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Extraction of Aniline from Wastewater: Equilibria, Model, and Fitting of Apparent Extraction Equilibrium Constants

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Abstract

The physical and reactive extraction equilibria of aniline at 298.2 ± 0.5 K were studied. N-Butylacetate (BA), *n*-decanol, *n*-heptane and methyl tert-butyl ether (MTBE) were used for physical extraction. The distribution coefficients (D) of aniline follows the sequence $BA > MTBE > n\text{-decanol} > n\text{-heptane}$. The largest distribution coefficient ($D=22.58$) can be obtained with BA owing to its strong polarity. The equilibrium temperature almost has no effect on distribution coefficient except for MTBE. Tributyl phosphate (TBP), acetamide (N503), trialkylamine (N235), Di-(2-ethylhexyl) phosphoric acid (D2EHPA) and (2-Ethylhexyl)2-Ethylhexylphosphonate (P507) were used as extractants with BA, kerosene and *n*-heptane as diluents for the reactive extraction. TBP, N503 and N235 show weak removal ability for their neutral and basic characteristics. For acidic phosphorus-containing extractants, D2EHPA and P507, equilibrium models are presented that employ the mass action law and used to determine model parameters and apparent extraction equilibrium constants (K_{11} , K_{12} , and K_{21}). The reactive extraction complexes are considered as 1:1, 1:2 aniline to D2EHPA complexes with BA as diluent, 1:2 aniline to D2EHPA complexes with kerosene and *n*-heptane as diluents, and 1:1, 1:2 aniline to P507 complexes with

kerosene and *n*-heptane as diluents. The distribution coefficients and loadings of D2EHPA and P507 calculated using the equilibrium model parameters and apparent extraction equilibrium constants agree with the experimental data well, which indicates that the models are valid in representing the equilibrium behavior of aniline with the selected extractants in reactive extraction. The effects of temperature on extraction abilities were investigated and the enthalpy change of the extraction process with D2EHPA in kerosene was obtained.

Keywords: aniline wastewater, physical and reactive extraction equilibria, loading of extractant, equilibrium model, apparent equilibrium constant

Introduction

As one of the important organic raw chemical materials and intermediates, aniline has been extensively used in the manufacture of dyes, rubbers, pharmaceutical preparation, plastic, paint, reagent intermediates, petrochemicals, and other industries.¹ There are over 840 000 and 600 000 tons aniline waste water produced in Europe and American per year.² It is bad smelly and generally regarded as toxic compound because of its carcinogenicity and high solubility in water (up to 3.6 wt.% at 293.16 K), which widely threatens public health and environmental quality.³ According to the United States Environmental Protection Agency (US EPA),⁴ the maximum concentration of aniline in water needs to be less than $0.262 \text{ mg}\cdot\text{L}^{-1}$ in US. Therefore, it's imperative for researchers to find out effective treatment methods to eliminate the aniline water pollution.

So far, there are several attempts to remove the chemicals or recover aniline and

recycle the water, such as liquid-liquid extraction,^{5,6} adsorption,⁷⁻⁹ ligand exchanger,¹⁰ biological treatment,¹¹ emulsion liquid membrane (ELM),¹² hollow fiber renewal liquid membrane,¹³ micellar-enhanced ultrafiltration (MEUF),¹⁴ dual-electrode oxidation,¹⁵ photocatalytic degradation,¹⁶ electro-fenton,¹⁷ electrochemical degradation,² and other processes. It is considered that liquid-liquid extraction process has advantages of simple equipment, effective operation and dealing with a large number of wastewaters in a short time.

In a commercial process, aniline is usually recovered by physical extractants (e.g., benzene, toluene, cyclohexane, nitrobenzene, etc.).^{5, 18} To improve the extraction efficiency of extractants, salts including both inorganic solid salts and ionic liquids were added as additives.^{4,5} However, these extractants, mostly poisonous, will pollute the aqueous again. In the 1980s, King¹⁹ came up with the idea based upon the reversible reaction of the specific functional groups of solute and extractants, called reactive extraction. Aniline is a typical Lewis alkali so that it can lead to satisfying distribution coefficient by reactive extraction according to Lewis Theory. Reactive extractants can be classified in two major types: phosphorus-bonded, oxygen-containing extractants and high molecular weight aliphatic amines.²⁰ Reactive extraction has been widely applied for separation of carboxylic acids, amines, alcohol, phenols and amphoteric compounds and other similar materials.^{21,22}

A series of extractants have been applied for removal of aniline from wastewater so far, such as tributyl phosphate,²³ trialkyl amine,²⁴ and so on. Unfortunately, few works have been reported on extraction equilibria of aniline by reactive extraction,

which obviously should play the fundamental roles in aniline recovery process.

Therefore, extraction equilibria of aniline were explored in this paper, including physical extraction with N-Butylacetate(BA), *n*-decanol, *n*-heptane and methyl tert-butyl ether (MTBE) as the extractants and reactive extraction with TBP, N503, N235, D2EHPA and P507 as the extractants and BA, kerosene, and *n*-heptane as the diluents. In order to treat the wastewater efficiently, the mechanism of extraction were investigated too. The influences of organic composition, pH, temperature, and initial aniline concentration in the feed solution were discussed. Besides, an equilibrium model was used to determine model parameters and apparent extraction equilibrium constants in reactive extraction.

