Studies on the effect of surfactants on the extraction rate by laser thermal lens spectrometry

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The effect of different kinds of surfactants on the extraction process of Nile Blue-I^- was investigated by laser thermal lens spectrometry. It was shown that the surfactants could accelerate or decelerate the extraction rate by varying the extractive's solubility and the interfacial tension of the extraction solution. The higher the concentration of surfactants was, the more obvious the effect.

Keywords Surfactant, extraction rate, thermal lens spectrometry

Surfactant can form micelles in a solution, which changes the physical and chemical characteristics of the solution, and leads to the reduction of the interfacial tension of the extraction solution and the enhancement of the extractive's solubility. So far, lots of papers on the application of micelle in liquid-liquid extraction have been reported.

It is important for the mineral separation, petroleum chemical industry and atomic energy industry *etc*. to study the extraction process. Many methods have been applied to study the extraction process, such as partition equilibrium method, two-phase titration method and so on.[1] However, the methods must determine the concentration in organic and aqueous phase, respectively and then calculate the distribution ratio in the solution. Nyma,[2] Fourre,[3] Richard[4] have studied the effect of micelles on the extraction process of some extraction systems and have given some meaningful results, respectively. Laser thermal lensspectrometry (TLS) is a high sensitive trace-analysis method.[5] In this paper, the extraction system of Nile Blue-I^- ion-pair was chosen as a model. The effect of different kinds of surfactant on the extraction rate was investigated by TLS as an on-line detection method and some results were given. These surfactants included: cetyl pyridinium bromide (CPB), octyl phenoxy polyethoxy ethanol (OP), triton X-100 (TX-100), sodium dodecyl benzene sulfonate (SDBS) and sodium dodecyl sulfonate (SDS).

Experimental

Apparatus

The instrument of Laser thermal lens spectrometry used in this experiment has been described in detail elsewhere.[6] A single mode He-Ne Laser ($\lambda = 632.8$ nm) acts as both exciting and probing beam. After being modulated and focused, the laser beam irradiates on the layer near $CHCl_3$-water interface in extraction and measurement cell. The TLS signals produced in the extraction solution systems were detected and processed by a photoelectric device and an M1052 lock-in amplifier. The results were recorded.

Reagents

Nile Blue stocking solution (12.0 μg/mL): The Nile Blue stocking solution was obtained by dissolving 1.20 mg Nile Blue in 100 mL of distilled water.

Nile Blue solution (4.80 μg/mL): 10.00 mL of Nile Blue stocking solution was diluted further to 25.00 mL containing 2.50 mL of HCl (pH = 1).

Nile Blue-surfactant (TX-100, OP, SDBS, SDS) solutions: 4.00 mL of Nile Blue stocking solution was

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diluted to 10.00 mL containing 1.00 mL of HCl (pH = 1) and certain volume of 0.5% surfactant solution.

CPB-$CHCl_3$ solutions (2.0%, 0.5%, 0.1% CPB), surfactant (TX-100, OP, SDBS, SDS) solutions and KI solution (0.05 mol/L) were prepared in the experiment.

All reagents used were of analytical grade. The distilled water was used in the experiment.

Procedure

2.00 mL of $CHCl_3$ and 1.00 mL of Nile Blue-surfactant solution (or 2.00 mL of CPB-$CHCl_3$ and 1.00 mL of Nile Blue solution (4.80 μg/mL)) were added in the extraction and measurement cell. Then 10 μL of KI solution was injected precisely into the cell. The signal change of TLS with time at the layer near $CHCl_3$-water interface in the cell was detected and recorded as S_{TLS}. In the meantime, the TLS signal of the blank solution (without surfactant) was detected and recorded as B_{TLS}. The S_{TLS} was divided by B_{TLS} and taken as the extraction ratio E_{TLS}% (S_{TLS}/B_{TLS}).

Results

The surfactants form the micelles in the determined solution, which change the thermal physical properties of the solution and affect the signals of the TLS. The result was described previously.[7,8] The affection has been corrected in order to study the effect of the surfactants on the extraction rate in the experiment.

The effects of different kinds of surfactant on the extraction system of Nile Blue-I^- were investigated and summarized as follows.

Anionic surfactant The effect of anionic surfactants (SDBS, SDS) on the extraction system was investigated. It was found that the change of the extraction rate was so small that it could hardly be observed in the extraction system containing anionic surfactant at the experimental time.

Nonionic surfactant The effect of nonionic surfactants (OP, TX-100) on the extraction rate of the system was shown in Fig. 1. It was shown that the extraction rate of the system containing nonionic surfactant was obviously smaller than that of blank solution. The nonionic surfactant could decelerate the extraction rate. The effect increased with increasing the concentration of surfactants.

