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Interfacial Behavior of Oil/Oil and Oil/Water Soluble Binary Surfactants and Their Effect on Stability of Highly Concentrated W/O Emulsions[1]

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Abstract—Instability of highly concentrated water-in-oil emulsions which contain a metastable inorganic salt solution in a form of drops arises from the crystallization of salt in the dispersed phase, both on the shelf and under high shear. In this work the interfacial properties of two binary mixtures of oil/oil soluble and oil/water soluble surfactants with different molar ratios were studied to determine their effect on the stability of manufactured emulsions. The two mixed surfactants used were mainly poly (isobutenyl) succinic anhydride (PIBSA)-based surfactant with either sorbitan monooleate (SMO) (oil/oil soluble) or with polyoxyethylene sorbitan monooleate (Tween 80) (oil/water soluble). Interfacial studies showed completely opposite behavior of these two mixtures with changing concentration of polymeric surfactant. A synergetic effect between PIBSA-Mea and Tween 80 molecules was evident. PIBSA/Tween 80 emulsions exhibited better shelf stability than the PIBSA-Mea/SMO mixtures due to the efficiently packed interfacial film produced by this synergetic binary surfactant mixture. In addition, a significant improvement in stability under high shear conditions was achieved with the oil/water soluble PIBSA/Tween 80 mixture. The results showed that the interfacial study are important for the understanding of instability due to crystallization in emulsions with an oversaturated dispersed phase

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INTRODUCTION

Highly concentrated water-in-oil emulsions with an oversaturated solution of inorganic salts as the dispersed phase are unique complex systems, playing an important role in manufacturing of explosives, nutritious foods and drug delivery systems. Instability of such emulsions arises from crystallization of the dispersed phase in the system during aging or under high shear conditions [1–3] and shear-induced coalescence. Crystallization decreases the efficiency of the application while the evolution of a droplet size is accompanied by changes in the rheological properties of the emulsions. Highly concentrated emulsions behave as gels and thus show viscoelastic and plastic properties [2, 4]. The compositions that can yield highly concentrated emulsions, which are stable both on the shelf and under intense shearing (e.g., during pumping) remain a challenging issue in this field [5].

Various combinations of two different surfactants have been studied over the last decade. The superior properties of the binary mixtures come from their interactions in the emulsion [6, 7]. Investigation of the interfacial behavior of these surfactants and their micelles can provide better understanding of the stability mechanism of the resulting emulsion [8–11]. However, the interfacial behavior of mixed surfactant systems in highly concentrated emulsions with an oversaturated dispersed phase, in which the stability is related more to crystallization than to coalescence of droplets, remain poorly explored [10, 12].

Binary mixtures of polymeric surfactant, polyisobutylene succinic anhydride derivative (PIBSA), and conventional oil soluble surfactant, sorbitan monooleate (SMO) are currently used as the main stabilizing system in the explosives industries. PIBSA-based surfactants provide long shelf stability through the formation of a large number of micelles which create a steric barrier between the emulsion droplets [13], while small SMO molecules quickly cover the fresh droplet surfaces and improve stability under high shear [12]. However, SMO accelerates crystallization during the storage, possibly by removing PIBSA molecules from the interface and by creating a multilayer around the droplets, which could initiate the crystallization [14–16]. Another possible mechanism of crystallization involves destabilization of the PIBSA micelles that can reduce the steric effects [13]. It is interesting therefore to study other co-surfactants which could increase the stability of the emulsion under high shear without a decrease of the stability during storage.

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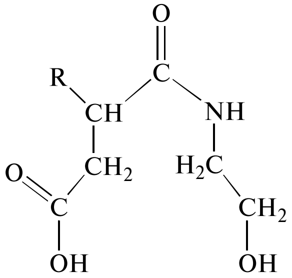

Fig. 1. Structural formula of the head group of PIBSA-Mea, in which R is the polyisobutylene chain with a repeat unit of $-C(CH_3)_2-CH_2-$.

