solution are measured by a digital pH meter of ArmField Instruments (PCT 40, Basic Process Module, U.K.). The uncertainty of the experimental measurements is calculated with the identification of its sources (aqueous and organic sample preparation, impurities of chemicals, tolerance of the glasswares, repeatability, and titration method) and is found to be ± 5 %.

The effectiveness of the reactive extraction process is analyzed by calculating the distribution coefficient (K_D), the degree of extraction (E), and loading ratio (Z) using eqs 1, 2, and 3, respectively.

$$K_D = \frac{\overline{C}_{HC}}{C_{HC}} \tag{1}$$

$$E = \frac{\overline{C}_{HC}}{C_{in}} = \frac{K_D}{1 + K_D} \tag{2}$$

$$Z = \frac{\overline{C}_{HC}}{[\overline{T}]_o} \tag{3}$$

where $\overline{C}_{HC}$ is the total (undissociated, dimer, and complex forms) concentration of carboxylic acid in the organic phase and C_{HC} is the total (dissociated and undissociated) concentration in the aqueous phase at equilibrium; C_{in} and $[\overline{T}]_o$ are the initial carboxylic acid concentration in the aqueous phase and the initial extractant concentration in the organic phase, respectively.

RESULTS AND DISCUSSION

The equilibrium results for physical (without extractant) extraction of both acids (BA and NA) are presented in Table 2, and chemical extraction of BA and NA using TBP and TOA as extractants dissolved in two different diluent mixtures, decane-1-ol ($w = 0.36$) + cyclohexane ($w = 0.64$) and 4-methylpentan-2-one ($w = 0.63$) + kerosene ($w = 0.37$), are given in Tables 3 and 4, respectively.

Table 2. Physical Equilibria for the Extraction of BA and NA Using Binary Diluent Mixtures at 298 ± 1 K

		C_{HC}	$\overline{C}_{HC}$				D		
acid	diluent	$mol \cdot dm^{-3}$	$mol \cdot dm^{-3}$	$K_D^{diluent}$	pH_{eq}	P	$dm^3 \cdot mol^{-1}$	R^2	SD
BA	decane-1-ol (w = 0.36) + cyclohexane (w = 0.64)	0.00168	0.0012	0.714	3.83	0.393	1193.63	0.98	0.183
		0.00263	0.00313	1.190	3.73				
		0.00445	0.00849	1.908	3.60				
		0.00636	0.01364	2.145	3.52				
		0.00659	0.01647	2.499	3.51				
	4-methylpentan-2-one (w = 0.63) + kerosene (w = 0.37)	0.00182	0.00106	0.582	3.81	0.189	4103.73	0.96	0.220
		0.00304	0.00272	0.895	3.69				
		0.00504	0.00649	1.288	3.57				
		0.00727	0.01273	1.751	3.49				
		0.00713	0.01593	2.234	3.50				
NA	decane-1-ol (w = 0.36) + cyclohexane (w = 0.64)	0.01817	0.00183	0.101	3.37	0.092	39.69	0.98	0.004
		0.04452	0.00548	0.123	3.18				
		0.06995	0.01005	0.144	3.08				
		0.08722	0.01278	0.147	3.03				
		0.10357	0.01643	0.159	2.99				
	4-methylpentan-2-one (w = 0.63) + kerosene (w = 0.37)	0.01862	0.00138	0.074	3.25	0.060	114.58	0.99	0.004
		0.04543	0.00457	0.101	3.05				
		0.07177	0.00823	0.115	2.95				
		0.08858	0.01142	0.129	2.90				
		0.10448	0.01552	0.149	2.87				

Physical Extraction. The understanding of the diluent effect on the reactive extraction of acids can be determined by taking into account three important factors: (i) partial dissociation of the acid molecules in the aqueous phase, (ii) partition of the undissociated acid molecules between aqueous and organic phase, and (iii) dimerization of the undissociated acid in the organic phase.

(i) NA has Lewis acid−base characteristics with a Lewis acid group (−COOH) and a Lewis base group (−N). Therefore, it acts both as proton donor and acceptor. BA is a Lewis acid having only a −COOH group. These acids can exist as the undissociated (HC), and the dissociated (C^-) forms in the aqueous solution. The dissociation of the acid in the aqueous solution depends upon the strength of the acid (pK_a) and is described by the eq 4.

$$HC \Leftrightarrow H^+ + C^- \tag{4}$$

The dissociation constant (K_a) is calculated by eq 5.

$$K_a = \frac{[H^+][C^-]}{[HC]} \tag{5}$$

The total acid concentration in the aqueous phase (C_{HC}) can be expressed in terms of undissociated acid ([HC]) concentration, K_a, and proton ($[H^+]$) concentration (eqs 6 and 7).

$$C_{HC} = [HC] + [C^-] \tag{6}$$

$$[HC] = \frac{C_{HC}}{\left(1 + \frac{K_a}{[H^+]}\right)} \tag{7}$$

(ii) The distribution of the undissociated acid molecules between aqueous and organic phases is represented by eq 8, and the corresponding partition coefficient is given by eq 9.

$$HC \Leftrightarrow \overline{HC} \tag{8}$$

$$P = \frac{\overline{[HC]}}{[HC]} \tag{9}$$

(iii) Because of the strong donor−acceptor interaction, the undissociated extracted acid molecules can be dimerized in the organic phase as the solute−solute hydrogen bond is stronger than the solute−solvent hydrogen bond. The dimerization of the undissociated extracted acid in the organic phase ($\overline{HC}$) is represented by eq 10.

