Emulsion stabilization by non-ionic surfactants: the relevance of surfactant cloud point

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The effect of various additives, electrolytes and non-electrolytes, on the cloud point of non-ionic surfactants has been studied. Additives which salt-out the polyoxyethylene chains of the surfactants cause decreased stability of oil-in-water emulsions by decreasing the true hydrophile-lipophile balance (HLB) of the surfactant; additives such as sodium iodide and propanol salt-in the non-ionic surfactants and result in an increase in the effective or true HLB of the system. The latter additives do not increase the hydration of the polyoxyethylene chains but their effect must be on the structure of water so that the heat of hydration of the chains is altered. Experiments with free films of the aqueous surfactant (Brij 96) show that thinning rates are markedly affected by the additives, but there is little effect on the equilibrium thickness of the films (*ca* 11 nm). Nonetheless the thickness at the transition from thick film to equilibrium black film decreases with increasing cloud point of the solution indicating increased stability. The importance of structure formation in the liquid film separating the emulsion globules was demonstrated.

Emulsions prepared with non-ionic polyoxyethylene surfactants are stabilized by steric interactions between the adsorbed hydrated polymer chains on close approach of the particles of the disperse phase (Elworthy & Florence, 1969). Extensive work by Napper and co-workers has demonstrated that for sterically stabilized dispersions a correlation exists between the point of instability and the corresponding theta (θ) point of the stabilizing molecules in free solution (Napper 1968, 1970a, b; Napper & Netschey, 1971; Evans, Davison & Napper, 1972). At the θ-temperature the partial molal free energy due to polymer-solvent interactions becomes zero, and the polymer shows ideal solution behaviour. Non-ionic surfactants in aqueous solution exhibit lower critical solution temperatures, and therefore cloud points, at which separation of surfactant from the isotropic solution occurs.

There are two components to the steric interactions between stabilizing polyoxyethylene chains, namely an enthalpic and entropic contribution. The former arises from the loss of water molecules of hydration on compression of the stabilizing chains so it is to be expected that changes in the affinity of the emulsifier for the aqueous phase will affect emulsion stability. Shinoda & Arai (1964) and Sunderland & Enever (1972) have, in fact, shown that there is a correlation between the phase inversion temperature of emulsions and the cloud point of the non-ionic stabilizers in free solution.

Many simple electrolytes decrease the solubility of non-ionic surfactants. This is

readily demonstrated by lowering of the solution cloud point. These electrolytes, such as sodium chloride, also decrease the stability of emulsions which are stabilized by non-ionic surfactants. A number of additives can, however, raise the cloud point of non-ionic surfactants and non-ionic polymers (Shakhova & Meerson, 1972; Ivanova, Alekseeva & Panich, 1973; Horne, Almeida & others, 1971). It is an interesting prospect that these additives may increase the stability of emulsions. The possibility of securing enhanced enthalpic stabilization by the addition of substances which increase surfactant cloud points is considered in this paper. In particular, the relation of cloud point to the true hydrophile-lipophile balance (HLB) of non-ionic emulsifiers in the presence of additives is examined. The deficiencies of calculated Griffin HLB values have been pointed out previously (Florence & Rogers, 1971; Lo, Legras & others, 1972).

In this paper we report results obtained with oil-in-water emulsions in the presence of additives which both raised and lowered solution cloud points. Thin films of some non-ionic detergents in air have also been studied in the hope that these simpler systems would shed some light on the effect of the additives on the intermolecular interactions between adjacent surfactant layers.

MATERIALS AND METHODS

Materials

Emulsifiers. The following commercial non-ionic surfactants were used without purification: Brij 92, Brij 96 and Brij 98 (Honeywill-Atlas, Carshalton, Surrey and Atlas-Seppic, Paris), are polyoxyethylene ethers of oleyl alcohol with calculated HLB values of 4·9, 12·4 and 15·0 respectively. Triton X–100 and Triton X–114 were Rohm & Haas products, through Sigma, London. The Tritons are nonyl phenol polyoxyethylene ethers with an average of 10 and 11·4 ethylene oxide units respectively.

Additives. Salts were analytical grade. Methanol, ethanol, propanol and n-butanol were reagent grade (BDH chemicals). Water was once distilled from an all-glass still.

Oils. Liquid paraffin (Primol 342, Esso), hexadecane (BDH) and *m*-xylene (BDH) were used as received. Polyoxyethylene glycol 400 was obtained from BDH Ltd.