In this work, the interfacial behavior of binary mixture of a polymeric PIBSA-based surfactant with SMO and polyoxyethylene sorbitan monooleate in a wide range of surfactant/co-surfactant ratios was studied in order to understand the stability mechanisms of super-concentrated emulsions with metastable dispersed droplets.

EXPERIMENTAL

Materials

Monoethanolamine derivative of polyisobutylene succinic anhydride surfactant (PIBSA-Mea) with a total molecular weight of 1109 g/mole and highly polar oil (Ash-H) with short alkyl chains, were supplied by Lake International Technologies (South Africa). The chemical composition of PIBSA-Mea is shown in Fig. 1. Ash-H mainly contains short chain paraffins (>99%) and small amount of aromatics (<0.1%) and has a density of 794 kg/m^3 at 20°C.

Sorbitan monooleate, SMO (trade name Span 80), with polyoxyethylene sorbitan monooleate (trade name Tween 80) as co-surfactant were purchased from Merck and Sigma-Aldrich respectively and were used without further purication (Fig. 2). Ammonium nitrate (AN), an inorganic salt, was purchased from Merck and added to ultra-pure water prepared by a Milli-Q purification system to prepare the aqueous phase.

Sample Preparation

For the interaction studies various concentrations of PIBSA-Mea were added to oil. Interfacial tension between the aqueous and the oil phases was measured to determine the critical micelle concentration (CMC) of PIBSA-Mea using the Wilhelmy plate method. In the next step, two sets of samples were prepared by adding a specific amount of PIBSA-Mea (below CMC and above CMC) mixed with different concentrations of two co-surfactants in the oil. Adding Tween 80, as a water soluble surfactant, to the aqueous phase was not possible because the aqueous phase was saturated with ammonium nitrate and there was insufficient water available to dissolve the surfactant molecules. However, Tween 80 was fully dispersed in the polar Ash-H oil, with an interfacial tension equal to 20 mN/m.

To manufacture the highly concentrated water-in-oil emulsions with an oversaturated dispersed phase, a 10 : 1 w/w ratio of PIBSA-Mea/co-surfactants was used. The surfactant mixtures (8 wt % in oil phase) were added to the oil prior to emulsification. The emulsion formulations consist of 80% AN solution with the ratio of aqueous to oil phases of 92.4 : 7.6 wt %. The two phases were mixed using Hobart N50 mixer at a temperature above the fudge point ($T_{\text{fudg}} \approx 60°C$) of the AN solution. After initial gentle mixing the pre-emulsions were refined at higher shear until the desired dispersed phase droplet size was reached (d_{32} = 10 μm). At ambient temperature (≈25°C) the solutions were thermodynamically unstable, but kinetically there were no changes in emulsion structure for a time sufficient to complete the investigation. Crystallization of the dispersed phase occurred over a period of several days to several weeks.

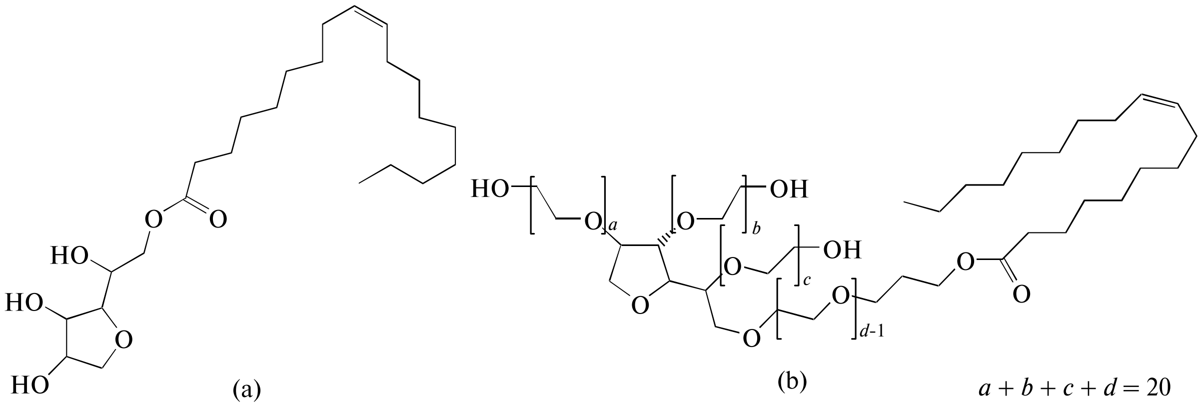

Fig. 2. Structures of (a) SMO and (b) Tween 80.

