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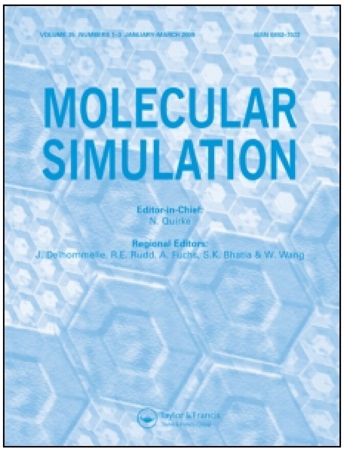

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A Study of the Stability of Emulsion with Mixed Surfactants using Electrolytic Conductivity

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Alcohols play an important role as cosurfactant in emulsions. The effects of cosurfactant chain length and concentration are discussed based on their particle size distribution (PSD) curves. A new model is established to determine the PSD by measuring the electrolytic conductivity of the emulsions.

Keywords: Cosurfactant; Emulsion stability; BSO equation; Particle size distribution

INTRODUCTION

Surfactants are used in a wide variety of industrial application [1]. Extensive research has been done on mixed surfactant systems since they can show superior performance compared to single surfactant systems alone [2]. But most of the previous literature has been concerned with monofunctional alcohols in microemulsions, focusing on the influence of the alcohol chain length [3,4], the temperature [5–7], the surfactant counter ion [8,9]; or with micelles [10–12]. Few papers have studied cosurfactant in emulsion. Various electrolytic conductivity techniques have been used to determine the stability of emulsion system [13–15]. But electrolytic conductivity measurements do not seem to have been used so far to determine particle size distribution (PSD) of emulsion directly.

In this paper, we focus on the stability study of emulsion with mixed surfactants according to the emulsion PSD, because it is one of the reliable parameters that are intimately related to the physical stability of an emulsion. At present, the main methods to determinate PSD are microscopic photography, sedimentation techniques, light scattering, instrument counting, IR and NMR spectroscopies, etc. [16]. Unfortunately, most of these methods are severely limited in their application because of the requirement to dilute the system under investigation, which changes the original emulsion state. Furthermore, these methods are usually used to determine some rather stable emulsion PSD (stable in days or months). We have established a new technique based on the electrolytic conductivity model to obtain the PSD of O/W emulsion without the need for dilution, and this new method is especially suitable for dense emulsions. In this work, the PSD curves of emulsions containing alcohol cosurfactant have been determined and the effects of cosurfactant chain length and concentration are discussed.

MODEL

The model is based on the fact that emulsion with ionic surfactant will gradually break into two phases after formation because of sedimentation and coagulation, and the oil fraction in electrode area will change because of the float. This will lead to a change of electrolytic conductivity in this area. According to the experiments of Hanai *et al.* [13], the following equation is established:

$$\kappa^{2/3} = \kappa_0^{2/3}(1-\varphi)/(1-\varphi_0) = k_m(1-\varphi) \qquad (1)$$

where κ, κ_0 are conductivities with the oil volume fractions φ and φ_0, respectively, k_m is the proportion coefficient and it can be determined by the initial state of the emulsion, when φ_0 is known. This relation is also supported by our experiment.

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The sedimentation (or float) velocity of a particle can be expressed by Stokes' equation [17]:

$$u = 2gr^2(d_1 - d_2)/(9\eta) \tag{2}$$

where u is sedimentation (or float) velocity, g is the acceleration of gravity, r is the droplet radius, η is the continuous phase viscosity, and d_1, d_2 are the densities of oil and water, respectively. In our model, we consider the emulsion system in which oil is lighter than water.

As for a given probe, there exists a relation:

$$u = h/t \tag{3}$$

where h is the probe height which is constant, and t is float time.

Substituting Eq. (3) into (2), we can relate the particle radius r and the floating time t by the following equation:

$$r = 3(h\eta/(2gt(d_1 - d_2)))^{1/2} \tag{4}$$

From Stokes' equation, if the emulsion is single-dispersed, the float velocity is constant, so the volume fraction of oil at the bottom (the electrolytic conductivity probe region) will decrease linearly to zero. The following equation is to describe this float process assuming that the single-dispersed particle radius is r_k:

$$\varphi_n = (1 - t_n/t_k)\varphi_k \tag{5}$$

where φ_k is the initial oil volume fraction in the electrode area, φ_n is oil volume fraction at time t_n, and t_k is the total float time calculated from equation (4) for the particle with radius r_k. In this equation, t_k must be larger than or equal to t_n. When t_n is beyond φ_k, φ_n equals to zero.