Methods

Cloud points were determined by noting the temperature at which a solution heated above the clouding temperature lost its last trace of turbidity on cooling.

Emulsions of *m*-xylene and hexadecane stabilized by Triton X-100 and Triton X–114 were prepared by repeated passage through a hand homogenizer. Emulsions of liquid paraffin in water stabilized by Brij 92/96 mixtures were prepared by adding the aqueous phase to the oil phase and homogenizing during a standard period of time using a turbine stirrer. Optimum HLB values were obtained as before (Seiller, Arguillère & others, 1968).

In both series, stock emulsions were diluted with the appropriate solutions of additives.

Thinning of vertical aqueous films of Brij 96 and some Brij 96/92 mixtures was studied using an apparatus similar to that used by Lyklema, Scholten & Mysels

(1965). The film, formed on a glass frame (1.6 cm $\times$ 4 cm) raised from a solution of the detergent at room temperature, was illuminated by light focussed from a mercury vapour lamp after passage through a monochromatizing filter (546 nm). The thickness of the soap film was measured by determination of the intensity of light reflected from the film. A photomultiplier (EMI, Middlesex, type 9663B) powered by a stable voltage source (Siemens Type R1184) received the reflected light; the signal was recorded on a Servoscribe recorder (Smiths, London). The reflected intensity (I) was obtained as a function of time and the equivalent film thickness δ_w calculated from

$$\frac{I}{I_{max}} = \sin^2 \frac{2\pi n_0 \delta_w}{\lambda}$$

where I_{max} is the intensity at maximum reflection (silver film), n_0 is the refractive index of water, δ_w is the equivalent water thickness ignoring the sandwich structure of the film—important only in very thin black films— and λ is the wavelength of light used. Thin equilibrium films of sodium dodecyl sulphate gave reproducible thicknesses in good agreement with values quoted by Lyklema & others (1965).

Viscosity measurements on surfactant solutions were made with a suspended level dilution viscometer at 25°; relative viscosity measurements on emulsions were made at the same temperature with an Ostwald (size D) viscometer.

The stability of the emulsions was assessed in several ways. A series of liquid paraffin emulsions was prepared with Brij 92/96 mixtures with a range of HLB values, with and without additives. The particle size of the resulting emulsions, treated identically, their rheological properties, evidence of creaming, inversion and emulsion type were recorded. In this way the HLB value at which a change in property, e.g. emulsion type, occurred could be noted.

RESULTS AND DISCUSSION

The effect of various electrolytes and alcohols, methanol to n-butanol, on the cloud points of representative non-ionic detergents is shown in Fig. 1a and b. Methanol, ethanol and propanol increase the cloud point, but, as has been observed by others (Horne & others, 1971; Ivanova & others, 1973), butanol depresses the cloud point of non-ionic polymers. Of the electrolytes studied, sodium and caesium iodide increase cloud points, the others depress the cloud point.

While dispersions stabilized by non-ionic surfactants and polymers are less sensitive to the action of electrolytes than those stabilized by ionic agents, presence of certain
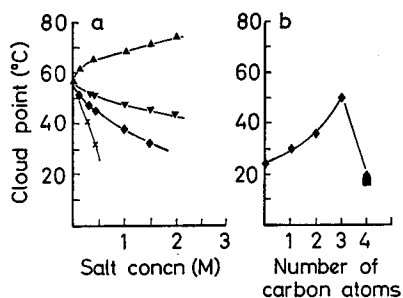
FIG. 1. a. The effect of salt concentration on the cloud point of 1 % w/v Brij 96 solutions ▲ NaI, ▼ KBr, ◆ NaCl, and × Na$_4$SO$_4$.
   b. The effect of the carbon chain length of M normal alcohols (◆) on the cloud point of 1 % w/v Triton X-114. ■ result obtained with isobutanol.

