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ORIGINAL CONTRIBUTION

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Phase behaviour and physicochemical properties of microemulsions with a non-ionic surfactant (IGEPAL)

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Abstract The non-ionic surfactant pentaethylenglycol-4-octylphenyl ether (igepal CA-520) represents a good industrial alternative to the long-tail members of the C_iE_j family. In this paper, the phase behaviour of the microemulsion system igepal CA-520/*n*-decane/brine is studied in detail. An isotropic phase was found, as well as liquid crystalline and cream-like structures, depending on composition and temperature. Such structures can either form single-phase homogeneous mixtures, or coexist with other structures when phase separation takes place. Below surfactant concentration of about 20%, more complicated phase equilibria develop as temperature changes. The presence of different additives shifts the temperature ranges where the different phases exist, while keeping the general shape of the phase diagram, which agrees with the general rules for non-ionic surfactants. Complementary rheology experiments reveal a change from non-Newtonian to Newtonian behaviour during the phase transition from a lamellar phase to the isotropic microemulsion. A structure of water droplets associated in clusters can be proposed from SANS and electrical conductivity.

Key words Microemulsions – non-ionic surfactants – phase behaviour – structure

Introduction

Mixtures of oil, water (with or without salt), and one or more surfactants (amphiphiles) can form transparent, homogeneous and thermodynamically stable (as opposed to kinetically stable) dispersions of one of the fluids within the other. Such dispersions are called microemulsions [1]. The formation of a microemulsion is due to a large reduction of the interfacial tension between water and oil phases driven by the surfactant. However, this is not always the case, and instead, many different other structures can develop (cloudly, lamellar, etc.). Individual phases do not necessarily constitute the whole system, and in many cases phase equilibria are obtained. All this phenomenology leads to very rich phase diagrams as a function of concentration, temperature or other parameters.

Phase diagrams constitute an essential first step for the study of a given system, because they provide information about the conditions which must be chosen to get the desired structure.

Applications of microemulsions show up increasingly, and range from oil recovery [2] to cosmetics and medicine industry [3] through fine and ultrafine particle synthesis [4]. Particularly, in our research group, microemulsions are used both for the study of hydrodynamic instabilities [5–7] and for the preparation of different kinds of particles with tailored composition and size [8, 9].

The most used non-ionic surfactants are the so-called *n*-alkyl polyglycol ethers (C_iE_j), and the systems in which they are included have been widely studied [10, 11]. The drawback of these surfactants is their high price, especially for the long-tail homologues.

In this paper, we report on the phase behaviour and selected physicochemical properties of microemulsions formed with the non-ionic surfactant Igepal CA-520 (pentaethylenglycol-4-octylphenyl ether) which is relatively cheaper than the long-tail C_iE_j, and is used for practical applications [12]. The main difference between igepal and the pure C_iE_j surfactants (e.g. C_8E_5) is that igepal is an industrial surfactant. This implies a certain polydispersity in the length of both the alkyl and polyglycol chains. In addition, igepal molecules contain a phenyl group, while the chain of the C_iE_j's is always linear. The outline of the paper is as follows: we present first a general view of the phase behaviour of the system igepal/*n*-decane/brine. Attention is then devoted to specific compositions where the isotropic microemulsion phase can exist in a given temperature range. The effect of different additives on such a temperature range is subsequently discussed. The findings can be confirmed by simple rheological and electrical conductivity measurements carried out to complement the characterization.

Experimental

All the chemicals were supplied by Aldrich Chemie, except *n*-butanol and sodium dodecyl sulphate (SDS), supplied by Merck. All of them were used without further purification. In every case double distilled water was used.

The procedure used to determine the phase diagrams is described next. First, samples with the desired composition were prepared. Mixing of the components was carefully performed to avoid externally inducing any order or preferred direction in the system. The samples were poured into graduated stoppered cylinders of 10 ml capacity, which in turn were introduced into a thermostatic bath (0.05 °C stability) with transparent walls. The temperature was increased every 0.1 °C. After mixing, the mixtures were allowed to rest at constant temperature for periods between 12 h and 2 weeks until equilibrium, as indicated by the formation of a single phase or a neat separation between well-differentiated phases, was reached.

