

# Extraction of phenol from wastewater by *N*-octanoylpyrrolidine

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Received 16 January 2004; received in revised form 7 July 2004; accepted 19 July 2004

Available online 27 September 2004

## Abstract

In this paper a new type of phenol extractant, *N*-octanoylpyrrolidine (OPOD), was synthesized. The behavior of phenol of wastewater extraction by *N*-octanoylpyrrolidine (OPOD) in kerosene was studied and the dependence of the extraction distribution ratios on the concentrations of extractant, phenol, acidity and temperature was investigated. The experimental results proved that OPOD could extract phenol effectively. The mechanism of the extraction of phenol by OPOD was studied in detail.

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**Keywords:** Wastewater treatment; *N*-octanoylpyrrolidine (OPOD); Solvent extraction; Phenol

## 1. Introduction

Phenols are present in waste water of various industries, such as refineries (6–500 mg/l), coking operations (28–3900 mg/l), coal processing (9–6800 mg/l), and manufacture of petrochemicals (2.8–1220 mg/l). Phenols are also the main organic constituents present in condensate streams in coal gasification and liquefaction processes. Other sources of waste stream water containing phenols are pharmaceutical, plastics, wood products, paint, and pulp and paper industries (0.1–1600 mg/l) [1]. Phenols are pollutants of high priority concerns because of their toxicity and possible accumulation in the environment [2].

During the review of technologies for treatment of synthetic organic compounds, especially phenols, phenolic wastewaters are usually treated by biodegradation, thermal decomposition and absorption. Under aerobic or anaerobic conditions, some aerobic bacteria and fungi utilize phenols as a source of carbon and energy, and can degrade it [3]. However, the major disadvantage of biological treatment is that the microorganisms cannot survive in high concentrations of phenol, e.g. more than 3000 mg/l. Furthermore, long time is

needed usually for degrading the phenol, e.g. more than 7 days. Thermal decomposition can be used to treat wastewater with concentrations of phenol as high as 15,000 mg/l, but it is only used in small scale for the high energy demand. Wet air oxidation, a typical thermal decomposition method, is usually operated at temperatures ranging from 200 to 330 °C and pressures ranging from 2 to 20 MPa [4,5]. So thermal treatment is not an economical effective method to phenol degradation. Absorption is an effective method of treating dilute phenolic wastewater [6–9]. However, for the relatively high cost of activated carbon or other sorbents, adsorption cannot be used to treat high concentrated phenolic wastewater.

The solvent extraction method has advantages on treating high concentrated phenol wastewater. Phenol has different solubility in extractants and water. In order to separate the phenol from wastewater, some extractants can be selected, in which the solubility of phenol is much higher than that in water. Distribution ratio is defined as the phenol concentration in wastewater to that in extractant. The key to promote the extraction efficiency is to enhance the distribution ratio. Alcohols, amines, and organic acids were applied as extractants in separation of phenol from the wastewater [10]. In this paper a new type of extractant (OPOD), was synthesized. The experimental results proved that OPOD could extract phenol

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effectively, and the distribution ratio was shown to be as high as 380 by pure OPOD. The mechanism of the extraction of phenol by OPOD was studied in detail.

## 2. Experimental

### 2.1. Synthesis of *N*-octanoylpyrrolidine and characterization

#### 2.1.1. Reagents and instruments

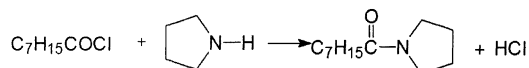
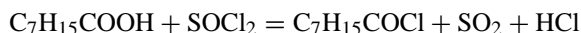
*N*-caprylic acid (Shanghai Chemical Reagents Company), Thionyl chloride (Shanghai Tingxin Chemical Plant), Pyrrolidine (Shanghai Chemical Reagents Company), Dichloromethane (Shanghai Chemical Reagents Company). The other reagents was of analytic purity.

