ELSEVIER

Chemical Engineering Journal 88 (2002) 95–101

Chemical Engineering Journal

www.elsevier.com/locate/cej

# Separation of phenol from aqueous solutions by polymeric reversed micelle extraction

Y.D. Wang [a,*], Q. Gan [b], C.Y. Shi [a], X.L. Zheng [a], S.H. Yang [a], Z.M. Li [a], Y.Y. Dai [a]

[a] *Solvent Extraction Laboratory, Department of Chemical Engineering, The State Key Laboratory of Chemical Engineering, Tsinghua University, Beijing 100084, PR China*

[b] *Department of Chemical Engineering, The Queen's University of Belfast, Belfast, Northern Ireland, UK*

Received 4 January 1999; received in revised form 31 October 2001; accepted 7 November 2001

## Abstract

Polyoxyalkylene block copolymers consisting of hydrophilic poly(ethylene oxide) (PEO) and hydrophobic poly(propylene oxide) (PPO) or poly(butylene oxide) (PBO) have not attracted much attention until recent years. Variations of the molecular characteristics (PPO/PEO ratio, molecular weight) of the copolymer during the synthesis allows the production of molecules with optimum properties that meet the specific requirements in different areas. Our present interest is focused, on the formation of the reversed polymeric micelles, which are formed in 'oil' phases with PEO–PPO–PEO-type as well as PPO–PEO–PPO-type triblock copolymers. A novel process of polymeric reversed micelle extraction is subsequently proposed based upon the concepts of reversed micelle extraction and polymeric micelle extraction. Extraction equilibrium partition of phenol between polymeric reversed micelle solutions was investigated to study the extraction behaviors. PPO content, copolymer and co-surfactant types affected the extraction process.

*Keywords:* Block copolymer; Polymeric reversed micelles; Extraction; Solubilisation

## 1. Introduction

Surfactants have long been playing an important role in a wide variety of industries. They are amphiphilic molecules containing a nonpolar hydrophobic tail, usually a straight or branched hydrocarbon chain at one end, and a polar hydrophilic group which can be either nonionic, zwitterionic or ionic at the another end. As a result of the solvophobic association, these molecules are capable of forming a rich variety of structurally organized assemblies such as micelles and reversed micelles. Reversed micelle solutions consist of aggregates that are formed spontaneously by self-aggregation of surfactant molecules in organic solutions [1]. Water-soluble block copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) are macromolecular surfactants. Variations of the molecular characteristics (PPO/PEO ratio, molecular weight) of the copolymer during the synthesis allows the production of molecules with optimum properties that meets the specific requirements in different areas. A number of examples block copolymers were found to be able to form reversed micelle structures in organic solvents [2–22].

Alexandridis and Andersson [7] have shown that polyoxyalkylene block copolymers can form reversed micelles in organic phase. The solubilisation of water by these polymeric reversed micelles has been investigated. Wu et al. [8], Wu and Chu [9], have also reported the water-induced micelle formation of a PEO–PPO–PEO copolymer in *o*-xylene.

In this paper, We investigate experimentally the possibility of block copolymer reversed micelle formation. Our specific objective in this paper is to explore the potential for using PEO–PPO–PEO block copolymer reversed micelles in the solubilisation of water for the determination of the solution critical micellisation concentration (CMC) as well as $W_o$, which is defined as the molar ratio of water solubilised in polymeric reversed micelle solution to molar surfactant values. The fact that reversed micelles can solubilise relatively large amount of water can be used to determine the onset of polymeric reversed micelle formation. We then look into polymeric reversed micelle extraction process based on the concepts of reversed micelle extraction and polymeric micelle extraction. We investigate experimentally the possibility of bringing micelle phase and aqueous into direct contact, extraction of polar and water-soluble solutes by polymeric reversed micelles. Our specific objective is to study the distribution equilibrium of phenols between aqueous solution and polymeric reversed micelle solution.

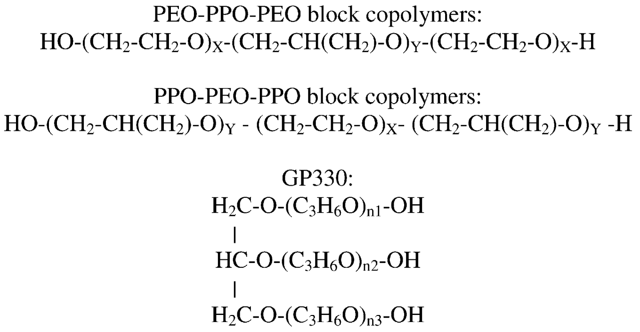
---

[*] Corresponding author.