The transparent walls of the bath permitted to follow visually the evolution of the system towards the equilibrium state, and to observe the number of coexisting phases, as well as their respective volumes. The presence of possible ordered lamellar phases (liquid crystals) was detected by means of a simple set-up consisting of a pair of crossed polarizers, which allow the pass of light when birefringent anisotropic structures are placed in between.

Viscosity measurements were performed in a Searle–Couette type rotational viscometer (Rotovisco Haake R-12). For the temperature dependence of the viscosity, a constant shear rate of 1385 s^{-1} was used.

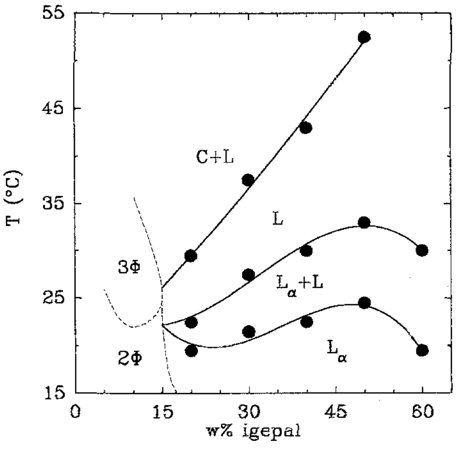
Electrical conductivity was measured with an RLC bridge (Databridge 452) coupled to a thermally stabilized cell. The measurements were made at three different frequencies of 100 Hz, 1 KHz and 10 KHz; then the conductivity value was obtained by extrapolation to infinite frequency [13].

Results and discussion

Phase diagrams

As a first step in the study of the phase behaviour of the system igepal/*n*-decane/brine, we arbitrarily chose as brine a KCl solution with weight fraction 3.3%, and a constant weight ratio *n*-decane/brine = 1. With these restrictions, we studied the phase behaviour when varying temperature, for surfactant contents lower than 60%. As shown in Fig. 1, when surfactant concentration is lower than 20%, two- and three-phase domains were found, which could not be clearly delineated, since even after two weeks no neat borders between phases had developed. The broken lines drawn on Fig. 1 are indicative of the temperature ranges at which the different phase equilibria were found. Note that at low temperature two isotropic phases coexist, while at high temperature it was unclear were the domain limits should be placed. Since no single-phase microemulsions were found to form at such low surfactant concentrations, we focused our attention on the right part of this diagram.

Fig. 1 Phase diagram measured for the system igepal/*n*-decane/brine with constant weight ratio *n*-decane/brine = 1 and varying surfactant concentration. Brine stands for a solution of KCl 3.3 w% in water. For surfactant concentration lower than 20%, two- and three-phase domains were found, which could not be clearly delineated



When surfactant weight fraction was larger than 20%, four main phase domains were found (at very low temperature other non-important phase equilibria were observed as well). At low temperature, the whole volume of the samples is a lamellar phase ($L\alpha$). When increasing temperature, an isotropic upper phase shows up in the system ($L\alpha + L$), whose volume fraction becomes increasingly larger until reaching a second boundary, above which the whole system is isotropic (L). We shall from now on call this phase microemulsion phase. When increasing temperature even further, another phase separation takes place, and a cream phase (C) with appearance of a dense white solid deposits, leaving a more diluted (weaker light scattering) isotropic phase on it (L).

The explanation of such a behaviour can be made on the following points: at low temperatures, surfactant molecules can organize themselves in more or less flat (flexible) layers, separating water and oil domains ($L\alpha$). The stability of this structure is possibly enhanced by the formation of hydrogen bonds between the polar heads of surfactant molecules and water molecules placed in between surfactant layers. When increasing temperature, these hydrogen bonds tend to break, increasing the curvature of surfactant films [14], and giving place to a more flexible structure, which can be bicontinuous or formed by microdroplets of one component dispersed in the other (L). Increasing further the temperature, the curvature of the system should also increase, giving place to the aggregation/flocculation of droplets. Such aggregates deposit as a compact cream (C) out of the isotropic microemulsion phase (L), which in turn becomes more diluted [15].

