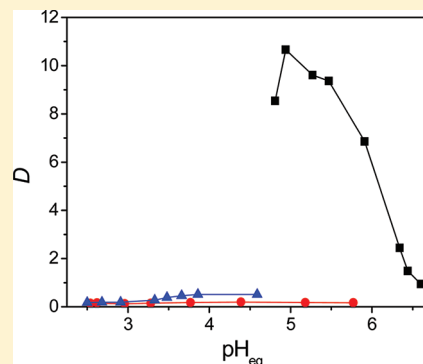


Extraction Equilibria of Picolinic Acid with Trialkylamine/*n*-Octanol

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ABSTRACT: The extraction equilibrium of picolinic acid using trialkylamine (N235) dissolved in *n*-octanol at 298 ± 0.5 K has been studied. The factors that affected distribution coefficients (D), such as aqueous equilibrium pH (pH_{eq}), N235 concentration, and diluents, were investigated. As diluents, *n*-octanol showed higher D values than those of tetrachloromethane and kerosene. The maximum D values appeared at a N235 concentration of $0.4218 \text{ mol}\cdot\text{L}^{-1}$, which were in agreement with the results of the apparent alkalinity of N235/*n*-octanol. The D values were also observed with peak values at pH_{eq} in the range of 4.5–6.0. In addition, D decreased with the increase of the initial picolinic acid concentration. Fourier transform infrared spectrometry confirmed that pH_{eq} had no influence on the complexes' structure and the extraction reaction belonged to the proton-transfer process. The expression of D was proposed based on the mass action law with reasonable assumptions, and the model parameters were calculated by fitting the experimental data. The D values obtained by the model were in good agreement with the experimental ones.



INTRODUCTION

Picolinic acid (pyridine-2-carboxylic acid), which can be used to produce mepivacaine, is an important intermediate for organic synthesis.¹ Picolinic acid is also commonly used as a ligand with metal for wastewater treatment, i.e., Lee² reported that the increase of picolinic acid concentration could enhance the removal of copper(II)–picolinic acid complexes by active carbon fibers. Every year, large amounts of wastewaters containing picolinic acid are discharged into rivers and leads to serious environmental pollution. Picolinic acid in these kinds of wastewaters has high recyclable values. However, the recovery, especially the separation, of picolinic acid has been rarely reported.

Reactive extraction, which is based upon the reversible reaction of the specific functional groups of solute and extractant, is an effective separation technique for organic compounds with high selectivity. It has received increasing attention for recoveries of polar organics from their dilute solutions.^{3–7} Long-chain aliphatic tertiary amines dissolved in suitable diluents have been considered as efficient extractants for the recoveries of carboxylic acids. Picolinic acid is a typical carboxylic acid compound, thus it is thought desirable to be extracted by amine extractants.

Recently, researchers have performed detailed experimental studies on the extractions of the isomers of picolinic acid like nicotinic acid (pyridine-3-carboxylic acid) and iso-nicotinic acid (pyridine-4-carboxylic acid) with various extractants and gained a series of encouraging results. Senol^{8,9} investigated the extraction equilibria of nicotinic acid using Alamine 336 (or 300) in various conventional diluents (proton donating and accepting, polar and nonpolar diluents). The results showed that conventional solvents were not suitable separation agents for nicotinic acid, yielding $D_0 \leq 1$, and there was synergistic

extraction efficiency in the amine/cyclic alcohol (such as cyclopentyl alcohol and methyl cyclohexanol) systems. Kumar^{10,11} aimed to intensify the recovery of nicotinic acid using reactive extraction with trin-octylphosphine oxide (TOPO) or tri-*n*-butylphosphate (TBP) in different diluents. His work provided lots of equilibrium data for separating nicotinic acid. Caşcaval¹² carried out a comparative study on reactive extraction of nicotinic acid using lauryl-trialkylmethylamine (Amberlite LA-2) and di(2-ethylhexyl)phosphoric acid (D2EHPA) and found that Amberlite LA-2 allowed the possibility to reach a higher extraction efficiency compared with D2EHPA. Li¹³ discussed the distribution of iso-nicotinic acid between water and Alamine 336 dissolved in *n*-octanol and kerosene. By infrared spectrometry analysis, he deduced the interaction between Alamine 336 and iso-nicotinic acid was a proton-transfer process and calculated the apparent extraction equilibrium constants and complexation ratios.