$$2\overline{HC} \Leftrightarrow \overline{(HC)}_2 \tag{10}$$

The dimerization constant (D) is expressed by eq 11.

$$D = \frac{\overline{(HC)_2}}{\overline{(HC)}^2} \tag{11}$$

The extraction efficiency (with diluent mixture alone) of carboxylic acid is calculated by the physical distribution coefficient, $K_D^{diluent}$ (eq 12).

$$K_D^{diluent} = \frac{\overline{C}_{HC}^{diluent}}{C_{HC}^{diluent}} \tag{12}$$

where $\overline{C}_{HC}^{diluent}$ is the total (undissociated and dimer forms) concentration of carboxylic acid in the organic phase and $C_{HC}^{diluent}$ is the total (dissociated and undissociated) concentration in aqueous phase at equilibrium with diluent mixture alone.

Table 3. Equilibrium Data for the Extraction of BA Using TBP and TOA Dissolved in Binary Diluent Mixtures at 298 ± 1 K

extractant			experimental results								model predicted values		
	$[\overline{T}]_o$		C_{HC}	$\overline{C}_{HC}$									
name	$\text{mol}\cdot\text{dm}^{-3}$	diluents	$\text{mol}\cdot\text{dm}^{-3}$	$\text{mol}\cdot\text{dm}^{-3}$	K_D^{total}	K_D^{chem}	E	Z	m	pH_{eq}	K_D^{total}	K_D^{chem}	Z
TBP	0.183	decane-1-ol (w = 0.36) + cyclohexane (w = 0.64)	0.00111	0.00177	1.594	0.568	61.42	0.010	0.007	3.93	2.591	1.564	0.016
			0.00166	0.00410	2.470	0.679	71.13	0.022	0.017	3.83	3.466	1.675	0.038
			0.00172	0.00981	5.703	1.014	85.10	0.054	0.046	3.83	6.363	1.674	0.090
			0.00216	0.01784	8.259	2.260	89.20	0.097	0.075	3.77	7.731	1.732	0.146
			0.00222	0.02084	9.387	2.339	90.39	0.114	0.090	3.77	8.779	1.731	0.175
	0.365		0.00105	0.00183	1.743	0.714	63.50	0.005	0.003	3.94	3.171	2.142	0.008
			0.00138	0.00438	3.174	1.133	75.99	0.012	0.009	3.88	4.280	2.239	0.019
			0.00163	0.00990	6.074	1.386	85.88	0.027	0.023	3.84	6.988	2.300	0.044
			0.00194	0.01806	9.309	2.981	90.30	0.049	0.037	3.80	8.685	2.357	0.072
			0.00194	0.02112	10.887	3.246	91.61	0.058	0.045	3.80	9.998	2.357	0.082
	0.183	4-methylpentan-2-one (w = 0.63) + kerosene (w = 0.37)	0.00055	0.00233	4.236	2.405	80.85	0.013	0.006	4.10	3.649	1.818	0.021
			0.00083	0.00493	5.940	2.827	85.54	0.027	0.015	4.00	5.105	1.992	0.043
			0.00155	0.00998	6.439	2.461	86.58	0.055	0.035	3.85	6.199	2.221	0.089
			0.00249	0.01751	7.032	2.175	87.55	0.096	0.070	3.74	7.210	2.353	0.144
			0.00222	0.02084	9.387	2.571	90.39	0.114	0.087	3.77	9.137	2.320	0.180
	0.365		0.00111	0.00177	1.595	0.735	61.42	0.005	0.003	3.93	2.134	1.275	0.014
			0.00166	0.00410	2.470	0.995	71.13	0.011	0.007	3.83	2.844	1.369	0.022
			0.00222	0.00931	4.194	1.563	80.76	0.026	0.018	3.77	4.051	1.420	0.044
			0.00332	0.01668	5.024	1.573	83.40	0.046	0.035	3.67	4.947	1.496	0.075
			0.00166	0.02140	12.892	4.255	92.82	0.059	0.044	3.83	10.006	1.369	0.087
TOA	0.115	decane-1-ol (w = 0.36) + cyclohexane (w = 0.64)	0.00018	0.00270	15.000	8.667	93.69	0.023	0.010	4.10	10.222	3.889	0.016
			0.00029	0.00547	18.862	8.609	94.90	0.048	0.027	3.97	15.069	4.816	0.038
			0.00044	0.01109	25.205	6.874	96.20	0.096	0.074	3.86	23.523	5.192	0.090
			0.00070	0.01930	27.571	9.060	96.50	0.168	0.119	3.74	23.986	5.475	0.146
			0.00081	0.02225	27.469	8.152	96.51	0.193	0.143	3.71	24.846	5.529	0.175
	0.229		0.00015	0.00273	18.200	11.000	94.73	0.012	0.005	4.15	12.213	5.013	0.008
			0.00026	0.00550	21.154	10.319	95.42	0.024	0.014	4.00	16.735	5.900	0.019
			0.00040	0.01113	27.825	8.723	96.55	0.049	0.037	3.89	25.190	6.088	0.044
			0.00062	0.01938	31.258	11.458	96.90	0.085	0.060	3.77	26.594	6.794	0.072
			0.00059	0.02247	38.085	12.961	97.46	0.098	0.072	3.79	31.827	6.703	0.082
	0.115	4-methylpentan-2-one (w = 0.63) + kerosene (w = 0.37)	0.00033	0.00255	7.727	4.676	88.49	0.022	0.009	3.94	7.318	4.266	0.021
			0.00050	0.00526	10.520	5.352	91.26	0.046	0.024	3.83	9.890	4.722	0.043
			0.00083	0.01070	12.892	5.463	92.82	0.093	0.056	3.70	12.331	4.903	0.089
			0.00089	0.01911	21.472	7.884	95.55	0.166	0.111	3.68	18.607	5.019	0.144
			0.00111	0.02195	19.775	6.141	95.21	0.191	0.139	3.63	18.649	5.015	0.180
	0.229		0.00039	0.00249	6.385	3.938	86.40	0.011	0.005	3.89	8.221	5.775	0.014
			0.00044	0.00532	12.091	6.527	92.30	0.023	0.012	3.86	11.450	5.886	0.022
			0.00066	0.01087	16.470	7.620	94.30	0.047	0.028	3.76	15.267	6.417	0.044
			0.00086	0.01914	22.256	8.934	95.70	0.084	0.056	3.69	19.971	6.649	0.075
			0.00083	0.02223	26.783	9.510	96.42	0.097	0.070	3.70	24.004	6.731	0.087

