Transfer kinetics of phenol between aqueous phase and N, N-di(1-methyl-heptyl) acetamide in kerosene

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Abstract: The transfer kinetics of phenol between aqueous phase and N,N-di(1-methyl-heptyl) acetamide (N503) in kerosene has been studied using Lewis cell technique. The effects of the factors including the concentrations of phenol in aqueous phase and organic phase, the concentration of N503 in organic phase, the acidity of aqueous phase, the stirring speed and the temperature on the rates of forward and backward extraction of phenol have been examined. The regularity of extraction rate has been obtained. According to experimental results, the rates of both forward and backward extraction of phenol might be controlled by diffusion process. The diffusion step of phenol from aqueous phase to interface for forward extraction and from interface to aqueous phase for backward extraction might be the rate-controlling steps.

Key words: phenol; transfer kinetics; N,N-di(1-methyl-heptyl) acetamide

CLC number: X703  Document code: A

Introduction

The solvent extraction is one of the methods for treatment of high concentration waste water containing phenol (Koreman, 1978; Lanouette, 1977; Inoue, 1984; Inoue, 1986; Braun, 1986; Wang, 1992; 1997). In China the extractant used widely in many plants is the N,N-di(1-methyl-heptyl) acetamide (N503) and excellent decontamination efficiency has been proved (Shanghai Environmental Protect Agency, 1992; 1994; Li, 1993). The component of solvate and regularity of distribution equilibrium for this extraction system has been studied by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences (Shanghai Institute of Organic Chemistry, 1980). However there has been no report on the transfer kinetics of phenol between aqueous phase and N503 in kerosene.

In this paper, the rates of forward and backward extraction of phenol between aqueous solution and N503-kerosene were determined using Lewis cell technique. The effect of concentration of phenol in both aqueous phase and organic phase, and that of hydrogen ion in aqueous phase and N503 in organic phase, temperature and stirring speed on both the forward and backward extraction were examined. In addition, the component and infrared absorption spectroscopy of solvate were measured. The mechanisms for the transfer process of phenol between aqueous solution and N503-kerosene are discussed. The results obtained will be of benefit to the treatment of waste water containing phenol.

1 Materials and methods

1.1 Materials

N503 was a product from Shanghai Kechuan manufacture of organic chemical engineering, and the quality index is specific gravity \(d_4^{25} = 0.8364\), viscosity \(\eta(25\, ^\circ\text{C}) = 19.2\) c.p., boiling range 155 ± 5°C (1 mm), burning point 190°C, solubility in water <10 ppm. Kerosene was purified by distillation and 180—240°C distillate was collected for use. Phenol and other reagents were all A.
R. grade.

1.2 Extraction rate measurements

The Lewis cell technique was employed as described else where (You, 1988; Jia, 1989). In this experiment, volume (V) of both organic phase and aqueous phase were 60 ml, and starting the two-paddle stirrer the two phases were stirred respectively without disturbing the interface area (A) which was 15.9 cm². The temperature (T) was controlled by a thermostat jacket in which constant temperature water was recycling. In order to obtain the kinetic data, aqueous phase was recycling via a micro pump, and sampled at suitable times (t) from the silica rubber recycling tube, and the concentration of phenol in aqueous (C_{phenol}) was analyzed with 4-amino-antipyrine spectrophotometric methods. Linear regression analysis for C_{phenol}·t gives the slope of ΔC_{phenol}/Δt, and forward extraction rate (R_f) and backward extraction rate (R_b) are defined by

\[ R_f = \frac{-ΔC_{phenol} \cdot V}{A \cdot Δt} \quad (\text{mol}/(\text{s} \cdot \text{cm}^2)), \]

\[ R_b = \frac{ΔC_{phenol} \cdot V}{A \cdot Δt} \quad (\text{mol}/(\text{s} \cdot \text{cm}^2)). \]

Unless specified differently, the basic experimental condition was as follows: C_{phenol} = 1.06 \times 10^{-3} \text{ mol/L}, C_{NS53(O)} = 0.15 \text{ mol/L}, C_{phenol(O)} = 3.78 \times 10^{-3} \text{ mol/L}, \text{ pH} = 5.0, \text{ stirring speed} = 150 \text{ r/min}, \text{ T} = 30 \pm 0.2°C.

1.3 Determination of distribution ratio

A quantitative volume (10 ml) of aqueous phase and organic phase were placed in the stoppered glass tubes, which were shaken for 15 minutes at 30°C, then the two phases were separated. The concentration of phenol in aqueous phase were determined. The concentration in organic phase was obtained by reducing the equilibrium concentration of phenol in aqueous phase from initial concentration of phenol in aqueous phase and the distribution ratio was calculated.

2 Results and discussion

2.1 The effect of stirring speed on the extraction rate

The effect of stirring speed on the extraction rate is one of the evidence to judge rate-controlling type in solvent extraction when the kinetics are studied with Lewis cell technique. If the rate increases linearly with increasing stirring speed, it is usually considered the extraction process is controlled by diffusion. If there is a plateau of rate when the stirring speed is higher than certain value, it is usually considered that is controlled by chemical reaction. The extraction rate as a function of the stirring speed are shown in Fig.1. It can be seen that both the rates of forward and backward extraction increase with the increasing stirring speed, and when the speed is greater than 150 r/min, the rates' increase with the stirring speed slows up gradually, but no plateau of rate appears. Therefore, the extraction processes (both the forward and backward extraction) under the experimental condition may be controlled by diffusion. The reason that there is no definitely linear relation between the extraction rates and the stirring speed may be the thickness of the liquid membrane of the interface does not decrease linearly with the increasing stirring speed. In order to make sure the region in which the diffusion rate was controlled, the effect of single phase stirring speed on the extraction rates has been examined and the results are also shown in Fig.1. It can be seen that both the forward and backward extraction rates increase with increasing stirring speed of aqueous phase, and the varying trend of the curve is similar to that of double phase stirring. But the both change slightly with the increasing stirring speed of organic phase. So it is
considered that the diffusion resistance may mainly exist in the aqueous phase.