*E-mail address:* wangyd@chemeng.tsinghua.edu.cn (Y.D. Wang).

1385-8947/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S1385-8947(01)00255-8

We describe the effect of polymer types and concentrations, co-surfactants on the equilibrium distribution. The effect of PPO content, polymer concentration, co-surfactant types and concentrations on the polymeric reversed micelle extraction process has also been discussed.



PEO-PPO-PEO block copolymers:
$HO\text{-}(CH_2\text{-}CH_2\text{-}O)_X\text{-}(CH_2\text{-}CH(CH_2)\text{-}O)_Y\text{-}(CH_2\text{-}CH_2\text{-}O)_X\text{-}H$

PPO-PEO-PPO block copolymers:
$HO\text{-}(CH_2\text{-}CH(CH_2)\text{-}O)_Y\text{ - }(CH_2\text{-}CH_2\text{-}O)_X\text{- }(CH_2\text{-}CH(CH_2)\text{-}O)_Y\text{ -}H$

GP330:
$$\begin{array}{l} H_2C\text{-}O\text{-}(C_3H_6O)_{n1}\text{-}OH \\ \quad | \\ HC\text{-}O\text{-}(C_3H_6O)_{n2}\text{-}OH \\ \quad | \\ H_2C\text{-}O\text{-}(C_3H_6O)_{n3}\text{-}OH \end{array}$$

Fig. 1. Schematic of the chemical structures of the polyoxyalklene block copolymers used in this study.

## 2. Experimental

### 2.1. Materials

Seven different polyoxyalkylene block copolymers were examined. The commercial notations of the copolymers, together with their nominal molecular masses, polyoxyethylene contents, and chemical formulas (calculated from the molecular masses and PPO contents), are listed in Table 1. Also tabulated there, are the hydrophilic–lipophilic balance (HLB) numbers and cloud point (CP) temperatures of the copolymers in aqueous solutions. Both HLB and CP are measures of the relative hydrophobicity of the amphiphilic polymers and depend on the copolymer PEO content, architecture, and molecular masses. The Pluronic® PE types of PEO–PPO–PEO as well as Pluronic® R types of PPO–PEO–PEO triblock copolymers were kindly supplied by BASF Corp., England, Chemicals Division of BASF in Washington DC, USA, and Shanghai Specialty Division, PR China. The chemical structures of the polyoxyalkylene block coploymers studied here are shown in Fig. 1. All copolymers were used as received.

### 2.2. Water solubilisation measurements

Water solubilisation experiments by polyoxyalklene block coploymers in organic solvent were adopted from Alexandridis and Andersson [7]. Copolymer-in-*p*-xylene solutions were prepared individually in the 0–40 wt.% copolymer concentration ranges. The samples were carefully sealed to avoid solvent evaporation. Water was titrated to the copolymer-in-oil solution in increments of 5–10 μl. Following the addition of each water drop, the samples were homogenized with shaker at 20 °C and left standing still for 20–30 min to equilibrate. When the resulting solutions were homogeneous and transparent, more water was added. The development in the samples of a persistently hazy or milky appearance after the addition of water was an indication that the maximum solubilisation was reached. Copolymer-in-*p*-xylene solutions of appropriate concentration were occasionally added to these hazy/milky samples in increments of less than 0.005 g in order to clear them up (by decreasing the water concentration) and ensure the reversibility of the phase separation. At the same time, the amount of water solubilised in the organic phase was also measured by Karl–Fischer titrator [24].

### 2.3. Particle size analysis of polymeric reversed micelles

The sizes of polymeric reversed micelles were measured by ZetaPlus Particle Sizer (Brookhaven Instruments, USA).

### 2.4. Equilibrium partitioning of phenol between water and polymeric reversed micelle solution

The extraction equilibrium experiments were performed by contacting equal volumes of polymeric reversed micelle solution with aqueous phenol solution with different concentrations in a conical flask in a water bath shaker at room temperature (25 ± 0.1 °C) for 1 h, at the vibration frequency of 200 rpm, then centrifuged for phase separation. After centrifugation, both phases were transparent with a distinct