IR spectrometer (Perkin-Elmer 577 spectrometer), NMR spectrometer (JEDLPS-100 NMR spectrometer), elemental analysis (Perkin-Elmer PE240C).

#### 2.1.2. Synthesis of *N*-octanoylpyrrolidine

OPOD has not been reported in the literatures. In this paper it was synthesized in our laboratory, the synthesis path is expressed as follows.

The Synthesis of octanoyl chloride referred to the literature [11]



The solution of octanoyl chloride (thionyl chloride solvent) was dripped slowly into pyrrolidine, then heated and circumfluented it for 8 h. The product was cleaned with water. The solvent was distilled, and the product was decompressed and distilled. We obtained OPOD.

#### 2.1.3. Characterization

The synthesized OPOD was analyzed by IR spectrometer, NMR spectrometer and elemental analysis. In the IR spectrum the characteristic absorption peak of C=O group is  $1647.1 \text{ cm}^{-1}$ . In the NMR spectrum the value of the chemical shift of protons was: 0.85 (CH<sub>3</sub>), 1.3–1.9 (CH<sub>2</sub>), 2.25 (CH<sub>2</sub>–CO) and 3.4 (CH<sub>2</sub>–N–CH<sub>2</sub>). The elemental analysis results of OPOD is N: 7.4%, C: 72.94%, H: 11.16%, which is approximately consistent with the calculated value (N: 7.11%, C: 73.1%, H: 11.68%). All these results indicate the structure and composition of the OPOD. The product was applied directly in the following extraction experiments.

## 2.2. Extraction test

### 2.2.1. Reagents and instruments

In the extraction experiments, sulfonated kerosene was chosen as solvent. Phenol was distilled. All other reagents used in experiments were analysis purity.

Model 752 spectrophotometer used for analysis of phenol was manufactured by Shanghai No. 3 Analytical Instrument Factory. Vibrator was manufactured by Jiangsu Yancheng Science Instrument Factory, and vibration frequencies was about 4.5 Hz. Temperature control was achieved in a cage and precision was about  $\pm 1 \text{ K}$ .

### 2.2.2. Experimental methods

OPOD was diluted with sulfonated kerosene. Extraction was carried out by shaking equal volumes of OPOD and phenol solution in a centrifugal tube at 298 K. After shaking 15 min, the distribution ratio was no more changed. The reaction reached the equilibrium. Phase disengagement was obtained by placing it for a while.

### 2.2.3. Analysis method

Phenol was analyzed by the  $\alpha$ -aminoantipyrin spectrophotometric method. A spectrophotometer at wavelength of 460 nm was used to determine phenol concentration. Phenol concentration in organic solution was calculated from the difference between total quantity and its quantity in aqueous solution.

## 3. Results and discussion

The influence of pH on the distribution ratio for phenol extraction by OPOD in kerosene was shown in Fig. 1. When pH less than 9, the pH value had small effects on the distribution ratio of phenol. The reason was that the acidic dissociation constant of phenol  $\text{p}K_a$  was 10, so phenol did not dissociate under the condition of  $\text{pH} < 10$ . When pH became higher than 9, the extraction distribution ratio decreased greatly due to phenol's dissociation. According to these results, in practical application, the extraction reaction should be conducted under the acidic condition. Meanwhile, using 10% NaOH to strip could achieve good extraction results. We separated the phenol with 10% NaOH from the oil phase effectively. And OPOD could be reused

$$[\text{OPOD}] = 0.06 \text{ mol/l}, \quad T = 298 \text{ K},$$

$$[\text{C}_6\text{H}_5\text{OH}] = 0.01 \text{ mol/l}$$

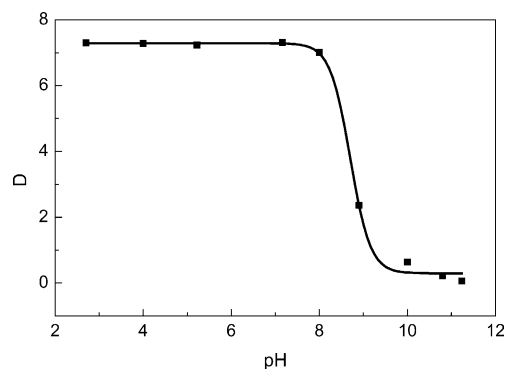


Fig. 1. The influence of pH on the distribution ratio for extraction phenol by OPOD in kerosene.

