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ORIGINAL CONTRIBUTION

Sodium dioctylphosphinate emulsifier properties

Paula V. Messina · Valeria Verdinelli · Pablo C. Schulz

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Abstract The properties of a scarcely studied twin-tailed surfactant, sodium dioctylphosphinate (SDOP), as emulsifier were studied. The SDOP hidrophile–lipophile balance (HLB) value was measured and the Davies HLB group number of the sodium phosphinate group was computed. The surfactant promotes the formation of water in petroleum ether emulsions. The emulsion was characterized by the employment of several techniques such as centrifuge test and turbidimetry and density measurements. The maximum stability was obtained by the surfactant concentration of 0.3 mol dm^{-3} with 14 g of water emulsified in 12.41 g oil/g surfactant was emulsified. Conductivity information was used to study the temperature effect on the emulsion droplets and the energy of the droplet clustering during percolation. The enthalpy of adsorption at the oil/water interface $\left(\Delta H_{\mathrm{s}}^{\mathrm{ads}}\right)$ was positive at all surfactant concentrations ([S]); its absolute value showed a maximum of [S]=0.1 mol dm^{-3} and subsequent decreased was attributed to a change in the droplet interface, which would provide the necessary energy for the adsorption of SDOP molecules. The determination of droplet clustering thermodynamic parameters during percolation showed that droplet clusters were formed spontaneously $\left(\Delta G_{\mathrm{cl}}^{0} < 0\right)$ and the process driving force was a negative enthalpy contribution.

Keywords Twin-tailed surfactant · W/O emulsion · Sodium dioctylphosphinate · HLB · Percolation

P. V. Messina (✉) · V. Verdinelli · P. C. Schulz
Departamento de Química, Universidad Nacional del Sur,
Bahía Blanca 8000, Argentina
e-mail: pau423ve@yahoo.com.ar

Introduction

Emulsions are metastable dispersions comprised of two immiscible fluids like oil and water and are kinetically stabilized by the addition of surface-active species. To reach the dispersed metastable state, energy has to be supplied and the way that emulsions are prepared is of importance to control their final properties.

Emulsions are not stable unless an appropriate surfactant is used. Because knowledge of the emulsification properties of different surfactants is then of paramount importance in the industry of emulsions, the determination of these properties in new possible emulsifier is highly desirable.

Research on emulsion systems is of considerable interest for numerous technical applications such as cosmetics, foods, pharmaceutics, paintings, and coatings.

We have recently focused our interest in the emulsifier properties of sodium dioctylphosphinate, Na $(CH_3(CH_2)_7)_2PO_2$ (SDOP).

SDOP is a little-studied twin-tailed surfactant, which can form, due to it short hydrocarbon tails and large polar group volume, a variety of different phases in the SDOP/water system at low temperatures [1, 2].

Hence, our aim in this article is to build upon the knowledge in this area in several ways. In the first part of this work, the SDOP hydrophile–lipophile character was determined by a water titration [3] and the hydrophile–lipophile balance (HLB) phosphinate group number, which is unknown until now, was estimated by the employment of the Davies and Rideal [4] equations.

Next, the SDOP emulsifying properties were evaluated in mixtures of petroleum ether and water. As could be assumed by the structure of this twin-tailed surfactant, it promotes the formation of water in oil (W/O) emulsions. As far as we know, the emulsification properties of SDOP are not reported in literature. The emulsion characterization was due by the utilization of several techniques such as analytical centrifugation and turbidimetry and density measurements.

Conductivity and viscosimetry information were employed to analyze the temperature effect on the emulsions and the energy of droplet clustering during percolation.

Theory

HLB group number

A systematic ranking of emulsifiers and of oils with respect to the HLB was undertaken by Griffin [5].

To obtain the HLB values, a quantity of techniques were proposed. We used a literature method [3] in which a suitable solution of oil and emulsifier is titrated with a liquid of limited solubility (water). The endpoint is detected by the appearance of a dense cloud, which is reproducible and the water added to obtain it indicates the HLB of the emulsifier blend.

Davies [4] proposed that the HLB value may be computed from the structure of an emulsifier and that it can be calculated as a function of the hydrophobic and hydrophilic group numbers according to the following equation:

$$HLB = 7 + \sum \text{(group numbers)} \tag{1}$$

Turbidity

The turbidity of a polydisperse system is the sum of all the contributions over the various particle sizes; the turbidity (τ) of the total distribution and the drop volume fraction (ϕ_i) expressed in integral form are:

$$\tau = \frac{N\lambda^2}{4\pi}\int_0^\infty \alpha^2 f(\alpha) Q(\alpha, m)\, d\alpha \tag{2}$$

$$\phi_i = \frac{N\lambda^3}{6\pi^2}\int_0^\infty \alpha^3 f(\alpha)\, d\alpha \tag{3}$$

where N is the particle concentration in particles per volume unit, $\alpha = \frac{2\pi r}{\lambda}$ is the dimensionless particle size, r is the particle radius, λ is the wavelength in the dispersing media, $f(\alpha)$ is the number fraction of particles with size between α and $\alpha+1$, Q is the scattering coefficient, and m is the ratio of the particle to the medium refractive index [6].

Because the volume fraction is either known only approximately or not at all, it can be eliminated by taking a ratio of turbidities at two widely separated wavelengths. Therefore, the turbidity ratio gives the information about the particle size distribution (PSD).

The changes in PSD under conditions of simultaneous flocculation and creaming for various times showed that the PSD shifts to large particle sizes, owing to the initial flocculation of the smaller particles. Because the stability to flocculation increases exponentially with increasing particle size, the smaller particles flocculate quickly to form relatively stable flocks [7]. If the prepared emulsions are relatively stable, shifts in PSD would occur slowly. Therefore, it is possible to evaluate the emulsion stability by measuring the change of PSD with time and the turbidity method is useful because the turbidity measurements are rapid and simple. Consequently, the change of turbidity ratio as a function of time exhibits the relative emulsion breaking process by simultaneous flocculation and coalescence more exactly than the measurements of turbidity at a single wavelength.