The distribution behavior of picolinic acid between water and Alamine 336 dissolved in various diluents has been studied by Senol.¹⁴ It was reported that the distribution degree of picolinic acid in pure diluent was very low ($D_0 \leq 1$) and the amine/alcohol always possessed a synergistic extraction effect. However, the effects of the aqueous solutions' pH, amine concentration, and interaction mechanism of the amine extractant with picolinic acid have not been completely discussed. Herein, systematic works on the extraction of picolinic acid with a kind of amine extractant N235 dissolved in *n*-octanol were performed. The influences of aqueous equilibrium pH (pH_{eq}), N235 concentration, and initial

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concentration of picolinic acid on distribution coefficients (D) were discussed. The organic phases loading picolinic acid were characterized by infrared spectroscopy to investigate the interaction mechanism between N235 and picolinic acid. Furthermore, an expression of D , used for estimating extraction efficiency, was proposed and the related model parameters were calculated.

EXPERIMENTAL SECTION

Materials. Trialkylamine (N235), a kind of C_8 – C_{10} saturated straight-chain tertiary amine mixture, was obtained from Rongcheng Petrochemical Plant (Shandong, China). It is a pale yellow liquid practically insoluble in water ($<10 \text{ mg}\cdot\text{L}^{-1}$) with an average molecular weight of $387 \text{ g}\cdot\text{mol}^{-1}$, a density of $0.816 \text{ kg}\cdot\text{dm}^{-3}$ ($25 \text{ }^\circ\text{C}$), and a viscosity of $10.4 \text{ mPa}\cdot\text{s}$ ($25 \text{ }^\circ\text{C}$). It was washed with high-purity water four times before use.

n-Octanol, analytical grade, was purchased from Tianjin Kermel Chemical Reagent Co., Ltd. and was used after being saturated with high-purity water. Kerosene was furnished by a local chemical plant and was pretreated as in ref 13.

Picolinic acid, chemical grade, was purchased from J&K Scientific Ltd. All of the other reagents used were analytical grade, and the water was of high purity.

Experimental Procedure. All extraction experiments were performed by shaking equal volumes (20 mL) and known concentrations of aqueous and organic phases, placed in 100 mL flasks, for 2 h in a SHZ-B constant temperature water bath-vibrator (Shanghai Yuejin Medical Instruments Factory) at 200 rpm, followed by settling of the mixture for 5 h at a fixed temperature ($298 \pm 0.5 \text{ K}$) and pressure (101.3 kPa). Picolinic acid with an initial concentration of $2.031 \text{ mmol}\cdot\text{L}^{-1}$ was used, except the experiments in the part which discussed the effect of the initial concentration of picolinic acid. The aqueous pH_{eq} was measured by a HI1200B composite with a pH 211 m (HANNA, Italy). To obtain different pH_{eq} values, the initial pH of the aqueous solution was adjusted with a saturated NaOH solution and diluent H_2SO_4 solution to the desired pH. After separation, the aqueous solution was adjusted to a pH of 2.0 ± 0.05 and then analyzed at 265 nm (the maximum adsorption wavelength of picolinic acid) with a UV spectrometer (LabTech Bluestar, Beijing Labtech, Ltd.). The concentration of picolinic acid in the aqueous solution was calculated by the equation $c = (A - 0.0283)/7140.5$ (correlation coefficient, 0.9992; linear scope, $0.2\text{--}3.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$), where c represented the concentration of picolinic acid in aqueous solution and A was the absorbance of the final aqueous solution. The loading of picolinic acid in the organic phase was calculated by mass balance. The deviation of this method was less than 3 %.

