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Reactive Extraction of iso-Nicotinic Acid with Trialkylamine in Different Diluents

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Distribution of iso-nicotinic acid (iNA) between water and trialkylamine (Alamine 336), dissolved in different diluents (1-octanol, tetrachloromethane, and kerosene), has been studied. The influence of the pH value of aqueous solutions, the Alamine 336 concentration, and diluents on distribution ratio (*D*) has been discussed. The extraction mechanism of Alamine 336 on iNA has been deduced according to the results of Fourier transformation infrared spectrometry. Results indicate that the diluents, the Alamine 336 concentration, the pH value of aqueous solutions, and the initial iNA concentration are the key factors that affect *D*. The polar diluent (1-octanol) is favorable for extracting iNA when Alamine 336 is used as extractant. *D* increases with the increasing Alamine 336 concentration and creates a higher *D* range vs the equilibrium aqueous pH range of 4.8 to 5.5. The proton-transfer reaction is demonstrated in the extraction process. An expression of equilibrium *D* was proposed, and the parameters of the apparent extraction equilibrium constants (*K*) and the complex ratio (*n*) (iNA vs Alamine 336) were calculated by fitting the experimental data. It was found that the *K* and *n* are 47.8 $(\text{mol}\cdot\text{dm}^{-3})^{-1/2}$ and 2:1 with 1-octanol as diluent and 4.72 $(\text{mol}\cdot\text{dm}^{-3})^{-2}$ and 1:2 with kerosene as diluent, respectively.

Introduction

The strong interaction between organic species and the extractant allows the formation of complexes and thus provides for a high equilibrium distribution coefficient, so reactive extraction has received increasing attention for the recovery of polar organic species from dilute aqueous solutions. Many organic acids and hydroxylbenzene compounds have been studied, for example, oxalic acid,[1] monocarboxylic acids,[2] phenol,[3] lactic,[4] *o*-dihydroxybenzene,[5] etc., but it was found that most studies on the organic species separated from aqueous solutions through reactive extraction are with only one Lewis functional group, Lewis acid (−OH, −COOH, $-SO_3H$) or Lewis base ($-NH_2$), for example, carboxylic acids, phenols, and organic amine solutions. Now many researchers are studying amphoteric functional groups, for example, *o*-aminophenol,[6] *meta*-aminophenol,[7] *p*-aminophenol,[8,9] amino acid,[10,11] etc.

Aliphatic tertiary amines are powerful extractants for acids, and the loss of the extractants is less in comparison to the physical extraction. According to the literature, this type of reactive extraction was used in the recovery of a single solute like phenol,[12] aniline,[13] and some carboxylic acids[14−16] successfully.

iso-Nicotinic acid (iNA) is a typical chemical with amphoteric functional groups, commonly used in the important production of chemical industry products. It is a key component in industrial effluent, which is not biodegradable and has serious toxic and contaminative effects. There is no known feasible processing method for removing iNA from such effluent. Thus, it is necessary to adopt a reactive extraction method to recover the organic species from the effluent to reduce pollution. Since iNA has both a Lewis functional group (−COOH) and a Lewis base functional group (−N), it can be extracted from an aqueous phase into an organic phase with a Lewis base extractant (amines and neutral phosphorus-bonded, oxygen-bearing extractants) and a Lewis acidic extractant (acidic phosphorus-bonded, oxygen-bearing extractants).

Senol[17] investigated extraction equilibria of nicotinic acid using Alamine 336 and conventional solvents. The results showed that conventional solvents are not suitable separation agents for nicotinic acid, yielding $D_0 < 1$, and there is the highest synergistic extraction efficiency in the amine/cyclic alcohol system. Chemodel presumes mainly the formation of two acid−amine aggregated structures of type (1,2) and (2,3) for cyclopentanol, (1,1) and (2,3) for MIBK, (1,1) for 1,2-DCE, and (1,2) and (1,9) for *n*-heptane. Later, he[18] took the same action to research extraction equilibria of nicotinic acid using Alamine 300/diluent and conventional solvent systems. A modified Langmuir equilibrium model and a chemodel approach comprising one or two acid−amine complex formations were taken using versions of the mass action law.

In spite of good results and further advances, the research on iNA has not been studied systematically, so in this work, iNA was selected as the species to be extracted, and Alamine 336 was studied for its ability to extract iNA. 1-Octanol, tetrachloromethane, and kerosene were also investigated for their ability to affect the extraction power of the extractants over a wide pH range. IR spectroscopic analysis of the organic phase loaded with iNA acid was investigated too.