Surfactant adsorption enthalpy

The surfactant adsorption at the oil/water droplet interface is described by:

$$\mu_s^{des} = \mu_s^{ads} \tag{4}$$

where s is the adsorbed surfactant. Considering the chemical potential dependence with temperature, Eicke et al. [8] deduced the following equation:

$$\frac{\partial T}{\partial x_s} = \frac{RT_p^2}{x_s \Delta H_s^{ads}} \tag{5}$$

where $\partial T/\partial x_s$ is the slope of the T_p vs x_s plot, R is the gas constant, x_s is the surfactant concentration, and $\Delta H_\mathrm{s}^\mathrm{ads}$ is the surfactant adsorption enthalpy at the oil/water drop interface.

Energy of droplet clustering percolation

It is generally accepted that conductivity percolation in W/O emulsions and microemulsions is a result of droplet clustering. Individual droplets maintain a low conductivity, the conductivity increases as droplets assemble in clusters and ion diffusion and/or exchange of droplet content is facilitated, and an infinite percolation droplet network is eventually formed.

Ray et al. [9] estimated the energy of the droplet clustering process utilizing the values of dispersed phase volume fraction (ϕ_d) at the percolation threshold for different temperatures. It was postulated that the threshold of electrical percolation corresponded to the formation of the first open structure of an infinite cluster [9]. The droplets above the percolation threshold, aggregates in clusters, were considered to be a phase different than that of nonpercolating droplets, with distinct physical properties such as conductivity. This is comparable to the pseudophase concept used for modeling the formation of micelles in amphiphilic solutions (association model) [10].

In the light of the concept of droplet association, the Gibbs free energy of droplet clustering (standard free energy change for the transfer of 1 mol of droplets from an infinite dilute solution to the percolating cluster), ΔG^0_{cl} was calculated from the relationship [9, 10]:

$$\Delta G^0_{cl} = RT \ln X_p \tag{6}$$

where R is the gas constant, T is the absolute temperature, and X_{p} is the mole fraction of droplets corresponding to the percolation threshold (ϕ_{d}) at temperature T. Another way of arriving to Eq. (6) is to assume equilibrium between individual droplets and droplet clusters [11]. Application of Gibbs–Helmholtz equation allows the standard enthalpy of cluster formation, ΔH^0_{cl}, to be expressed as:

$$\Delta H^0_{cl} = -RT\left[\partial \ln\left(X_p\right)/\partial T\right] = R\left[\partial \ln\left(X_p\right)/\partial(1/T)\right] \tag{7}$$

Finally, the standard entropy of cluster formation per mole of droplets, ΔS^0_{cl}, can be obtained from:

$$\Delta S^0_{cl} = \left(\Delta H^0_{cl} - \Delta G^0_{cl}\right)/T \tag{8}$$

It has been shown for surfactant micellization and block copolymers [11] that within experimental error:

$$\frac{\partial \ln\left(X_p\right)}{\partial(1/T)} = \frac{\partial \ln(X)}{\partial\left(1/T_p\right)} \tag{9}$$

where X is the droplet concentration expressed in mole fraction and T_{p} is the percolation temperature for a given ϕ_{d}; Eq. (8) thus becomes:

$$\Delta H^0_{cl} = R\left[\partial \ln(X)\Big/\partial\left({}^{1}\!/_{T_p}\right)\right] \tag{10}$$

Materials and methods

Materials All reagents were 99% pure and used as received. Petroleum Eter 60–80 °C was purchased from Cicarelli Laboratories. Dioctylphosphinic acid was synthesized and purified according to the method in the literature [12]. The acid was neutralized with a concentrated NaOH solution and then dried under vacuum to constant weight.

Oleic acid, sodium oleate, sodium dodecyl sulfate (SDS), and the solvents benzene and dioxane were from Sigma.

HLB value determination The surfactant HLB value was estimated by the method described by Greenwald et al. [3]. Samples of 1 g of emulsifier were accurately weighed into 125-ml Erlenmeyer flasks and 30 ml of solvent (4% v/v benzene in dioxane) was added to dissolve the sample. To ensure the dissolution, the samples were sonicated. This clear solution was titrated with distilled water from a burette until the first persistent turbidity was obtained. The volume of added water up to the endpoint is called the water index.

Using this procedure, a calibration curve was plotted by using mixtures of oleic acid (HLB=1), sodium oleate (HLB=18), and sodium oleate with sodium dodecyl sulfate (HLB=40) mixtures [7]. To obtain the intermediate HLB values, mixtures of these surfactants were used and the following equation was employed:

$$\begin{aligned} &\mathrm{HLB_{mix}}=w_{\mathrm{A}}\mathrm{HLB_A}+w_{\mathrm{B}}\mathrm{HLB_B} \\ &w_A+w_{\mathrm{B}} = 1\ \mathrm{g} \end{aligned} \tag{11}$$

where $\mathrm{HLB_{mix}}$, $\mathrm{HLB_A}$, and $\mathrm{HLB_B}$ are the HLB values for the mixture, the surfactant A, and the surfactant B (the weights of the last two in the mixture are w_{A} and w_{B}). The different mixtures were then treated as described above to obtain the respective water index, and then the HLB values were plotted as a function of the water index to obtain a calibration curve. A range of 1 to 26 HLB values were tested and are summarized in Table 1. The SDOP sample was then tested following the same procedure.

Emulsions system Experiments were performed on water/SDOP/oil emulsion systems. The oil phase tested was petroleum ether 60–80 °C (composed by a linear hydrocarbon mixture with boiling point in the 60–80 °C temperature range) as a model for aliphatic Argentinean petroleum. The composition of the emulsion is given here in terms of W_0, the ratio of water to surfactant concentration, and S_0, the ratio of oil to surfactant concentration. Emulsions of S_0=0–60 and W_0=16–43 were investigated.

Emulsions were prepared by mixing 26 ml of oil with 14 ml of SDOP aqueous solutions having different surfactant concentrations. The mixture was sonicated in a laboratory ultrasound generator (MADA no. 6000) during different times. The resulting emulsions were then placed in stoppered test tubes and left to equilibrate at room temperature for approximately 24 h before the experimental measurements.

To obtain the data as a function of W_0, an emulsion made with concentrated surfactant aqueous solution was titrated with water before each measurement.