From eqs 7, 9, and 12, K_D^{diluent} is expressed in terms of partition coefficient (P) and dimerization constant (D) for dilute acid concentration by eq 13.[12,27]

$$K_D^{\text{diluent}} = P + 2DP^2[\text{HC}] \tag{13}$$

Using plots of K_D^{diluent} versus [HC] in the Origin 6.0 (software package) and fitting the data linearly, the value of P as an intercept and $2DP^2$ as a slope are determined. In the linear fit program of Origin 6.0, the χ-squared minimization or "weighted least-squared" method is used to estimate the parameters (P and D). The physical extraction of BA and NA using a binary mixture of diluents is presented in Table 2. The degree of extraction is affected by two more significant factors: (i) the strength of the acid (pK_a) and (ii) the hydrophobicity of acid molecule (log P). The extraction efficiency is found to be increased with an increase in acid strength and hydrophobicity of acid [BA (pK_a = 4.204, log P = 1.87); NA (pK_a = 4.75, log P = −0.65)]. The maximum values of K_D^{diluent} of BA and NA with a diluent mixture of decane-1-ol (w = 0.36) + cyclohexane

Table 4. Equilibrium Data for the Extraction of NA Using TBP and TOA Dissolved in Binary Diluent Mixtures at 298 ± 1 K

