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Interfacial Behavior of Phase Transfer Catalysis of the Reaction between Potassium Thiocyanate and *p*-Nitrobenzyl Bromide with Crown Ethers as Catalysts[1]

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Abstract—A very simple and novel method is devised to study the mechanism of phase transfer catalysis (PTC) for a nucleophilic substitution reaction between potassium thiocyanate and p-nitrobenzyl bromide (*p*-NB); the mechanism of the nucleophilic substitution reaction is illustrated by characterizing the interfacial dilational viscoelastic properties of the crown ether catalysts and intermediates, which are closely related to the interfacial behavior of the species in the PTC reaction. The results obtained from this study can be used to infer the mechanism of the nucleophilic substitution reaction that uses 18-crown-6 (18C6) and dibenzo-18-crown-6 (DB18C6) as phase transfer catalysts. This mechanism begins with formation of the intermediates $[K \cdot \text{Crown ether}]^+$ and $[K \cdot \text{Crown ether}]^+SCN^-$ through mutual collisions between crown ethers and KSCN in the aqueous phase near the interface. Then the complex, $[K \cdot \text{Crown ether}]^+Br^-$, was obtained due to the collision between $[K \cdot \text{Crown ether}]^+SCN^-$ and *p*-NB in the organic phase near the interface and simultaneously the products were obtained.

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INTRODUCTION

Since Pedersen's first discovery in 1967 [1], crown ethers have been of great interest in many areas of science and technology including the chemistry of "host-guest" complexes, extraction, phase transfer catalysis, organic synthesis, analytical chemistry, biology, medicine, ecology, etc. [2, 3]. In particular, crown ethers have been widely used in recent decades as phase transfer catalysts in organic reactions and industrial processes due to their special structures and properties [4]. In a review on macrocyclic polyethers and their complexes, Pedersen and Frendsdorff listed some early examples of the use of crown ethers as phase transfer catalysts [5]. Stott and co-workers compared the catalytic activity of simple crown ethers used to catalyze two-phase nucleophilic substitution reactions between potassium thiocyanate and *p*-nitrobenzyl bromide (*p*-NB), with those of several series of substituted dibenzo and dicyclohexano crown ethers, and discussed the relationship between the structures of crown ethers and their catalytic performance. Their experimental results indicated that 18C6 binds ability of potassium cations 2.3-fold higher as compared to DB18C6, whereas 18C6 can only accelerate the reaction 1.4 times faster than DB18C6 [6]. In recent years, many new types of crown ether have been synthesized and used as phase-transfer catalysts [3, 7–10]. In contrast to the extensive synthetic applications of crown ethers, the detailed mechanisms of these processes are very controversial. It is well-known that the physicochemical properties of crown ethers are relevant not only in the two phases but also at interfaces between them. It is therefore very important for us to understand the mechanism of PTC in order to optimize applications of these systems and to determine the relevant kinetic and thermodynamic parameters. However, progress in this field has been rather slow for many years, mainly due to the lack of suitable experimental techniques. Traditional methods such as tension measurements have been employed to detect the phase transfer catalysts at air-water and aqueous-organic solvent interfaces [11, 12], but to what extent the interface tension is low enough to be advantageous to a reaction still needs further investigation. Rheological properties are the main characteristics of the dynamic properties of a film. There are two rheological properties of interfacial films, interfacial shears and dilational viscoelasticities. The interfacial shear property has been the most investigated viscoelastic property of liquid-liquid interface films in the past [13, 14]. However, it seems that shear deformations are connected mainly with the processes of structural reorganization which have been characterized by a broad and almost continuous spectrum of relaxation times. On the other hand, measurements of dynamic

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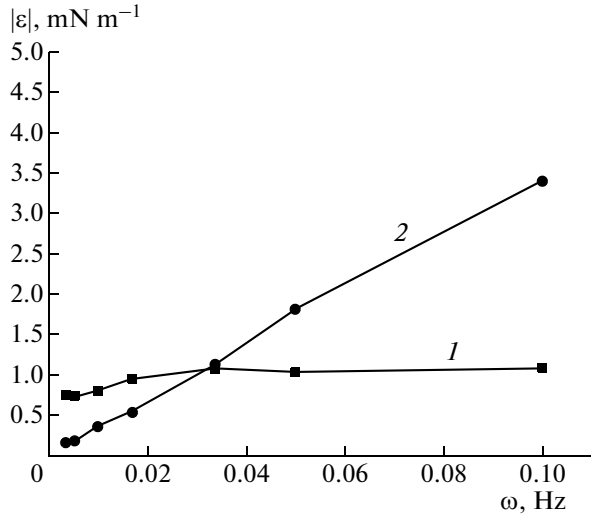