As for multi-dispersion emulsion:

$$\begin{aligned}\varphi_n &= \sum_{k=n}^{\infty}\left(1 - \frac{t_n}{t_k}\right)\phi_k \\ &= \left(1 - \frac{t_n}{t_n}\right)\phi_n + \left(1 - \frac{t_n}{t_{n+1}}\right)\phi_{n+1} \\ &\quad + \left(1 - \frac{t_n}{t_{n+2}}\right)\phi_{n+2} + \left(1 - \frac{t_n}{t_{n+3}}\right)\phi_{n+3} + \cdots \\ &= \left(1 - \frac{t_n}{t_{n+1}}\right)\phi_{n+1} + \left(1 - \frac{t_n}{t_{n+2}}\right)\phi_{n+2} \\ &\quad + \left(1 - \frac{t_n}{t_{n+3}}\right)\phi_{n+3} + \cdots\end{aligned} \tag{6}$$

where the meaning of ϕ_n, the volume fraction of oil drop with radius r_n in emulsion, is different from the concept φ_n which is the linear summation of the volume fractions of all the different size oil droplets at time t_n.

A small time interval Δt is used to discretize t_n. That is:

$$t_n = n\Delta t \tag{7}$$

Substituting Eq. (7) into (6) gives:

$$\begin{aligned}\varphi_n &= \phi_{n+1}/(n+1) + 2\phi_{n+2}/(n+2) \\ &\quad + 3\,\phi_{n+3}/(n+3) + \cdots\end{aligned} \tag{8}$$

On the same basis:

$$\varphi_{n-1} = \phi_n/n + 2\phi_{n+1}/(n+1) + 3\phi_{n+2}/(n+2) + \cdots \tag{9}$$

In order to relate φ to electrolytic conductivity κ, the Eq. (1) can be rearranged as:

$$\begin{aligned}\left(\kappa(\varphi)^{2/3} - \kappa_0^{2/3}\right)/k_m &= (1 - \varphi) - (1 - \varphi_0) \\ &= \varphi_0 - \varphi\end{aligned} \tag{10}$$

Combining Eq. (10) with Eqs. (8) and (9) gives:

$$\begin{aligned}&\left(\kappa(\varphi_n)^{2/3} - \kappa(\varphi_{n-1})^{2/3}\right)/k_m \\ &\quad = \varphi_{n-1} - \varphi_n \\ &\quad = \phi_n/n + \phi_{n+1}/(n+1) + \phi_{n+2}/(n+2) + \cdots\end{aligned} \tag{11}$$

Then we can obtain the similar equation:

$$\begin{aligned}&\left(\kappa(\varphi_{n+1})^{2/3} - \kappa(\varphi_n)^{2/3}\right)/k_m \\ &\quad = \varphi_n - \varphi_{n+1} \\ &\quad = \phi_{n+1}/(n+1) + \phi_{n+2}/(n+2) + \phi_{n+3}/(n+3) + \cdots\end{aligned} \tag{12}$$

Subtract Eq. (12) from Eq. (11), then:

$$\phi_n = n\left(2\kappa(\varphi_n)^{2/3} - \kappa(\varphi_{n-1})^{2/3} - \kappa(\varphi_{n+1})^{2/3}\right)/k_m \tag{13}$$

Thus, we can get the emulsion particle size distribution curve by plotting ϕ_n versus r_n which is calculated from Eq. (4) when t equal to t_n. From Eq. (1) we can deduce that the normalized $\kappa^{2/3}$ is equal to the normalized $(1 - \phi)$. So, when we substitute $\kappa^{2/3}$ and $(1 - \phi)$ with the normalized ones in the above equations, then k_m will equal 1. Thus, as for the normalized data, we need not calculate k_m.

