9 Foaming in non-aqueous liquids

> Nernst was a great admirer of Shakespeare, and it is said that in a conference concerned with naming units after appropriate persons, he proposed that the unit of rate of liquid flow should be called the falstaff.
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> *James Riddick Partington*, "The Nernst Memorial Lecture",
> *Journal of the Chemical Society, Part 3, 2855, 1953.*

9.1 Introduction

Foaming is less commonly encountered in non-aqueous fluids than in water-based media, but it is generally accepted that similar physico-chemical principles are applicable, such as the adsorption to the bubble interface. This enables some analogies to be drawn with aqueous systems but there are problems which need to be resolved, since it was originally thought that the degree of dissociation of solubilized chemical additives was limited in non-aqueous systems and free ions were almost absent. The physical properties of the liquid also play a more important role in determining the stability of the non-aqueous foam, and if one considers the many different types of non-aqueous liquids, for example liquid metals, liquid polymers, crude oils, drilling fluids, lubricants and solvents (base cleaners), then it is clear that wide variations in physical properties need to be considered. With these liquids, distinct differences in, for example, viscosity, conductivity, dielectric constant and density are evident.

This makes it difficult to generalize the prediction of foaming behavior in non-aqueous systems, but usually some type of surface activity is needed as in aqueous systems. For example, in the generation of aluminum foams, silicon carbide particles are added which are captured by the bubbles and act to stabilize the gas/liquid metal interface (1). In mixed hydrocarbon media, lyotropic liquid crystals which are surface-active self-organized assemblies play a role in foaming performance (2, 3, 4). It has also been shown that the addition of inorganic electrolytes to organic liquids inhibits bubble coalescence by reducing drainage, but it is only recently that an improved understanding of bubble stability and interfacial drainage in non-aqueous liquids has been achieved. In these systems, it has been shown that drainage rates may be influenced by the particular arrangement of ions in the interfacial region (5, 6). For non-aqueous liquids with high bulk viscosity such as molten polymers, thick oils and metal foams, the drainage can be relatively slow, and this will reduce the foam decay rate to some degree. In addition, the importance of electrostatic double-layer repulsion in stabilizing thin foam lamellae in

organic media has not yet been completely resolved, and experimental studies over the past decade indicate that it cannot be totally neglected (7).

Non-aqueous foaming occurs in a wide range of industrial processes and several literature surveys have been published over the past 50 years. For example, surfactant-stabilized foams are used for mobility control in gas-enhanced oil recovery processes in which gas blockage is frequently encountered. Callaghan and Neustader (8) highlighted the causes of foaming and the use of foam control agents in the petroleum industry. Blazquez and coworkers (9) discussed non-aqueous foams in crude oils. Mannhardt and Novosad (10) investigated the surface activity of several different types of surfactants such as α-olefins, olefin sulfonates and betaines in hydrocarbon miscible flooding under conditions of high salinity. Schmidt (11) has extensively reviewed some of the different mechanisms involved in stabilizing non-aqueous foams. The stabilization of liquid metal foams by ceramic particles has been covered by Banhart (1), and this aspect will be further reviewed in Chapter 12.

In the following sections, different types of stabilizing agents and mechanisms which are relevant to non-aqueous foam systems are discussed. In hydrocarbon media the most important surfactants are the polmethylsiloxane (silicone) and fluoroalkyl types which have been widely used as both foamers and antifoaming agents. Gibbs surface elasticity (the build-up of surface tension gradients) and the formation of surface viscous layers are usually considered to be the most important stabilizing mechanisms in foaming, whereas electrostatic double layers and entropic repulsion that account for stability of extremely thin films in aqueous media are mostly considered to be less important in hydrocarbon systems. In situations where low molecular weight silicone surfactants confer film elasticity, they act as foam promoters, but in situations where the high molecular weight silicones reduce elasticity and cause film rupture, they act as defoamers.

9.2   Hydrocarbon-type surfactants

Water is unique in that it has a low viscosity and a high surface tension and boiling point resulting from the extensive hydrogen bonding. Although surface-active chemicals readily dissolve in water and adsorb at the air/water interface, reducing the surface tension from around $72–73$ mN/m^{-1} to values as low as 25 mN/m^{-1}, for most hydrocarbons, it is difficult to reduce the surface tension since it is already relatively low (in the region of 30 to 25 mN/m). However, in the early literature, several authors have reported that weak adsorption of surfactants at the air/hydrocarbon liquid interface can cause small reductions in surface tension. For example, studies by Mc Bain and Perry (12) in 1940 reported that the surface tension of mineral oils, tetra-isobutylene and hydrogenated tetra-isobutylene was reduced by small amounts (from about 3 to 5 mN/m) by lauryl sulfonic acid, but this surfactant had a less pronounced effect on the surface tension of benzene, xylene, heptane and iso-octane. Several years later, Jones and Saunders (13) carried out experiments with a series of *n*-aliphatic acid surfactants in nitromethane and found that the amount adsorbed was critically controlled by the bulk concentration, and to reduce the surface tension by about 3 mN/m, a fairly high concentration was required.