extractant			experimental results								model predicted values		
name	$[\overline{T}]_o$ mol·dm^{-3}	diluents	C_{HC} mol·dm^{-3}	$\overline{C}_{HC}$ mol·dm^{-3}	K_D^{total}	K_D^{chem}	E	Z	m	pH$_{eq}$	K_D^{total}	K_D^{chem}	Z
TBP	0.183	decane-1-ol (w = 0.36) + cyclohexane (w = 0.64)	0.01495	0.00505	0.338	0.222	25.25	0.028	0.010	3.60	0.194	0.078	0.096
			0.04043	0.00957	0.237	0.108	19.14	0.052	0.030	3.38	0.208	0.079	0.233
			0.06536	0.01464	0.224	0.078	18.30	0.080	0.055	3.27	0.225	0.079	0.386
			0.08197	0.01803	0.220	0.072	18.03	0.099	0.070	3.22	0.227	0.079	0.514
			0.09693	0.02307	0.238	0.077	19.23	0.126	0.090	3.18	0.240	0.079	0.604
	0.365		0.01219	0.00781	0.641	0.506	39.05	0.021	0.005	3.64	0.300	0.165	0.058
			0.03600	0.01400	0.389	0.252	28.00	0.038	0.015	3.40	0.305	0.168	0.160
			0.05982	0.02018	0.337	0.186	25.23	0.055	0.028	3.29	0.319	0.168	0.276
			0.07643	0.02357	0.308	0.158	23.57	0.065	0.035	3.24	0.318	0.168	0.358
			0.09139	0.02861	0.313	0.151	23.84	0.078	0.045	3.20	0.328	0.166	0.425
	0.183	4-methylpentan-2-one (w = 0.63) + kerosene (w = 0.37)	0.01551	0.00449	0.289	0.205	22.45	0.025	0.008	3.59	0.193	0.108	0.043
			0.04043	0.00957	0.237	0.129	19.14	0.052	0.025	3.38	0.217	0.110	0.126
			0.06480	0.01520	0.235	0.114	19.00	0.083	0.045	3.27	0.230	0.109	0.200
			0.08087	0.01913	0.237	0.102	19.13	0.105	0.062	3.22	0.242	0.108	0.253
			0.09527	0.02473	0.260	0.105	20.61	0.135	0.085	3.19	0.262	0.107	0.309
	0.365		0.01440	0.00560	0.389	0.303	28.00	0.015	0.004	3.60	0.212	0.126	0.024
			0.03988	0.01012	0.254	0.151	20.24	0.028	0.013	3.38	0.231	0.128	0.074
			0.06425	0.01575	0.245	0.130	19.69	0.043	0.023	3.27	0.243	0.128	0.123
			0.08059	0.01941	0.241	0.113	19.41	0.053	0.031	3.23	0.255	0.127	0.151
			0.09416	0.02584	0.274	0.126	21.53	0.071	0.043	3.19	0.275	0.127	0.183
TOA	0.115	decane-1-ol (w = 0.36) + cyclohexane (w = 0.64)	0.00596	0.01404	2.356	2.064	70.20	0.122	0.016	3.80	1.852	1.56	0.096
			0.01511	0.03489	2.309	1.965	69.78	0.303	0.048	3.59	1.773	1.428	0.233
			0.02783	0.05217	1.875	1.532	65.21	0.454	0.087	3.46	1.595	1.252	0.386
			0.04373	0.05627	1.287	1.009	56.27	0.489	0.111	3.36	1.352	1.074	0.514
			0.05565	0.06435	1.156	0.876	53.63	0.560	0.143	3.31	1.248	0.968	0.604
	0.229		0.00239	0.01761	7.368	6.679	88.05	0.077	0.008	4.00	5.557	4.868	0.058
			0.00676	0.04324	6.396	5.667	86.48	0.189	0.024	3.77	5.420	4.690	0.160
			0.01272	0.06728	5.289	4.578	84.10	0.294	0.044	3.63	4.969	4.258	0.276
			0.01800	0.08200	4.556	3.917	82.00	0.358	0.056	3.55	4.555	3.916	0.358
			0.02266	0.09734	4.296	3.643	81.12	0.425	0.072	3.50	4.295	3.642	0.425
	0.115	4-methylpentan-2-one (w = 0.63) + kerosene (w = 0.37)	0.01302	0.00698	0.536	0.435	34.90	0.061	0.012	3.63	0.380	0.279	0.043
			0.03711	0.01289	0.347	0.230	25.78	0.112	0.040	3.40	0.390	0.273	0.126
			0.05816	0.02184	0.376	0.241	27.30	0.190	0.072	3.30	0.395	0.261	0.200
			0.07200	0.02800	0.389	0.238	28.00	0.243	0.099	3.25	0.404	0.253	0.253
			0.08364	0.03636	0.435	0.258	30.30	0.316	0.135	3.22	0.425	0.249	0.309
	0.229		0.01108	0.00892	0.805	0.693	44.60	0.039	0.006	3.66	0.496	0.384	0.024
			0.03323	0.01677	0.505	0.381	33.54	0.073	0.020	3.42	0.510	0.386	0.074
			0.05539	0.02461	0.444	0.311	30.76	0.107	0.036	3.31	0.509	0.375	0.123
			0.06591	0.03409	0.517	0.361	34.09	0.149	0.050	3.27	0.525	0.369	0.151
			0.07699	0.04301	0.559	0.377	35.84	0.188	0.068	3.24	0.544	0.363	0.183

(w = 0.64) are found to be 2.50 and 0.16, respectively, and with 4-methylpentan-2-one (w = 0.63) + kerosene (w = 0.37), the $K_D^{diluent}$ values are 2.23 and 0.15, respectively (Table 2). Since the acid strength of NA is slightly higher than that of BA, it will dissociate less in the aqueous phase and should be extracted by the diluent mixture in greater amounts, but a much higher hydrophilicity and presence of pyridine group in NA makes it poorly extractable by the diluent mixture.

The values of physical extraction parameters (P and D) are obtained for both acids using two different diluent mixtures by fitting eq 13 to the experimental data (Table 2). In the physical extraction of both acids, higher P values (0.393 for BA and 0.092 for NA) and lower D values (1193.63 for BA and 39.69 for NA) are obtained with decane-1-ol (w = 0.36) + cyclohexane (w = 0.64) than that of 4-methylpentan-2-one (w = 0.63) + kerosene (w = 0.37) (P = 0.189 for BA and 0.06 for NA; D = 4103.73 for BA and 114.58 for NA). This indicates that the solute−solvent interaction is rather more than the solute−solute interaction in the case of physical extraction by decane-1-ol (w = 0.36) + cyclohexane (w = 0.64). Here, the decane-1-ol (w = 0.36) + cyclohexane

($w = 0.64$) diluent mixture shows a better solvation of acid by making hydrogen bonds with acid and limits the formation of dimers in the organic phase. The higher D values in the physical extraction of BA with both diluent mixtures signify that BA has a greater tendency to dimerize in the organic phase as compared to NA. This is because the dissociation of BA is comparatively more ($K_a = 6.25 \cdot 10^{-5}$) in the aqueous phase than that of NA ($K_a = 1.78 \cdot 10^{-5}$). In the physical extraction of BA with both diluent mixtures, solute—solute interactions may dominate. The use of nonpolar solvents such as cyclohexane and kerosene in the extraction of carboxylic acid at higher initial acid concentrations may also lead to the formation of a stable emulsion and dimer in the organic phase. Therefore, a modifier (active diluent) is generally added with the inert diluent to avoid the formation of a stable emulsion and dimer in the organic phase. This also assures a higher solubility of the formed acid—extractant complex in the organic phase. The active diluents, decane-1-ol and 4-methylpentan-2-one are having active groups such as —OH (proton donor) and ═CO (proton acceptor), respectively, which enhance the extracting capability of low polar extractant (TBP and TOA) and allow polar—extractant complexes to stay in the organic phase. Hence, in this study, the equal volume mixtures of inert and active diluent (modifier) are used.