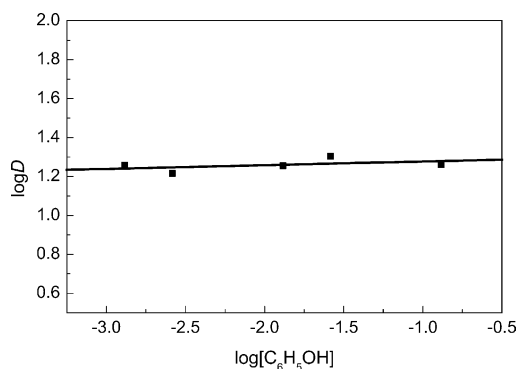


Fig. 2. Dependence of the distribution ratio of phenol on phenol concentration.

The composition of the extracted complex was deduced by the slope method. The extraction reaction in this system could be supposed as follows:



The acidic dissociation constant of phenol could be neglected because it was very small. The equilibrium constant of this reaction,  $K_{\text{ex}}$ , could be expressed as

$$K_{\text{ex}} = \frac{[m\text{C}_6\text{H}_5\text{OH} \cdot n\text{OPOD}_{\text{oil}}]}{[\text{C}_6\text{H}_5\text{OH}_{\text{aqueous}}]^m [\text{OPOD}_{\text{oil}}]^n} \quad (1)$$

The distribution ratio  $D$  could be expressed as

$$D = \frac{[m\text{C}_6\text{H}_5\text{OH} \cdot n\text{OPOD}_{\text{oil}}]}{[\text{C}_6\text{H}_5\text{OH}_{\text{aqueous}}]^m} \quad (2)$$

Eqs. (1) and (2) could be rearranged as

$$\log D = \log K_{\text{ex}} + (m - 1) \log [\text{C}_6\text{H}_5\text{OH}_{\text{aqueous}}] + n \log [\text{OPOD}_{\text{oil}}] \quad (3)$$

The distribution ratio dependence on phenol concentration was shown in Fig. 2, the concentration of OPOD was 0.2 mol/l.

In Fig. 2 the slope of the line  $\log D$  versus  $\log [\text{C}_6\text{H}_5\text{OH}]$  was approximately zero. In the same way, we extracted phenol by kerosene. The plot of  $\log D$  versus  $\log [\text{C}_6\text{H}_5\text{OH}]$  also gave a slope of zero. Because the distribution ratio of the extraction of phenol by kerosene was much smaller than that of by OPOD, the extraction of phenol by kerosene could be neglected. So in Eq. (3), we got  $m - 1 = 0$ ,  $m = 1$ .

$$[\text{OPOD}] = 0.2 \text{ mol/l,}$$

$$[\text{C}_6\text{H}_5\text{OH}] = 0.001 \sim 0.3 \text{ mol/l,} \quad T = 298 \text{ K}$$

The distribution ratio dependence on OPOD concentration was shown in Fig. 3. The concentration of phenol was 0.2 mol/l. The slope of the line  $\log D$  versus  $\log [\text{OPOD}]$  was 0.915, approximately equal to 1, which indicated  $n = 1$ . Therefore the extracted complex could be deduced to be  $\text{C}_6\text{H}_5\text{OH}$ ,  $K_{\text{ex}}$  was calculated to be 97.05.

$$[\text{C}_6\text{H}_5\text{OH}] = 0.01 \text{ mol/l,}$$

$$[\text{OPOD}] = 0.001 \sim 0.3 \text{ mol/l,} \quad T = 298 \text{ K}$$

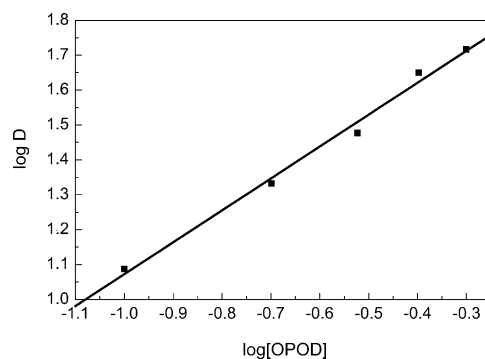


Fig. 3. Dependence of the distribution ratio of phenol on OPOD concentration.

