Chinese Chemical Letters Vol. 15, No. 9, pp 1101-1104, 2004
http://www.imm.ac.cn/journal/ccl.html

Effect of Addition of Cosurfactant on the Phase Behaviour of Oil-in-water Aminosilicone Oil Microemulsion

Zheng Hong LUO[1]*, Xiao Li ZHAN[2], Peng Yong YU[3]

[1]Department of Chemical Engineering, Xiamen University, Xiamen 361005
[2]Department of Chemical Engineering , Zhejiang University, Hangzhuo 310027
[3]Shanghai Toyocosmetic Industrial Co., LTD., Shanghai 200135

Abstract: Stable and transparent aminosilicone oil microemulsion of the average particle size below 0.05 micron was prepared. The interaction of the aminosilicone oil, water, complex surfactants and cosurfactant was studied by part pseudoternary phase diagram. The effect of cosurfactants (such as alcohol) and the mechanism of its effect on the phase behaviour of the pseudoternary system were investigated.

Keywords: Aminosilicone oil microemulsion,cosurfactant, phase diagram.

The studies of using water as a substitute of organic solvents for reducing environment problems have steadily gained importance, especially in the coating industry. A waterborne microemulsion is a binary colloidal system in which particles are dispersed in a continuous aqueous phase.

Most studies were concentrated on micromolecules and their microemulsion, but less attention has been paid to macromolecules in aqueous solution, due to difficulty of preparation of their microemulsions. Recently, Jiang *et al.*[1] reported that lightly carboxylated hydrogenated poly (styrene-block-butadiene-block-styrene) triblock (SEBS) copolymer and randomly carboxylated polystyrene ionomers can form stable aggregations in water by a special procedure. Alany *et al.*[2] also prepared stable microemulsion with help of addition of cosurfactant and investigated the effects of the addition of cosurfactant on the phase behaviour of quaternary systems. However, most investigations were concentrated on the polymers with flexible hydrocarbone as main chain. The microemulsion of organsilicone polymer were rarely reported in theoretical aspect. In this article, the oil-in-water aminosilicone oil microemulsion was studied, and the influences of addition of cosurfactant on the phase behaviour of the pseudoternary system water: aminosilicone oil: complex surfactant blend were studied.

In the studies, the stable and transparent aminosilicone oil microemulsion of the average particle size below 0.05 micron was prepared without or with the help of cosurfactant. Aminosilicone oil (made in our laboratory) of average molecular weight

* E-mail: luozhenghong@sina.com

between 10,000 and 20,000, amino content of 0.45%, and viscosity of 1200 mPa·s at 25°C, was used as the oil component of pseudoternary system. Polyoxyethylene (4) octylphenyl ether (NP-55/015, Hefti Ltd., Switzerland), polyoxyethylene (7) octylphenyl ether (NP-55/22, Hefti Ltd., Switzerland), were used as surfactant. Deionised water was used as the aqueous phase. 1-pentanol from Chemical Reagent Company of Shanghai, was used as cosurfactant. Acetic acid from Chemical Reagent Company of Shanghai, was used as pH regulator. Composition for each point in the pseudoternary phase diagram was constructed at certain mass ratio of water: complex surfactant blend: aminosilicone: cosurfactant, the optimal ratio for maximum water solubilization was determined previously, and the phase boundary was determined by both clarity and particle size. The conductivity of the system was also measured by the conductometer (DDS-11A, manufactured by the Electric Factory of Shanghai, China). TEM photographs were obtained by TEM (JEM-1200CX). Particle size of the (micro) emulsions were measured by photo correlation spectroscopy with a Malvern Zeta-sizer 3000, Malvern Instruments GmbH, Herrenberg, Germany, at ambient temperature. Particle size is reported as the cumulant average diameter calculated by the cumulants method of Koppel3. Because oil-in-water aminosilicone oil microemulsion was the emphasis of this work, we only gave part phase diagram of oil-in-water area. Systems were prepared by mixing water, surfactants and cosurfactants prior to the addition of the appropriate mass of aminosilicone oil in a beaker with constant agitation. The samples were vortexed and left overnight to equilibrate and then characterized by visual inspection, light microscopy and conductivity measurements.