Chemical Extraction. Conventional solvents are generally not able to fulfill the basic requirements of high distribution coefficients and high acid selectivities. The use of conventional solvents with extractants (higher K_D) may improve the extraction efficiency of the recovery process. Therefore, the equilibrium chemical extraction experiments for the recovery of carboxylic acids (BA and NA) are also carried out by considering five different concentrations of both acids and two different concentrations of both extractants (TBP and TOA) dissolved in two different diluent mixtures, decane-1-ol ($w = 0.36$) + cyclohexane ($w = 0.64$) and 4-methylpentan-2-one ($w = 0.63$) + kerosene ($w = 0.37$). The results for the reactive extraction of BA and NA are shown in Tables 3 and 4, respectively. It can be seen that K_D values for both acids are found to be increased 3 to 4 times with TBP and 5 to 24 times with TOA, dissolved in diluent mixtures over when these diluent mixtures are used alone.

The experimentally determined K_D values depend on the acid strength ($pK_{a,BA} = 4.204$ and $pK_{a,NA} = 4.75$) and the dipole moment ($\mu_{BA} = 2.54 \cdot 10^{-30}$ Cm and $\mu_{NA} = 8.44 \cdot 10^{-30}$ Cm) of both acids. There is not much difference between acid strengths of BA and NA, but the presence of pyridine group (—N) in NA increases its hydrophilicity than BA. The benzene ring of BA makes this acid more hydrophobic and, thus, more easily extractable by polar (decane-1-ol) and protic (4-methylpentan-2-one) diluents as compared to less hydrophobic NA. In NA, there is a possibility to make an intramolecular hydrogen bond due to the presence of second proton accepting group (—N). The higher values of K_D are observed in the extraction of BA with both extractants (TBP and TOA) dissolved in both diluent mixtures [decane-1-ol ($w = 0.36$) + cyclohexane ($w = 0.64$) and 4-methylpentan-2-one ($w = 0.63$) + kerosene ($w = 0.37$)]. The extraction efficiency is also affected by initial acid concentration at constant extractant concentration. The values of E for BA are found to be increased with an increase in the initial BA concentration due to a lower concentration range as compared to when the extractant concentration is used. Moreover, the hydrophilic nature of NA makes its molecules more likely to attach with water molecules before coming in contact with the extractant/diluent molecules.

Decane-1-ol (protic or proton donor, $\mu = 8.74 \cdot 10^{-30}$ Cm, $E_T = 47.7$) and 4-methylpentan-2-one (aprotic or proton acceptor, $\mu = 9.31 \cdot 10^{-30}$ Cm, $E_T = 39.4$) are used as active diluents, which show a higher extractability than that of inactive diluents. E_T, an empirical parameter, gives the assessment of solvation energy of the solute and is based on the absorption spectrum of pyridinium-*N*-phenolbutane.[38] It provides anion solvation by ion—dipole and ion-induced dipole forces. The cyclohexane ($\mu = 0$) and kerosene ($\mu \approx 0$) are inactive and nonpolar diluents used to control density and viscosity of the organic phase. The experimental data obtained for the reactive extraction of BA and NA show that the decane-1-ol ($w = 0.36$) + cyclohexane ($w = 0.64$) mixture provides a higher extraction efficiency with both extractants (TBP and TOA) as compared to the 4-methylpentan-2-one ($w = 0.63$) + kerosene ($w = 0.37$) mixture. With TBP ($0.365\ \text{mol} \cdot \text{dm}^{-3}$) dissolved in decane-1-ol ($w = 0.36$) + cyclohexane ($w = 0.64$), the maximum values of K_D are found to be 10.887 for BA ($0.023\ \text{mol} \cdot \text{dm}^{-3}$) and 0.641 for NA ($0.02\ \text{mol} \cdot \text{dm}^{-3}$) and TBP in 4-methylpentan-2-one ($w = 0.63$) + kerosene ($w = 0.37$); the maximum values of K_D are found to be 12.892 for BA ($0.023\ \text{mol} \cdot \text{dm}^{-3}$) and 0.389 for NA ($0.02\ \text{mol} \cdot \text{dm}^{-3}$). With TOA ($0.229\ \text{mol} \cdot \text{dm}^{-3}$) in decane-1-ol ($w = 0.36$) + cyclohexane ($w = 0.64$), the maximum values of K_D are found to be 38.085 for BA ($0.023\ \text{mol} \cdot \text{dm}^{-3}$) and 7.368 for NA ($0.02\ \text{mol} \cdot \text{dm}^{-3}$) and TOA in 4-methylpentan-2-one ($w = 0.63$) + kerosene ($w = 0.37$); the maximum values of K_D are found to be 26.783 for BA ($0.023\ \text{mol} \cdot \text{dm}^{-3}$) and 0.805 for NA ($0.02\ \text{mol} \cdot \text{dm}^{-3}$). With an increase in the concentration of TBP and TOA, it is found that there is an increase in the extraction efficiency for both acids. The maximum values of E are found to be 97.46 % for BA ($0.023\ \text{mol} \cdot \text{dm}^{-3}$) and 88.05 % for NA ($0.02\ \text{mol} \cdot \text{dm}^{-3}$), with the extractant—diluent system TOA ($0.229\ \text{mol} \cdot \text{dm}^{-3}$) + decane-1-ol ($w = 0.36$) + cyclohexane ($w = 0.64$).