Fig. 1. Interfacial dilational moduli as a function of dilational frequency with 0.1 mmol/l crown ether dissolved in *n*-decane: (*1*) 18-crown-6 and (*2*) dibenzo-18-crown-6.

dilational viscoelasticity can be used to study each single chemical and physical process in the system and can provide more information on the dynamics of the surfactant molecules at the interfaces [15]. In our previous study, we investigated the interfacial behavior of quaternary ammonium bromides as phase transfer catalysts for reactions initiated by hydroxide ion by means of the interfacial tension response to sinusoidal area variations [16]. The results are in good agreement with Rabinovitz's experimental results [17].

In the present work, a very simple and novel method is devised to study the mechanism of phase transfer catalysis (PTC) for a nucleophilic substitution reaction between potassium thiocyanate and *p*-NB; the mechanism of the nucleophilic substitution reaction is illustrated by characterizing the interfacial dilational viscoelastic properties of the crown ether catalysts and intermediates, which are closely related to the interfacial behavior of the species in the PTC reaction. The results obtained from this study can be used to infer the mechanism of the nucleophilic substitution reaction that uses crown ethers as phase transfer catalysts.

EXPERIMENTAL

The 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane, abbreviated as 18C6, ≥99%) and dibenzo-18-crown-6 (2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene, abbreviated as DB18C6, ≥98%) were purchased from Yiri Chemical Science and Technology Co., Ltd., Shanghai, China, and used as received. *n*-Decane was supplied from Regent Chemicals Co., Ltd., Tianjin, China. Potassium thiocyanate (≥98.5%) was acquired from Sinopharm Chemical Reagent Co., Ltd., China. *p*-Nitrobenzyl bromide (*p*-NB, 99%) was obtained from Special Chemicals Co., Ltd. Chloroform (≥99.0%) was purchased from Shenyang Chemical Reagent Factory, China. Other chemicals, unless specified, were all of reagent grade and used without further purification. High purity water with resistivity higher than 18.0 MΩ cm was used in all the preparations.

An interfacial dilational viscoelasticity meter JMP2000A (Powereach Ltd., Shanghai, China) which has been described elsewhere [18–20], was employed. The working principle is similar to that reported by Lucassen and Giles [21]. The dilational rheology gives a measure of the interfacial resistance to changes in area. The interfacial dilational modulus ε at a particular frequency is characterized by its absolute value |ε| and by a phase angle θ describing the phase difference between dynamic interfacial tension variation and interfacial area variation.

$$\varepsilon \equiv \frac{d\gamma}{d\ln A} = |\varepsilon|\exp(i\theta), \quad (1)$$

where ε is the dilational modulus, γ is the interfacial tension, θ is phase angle, and A is the area of the interface. When a relaxation process takes place at or near the interface as a result of a disturbance, the interface will exhibit viscoelastic rather than pure elastic behavior. Dilational modulus can also be expressed as the summation of elastic and viscosity contribution.

$$\varepsilon = \varepsilon_d + i\omega\eta_d, \quad (2)$$

where the real part (storage modulus) represents the elastic energy stored in the interface and is known as the dilational elasticity ε_d, and the imaginary part (loss modulus) may be expressed in terms of the interfacial dilatonal viscosity η_d, because it accounts for the energy dissipated in the relaxation process [15, 21].

In order to probe the dilational viscoelasticty of an interfacial film, a Langmuir trough with a pair of polytetrafluoroethene barriers was used. In the interfacial dilational viscoelasticity measurements, the interface areas can be changed in a sinusoidal oscillation mode by horizontal sliding of the barriers. Dynamic interfacial tensions were measured by the Wilhelmy plate method, using a platinum plate suspended in the middle of a trough with a sensitive force transducer. 18C6, DB18C6, or *p*-NB was dissolved in *n*-decane as the oil phase. KSCN was added to deionized water to act as the aqueous phase. The aqueous phase (90 ml) and the oil phase (50 ml) were poured carefully one after the other into the trough. The Wilhelmy plate was completely submerged under the surface of the oil phase. The dilational viscoelasticity experiment was begun