Table 1
Physicochemical properties of copolymers

| Name | Formula | MW | Density (g/cm$^3$ (23 °C)) | PPO (wt.%) | Cloud point (°C)[a] | HLB[b] |
|---|---|---|---|---|---|---|
| PE6100 | $E_3P_{30}E_3$ | 2000 | 1.02 | 85 | 24 | 1–7 |
| PE6200 | $E_6P_{34}E_6$ | 2500 | 1.04 | 80 | 32 | 1–7 |
| PE6400 | $E_{13}P_{30}E_{13}$ | 2900 | 1.05 | 60 | 58 | 12–18 |
| PE9200 | $E_8P_{50}E_8$ | 3650 | 1.03 | 80 | 26 | 1–7 |
| 17R4 | $P_{14}E_{24}P_{14}$ | 2650 | 1.05 | 60 | 46 | 7–12 |
| 25R4 | $P_{19}E_{33}P_{19}$ | 3600 | – | 60 | 40 | 7–12 |
| GP330[c] | $P_{n1}P_{n2}P_{n3}$ | 3000 | 1.05 | 100 | – | – |

[a] Data were taken BASF product specifications.
[b] Hydrophilic–lipophilic balance; the HLB values for the pluronic copolymers were taken from BASF product specifications.
[c] Purchased from Jiangsu Haian Petrochemicals Plant, PR China.

phase boundary. The phenol concentration in the aqueous phase was measured by UV-visible spectroscopy (HP-8452 UV spectroscopy) [23]. The phenol concentration in the polymeric reversed micelle phase was then calculated by subtracting the initial phenol concentration with that of the aqueous one at equilibrium. The partition coefficient, $D$, was eventually calculated.

## 3. Results and discussion

### 3.1. Reversed micelle formation and CMC determination

Water solubilisation by triblock copolymers in organic solvents is used as an indication of polymeric reversed micelle formation and determination of CMC. The amount of water solubilised in copolymer-alkyl hydrocarbon solutions (expressed as $W_o$, i.e. moles of water solubilised per moles of copolymer) over a wide range of PE6200 and 25R4 concentrations is shown in Fig. 2. At low PE6200 and 25R4 concentrations, the ability of the PE6200 and 25R4 aromatic hydrocarbon solutions to take in water is very limited and the water solubilisation (expressed in moles of water per mole of copolymers) varies little with the PE6200 and 25R4 concentrations. A sharp increase in the water solubilisation capacity is observed at a certain PE6200 and 25R4 concentrations. This is indicative of the polymeric reversed micelle formation, which provides a hydrophilic microenvironment for water solubilisation. The copolymer concentrations at which water solubilisation increases abruptly vary with different types of copolymers. The solubilisation of water can thus be used to determine the CMC of amphiphilic block copolymers in organic solvents. This is similar to the use of the solubilisation of organic compounds for detecting micelle formation in aqueous solutions. The CMC for polymeric reversed micelles is then determined from the copolymer concentration at which the water solubilisation capacity starts to increase sharply as shown in Fig. 2.

Water solubilisation in polymeric reversed micelle solutions formed with different types of hydrocarbons is illustrated in Fig. 3. It has been noted that the water solubilisation capacity of polymeric reversed micelle solutions with aromatic hydrocarbons is much higher than that with straight chain alkyl hydrocarbons.

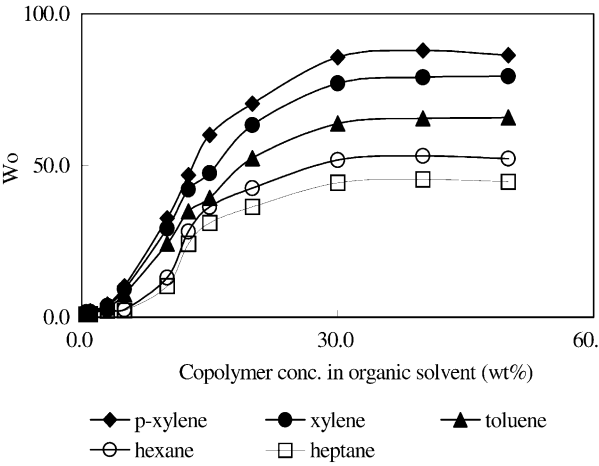


Fig. 3. Effect of organic solvents on polymeric reversed micelle formation and water solubilisation ability for 25R4/10%1-octanol/systems.

The particle size of copolymer-organic reversed micelle solutions over a wide range of copolymer concentrations has been measured using ZetaPlus particle sizer (Brookhaven Instrument Corporation). Typical result was given in Fig. 4. During the micelle size measurement, water was gradually added to different polymeric-solvent solutions. At low polymer concentrations, water solubilisation was very low and the micelle size was either small or unable to be detected. As polymer concentration increases, micelle size increases too so as the water solubilisation. The turning point of the micelle diameter in Fig. 5 is exactly the same as the water solubilisation experiments shown in Fig. 2. Therefore, both water solubilisation and micelle size measurement proves the existence of polymeric reversed micelles [24,25].