The structure of both lamellar and isotropic phases was determined by SANS and published elsewhere [16]. These studies confirmed the ordered structure of $L\alpha$ and show that L contains a high volume fraction of polydisperse hard spheres with an average radius of the order of 2.6 nm and polydispersity of the order of 20%.

Once we have determined the different possible phases for the system with equal weight fractions of brine and oil, we want to see how such a phase behaviour changes when varying their weight ratio. We performed studies with two constant surfactant weight fractions, namely 20% and 40%, and variable oil/brine ratio (see Fig. 2). A similar phase behaviour is observed, and only the transition temperatures between the different domains change with composition. It can be observed that the L region becomes broader as igepal concentration increases. As a rule, the L region exists at higher temperatures as igepal content increases.

Given that in many of the applications mentioned in the introduction it is necessary to include in the water phase of the microemulsion variable concentrations of several additives, it is important to know the influence of additive concentration on the phase diagram (temperature shifts, variation of the existence range of the isotropic region, etc.).

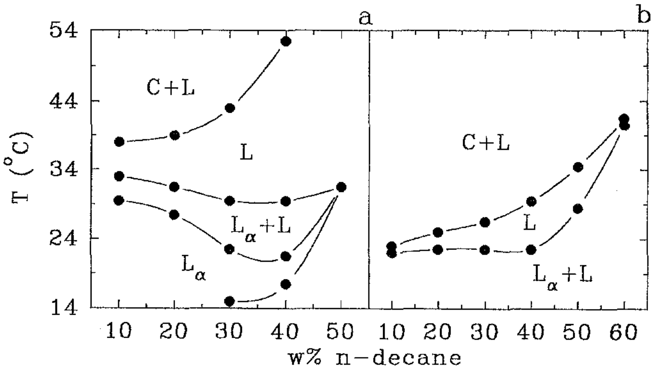


Fig. 2 Phase diagram dependency on the n-decane/brine ratio, expressed as oil content for constant weight fraction of surfactant: (a) 40 w% igepal and (b) 20 w% igepal. Brine stands for a solution of KCl 3.3 w% in water

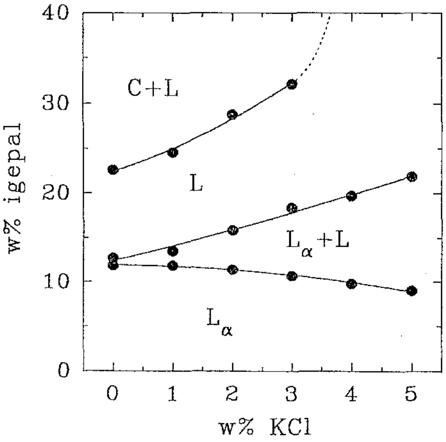


Fig. 3 Influence of KCl concentration in brine on the phase behaviour for constant weight ratio n-decane/water = 1 and different surfactant concentrations at a constant temperature of T = 30.1 °C

First, the influence of KCl concentration on the phase diagram was studied. For different surfactant concentrations and constant weight ratio n-decane/brine = 1, the concentration of KCl in the aqueous solution was varied. The results obtained at 30.1 °C are shown in Fig. 3. Furthermore, one should notice that when KCl concentration increases, higher surfactant concentrations are necessary to reach the microemulsion phase. However, the width of the surfactant concentration range in which the microemulsion exists does not appreciably change until KCl concentrations of about 3%. This is easy to understand on the basis of a screening of the repulsive interactions between surfactant heads. Such a screening reduces the curvature of the surfactant film, favouring a flat geometry.