electrolytes induces flocculation and coalescence (Elworthy, Florence & Rogers, 1971). Decreased stability has been attributed (Napper, 1969) to the influence which the ions exert on the structure of water in their immediate environment, rather than in terms of dehydration of the stabilizing species, a view to which Volkov & Ezhov (1972) subscribe. Dehydration of the polyoxyethylene chain on heating has often been assumed to be the cause of clouding. Sodium iodide and the alcohols with a carbon chain length less than 3 have an effect on the solution properties of the stabilizing chains opposite to that of sodium chloride. It might be assumed that these compounds increase by some mechanism the hydration of the polyoxyethylene chain, but the viscosity results show that this is not so. Fig. 2 shows representative results for the reduced specific viscosity of Triton X–100 and polyoxyethylene glycol 400 in the presence of M propanol. As the micelles of Triton X–100 are spherical (Kushner & Hubbard, 1954) a decrease in the intrinsic viscosity, $[\eta]$, can only be ascribed to a *decrease* in the total amount of water bound to the micelle. This implies that the effect of the iodide and the alcohols is not on the non-electrolyte species but is indeed an effect on the water structure surrounding the chains; whether trapped or hydrogen bonded water is not known. The point for potassium bromide shows the expected decrease in reduced specific viscosity on dehydration.
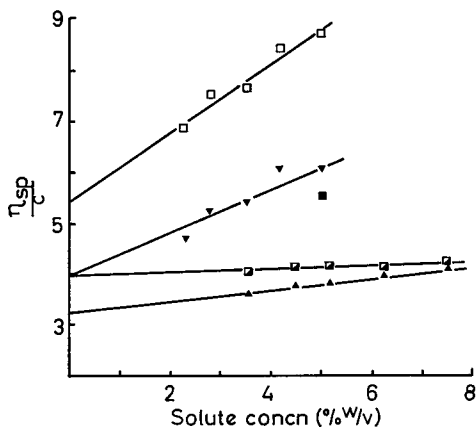

FIG. 2. Reduced specific viscosities (ml g^{-1}) as a function of solute concentration, c, of □ Triton X–100 in water, ▼ Triton X–100 in M propanol and ■ M KBr; ▨ PEG 400 in water and ▲PEG 400 in M propanol.

The micelle surface is not strictly analogous to the emulsion globule interface. Nevertheless the results on the glycol, while not unambiguous because of the possibility of change in solute conformation, support the view of *loss* of hydrating water in the presence of propanol and iodide.

Results on whole emulsions. Decrease in stability of Triton-stabilized emulsions was readily shown to be caused by addition of butanol which caused rapid breaking. Addition of sodium chloride and other electrolytes cause a shift in the optimal HLB for stabilization of the liquid paraffin emulsions stabilized by Brij 92–96 mixtures (Puisieux and Madsen, unpublished). As these emulsions were stabilized by mixtures of surfactants, one of which is insoluble, no solution cloud point can be determined. Nevertheless as it is the protruding long polyoxyethylene chain which is controlling stability, consideration of the cloud point of the soluble surfactant is useful. Decrease in the

hydrophile-lipophile balance of non-ionic surfactants results in decreases in the cloud point of their solutions (Fig. 3).   A substance which decreases the cloud point of a given surfactant therefore can be considered to lower its effective HLB.   Hence we would expect a shift of optimal HLB (i.e. calculated values) to higher values on addition to the emulsion system of electrolytes which salt-out the surfactant chains.   The shift in optimal or critical HLB to lower values on the addition of sodium iodide and the shift to higher values on the addition of sodium chloride is shown in Fig. 4.   If the reasonable assumption is made that the effective HLB required to stabilize an oil-in-water emulsion remains the same on addition of sodium chloride, the change in true or effective HLB of the stabilizers will result in the shift of calculated HLB. On addition of 15 % NaCl to the liquid-paraffin–water system the calculated HLB for maximum stability rises from 7·8 to 9·5; the cloud point of the water-soluble surfactant
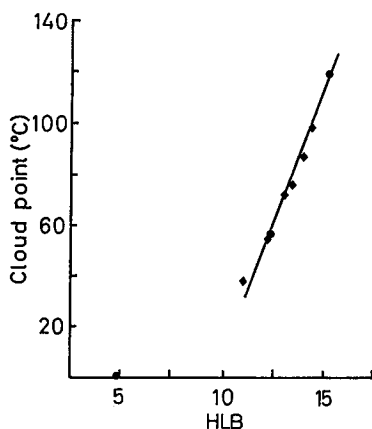

FIG. 3.   Variation of cloud point of surfactant solutions as a function of calculated HLB value.   ◆ values for linear primary dodecanol-polyoxyethylene condensates from Schott (1969); ●Brij 96 and Brij 98, the latter point being obtained by extrapolation to zero salt concentration of cloud points in a series of NaCl solutions.
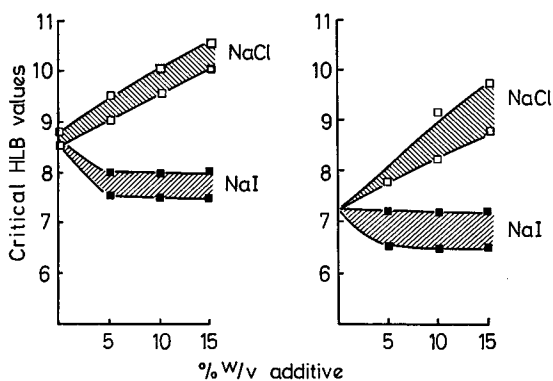