Temperature also affects the water solubilisation of the polymeric reversed micelle solutions [26]. Fig. 6 shows water solubilisation of PEO–PPO–PEO and PPO–PEO–

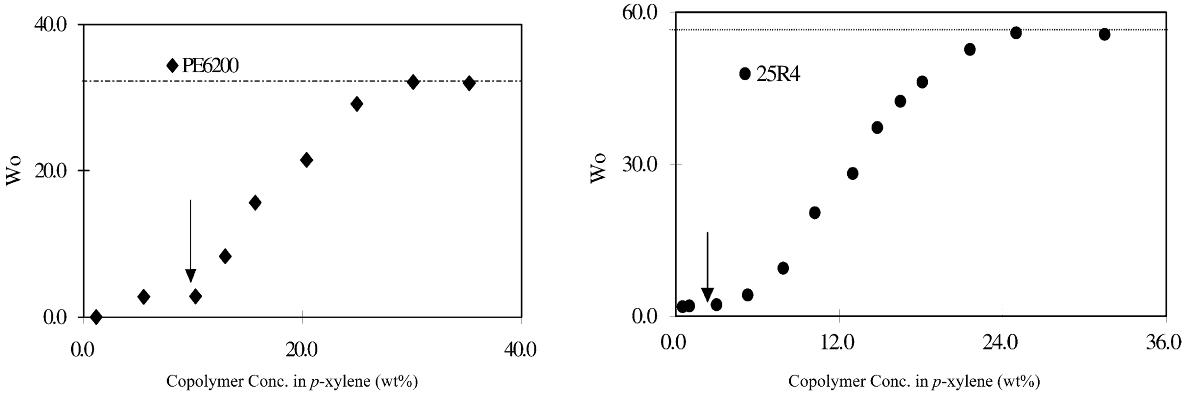


Fig. 2. Typical water solubilization curve of PEO–PPO–PEO (PE6200) and PPO–PEO–PPO(25R4) in $p$-xylene, plotted as $W_o$ to weight fraction of copolymer in $p$-xylene.

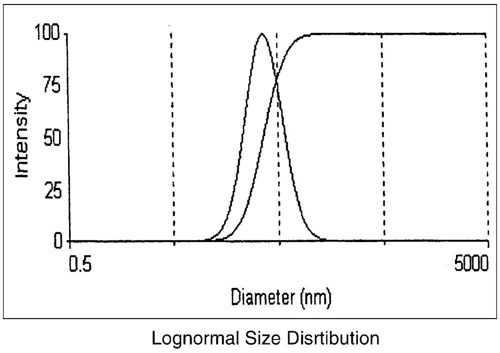


Fig. 4. Particle size distribution of PE6200/*p*-xylene micelle solution.

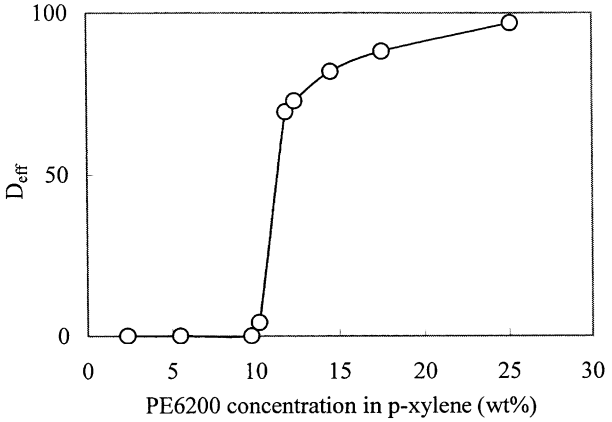


Fig. 5. Relationship between effective diameter of particle and copolymer concentration in PE6200/$H_2O$/*p*-xylene system.

PPO-types of copolymers at different temperature. As temperature increases, minimum polymer concentrations required for polymeric micelle formation in polymer-organic solvent solutions increase. In other word, CMC increases. A large amount of polymer is needed for polymeric reversed micelle formation.