In Fig. 4 the IR spectrum of the extracted complex was shown. The characteristic absorption peak of C=O group shifted from 1647.1 to 1593.5  $\text{cm}^{-1}$  after the extracted complex was formed. This result indicated that OPOD was coordinated with phenol through its C=O groups. The NMR spectrum showed the chemical shift of the hydroxyl proton in phenol increased to 9.12 ppm in the extracted complex, resulting from the effect of the intermolecular hydrogen bonding  $\text{C} = \text{O} \cdots \text{HO}$ . These results also indicated the extracted complex was  $\text{C}_6\text{H}_5\text{OH-OPOD}$ .

Extraction of 0.01 mol/l phenol with 0.2 mol/l OPOD at different temperatures was investigated. The result was shown in Fig. 5.

$$[\text{OPOD}] = 0.2 \text{ mol/l,} \quad [\text{C}_6\text{H}_5\text{OH}] = 0.01 \text{ mol/l}$$

In Fig. 5, the  $\log D$  increased linearly with  $1/T$ , which indicated that the extraction reaction was an exothermic reaction, and low temperature was beneficial to the extraction reaction.

As the distribution ratio  $D$  was in direct proportion to the equilibrium constant  $K_{\text{ex}}$ , The Clausius–Clapyron equation:

$$\frac{\partial \log K_{\text{ex}}}{\partial (1/T)} = -\frac{\Delta H^\circ}{2.303R} \quad (4)$$

can be rearranged as

$$\frac{\partial \log D}{\partial (1/T)} = -\frac{\Delta H^\circ}{2.303R} \quad (5)$$

In Fig. 5,  $\Delta H^\circ$  could be calculated to  $-13.15 \text{ kJ/mol}$ , which was similar to the bond energy of hydrogen bond. Therefore it could be considered that phenol was extracted into organic phase by forming a complex compound of hydrogen bond with OPOD.

According to thermodynamic equations:

$$\Delta G^\circ = -RT \ln K_{\text{ex}}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Gibbs free energy  $\Delta G^\circ$  was calculated to be  $-11.34 \text{ kJ/mol}$ , and  $\Delta S^\circ$  was calculated to be  $-6.07 \text{ J/mol K}$ .

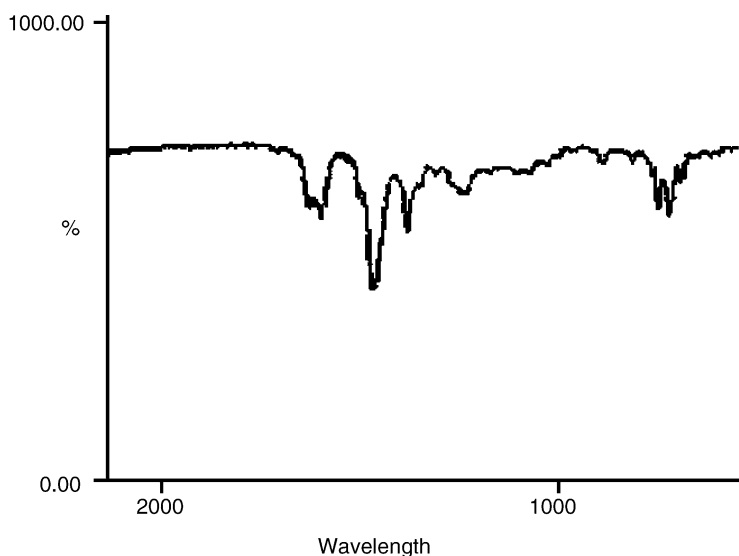


Fig. 4. The IR spectrum of the extracted complex  $C_6H_5OH \cdot OPOD$ .