Although at first sight, it would appear that these small reductions in surface tension are insufficient to play a major role in foaming, it is possible they can produce small surface tension gradients which may be of sufficient magnitude to give weak Gibbs–Marangoni effects and generate transient foams. However, several other mechanisms have been proposed for foaming in hydrocarbons in the presence of surfactants with limited solubility. For example, in 1984, Ross (14) detected weak foaming in lubricating oils; this was explained by surface shear viscosity, electrostatic repulsion and Gibbs–Marangoni flow. In the petroleum industry, strong agitation is frequently encountered during cracking, coking and asphalt processing, and this gives rise to entrained air and stable foams. In the 1980s, Callaghan and coworkers (8, 15, 16) published a series of papers showing that foaming in several different types of crude oils was due to the presence of surface-active organic materials. Short-chain, low molecular weight car-boxylic acids and phenols produced transient foams, possibly due to surface tension gradients and/or changes in surface viscosities which altered the non-slip boundary conditions during thin film drainage. In addition, it was found that the stability could also be related to bulk liquid viscosity.

From the early literature, it was established that certain types of hydrocarbon surfac-tant with specific functional groups (i.e. alcohols, glycols, soaps, acids, amines) were capable of stabilizing foams in mineral oils. For example, it was reported that glycerol and mineral oil foams were stabilized by ethoxylated stearyl alcohol and polyethylene glycol base surfactants (17). This was one of the early papers where the solubility of the surfactant was found to be critical and it was suggested that foam stability could be due to the precipitation of solid particles at the bubble surface. It is important to also consider other stabilizing mechanisms based on the generation of charge in non-aqueous fluids containing low concentrations of surfactants. In these systems, the electrostatic double-layer repulsion has been shown to contribute significantly to the thin film disjoining pressure as in aqueous systems. Briscoe and Horn (7) were the first to measure interfacial repulsive forces due to charging in non-polar liquids and showed that the magnitude of such effects is extremely dependent on the dielectric constant of the liquid. In order to achieve higher foaming performance in hydrocarbons, special types of chemical surfac-tants have been developed, such as polyalkylsiloxanes and perfluoroalkyls, which can substantially reduce the surface tension of several organic liquids (by about 12 to 25 nmN/m). More details of the characteristics and foaming properties of these surfac-tants are covered in the following section.

9.3   Polymethylsiloxane and fluoroalkyl-type surfactants

Polymethylsiloxane (PMS) (silicon)-type surfactants structurally consist of an inor-ganic siloxane backbone with attached pendant methyl groups. The low molecular weight polymers are fairly soluble in hydrocarbons and lower the surface tension and generate moderately stable foams. The principal cause of the surface activity is the unique flexibility of the siloxane backbone and its ability to present the attached organic groups (which can adopt various orientations) to the hydrocarbon/air interface.

In the case of PMS, this can lead to an array of adsorbed densely packed methyl groups which act to minimize the surface energy. PMS polymers within a critical molecular weight range can provide marginal solubility in hydrocarbons and give high foaming performance, but the higher molecular weight insoluble polymers act as defoamers. Low molecular weight PMS have greater surface activity than those commonly encountered by other organic foaming agents and are widely used as foam stabilizers (in combination of polyols) in the production of polyurethane foams. Linear, branched, di- and tri-block polysilane structures have been manufactured, and Owen and Kendrick (18a and b) in 1967/8 studied the polyurethane foam system and measured the surface tension of polysiloxane-polyether block copolymers in polyol and found the CMC decreased with increasing siloxane content of the copolymer. It was suggested that the surface tension was determined by the configuration of the polydimethyl siloxane chain adsorbed at the bubble interface. It was also reported that the polysiloxane-polyether block copolymers were less effective foam stabilizers in polyol than the branched polysiloxane–polyether block copolymers, possibly due to differences in surface viscosity. Gas diffusion between bubbles and the surface viscosity was reported to influence stability.