Cationic surfactant Fig. 2 shows the effect of the cationic surfactant (CPB) on the extraction rate of the system. The cationic surfactant could accelerate the extraction, and the higher the concentration of CPB was, the more obvious the effect.

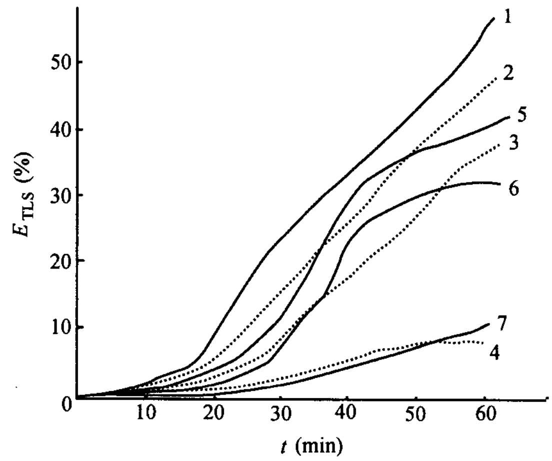

Fig. 1 Deceleration effect of OP and TX-100 on extraction. 1. blank, 2. OP (0.1%), 3. OP (0.5%), 4. OP (2.0%), 5. TX-100 (0.1%), 6. TX-100 (0.5%), 7. TX-100 (2.0%).

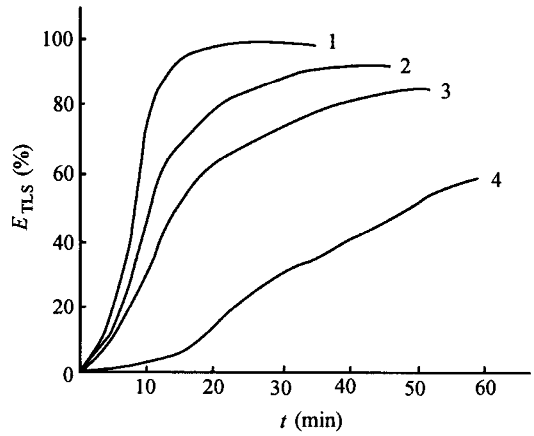

Fig. 2 Acceleration effect of CPB on extraction. 1. CPB (2.0%), 2. CPB (0.5%), 3. CPB (0.1%), 4. blank.

Mixture of surfactants In a system containing mixture of the surfactants, the extraction rate is the combination of the extraction rates in these two micelles. For example, the extraction rate in the system containing CPB and OP is faster than that containing OP, but slower than that containing CPB. This phenomenon is the result of the interaction of surfactants. The effects of extraction rates for the systems are ordered as below:

CPB > CPB + OP > BLANK > OP > CPB + SDS > OP + SDS ≈ SDS.

Discussion

In the extraction system, Nile Blue cations form hydrophobic ion-association species with I^- in aqueous phase. It can be extracted to $CHCl_3$ phase. The extraction rate is followed to the formula:[4] $dM/dt = kA\Delta C$, where dM/dt is the mass transfer velocity, k is the mass transfer coefficient, A is the interfacial area, and ΔC is the difference of solute concentration between two phases. When surfactant is added into the solution, there is an interaction between the surfactant molecule and the extracting species, which may be electrostatic attractions, or the extracting species enter the "water pool" of the micelles or are absorbed on the surface of the micelles. It changes the chemical potential of extracting species in the solution and the characteristics of the interface between two phases. The results produce two effects: the reduction of interfacial tension and the solubilization, the enhancement of extractive's solubility in water. The former increases the interfacial area A, resulting in the increase of dM/dt. The latter decreases the mass transfer coefficient k, resulting in the decrease of dM/dt. In the extraction system, the effect of surfactant on the extraction rate is the common result of these two effects.

When the concentration of surfactant being added reached its critical micelle concentration (cmc), the reduction of interfacial tension π_{cmc} could be described by Gibbs formula.[9] The π_{cmc} (mN/m) of SDS, TX-100, OP are 33.5, 38.5 and 37 at 25℃, respectively.[9] The higher the π_{cmc} is, the lower the interfacial tension.

It is clear that the reduction of interfacial tension for anionic surfactant micelle is less than that for nonionic surfactant micelle. Thus the increase of interfacial area A in SDS or SDBS micelle systems is not as much as that in TX-100 or OP micelle system. In the extraction system containing anionic surfactant (SDBS or SDS), the solubility of Nile Blue in water is enhanced by the ion-pair interaction between Nile Blue's positive charge and micelle's negative charge. It increases the aggregation of the micelles and the strength of interfacial film. The characteristic restrains Nile Blue dispersing to organic phase, which leads to the decrease of mass transfer coefficient of k. The stronger the ion-pair interaction, the more obvious the decrease of k is. As a result, the extraction was hardly observed in the system containing anionic surfactant during the experimental time (1 h).