Table 1 Change in water titration values for the different HLB systems

HLB[a]	Sodium oleate/g	Oleic acid/g	SDS/g	HLB[b]	Water index/ml
1	0	1.0011	0	1.0011	11.2
4	0.1764	0.8236		3.9988	12.6
6	0.2942	0.7063		6.0019	13.7
8	0.4121	0.5881		8.0059	15.3
10	0.5293	0.4704		9.9978	17.1
12	0.6472	0.3517		12.0013	19.8
16	0.8824	0.1170		16.0002	31.8
18	1.0001	0	0	18.0018	38.8
20	0.9090		0.0908	19.994	40.2
22	0.8182		0.1820	22.0076	40.4
24	0.7274		0.2727	24.0012	39.9
26	0.6364		0.3635	25.9952	42.3

[a] Theoretical HLB system value

[b] Calculated HLB system value in accordance with the weighted quantities of surfactants (Eq. 11).

Centrifuge test Experiments were carried out in an ACL PK 120 centrifuge. The samples were centrifuged during 10 min and the acceleration was varied from 0 to 2,000 rpm.

Turbidity ratio measurements All emulsions were allowed to age for 24 h at room temperature and were diluted four times in oil.

Spectral absorbance was measured after dilution by using a Spectronic 21D UV–Visible spectrophotometer at 850 and 450 nm with time. The turbidity ratio was defined as the ratio of turbidity at wavelengths of 850 and 450 nm and the slope was calculated within 50 min.

Conductivity measurements The emulsions' conductivity was measured as a function of temperature with an OAKTON con 510 series conductivimeter, an OAKTON conductivimeter cell, and a OAKTON ATC probe.

The test tube with a certain amount of sample (prepared as mentioned above) was placed in an Edmund Bühler bath with a CRIBABB-selected CT-47 heating head ($T \pm 0.02$ °C). The sample was equilibrated for at least 10 min after any temperature change and before any conductivity reading was done.

The temperature range was 22–50 °C, upper temperature studies were limited due to the oil phase evaporation.

Density measurements Emulsion density was measured by the employment of a Becker's Sons balance. During the experiments the temperature was kept constant at 22 °C. For all experiments only double-distilled water was used.

Results and discussion

HLB value and HLB phosphinate group number determination

For the water titration of SDOP 4% benzene in dioxane solution the cloud point was reached when 27.5 ml of water was added. The introduction of this data in the calibration curve resulted in an $HLB_{SDOP}=14.86$. By the application of Eq. (1) and using the value of −0.475 for the HLB group number of $–CH_2–$ and $–CH_3$ [4], the HLB group number for the phosphinate was calculated as 15.46.

Water/SDOP/oil emulsion stability

The effect of SDOP molecules in emulsion stability was evaluated. It was determined that all water was emulsified, but the sedimentation of water droplets liberates some petroleum ether as a supernatant. The effect of sonication time and surfactant concentration on the emulsion stability to sedimentation was evaluated as the volume of separated oil after 24 h. It may be seen that the system had its maximum stability when $[S]=0.3$ mol dm^{-3}.

Centrifugation is a useful tool to investigate the emulsions stability. During the centrifuge test, the droplets were accelerated beyond the earth acceleration (g) to raise their mobility. The influence of centrifugal acceleration on the emulsion stability must be evaluated to ensure that results of accelerated testing are valid for conditions of normal gravity. Figure 1 shows the effect centrifugal speed on the volume of separated oil after 10 min of centrifugation vs surfactant concentration in water.

The stability to sedimentation increased with the sonication time and decreased with centrifugal acceleration (Fig. 1). It may also be seen that the maximum of emulsion volume and sedimentation stability was obtained with a surfactant concentration of 0.3 mol dm^{-3} and a further increase in SDOP concentration does not improve the surfactant performance. This fact was probably due to the saturation of the water drop interface with surfactant molecules.

Increasing the processing time, the sedimentation velocity of water droplets was reduced, leading to an increase in stability. On the contrary, an augment of the centrifugal acceleration increased the sedimentation velocity and caused a reduction in the emulsion stability. The differences in the dependence on processing time or in the effect of centrifugal acceleration were therefore related to the stabilization and partition efficiency of the surfactant molecules to the droplet surface.

Turbidity measurements were also used to determined emulsion stability, and a technique utilizing spectral absorbance at two different wavelengths [13] was applied to allow the determination within a relatively short period of time.

Fig. 1 Effect of centrifugal speed on the amount of separated oil phase vs [S]