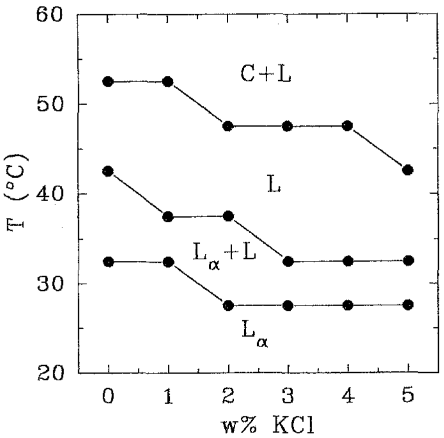


Fig. 4 Influence of KCl expressed as weight % in brine on the phase behaviour of the system with volume fractions 40% igepal, 30% *n*-decane and 30% brine

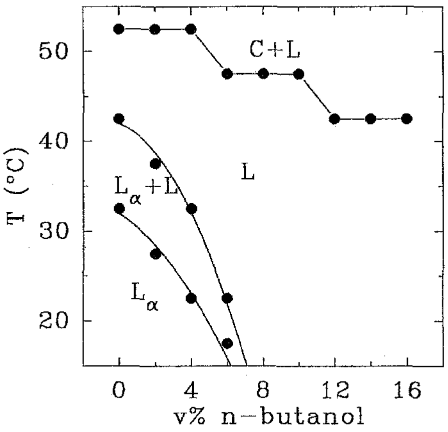


Fig. 5 Influence of *n*-butanol (cosurfactant) on the phase behaviour of the system 40 v% igepal, 30 v% *n*-decane and 30 v% brine

For KCl concentrations larger than 4%, the transition from the isotropic single-phase region (L) to the upper two-phase region ($C + L$) occurs (if ever) at surfactant concentration larger than 50%.

Another interesting system to study, with regard to industrial applications is that where water and oil phases occupy equal volumes. The phase diagram obtained for the system with volume ratio *n*-decane/brine = 1 was similar to that shown in Fig. 1. From Fig. 1, we see that when increasing surfactant concentration, the temperature range where the microemulsion system (L) exists, gets broader. As a compromise with reasonable surfactant concentration, we chose a composition in volume fractions 40% igepal/30% *n*-decane/30% brine. Next, we discuss the effect of different additives on the phase diagram.

First, the phase behaviour of that system for KCl weight concentrations in brine between 0 and 5% was investigated from 10° to 60 °C. As shown in Fig. 4, KCl has a clear lyotropic effect (the mutual solubility water-surfactant decreases), which promotes a shift of the microemulsion region (L) towards lower temperatures.

The effect of cosurfactant addition was also investigated. In this case *n*-butanol was used, and its volume fraction was changed from 0 to 16%, while keeping 40% igepal and volume ratio *n*-decane/water = 1. The whole phase diagram gets drastically shifted to lower temperatures as butanol concentration increases (see Fig. 5). However, the decrease of the transition temperatures from the ordered phases to the isotropic phase is much larger than that of the upper separation limit. The introduction of *n*-butanol molecules (with a short aliphatic chain) among surfactant molecules lowers the interfacial tension and increases the curvature of surfactant layers, towards water or oil, depending on the facility for each possibility. The degree of curvature needed to reach the last phase transition (separation) is more difficult to achieve, and consequently the shift of the corresponding temperature is not so marked.

The influence of the addition of an ionic surfactant, namely SDS was also studied. These experiments were performed varying SDS weight concentration in the aqueous phase from 0 to 10%. As one can see in Fig. 6, there is no appreciable effect of SDS on the transition temperatures where ordered phases are involved ($L\alpha \rightarrow L\alpha + L$ and $L\alpha + L \rightarrow L$), because SDS contains an aliphatic chain of similar size to that of igepal, what means that no additional disorder is introduced in the structure. On the contrary, the effect on the transition ($L \rightarrow C + L$) is opposite to that originated by the presence of KCl and butanol. In this case, SDS molecules lead to an increase in water-surfactant solubility, and when increasing SDS concentration, higher temperatures are needed to destabilize the microemulsion structure [10].