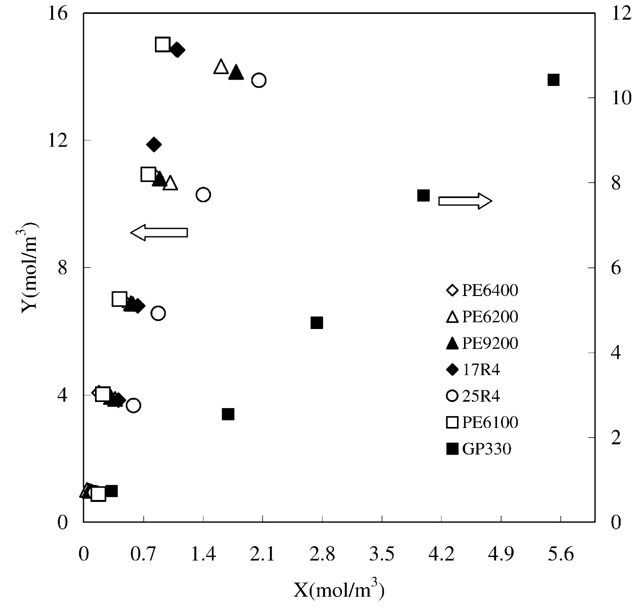


Fig. 7. Effect of copolymer type on equilibrium extraction partition of phenol between water and 10 wt.% copolymer-12.5 wt.% 1-octanol-*p*-xylene solution (*X*, equilibrium concentration of phenol in the aqueous phase; *Y*, equilibrium concentration of phenol in the organic phase).

### 3.2. Extraction of phenol from water to polymeric reversed micelles

Six copolymers, four types PEO–PPO–PEO (PE6100, PE6200, PE6400, and PE9200) and two PPO–PEO–PPO-types (17R4 and 25R4) as well as GP330 (100% of PPO) were used for phenol extraction. All copolymers have a weight concentration of 10 and 12.5 wt.% of 1-octanol was added into *p*-xylene. The results are illustrated in Fig. 7. The figure was plotted with phenol concentration in aqueous phase (*X*) against phenol concentration in polymeric reversed micelle phase (*Y*). A straight line was obtained for each extraction case. The slope of the line is defined as partition coefficient or distribution ratio of phenol between

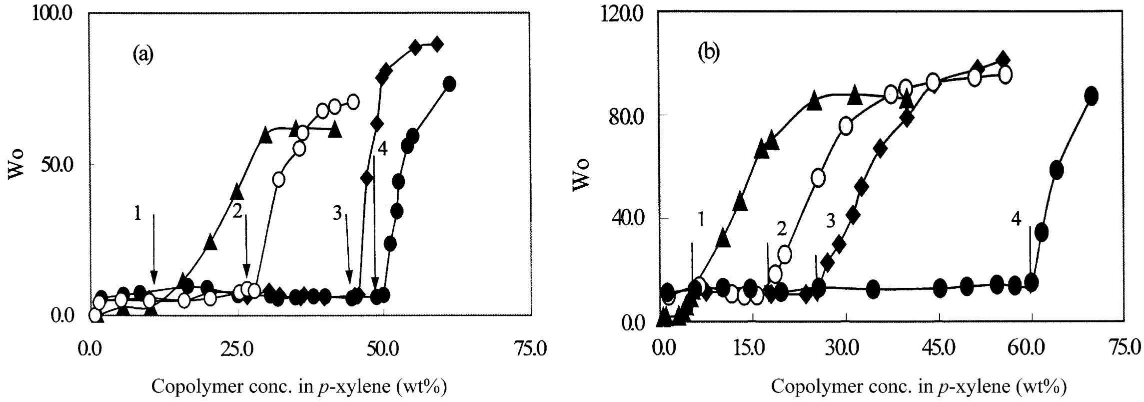


Fig. 6. Effect of temperature on water solubilisation: (a) PE6200/10%1-octanol/*p*-xylene system (1–20, 2–30, 3–35 and 4–40 °C); (b) 25R4/10% 1-octanol/*p*-xylene system (1–20, 2–30, 3–40 and 4–50 °C).

water and polymeric reversed micelle solution. It can be seen that PPO (or PEO) content, molecular weight and type of copolymer influence the extraction partitioning. Extraction of phenol in PE6100 polymeric reversed micelle solution (PPO content of 85 wt.%) exhibits highest partition coefficient. Reversed micelle solutions generated from PEO–PPO–PEO-type copolymers do not have much different equilibrium partition coefficients although they have different molecular weights and PPO contents. However, copolymers with high PPO content do have a slightly higher partition coefficient of phenol between aqueous phase and polymeric reversed micelle phase. This may contribute to the hydrogen bond interaction between copolymer and solute apart from the hydrophilic environment in the polymeric reversed micelle solutions. The later contributes most of the phenol loading in the solution. The hydrogen bond interaction between copolymer and solute only contributes a little as GP 330 (100% of PPO)/*p*-xylene solution has the lowest partition coefficient of phenol. Both 17R4 and 25R4 are PPO–PEO–PPO-type block copolymer. They have the same percentage of PPO content (60 wt.%). Extraction by polymeric reversed micelle solution formed with 17R4 (lower molecular weight and absolute PPO content) exhibits higher partition coefficient.