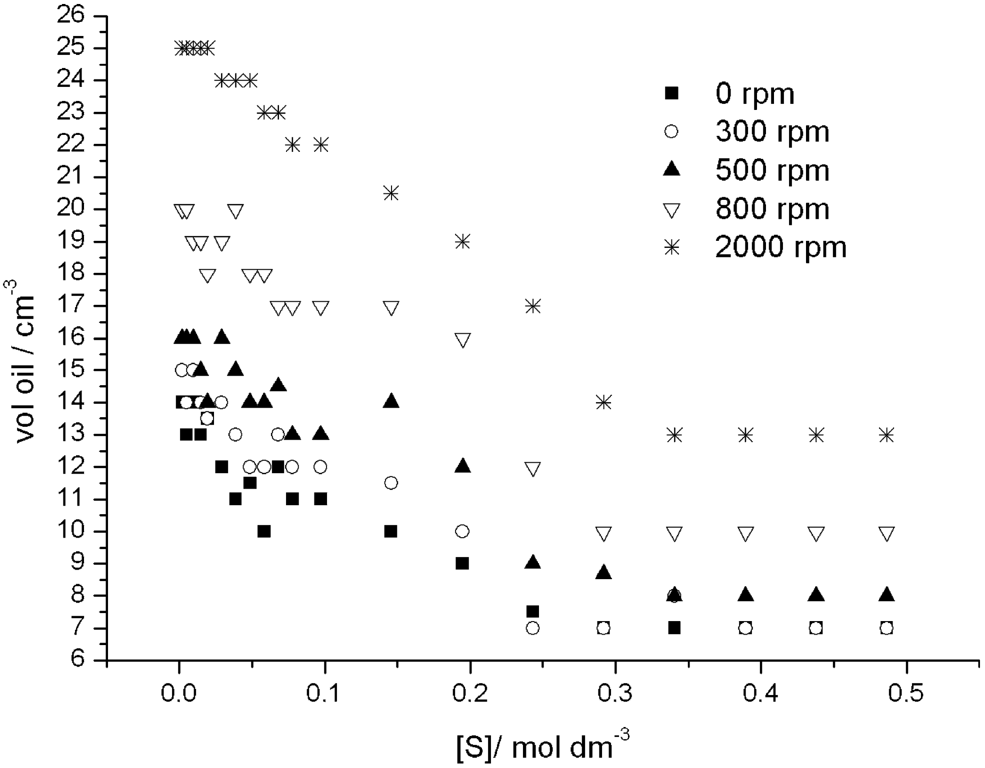
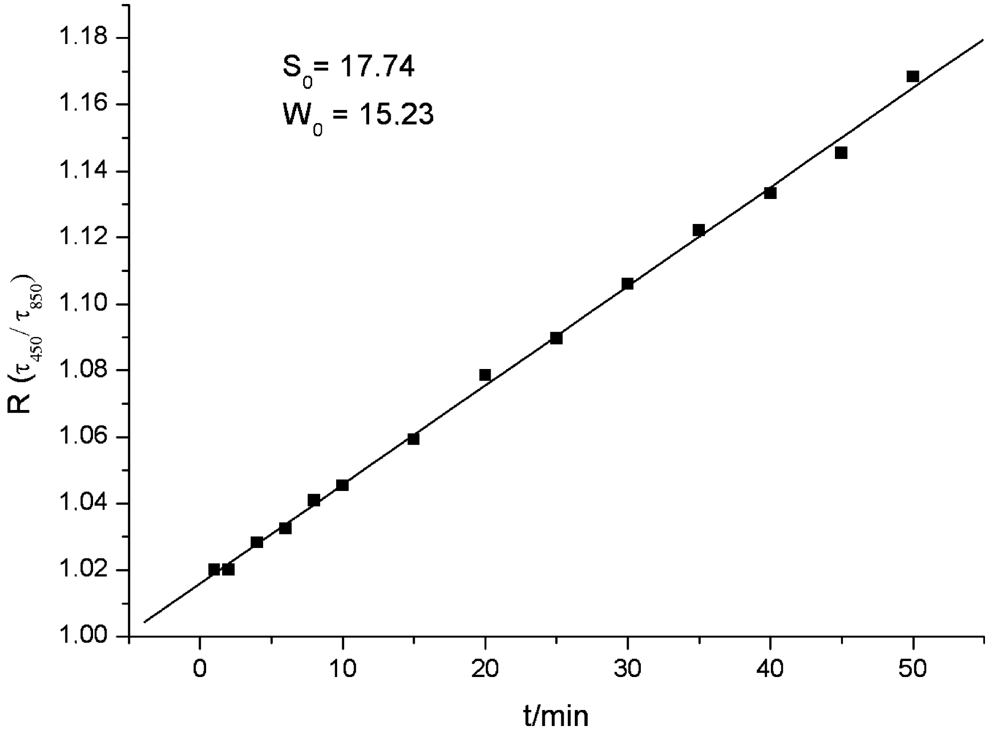


Figure 2 shows the turbidity ratio dependence on time for the water/SDOP (0.3 mol dm^{-3}/ether emulsion) system. The slopes were calculated from the linear increases of turbidity ratios with time. The change of slope turbidity ratio for diluted emulsions prepared from water/SDOP/oil at the maximum stability surfactant concentrations (0.25–0.5 mol dm^{-3}) were plotted in Fig. 3. The minimum slope turbidity ratio was at [S]=0.3 mol dm^{-3}, corresponding to the most stable emulsion. An increase of emulsifier concentration slightly decreased the emulsion stability confirming our previous obtained results.

Fig. 2 Turbidity ratio variation as a function of time



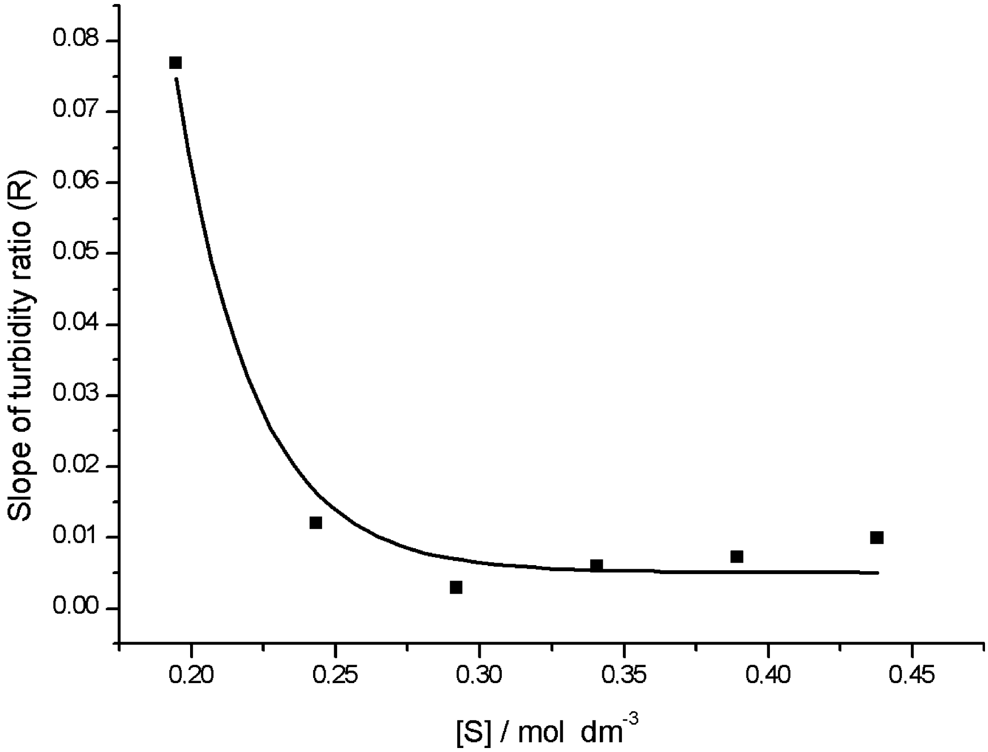


Fig. 3 Change of slope turbidity ratio for diluted emulsions vs [S]

The emulsion density variation with the surfactant concentration (Fig. 4) was then evaluated. There was a decrease of emulsion density with the increase of surfactant concentration; this fact was due to the increase of the proportion of oil incorporated to the emulsion as the surfactant concentration increases.