All these results agree with the "general rules" for pure non-ionic surfactants recently summarized by Kahlweit [17]. This shows that such rules can be applied to industrial surfactants like igepal.

Physicochemical properties

As a complement of the characterization, a simple rheological study of the system composed by 40 w% surfactant, 30 w% *n*-decane and 30 w% brine (3.3% KCl) was performed at temperatures ranging both the coexistence region ($L\alpha + L$) and the microemulsion region (see Figs. 1 or 2). Stress-strain curves were obtained for this system which clearly show the differences between the $L\alpha$ and L phases. The $L\alpha$ phase shows a non-linear behaviour of

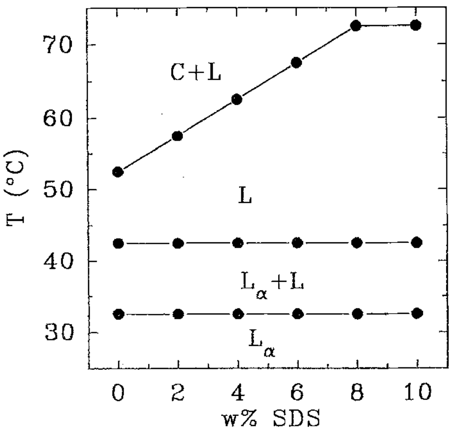


Fig. 6 Influence of SDS, expressed as weight % in brine, on the phase behaviour of the system with volume fractions 40%, igepal, 30% *n*-decane and 30% brine

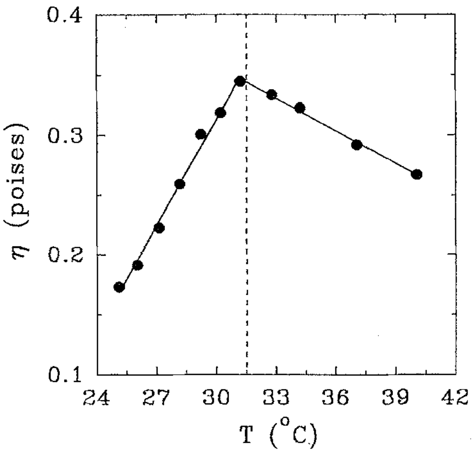


Fig. 7 Change of viscosity with temperature for the system with composition 40 w% igepal, 30 w% *n*-decane and 30 w% brine (3.3 w% of KCl in the aqueous phase). The dashed line shows the transition temperature from the $L\alpha + L$ region to the L region of the phase diagram

the viscosity, which is accompanied by a shear fracture, i.e. at a certain critical value of the shear rate a sudden decay of the stress is observed. On the contrary, the *L* phase shows a Newtonian behaviour in the considered temperature range. When both phases coexist (from 24 to 31 °C) non-linear effects show up, mainly close to the phase transition to $L\alpha$ ($T = 24$ °C), i.e. for temperatures in which the lamellar phase is dominant. Above 26 °C the response is almost linear and fracture is not observed. It must be pointed out that positive "Weissenberg effect" was observed in the interface by means of the rotation of an immersed rod, which evidences the existence of non-zero normal stress in the lamellar phase. This effect can be observed even at slow shear rates, due to the small density difference between both phases.

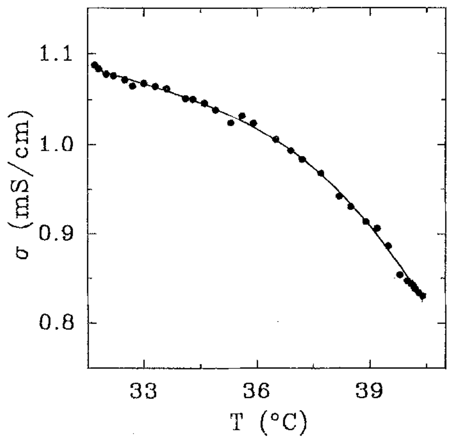


Fig. 8 Variation of electrical conductivity with temperature in the *L* phase for the system 40 w% igepal, 30 w% *n*-decane and 30 w% brine (3.3 w% KCl in the aqueous phase)