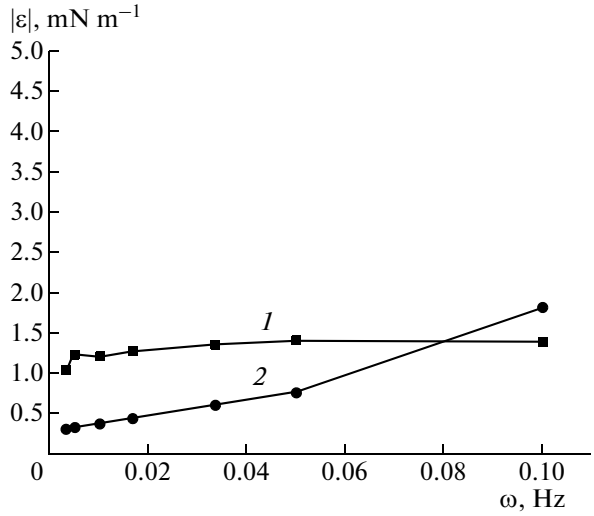


Fig. 2. Interfacial dilational moduli as a function of dilational frequency with 0.1 mmol/l crown ether and 13.9 mmol/l KSCN dissolved in *n*-decane and water, respectively: (*1*) 18-crown-6 + KSCN and (*2*) dibenzo-18-crown-6 + KSCN.

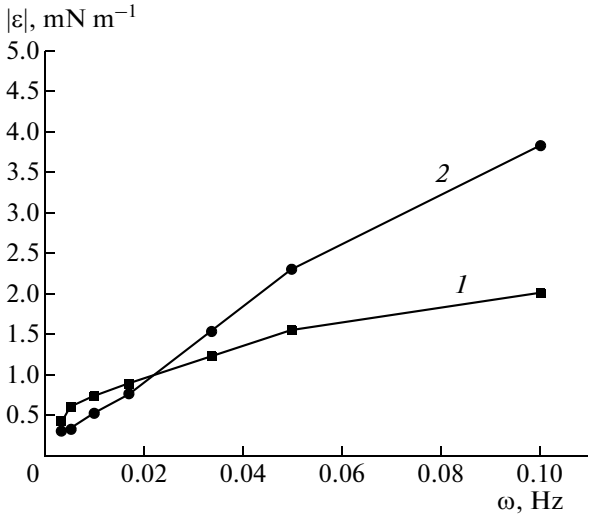


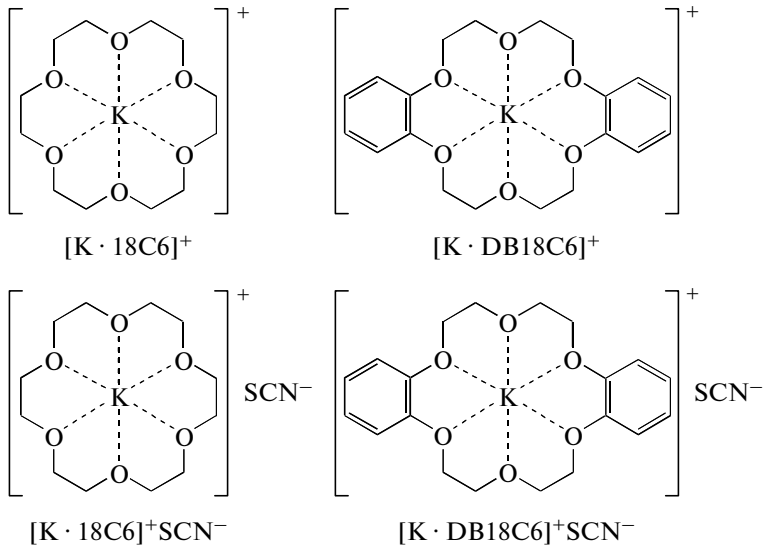
Fig. 3. Interfacial dilational moduli as a function of dilational frequency with 0.1 mmol/l crown ether and 3.8 mmol/l *p*-NB dissolved in *n*-decane as well as 13.9 mmol/l KSCN dissolved in water: (*1*) (18C6 + *p*-NB)–KSCN and (*2*) (DB18C6 + *p*-NB)–KSCN.

after 6 h of pre-equilibrium of the oil-water system at 35°C.