Experimental turbidimetry and density measurements in addition to centrifugal test determined that SDOP surfactant molecules stabilized the W/O emulsion without the incorporation of additives or a cosurfactant. The maximum stabilization required a surfactant concentration of 0.3 mol dm^{-3} and the corresponding emulsion had 12.54 g of petroleum ether and 14 g water/g surfactant (Fig. 5).

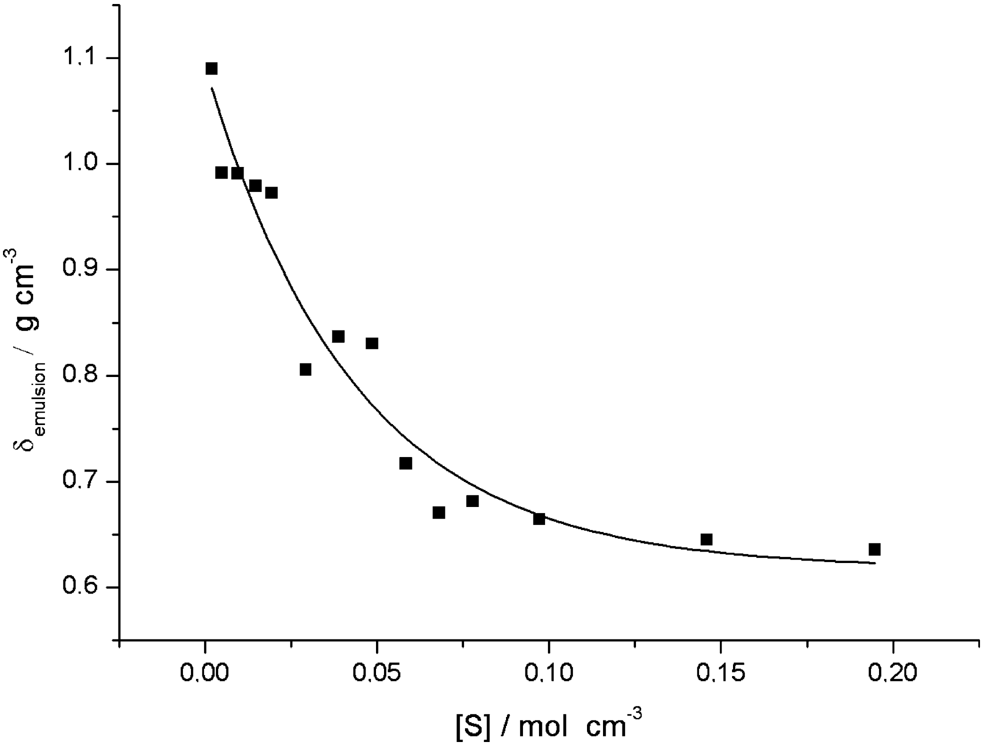
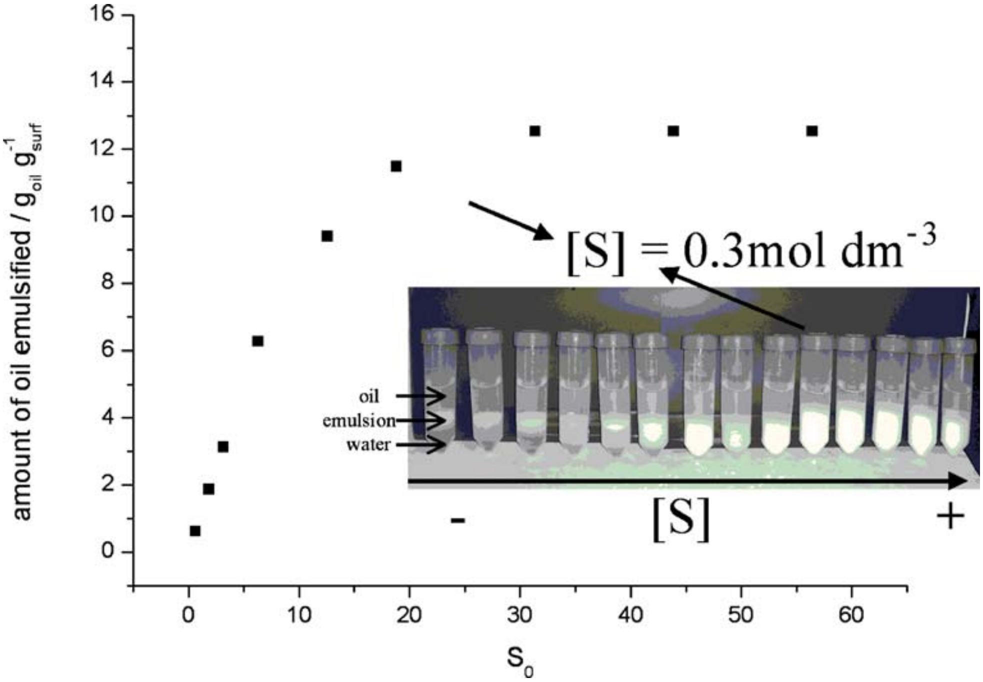


Fig. 4 Emulsion density, δ, variation with surfactant concentration [S]

Fig. 5 Amount of emulsified oil vs S_0 (oil to surfactant ratio)