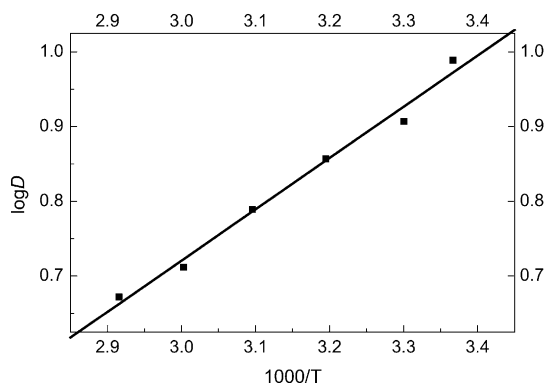


Fig. 5. The temperature effects on the distribution ratio.

#### 4. Conclusions

In this paper a new phenol extractant, *N*-octanoylpyrrolidine (OPOD), was synthesized. Under acidic condition, OPOD in sulfonated kerosene could extract phenol effectively. The structure of extracted complex could be deduced to be  $C_6H_5OH \cdot OPOD$ .

#### Acknowledgements

This work was financially supported by Shanghai-Applied materials research and development fund (project 0318) and Shanghai Committee of Science and Technology (Qimingxin project 03QB14017), China, which was gratefully acknowledged.

#### References

- [1] M.J. González-Muñoz, S. Luque, J.R. Álvarez, J. Coca, Recovery of phenol from aqueous solutions using hollow fibre contactors, *J. Membr. Sci.* 213 (2003) 181–193.
- [2] Y. Ku, K.-C. Lee, Removal of phenols from aqueous solution by XAD-4 resin, *J. Hazard. Mater. B* 80 (2000) 59.
- [3] M.M. Broholm, A. Erik, Biodegradation of phenols in a sandstone aquifer under aerobic conditions and mixed nitrate and iron reducing conditions, *J. Contamin. Hydro.* 44 (2000) 239–273.
- [4] J.L. Yu, E.S. Phillip, Phenol oxidation over  $CuO/Al_2O_3$  in supercritical water, *Appl. Catal. Part B: Environ.* 28 (2000) 275–288.
- [5] J.R. Portela, E. Nebot, E.M. Ossa, Kinetic comparison between subcritical and supercritical water oxidation of phenol, *Chem. Eng. J.* 81 (2001) 287–299.
- [6] F.A. Banat, B. Al-Bailey, S. Al-Asheh, O. Hayajneh, Adsorption of phenol by bentonite, *Environ. Pollut.* 107 (2000) 391–398.
- [7] V.M. Hebatpuria, A.H. Hassan, H.S. Rho, Immobilization of phenol in cement-based solidified/stabilized hazardous wastes using regenerated activated carbon: leaching studies, *J. Hazard. Mater.* 70 (1999) 117–138.
- [8] S. Rengaraj, S.H. Moon, R. Sivabalan, B. Arabindoo, V. Murugesan, Removal of phenol from aqueous solution and resin manufacturing industry wastewater using an agricultural waste: rubber seed coat, *J. Hazard. Mater.* 89 (2002) 185–196.
- [9] T. Viraraghavan, F.D.M. Alfaro, Adsorption of phenol from wastewater by peat, fly ash and bentonite, *J. Hazard. Mater.* 57 (1998) 59–70.
- [10] H. Jiang, Y. Fang, Y. Fu, Q.X. Guo, Studies on the extraction of phenol in wastewater, *J. Hazard. Mater. B* 101 (2003) 179–190.
- [11] S. Li, R. Fan, *Practical Handbook of Organic Chemistry*, Shanghai Science and Technology Publishing Company, 1981, p. 345.