

Double-Tailed Surfactants and Their Chain Length Compatibility in Water-in-Oil Emulsions

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The effect of carbon number has been studied with three different series of double tailed surfactants, viz. poly(isobutylene)succinic anhydride esterified with di- and triethanolamine esters of *n*-alkylsuccinic anhydride and poly(isobutylene)succinic anhydride esterified with ((*n*-alkyloxy)propyl)diethanolamine. The primary hydrocarbon chain of the surfactants comprised polyisobutylene of approximately 34 backbone carbon number and the secondary hydrocarbon chain comprises *n*-alkyl groups varying from C₈ to C₂₀. The results indicate that the surface properties at the water-oil interface correlate well with chain length compatibility effects in the mixed surfactant and cosurfactant systems.

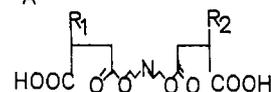
Introduction

The effects of chain length compatibility and surface properties of mixed surfactant systems are well documented with regard to the formation and stability of foams and emulsions.¹⁻⁹ The formation and various physicochemical properties of emulsions are reported to be influenced by the alkyl chain length of cosurfactants and oils. It has also been reported that the structure as well as the nature of the cosurfactants has a strong influence on the properties of microemulsions.⁴ However, no such study has been made on surfactants containing two dissimilar hydrocarbon chains. The present study involved the investigation of the ester derivatives of poly(isobutylene)succinic anhydride of di- and triethanolamine esters of *n*-alkylsuccinic anhydride (series A and series B respectively)¹⁰ and ((*n*-alkyloxy)propyl)diethanolamine (series C). The structural formulas of these three classes of surfactants are shown in Chart I. The surface properties of the water-oil interface and the properties of emulsions based on these double tailed surfactants were studied as a function of secondary alkyl chain length (C₈-C₂₀).

The efficacy of these emulsifiers was examined in water-in-oil (w/o) emulsions, particularly useful for explosives purposes. In order to suit the redox stoichiometry, such w/o emulsions comprise a very large volume of supersaturated nitrate salt solutions finely dispersed in a small

Chart I

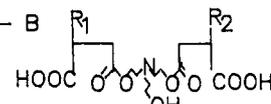
Series - A



R₁ = Polyisobutylene

R₂ = *n*-alkyl(C₈, C₁₀, C₁₂, C₁₄, C₁₆ & C₁₈)

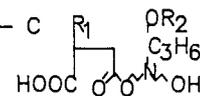
Series - B



R₁ = Polyisobutylene

R₂ = *n*-alkyl(C₈, C₁₀, C₁₂, C₁₄, C₁₆ & C₁₈)

Series - C



R₁ = Polyisobutylene

R₂ = *n*-alkyl(C₁₀, C₁₂, C₁₃, C₁₆, C₁₈ & C₂₀)

volume of hydrocarbon oil.^{10,11} The primary functions of the surfactants used for these emulsions are to form and stabilize the high internal phase w/o emulsions, to maintain the supercooled state of the dispersed droplets, and to prevent the emulsions from crystallizing.

The formation and stability of the w/o emulsions studied with these surfactants were found to have some dependence on the chain length compatibility.

Experimental Section

Poly(isobutylene)succinic anhydride of average molecular weight 1050 (supplied by Paramins Exxon) was further purified by chromatographic separation in order to avoid contaminations from free oils or poly(isobutylene) components.

((*n*-Alkyloxy)propyl)diethanolamines of Tomah Products, *n*-alkylsuccinic anhydride of Humphery Chemicals, and reagent grade di- and triethanolamines (BDH) were used without any further purification.

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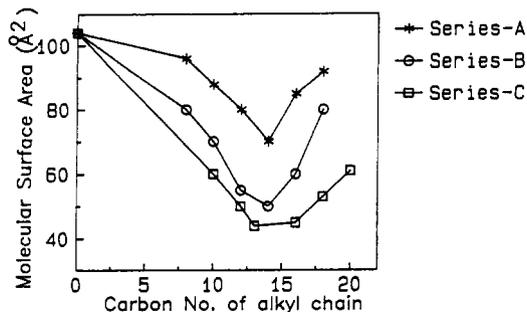


Figure 1. Molecular surface area versus carbon number of secondary alkyl chain plots for the series A, series B, and series C surfactants.