Experimental

Chemicals. iNA, analytical grade with a purity of > 99 %, was furnished by Sinopharm Chemical Reagent Co., Ltd. 2-Ethyl hexylphosphic mono-2-ethyl-hexylester (P507), tributyl phosphate (TBP), and trialkylamine (Alamine 336) were obtained

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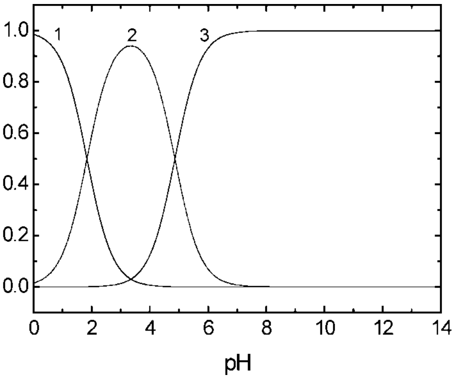

Figure 1. Molar fractions of various iNA species vs pH. 1, the charged cations (H_2^+A); 2, neutral iNA (HA); 3, the anions (A^-).

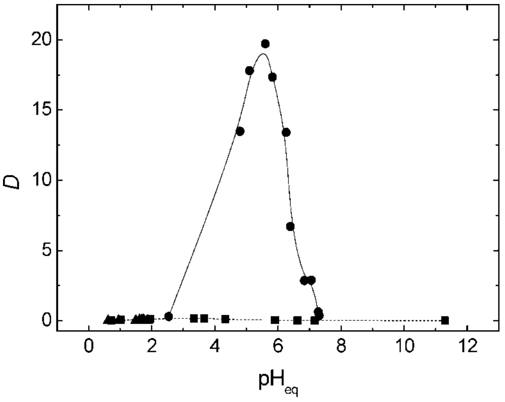

Figure 2. *D* values of various extractants in 1-octanol. ■, 20 % TBP; ●, 20 % Alamine 336; ▲, 20 % P507; and lines, represent correlation results.

Table 1. Equilibrium Data of iNA between Water and Alamine 336/1-Octanol

init conc of Alamine 336		total equil conc of iNA/mg·dm^{-3}		
mol·dm^{-3}	init/equil pH in aq phase	in aq phase	in org phase	*D*
0	1.14/1.13	250	0	0
0	1.89/1.74	246.3	3.7	0.0149
0	3.35/3.31	233.7	16.3	0.0698
0	3.66/3.66	234.7	15.3	0.0652
0	4.47/4.64	245.5	4.5	0.0184
0	5.98/6.09	250	0	0
0.01033	1.11/1.15	250	0	0
0.01033	1.72/1.83	245.1	4.9	0.0199
0.01033	2.00/2.32	231.6	18.4	0.0793
0.01033	3.06/4.38	63.1	186.9	2.9604
0.01033	3.99/4.99	54.5	195.5	3.5867
0.01033	5.00/6.16	154.5	95.5	0.6184
0.01033	6.06/7.02	235.4	14.6	0.0618
0.01033	10.03/7.44	250	0	0
0.04132	1.15/1.23	250	0	0
0.04132	1.50/1.89	247.8	2.2	0.0087
0.04132	1.93/4.16	70.4	179.6	2.5508
0.04132	2.93/5.29	23.3	226.7	9.7299
0.04132	3.99/6.08	56.5	193.5	3.4216
0.04132	5.02/6.82	160.0	90.0	0.5622
0.04132	6.03/6.90	236.8	23.2	0.0559
0.04132	9.63/7.37	250	0	0
0.04132	10.95/9.48	250	0	0
0.2066	1.02/1.46	247.3	2.7	0.0110
0.2066	1.42/4.48	29.4	220.6	7.5123
0.2066	1.93/5.40	12.2	237.8	19.5594
0.2066	2.99/6.27	30.3	219.7	7.2533
0.2066	5.00/6.93	154.5	95.5	0.6181
0.2066	8.98/7.72	228.2	21.8	0.0955
0.2066	10.49/8.03	240.9	9.1	0.0376
0.2066	11.04/8.72	250	0	0
0.4132	0.97/2.54	193.4	56.6	0.2929
0.4132	1.11/4.80	17.3	232.7	13.4806
0.4132	1.14/5.10	13.3	236.7	17.7937
0.4132	1.38/5.60	12.1	237.9	19.7179
0.4132	1.73/5.83	13.6	236.4	17.3330
0.4132	1.95/6.26	17.4	232.6	13.4030
0.4132	2.38/6.40	32.5	217.5	6.6978
0.4132	3.70/6.84	64.9	185.1	2.8501
0.4132	6.67/7.28	154.8	95.2	0.6149
0.4132	7.48/7.31	185.5	64.5	0.3474
0.8264	0.53/0.72	242.0	8.0	0.0331
0.8264	0.82/4.49	15.5	234.5	15.0838
0.8264	1.00/4.88	12.7	237.3	18.7429
0.8264	1.20/5.22	11.6	238.4	20.6026
0.8264	1.46/5.64	10.0	240.0	24.0291
0.8264	1.92/5.85	15.3	234.7	15.3002
0.8264	2.53/6.40	28.4	221.6	7.8151
0.8264	3.66/6.83	53.2	196.8	3.6956
0.8264	6.73/7.41	212.4	37.6	0.1769
0.8264	9.42/7.50	213.9	36.1	0.1688
0.8264	11.33/8.48	250	0	0