Experimental

Materials

Aniline (purity >99.5%wt, Tianjin GuangFu Chemical Reagents Company) is a colorless oily liquid and model organic pollutant with a molecular weight of 93.128 and a Lewis basic group -NH₂. Methyl tert-butyl ether (MTBE, analytical grade, Tianjin GuangFu Chemical Reagents Company), *n*-decanol (Analytical grade, Tianjin Jinke Institute of Fine Chemicals), N-Butylacetate (BA) and *n*-heptane (Analytical grade, Beijing Chemical Works) were used to extract aniline in physical extraction. Besides, BA, *n*-heptane and kerosene (analytical grade, Tianjin Fuchen Chemical Reagent Plant) were also used to dilute extractants to prepare organic solution in reactive extraction. Di-(2-ethylhexyl)phosphoric acid (D2EHPA, analytical grade, Tianjin Jinke Institute of Fine Chemicals), tributyl phosphate (TBP, analytical grade,

Beijing Chemical Works). N, N-di(1-methyl-heptyl) acetamide (N503) and trialkylamine (N235) (analytical grade, Zhengzhou qinshikeji Co., Ltd.). Purities of the above chemicals were larger than 95% in mass and were used without further purification. Phosphate buffer were prepared by NaOH (purity>96.0%wt, Beijing Chemical Works) and KH_2PO_4 (analytical grade, Sinopharm Chemical Reagent Co., Ltd).

Procedure

1) Physical extraction. The aqueous solution of aniline was prepared using distilled water. Several different pH values of aniline solution were considered to investigate the influence of pH value. Various initial concentrations of aniline were also used for the investigation of the equilibrium of physical extraction.

2) Reactive extraction. Over six different concentrations of extractants (range from 0.1 to 0.7 $\text{mol}\cdot\text{L}^{-1}$), such as TBP, N235, N503, D2EHPA and P507 were considered to prepare the extract phase and dissolved in three different diluents (BA, kerosene, and *n*-heptane) to perform experiments on the equilibrium of reactive extraction.

All the extraction experiments were conducted in 50 mL stoppered flasks at 298.2 \pm 0.5 K (except for experiments of the effect of temperature) in a thermostated shaker bath. Equal volumes (10 mL) of the aqueous and organic phase were added to each flask. The flask containing the mixture was shaken for about 1 h, which was found to be sufficient for reaching the equilibrium. The aqueous raffinate were removed for assay after a few minutes standing.

Sample Analysis.

The aqueous samples were analyzed for aniline concentration by using spectrometric absorption measurements (UV-1800, Shimadzu Corporation) at 230 nm. The samples were appropriately diluted and analyzed at pH 7 adjusted by the phosphate buffer. The aniline concentration in the organic phase was calculated by material balance based on the volumes of the two phases and the aniline concentration in the aqueous phase at equilibrium. A digital precision ionometer (PXS-450, Shanghai Dapu Co. Ltd.) with a combined glass electrode was used for pH measurements (± 0.01 pH).

The distribution coefficient (D) and extraction rate (E) in the extraction process, are defined by Eq. 1 and 2, respectively.

$$D = \frac{\overline{C_{\text{RNH}_2}}}{C_{\text{RNH}_3^+} + C_{\text{RNH}_2}} \quad (1)$$

$$E = \frac{\overline{C_{\text{RNH}_2}}}{C_{\text{in}}} = \frac{D}{1 + D} \quad (2)$$

where $\overline{C_{\text{RNH}_2}}$ represents the total concentration of aniline in the organic phase at equilibrium; C_{RNH_2} represents the overall concentration in the aqueous phase at equilibrium, including the dissociated aniline; C_{in} represents the initial aniline concentration in the aqueous phase.

Results and Discussion

Aniline has a Lewis base group $-\text{NH}_2$, which exhibits Lewis base characteristics. The dissociation equilibrium exists in the aqueous solutions is as follows:



The dissociation constant (K_a) can be written as follows:

$$K_a = \frac{C_{\text{RNH}_2} \cdot C_{\text{H}^+}}{C_{\text{RNH}_3^+}} \quad (4)$$

Physical Extraction

Effect of initial concentration of aniline

The effects of initial concentration of aniline on the extraction equilibrium of aniline in physical extraction are shown in Fig. 1. The distribution coefficient of aniline follows the sequence BA > MTBE > *n*-decanol > *n*-heptane. As we all know, the polarity of the solvent follows the sequence BA > MTBE > *n*-decanol > *n*-heptane. According to the “like dissolves like” principle, since BA, MTBE, *n*-decanol and aniline are polar molecules, the stronger the solvent polarity is, the higher the concentration of aniline in the organic phase is. As there are hydrogen atoms and lone pair electron of nitrogen atom existing in $-\text{NH}_2$ group, BA, MTBE and *n*-decanol can form hydrogen bond with aniline respectively. Besides, it is considered that *n*-heptane is a typical inert solvent which nearly has no effect on aniline removal. Moreover, the distribution coefficient of all extractants except for *n*-heptane increase with the increase of initial aniline concentration. Thus, BA may be the best extractant in physical extraction.

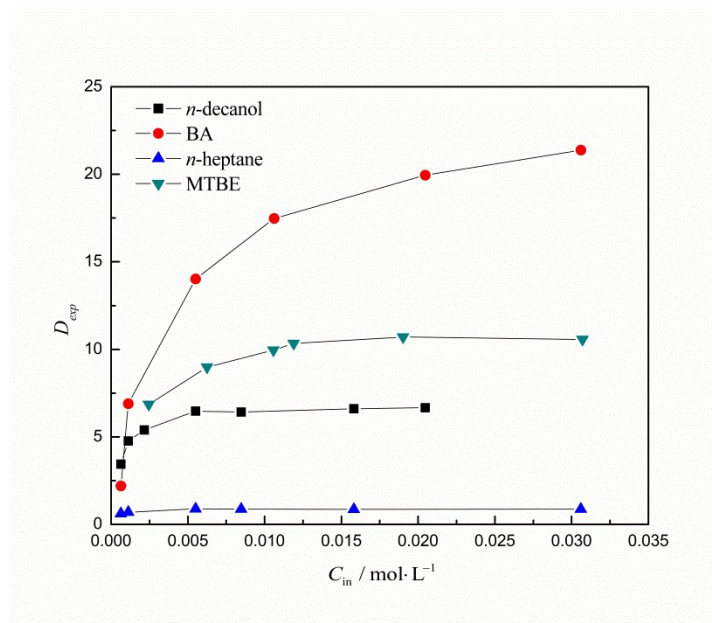


Fig.1 Effect of initial aniline concentration (C_{in}) on extraction equilibrium of aniline in physical extraction at 298.2 K