The detailed synthetic methods for series A and series B surfactants are disclosed elsewhere.¹⁰ Surfactants of series C were synthesized by reacting ((*n*-alkoxy)propyl)diethanolamines with poly(isobutylene)succinic anhydride at 80 °C.

Interfacial tensions were measured by the Du Nouy ring detachment method. Molecular surface areas were calculated from the γ_{12} vs $\ln C$ plots using Gibb's equation for surface excess concentration,¹² where γ_{12} is the interfacial tension between water and oil and C is the concentration of surfactants.

The w/o emulsions of particular interest^{10,11} were prepared in a Hobart vertical mixer by dispersing 94.0 parts by weight of ammonium nitrate salt solutions in 6 parts by weight of oil phase. The oil phase comprised a blend of oil and emulsifiers mixed in the ratio of 3:1.

The paraffin oil used for the present study was obtained from Petro Canada. The equivalent alkane carbon number (EACN) of the paraffin oil was determined by chromatographic analysis of the oil and it was found to be 17.64.

The low-frequency electrical resistance measurements were done on a LCR Databridge 452 ex. Aimtest Limited with an IEEE-488/RS232 interface. The measurements were done at limited frequency ranges, i.e. at the line frequency (60 Hz), 120 Hz, 1 kHz, and 10 kHz, and by extrapolation the low-frequency resistances were calculated. More accurate results would have been obtained by using instruments with larger frequency ranges, however, the method proved satisfactorily reproducible since we were more interested in the trend of results rather than the absolute values. All measurements reported in this paper were carried out at 30 °C in a parallel plate conductivity cell of area 24 cm² with a cell gap of 3 mm.

Results and Discussion

In a particular series of surfactants secondary *n*-alkyl chains were varied from C₈ to C₂₀. The interfacial tensions were measured at a water-paraffin oil interface. The experimental results showed that (Figures 1 and 2) irrespective of the type of surfactants studied a minimum in interfacial tension and a minimum in molecular surface area were found when the secondary alkyl chains of the double-tailed surfactants composed approximately 14 carbon atoms. Shah et al.³⁻⁸ demonstrated the validity of the relationship

$$L_s = L_o + L_a$$

in various systems where L_s is the carbon number of the surfactant, L_a is the carbon number of the cosurfactant (normally an alcohol), and L_o is the carbon number of the oil or EACN of the oil.^{7,8}

Here, we apply the above relationship to the double-tailed surfactants where L_s is considered as the principal hydrocarbon chain length (i.e. polyisobutylene chain present in the poly(isobutylene)succinic anhydride de-

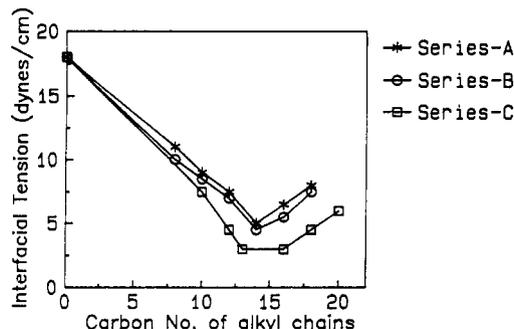


Figure 2. Interfacial tension versus carbon number of secondary alkyl chain plots for the series A, series B, and series C surfactants.

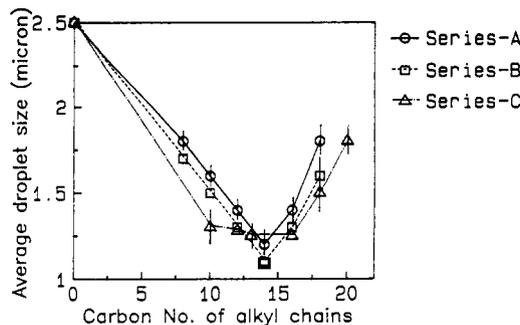


Figure 3. Emulsion droplet size versus carbon number of secondary alkyl chain plots for the series A, series B, and series C surfactants.