Low molecular weight fluoroalkyl-type surfactants behave similar to PMS surfactants in that they are capable of lowering the surface tension of essentially all organic liquids. Kiss (19) gives an overview of the syntheses, properties and applications of fluorinated surfactants. The polyoxyalkylene chain is usually attached to the fluoroalkyl group through a connecting group such as $-CH_2CH_2S$ or $-SNH$ $(O_2)-CH_2CH_2$, and structurally, the covalent radii of the fluoride ion shield the carbon atoms, producing extremely low interactions both between like molecules and also between different types of molecules. Several commercial products have been manufactured by the 3M Company; for example, the nonionic fluorocarbon surfactant Fluorad FC-95, which is the potassium salt of perfluorooctane sulfonic acid, lowers the surface tension of many organic liquids and produces relatively stable foams (20).

In the laboratory, Eastoe and coworkers (21) prepared an interesting series of surfactants based on the perfluoroalkyl triethylene oxide methyl ethers-type structure (designated as $X-(CF_2)_m-CH_2-O-(C_2H_4O)_3-CH_3$, with X being either H of F and m = 4 or 6). From this study, it was shown that altering the chain length of $X-(CF_2)_m$ groups or replacing the F atom for H on the terminal group can have dramatic effects on both adsorption and aggregation characteristics (21). Other types of structurally modified nonionic (ethylene oxide EO) fluorinated surfactants were also synthesized in order to investigate how variations in the molecular architecture affect surfactant properties (22). These molecules included a linear surfactant (L) comprising one fluorinated hydrophobic group and one nonionic head group; a bolaform (B), which may also be considered as a unique mini monodispersed fluorinated block copolymer EO-CF-EO; and a Y-shaped surfactant (Y) in which both head groups were at the same end of the hydrophobic group as shown in Fig. 9.1. Although these surfactants had widely different molecular architectures they were found to exhibit classical surfactant behavior in both non-aqueous solvents and also in water and give strong structural interfacial packing and structural-aggregation relationships. It would
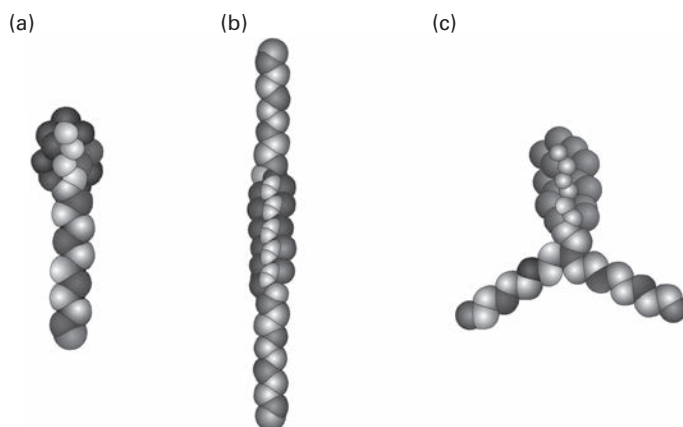
Fig. 9.1 3D structures of modified nonionic (ethylene oxide EO) fluorinated surfactant: (a) the linear form L (b) the bolaform B and (c) the Y-shaped surfactant. From ref (22).

be of considerable interest to study the foaming and defoaming performance of these types of nonionic fluorinated surfactants.

Prudhomme and Khan (23) reviewed the stabilizing action of fluoroalkyl surfactants in different organic liquids, and Bergeron and coworkers (24) carried out foam film studies with fluoroalkyl surfactants in dodecane as a model for gas blocking oil foams. Two fluoroalkyl esters (designated FC-740 with molecular weights from 5,000 to 10,000 manufactured by 3M Company) and also a larger fluorosilicone surfactant (designated FS-2 K with a molecular weight of about 20,000 manufactured by Hoechst) were used in the investigation. The surfactants were reported to reduce the surface tension of the air/dodecane interface, and it was also reported that both surfactants produced robust foam films stabilized by stearic forces. With FC-740, highly stable dimples were detected within the film, and the higher molecular weight FS-2 K produced a gel-like structure.

Islam and Bailey (25) carried out experimental studies with a nonionic fluorocarbon surfactant (FC-740) in a hydrocarbon mixture consisting of n-decane/decalin (50/50 w%) which was used to model a crude oil. An attempt was made to correlate the foam stability to the shear viscosity, determined using a deep channel viscometer. The surface dilational properties were determined from dynamic surface tension measurements made using a stress relaxation technique based on a Langmuir trough with a Wilhelmy plate attachment. It was found that the FC-740 formed a gel-like structure at the air/oil interface in agreement with the studies by Bergeron and coworkers (24), and values of the relative shear viscosity were found to be time dependent. The results were explained by the cohesive entanglement of the adsorbed surfactant molecules at the air/hydrocarbon interface. Relaxation of surface tension gradients was observed and explained in terms of molecular diffusion and orientation of the adsorbed molecules. High foam stability was attributed to the dilational and relative shear viscosity. Bink and coworkers (26) coated silica particles with perfluoro-alkoxysilane reagents to produce surfaces with different levels of surface hydrophobicity. This enabled the surface energy of the particles to be tuned so that stable foams could be produced in both polar and non-polar hydrocarbons.