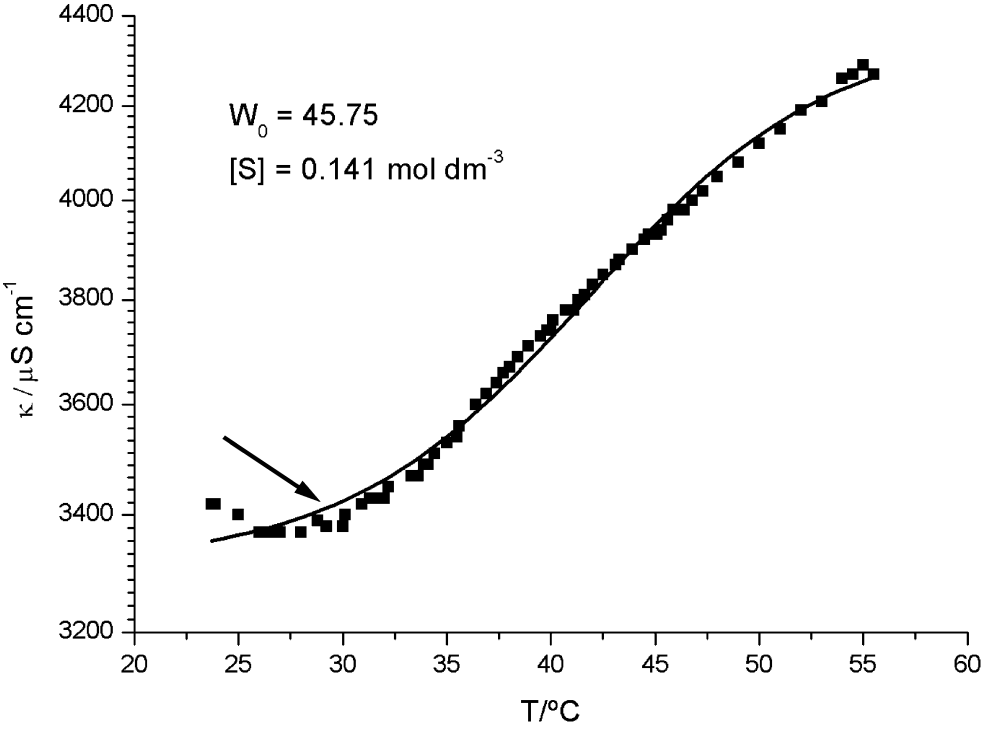
Temperature effect on water/SDOP/oil microemulsions

SDOP adsorption enthalpy at the oil/water droplet interface

The temperature effect on conductivity is presented in Fig. 6 for W/O emulsions of varying W_0, which is proportional to the droplet radii and concentration ($\approx 1/S_0$ for any given W_0).

The logarithm of emulsion conductivity exhibited a characteristic sigmoidal behavior as the temperature increased for all emulsions tested. This conductivity increase is indicative of percolation [14–16]. Both charge-hopping and coalescence percolation mechanism can adequately explain this influence of temperature on conductivity. An increase in temperature would increase the probability of surfactant ionization and the range of ion diffusion (charge-hopping percolation mechanism) and also increase the

Fig. 6 Temperature effect on emulsion conductivity for different W_0 systems. The *arrow* indicates the percolation temperature T_P



frequency of droplet collisions and solubilizate exchange (coalescence mechanism). The percolation temperature, T_P, is defined as the point at which a dramatic change in slope (break) in the conductivity vs temperature curve occurs (as shown by an arrow in Fig. 6), indicating the transition from a nonpercolating to a percolating state.

This effect can be attributed to enhanced interdroplet interaction with increasing droplet size as the overlap volume of the surfactant tails when two droplets approach each other increases, and to an increase fluidity of the surfactant interface.

The application of Eq. (5) to the water/SDOP/oil emulsion system resulted in $\Delta H_s^{ads} > 0$ values (Fig. 7). ΔH_s^{ads} augmented with surfactant concentration until a maximum of [S]=0.1 mol dm^{-3} and then decreased. This fact would probably be due to the surfactant molecules becoming increasingly soluble in oil with raising temperature. Similar results were obtained by Eicke et al. [17] for the water/AOT/oil emulsion system. AOT, Aerosol–OT (sodium bis(2-ethylhexyl)sulfosuccinate), is a twin-tailed ionic surfactant, too. The maximum ΔH_s^{ads} value would bee possible due a change in the droplets structure. The change of droplet to clusters would provide the necessary energy for the adsorption of SDOP molecules at the droplet interfaces.

Notice that emulsion density (Fig. 4) also became constant at [S]≈0.1 mol dm^{-3}, which indicates that the water/oil ratio per unit volume does not change above this concentration value. This probably means that the mechanism in emulsion formation and stabilization changes at this surfactant concentration. In the presence of a large amount of surfactants molecules, [S]>0.1 M, the total forces between surfaces may oscillate due to the occurrence of oscillatory structural forces. Structural forces are a consequence of variations in the density of packing of small surfactant molecules around a surface on the approach of a second (stratification). Stratification of particles such as surfactants or micelles in thin liquid films explains, for example, the stepwise thinning occurring in large soap or emulsion films during water drainage. At low surfactant concentration, [S]<0.1 M, the force between the surfaces becomes monotonically attractive and structural forces transform into the depletion attraction. The depletion attraction has an entropic origin: If two large oil droplets approach one another, surfactant coils are excluded from the region in between, leading to an uncompensated pressure within the depleted region. The simplest description of the depletion interaction consists in ascribing a characteristic separation at which the small surfactant molecules are excluded [18].