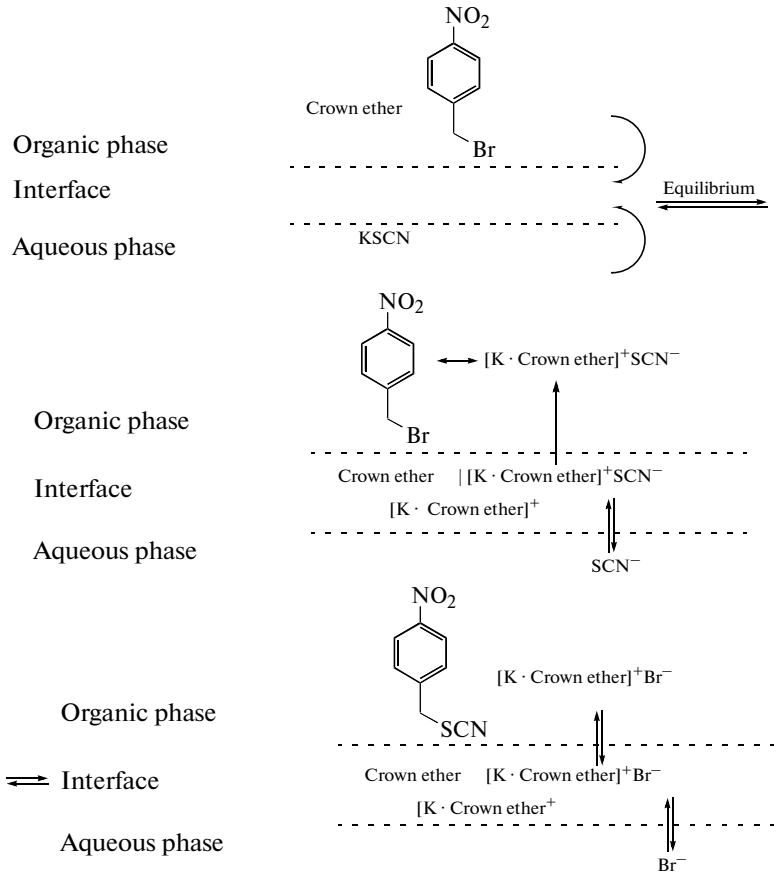
RESULTS AND DISCUSSION

The typical dependence of the interfacial dilational moduli of the crown ethers on the dilational frequencies is shown in Fig. 1. It can be clearly seen from these experimental results that the curve of the plot of |ε| versus ω in the presence of DB18C6 exhibits a greater slope than that in the presence of 18C6. By recalling the fact that a greater slope arises because more surface-active substances diffuse from the bulk towards a interface newly formed to repair the interfacial tension gradient caused by an interface deformation [22], it can be inferred that the proportion of DB18C6 diffusing from bulk phase to interface newly formed is greater than that of 18C6 when the interface was destroyed. The values of the dilational moduli of DB18C6 decreased with the dilational frequencies. This is because the DB18C6 molecules have enough time to diffuse from the bulk and interface to the interface newly formed to repair the interfacial tension gradient resulting from the change of interfacial area when the speed of interfacial deformation is slow. Thus the interfacial dilational moduli decrease with dilational frequency. The values of the dilational moduli of 18C6 change slightly with the dilational frequencies, showing the character of an elastic film and indicating that 18C6 diffuses mainly from the interface to interface newly formed to repair the interfacial film when the interface was destroyed. The speed with which 18C6 diffuses from interface to interface newly formed is high, thus the values of the dilational moduli change only slightly with dilational frequency. These results suggest that a greater quantity of 18C6 would settle at the interface through diffusion and arrangement over a long pre-equilibrium time, whereas a greater quantity of DB18C6 would remain in the organic phase. Thus there is a greater probability of mutual collisions between 18C6 and potassium cations dissolved in the aqueous phase than there is with DB18C6; this may explain the fact that 18C6 binds potassium cations 2.3 times better than DB18C6 [6]. According to Stott [6], the binding ability of crown ethers had strong effects on catalyst performance, so the rate of the nucleophilic substitution reaction between potassium thiocyanate and *p*-NB by using 18C6 as phase transfer catalyst is higher than that of DB18C6.