Instrumentation

To determine the interfacial tension (σ) at the water–oil interface in the presence of surfactants, the Wilhelmy plate method was applied using a Krüss K100 tensiometer with a platinum plate. All measurements were done at a temperature of 25.0 ± 0.1°C. Each measurement was made by adding 12 mL of 60% AN solution and 50 mL of oil phase containing surfactants to the 70 mL glass cup. Each test ran for 2 hours to ensure the equilibrium value of interfacial tension was measured for each system. Crystallization in the emulsions was examined under a Leica optical microscope with ×500 magnification to corroborate the stability of the samples before experiments and also to monitor the aging (initiation and kinetics of crystallization) of the emulsions.

The droplet size (d_{32}) of the emulsions was monitored during refinement using a light scattering method with Malvern Mastersizer 2000 instrument. The refinement was stopped at $d_{32} = 10$ μm for all samples. To investigate the stability for pumping applications, fresh emulsion samples were subjected to high shear (~1200 Pa) by passing them five times, at a pressure of 4 bar, through a ∅ 4 mm orifice hole with the length of 3 mm in a double cylindrical chamber.

RESULTS AND DISCUSSION

Interfacial Study

The measured values of CMC and minimum interfacial tension at CMC of PIBSA-Mea, SMO and Tween 80 are listed in Table 1. The measurements showed that the adsorption efficiency of Tween 80 is higher than that of PIBSA-Mea and SMO.

Table 1. Values of CMC and corresponding values of interfacial tension for the surfactants used

Surfactant	CMC × 10^5 (mol/L)	σ (mN/m)
PIBSA-Mea	7.6	9.5
SMO	59.3	<1
Tween 80	1.3	<1

For interfacial tension measurements, different oil phases were prepared from certain amounts of PIBSA-Mea (below and above the CMC) with various concentrations of co-surfactants. The interfacial behavior of PIBSA-Mea/SMO and PIBSA-Mea/Tween 80 (below and above PIBSA-Mea's CMC) is illustrated in Figs. 3 and 4, respectively. The interfacial properties of these two systems differ significantly. For PIBSA-Mea/SMO system, the rate of the decrease of interfacial tension is higher in the region below PIBSA-Mea's CMC when compared with the region above this point (Fig. 3). The PIBSA-Mea/Tween 80 mixture shows the opposite behavior (Fig. 4).

The results suggest that, when the amount of polymeric surfactant to form micelles is insufficient (i.e., the system is below the CMC), the SMO molecules cover the interface rapidly decreasing the interfacial tension. When the system is above the CMC, the amount of PIBSA-Mea is large enough for the formation of interfacial coating and micelles. The rate of SMO-induced lowering of interfacial tension therefore decreases, and $\sigma < 1$ that is close for the value of pure SMO. The observed effect implies an antagonistic interaction between the surfactants at the interface [17]. Furthermore, the slow decrease of interfacial tension in the region above the CMC suggests that the SMO molecules exhibit a pronounced tendency to interact with the PIBSA micelles.

For the PIBSA-Mea/Tween 80 system, we observed the opposite behavior. In both regions, the minimal interfacial tension ($\sigma < 1$) was reached remarkably earlier than with Tween 80 alone. This effect is, most likely, due to solubility of Tween 80 in the aqueous phase. In addition, a strong synergism exist between PIBSA-Mea and Tween 80 [17] which accelerates the reduction of σ in both regions. The dramatic decrease of interfacial tension in the region above the