The experimental results are also interpreted in terms of the distribution coefficient of acid by chemical extraction (K_D^{Chem}) with extractants (TBP and TOA) dissolved in diluent mixtures and given by eq 14.

$$K_D^{\text{chem}} = \frac{\overline{C}_{HC} - \nu \overline{C}_{HC}^{\text{diluent}}}{C_{HC}} \tag{14}$$

where ν is the volume fraction of diluent mixture.

The overall distribution coefficient (K_D^{total}) by physical and chemical extraction is obtained by adding eqs 12 and 14.

$$K_D^{\text{total}} = \nu K_D^{\text{diluent}} + K_D^{\text{chem}} \tag{15}$$

The equilibrium reactive extraction of monocarboxylic acids (HC) using TBP and TOA as extractants (T) with diluent mixtures is described by eq 16, showing formation of complexes between acid and extractant molecules in the organic phase with the corresponding equilibrium constant (K_E) as given by eq 17.

$$HC + p\overline{T} \Leftrightarrow \overline{(HC)(T)_p} \tag{16}$$

$$K_E = \frac{[\overline{(HC)(T)_p}]}{[HC][\overline{T}]^p} \tag{17}$$

where [HC], $[\overline{T}]$, and $[(\overline{HC})(\overline{T})_p]$ represent undissociated acid-, free extractant-, and acid/extractant complex concentrations, respectively, and p is the number of extractant molecules reacting with one acid molecule. Niitsu and Sekine[39] reported that the value of p for the carboxylic acid is the same as the

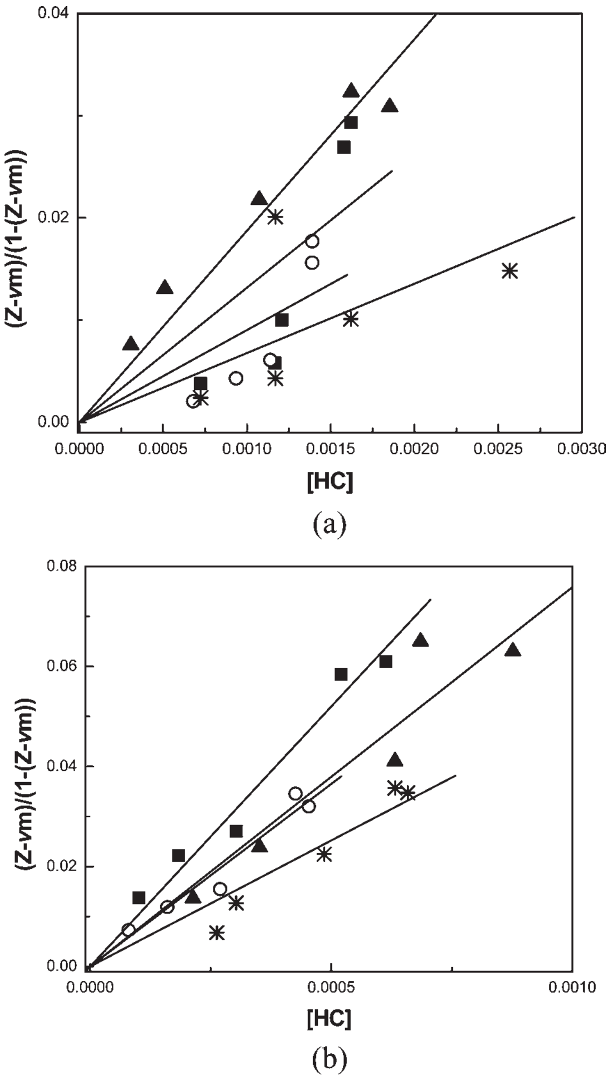

Figure 1. Equilibrium complexation constant (K_E) determination for the extraction of BA at 298 ± 1 K with (a) TBP in decane-1-ol ($w = 0.36$) + cyclohexane ($w = 0.64$): ■, 0.183 mol·dm^{-3}; ○, 0.365 mol·dm^{-3} and in 4-methylpentan-2-one ($w = 0.63$) + kerosene ($w = 0.37$):▲, 0.183 mol·dm^{-3}; ∗, 0.365 mol·dm^{-3} and (b) TOA in decane-1-ol ($w = 0.36$) + cyclohexane ($w = 0.64$): ■, 0.115 mol·dm^{-3}; ○, 0.229 mol·dm^{-3} and in 4-methylpentan-2-one ($w = 0.63$) + kerosene ($w = 0.37$): ▲, 0.115 mol·dm^{-3}; ∗, 0.229 mol·dm^{-3}; —, linear fit lines.

numbers of the carboxyl groups present on each acid with phosphorus-based extractants, and hence the value of p for BA and NA can be considered as one, which indicates a stoichiometric (1:1) association of the individual acid molecule with TBP. The loading ratio (Z) is also an important parameter which helps to predict the stoichiometry of the overall reactive extraction of the acid in the organic phase. In the extraction of both acids using TOA in decane-1-ol ($w = 0.36$) + cyclohexane ($w = 0.64$) and 4-methylpentan-2-one ($w = 0.63$) + kerosene ($w = 0.37$), the values of Z are found to be between 0.005 and 0.566. The Z values less than 0.5 indicate a formation of (1:1) acid/TOA complex in the organic phase.[21,40,41] Therefore, with the assumption of (1:1) acid/extractant complexes in the organic phase, the following model equations of reactive extraction mechanism are developed.