FIG. 4. The change in critical HLB values as a function of added salt concentration, where the salt is either NaCl or NaI.   Results were obtained from measurements of particle size, stability, viscosity and emulsion type as a function of HLB for liquid paraffin-in-water emulsions stabilized by Brij 92–Brij 96 mixtures. Data from different experiments showed different critical values hence on each diagram hatching represents the critical regions while data points actually recorded are shown.   Results on the left-hand diagram show, respectively, particle size and stability data: those on the right-hand diagram show the HLB at transition from pseudoplastic to Newtonian flow properties and emulsion type (o/w→w/o) transitions.

decreases by 35° in the presence of this concentration of NaCl. From Fig. 3 a decrement of 35° in cloud point is equivalent to a decrease of real HLB of 1·6 which is in agreement with the experimentally determined change. Shinoda & Takeda (1970) also observed a decrease in optimal HLB of about 1 unit on the addition of 6% NaCl to an oil-in-water non-ionic emulsion.

The lesser effect of sodium iodide on the cloud point is reflected in the less pronounced effect on optimal or critical HLB value (Fig. 4).

The Triton-emulsions were stabilized with a single surfactant species, therefore it was not possible to carry out similar experiments with them. It was difficult to detect increases in stability of the emulsions in the presence of methanol, ethanol and propanol although there were two pieces of evidence which suggest increased stability: the relative viscosity of the series of emulsions containing the same weight of hexadecane and percentage of Triton X–100 but having M alcohols added showed an increase up to propanol. This could be due to either decreasing particle size (Sherman, 1967) or to increased repulsion between the particles.

The apparent inability to effect larger or demonstrable increases in emulsion stability by the addition of substances which raise the cloud point of the stabilizing molecules may be due to several factors. Increase in aqueous solubility may decrease the concentration of emulsifier at the interface, although interfacial tension measurements do not indicate that this is so; as there is an optimal HLB for each oil to achieve stability, any change in HLB by addition of agents which salt-in or salt-out the stabilizing molecules will shift the stability index from the optimum position.

Results on free films

Although it has been suggested that stabilizers act by keeping the emulsion droplets far apart, actual measurements have shown that the distance between neighbouring droplets in a stabilized system is smaller than in a non-stabilized emulsion and that the stabilizing action depends on increasing the stability at any given film thickness (van den Tempel, 1960). We have measured the thinning rates of aqueous films of Brij 96 and have determined the thickness of the equilibrium black films in the presence of electrolytes and non-electrolytes. Fig. 5 shows typical thickness-time profiles for the surfactant films and shows the sudden point of transformation into black film. Considerable variation was found in the drainage times of the films as can be seen in the insert to Fig. 5 which shows film thickness as a function of log t for a number of Brij 96 solutions. The high viscosity of the NaCl–Brij 96 mixtures results in the long drainage time of their films. Structure-formation in the bulk of the film undoubtedly affects the thinning process and it seems to maintain an abnormally high final thickness. This will affect emulsion stability. Although the salting-out caused by high concentrations of sodium chloride would be expected to drastically decrease steric stabilization, the maintenance of a thick, slow-draining film must to some extent counteract the dehydration of the polyoxyethylene chain.