Infrared (IR) spectra were collected on an AVATAR 30 Fourier transform infrared spectrometer (Nicolet, America). In order to obtain good spectra, organic phases were centrifuged at 4000 rpm for 30 min to completely eliminate water before the IR spectra collection.

RESULTS AND DISCUSSION

Because of high viscosity, N235 was usually used diluted with diluents. A good diluent should not only improve the extraction operation process but also increase the extraction capacity. Figure 1 shows a D of $2.031 \text{ mmol}\cdot\text{L}^{-1}$ picolinic acid extracted by $0.4218 \text{ mol}\cdot\text{L}^{-1}$ N235 in *n*-octanol, tetrachloromethane, or kerosene. It is observed that D values in three diluents are in the order of n -octanol \gg tetrachloromethane \geq kerosene ≈ 0 ,

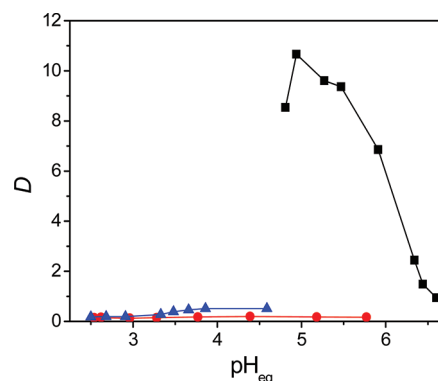


Figure 1. D vs pH_{eq} of $0.4218 \text{ mol}\cdot\text{L}^{-1}$ N235/diluents: ■, *n*-octanol; ▲, tetrachloromethane; and ●, kerosene.

which is similar with the results reported by Senol.¹⁴ Generally, the effects of diluent on extraction equilibrium are mainly in three aspects:¹⁵ (i) the physical extraction by diluent itself, the physical extraction abilities of polar diluents are higher than those of nonpolar diluents; (ii) the dissolving capacities of diluents for complexes, the polar complexes are apt to dissolve in polar diluents; and (iii) the apparent alkalinity of extractant. Eyal¹⁶ defined apparent alkalinity as the aqueous equilibrium pH of $1/2c \text{ mol}\cdot\text{L}^{-1}$ strong acid (like hydrochloric acid) after reacting with $c \text{ mol}\cdot\text{L}^{-1}$ extractant. The apparent alkalinity for an extractant/diluent system usually depended on the concentration of extractant and the type of diluent. Usually, an extractant/diluent system with higher apparent alkalinity could provide higher extraction capacity for the acidic solute. Figure 2 shows the apparent alkalinity of N235 with various

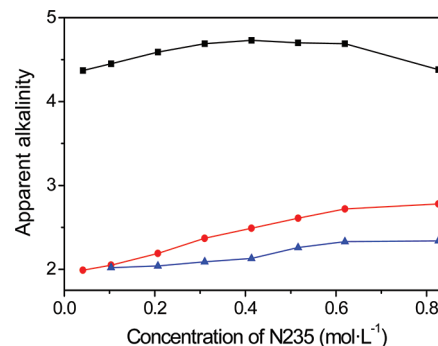


Figure 2. Apparent alkalinities of N235/diluents under various concentrations: ■, *n*-octanol; ●, tetrachloromethane; and ▲, kerosene.

concentrations in *n*-octanol, tetrachloromethane, and kerosene. It is obvious that the apparent alkalinities of N235/*n*-octanol are far higher than those of N235/tetrachloromethane and N235/kerosene. From a summary of the above discussions, it is easy to understand why D values of N235/*n*-octanol are higher than those of N235/tetrachloromethane and N235/kerosene.