from Dalian Chemical Reagent Plant with a purity of > 99 %. 1-Octanol and tetrachloromethane, analytical grade, were purchased from Tianjin Kermel Chemical Reagent Co., Ltd.

Alamine 336, a C_8–C_{10} saturated straight-chain tertiary amine mixture, is a pale yellow liquid practically insoluble in water < 5 mg·dm^{-3} with an average molecular weight of 392 g·mol^{-1} and a density of 0.81 kg·dm^{-3} (25 °C) and a viscosity of 0.11 Pa·s.

Kerosene, a mixture (C_{10}–C_{16}) of alkyl (68.4 %), naphthenic hydrocarbon (22.1 %), aromatic hydrocarbon (6.3 %), and alkene (3.2 %), is obtained from a local chemical plant. Before being used in experiment, it was washed with H_2SO_4 (98 %) (V_{H2SO4}:$V_{kerosene}$ = 1:5) until the bottom became achromatism transparent. It was then washed with distilled water several times until the aqueous layer became neutral. The final product's density is about 0.78 g·cm^{-3}, and its content of arene is less than 10 %.

All of the other reagents were used with analytical grade and water was of high purity.

Experimental Procedure. All extraction experiments were performed with 100 cm^3 flasks at 25 °C. The equal volumes (20 cm^3) of initial aqueous (250 mg·dm^{-3} iNA solution) and organic phases (about 0.01, 0.04, 0.20, 0.40, 0.60, and 0.80 mol·dm^{-3} Alamine 336 in 1-octanol or kerosene) were agitated for 2 h in a constant temperature water bath–vibrator (SHZ-B, Shanghai Yuejin Medical Instruments Factory) at 200 rpm and then left to settle for 5 h at fixed temperature (25 °C) and pressure (101.3 kPa). Before the organic phase was added, the aqueous-phase pH, which was measured by a HI1200B composite electrode with a pH meter (pH211 Microprocessor pH meter, HANNA, Italy), was adjusted with saturated NaOH solution and diluent H_2SO_4 solution. After separation, the same method was used to measure aqueous-phase pH. It was then adjusted to pH of 3.4 ± 0.1. It was finally analyzed at 261 nm (the maximum adsorption wavelength of iNA) with a UV spectrometer (LabTech Bluestar, Beijing Labtech, Ltd.). The interest concentrations in organic phases were calculated by material balance. The deviation of this method was less than 3 %.

For recording Fourier transformation infrared spectra, the organic phases were centrifugated under 4000 rpm for 30 min to eliminate water completely and the IR spectra were recorded on an AVATAR 30 Fourier transformation infrared spectrometer (Nicolet, America) by injecting the organic phase into the sample cell with a thickness of 0.05 mm between two CaF_2 plates.

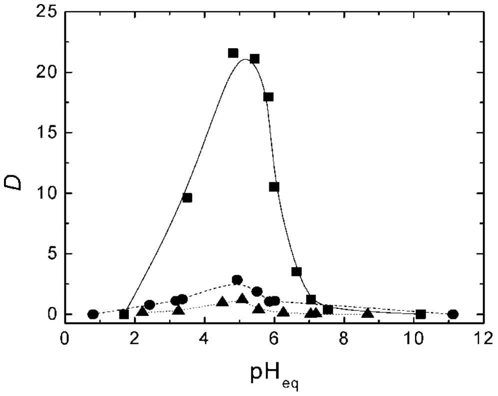

Figure 3. *D* values of 30 % Alamine 336 in various diluents. ■, 1-Octanol; ●, Tetrachloromethane; ▲, Kerosene; and lines, represent correlation results.