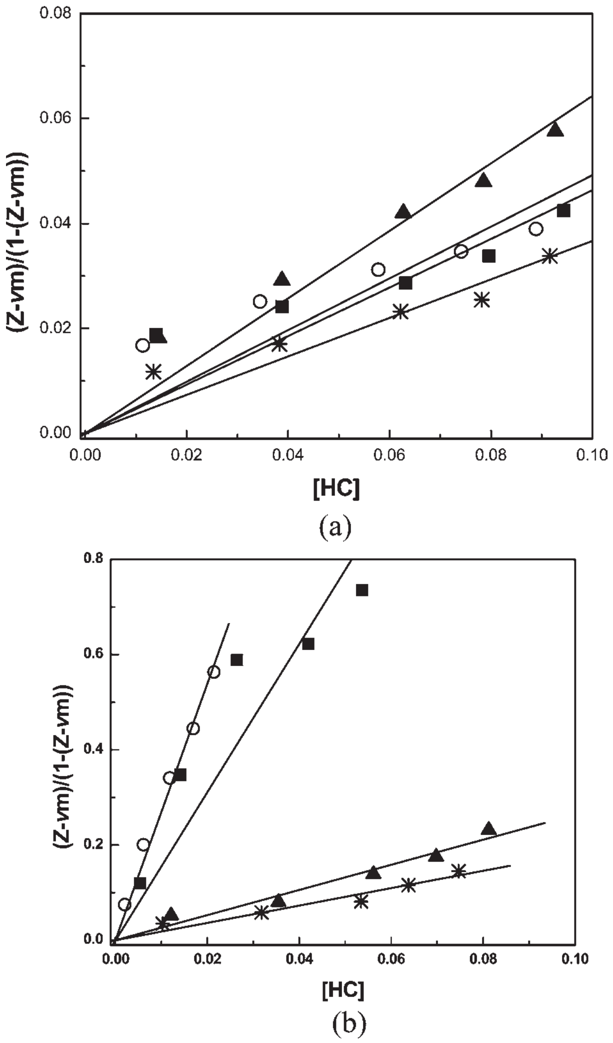

Figure 2. Equilibrium complexation constant (K_E) determination for extraction of NA at 298 ± 1 K with (a) TBP in decane-1-ol ($w = 0.36$) + cyclohexane ($w = 0.64$): ■, 0.183 mol·dm^{-3}; ○, 0.365 mol·dm^{-3} and in 4-methylpentan-2-one ($w = 0.63$) + kerosene ($w = 0.37$):▲, 0.183 mol·dm^{-3}; ∗, 0.365 mol·dm^{-3} and (b) TOA in decane-1-ol ($w = 0.36$) + cyclohexane ($w = 0.64$): ■, 0.115 mol·dm^{-3}; ○, 0.229 mol·dm^{-3} and in 4-methylpentan-2-one ($w = 0.63$) + kerosene ($w = 0.37$): ▲, 0.115 mol·dm^{-3}; ∗, 0.229 mol·dm^{-3}; —, linear fit lines.

The equilibrium free extractant concentration in the organic phase is given by eq 18.

$$\overline{[\mathrm{T}]} = \overline{[\mathrm{T}]}_{\mathrm{o}} - \overline{[(\mathrm{HC})(\mathrm{T})]} \qquad (18)$$

Substituting the value of $\overline{[\mathrm{T}]}$ from eq 18 into eq 17, eq 19 is derived.

$$K_{\mathrm{E}}[\mathrm{HC}] = \frac{\overline{[(\mathrm{HC})(\mathrm{T})]}}{\overline{[\mathrm{T}]}_{\mathrm{o}} - \overline{[(\mathrm{HC})(\mathrm{T})]}} \qquad (19)$$

In general the diluent alone also solvates some amount of solute (acid) from aqueous solution by physical extraction which is described in the previous section. The expression for $[\overline{(\mathrm{HC})}(\overline{\mathrm{T}})_p]$ is represented by eq 20.

$$\overline{[(\mathrm{HC})(\mathrm{T})]} = \overline{C}_{\mathrm{HC}} - \nu \overline{C}_{\mathrm{HC}}^{\mathrm{diluent}} \qquad (20)$$

Table 5. Values of Equilibrium Constants (K_E) with the Coefficient of Determination (R^2) and Standard Deviation (SD)