Figure 3 illustrates D values under various concentrations of N235 in *n*-octanol vs aqueous equilibrium pH (pH_{eq}). Comparing D values at the same pH_{eq} it can be seen that, as N235 concentration increases, D values first increase and then decrease and appear as a maximum value when the N235 concentration is $0.4218 \text{ mol}\cdot\text{L}^{-1}$. The result attributes to the apparent alkalinity N235/*n*-octanol which displayed with

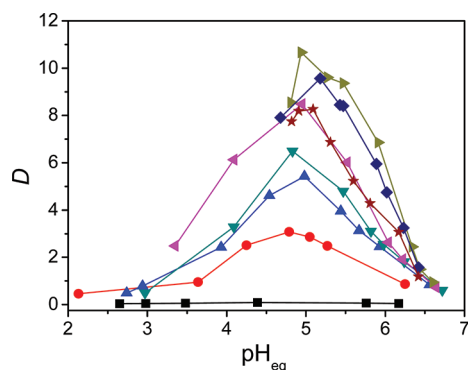


Figure 3. D vs pH_{eq} at various concentrations of N235 in n -octanol: ■, 0; ●, 0.04218; ▲, 0.1055; ▼, 0.2109; ◀, 0.3164; ▶, 0.4218; ◆, 0.6327; and ★, 0.8436. (in $\text{mol}\cdot\text{L}^{-1}$).

relatively higher values at a N235 concentration in the range of 0.3–0.6 $\text{mol}\cdot\text{L}^{-1}$.

In Figure 3, D values vary with the increase of pH_{eq} and the highest D values always appear at pH_{eq} of 4.5–6.0. Picolinic acid has two active groups: carboxyl group and pyridine nitrogen atom. It can exist in four forms, viz., charged cations, zwitterion molecules, neutral molecules, and charged anions. Wang¹⁷ and Liang¹⁸ reported that, in aqueous solution, the zwitterion form could be neglected, the charged cations and the neutral molecules dominated at $\text{pH} < 3.2$, the neutral molecules and the charged anions dominated at pH of 3.2–7.0, and the charged anions dominated at $\text{pH} > 7.0$. The highest D values appeared at a pH_{eq} of 4.5–6.0 and indicated N235 mainly reacted with the neutral and anionic picolinic acids in the extraction process.

The initial concentration of solute was also of influence on reactive extraction equilibrium. Picolinic acid solutions with different initial concentrations were examined by extraction with 0.4218 $\text{mol}\cdot\text{L}^{-1}$ N235/ n -octanol, and the D values were shown in Figure 4. As seen, D values decrease gradually with

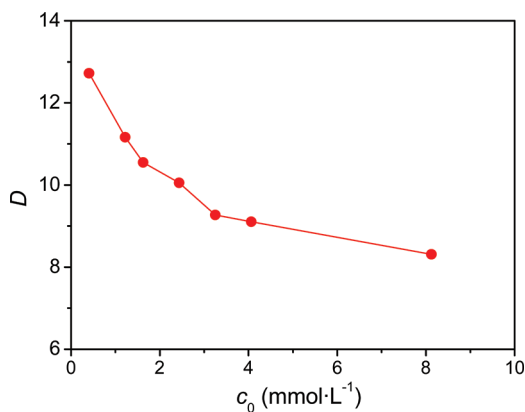


Figure 4. D vs initial concentrations of picolinic acid.

the increase of initial concentrations of picolinic acid. This might be attributed to that the gradual increase of picolinic acid concentration made the extractant's loading solute close to stoichiometric saturation. The amount of extracted solute increased but extraction efficiency decreased. By taking into account the principle of chemical balance motion, this phenomenon could be easily explained. The result indicated

that reactive extraction was much more suitable for separating solutes from dilute solutions.