Results and Discussion

Existing Forms of iNA. iNA has a Lewis acid group (−COOH) and a Lewis base group (−N−), with Lewis acid−base character. There are three forms in aqueous solution: the charged cations (H_2^+A), neutral iNA (HA), and the anions (A^-). Two dissociation balances exist in aqueous solution as follows

$$H_2^+A \xleftrightarrow{K_{a1}} HA + H^+$$

$$HA \xleftrightarrow{K_{a2}} A^- + H^+$$

where the dissociation balance constants are

$$K_{a1} = \frac{[HA][H^+]}{[H_2^+A]} \tag{1}$$

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

and pK_{a1} and pK_{a2} are 1.84 and 4.86,[19] respectively.

The effect of the aqueous pH on molar fractions of various iNA is shown in Figure 1. Apparently, the cation iNA exists at lower pH (pH < pK_{a1}), while the anion appears at higher pH (pH > pK_{a2}) and neutral iNA dominates at an intermediate pH (pK_{a1} < pH < pK_{a2}). The extraction behavior is distinct at different pH.

Effect of Extractants. iNA is extracted by Alamine 336, TBP, and P507 in 1-octanol (20 % in volume fraction), respectively, over a long-range pH. The various *D* vs equilibrium aqueous pH (pH_{eq}) were shown in Figure 2. It demonstrated that, compared with unsatisfactory results of TBP and P507, the *D* values are far higher when Alamine 336 was used as extractants.

Effect of Diluents. 30 % Alamine 336 in 1-octanol, kerosene, and tetrachloromethane (in volume fraction) were used to investigate the effect of diluents on *D*. Figure 3 shows the *D* values vs pH_{eq} at the same Alamine 336 concentration in various diluents. As can be seen from Figure 3, *D* values increased in the order 1-octanol > tetrachloromethane > kerosene, which is similar to the order of the diluents' polarity. Alamine 336 reacted with iNA forming an ion-pair complex which has certain polarity. Generally, the stronger the polarity of the diluents is, the stronger its solubility vs the complexes. As 1-octanol can provide more favorable soluble conditions for the complexes, a higher *D* was demonstrated.

Table 2. Equilibrium Data of iNA between Water and Alamine 336/Kerosene

init conc of Alamine 336		total equil conc of iNA/mg·dm^{-3}		
mol·dm^{-3}	init/equil pH in aq phase	in aq phase	in org phase	*D*
0	0.92/0.90	250	0	0
0	1.90/1.20	250	0	0
0	2.02/2.01	250	0	0
0	3.36/3.34	250	0	0
0	3.65/3.64	250	0	0
0	4.52/4.49	250	0	0
0	5.96/5.94	250	0	0
0	6.29/6.34	250	0	0
0	7.04/7.00	250	0	0
0	11.02/11.00	250	0	0
0.1033	1.22/1.55	250	0	0
0.1033	1.98/2.54	250	0	0
0.1033	3.05/4.42	244.8	5.2	0.0211
0.1033	4.21/4.88	242.5	7.5	0.0311
0.1033	5.09/5.47	250	0	0
0.1033	6.00/6.12	250	0	0
0.1023	9.98/6.61	250	0	0
0.1033	11.28/8.53	250	0	0
0.2066	0.82/1.11	250	0	0
0.2066	1.11/1.71	249.5	0.5	0.0018
0.2066	2.04/3.81	225.1	24.9	0.1108
0.2066	3.37/5.16	234.5	16.5	0.0662
0.2066	3.72/5.23	235.5	15.5	0.0618
0.2066	4.51/5.40	244.2	5.8	0.0239
0.2066	5.98/6.32	250	0	0
0.2066	8.16/6.51	250	0	0
0.2066	10.21/6.68	250	0	0
0.2066	11.38/9.09	250	0	0
0.4132	0.82/1.72	250	0	0
0.4132	1.11/2.15	246.1	3.9	0.0156
0.4132	1.15/2.4	238.8	11.2	0.0471
0.4132	1.23/2.5	240.0	10.0	0.0594
0.4132	1.98/4.89	155.4	94.6	0.6088
0.4132	2.44/5.05	184.0	66.0	0.3585
0.4132	3.69/5.67	225.5	24.5	0.1086
0.4132	6.67/6.80	250	0	0
0.4132	9.08/6.90	250	0	0
0.4132	11.21/7.43	250	0	0
0.6198	0.72/2.22	217.2	32.8	0.1510
0.6198	1.13/3.25	199.9	50.1	0.2506
0.6198	1.53/4.51	128.5	121.5	0.9450
0.6198	1.98/5.08	113.2	136.8	1.2088
0.6198	2.52/5.55	181.5	168.5	0.3777
0.6198	3.58/6.26	226.5	23.5	0.1036
0.6198	6.48/7.04	245.9	4.1	0.0167
0.6198	9.86/7.19	249.5	0.5	0.0020
0.6198	11.38/8.68	250.0	0	0