In practice, the electrolytic conductivity curves are not precise enough to get the reasonable PSD directly from solving Eq. (13) (sometimes the distribution values for some radius is minus). A more practical and effective method is to define the PSD in the following form:

$$\begin{aligned}\phi(r) = {} & a\exp\left(-(r - r_{c1})^2/(2w_1^2)\right) \\ & + (1 - a)\exp\left(-(r - r_{c2})^2/(2w_2^2)\right).\end{aligned} \tag{14}$$

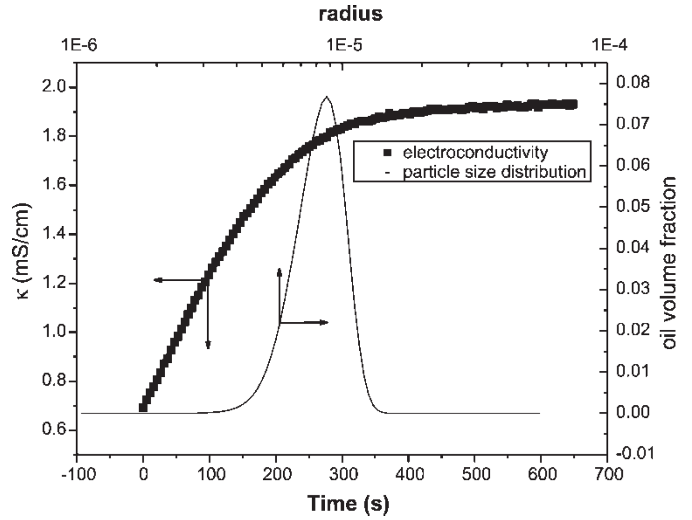

FIGURE 1 The electrolytic conductivity curve of 4 mM SDS/cyclohexane/propanol system and the deduced PSD curve by our model.

ϕ is the fraction of oil drops with radius r. a, r_{c1}, r_{c2}, w_1, w_2 are the parameters to define the PSD curve. Here, a is between 0 and 1, and r_{c1}, r_{c2}, w_1, w_2 are greater than zero. Then from Eqs. (4), (6) and (14), we can also calculate the electrolytic conductivity curve. Using constrained non-linear optimization method we can get the best fitting parameters.

Here an example of electrolytic conductivity curve and the deduced PSD curve by the model are given (as shown in Fig. 1).

EXPERIMENTAL

Reagents

Sodium dodecylsulfate (SDS, ≥99%, Sigma Co.), cyclohexane and 1-octanol (AR., Shanghai Reagent Plant I), methanol, ethanol, 1-propanol and 1-butanol (AR., Hangzhou Shuanglin Chemical Reagent Plant), 1-hexanol and 1-decanol (AR., China Medical Group Shanghai Chemical Reagent Co.), distilled water.

Instruments

CS501 super thermostatic water bath (Chongqing Experiment Education factory), DOSJ-308 electrolytic conductivity instrument (Shanghai LEICI Instruments Plant), WH-861 vortex mixer (Taicang Experiment Education Instrument Plant), AE204 electrical balance (Mettler-Toledo Instruments ⟨Shanghai⟩ Co., Ltd.), modified 260 style conduction electrode (the electrode end is truncated in order to completely touch the conductivity cell bottom, shown in Fig. 2), a series of comparison tubes as conductivity cells. Ubbelohode viscometer, Model 80-2 Centrifuge (Shanghai Surgical Instruments Factory) and home made electrolytic conductivity sample system.

Experiment Details

A series of quaternary emulsion systems: 4 mM SDS aqueous solution (10 ml)/cyclohexane (5 ml)/1-alkanol (at different volume), were prepared by WH-861 vortex mixer. The ratio of SDS solution and cyclohexane was 2:1 for convenience to determine the electrolytic conductivity of the water-rich phase. The electrolytic conductivities were recorded by computer as soon as the emulsion was prepared, and until the conductivity did not change much. The sample was taken off, and put into the centrifuge to segregate oil and water. Then the viscosity of water phase was measured, and the density of oil and water phase by volume–weight method.

All the experiments are carried out at a temperature of 25 ± 0.1°C, and the shaking time was 60 s for

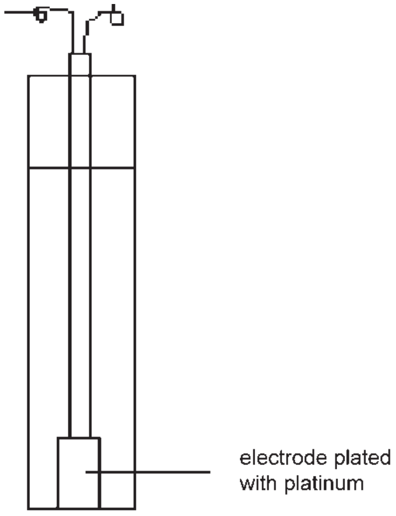

FIGURE 2 The electrolytic conductivity sample system.