acids	extractants	$[\overline{T}]_o$ mol·dm^{-3}	diluent mixtures	K_E	R^2	SD
BA	TBP	0.183	decane-1-ol (w = 0.36) + cyclohexane (w = 0.64)	13.22 ± 2.80	0.92	0.008
		0.365		9.12 ± 1.84	0.94	0.005
		0.183	4-methylpentan-2-one (w = 0.63) + kerosene (w = 0.37)	17.85 ± 1.40	0.99	0.003
		0.365		5.37 ± 0.46	0.99	0.002
	TOA	0.115	decane-1-ol (w = 0.36) + cyclohexane (w = 0.64)	103.96 ± 4.61	0.98	0.004
		0.229		73.01 ± 4.09	0.97	0.003
		0.115	4-methylpentan-2-one (w = 0.63) + kerosene (w = 0.37)	75.84 ± 5.81	0.94	0.008
		0.229		50.38 ± 3.77	0.99	0.004
NA	TBP	0.183	decane-1-ol (w = 0.36) + cyclohexane (w = 0.64)	0.46 ± 0.05	0.97	0.007
		0.365		0.49 ± 0.06	0.99	0.008
		0.183	4-methylpentan-2-one (w = 0.63) + kerosene (w = 0.37)	0.64 ± 0.04	0.99	0.005
		0.365		0.37 ± 0.03	0.98	0.004
	TOA	0.115	decane-1-ol (w = 0.36) + cyclohexane (w = 0.64)	15.56 ± 1.64	0.94	0.122
		0.229		26.98 ± 0.83	0.99	0.025
		0.115	4-methylpentan-2-one (w = 0.63) + kerosene (w = 0.37)	2.64 ± 0.13	0.98	0.016
		0.229		1.82 ± 0.11	0.97	0.012

Therefore, eq 19 could be obtained by including the term for physical extraction as

$$K_E[HC] = \frac{\overline{[(HC)(T)]}}{[\overline{T}]_o - \overline{[(HC)(T)]}} = \frac{\overline{C}_{HC} - \nu \overline{C}_{HC}^{diluent}}{[\overline{T}]_o - (\overline{C}_{HC} - \nu \overline{C}_{HC}^{diluent})} = \frac{(Z - \nu m)}{1 - (Z - \nu m)} \tag{21}$$

m is the loading of acid in the organic phase by a diluent mixture.

$$m = \frac{\overline{C}_{HC}^{diluent}}{[\overline{T}]_o} \tag{22}$$

The plots of $[(Z - \nu m)/(1 - (Z - \nu m))]$ versus [HC] yield a straight line with a slope representing the corresponding K_E value of the reactive extraction [Figure 1a,b for BA; Figure 2a, b for NA]. The equilibrium complexation constants (K_E) predicted by the eq 21 are presented in Table 5 with the coefficient of determination (R^2) and standard deviation (SD). The model predicted values of K_E are showing a good correlation with $R^2 > 0.92$ and a maximum value of SD = 0.122. The maximum values of K_E are found to be 103.96 dm^3·mol^{-1} for BA and 26.98 dm^3·mol^{-1} for NA with TOA dissolved in decane-1-ol (w = 0.36) + cyclohexane (w = 0.64) diluent mixture. The solvation ability of the formed acid—extractant complexes at equilibrium are strongly affected by both polarity and ionizing strength of acid. This is in accordance with the lower K_E values for NA clarifying weaker interactive forces appear during NA—extractant complexation. BA is more sensitive to form complexes with the extractants (TBP and TOA) due to the easy solvation of BA molecules by the diluent mixtures, giving higher values of K_E. The highest values of K_E for both acids with TOA in the decane-1-ol (w = 0.36) + cyclohexane (w = 0.64) mixture also emphasize the fact that the extraction power of TOA/alcohol system is remarkably higher due to the simultaneous effect of physical extraction and chemical interaction of acid and extractant molecule through hydrogen bonding and ion pair formation. Hence, TOA in decane-1-ol (w = 0.36) + cyclohexane (w = 0.64) diluent mixture is the efficient and effective extractant—diluent system for the recovery of these two carboxylic acids from the aqueous solution. In the reactive extraction of BA and NA with TBP and TOA, the predicted values of K_D^{total} are found to be comparable with experimental values of K_D^{total} except for very low concentrations of acid. Minor errors in the experimental concentration of the aqueous phase may lead to a very high error in the experimental values of K_D ($\overline{C}_{HC}/C_{HC}$). Therefore, the experimental and predicted values of loading ratio ($Z = \overline{C}_{HC}/[\overline{T}]_o$) are found to be closer for both acids with TBP/TOA/diluent systems. The deviations between the predicted and the experimental values of K_D^{chem} indicate that the diluent mixture is not completely involved in the physical extraction.

■ CONCLUSIONS

The equilibrium reactive extraction of BA and NA is studied with two different extractants, TBP and TOA, dissolved in two different diluent mixtures at isothermal conditions (298 ± 1 K). The solvation ability of the formed acid—extractant complexes at equilibrium are strongly affected by both polarity and ionizing strength of acid. The study shows that the acid strength (pK_a) and hydrophobicity (log P) are responsible for the distribution of acid between the aqueous and the organic phase. The hydrophobicity of the BA makes it easily extractable by the extractant—diluent system and contributes to the higher values of extraction efficiency in terms of K_D and E. The values of Z (between 0.005 and 0.566) for the extraction of both acids using TBP and TOA in both diluent mixtures indicate a formation of (1:1) acid/extractant complex in the organic phase. The experimental results (K_D and E) and the values of K_E for the reactive extraction of BA and NA show that the decane-1-ol (w = 0.36) + cyclohexane (w = 0.64) is found to be a better diluent system with both extractants (TBP and TOA) as compared to

4-methylpentan-2-one ($w = 0.63$) + kerosene ($w = 0.37$). The maximum values of the K_D in the chemical extraction are found to be 38.025 for BA and 7.368 for NA with TOA (0.229 mol·dm^{-3}) in the decane-1-ol ($w = 0.36$) + cyclohexane ($w = 0.64$) diluent mixture.

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