Effect of initial pH value

As shown in Fig. 2, the distribution coefficients for all four extractants increase with increasing the initial pH value. Since the pH value plays a vital role on the existential form of aniline in the aqueous phase, higher the pH values, larger the D values. When the equilibrium pH values in the aqueous solution is smaller than the pK_a (4.60) of aniline,²⁵ RNH_3^+ dominates the existential form of aniline, which makes against the physical extraction process; when the equilibrium pH value in the aqueous solution is larger than the pK_a (4.60) of aniline, RNH_2 dominates the existential form of aniline, which benefits to the physical extraction process. Thus, the pH value in the aqueous solution is usually maintained at 6.0 to 8.0 to remain the aniline as a moderate state. According to Fig. 2, the distribution coefficients follows the sequence: $\text{BA} > \text{MTBE} > n\text{-decanol} > n\text{-heptane}$. As the $n\text{-heptane}$ molecule is nonpolar which prefers

to combine with nonpolar molecules according to “like dissolves like” principle, the distribution coefficients of *n*-heptane are approximately 0.

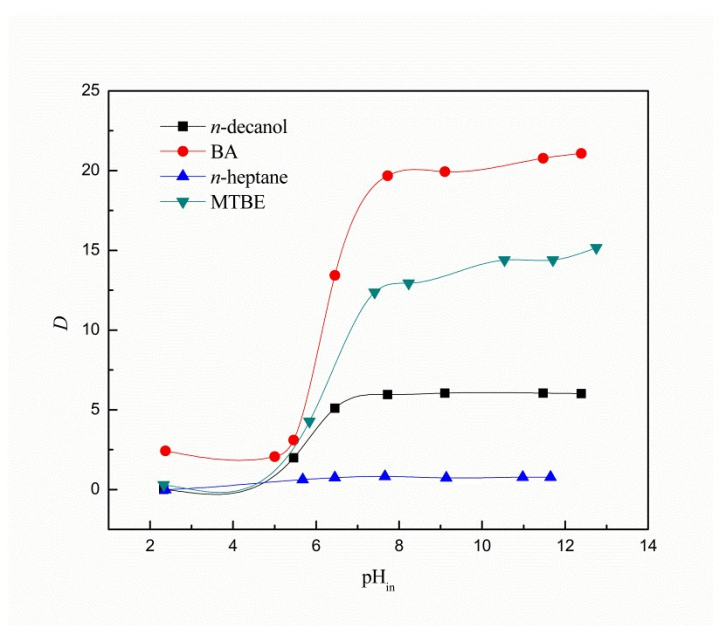


Fig.2 Effect of initial pH value on extraction equilibrium of aniline at 298.2 K, $C_{in}=0.01 \text{ mol}\cdot\text{L}^{-1}$.

Effect of temperature

Temperature generally has influence on extraction equilibrium. When the extraction process is exothermic, the distribution coefficient decreases with the increase of temperature. Otherwise, the distribution coefficient increases with the increase of temperature. As shown in Fig. 3, the extraction rate and distribution coefficient of BA and *n*-decanol have little change with increasing temperature, which indicates that they are not sensitive to temperature changes. Since the extraction process with MTBE is exothermic,⁴ the extraction rate and distribution coefficient decrease with the increase of temperature, which agrees with the experimental data well. For *n*-heptane, the extraction rate and distribution coefficient slightly increase with increasing the temperature, which indicates that the process is endothermic.

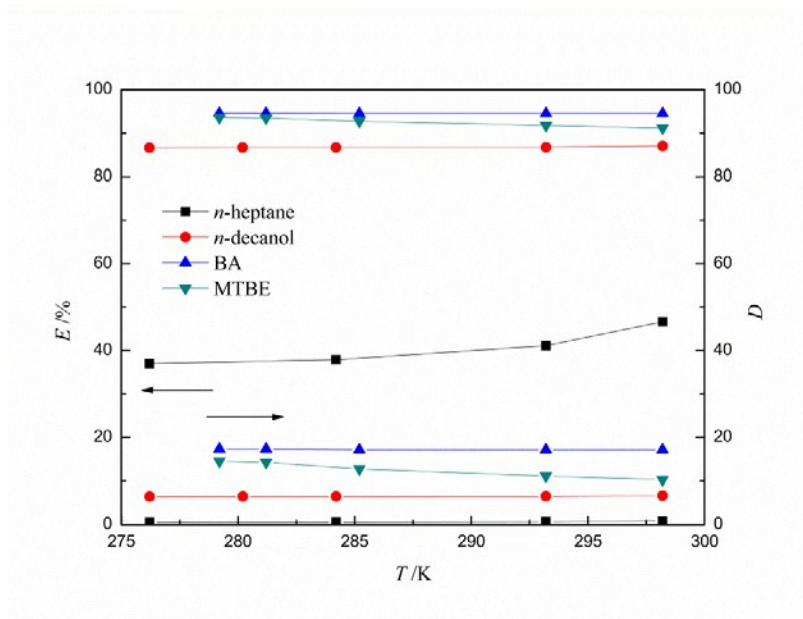


Fig. 3 Effect of temperature on extraction equilibrium of aniline, $C_{in}=0.01 \text{ mol}\cdot\text{L}^{-1}$.

Reactive Extraction

TBP, N503, N235, D2EHPA and P507 were used as extractants in the range of 0.1 to 0.7 $\text{mol}\cdot\text{L}^{-1}$ with BA, kerosene, and *n*-heptane as the diluents. Most extractants always need to be diluted owing to their high viscosity. A good diluent should not only improve the extraction operation process but also increase the extraction capacity.