As a comparative work, D of picolinic acid between water and 0.6327 $\text{mol}\cdot\text{L}^{-1}$ N235, TBP, and D2EHPA in n -octanol were investigated, respectively. As shown in Figure 5, the extraction

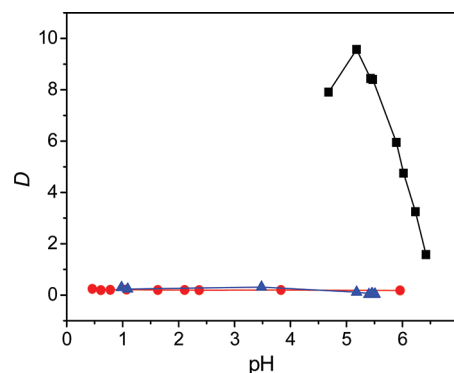


Figure 5. D vs pH_{eq} in various 0.6327 $\text{mol}\cdot\text{L}^{-1}$ extractants in n -octanol. ■, N235; ▲, P507; and ●, TBP.

capacities of TBP and D2EHPA in n -octanol are rather poor with $D < 1.0$, while N235/ n -octanol demonstrates very good separation ability for picolinic acid. The results further confirmed N235/ n -octanol was suitable for separating picolinic acid.

Infrared Spectra Analysis. Infrared spectra of N235/ n -octanol loading with picolinic acid were recorded on an infrared spectrometer as well as the original N235/ n -octanol and pure picolinic acid. Figure 6 shows the IR spectra of N235/ n -octanol

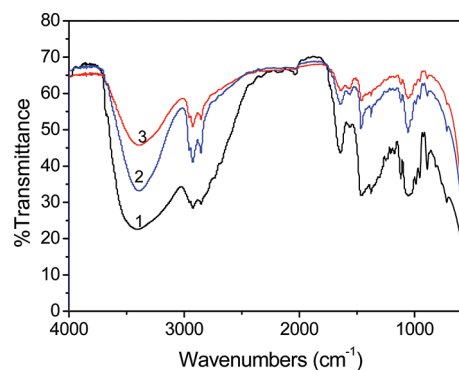


Figure 6. IR spectra of loading organic phases at pH_{eq} : 1, 3.87; 2, 6.53; and 3, 8.88.

loading with picolinic acid at different pH_{eq} values. It shows no significant difference, indicating that pH had an ignorable influence on the complexes' structure, namely, pH did not affect the interaction forms between N235 and picolinic acid. Figure 7 shows the comparison of IR spectra of N235/ n -octanol loading with picolinic acid, original N235/ n -octanol and pure picolinic acid. As seen, the band at 1720 cm^{-1} in picolinic acid, assigned to the characteristic stretching vibration of $\text{C}=\text{O}$, was not observed in the N235/ n -octanol loading phase, while two new bands appeared at 1640 and 1557 cm^{-1} , which could be assigned to the characteristic asymmetry and symmetry stretching of COO^- . It indicated that the ion-pair complex has been formed between N235 and picolinic acid; in

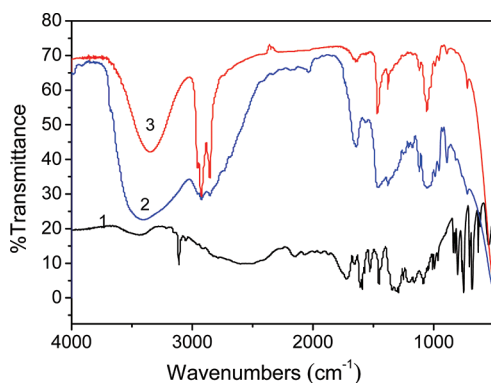
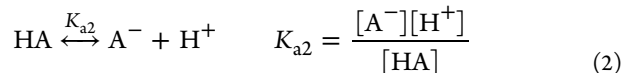
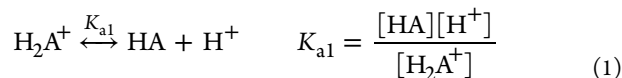


Figure 7. IR spectra of 1-picolinic acid, 2-N235/*n*-octanol, and 3-picolinic acid + N235/*n*-octanol.

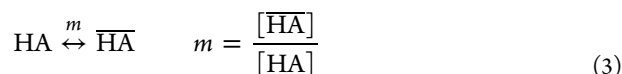
other words, the extraction reaction was a proton-transfer process.