Effect of pH. The Alamine 336 molecule is a Lewis alkali and can receive a proton. As such, it can react with the cationic and neutral forms of iNA to produce the complex that is extracted into the organic phase. Because the molar fractions of neutral and positive ions of iNA acid are a function of pH, *D* greatly depends on the pH of the aqueous phase. As is indicated by the data given in Tables 1 and 2 and Figures 4 and 5, *D* increases with a sharp increase and then decreases in pH_{eq} at the same concentration of Alamine 336, and there is a peak value when the pH_{eq} value is around 4.8 to 5.5.

Generally, Alamine 336 can react with iNA through proton transfer. *D* is lower when pH_{eq} is lower (1 to 4), and the key is that Alamine 336 and iNA acid will be all protonated, which will hamper combination of Alamine 336 and iNA. However, *D* will increase when pH_{eq} is higher (4.8 to 5.5) and there is proton transfer between Alamine 336 and iNA, so the maximum *D* will occur with the increase of pH_{eq}. While pH_{eq} increases continuously, the anionic form appears, and there is little reaction between Alamine 336 and anionic iNA, so *D* decreases.

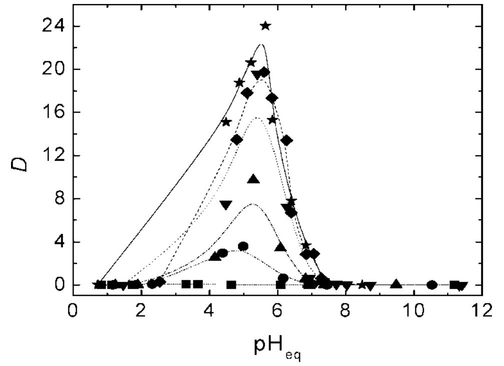

Figure 4. *D* vs pH in various concentrations of Alamine 336/1-octanol (in mol·dm^{-3}). ■, 0; ●, 0.01033; ▲, 0.04132; ▼, 0.2066; ◆, 0.4132; ★, 0.8264; and lines, represent correlation results.

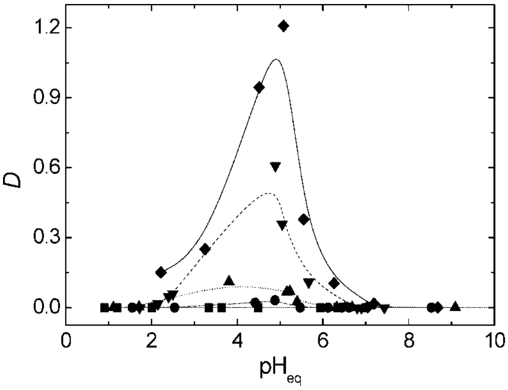

Figure 5. *D* vs pH in various concentrations of Alamine 336/kerosene (in mol·dm^{-3}). ■, 0; ●, 0.01033; ▲, 0.2066; ▼, 0.4132; ◆, 0.6198; and lines, represent correlation results.

Effect of Extractant Concentration. Alamine 336 concentration has a strong effect on the equilibrium distribution of acid as shown in Figures 4 and 5. iNA is extracted into the organic phase effectively at higher Alamine 336 concentration. *D* increases as the extractant concentration increases, which likely results from the extraction equilibrium moving toward the direction of forming an extraction complex. It is also indicated in Figures 4 and 5 and Tables 1 and 2 that *D* is affected by the concentration of extractant more greatly in the Alamine 336/1-octanol system than in the Alamine 336/kerosene system at the same concentration of Alamine 336, and its cause is related to the effect of diluents (see the Effect of Diluents). Therefore, an optimal Alamine 336 concentration should be considered with an active diluent in use.

Effect of the Initial iNA Acid Concentration. When the initial iNA concentrations are (0.4061, 0.8122, 2.031, 4.062·10^{-3}, and 0.4132) mol·dm^{-3}, Alamine 336 dissolved in the 1-octanol and the kerosene, and the experiment equilibrium is performed. The initial iNA concentration is the key factor in the extraction process as shown in Figures 6 and 7: *D* increases with the increase of the given initial iNA concentration. As a result, the initial iNA acid concentration must be considered in the extraction process before using extraction technology.