A stable and transparent microemulsion can not be obtained if the surfactants of the system are not selected appropriately. The selection and combination of surfactants are mainly based on the theory of hydrophilic-lipophilic balance, which means that the hydrophilic-lipophilic balance value of complex surfactants should be equal to that of aminosilicone oil approximately. Furthermore, according to the experimental results, we obtained the fine complex surfactants (B) NP-55/015 and NP-55/22. This article discusses complex surfactants (B).

When NP-55/015 and NP-55/22 are mixed at 3:7 (weight), the hydrophilic-lipophilic balance value of the complex surfactants is about 9.9, which is equal to that of aminosilicone oil approximately. This result is in accord with other report[4]. The resulting aminosilicone oil microemulsion was measured TEM by transmission electron microscopy (see **Figure 1**). The TEM photograph showed the colloid particles are very small, the size of all particles is below 0.05 microns. The microemulsion examined by photo correlation spectroscopy revealed that the mean volume-based diameter of particles is 6.4 nm and the size of particles is in the range of 4~10 nm. According to these results, it is believed that the stable and transparent aminosilicone oil microemulsion, the particle size of which is below 50 nm and in narrow range, can be prepared with some complex surfactants.

Based on above results, we mixed NP-55/015 and NP-55/22 in 3:7 by weight to get the complex surfactants, then mixed water and the complex surfactants at 19:1, 15:1, 9:1, 7.5:1 by weight to obtain surfactants solutions with different concentration. The aminosilicone oil was added into surfactants solutions slowly. Simultaneously, we recorded the average particle size and percent transmittance of (micro)emulsion as a function of the contents of aminosilicone. Furthermore, a part pseudo-ternary phase diagram of oil-in-water area was constructed as **Figure 2**.

Figure 2 showed that the formation of microemulsion is closely connected with the concentration of complex surfactants. When too much aminosilicone oil was added in the complex surfactants solution of certain concentration (up point B in **Figure 2**), the stable microemulsion could not form, because there were not enough complex surfactants to produce microparticles. On the contrary, as the amount of aminosilicone oil was small, which meant the concentration of complex surfactants was high (under point A in **Figure 2**), only opaque emulsion formed. This result can be explained as follows: when too much complex surfactants, much hydrophilic NP-55/22 can be dissolved in water to form true solution, while high content of NP-55/015 can only be dispersed in water. So the resulting emulsion is opaque, and some precipitate can be observed after a period of time. In short, according to **Figure 2**, to form aminosilicone oil microemulsion often requires the high concentration of surfactant, which can lead to issues of bioincompatibility[2].

In general, the concentration of surfactant can be reduced by the addition of the cosurfactants. Low molecular weight alcohols can be used for this purpose. The complex surfactants (made by mixing NP-55/015 and NP-55/22 at 3:7 by weight) were mixed with 1-pentanol at 9:1, 8:2–2:8, 1:9 by weight to gain different solutions containing 6 wt% surfactant (complex surfactants + 1-pentanol), then aminosilicone oil was added slowly. The part pseudo-ternary phase diagram is shown in **Figure 3**.

Figure 3 showed that 1-pentanol is helpful to form a stable and transparent aminosilicone oil microemulsion. Acting a cosurfactant, 1-pentanol can influence the formation of microemulsion by both interfacial and bulk effects[5]. The amphiphilic na-

Figure 1 The TEM photograph of microemulsion

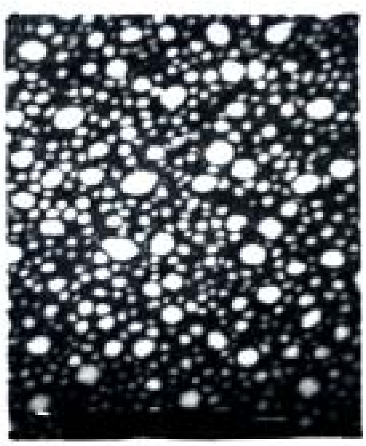


Figure 2 The part pseudo-ternary phase diagram aminosilicone oil (O), water (W) and complex surfactants (S)