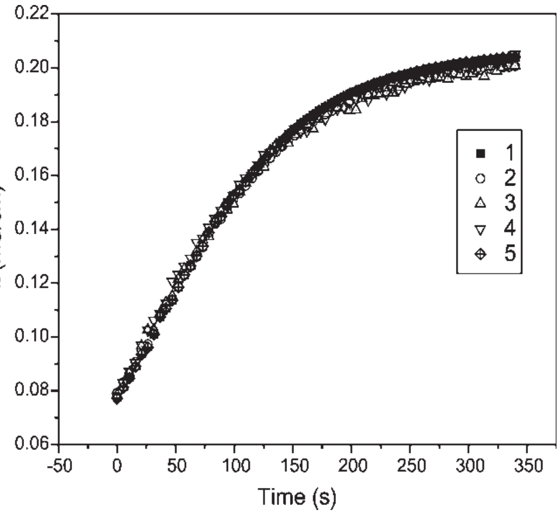

FIGURE 3 The reproducibility of electrolytic conductivity of 4 mM SDS/cyclohexane/ethanol system.

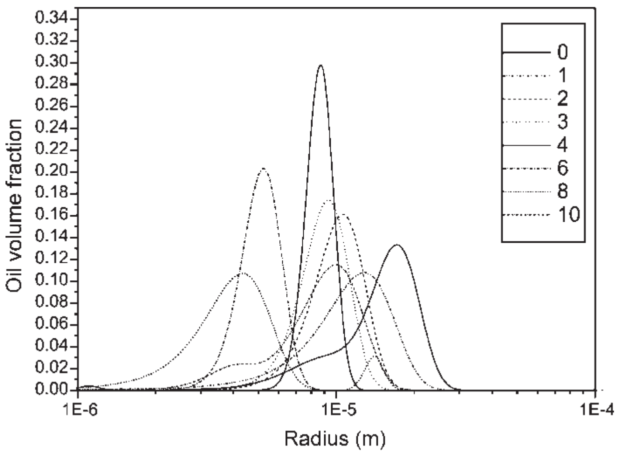

FIGURE 5 PSD curves for 4 mM SDS/cyclohexane/1-alkanol system with different numbers of carbons in the alcohol chain. 0 represents the care when no alcohol has been added.

all the emulsions under investigation. For any emulsion system in our study, we repeated the same process from preparation to measurement, and the reproducibility was satisfying as shown in Fig. 3.

RESULTS AND DISCUSSION

Effect of Cosurfactant Length on Emulsion Stability

In our experiment, the PSD curves of emulsions containing different 1-alkanol with the same amount (0.6 ml in 15 ml emulsion) are determined. For the sake of comparison, the electrolytic conductivity curves ($\kappa^{2/3}$) are normalized as shown in Fig. 4. The PSD curves deduced from the electrolytic conductivity curves are shown in Fig. 5. And the volume mean droplet radius is shown in Fig. 6. From these figures, one sees that the emulsion tends to be more stable with the increase of alcohol chain length. But the emulsion stability will go through a maximum when the carbon number is 8, then decrease after that.

It is well known that the addition of appropriate chain length cosurfactant can increase the stability of microemulsion system, which is due to either the maximum cohesive interaction between hydrocarbon chains or the minimum disruption in the interfacial region [18,19]. The optimal chain length of cosurfactant can be calculated from BSO equation [20]: $l_c + l_o = l_s$, where l_c, l_o, l_s, are carbon chain lengths of cosurfactant, oil and surfactant, respectively.

In our SDS/cyclohexane/1-alkanol system, the optimal cosurfactant carbon number is 8. It must be taken into consideration that the effective chain length of cyclohexane is equivalent to 4. So it can be found from our investigation that medium chain

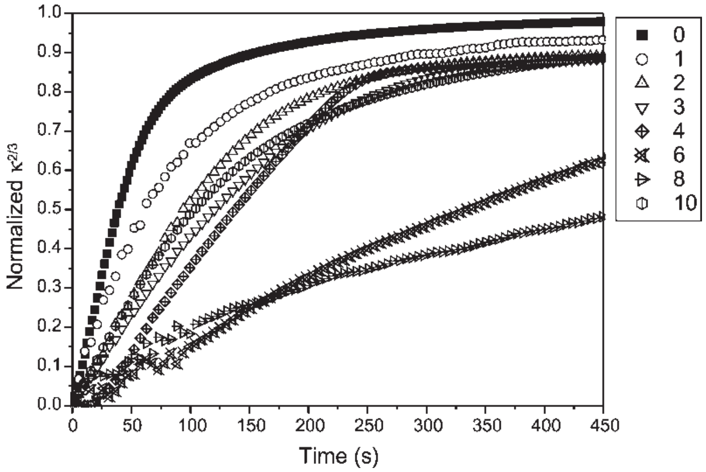

FIGURE 4 Normalized electrolytic conductivity curves for 4 mM SDS/cyclohexane/1-alkanol system with different numbers of carbons in the alcohol chain. 0 represents the care when no alcohol has been added.