Description of Extraction Equilibria. Equilibrium was governed by the mass action law;¹⁹ physical extraction of diluents was also taken into account. It was also under the following assumptions: the systems were diluent solutions and the activities of the interests and the complexes are proportional to their concentrations; the concentration of N235 in the organic phase is far higher than that of picolinic acid, and the complexes are mainly in the 1:1 form (N235/picolinic acid); reactive extraction and physical extraction accord with the simple addition; and the chemical reaction takes place at the phase interface. If N235 is defined as R_3N and picolinic acid as HA, the following reaction equilibria exists.

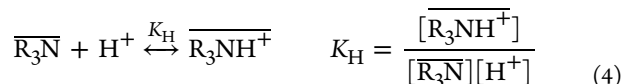
The two dissociation equilibria of picolinic acid:



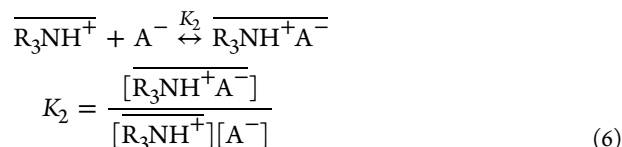
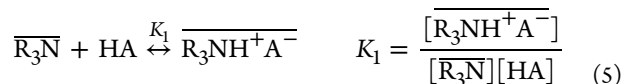
Physical extraction equilibrium of diluents vs picolinic acid:



Equilibrium of N235 reacting with a proton:



Chemical extraction equilibria of N235 reacting with picolinic acid:



where K_{a1} and K_{a2} are dissociation constants of picolinic acid with $pK_{a1} = 2.21$ and $pK_{a2} = 5.29$,²⁰ respectively; m denotes the physical extraction equilibrium constant; K_H represents the apparent reaction equilibrium constant of N235 with H^+ ; and

K_1 and K_2 represent the apparent extraction equilibrium constants of N235 reacting with neutral picolinic acid and protonated N235 reacting with anion picolinic acid, respectively. It is obvious that

$$\begin{aligned} K_1 &= \frac{[\overline{R_3NH^+}][A^-]}{[\overline{R_3N}][HA]} \\ &= K_2 K_H \frac{[H^+][A^-]}{[HA]} \\ &= K_2 K_H K_{a2} \end{aligned} \quad (7)$$

So, the distribution coefficient, D , can be written as

$$D = \left(\frac{K_1 B_0}{K_H [H^+] + 1 + K_1 [HA]} + vm \right) / (10^{pK_{a1}-pH} + 1 + 10^{pH-pK_{a2}}) \quad (8)$$

$$\begin{aligned} B_0 &= [\overline{R_3NH^+}] + [\overline{R_3N}] + [\overline{R_3NH^+A^-}] \\ &= [\overline{R_3N}](K_H [H^+] + 1 + K_1 [HA]) \end{aligned} \quad (9)$$

where B_0 is the initial concentration of N235 (ignoring its dissolution in aqueous solution), pH is aqueous equilibrium pH , and v is volume fraction of diluent in the organic phase. Because the concentration of N235 was far higher than that of picolinic acid, namely, $[\overline{R_3NH^+}] + [\overline{R_3N}] \gg [\overline{R_3NH^+A^-}]$, B_0 could be rewritten as

$$B_0 = [\overline{R_3N}](K_H [H^+] + 1) \quad (10)$$

Substituting eqs 9 and 10 into eq 8, D was revised as

$$D = \left(\frac{K_1 B_0}{K_H [H^+] + 1} + vm \right) / (10^{pK_{a1}-pH} + 1 + 10^{pH-pK_{a2}}) \quad (11)$$

By fitting the experimental data, m was calculated to be 0.15. K_H could be received from the apparent alkalinity, which was equivalent to $\lg K_H$. Figure 8 shows $\lg K_H$ vs B_0 according to a polynomial eq 12.