Effect of initial concentration of neutral and basic extractants

As shown in Fig. 4, since the BA molecule is polar, which prefers to combine with polar molecules according to “like dissolves like” principle, the distribution coefficient of aniline with TBP in BA is much larger than that in kerosene and *n*-heptane. Thus, it is considered that BA plays a leading role in aniline removal process. However, the values of D decreased with increasing the concentration of N235 and N503. These two typical Lewis basic extractants, may drag on the organic phase capacity by decreasing the concentration of BA. However, the general rule is that the

extraction capacity depends on three factors: physical extraction of diluent, dissolving capacity of complexes and apparent basicity of extractant.²¹ It is apparently that N235 and N503 show their basicities. Since N235 has stronger basicity than N503, the distribution coefficient of N235 is smaller than that of N503 in BA. Thus, it can be concluded that N235 and N503 exhibit weak selective extraction ability for aniline.

Actually, since TBP is a neutral phosphorus-based extractant, which has a certain extraction capability for basic solute aniline, the distribution coefficient of aniline increases with increasing the concentration of TBP in a certain range. It also can be found that the difference between kerosene and *n*-heptane as diluents can be negligible, due to their very weak polarity. Therefore, the basicity of N235 and N503 dominate the extraction capacity of aniline in nonpolar solvent. Thus, the distribution coefficient with N235 as extractant is lower than that with N503 in kerosene and *n*-heptane owing to N235's stronger basicity.

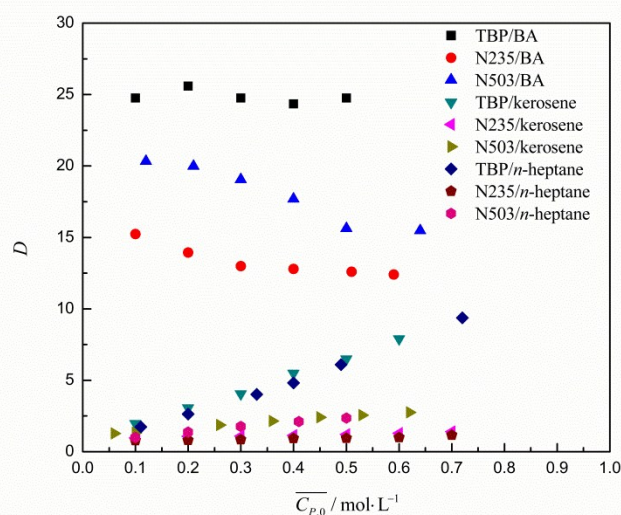


Fig. 4 Effect of initial concentration ($\overline{C_{P,0}}$) of TBP, N235, N503 in three diluents on extraction

equilibrium of aniline in reactive extraction at 298.2 K, $C_{in}=0.01 \text{ mol}\cdot\text{L}^{-1}$.

Effect of initial concentration of acidic phosphorus-containing extractants

The effects of initial concentration of D2EHPA and P507 in three diluents on the extraction distribution of aniline are presented in Fig. 5. BA is considered as the best diluent for D2EHPA, which shows much larger D values than that of kerosene and n -heptane. Since higher concentration of the extractants can favorably promote the reaction equilibrium to increase the products concentration, the distribution coefficient increases with increasing the concentration of D2EHPA and P507, which leads to a more satisfying extraction rate but worse loading of extractants, as shown in Fig. 6. However, since the concentration of aniline molecule in the aqueous phase decreases with decreasing the equilibrium pH value by Eq. 3, the distribution coefficient and extraction rate decrease with decreasing the equilibrium pH values.

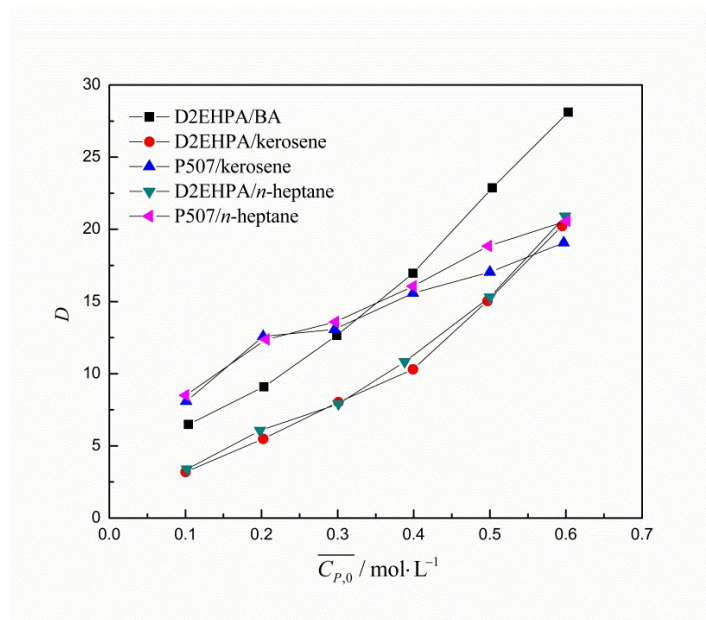


Fig. 5 Effect of initial concentration ($\overline{C}_{P,0}$) of D2EHPA and P507 in three diluents on extraction

distribution of aniline in reactive extraction at 298.2 K, $C_{in}=0.01 \text{ mol}\cdot\text{L}^{-1}$.