Fig. 1 shows that the nonionic surfactants (OP or TX-100) can decrease the extraction rate. When the nonionic surfactant forms the micelle in the solution, the mass transfer coefficient of k decreases and the interfacial area A increases. The decrease of k is due to the enhancement of solubility of Nile Blue-I^- association species in water, because it can be contained in the hydrophilic chain of micelle's polyoxyethylene, which decreases the chemical potential of the extractive species and the interfacial tension in the solution. The reduction effect of OP or TX-100 on the interfacial tension makes interfacial area A increase. The effect of nonionic surfactants on the extraction rate is mainly dominated by k. Therefore, the extraction rate is decelerated in the systems containing OP or TX-100.

But what is different from anionic surfactants is that the deceleration effects of OP and TX-100 are far weaker than those of SDBS and SDS. It results fromtwo reasons: the first is that the combination between polyoxyethylene chain and Nile Blue association species is weaker, thus the decrease of k is little; the second is that π_{cmc} of OP and TX-100 are bigger, thus the increase of interfacial area A is more obvious. The extraction can be observed during the experimental time (1 h). After the concentration of surfactant reached its cmc, the interfacial area A kept constant. The increase of concentration leads to the formation of large amount of micelle and the aggregation. The enhancement of solubility leads to the decrease of k, so the extraction rate gets slower with the increase of the concentration of OP, TX-100.

Cationic surfactant CPB can reduce the interfacial tension in $CHCl_3$, thus make A increase. Besides, CPB forms reverse micelles in organic phase. In the reverse micelles, the surfactant's polar head groups outline a water-soluble polar core region of the micelles shielded by its nonpolar hydrocarbon tails. Consequently, the reverse micelle contains a small water pool, in which the Nile Blue can be dissolved. The effect enhances the species solubility in organic phase. The result leads to the increase of k. Because of the reduction of interfacial tension and the enhancement of extractive's solubility in $CHCl_3$, CPB can accelerate the extraction obviously. In addition, the extraction rate changes slowly with the decrease of ΔC gradually in the extraction process. The result is shown in Fig. 2.

Similar to nonionic surfactants, with the increase of the concentration of CPB, A keeps constant, but the extractive's solubility in $CHCl_3$ is enhanced and k increased, so the acceleration effect becomes obvious.

In the system containing mixture of surfactant, the extraction rate is strongly affected by the interaction of surfactant molecules. The extraction rate is the combination of the extraction rates of these micelles.

In the mixture micelle extraction system containing nonionic surfactant OP and cationic surfactant CPB, the molecules of OP "insert into" the micelle of CPB, thus it forms the mixture of micelle on the interface. The reduction of interfacial tension in OP-CPB micelle is more than that in OP micelle, and simultaneously A is increased. The extraction rate in such micelle is faster than that in OP micelle. But due to the solubility enhancement of Nile Blue association species in water by OP, k is decreased, and the extraction rate of the mixture micelle is slower than that in CPB micelle.

In the mixture micelle extraction system containing cationic surfactant CPB and anionic surfactant SDS, similar to the above OP-CPB micelle, SDS lies in aqueous phase, and CPB lies in organic phase. SDS and CPB form mixture of micelle on the interface by ion-pair interaction. The A decreases because the surface activation becomes weaker. Besides, k also decreases because of the enhancement of extractive's solubility in water by SDS. The extraction rate in CPB-SDS micelle is far slower than that in CPB micelle. In CPB-SDS mixture micelle system, k is increased as a result of the enhancement of extractive's solubility in $CHCl_3$ caused by CPB. On the contrary, the enhancement of extractive's solubility in water caused by SDS results in the decrease of k. But the final result is the increase of k. Obviously, the extraction rate in CPB-SDS micelle is faster than that in SDS micelle.

In the mixture micelle containing nonionic surfactant OP and anionic surfactant SDS system, the interfacial activation is enhanced due to the insertion of OP molecules into SDS micelle, thus A is increased. But the effect of the increase of A on extraction rate is far weaker than the enhancement of extractive's solubility in water by OP and SDS, the decrease of k is the main effect. The extraction is hardly detected during the experimental time (1 h).

Conclusion

Surfactant can form the micelle in a solution, thus will change the extraction rate by enhancing the extractive's solubility and reducing the interfacial tension. The studies of the effect of various surfactants on the extraction rate provide a meaningful result. It will be useful in the study of mechanism of extraction, purification of medicine and mineral separation in metallurgical industry, *etc*.

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