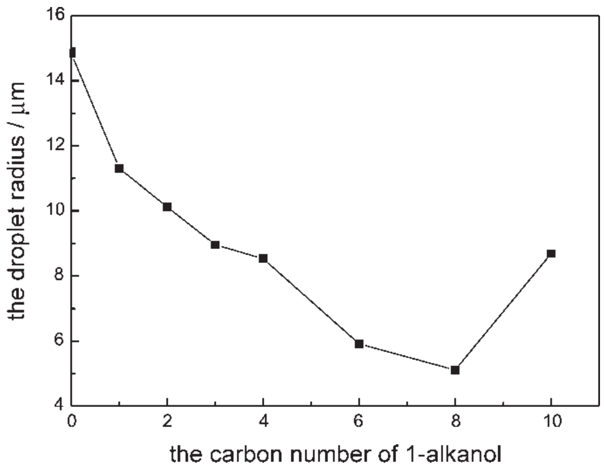

FIGURE 6 The mean droplet radius in 4 mM SDS/cyclohexane/1-alkanol system for different alcohol carbon numbers.

length alkanol has the same enhancement to stability of emulsion and agrees with the BSO rule.

Effect of Cosurfactant Concentration on Emulsion Stability

It is known from the chain length compatibility experiment that the octanol emulsion in our investigation is most stable. Then the effect of different cosurfactant concentrations in this emulsion system is investigated.

The volume mean droplet radius of SDS/cyclohexane/1-octanol emulsion system at different octanol volumes are demonstrated in Fig. 7. It can be seen from this figure that with an increase of cosurfactant concentration, the emulsion stability increases first, before the increment degree slows down.

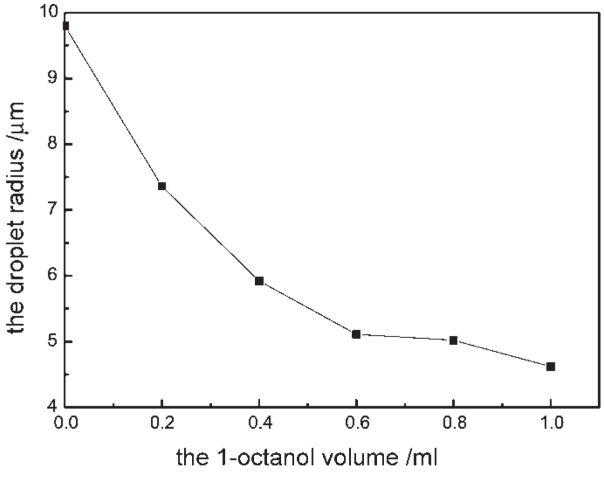

FIGURE 7 The volume mean droplet radius in 4 mM SDS/cyclohexane/1-octanol system for different octanol concentrations.

It has been mentioned earlier how the addition of cosurfactant (1-octanol here) affects the emulsion stability. With the increase of the octanol concentration, the emulsion becomes more stable. But when the octanol concentration reaches a certain value, octanol will be saturated in the interface. When it is near the saturation region, the composition and the properties of the interface will change little when more octanol is added.

It should be noted that the method is adapted to determine the PSD of O/W emulsions (not suitable for very dilute emulsion, because the electrolytic conductivity does not change sufficiently for this system). It is difficult to directly compare our PSD results with other methods, because this emulsion is too unstable to be determined by other methods. But the PSD curves of the emulsions deduced from the electrolytic conductivity are more meaningful than the latter one. Further work is in progress.

CONCLUSION

A new method based on the electrolytic conductivity model to obtain the PSD of O/W emulsion was developed, and the effects of cosurfactant chain length and concentration to emulsion stability were investigated. The following conclusions were obtained.

1. Our new technique of PSD measurement without the need for dilution can give the PSD results with high reproducibility and reasonable accuracy.
2. Medium chain length 1-alkanol cosurfactant can enhance the emulsion stability and also agree with the BSO equation as in microemulsion systems.
3. Cosurfactant can saturate the oil/water interface in our SDS/cyclohexane/1-octanol system, and the addition of octanol near the saturation region affects a little.