Fig. 6 shows the thickness of the silver film at the silver-black film boundary, considered to be the "critical" thickness, δ_{crit}, plotted as a function of solution cloud point. Although the recorded critical thicknesses are not identical with the thicknesses of the film at the point when black film just forms, (the point of measurement is not at the top of the film where black film first forms) the trend of results may be informative with regard to relative stabilities.
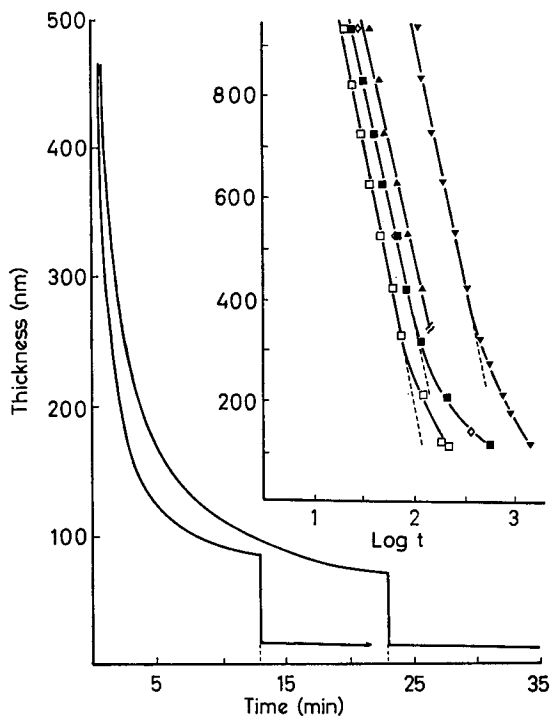
FIG. 5. Typical thickness profiles of thinning films of Brij 96 showing the sudden transition to black film at 13 and 23 mm respectively. So-called critical thicknesses as recorded in Fig. 6 were determined at the point of this transition to thin film. Inset shows thickness *vs* log t relations showing the influence of additive on the thinning behaviour of 2% Brij 96 in water. ◇ M NaI, ■ no additive, ▲ 0·5 M NaCl, ▼ M NaCl □ 0·5 M KBr.

A thin, non-equilibrium film loses its stability at a certain critical thickness (δ_{crit}) and either ruptures or forms with a sudden change in thickness thinner, more stable films (Sheludko, 1967; Vrij, 1966). Sheludko (1967) obtained the following expression for δ_{crit}

$$\delta_{crit} = \left(\frac{3A}{64\sigma}\right)^{\frac{1}{4}} \lambda^{\frac{1}{2}}$$

where A is the van der Waals-Hamaker constant, σ is the surface tension and λ the wavelength of the random surface deformations which lead to rupture (Ruckenstein & Jain, 1974).

Unstable systems reach critical dimensions when relatively thick and if insufficient surfactant is present the films will then rupture. More stable films show the transition to black film. The trends shown in Fig. 6 are the expected trends—on salting-out the surfactant molecules δ_{crit} increases (although no value could be obtained in the very viscous NaCl–Brij 96 mixtures), and on addition of sodium iodide (cloud point values >57°) the critical thickness at the boundary decreases. Using a value of 40 mN m^{-1} for σ and 2×10^{-5}m for λ a critical thickness of 64·4 nm is obtained when A is $3·7 \times 10^{-20}$J, the value for water or for a hydrated polyoxyethylene layer; dehydration of the layer would, it may be assumed, change the value of A *in extremis* to that for a hydrocarbon, namely $5·8 \times 10^{-20}$J (see Ottewill & Walker, 1974). A
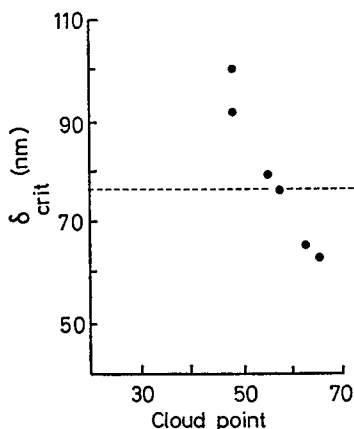
FIG. 6. Change of critical thickness as a function of solution cloud point for films of 5% w/v Brij 96 at 22°. Changes in cloud point caused by addition to the solution of NaCl, KBr and NaI. Dotted line represents value for film in absence of additives.

concomitant reduction of σ due to the increased surface activity ($\sigma = 30$ mN m^{-1}) results in a δ_{crit} of 80·4 nm. Therefore the trend of the experimentally determined values, although subject to experimental artifact due to the different thinning times of the films, is explicable in terms of changes in the value of the effective van der Waals-Hamaker constant.

The equilibrium thicknesses of the black film show little trend with additive (Table 1). The limiting thickness is determined by the balance of the forces of attraction and repulsion. The modification of the degree of hydration and extension of the polyoxyethylene chains will change both steric interactions and the value of A and hence the attractive interactions, π_{vdw}, since (Hamaker, 1937)

$$\pi_{vdw} = -A/6\pi\delta^3$$

Our prediction was that in the presence of sodium chloride steric interactions would decrease and that in the presence of sodium iodide the enthalpic barrier would be greater. It might be expected that solutions with high cloud points would therefore produce equilibrium films thicker than those with lower cloud points. Our results show no obvious trend but there is clear evidence that structure formation in the bulk film affects equilibrium thickness. The results for Brij 96 in the presence of sodium chloride (Table 1) are therefore unclear but could be partly due to the unwinding of the coiled PEG chains, i.e. destabilization of the coil as deduced by Assarson, Leung & Stafford (1969).