9.4   Phase separation from partially immiscible liquids

Foaming frequently occurs in multiphase systems during the processing (fractionation or distillation) of hydrocarbon mixtures where changes in composition, solubility and surface tension occur (27). Ross and coworkers (27, 28, 29, 30) carried out fundamental studies with a model consisting of partially miscible liquids (consisting of two, three or more component systems) and observed that the foaminess attained a maximum value as the composition of the mixtures approaches a region of limited or partial solubility. This corresponded to the regions of imminent phase separation. Incompatibility or insolubility between the dissolved substances and the solvent causes the solute to migrate to the interface, resulting in phase separation, which increased the surface activity. Under practical conditions, for example during the distillation of mixtures of hydrocarbon fractions, one of the constituents is more easily removed (e.g. the lower surface tension component), which causes the surface tension of the residual liquid to increase. This results in higher surface tension of the liquid, drawing liquid away from the region of lower surface tension (Marangoni flow) and causing an increase in the stability of the liquid film and thus stabilizing the bubbles generated in these systems. In the opposite situation, where the higher surface tension component is removed the surface tension of the residual liquid decreases and wetting and spreading occur producing defoamer action. In addition, changes in the foaming and phase behavior could be achieved by changing the temperature. Ross and coworkers (27, 28) reported several more examples of mixtures of organic liquids where both foaming and defoaming could be related to regions of partial immiscibility. In a specific example, Ross and Nishioka (29, 30) showed that the phase behavior of a binary liquid system of ethylene glycol (EG) in methyl acetate (MA) could be related to foam stability, as shown in Fig. 9.2.

In this system, MA has a lower surface tension and as the composition of the mixture is reduced from 100% EG, foam stability gradually increases due to the onset of phase separation. However, when the phase separation region is exceeded (at about 60% EG level), MA is completely dispersed in EG. This is represented in the diagram by the region MA/EG and, within this narrow range of composition, the system acts essentially as a defoamer. This action is caused by the insoluble droplets of MA depositing from the solution on the foam lamellae, but as indicated in this plot, the antifoaming action ceases when the phase inversion is reversed and EG is dispersed in MA which causes a slight increase in foam stability. This reaches its maximum at the opposite phase boundary and then declines to zero foam stability at the composition of pure MA. It was speculated that the phase separation at the interface causes viscoelastic forces to build-up, which reduces the thin film drainage, resulting in transitional foam structures.

Ross (28) also discussed how the relationship between phase behavior and foaming was used as a method of measuring the strength (proof) of whiskey. It was originally shown by Davidson (31) that a sudden increase and then decline in bubble stability occur in whiskey on diluting with water. The maximum in bubble stability occurs at about 42% alcohol by volume and this has been used as an observable test of strength which enables an inspector to detect if whiskey is above or below proof. Although this is an
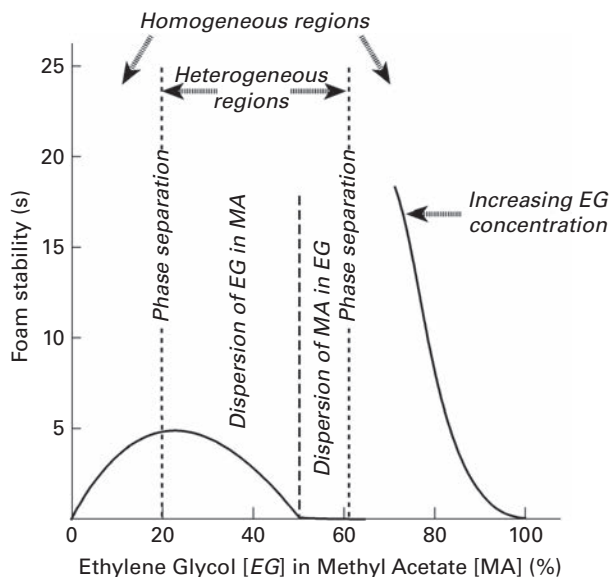
Fig. 9.2   Foam stability of a two-component mixture of methyl acetate (MA) and ethylene glycol (EG) versus composition (% MA) at 20°C. From ref (27, 28).

an empirical test, it was accepted by the US Congress as a legal definition of proof and can indicate if the sample is above or below proof (actually, the official US proof scale is twice the volume percent of alcohol). Ethanol with water levels above or below the 42% alcohol/ethanol level shows lower bubble stability, and when over-proof whiskeys (containing lower water content than the official proof) are diluted with water, some secondary organic constituents such as tannin, fusel oils and aldehydes approach their solubility limit. This is due to the lower concentration of alcohol in the mixture, and the stability of the bubbles increases due to the increase in surface activity. The relationship between bubble stability with alcohol content of a bottled overproof bourbon and an alcohol content of 107 proof which was titrated with water is shown in Fig. 9.3. The bubble stability tests were carried out by shaking small vials and measuring the bubble persistence time. The maximum bubble stability occurs at 97 proof at 60°F.