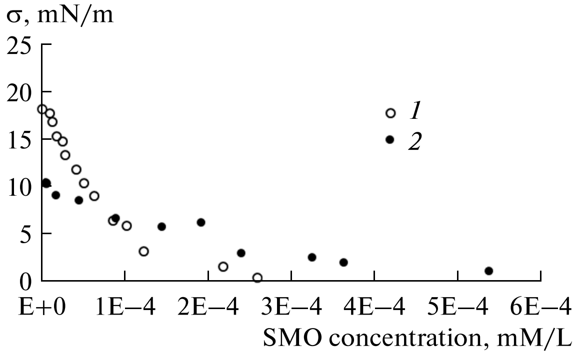

Fig. 3. Interfacial tension dependencies on SMO concentration for PIBSA-Mea/SMO mixtures in the regions below (*1*) and above (*2*) the CMC of PIBSA-Mea system.

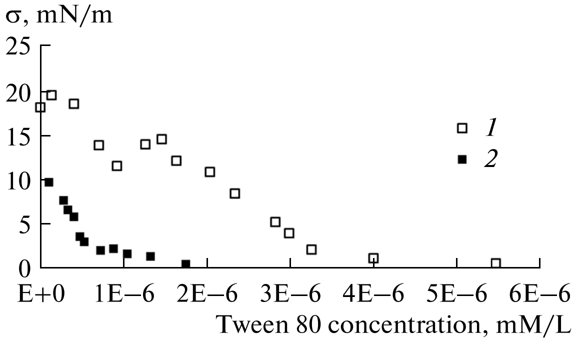

Fig. 4. Interfacial tension dependencies on Tween 80 concentration for PIBSA-Mea/Tween 80 mixtures in the regions below (*1*) and above (*2*) the CMC of PIBSA-Mea system.

Table 2. Refinement and aging times for un-pumped emulsion formulations

Sample	Refinement time (min)	Ageing time after preparation (day)
PIBSA-Mea	55	45
PIBSA-Mea/SMO	29	16
PIBSA-Mea/Tween 80	8	30

Table 3. Droplet size and aging time for the pumped emulsions after 5 pumping cycles

Sample	d_{32} after pumping (μm)	Aging time after pumping (day)
PIBSA-Mea	Not available	0
PIBSA-Mea/SMO	5.5	3
PIBSA-Mea/Tween 80	6.0	10

CMC can be explained by the capturing of PIBSA-Mea micelles by Tween 80 molecules at the interface that increases the adsorption rate [18].

Stability Study

Emulsification. The dynamic instability during emulsification is related to rapturing of large droplets into smaller ones caused by mechanical forces. Splitting of droplets is determined by capillary number, which depends on interfacial tension and viscosity of both internal phase and emulsions. In this study viscosity of the aqueous phase of approximately 41 cP, and the viscosity of the emulsions was close to 640 cP. Therefore, the emulsification process was affected mainly by interfacial properties of the system.

Refinement times (i.e. manufacturing time required to achieve a dispersed phase droplet size $d_{32} = 10$ μm) for the different emulsion samples are presented in Table 2. Adding co-surfactant to the emulsion formulations decreased the refinement time due to the higher packing efficiency of the mixture, which decreases the opportunity for droplets to re-coalesce during refinement. Droplet size reduction was enhanced by the addition of Tween 80 as the co-surfactant. This effect was a consequence of the higher adsorption efficiency of the PIBSA-Mea/Tween 80 mixture, which favors a higher rate of break up in the emulsification process.

Pumping. When the emulsion is subjected to high shear, the larger droplets undergo severe deformation resulting in their splitting to smaller ones. Pumping therefore can be considered as a second stage of refining. Previous studies showed the instability of PIBSA-Mea emulsions when pumped [19]. Small SMO molecules were added to improve the pumpability (that is, the stability under high shear) through the rapid formation of coverage on a newly formed droplet surfaces [12]. In this study, better pumpability was, however, achieved by using Tween 80 with high molecular weight.

This result implies that, for the high shear conditions, not only the rate of diffusion of surfactant within the emulsion to cover newly formed surfaces is important, but also the dense packing of the interfacial film, which increases resistance to droplet splitting. As it is shown in Table 3, the d_{32} of emulsions stabilized with PIBSA-Mea/Tween 80 is larger than the d_{32} of PIBSA-Mea/SMO stabilized emulsions after five pumping cycles.