Fig. 8 shows the partition coefficient changes with copolymer concentration in *p*-xylene. The equilibrium partitioning of phenol in polymeric reversed micelle solution increases with the increase of copolymer concentration. The similar trends were also found in water solubilization and micelle diameter. The more water solubilized in polymeric micelle solution, the larger the micelle diameter and the more phenol extracted in the polymeric micelle solution.

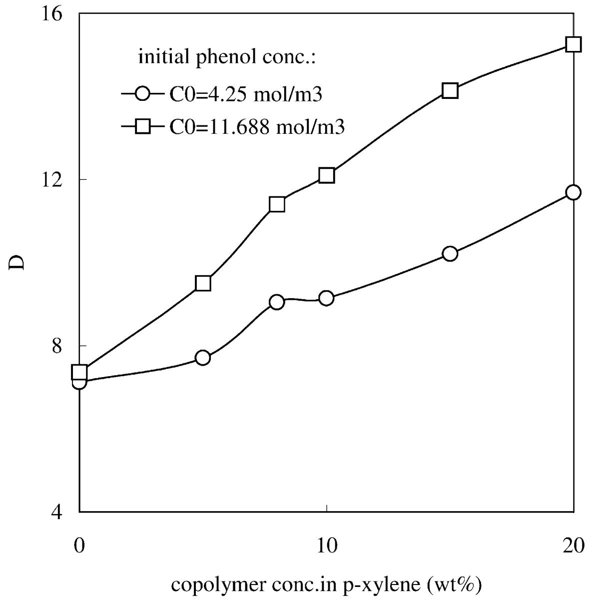


Fig. 8. Effect of polymer concentration on the extraction equilibrium partition of phenol in PE6100/10 wt.%1-octanol/*p*-xylene system.

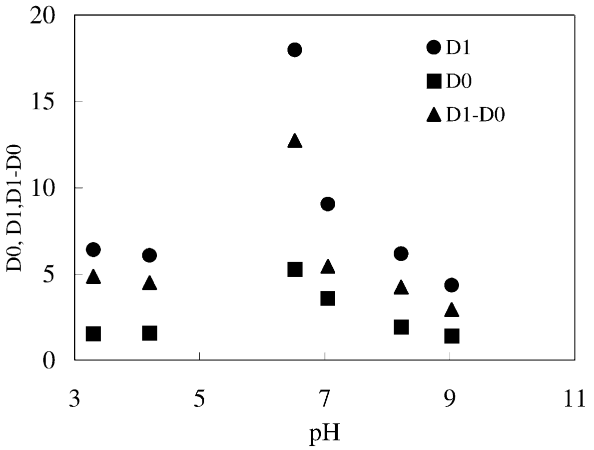


Fig. 9. Effect of the aqueous phase pH on equilibrium partition of phenol between water and 10 wt.% PE6100/10 wt.% 1-octanol/*p*-xylene reversed micelle solution.

Aqueous phase pH also influences the extraction equilibrium partitioning as indicated in Fig. 9. *D*1 is overall partition coefficient, *D*0 is partition coefficient without the copolymer and *D*1-*D*0 is the net increase of partition coefficient after copolymers were added to *p*-xylene solution. Sulfuric acid and sodium hydroxide were used to regulate pH of the aqueous phenolic solution. The highest extraction partitioning happened around $\mathrm{pH} = 6$ when phenol exists in a molecular form. When $\mathrm{pH} > 7$, salt was formed and phenol exists in a form of ion. Extraction partitioning dramatically decreases. At low pH value, extraction partition coefficient is small because of the high ionic strength.

Straight chain aliphatic alcohol (number of carbon atom in the alcohol $\geq 5$) can act as co-surfactants. Introduction of them into the polymeric reversed solution significantly affects reversed micelle formation, micelle diameter and the extraction equilibrium. Within the experimental range in this study, it is supposed that the contributions to the extraction partition coefficient by polymeric reversed micelle phase and co-surfactants are in coincidence with additivity. Before undertaking polymeric reversed micelle extraction, the extraction partitioning isotherms of phenol in 10 wt.% co-surfactant (1-pentanol, 1-hexanol, 1-heptanol and 1-octanol, 1-nananol and 1-decanol) in *p*-xylene solution, have been obtained. Then, the mixed solution of polymer-co-surfactant in *p*-xylene with PE6100 concentration of 10 wt.% made and the extraction partitioning isotherms were measured. The results were plotted in Fig. 10, with solid dots representing extraction using PE6100/co-surfactant/*p*-xylene solution and hollow dots representing extraction using co-surfactant/*p*-xylene solution. It was found that partition coefficient, *D*1, reached maximum when the number of carbon atom in alcohol was 7, i.e. when 1-heptanol was used as a co-surfactant. This is because the partition coefficient, *D*1, is not only affected by co-surfactant, but also