Lubrication oils used for internal combustion engines consist of branched, saturated hydrocarbon mineral oil and a mixture of additives (oxidation inhibitors, viscosity index improvers, dispersing agents and detergents, pour point depressants, etc.). In order to neutralize the corrosive acids, colloidal dispersions of alkali metal carbonates are also added, and carbon particles are formed during combustion which deposit as sludge in the oil. These particles can be dispersed in the oil with surfactants such as polyisobutylene (32) (a) and (b). During the operation of an internal combustion engine, agitation causes air entrainment and foaming, resulting in oil starvation, cavitation and impairing heat transfer, which eventually leads to engine and gearbox failure. Over the years, there has been a lack of basic studies on the nature of foaming in lubrication systems, although several theories have been put forward to explain this behavior which may be partly due to high viscosity but enhanced by contributions from various dispersions of carbon or inorganic particles (33).
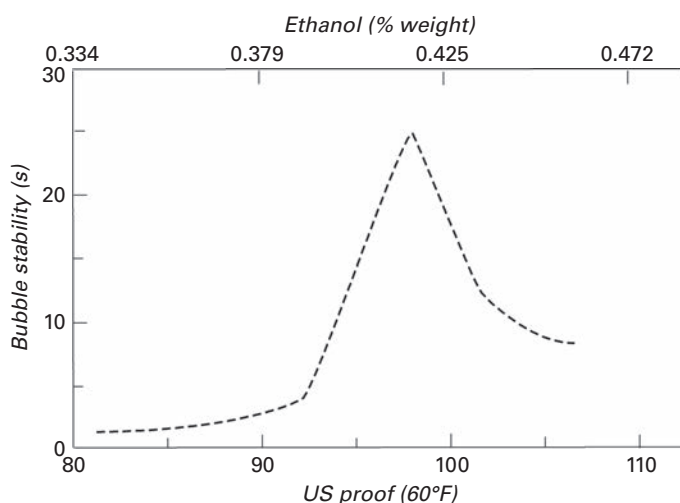
Fig. 9.3   A plot of bubble stability (bubble persistence time) versus concentration of ethanol. All samples were prepared from bottled 107-proof bourbon, either by direct titration with water or by addition of absolute alcohol followed by titration with water. The maximum stability occurs at 100 proof. From ref (27).

Binks and coworkers (34) took an alternative approach to this foam stability problem based on the phase separation principles developed by Ross (28). They suggested that the additives were completely soluble in the oil phase during engine start-up, but during the aging process, in which increases in temperature, pressure and vaporization occur, the single-phase system gradually approaches a phase separation boundary. In this region the solute's affinity for the solvent was reduced, causing the additives to separate and adsorb at the gas/hydrocarbon interface, thus promoting foam stability. Foaming experiments were carried out with the single-phase mixtures consisting of a hydrocarbon solvent composed of various additives, such as low molar mass, polymeric and over-based detergent particles, as used in lubricating oils. It was found that foam formation correlated with the phase separation process, and it was also shown that the phase boundary for these systems occurred at a fairly high solute concentration (about 1 w%) and wet transient foams (with volume fraction > 20 w%) were generated. From this study, it was suggested that adsorbed solute films at the air/hydrocarbon interface reduced drainage but were also incapable of resisting coalescence between contacting bubbles. The foam half-life stability was shown to be proportionate to the kinematic viscosity of the liquid, which validated a non-coalescence model.