Infrared Spectra of the Loading Organic Phases. To investigate the interaction between Alamine 336 and iNA in organic phases, IR spectra of the loading organic phase were studied by the FT-IR spectra, as well as original organic phase, Alamine 336, diluents (1-octanol and kerosene), and iNA. Figures 8 and 9 demonstrate the infrared spectra of the 30 % Alamine 336/1-octanol phase and 30 % Alamine 336/kerosene phase, respectively.

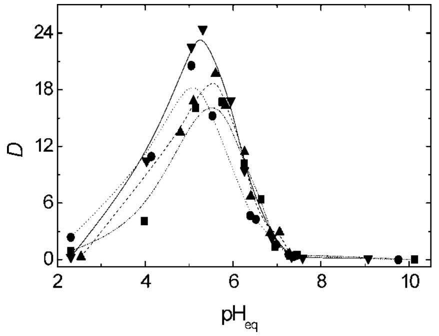

Figure 6. Effect of initial iNA concentration on *D* with 0.4132 mol·dm^{-3} Alamine 336/1-octanol. Concentration of iNA (·10^{-4} mol·dm^{-3}): ■, 4.061; ●, 8.122; ▲, 20.31; ▼, 40.62; and lines, represent correlation results.

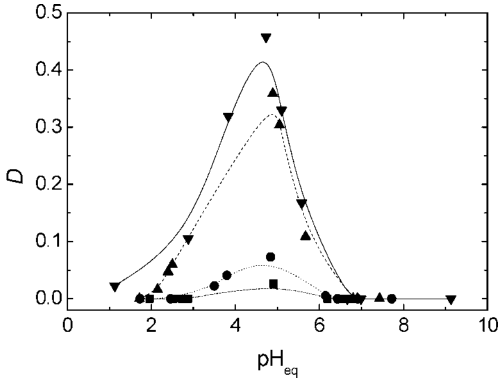

Figure 7. Effect of initial iNA concentration on *D* with 0.4132 mol·dm^{-3} Alamine 336/kerosene. Concentration of iNA (·10^{-4} mol·dm^{-3}): ■, 4.061; ●, 8.122; ▲, 20.31; ▼, 40.62; and lines, represent correlation results.

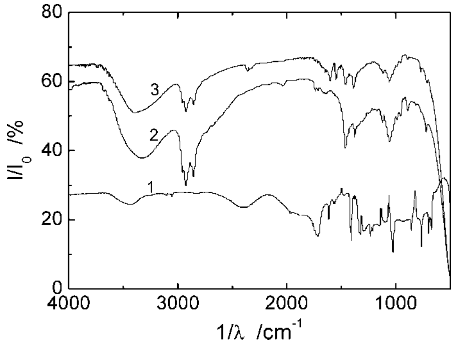

Figure 8. IR spectra of 1, iNA; 2, Alamine 336/1-octanol; and 3, iNA + Alamine336/1-octanol (pH$_{eq}$ = 5.14).

As shown in Figure 8, the band at 1717 cm^{-1} in iNA, the characteristic C═O stretching vibration absorption disappeared in iNA + Alamine 336/1-octanol, while the two bands at (1603 and 1549) cm^{-1}, which are attributed to characteristics of the asymmetry and symmetry stretching of COO^{-}, appeared. These results indicate that the ion-pair complex of iNA and Alamine 336 has been formed when 1-octanol was used as diluent; in other words, the extraction reaction is a proton-transfer reaction.

As shown in Figure 8, the C═O stretching vibration absorption disappeared in iNA + Alamine 336/kerosene. The difference is that only a band at 1604 cm^{-1} (asymmetry stretching of COO^{-}) appeared, which may be attributed to the lower loadings of iNA. Even so, it still suggested that the extraction reaction is also a proton-transfer reaction when kerosene was used as diluent.

According to the discussions above, it is obvious that a proton-transfer reaction was demonstrated between Alamine 336 and iNA without reference to 1-octanol or kerosene as diluent.

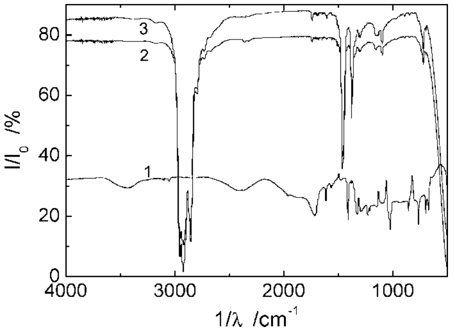

Figure 9. IR spectra of 1, iNA; 2, Alamine 336/kerosene; and 3, iNA + Alamine 336/kerosene ($\mathrm{pH_{eq}} = 4.88$).