Aging. Instability of highly concentrated emulsions over time (their aging) is a consequence of slow crystallization of the oversaturated inorganic salt solutions in the emulsion. Aging can be accelerated by high shear conditions [1]. The results of aging studies, given as the number of days until crystallization begun (that is, the period after which first crystals formed within the sample were observed under the microscope), are presented in Tables 2 and 3 for un-pumped and pumped emulsion, respectively. A binary mixture of PIBSA-Mea/Tween 80 significantly increased the aging time of pumped samples and improved the stability of the un-pumped emulsion with time in comparison with that of PIBSA-Mea/SMO samples. Crystallization of inorganic salts in such emulsions initiates within the droplets. When the crystal size reaches certain critical value, the crystals rupture the interfacial layer and the content of the droplet spread into the emulsion until it is fully crystallized [20]. To prevent or slow down the kinetics of crystallization of the dispersed phase it is thus necessary to provide both a tightly packed interfacial layer and a strong steric barrier.

The microphotographs in Fig. 5 show that the nucleation of crystals occurs later and the kinetics of the crystallization from nucleation to fully crystallized emulsion is much slower for the PIBSA-Mea/Tween 80 samples than that for the PIBSA-Mea/SMO system. This difference is, most likely, due to the stability of the micelles as well as that of the packed interfacial layer in PIBSA-Mea/Tween 80. Destabilization of PIBSA-Mea micelles by adding SMO, due to the incompatibility between SMO and the hydrophobic portion of PIBSA-Mea, has been reported [21, 22]. It is possible that there is a synergism in mixed micelles of PIBSA/Tween 80 which enhances emulsion stability, but further investigation is needed to clarify the effect of Tween 80 molecules on PIBSA micelles.

CONCLUSION

The interfacial behavior of binary mixtures of oil/oil (PIBSA-Mea/SMO) and oil/water (PIBSA-Mea/Tween 80) soluble surfactants was investigated and it was related to the stability of highly concentrat-

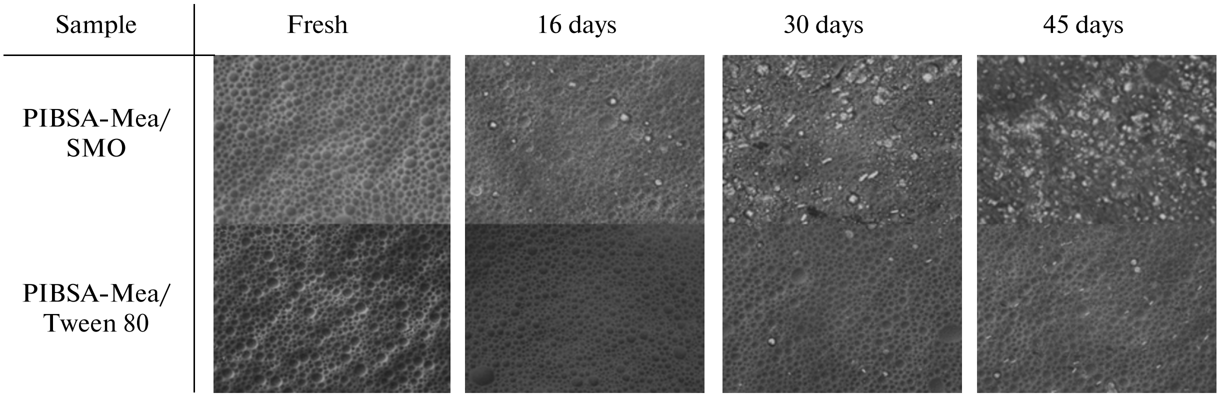

Fig. 5. Optical microphotographs of fresh and aged un-pumped emulsions (×500 magnification).

ed water-in-oil emulsions with an oversaturated dispersed phase. There was a remarkable difference in interfacial behavior of these two binary mixtures. Synergism was clearly present between PIBSA-Mea/Tween 80 molecules forming interfacial film. The ability of Tween 80, in spite of its high molecular weight, to improve the stability of the emulsion both during storage and under high shear conditions results from the formation of tightly packed interfacial film through the synergetic interaction between the PIBSA-Mea and Tween 80 molecules. The PIBSA-Mea/SMO mixture improved emulsion pumpability due to rapid formation of surface coating by the small SMO molecules, but it significantly assists crystallization of the emulsion.