The interfacial dilational moduli versus the dilational frequency in the presence of the crown ethers and KSCN are shown in Fig. 2. The curves of the plots of |ε| versus ω in the presence of crown ethers and KSCN exhibit a different slope to those with only crown ethers as in Fig. 1. The results imply that new intermediates, namely the coordination compounds of crown ethers and K^+ ($[K \cdot \text{Crown ether}]^+$) and known as "crown ether salt", and the complex of crown ether salt and SCN^- ($[K \cdot \text{Crown ether}]^+SCN^-$), were formed through mutual collisions between the crown ethers and KSCN (see Scheme 1). In comparison with the result in the presence only of 18C6 (Fig. 1), it is found that the interfacial dilational moduli in the presence of both 18C6 and KSCN have slightly higher values (Fig. 2). This is due to the fact that the intermediates $[K \cdot 18C6]^+$ and



Scheme 1. Schematic representation of structures of the "crown ether salt" and the complex of crown ether salt and SCN^-.



Scheme 2. The mechanism of the nucleophilic substitution reaction inferred from the data of the interfacial dilational properties.

$[K \cdot 18C6]^+SCN^-$, as well as 18C6, coexist on the interface; the $[K \cdot 18C6]^+$ ion should be more regularly arranged because of the mutual electrostatic repulsion from its positive charge, resulting in an increase of the intensity of the interfacial film and higher values of the interfacial dilational moduli. The curve of the plot of $|\varepsilon|$ versus ω in the presence of DB18C6 and KSCN in Fig. 2 exhibits lower values of the dilational moduli and slope than that in the presence of DB18C6 alone (Fig. 1). It can be inferred that the formation of the intermediates, $[K \cdot DB18C6]^+$ and $[K \cdot DB18C6]^+SCN^-$, leads to a decrease of the quantity of DB18C6 both at the interface and in the organic phase. Moreover, $[K \cdot DB18C6]^+$ is easier to condense on to the interface due to its stronger hydrophilicity compared with DB18C6, so there are more $[K \cdot DB18C6]^+$ to diffuse from the interface towards a interface newly formed and less DB18C6 diffuses from the bulk phase towards a interface newly formed to repair the interfacial film when the interface has been destroyed. In this repairing of the destroyed interface becomes faster and so exhibits lower values of the dilational moduli and slope.

The curves of the plots of $|\varepsilon|$ versus ω in the presence of crown ethers and all of the reactants are shown in Fig. 3. Comparing the results in the presence of the crown ethers and KSCN in Fig. 2, it is clear that the curves of the plots of $|\varepsilon|$ versus ω in the presence of the crown ethers and all reactants exhibit higher slopes, indicating that new surface-active substances, i.e., $[K \cdot 18C6]^+Br^-$ and $[K \cdot DB18C6]^+Br^-$, were formed when all reactants were present in the system. It is believed that the degree of ionization of $[K \cdot 18C6]^+Br^-$ and $[K \cdot DB18C6]^+Br^-$ in the organic phase is lower than that of the relevant SCN^- complexes $[K \cdot 18C6]^+SCN^-$ and $[K \cdot DB18C6]^+SCN^-$. Thus the concentrations of $[K \cdot 18C6]^+Br^-$ and $[K \cdot DB18C6]^+Br^-$ in the organic phase are higher, and there are more $[K \cdot 18C6]^+Br^-$ and $[K \cdot DB18C6]^+Br^-$ species diffusing from the bulk towards a interface newly formed when the interface has been destroyed, making the curves of the plots of $|\varepsilon|$ versus ω exhibit higher slopes.

It is worth noting that the values of the dilational moduli for DB18C6 are lower than those for 18C6 in low dilational frequencies (Figs. 1–3). However, the opposite is true for high dilational frequencies. This may indicate that diffusion between the interface and the bulk predominates the interfacial dilational viscoelasticities in the case of DB18C6, while the rearrangement at the interface plays the important role in the case of 18C6. This may account for the fact that although 18C6 binds potassium cations 2.3 times better than DB18C6, 18C6 can only accelerate the reaction 1.4 times faster than DB18C6 [6]. Thus, it can be inferred that not only the binding ability of crown ethers but also the interfacial behavior of crown ethers has an effect on the catalysis performance.