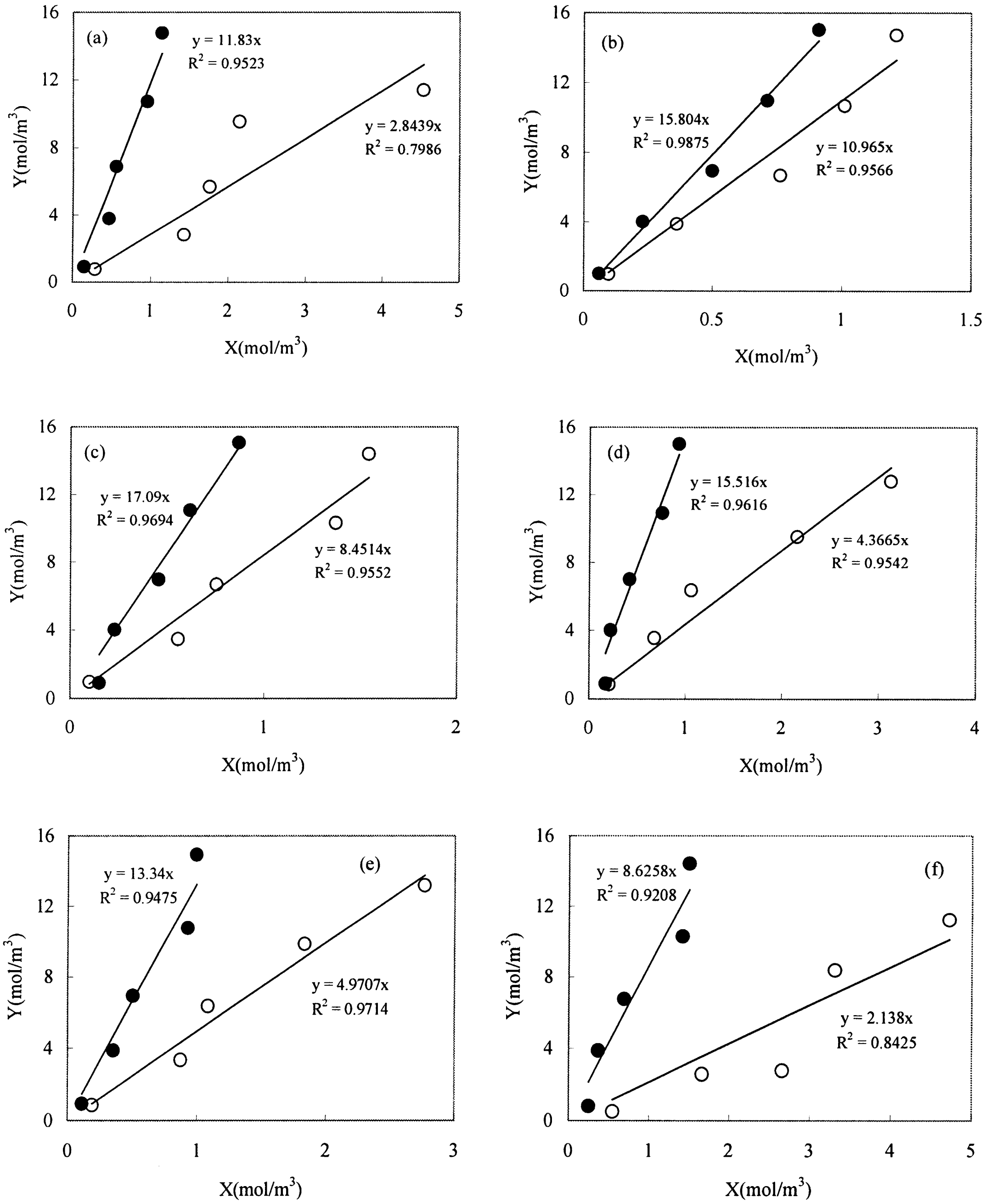


Fig. 10. Equilibrium partitioning of phenol between water and 10 wt.% PE6100-10 wt.% alkanol-*p*-xylene polymeric reversed micelles (*X*, equilibrium concentration of phenol in the aqueous phase; *Y*, equilibrium concentration of phenol in the organic phase); (○), extraction with 10 wt.% alkanol-*p*-xylene; (●), extraction with 10 wt.% PE6100-10 wt.% alkanol-*p*-xylene; (a) 1-pentanol; (b) 1-hexanol; (c) 1-heptanol; (d) 1-octanol; (e) 1-nananol; (f) 1-decanol.

by solubilization in polymeric reversed micelles. The addition of co-surfactants to the system improved the extraction capacity as well as the micelle formation. As the carbon atom number in co-surfactant increases, the net increase of partitioning, *D*1-*D*0, trends to increase. The addition of co-surfactants made the micelle volume increase, hence the solubilization of solute was improved. On the other hand, the partition coefficient of phenol by co-surfactant, *D*0, decreases as the carbon number in co-surfactant increases. These two adverse actions result in the appearance of a peak value at the carbon number of 7 (1-heptanol).