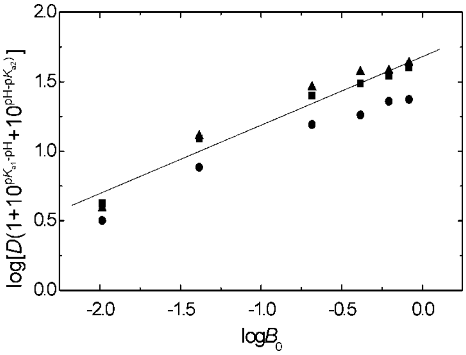

Figure 10. Relation between $\log[D(1 + 10^{\mathrm{p}K_{\mathrm{a1}}-\mathrm{pH}} + 10^{\mathrm{pH}-\mathrm{p}K_{\mathrm{a2}}})]$ and $\log B_0$ in Alamine 336/1-octanol. $\mathrm{pH_{eq}}$: ■, 4.83; ●, 4.52; ▲, 5.64; and —, linear fitting curve: $\log[D(1 + 10^{\mathrm{p}K_{\mathrm{a1}}-\mathrm{pH}} + 10^{\mathrm{pH}-\mathrm{p}K_{\mathrm{a2}}})] = 1.68 + 0.491 \log B_0$.

Description of Extraction Equilibrium. Equilibrium was governed by the mass action law,[20] and diluents' physical extraction was also taken into account in the equilibrium. It was also under the following assumptions: the systems were diluent solutions; the activities of the interest and the complexation are proportional to their concentrations; an iNA molecule (HA) reacts with n Alamine 336 (R_3N) molecules to form (1, n) complexes; reactive extraction and physical extraction accord with the simple addition. Thereinto:

Equilibrium of chemical reaction between iNA and Alamine 336

$$\mathrm{HA} + n\overline{\mathrm{R_3N}} \overset{K}{\leftrightarrow} \overline{(\mathrm{R_3N})_n\mathrm{H^+}\cdot\mathrm{A^-}}$$

Equilibrium of physical extraction of diluents

$$\mathrm{HA} \overset{m}{\leftrightarrow} \overline{\mathrm{HA}}$$

with the equilibrium constants

$$K = \frac{[\overline{(\mathrm{R_3N})_n\mathrm{H^+}\cdot\mathrm{A^-}}]}{[\mathrm{HA}]\cdot[\overline{\mathrm{R_3N}}]^n} \tag{3}$$

$$m = \frac{[\overline{\mathrm{HA}}]}{[\mathrm{HA}]} \tag{4}$$

where the overbar denotes species in the organic phase (ignoring dissolution of Alamine 336 in the water). So, the distribution coefficient, D, can be written as

$$D = \frac{\overline{[(\mathrm{R_3N})_n\mathrm{H^+}\cdot\mathrm{A^-}]} + [\overline{\mathrm{HA}}]}{[\mathrm{H_2}^+\mathrm{A}] + [\mathrm{HA}] + [\mathrm{A^-}]} = \frac{K[\overline{\mathrm{R_3N}}]^n}{1 + 10^{\mathrm{p}K_{\mathrm{a1}}-\mathrm{pH}} + 10^{\mathrm{pH}-\mathrm{p}K_{\mathrm{a2}}}} + \frac{vm}{1 + 10^{\mathrm{p}K_{\mathrm{a1}}-\mathrm{pH}} + 10^{\mathrm{pH}-\mathrm{p}K_{\mathrm{a2}}}} \tag{5}$$

where pH denotes the pH value in the aqueous phase under the equilibrium condition; K denotes the apparent extraction equilibrium constant; m denotes the equilibrium constant of physical extraction of diluents; and v is the volume fraction of diluents in organic phase.