Energetic of droplet clustering during percolation

Figure 8 shows the emulsion conductivity as a function of W_0 at various temperatures. For relatively low temperatures (T=22 °C), the conductivity decreased after the maximum at W_0=23 and no percolation was observed with further increase of W_0. At intermediate temperatures, the conductivity values exhibited a maximum at W_0=23, then decreased and passed through a minimum before increasing monotonically for higher W_0 values. Similar results were reported by Peyrelasse and Poned [19] who argued that the maxima and minima did not correspond to

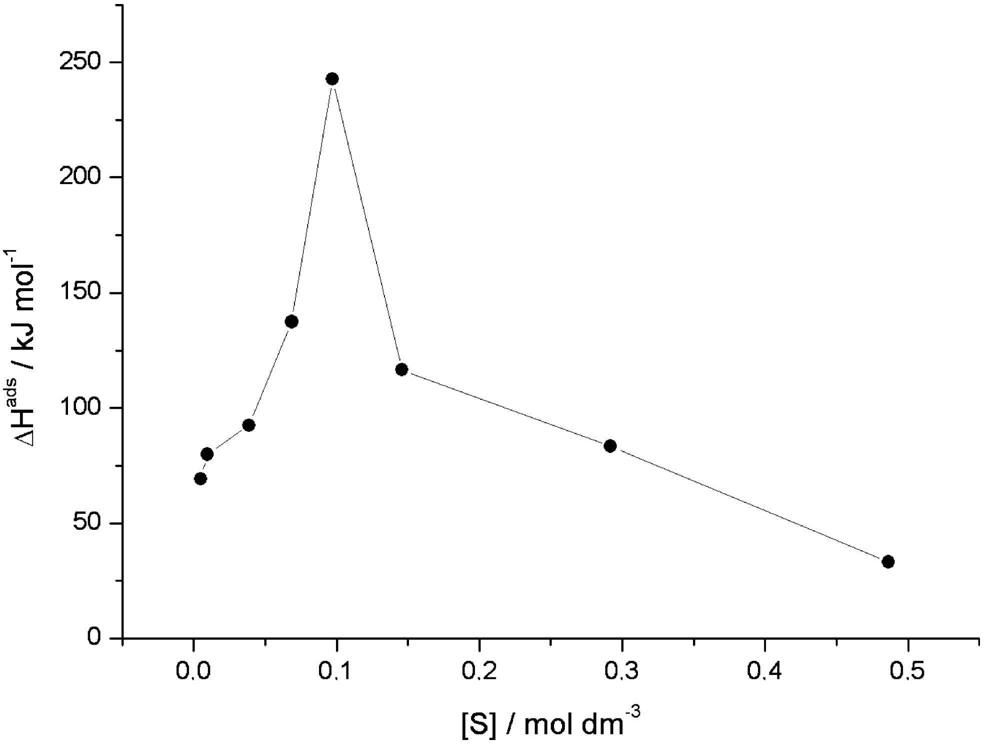
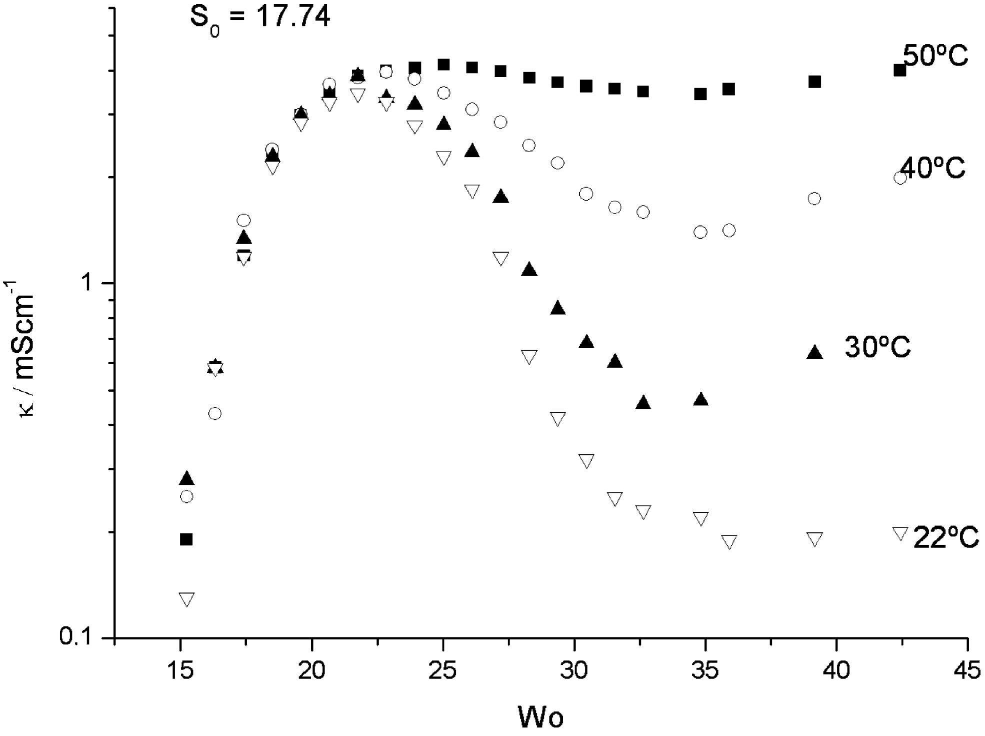


Fig. 7 SDOP adsorption enthalpy at the water/oil interface, ΔH^{ads}, vs [S]

Fig. 8 Emulsion conductivity, κ, as a function of W_0 at 22 °C (*inverted triangle*), 30 °C (*triangle*), 40 °C (*circle*), and 50 °C (*square*)



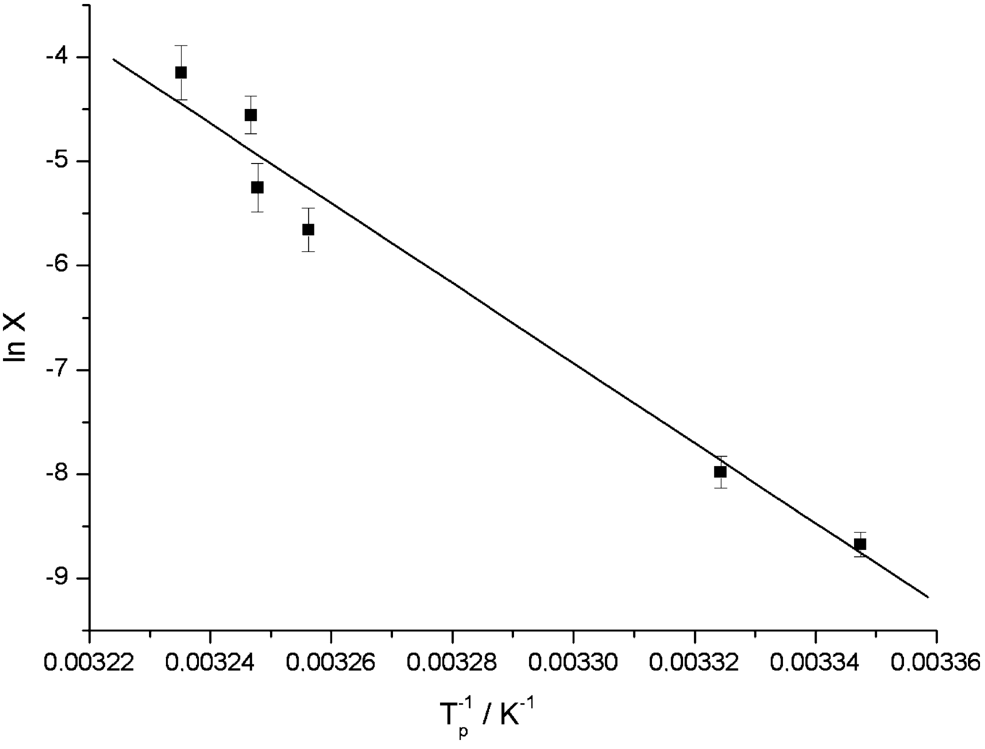
the structural changes but were linked to $|\phi - \phi_c(W_0)|$ where $\phi_c(W_0)$ is the volume fraction of water at the percolation threshold.