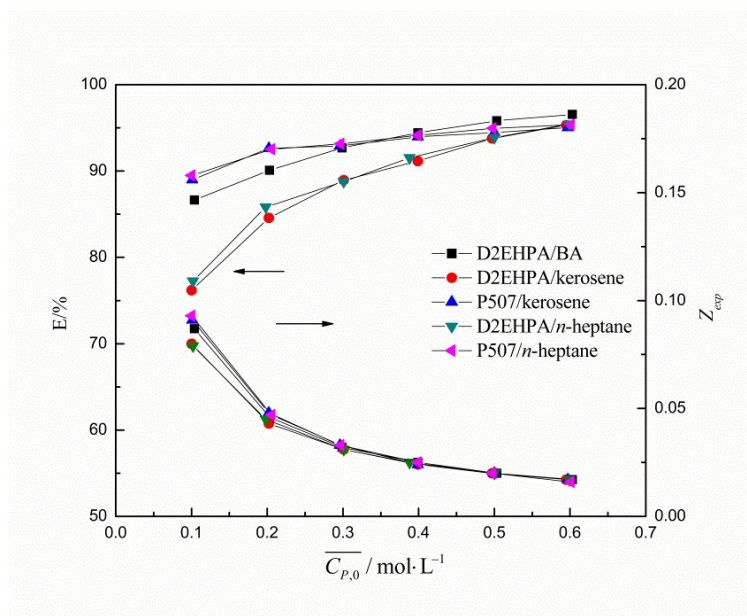
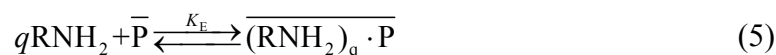


Fig. 6 Effect of initial concentration ($\overline{C_{P,0}}$) of D2EHPA and P507 in three diluents on extraction rate (E) and loading of aniline (Z_{exp}) in reactive extraction at 298.2 K, $C_{\text{in}}=0.01 \text{ mol}\cdot\text{L}^{-1}$.

Equilibrium model for D2EHPA and P507

In order to simplify the model, the mechanism of reactive extraction for D2EHPA and P507 can be written as:



where $\overline{(\text{RNH}_2)_q \cdot \text{P}}$ represents the complexing extractants in the organic phase; q is the stoichiometric ratio of the aniline to extractant.

The equilibrium constant K_E can be defined as:

$$K_E = \frac{\overline{C_{q1}}}{C_{\text{RNH}_2}^q \cdot C_{\text{p}}} \quad (6)$$

where $\overline{C_{q1}}$ represent the equilibrium concentration of $\overline{(\text{RNH}_2)_q \cdot \text{P}}$ in the organic phase.

The total concentration of RNH_2 in the aqueous phase can be expressed in terms of undissociated RNH_2 concentration (C_{RNH_2}), K_a , and H^+ concentration (C_{H^+}),

$$\begin{aligned}
 C_{\text{RNH}_2, \text{Tot}} &= C_{\text{RNH}_2} + C_{\text{RNH}_3^+} \\
 &= C_{\text{RNH}_2} + \frac{C_{\text{RNH}_2} \cdot C_{\text{H}^+}}{K_a} \\
 &= \left(1 + \frac{C_{\text{H}^+}}{K_a}\right) C_{\text{RNH}_2}
 \end{aligned} \tag{7}$$

The physical extraction can be expressed as:



$$s = \frac{\overline{C_{\text{RNH}_2}}}{C_{\text{RNH}_2}} \tag{9}$$

where $\overline{C_{\text{RNH}_2}}$ represents the concentration of aniline extracted by physical extraction in the organic phase; s is the physical extraction constant of the aniline for the pure diluent obtained from the distribution coefficient with the same initial concentration of aniline.

The distribution coefficient can be derived by Eq.4, 7 and 9:

$$\begin{aligned}
 D &= \frac{\overline{C_{\text{RNH}_2}}}{C_{\text{RNH}_2} + C_{\text{RNH}_3^+}} \\
 &= \frac{q\overline{C_{q1}}}{C_{\text{RNH}_2} + C_{\text{RNH}_3^+}} + \frac{sC_{\text{RNH}_2}}{C_{\text{RNH}_2} + C_{\text{RNH}_3^+}} \\
 &= \frac{qK_E C_{\text{RNH}_2}^{q-1} \overline{C_p}}{1 + \frac{C_{\text{H}^+}}{K_a}} + \frac{s}{1 + \frac{C_{\text{H}^+}}{K_a}}
 \end{aligned} \tag{10}$$

The material balance of extractant in the organic phase can be written as:

$$\overline{C_p} = \overline{C_{p,0}} - \overline{C_{q1}} \tag{11}$$

The concentration of extractant in the organic phase at equilibrium can be derived by Eq. 6 and 11:

$$\overline{C_p} = \frac{\overline{C_{p,0}}}{1 + K_E C_{\text{RNH}_2}^q} \tag{12}$$

Thus, the distribution coefficient can be deduced by Eq. 10 and 12:

$$\begin{aligned}
 D &= \frac{\overline{C_{\text{RNH}_2}}}{C_{\text{RNH}_2} + C_{\text{RNH}_3^+}} \\
 &= \frac{q\overline{C_{\text{q1}}} + s\overline{C_{\text{RNH}_2}}}{C_{\text{RNH}_2} + C_{\text{RNH}_3^+}} \\
 &= \frac{qK_{\text{E}}C_{\text{RNH}_2,\text{Tot}}^{q-1}\overline{C_{\text{P},0}}}{K_{\text{E}}C_{\text{RNH}_2,\text{Tot}}^q + (1 + 10^{pK_a - \text{pH}})^q} + \frac{s}{1 + 10^{pK_a - \text{pH}}} \quad (13)
 \end{aligned}$$

The Error function can be defined as root-mean-square deviation (rmsd):

$$\text{rmsd} = \sqrt{\frac{\sum_{i=1}^n (D_{\text{exp}} - D_{\text{cal}})^2}{n}} \quad (14)$$

The stoichiometric ratio of aniline to acidic extractants q , physical extraction constant of the aniline s , correlation coefficient R^2 and rmsd in different diluents are determined by fitting the experimental data for D with Eq. 13 and 14 using least square regression method. For all these extraction systems used in this work, the values of q range from 0 to 1, which indicates that more than one form of the aniline to acidic extractant complex exist in the organic phase. Besides, all the values of s are 0 except for D2EHPA in BA, which indicates that the physical extraction can be totally ignored for extractants in kerosene and n -heptane. In other words, kerosene and n -heptane are inert diluents and barely have extraction capacity for aniline. Thus, reactive extraction plays the leading role in aniline removal with D2EHPA and P507 in kerosene and n -heptane. However, the value of s for D2EHPA in BA reveals that physical extraction should be considered in BA and other polar solvents.