![Graph](image_url)

*Fig. 1* Effect of stirring speed on the extraction rates
- • double phase stirring
- ○ aqueous phase stirring
- × organic phase stirring

### 2.2 The effect of temperature on the extraction rates

The effect of temperature on the extraction rate is also one of the evidences to judge the controlling type of the extraction process. The effect on the extraction rate controlled by a chemical reaction is more obvious than that controlled by diffusion. *Fig. 2* gives the dependence of rates on the temperature. It shows that the temperature effect on the forward and backward extraction rates is not obvious. According to the Arrhenius equation and pseudo-first order reaction \( R_t = k_t' \cdot C_{\text{phenol}} \), \( R_b = k_b' \cdot C_{\text{phenol}(O)} \), linear regression analysis for \( 1g k_t' - 1/T \) and \( 1g k_b' - 1/T \) gives the apparent activation energies which are 14.3 kJ/mol for forward extraction and 24 kJ/mol for backward extraction respectively. This result is in accordance with above conclusion of diffusion controlling.

### 2.3 The effect of the concentrations of phenol on the extraction rates

*Fig. 3* gives the dependence of rates on the concentration of phenol in aqueous phase for forward extraction and in organic phase for backward extraction. It shows that the rates increase linearly with the increasing concentrations of phenol. The linear relationship for \( 1gR_t \) vs. \( 1gC_{\text{phenol}} \) gives a slope of 1.0 and that for \( 1gR_b \) vs. \( 1gC_{\text{phenol}(O)} \) is 0.98. That is to say the forward extraction rate is first order with respect to the concentration of phenol in aqueous phase and the backward extraction rate is first order with respect to the concentration of phenol in organic phase.

### 2.4 The effect of the concentration of N503 in organic phase on the extraction rates

The effect of the concentration of N503 in organic phase on the extraction rates is shown in *Fig. 4*. As is seen, the forward extraction rate increases slightly with the increasing concentration of N503 in organic phase, and linear regression analysis for \( 1gR_t - 1gC_{\text{N503(O)}} \) gives a slope of...
0.26; the backward extraction rate decreases obviously with the increasing concentration of N503 in organic phase, and linear regression analysis for $\log R_b - \log C_{N503(o)}$ gives a slope of $-0.82$. In order to contrast with the influence of the concentration of N503 on the distribution equilibrium, Fig.4 also shows the effect of the concentration of N503 on the distribution ratio. It shows that in a wide range the distribution ratio increases linearly with the increasing concentration of N503. Linear regression analysis gives a slope of 1, which indicates the solvate is $C_6H_5OH \cdot N503$.

2.5 The effect of the acidity in aqueous phase on the extraction rates

The extraction rates as a function of the acidity in aqueous phase are shown in Fig.5. It can be seen that the trend of the curve of the forward rate is reversed extraction with that of the backward extraction rate. When the pH value in aqueous phase is less than 10.5, there is no change of the rates. But when it is greater than 10.5, with the increasing pH value, the forward extraction rate decreases sharply while the backward extraction rate increases obviously. It is due to that the phenol is a weak acid whose $P_k_a$ is about 10. When pH value is greater than $P_k_a$, the phenol will dissociate obviously, which hinders the combination of phenol and N503 for forward extraction while facilitates the backward extraction.

2.6 Infrared absorption spectroscopy

Fig.6 is the infrared absorption spectroscopy of the solvate. As is seen, 0.15 mol/L N503-kerosene (Fig.6a) shows the characteristic absorption peak of the carbonyl group of substitutive amide at 1656.2 cm$^{-1}$ but when N503 is almost completely saturated by phenol (Fig.6b), the peak of 1656.2 cm$^{-1}$ diminishes obviously, and the characteristic absorption peak of combined carbonyl group appears at 1625.0 cm$^{-1}$, in
addition, the characteristic peaks of the benzene ring frame appears at 1606.2 cm\(^{-1}\), 1593.7 cm\(^{-1}\) and 1500 cm\(^{-1}\). So it verifies that the N503 combined with phenol molecule by hydrogen bond in extraction reaction.

### 3 Conclusions

According to experimental results obtained, the reaction formula in solvent extraction of phenol with N503 can be written as:

\[
C_6H_5\cdot OH + N503_{(O)} = C_6H_5OH \cdot N503_{(O)}.
\]

The rates of forward and backward extraction can be controlled by chemical reaction or diffusion process. Experimental data show that there is no rationally quantitative relation between rates of forward or backward extraction and the concentrations of components, the temperature effect on both forward and backward extraction rates is not obvious and the stirring speed affects the both obviously. Therefore, both the forward and backward extraction might be controlled by diffusion process under our experimental condition. Additional results of single stirring experiments indicate that the diffusion resistance mainly in the aqueous phase. So the diffusions of phenol from aqueous phase to interface for forward extraction and phenol obtained by dissociation of solvate from the interface to the aqueous phase for backward extraction might be rate-controlling step, respectively.

Therefore, it is necessary to applying the suitable condition in the treatment of waste water containing phenol with N503 solvent extraction. According to our experimental results, keeping pH value in aqueous phase less than 10.5, raising concentration of N503 in organic phase and stirring speed of aqueous phase, can raise the rate of forward extraction so as to obtain high cleaning efficiency.

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(Received for review October 20, 1998. Accepted December 7, 1998)