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References

[1] Falbe, J. (1994) *Daily Surfactants-Theory, Technology and Application* (China Petrochemical Press, Beijing), Translated by Zhang, Z.Y. and Zhao, H.W.

[2] Patist, A., Devi, S. and Shah, D.O. (1999) "Importance of 1:3 molecular ratio on the interfacial properties of mixed surfactant systems", *Langmuir* **15**, 7403.

[3] Fontell, K., Khan, A., Lindstrom, B. and Puang, N.S. (1991) "Phase equilibria and structures in ternary systems of

a cationic surfactant (C_{16}TABr of $(C_{16}TA)_2SO_4$), alcohol, and water", *Colloid Polym. Sci.* **269**, 727.

[4] Gamboa, C., Olea, A., Rios, H. and Henriquez, M. (1992) "Association of alcohol with cationic micelles", *Langmuir* **8**, 23.

[5] Sasaki, M., Imae, T. and Ikeda, S. (1989) "Aqueous sodium halide solutions of cationic surfactants with consolute phase boundary. Viscosity behavior in semidilute regime", *Langmuir* **5**, 211.

[6] Makhloufi, R. and Cressely, R. (1992) "Temperature dependence of the non-Newtonian viscosity of elongated micellar solutions", *Colloid Polym. Sci.* **270**, 1035.

[7] Nagao, M., Seto, H., Kawabata, Y. and Takeda, T. (2001) "Effects of temperature and pressure on phase transitions in a ternary microemulsion system", *J. Chem. Phys.* **115**, 10036.

[8] Ikeda, S. (1991) "Stability of spherical and rod-like micelles of ionic surfactants in relation to their counterion binding and modes of hydration", *Colloid Polym. Sci.* **269**, 49.

[9] Wärnheim, T., Jönsson, A. and Sjöberg, M. (1990) "Phase diagrams for cationic surfactants in polar solvent systems", *Prog. Colloid Polym. Sci.* **82**, 271.

[10] Leung, R. and Shah, D.O. (1986) "Dynamic properties of micellar solutions I. Effects of short-chain alcohols and polymers on micellar stability", *J. Colloid Interface Sci.* **113**(2), 484.

[11] Patist, A., Axelberd, T. and Shah, D.O. (1998) "Effect of long chain alcohols on micellar relaxation time and foaming properties of sodium dodecyl sulfate solutions", *J. Colloid Interface Sci.* **208**, 259.

[12] Zhou, M.F. and Rhue, R.D. (2000) "Effect of interfacial alcohol concentrations on oil solubilization by sodium dodecyl sulfate micelles", *J. Colloid Interface Sci.* **228**, 18.

[13] Hanai, T., Koizumi, N., Sugano, T. and Gotoh, R. (1960) "Dielectric properties of emulsions II. Electrical conductivities of O/W emulsions", *Kolloid-Z.* **171**, 20.

[14] Gundersen, S.A. and Sjoblom, J. (1999) "Original contribution: high- and low-molecular-weight lignosulfonates and Kraft lignins as oil/water-emulsion stabilizers studied by means of electrical conductivity", *Colloid Polym. Sci* **277**, 462.

[15] Gundersen, S.A., Sæther, Ø. and Sjoblom, J. (2001) "Salt effects on lignosulfonate and Kraft lignin stabilized O/W-emulsions studied by means of electrical conductivity and video-enhanced microscopy", *Colloids Surf., A* **186**, 141.

[16] Becher, P. (1965) *Emulsions Theory and Practice* (Reinhold Publishing Corporation, New York), Chapter 3, pp 49–60.

[17] Stokes, G.G. (1851) "On the effect of the internal friction of fluids on motion of pendulums", *Trans. Cambridge Phil. Soc.* **9**, 8.

[18] Cui, Z.G. and Yin, F.S. (1999) *Microemulsification Technology and Application* (China Light Industry Publishing Press), pp 219–221.

[19] Shiao, S.Y., Chhabra, V., Patist, A. and Shah, D.O. (1998) "Chain length compatibility effects in mixed surfactant systems for technological applications", *Adv. Colloid Interface Sci.* **74**, 1.

[20] Bansal, V.K., Shah, D.O. and O' Connel, J.P. (1980) "Influence of alkyl chain length compatibility on microemulsion structure and solubilization", *J. Colloid Interface Sci.* **75**, 462.