Table 1

Value of stoichiometric ratio of aniline to D2EHPA and P507 q , physical extraction constant s , correlation coefficient R^2 , and rmsd in different diluents at 298.2 K

Extractant	Diluent	q	s	R^2	rmsd
	BA	0.5943	23.7237	0.9997	0.1396
D2EHPA	kerosene	0.4570	0	0.9984	0.2277
	<i>n</i> -heptane	0.4837	0	0.9964	0.3574
P507	kerosene	0.6049	0	0.9934	0.2861
	<i>n</i> -heptane	0.5853	0	0.9996	0.0854

The comparison of experimental and calculated data for the distribution coefficient of aniline in reactive extraction are shown in Fig. 7. The calculated values of D agree with the experimental values of D very well, which indicates that the model is valid in representing the equilibrium behavior of aniline with the selected extractants in reactive extraction.

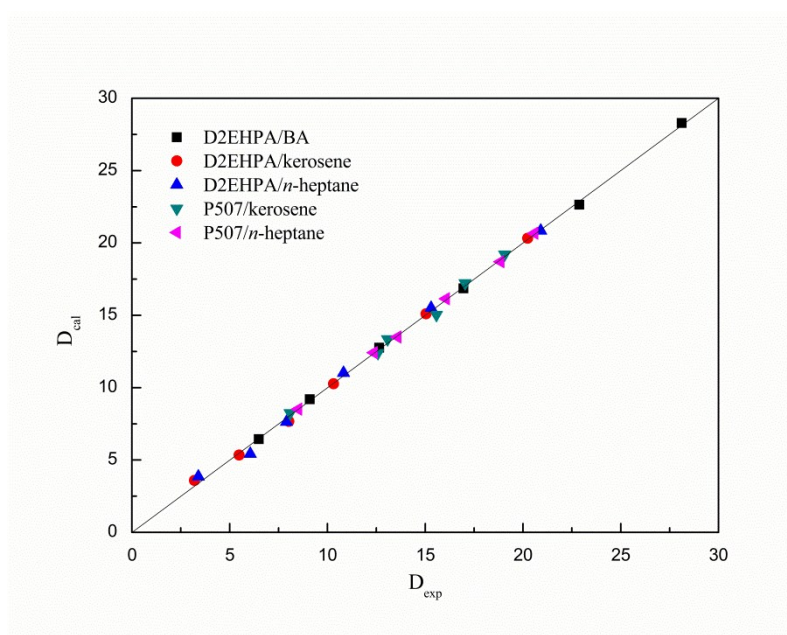
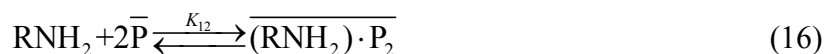


Fig. 7 Comparison of experimental and calculated data for distribution coefficient of aniline in reactive extraction.

For D2EHPA and P507, since all the values of q are smaller than 1, reactive extraction productions are considered as the formation of 1:1, 2:1 and 1:2 aniline to acidic extractant complexes, where the 2:1 complex results from the dimer of the aniline in the organic phase and the 1:2 complex results from ion-pair or

hydrogen-bond association between the 1:1 complex and acidic extractants. The complexes are formed by reactions as follows:



The equilibrium constants (K_{11} , K_{12} and K_{21}) can be given:

$$K_{11} = \frac{\overline{C_{11}}}{C_{\text{RNH}_2} \cdot C_{\text{P}}} \quad (18)$$

$$K_{12} = \frac{\overline{C_{12}}}{C_{\text{RNH}_2} \cdot C_{\text{P}}^2} \quad (19)$$

$$K_{21} = \frac{\overline{C_{21}}}{C_{\text{RNH}_2}^2 \cdot C_{\text{P}}} \quad (20)$$

where $\overline{C_{11}}$, $\overline{C_{12}}$ and $\overline{C_{21}}$ represent the concentrations of the formation of 1:1, 1:2 and 2:1 aniline to acidic extractant complexes, respectively.

The concentrations of aniline by reactive extraction and free extractants in the organic phase can be calculated by Eq. 21 and 22, respectively,

$$\begin{aligned} \overline{C_{\text{RNH}_2, \text{React}}} &= \overline{C_{11}} + 2\overline{C_{21}} + \overline{C_{12}} \\ &= K_{11} C_{\text{RNH}_2} \overline{C_{\text{P}}} + 2K_{21} C_{\text{RNH}_2}^2 \overline{C_{\text{P}}} + K_{12} C_{\text{RNH}_2} \overline{C_{\text{P}}}^2 \end{aligned} \quad (21)$$

$$\begin{aligned} \overline{C_{\text{P}}} &= \overline{C_{\text{P},0}} - (\overline{C_{11}} + \overline{C_{21}} + 2\overline{C_{12}}) \\ &= \overline{C_{\text{P},0}} - (K_{11} C_{\text{RNH}_2} \overline{C_{\text{P}}} + K_{21} C_{\text{RNH}_2}^2 \overline{C_{\text{P}}} + 2K_{12} C_{\text{RNH}_2} \overline{C_{\text{P}}}^2) \end{aligned} \quad (22)$$

where $\overline{C_{\text{RNH}_2, \text{React}}}$ represents the total concentration of aniline extracted by reactive extraction in the organic phase.