9.5   Lamellar liquid crystals, surfactant solid particles and lipid phases

At fairly high concentrations, surfactants (such as Aerosol OT and polyethylene glycol ethers with a polyethylene glycol chain of four or five units) are sufficiently hydrophobic to dissolve in hydrocarbons and formed micelles. However, they are also well known to associate in the presence of small amounts of water to form inverse micelles. At even
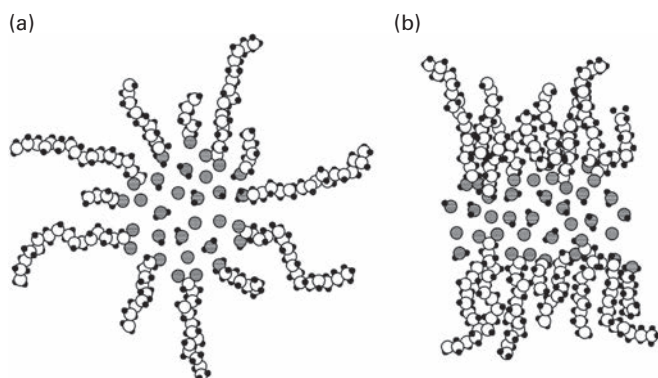
Fig. 9.4   Non-polar media hydrophobic surfactants or surfactant combinations giving (a) inverse micelles; (b) at higher surfactant or water concentrations a lamellar liquid crystal is formed. From ref (4).

higher surfactant concentrations (in excess of a critical value required for the inverse micelle formation), in the presence of excess water and with a small amount of hydrocarbon, lamellar liquid crystals are formed. These liquid crystal structures are denoted as the L_α phase and are shown to be strongly birefringent and often sensitive to changes in temperature. It is important to note that whereas the micellar solution is an isotropic liquid that contains isolated colloidal-sized micellar species, the lyotropic liquid crystals exist as lamellar-associated single-phase structures produced from three separate components (in between micellar solutions and liquid crystals). In Fig. 9.4(a), a typical structure of an inverse micelle is shown with the polar parts of the surfactant orientated toward the center of the micelle and the hydrocarbon parts oriented outward to the hydrocarbon environment; in Fig. 9.4(b), the lamellae liquid crystal is shown.

During the 1970s, Friberg and coworkers (2, 3, 4) constructed several multiphase diagrams from different components (surfactant, organic solvents and water) and correlated the foaming to the different phase regions. From the studies it was established that two-phase regions which consisted of the hydrocarbon solution and a lamella liquid crystal phase (designated L_α) generated extremely stable foams. It was proposed that lamellar crystals possessed a lower surface tension than the corresponding solution of similar composition, and hence they adsorb at the interface of the thin film foam lamella produced during the generation of bubbles. A typical phase diagram as presented by Friberg (4) is shown in Fig. 9.5.

In this diagram, none of the single phases – the inverse micellar solution (A), the lyotropic liquid crystal (B) or the water – gives stable foams. In the case of the three *two*-phase areas (indicated by 1, 2 and 3) and the one *three*-phase and two-phase area (corresponding to 4), only one will give a stable foam. It is the *two*-phase area (indicated by 2) which contains the isotropic solution and the lyotropic liquid crystal. Inside this two-phase area the foam is extremely stable, but outside this two-phase area, there was no evidence of foam stability. From these studies, it was concluded that the structure of the dispersed phase was crucial in controlling the stability of non-aqueous foams, and essentially the phase behavior is mainly determined by the surfactant type and concentration and the nature of the oil and temperature. Small changes in total composition or
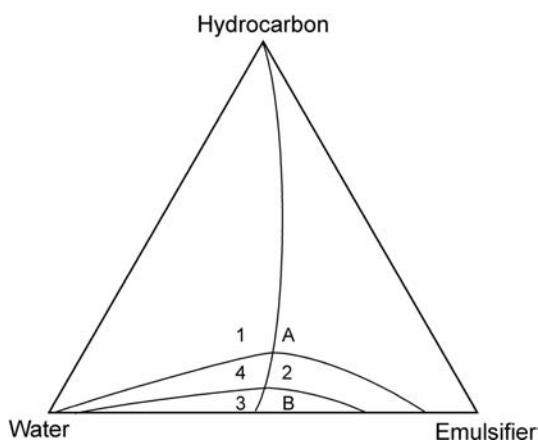
Fig. 9.5   A typical phase diagram for a hydrophobic emulsifier. From ref (3).
A = Isotropic solution with inverse micelles, B = Lamellar liquid crystals, 1 = two-phase area of water plus the isotropic liquid A, 2 = two-phase area of the isotropic liquid A plus the lamellar liquid crystal B, 3 = two-phase area of water plus the lamellar liquid crystal B, 4 = three-phase area of water plus the isotropic solution A plus the lamellar liquid crystal B.

small changes in temperature are sufficient to move the system from a homogeneous solution to a mixture of two or three phases.