Since the $m_{\max}$ of kerosene and 1-octanol are about 0 and 0.070, respectively, they can be neglected. In addition, suppose the initial concentration of Alamine 336 is B_0, which is far higher that that of iNA, and we can think that the concentration of Alamine 336 is of no change before and after extraction. So, eq 5 can be revised as follows

$$D = \frac{KB_0{}^n}{1 + 10^{\mathrm{p}K_{\mathrm{a1}}-\mathrm{pH}} + 10^{\mathrm{pH}-\mathrm{p}K_{\mathrm{a2}}}} \tag{6}$$

If logarithm is adopted by eq 6, it was deduced that

$$\log D = \log K + n \log B_0 - \log(1 + 10^{\mathrm{p}K_{\mathrm{a1}}-\mathrm{pH}} + 10^{\mathrm{pH}-\mathrm{p}K_{\mathrm{a2}}}) \tag{7}$$

So

$$\log[D(1 + 10^{\mathrm{p}K_{\mathrm{a1}}-\mathrm{pH}} + 10^{\mathrm{pH}-\mathrm{p}K_{\mathrm{a2}}})] = \log K + n \log B_0 \tag{8}$$

On the basis of D values and pH values of different concentrations of Alamine 336, K and n were then calculated. The relationships between $\log[D(1 + 10^{\mathrm{p}K\mathrm{a1}-\mathrm{pH}} + 10^{\mathrm{pH}-\mathrm{p}K\mathrm{a2}})]$ and $\log B_0$ at three different $\mathrm{pH_{eq}}$ in Alamine 336/1-octanol and Alamine 336/kerosene were demonstrated in Figures 10 and 11. Figure 10 shows that the linear slope n is 0.491 ($n = 0.5$, approximately) and that the intercept $\log K$ is 1.68 with the correlation coefficient $r = 0.9855$ in Alamine 336/1-octanol, while Figure 11 demonstrates n is 1.92 ($n = 2$, approximately) and $\log K$ is 0.674 with $r = 0.9834$ in Alamine 336/kerosene. These results suggested that (2, 1) and (1, 2) complexes were formed in Alamine 336/1-octanol and Alamine 336/kerosene, respectively. In addition, taking into account 20 % deviation, K was calculated to be 47.8 $(\mathrm{mol\cdot dm^{-3}})^{-1/2}$ in Alamine 336/1-octanol and 4.72 $(\mathrm{mol\cdot dm^{-3}})^{-2}$ in Alamine 336/kerosene.

According to the K and n obtained above, eq 6 could be denoted by the following.

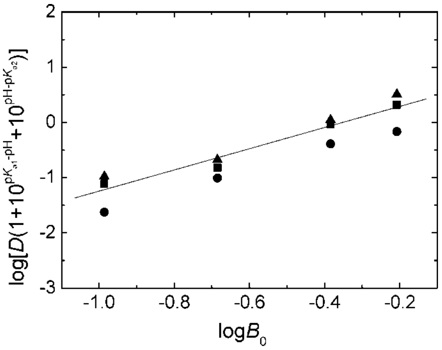

Figure 11. Relation between $\log[D(1 + 10^{\mathrm{p}K_{\mathrm{a1}}-\mathrm{pH}} + 10^{\mathrm{pH}-\mathrm{p}K_{\mathrm{a2}}})]$ and $\log B_0$ in Alamine 336/kerosene. $\mathrm{pH_{eq}}$: ■, 3.89; ●, 4.84; ▲, 5.34; and —, linear fitting curve: $\log[D(1 + 10^{\mathrm{p}K_{\mathrm{a1}}-\mathrm{pH}} + 10^{\mathrm{pH}-\mathrm{p}K_{\mathrm{a2}}})] = 0.674 + 1.92 \log B_0$.

For the Alamine 336/1-octanol system

$$D = \frac{47.8 B_0^{0.5}}{1 + 10^{\mathrm{p}K_{\mathrm{a1}} - \mathrm{pH}} + 10^{\mathrm{pH} - \mathrm{p}K_{\mathrm{a2}}}} \qquad (9)$$

For the Alamine 336/kerosene system

$$D = \frac{4.72 B_0^{2}}{1 + 10^{\mathrm{p}K_{\mathrm{a1}} - \mathrm{pH}} + 10^{\mathrm{pH} - \mathrm{p}K_{\mathrm{a2}}}} \qquad (10)$$

Thus, eqs 9 and 10 can be used to predict D of extraction equilibrium when Alamine 336 was used for extracting iNA.

Conclusions

In the present work, distribution of iNA between water and Alamine 336 dissolved in 1-octanol and kerosene has been studied in detail. It was found that the diluents, the Alamine 336 concentration, the pH of aqueous solutions, and the initial iNA concentration are the key factors that affect D. The polar diluent 1-octanol is favorable for extracting iNA when Alamine 336 is used as extractant. The proton-transfer reaction between Alamine 336 and iNA was deduced from Fourier transformation infrared spectra analysis. An expression of equilibrium D was proposed to evaluate the extraction efficiency of Alamine 336 vs iNA when 1-octanol and kerosene were selected as diluents.

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