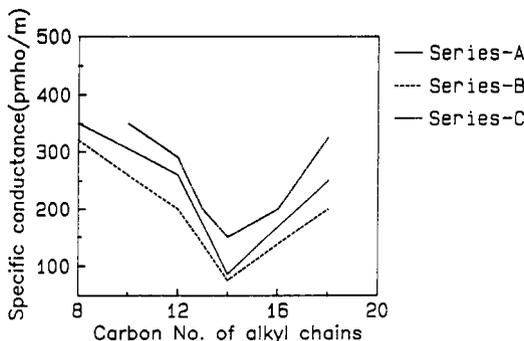


Figure 4. Specific conductance of emulsions versus carbon number of secondary alkyl chain plots for the series A, series B, and series C surfactants.

riivative of molecular weight 1050 which has a backbone carbon number of 34), L_a as secondary hydrocarbon chain length (i.e. *n*-alkyl chain present in *n*-alkylsuccinic anhydrides or in ((*n*-alkoxy)propyl)diethanolamines) and L_o as the oil chain length, i.e. paraffin oil of EACN 17.64. It is quite evident that at L_a close to $L_s - L_o$ maximum packing of the double-tailed surfactants occurs at the oil-water interface.

Figures 3 and 4 show the average droplet size and specific conductance of emulsions containing the double-tailed surfactants. Results indicate that at a given aqueous/oil phase ratio the droplet size and the specific conductivity of emulsions decrease as L_a approaches close to $L_s - L_o$. Under identical manufacturing conditions the average size of the emulsion droplets is controlled by the interfacial tension between the aqueous and oil phases. The variation in average droplet size can be attributed to the efficiency of surfactants to reduce the interfacial tension. The work done in expanding an interface is $\gamma_{12} \Delta A$, where γ_{12} and ΔA are the interfacial tension and increase in interfacial area, respectively. Thus, for the same input of emulsi-

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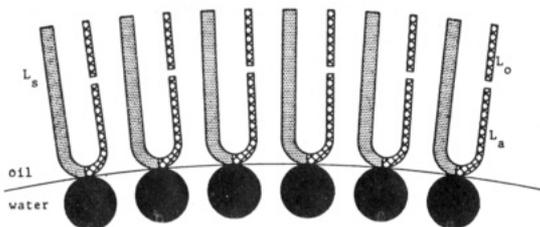


Figure 5. Schematic illustration of the chain length compatibility effect and ordering of alkyl chains at the oil-water interface. L_s and L_a are the chain lengths of principal hydrocarbon chain and secondary hydrocarbon chain of the double-tailed surfactant, respectively. L_o is the chain length of oil.

fication energy, a lower value of γ_{12} yields a higher value of ΔA (i.e. a smaller droplet size) in the oil-water-emulsifier system. The average droplet size measured from the optical micrographs of each emulsion sample demonstrates the importance of the length of secondary alkyl chain in the dispersion process while keeping the input of emulsification energy constant (Figure 3).

It should also be emphasized that the electrical conductivity values show that the present system forms water-in-oil type emulsions in spite of the fact that the volume fraction of the dispersed aqueous phase is around 90.5% (considering the density of the aqueous phase as 1.4 g/cm³ and the density of the oil phase as 0.85 g/cm³).

The packing of the spherical droplets in an emulsion comprising an internal phase volume fraction greater than 0.74 is possible with increased degree of polydispersity in droplet size distribution. Under such circumstances, smaller droplets occupy the interdroplet spaces.^{12,13} It is also to be noted that a monodisperse emulsion is also possible to form with such high internal phase volume by enhancing the energy of emulsification. However, the spherical shape of the droplets in such cases suffers a great deal of distortion and results into the formation of distorted polyhedral structure.¹²

As the system forms the water-in-oil type emulsions, it can be concluded that v/aL is greater than unity according to Israelachvili et al., where v is the volume of the hydrophobic moiety, a is the effective area of the polar head group, and L is the effective length of the nonpolar chain of the surfactant molecule.¹⁴

The droplets of the dispersed aqueous phase can be considered as conducting spheres with fully polarized interfaces when subjected to an electrical field. Conduction in emulsions occurs due to the transport of charges (both conductive and inductive).¹⁵ Because the films of the present emulsions are largely composed of hydrocarbons, their conductance is usually very low, typically in the range of pmho/m. Such conduction is facilitated by the fluidity of the films.¹² The more rigid the film, the less conducting the emulsion.