Table 1 also shows results for some surfactant mixtures. The addition of small amounts of Brij 92 to Brij 96 solutions results in different thinning profiles but little change in equilibrium thickness in spite of the presence at the film surface of the shorter Brij 92 molecules. Addition of sodium iodide and chloride cause an increase in δ_w due in the latter case to structure formation in the interior of the film, as bulk solutions are very viscous.

The effect of the minor component in stabilizing oil-in-water emulsions has been previously ascribed to increases in surface shear viscosity or slow drainage of the aqueous film caused by structure formation. In the systems examined aqueous films of Brij 96 containing dispersed Brij 92 were mobile at ratios equivalent to HLB

Table 1. *Equilibrium thicknesses of black films formed from Brij 96 solutions*

Surfactant solution	δw*, nm	Surfactant solution	δw*, nm
Brij 96 5%	11	Brij 96 2%	13
" + 0.5 M NaI	13	" + 1.3 M NaI	14
" + 1.0 M NaI	14	+ 1.3 M NaCl	10
" + 0.5 M KBr	12	Brij 96 2% ⎫	
1.0 M KBr	12	Brij 92 0.2% ⎬	14
0.5 M NaCl	12	" +1.3 M NaI	20
1.0 M NaCl	13	+1.3 M NaCl	(25)†
2.8% propanol	12		
3.0% butanol	11		

* Equivalent water thickness assuming refractive index of film to be that of water n = 1·33. Uncertainty in estimation of thicknesses ∿± 1 nm.
† Very slow approach to equilibrium did not allow measurement of true equilibrium thickness.

values of 12 and 11 but gave rigid films in the presence of higher concentrations of Brij 92. High-viscosity solutions could be produced in the mixtures more readily than in solutions of single surfactant. A 2% Brij 96 solution in 1·3M NaCl gave a free-draining mobile film; a 2% Brij 96—0·2% Brij 92 mixture in 1·3 M NaCl produced viscous films which had a high equilibrium thickness. Formation of asymmetric, rigid mixed micelles in the film could perhaps explain this result. Quite marked differences are observed in the thinning profiles of the mixed systems below 200nm which warrants further study of films in air and in oil.

Conclusions

The presence in emulsion systems of agents which salt-in and salt-out non-ionic surfactants has been shown respectively to increase and decrease the effective HLB values of the surfactants. Even in emulsions stabilized by surfactant mixtures the magnitude of the shift in HLB value can be reasonably predicted from changes in cloud point of solutions of the soluble surfactant.

The mechanism of action of the additives which alter the solution properties of the non-ionic surfactants is not yet clear. The measurable hydration of the polyoxyethylene chains is not increased by the compounds which salt-in the surfactant molecules, as the viscosity results demonstrate. These substances must so alter the structure of water that the thermodynamic properties of the system are altered. Racz & Orban (1965) showed that for a homologous series of liquid non-ionic polyethers

$$HLB = 0.42Q + 7.5$$

where Q is the heat of hydration of the surfactant (in g cal^{-1} g^{-1}). An increase in intrinsic HLB caused by the addition of, say sodium iodide or thiocyanate, should result in an increase in Q. This expectation is borne out by the fact that the heat of dilution of non-ionic surfactant in sodium thiocyanate solution is greater than the heat of dilution in sodium chloride (Doren & Goldfarb, 1970). An increase in the heat of hydration caused by agents which salt-in the stabilizing chains of the surfactants should result in an increase in the enthalpic element of the steric barrier to coalescence. All the evidence points to the possibility of increasing the enthalpic barrier but experimental evidence is less easily gained. Preliminary results show that the phase inversion temperature of xylene in water emulsions stabilized by Triton X–100 is increased by ethanol and propanol.

The evidence from the thin films also points in the right direction but more data are required on phase inversion and stability in the presence of thiocyanate, iodide, perchlorate ions and the short-chain alcohols.

During this work the importance of structure formation in the liquid film in determining the properties of the film and to a great extent overriding the simple thermodynamic considerations was seen. Sodium chloride although it dehydrates the polyoxyethylene chains, and decreases the enthalpic contribution to steric stabilization, in high concentrations increases the viscosity of the bulk phase sufficiently to produce stable emulsions, albeit at a higher calculated HLB than in the absence of salt.

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