REFERENCES

1. Masalova, I., Malkin, A.Ya., Ferg, E., Kharatiyan, E., Taylor, M., and Haldenwang, R., *J. Rheol.*, 2006, vol. 50, p. 435.
2. Masalova, I. and Malkin, A.Ya., *Appl. Rheol.*, 2007, vol. 17, p. 42250.
3. Masalova, I. and Malkin, A.Ya., *Colloid J.*, 2007, vol. 69, p. 198.
4. Mason, T.G., *Curr. Opin. Colloid Interface Sci.*, 1999, vol. 4, p. 231.
5. Masalova, *I.* and Malkin, A.Ya., *Chem. Eng. Res. Design*, 2013, vol. 91, p. 204.
6. *Encyclopedia of Pharmaceutical Technology. Vol. 2. Biodegradable Polyester Polymers as Drug Carriers to Clinical Pharmacokinetics and Pharmacodynamics* / Ed. by Swarbrick, J. and Boylan, J.C., New York: Taylor & Francis, 1989.
7. Lu, D. and Rhodes, D.G., *Langmuir*, 2000, vol. 16, p. 8107.
8. Chow, M.C. and Ho, C.C., *J. Am. Oil Chem. Soc.*, 1996, vol. 73, p. 47.
9. Campana, M., Webster, J.R.P., Gutberlet, T., Wojciechowski, K., and Zarbakhsh, A., *J. Colloid Interface Sci.*, 2013, vol. 398, p. 126.
10. Ghaicha, L., Leblanc, R.M., Villamagna, F., and Chattopadhyay, A.K., *Langmuir*, 1995, vol. 11, p. 585.
11. Ortiz, D.P., Baydak, E.N., and Yarranton, H.W., *J. Colloid Interface Sci.*, 2010, vol. 351, p. 542.
12. Masalova, I., Kovalchuk, K., and Malkin, A.Ya., *J. Disp. Sci. Technol.*, 2011, vol. 32, p. 1547.
13. Reynolds, P.A., Gilbert, E.P., Henderson, M.J., and White, J.W., *J. Phys. Chem. B*, 2009, vol. 113, p. 12231.
14. Drelich, A., Gomez, F., Clausse, D., and Pezron, I., *Colloids Surf. A*, 2010, vol. 365, p. 171.
15. Kovalchuk, K. and Masalova, I., *S. Afr. J. Sci.*, 2012, vol. 108, Art. no. 178, http://dx.doi.org/10.4102/sajs.v108i3/4.178
16. Opawale, F.O. and Burgess, D.J., *J. Colloid Interface Sci.*, 1998, vol. 197, p. 142.
17. *Mixed Surfactant Systems* / Ed. by Holland, P.M. and Rubingh, D.N., Washington, DC: Am. Chem. Soc., 1992.
18. Jiao, J. and Burgess, D., *AAPS Pharm. Sci.*, 2003, vol. 5, p. 62.
19. Reynolds, P.A., McGillivray, D.J., Gilbert, E.P., Holt, S.A., Henderson, M.J., and White, J.W., *Langmuir*, 2003, vol. 19, p. 752.
20. Tshilumbu, N.N., Kharatyan, E. and Masalova, I., *J. Disp. Sci. Technol.*, 2013, vol. 35, p. 283.
21. Reynolds, P.A., Gilbert, E.P., Henderson, M.J., and White, J.W., *J. Phys. Chem. B*, 2009, vol. 113, p. 12243.
22. Shiao, S.Y., Chhabra, V., Patist, A., Free, M.L., Huibers, P.D.T., Gregory, A., Patel, S., and Shah, D.O., *Adv. Colloid Interface Sci.*, 1998, vol. 74, p. 1.