## 4. Conclusions

The polymeric reversed micelle formation by PPO/PEO/PPO triblock copolymers in various organic solvents and the water solubilisation in these systems are presented here.

The ability of the polymeric reversed micelles to solubilise water has been used to detect the formation of the polymeric reversed micelles and determine the copolymer CMC in organic solvent. Water solubilisation in polymeric reversed micelle solutions varies with different types of hydrocarbons, and is much higher with aromatic hydrocarbons than that with straight chain alkyl hydrocarbons.

Polymeric reversed micelle extraction has been proposed based on polymeric micelle extraction and reversed micelle extraction. This novel extraction process has been used to separate phenol aqueous solution. The results showed that polymeric reversed micelle extraction is affected by polymer composition and structure, and aqueous phase pH. The extraction process also strongly depends on the addition of co-surfactants, which affect the solubilisation of solute. A co-surfactant with long chain (6–8) is beneficial to extraction equilibrium partition.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China, No. 29290500 and 29836130, and was carried out in Solvent Extraction Laboratory of the State Key Laboratory of Chemical Engineering, PR China.

## References

[1] H.F. Eicke, Top Curr. Chem. 87 (1980) 85.
[2] K.A. Cogan, A.P. Cast, Macromolecules 23 (1990) 745.
[3] M.C. Barker, B. Vincent, Colloids Surf. 8 (1984) 297.
[4] P. Marie, Y. Callot, Macromol. Chem. 185 (1984) 205.
[5] A. Sikora, Z. Tuzar, Macromol. Chem. 184 (1983) 2049.
[6] C. Price, Pure Appl. Chem. 55 (1983) 1563.
[7] P. Alexandridis, K. Andersson, J. Phys. Chem. B101 (1997) 8103.
[8] G. Wu, Z. Zhou, B. Chu, Macromolecules 26 (1993) 2117.
[9] G. Wu, B. Chu, Macromolecules 27 (1994) 1766.
[10] A. Caragheorgheopol, J. Pilar, S. Schlick, Macromolecules 30 (1997) 2923.
[11] P. Alexandridis, U. Olsson, B. Lindman, J. Phys. Chem. 100 (1996) 280.
[12] P. Holmqvist, P. Alexandridis, B. Lindman, Macromolecules 30 (1997) 6788.
[13] P. Alexandridis, U. Olsson, B. Lindman, Macromolecules 28 (1995) 7700.
[14] P. Holmqvist, P. Alexandridis, B. Lindman, Langmuir 13 (1997) 2471.
[15] D. Izzo, C.M. Marques, Macromolecules 30 (1997) 6544.
[16] P. Alexandridis, U. Olsson, B. Lindman, Langmuir 14 (1998) 2627.
[17] P. Holmqvist, P. Alexandridis, B. Lindman, J. Phys. Chem. B 102 (1998) 1149.
[18] K. Khougaz, Z.S. Gao, A. Eisenberg, Langmuir 13 (1997) 623.
[19] J.R. Lopes, L. Watson, Langmuir 14 (1998) 750.
[20] L.R. Zhou, S. Schllick, Polym. Prepr. 37 (1996) 829.
[21] H. Mays, M. Almgren, W. Brown, Langmuir 14 (1998) 723.
[22] P. Alexandridis, K. Andersson, J. Colloid Interf. Sci. 194 (1997) 166.
[23] S.-H. Yang, Study on Properties of Extraction by Polymeric Reversed Micelles, M.Sc. Thesis, Tsinghua University, Beijing, China, 1996.
[24] Z.-M. Li, Study on Polymeric Reverse Micelle Formation and its Properties of Extraction, M.Sc. Thesis, Tsinghua University, Beijing, China, 1999.
[25] C.-Y. Shi, Study on Properties of Reverse Micelles by $EO_XPO_YEO_X$ and $PO_XEO_YPO_X$ Type Triblock Copolymer, M.Sc. Thesis, Tsinghua University, Beijing, China, 2000.
[26] C.-Y. Shi, Y.-D. Wang, Y.-Y. Dai, Q. Gan, Chinese J. Appl. Chem. 17 (2000) 581.