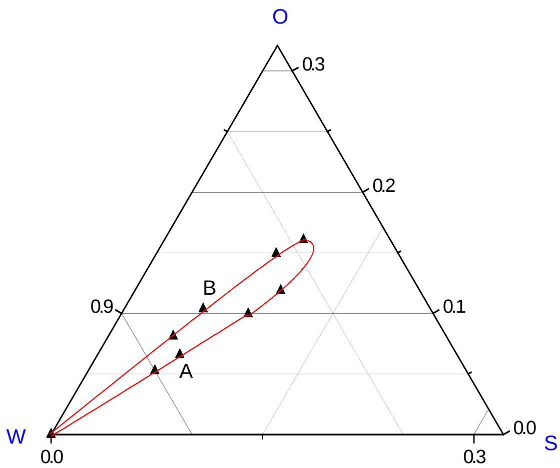
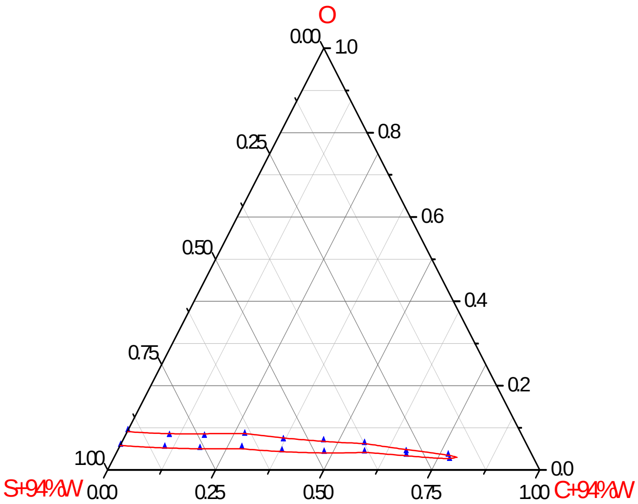


Figure 3 The part pseudo-ternary phase diagram microemulsion aminosilicone oil (O), water (W) , complex surfactants (S), and 1-pentanol (C)



nature, short hydrophobic chain and terminal hydroxyl group of 1-pentanol, makes it to interact with surfactant monolayers at the interface, affect the packing of the interface, and in turn influence the curvature of the interface and interfacial energy. The amphiphilic nature of low molecular cosurfactants also can distribute between the aqueous and oil phase, altering the chemical composition and the relative ratio of hydro/lipophilicity. These two properties render short chain alcohols useful for the preparation of microemulsion. But in this system the cosurfactant are not absolutely necessary, it is only a substitute for part primary surfactants. In the classic theory of microemulsion, the cosurfactant (such as alcohol) is necessary in the preparation of microemulsion, but in fact some kinds of ionic or nonionic surfactants can help to make microemulsion without cosurfactant, and the aminosilicone oil microemulsion is a good example for this instance.

References

1. M. Li, M. Jiang, L. Zhu, C. Wu, *Macromolecules*, **1997**, *30*, 2201.
2. R. G. Alany, T. Rades, S. Agatonovic-Kustrin, N. M. Davies, I. G. Tucker, *International Journal of Pharmaceutics*, **2000**, *196*, 141.
3. D. Koppel, *J. Chem. Phys.*, **1972**, *57*, 4814.
4. Q. L. Chen, Y. Kong, *Textile Auxiliaries* (in Chinese), **1997**, *14*(4), 9.
5. M. T. Kahlweit, G. Busse, B. Faulhaber, H. Eibl, *Langmuir*, **1995**, *11*, 4185.

Received 28 July, 2003