The trend observed with conductivity results can be attributed to the rigidity of the films. As $L_s - L_a$ approaches L_o , the disruptive effect due to the disordered terminal segments of the hydrocarbon chains in w/o type emulsions reaches a minimum⁴⁻⁶ (Figure 5).

Using mixed monolayers, it has already been shown that the thermal motion of the disordered terminal segment produces a disruptive effect on packing of surfactant molecules that increases the surface area per molecule at the interface.³⁻⁶ This in turn influences surface viscosity,

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Table I

surfactant	mol wt	molecular surface area, Å ²	av droplet size, μm	X_i , Å ²	X_e , Å ²
series A, $R_2 = 14$	1450	70.5	1.2	0.44×10^{23}	0.45×10^{23}
series B, $R_2 = 14$	1494	50	1.1	0.30×10^{23}	0.49×10^{23}
series C, $R_2 = 13$	1395	44	1.25	0.29×10^{23}	0.43×10^{23}

surface tension, contact angle, boundary lubrication, melting point of crystals, and the stability of foams and emulsions based on mixed surfactant systems.^{1,2,16-18}

In the context of chain length compatibility and packing of surfactant molecules at the interface, it would be worthwhile to show an estimate of the fraction of the total surfactant molecules present at the interface of emulsion droplets by following simple mathematical calculations. The total interfacial area can be estimated from (i) surfactant's molecular surface area as calculated from the Gibb's equation and (ii) average droplet size of the emulsion.

If we are to assume that after the emulsification all surfactant molecules are at the interface, we can calculate the total interfacial area (X_i) by the following expression

$$X_i = \frac{m}{M} NA \quad (\text{Å}^2)$$

where m is the weight of surfactant used for emulsification (i.e. 1.5 g/100 g of emulsion), M is the molecular weight of the surfactant, N is Avogadro's number, and A is the molecular surface area of the surfactant obtained from γ_{12} vs $\ln C$ plot. Similarly, the total interfacial area (X_e) can also be calculated from the average droplet size by the following expression

$$X_e = 100\phi a_d / V_d$$

where ϕ is the volume fraction of the aqueous phase, V_d is the average volume of the droplets, and a_d is the average surface area of the droplets. This can further be simplified as

$$X_e = \frac{6\phi 10^{26}}{D} \quad (\text{Å}^2)$$

where D is the average diameter of the emulsion droplets. Ideally X_i should be equal to X_e , if all surfactant molecules are present at the interface. In Table I results of the calculations are shown for the molecules which exhibited maximum chain length compatibility effect in each series of surfactants studied.

The results show that for the molecule of series A ($R_2 = 14$) the X_i and X_e values are quite comparable, whereas for the molecules of series B ($R_2 = 14$) and series C ($R_2 = 13$), X_i is smaller compared to X_e . Such anomalies for those two compounds can be explained by interpenetration of oil molecules at the interface and subsequent swelling. Probably, the molecules of series A ($R_2 = 14$) offer enough room to accommodate the interpenetrating oil molecules at the interface. It seems that the interface comprising the molecules of series B ($R_2 = 14$) and series C ($R_2 = 13$) swells most during the oil penetration.

To summarize, the interfacial area and surface tension experiments are the interesting consequences of the mo-

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lecular packing theories.¹⁹ In all our experiments it was noticed that the minima in interfacial tension, surface area, emulsion droplet size, and specific conductivity of emulsions occurred at $L_a + L_o \sim L_s$. However, the minor deviations observed could be due to the polydispersity of

the polyisobutylene chains of the surfactant molecules and compositional uncertainties in the mixture of branched and straight alkyl chains.⁹

Nevertheless, the secondary alkyl chain length of the surfactant has been found to strikingly influence the properties of the two contacting phases and the phenomena are quite consistent with the structural chain length compatibility effect.

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