CONCLUSIONS

Our results have shown that interfacial dilational properties can provide information on interfacial interaction and the structure of films and give insights onto the mechanism of the chosen nucleophilic substitution reaction. This mechanism begins with formation of the intermediates $[K \cdot \text{Crown ether}]^+$ and $[K \cdot \text{Crown ether}]^+SCN^-$ through mutual collisions between crown ethers and KSCN in the aqueous phase near the interface. Then the complex, $[K \cdot \text{Crown ether}]^+Br^-$, was obtained due to the collision between $[K \cdot \text{Crown ether}]^+SCN^-$ and *p*-NB in the organic phase near the interface and simultaneously the products were obtained (as shown in Scheme 2).

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REFERENCES

1. Pedersen, C.J., *J. Am. Chem. Soc.*, 1967, vol. 89, p. 2495.
2. Gokel, G.W., Leevy, M.W., and Weber, M.E., *Chem. Rev.*, 2004, vol. 104, p. 2723.
3. Shishkina, S.V., Shishkin, O.V., Grygorash, R.Ya., Mazepa, A.V., Rakipov, I.M., Yakshin, V.V., Kotlyar, S.A., and Kamalov, G.L., *J. Mol. Struct.*, 2007, vol. 832, p. 199.
4. Naik, S.D. and Doraiswamy, L.K., *AIChE J.*, 1998, vol. 44, p. 612.
5. Pedersen, C.J. and Frensdorff, H.K., *Angew. Chem., Int. Ed. Engl.*, 1972, vol. 11, p. 16.
6. Stott, P.E., Brandshaw, J.S., and Parish, W.W., *J. Am. Chem. Soc.*, 1980, vol. 102, p. 4810.
7. Yamato, K., Bartsch, R.A., Broker, G.A., Rogersb, R.D., and Dietzc, M.L., *Tetrahedron Lett.*, 2002, vol. 43, p. 5805.
8. Yamato, K., Fernandez, F.A., Vogel, H.F., Bartscha, R.A., and Dietzc, M.L., *Tetrahedron Lett.*, 2002, vol. 43, p. 5229.
9. Maia, A., Landini, D., Leska, B., and Schroeder, G., *Tetrahedron Lett.*, 2003, vol. 44, p. 4149.
10. Leska, B., Pankiewicz, R., Schroeder, G., and Maiab, A., *J. Mol. Catal. A: Chem.*, 2007, vol. 269, p. 141.
11. Azizian, S., Kashimoto, K., Matsuda, T., Matsubara, H., Takiue, T., and Aratono, M., *J. Colloid Interface Sci.*, 2007, vol. 316, p. 25.
12. Zeng, Y.H., Lu, X.F., and Du, W.Y., *Acta Chem. Sin.*, 2000, vol. 58, p. 34.

13. Lee, H.O., Jiang, T.S., and Avramidis, K.S., *J. Colloid Interface Sci.*, 1991, vol. 146, p. 90.

14. Xia, L.X., Li, M.Y., Gu, P.X., Cao, G.Y., Lu, S.W., and Liu, Q., *Colloids Surf., A,* 2004, vol. 247, p. 85.

15. Wang, Y.Y., Dai, Y.H., Zhang, L., Luo, L., Chu, Y.P., Zhao, S., Li, M.Z., Wang, E.J., and Yu, J.Y., *Macromolecules*, 2004, vol. 37, p. 2930.

16. Xia, L.X., Tong, S.R., Jiang, Y., Jia, Y., and Wang, J., *Colloids Surf., A*, 2008, vol. 317, p. 747.

17. Rabinovitz, M., Cohen, Y., and Halpern, M., *Angew. Chem., Int. Ed. Engl.*, 1986, vol. 25, p. 960.

18. Sun, T.L., Zhang, L., Wang, Y.Y., Zhao, S., Peng, B., Li, M.Y., and Yu, J.Y., *J. Colloid Interface Sci.*, 2002, vol. 255, p. 241.

19. Wang, Y.Y., Zhang, L., Sun, T.L., Zhao, S., and Yu, J.Y., *J. Colloid Interface Sci.*, 2003, vol. 270, p. 163.

20. Xia, L.X., Wang, Y.Y., Luo, L., Zhang, L., Cao, G.Y., Zhao, S., Lu, S.W., Liu, Q., and Yu, J.Y., *Colloids Surf., A*, 2006, vol. 289, p. 53.

21. Lucassen, J. and Giles, D., *J. Chem. Soc., Faraday Trans.*, 1975, vol. 71, p. 217.

22. Tempel, M. and Lucassen-Reynders, E.H., *Adv. Colloid Interface Sci.*, 1983, vol. 18, p. 281.