Figure 7 shows the temperature dependence of the viscosity from 24° to 40 °C under a constant shear rate of 1385 s^{-1}. A change from an anomalous behaviour, in which viscosity behaves as an increasing function of temperature, to a normal behaviour can be observed. This anomalous behaviour has also been reported for other systems and corresponds to near-critical systems [18]. When the *L* phase coexists with $L\alpha$, the system behaves as a critical fluid, changing drastically this behaviour in the single phase domain, where viscosity decreases with temperature (as in the case of pure fluids).

Electrical conductivity was measured in the isotropic phase (*L*) for the system 40 w% igepal, 30 w% *n*-decane and 30 w% brine, in the temperature range where it exists as a single phase (Fig. 8). The measured electrical conductivity (of the order of 1 mS · cm^{-1}) was much higher than that corresponding to a continuous oil phase, but also much lower than that of a KCl solution of the same concentration (of the order of 50 mS · cm^{-1}).

When SDS, instead of KCl, was added together with the aqueous phase, the same tendency was observed (see Fig. 9), though a slightly lower conductivity was measured. When *n*-butanol was added to the 40 : 30 : 30 system, a very low conductivity was measured, due to the absence of ionic species in the microemulsion, so that meaningful results could not be obtained. However, when *n*-butanol was added to the system containing KCl, an increase of the electrical conductivity was observed at temperatures close to the lower phase transition, being the trend at higher temperatures similar to that observed when *n*-butanol was not present (see Figs. 8 and 9-b).

It is remarkable that from SANS measurements, a W/O structure was proposed for this system [16]. From these results the relatively high conductivity measured

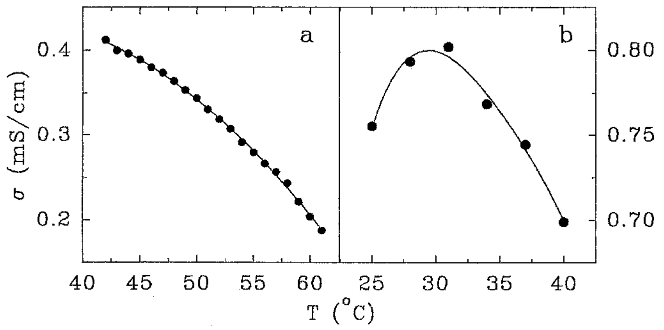


Fig. 9 Temperature dependency of the electrical conductivity in the *L* phase of the system composed by 40 v% igepal, 30 v% *n*-decane and 30 v% brine. (a) 4 w% of SDS in the aqueous phase; (b) 6 v% *n*-butanol, 3 w%KCl in the aqueous phase

must be explained using a percolation model [19] where charge transfer is efficiently performed by the droplets themselves, which form a dynamic structure of permanently changing clusters. The decrease of conductivity with temperature, as well as the slight differences found between the systems with different additives, is probably due to small changes in the shape and the clustering behaviour of the droplets.

Conclusions

The phase behaviour of the system igepal CA-520/*n*-decane/brine was shown to follow the general rules for non-ionic surfactants, i.e., KCl and *n*-butanol move the phase diagrams to lower temperatures (Iyotropic effect). When SDS is present, droplet aggregation takes place at higher temperatures. On the other hand, when surfactant concentration is lower than ≈ 20% two- and three-phase domains are found, but not well defined, probably due to the polydispersity characteristic of this commercial surfactant. It seems that the phenyl group present in igepal molecules has no influence on the properties of the system.

The isotropic phase seems to consist of clusters of water droplets, responsible for a relatively high electrical conductivity.

In summary, the system is suitable for most applications where a high concentration of water pools in a non-polar continuum is needed.

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