Friberg and coworkers (2, 3) also related the phase behavior to foam stability for several different surfactant/oil/water systems. For example, studies were reported for the lecithin and ethylene glycol system which forms a lamellar liquid crystal phase corresponding to the maximum ethylene glycol content of 60 w% (4). The liquid crystals were also found to be in equilibrium with an ethylene glycol solution containing low concentrations of lecithin. Friberg and Green (2) investigated the triethanolammonium oleate/p-xylene system and showed that at low p-xylene concentrations (< 3 w%) lamellar liquid crystals were formed at higher concentrations (> 13 w%) and the liquid was isotropic, but foaming could only be achieved in the presence of the crystalline liquid. Further studies using glycerol/sodium dodecyl sulfate and glycerol/sodium octanoate systems confirmed the importance of the liquid crystalline phase in foaming. Presumably, foaming was enhanced by modification of the surface rheology which retarded the drainage of the liquid between the lamellae films. This mechanism has been reported in both aqueous and non-aqueous foams, and it is of interest to note that Garrett and Gratton (35) monitored the transport of the dispersed liquid crystalline species (LCS) to the air/water interface using dynamic surface tension measurements and reported diminished rates of transport compared with micellar species. This result implied that in aqueous systems, although the foam stability may be enhanced due to the accumulation of the liquid crystalline materials in Plateau borders, the generation of the foam may not be necessarily improved.

Based on the systematic and logical application of these principles, many industrial foaming problems were solved and new formulations developed in Sweden. For example, personal care and pharmaceutical aerosols formulation are extruded as rich foam produced from pressurized containers, and traditionally, chlorofluorocarbons were used
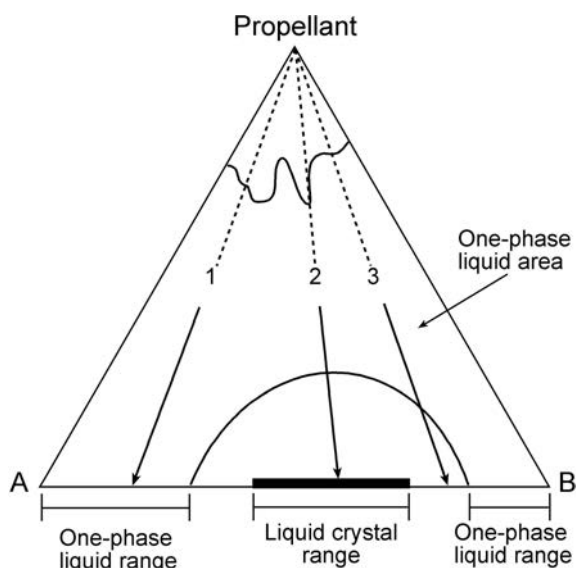
Fig. 9.6   The principal features of an aerosol formulation system at the pressure of the aerosol package. The A and B corners represent combinations of the non-propellant compounds. From ref (37).

as the effective propellant gas. However, due to environmental concern, this gas was replaced by inert alternatives such as N_2 or CO_2. Due to differences in the nature of foaming of these gases, it was found necessary to change the aerosol formulation and develop new systems that gave improved foaming. A considerable amount of progress was made by Pharmacia AB, in Uppsala, Sweden (36), in successfully developing new formulations based on phase diagrams for entire new systems (including propellant under pressure). This work has been well documented by Friberg (37), and a typical phase diagram is shown in Fig. 9.6, which illustrates a formulations of a liquid composition with two other components, except in regions where the propellant concentrations were relatively low. This type of phase diagram enabled formulations to be designed for extruded foams with specific degrees of foamability and foam stability.

In this diagram, the straight line along the base of the diagram phase (from A to B) defines the evaporation path that starts from A where the composition has no propellant. Three evaporation paths are indicated (1, 2 and 3), which begin with the propellant phase. Each path defines a different type of extrusion formulation, and these were constructed by addition of the two components (A and B). In the case of the extrusion composition following the evaporation in path 2, which ends within the liquid crystal range at the base line, extremely stable foams lasting more than 10 mins with no reduction in foam height were produced. However, paths such as 3, which end in the multi-phase range B, lead to foams of intermediate stability, and path 1 ends in the one-phase span, resulting in unstable foams.

More recent advances have identified another surface-active dispersed solid crystal-line phase (designated as a β crystal or a-gel phase which precipitates from the solution as fine particles) as an important foam stabilizing agent. It has been shown that this phase

can lead to the generation of super-stable non-aqueous foams in glycerol fatty acid esters/oil formulations that have several potential practical applications in shaving creams, whipped creams and food ingredient formulations. Shrestha and coworkers (38, 39, 40, 41) carried out studies with several different types of glycerol fatty acid esters such as glycerol-α-mono-laurate (GML), diglycerol mono-myristate (DGMM) and a tris-2-ethylhecanoate glycerol ester (designated T10) which have different alkyl chain lengths and form different structures in different types of non-polar oils (squalene, squalene and liquid paraffin LP 70). The foaming performance of these systems was correlated to the phase behavior. The structure of these glycerol fatty acid ester surfactants and non-polar oils is shown in Fig. 9.7.