$$\begin{aligned} \lg K_H &= -0.7676B_0^3 - 1.317B_0^2 + 1.716B_0 \\ &\quad + 4.297 \quad (R^2 = 0.9923, B_0 = 0.04 - 0.85) \end{aligned} \quad (12)$$

Then, K_1 was calculated by eq 10 with experimental data (pH_{eq} and D), and finally K_2 was obtained from eq 6. Table 1 lists the fitting parameters of m , K_1 , K_2 , and K_H . It was in the order of $\lg K_H > \lg K_2 > \lg K_1$, suggesting that under the equilibrium conditions involved in the present work, the trend of forming complexes tend to be through eqs 4 and 6 rather than eq 5. According to the parameters m , K_1 , K_2 , and K_H , D (D_{cal}) were calculated. Comparing experimental D (D_{exp}) with D_{cal} , the fitting precision was examined. Figure 9 demonstrates the relationship of D_{cal} vs D_{exp} , which suggests the results are satisfactory.

CONCLUSIONS

Extraction equilibria of picolinic acid between water and N235/*n*-octanol were examined in detail. The D values were found to

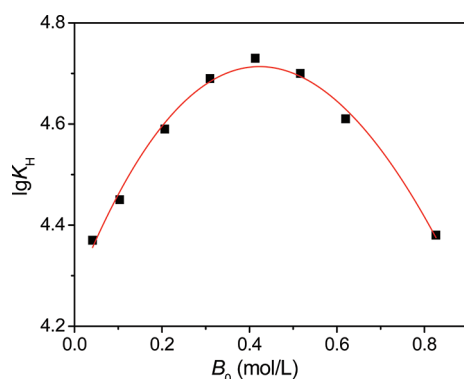


Figure 8. $\lg K_H$ vs B_0 .

Table 1. Model Parameters for Picolinic Acid + N235/*n*-Octanol Systems

$B_0/\text{mol}\cdot\text{L}^{-1}$	ν	m	$\lg K_H$	$\lg K_1$	$\lg K_2$
0	1.00	0.15			
0.0422	0.98	0.15	4.367	2.104	3.027
0.1055	0.95	0.15	4.462	2.021	2.849
0.2109	0.90	0.15	4.593	1.838	2.535
0.3164	0.85	0.15	4.684	1.760	2.366
0.4218	0.80	0.15	4.729	1.734	2.295
0.6327	0.70	0.15	4.661	1.562	2.191
0.8436	0.60	0.15	4.347	1.321	2.264

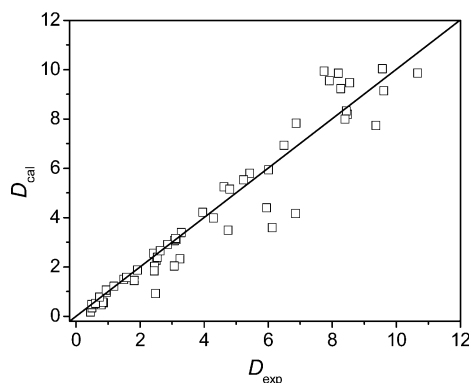


Figure 9. D_{cal} vs D_{exp} .

be highly dependent on the aqueous equilibrium pH and the apparent alkalinity of N235/*n*-octanol. The optimum operation conditions were N235/*n*-octanol with the concentration of $0.4218 \text{ mol}\cdot\text{L}^{-1}$ at the equilibrium pH of 4.5–6.0. IR spectra analysis confirmed that equilibrium pH did not affect the structures of the complexes, and the ion-pair complexes were formed between N235 and picolinic acid, namely, the extraction reaction was a proton-transfer process. Both the reactions of N235 accepting a proton followed by reaction with anion picolinic acid and N235 directly reacting with neutral picolinic acid were the main processes, through which picolinic acid transferred into organic phases from aqueous phases. An extraction equilibrium model was established and fitted with experimental data.

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