Then, the calculated loading of D2EHPA and P507, Z_{cal} can be expressed as:

$$\begin{aligned}
 Z_{\text{cal}} &= \frac{\overline{C_{\text{RNH}_2, \text{React}}}}{C_{\text{P},0}} \\
 &= \frac{\overline{C_{\text{P}} C_{\text{RNH}_2}}}{C_{\text{P},0}} (K_{11} + 2K_{21} C_{\text{RNH}_2} + K_{12} \overline{C_{\text{P}}})
 \end{aligned} \quad (23)$$

The experimental loading, Z_{exp} can be written as:

$$Z_{\text{exp}} = \frac{\overline{C_{\text{RNH}_2, \text{Tot}} - \varphi S C_{\text{RNH}_2}}}{C_{\text{P},0}} \quad (24)$$

where φ is the volume fraction of diluent in the organic phase.

The error function also can be defined:

$$\text{rmsd} = \sqrt{\frac{\sum_{i=1}^n (Z_{\text{exp}} - Z_{\text{cal}})^2}{n}} \quad (25)$$

Then, the values of K_{11} , K_{12} and K_{21} also can be calculated and are listed in Table 2. As all the values of K_{21} equal to 0, it is obvious that the 2:1 complex results from the dimer of the aniline in the organic phase can be neglected. It is considered that the dominating formation of D2EHPA is the dimer form in inert solvent with D2EHPA as extractant, and the solute would be extracted by reacting with the dimer. Thus, the values of K_{11} should equal to 0 in kerosene and *n*-heptane with D2EHPA as extractant, which agrees with the experiment results well. It is also be noticed that the values of K_{11} and K_{12} is not zero with BA as diluent, which indicates that both the monomer and dimer forms of D2EHPA exist in the organic phase with BA as diluent.

For P507 in both kerosene and *n*-heptane, it is considered that there are two major formations of 1:1 and 1:2 aniline to P507 complexes existing in the organic phase, which indicates that both the monomer and dimer forms of P507 exist in the organic phase with kerosene and *n*-heptane as diluents. As shown in Fig. 8, the calculated

values of Z agree with the experimental values of Z and most points are within the deviation of $\pm 10\%$, which indicates that the model is valid in representing the equilibrium behavior of aniline with the selected acidic extractants.

Table 2

Value of aniline molecules to D2EHPA and P507 equilibrium constants (K_{11} , K_{12} and K_{21}), correlation coefficient (R^2) and rmsd in different diluents at 298.2 K

Extractant	Diluent	K_{11}	K_{12}	K_{21}	R^2	rmsd
D2EHPA	BA	777.97	5677.55	0	0.9991	0.0006
	kerosene	0	9863.14	0	0.9782	0.0068
	<i>n</i> -heptane	0	10903.25	0	0.9492	0.0065
P507	kerosene	79.57	985.35	0	0.9944	0.0020
	<i>n</i> -heptane	76.01	1107.24	0	0.9982	0.0011

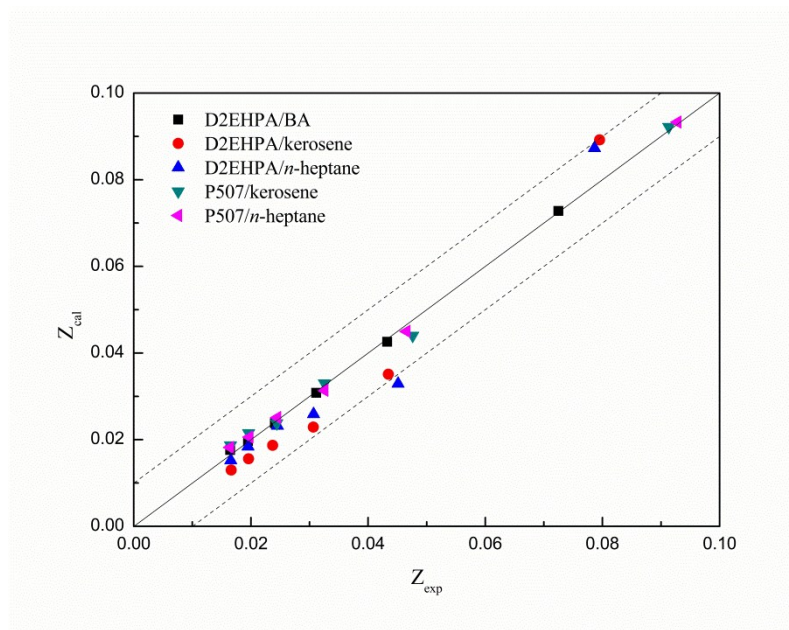


Fig. 8 Comparison of experimental and calculated data for loading of D2EHPA and P507

Effect of temperature

As shows in Fig. 9, the distribution coefficient has little change with increasing temperature with P507, TBP, N235 and N503 as the extractants. However, the distribution coefficient remarkably decreases with increasing temperature for D2EHPA.