In accordance with Eq. (9), the natural logarithm of X ($\approx 1/S_0$) was plotted as a function of inverse percolation temperature (Fig. 9) and ΔH^0_{cl} was calculated using Eq. (10).

The free energy (ΔG^0_{cl}, calculated from Eq. (6)) plotted as a function of T, is shown in Fig. 10 and the ΔS^0_{cl} values were obtained from Eq. (8). The droplet-clustering thermodynamic parameters are summarized in Table 2.

The free energy is negative because the droplet clusters were formed spontaneously. ΔS^0_{cl} was negative, indicating that the transference of microemulsion droplets from

Fig. 9 Logarithm of droplet concentration (X) variation with $1/T_p$



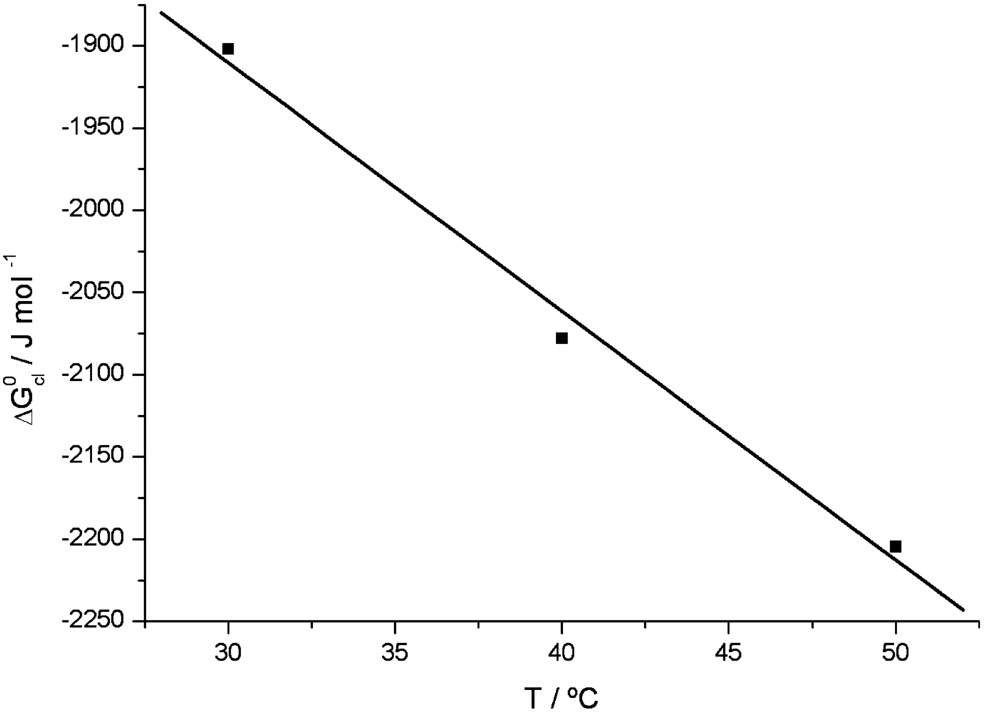


Fig. 10 Gibbs free energy of droplet clustering vs *T*

solution to the percolating cluster is an entropically disfavored process. It was therefore clear that the driving force for clustering during conductivity percolation is the negative enthalpy contribution.

The phenomenon of emulsion droplet clustering can be related to the reversible flocculation of sterically stabilized colloidal particles [20, 21].

The enthalpic stabilization is typical in aqueous dispersions and entropic stabilization is more common in nonaqueous media; however, both stabilization types were observed in both aqueous and nonaqueous media [17].

Concluding remarks

SDOP HLB is 14.86 and the HLB group number for the phosphinate was calculated as 15.46. Then the emulsifier SDOP properties were analyzed. It was determined that the tested surfactant stabilized W/O emulsions without the incorporation of additives or a cosurfactant. The maximum stabilization to sedimentation was obtained with an aqueous medium of 0.3 mol dm^{-3}, which emulsifies 14 ml of water and 12.54 g oil/g surfactant.

Table 2 Droplet-clustering thermodynamic parameters

T/°C	ΔH^0_{cl}/kJ mol^{-1}	ΔG^0_{cl}/kJ mol^{-1}	ΔS^0_{cl}/kJ mol^{-1} K^{-1}
30	−305.79	−1.99	−1.00
40		−2.08	
50		−2.22	

Conductivity information was employed to analyze the temperature effect on the emulsions; the droplet clustering energy during percolation SDOP adsorption enthalpy at the oil/water droplet interface was always positive. ΔH_s^{ads} augmented with surfactant concentration until a maximum of [S]=0.1 mol dm^{-3} and then decreased. The maximum ΔH_s^{ads} value probably corresponded to the change in the structure of the droplets. The determination of droplet-clustering thermodynamic parameters during percolation showed that droplet clusters were formed spontaneously $\left(\Delta G^0_{cl} < 0\right)$ and the process driving force was a negative enthalpy contribution.

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