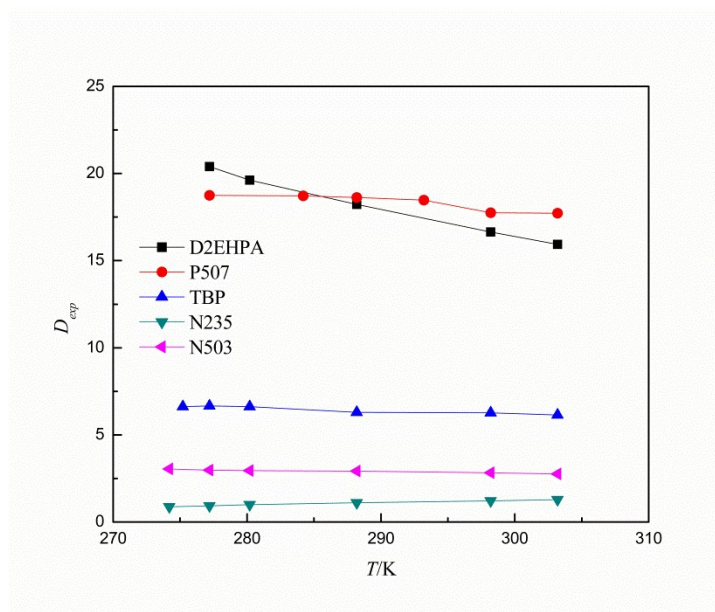


Fig. 9 Effect of temperature on extraction distribution of aniline with various extractants in

kerosene, $\overline{C}_{p,0} = 0.6 \text{ mol}\cdot\text{L}^{-1}$, $C_{in} = 0.01 \text{ mol}\cdot\text{L}^{-1}$.

As for $q = 0.4570$, $s = 0$ for D2EHPA in kerosene, K_E of aniline with D2EHPA can be written by Eq. 13 as:

$$K_E = \frac{D(1 + 10^{pK_a - pH})^q}{C_{RNH_2, Tot}^{q-1} (q\overline{C}_{P,0} - DC_{RNH_2, Tot})} \quad (26)$$

The relationship between the extraction equilibrium constant K_E and the enthalpy change of the extraction process ΔH can be expressed as

$$\ln K_E = -\frac{\Delta H}{RT} + c \quad (27)$$

where R is the molar gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), T is the absolute temperature, c is a constant. Fig. 10 shows the linear change of the logarithmic distribution coefficient with inverse temperature. The enthalpy change of the extraction process and correlation coefficient (R^2) with D2EHPA in kerosene are deduced to be $-4.183 \text{ kJ}\cdot\text{mol}^{-1}$ and 0.9332 , which means that the extraction process with D2EHPA in kerosene is exothermic. It is concluded that temperature variation has greater effect on

the extraction process with D2EHPA than P507. Besides, P507 can obviously be regarded as suitable extractant in aniline wastewater treatment in large temperature difference range.

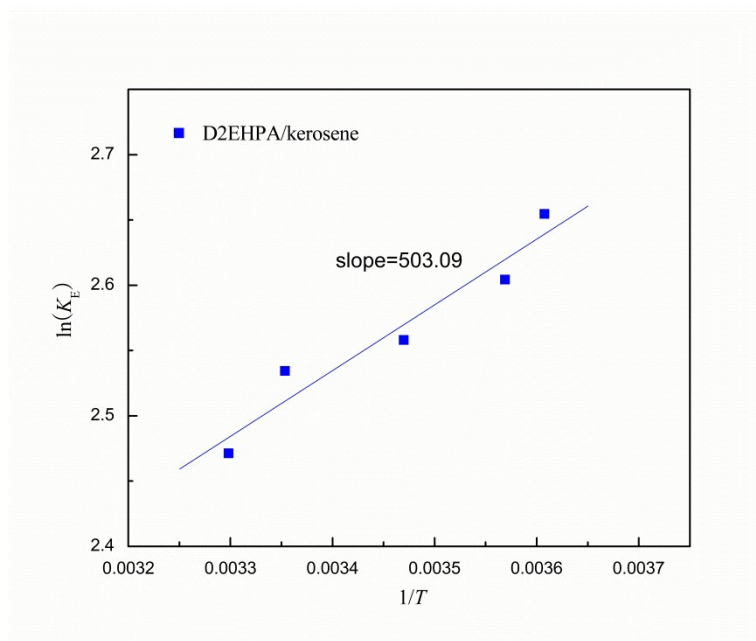


Fig. 10 Dependence of $\ln K_E$ on $1/T$ for aniline extraction with D2EHPA in kerosene, $C_{in}=0.01$ mol·L⁻¹, $C_{p,0}=0.60$ mol·L⁻¹.

Conclusions

In this work, physical and reactive solvent extraction equilibria and complex structure investigation for aniline with several extractants and diluents were conducted at 298.2 ± 0.5 K. In physical extraction, the distribution coefficients of aniline follows the sequence $BA > MTBE > n$ -decanol $> n$ -heptane. The equilibrium temperature almost has no effect on distribution coefficient except for MTBE. In reactive extraction, TBP, N503 and N235 have very weak interaction with aniline owing to their neutral and basic characteristics. For acidic phosphorus-containing extractants, the distribution coefficient increases with increasing the concentration of D2EHPA and P507, which

leads to more satisfying extraction rate but worse loading of extractants. When the mass action law and suitable assumptions are used, models for extraction equilibrium were evaluated and the apparent extraction equilibrium constants (K_{11} , K_{12} , and K_{21}) were determined by fitting the experimental data using a least-squares regression method. 1:1, 1:2 aniline to D2EHPA complexes with BA as diluent, 1:2 aniline to D2EHPA complexes with kerosene and *n*-heptane as diluents and 1:1, 1:2 aniline to P507 complexes with kerosene and *n*-heptane as diluents could be formed. By using the equilibrium model parameters and apparent extraction equilibrium constants, the distribution coefficients and loadings of P507 agree with the experimental data well. The reactive extraction process with D2EHPA in kerosene is exothermic, and the enthalpy change is $-4.183 \text{ kJ}\cdot\text{mol}^{-1}$.

Acknowledgements

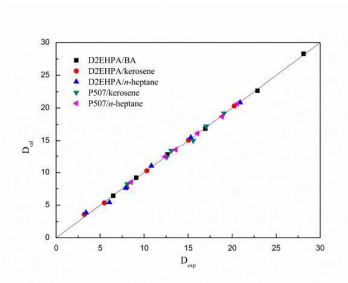
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Reactive extraction complexes of aniline to D2EHPA or P507 in various diluents are obtained by fitting equilibrium models presented.