From initial observation, it was found that on dispersing low concentrations of the glycerol fatty acid esters in the different oils at 25°C, finely divided solid was precipitated. Foams were generated in these systems by mixing the surfactant/oil dispersions in liquid petroleum gas which was enclosed in an airtight bottle fitted with a nozzle. The bottle was shaken and the contents extruded from the nozzle into a measuring cylinder,
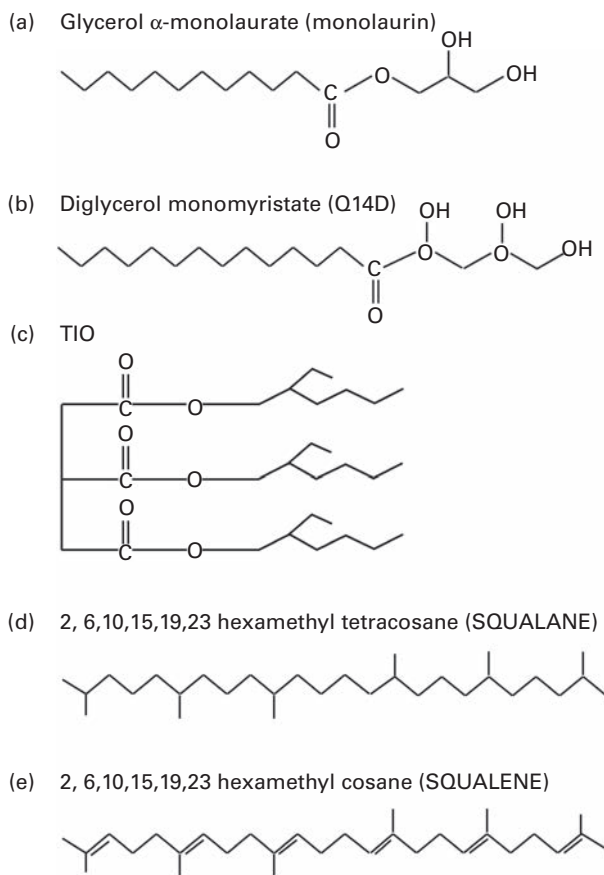
Fig. 9.7   (a) (b) and (c) Structure of the glycerol fatty acid ester chemical surfactants and (d and c) the structures of non-polar oils. From ref (38, 39).
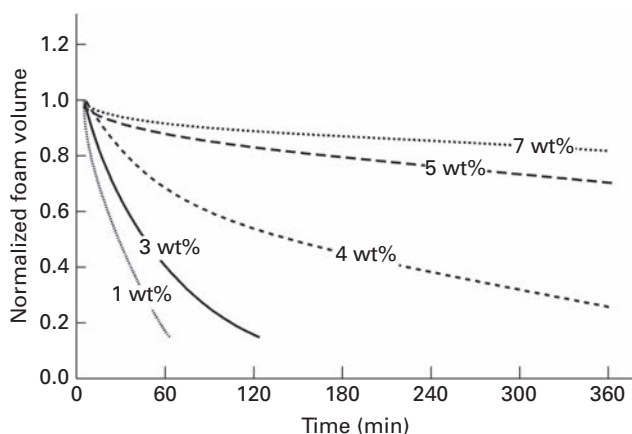
Fig. 9.8 Foam volume (normalized) versus time at different surfactant concentrations for glycerol α-monolaurate/squalane systems at 25°C. From ref (37).

resulting in the building-up of a foam column, and the change in volume as a function of time was used as a measure of stability. In Fig. 9.8, the effect of increasing the concentration of GML (from 1 to 7 w%) in the squalene solvent at 25°C is shown. This can be seen to increase the stability of the foam column, and at 5 w% the foams were found to be stable for about 14 hours.

It was also reported that on changing the type of non-polar oil from squalane to a mixture of LP 70 and squalene, the foams were generally less stable. In addition, the chain length of the fatty acid esters was found to have an influence on stability; for example, on decreasing the chain length of the surfactant from GML-squalane to glycerol α-monodecanoate (GMD) the foams were found to be stable for a shorter time period (about 3 to 4 hours). On further reducing the chain length by changing to glycerol α-mono-octanoate (GMO) the foam rapidly coarsened and collapsed. From wide-angle X-rays scattering, fine solid particles in the system were identified as β crystals (L_β), and the shape and size of these solid particles appeared to play an important role in the efficiency of the stabilizing process. On increasing the temperature of the dispersed systems, the solid particles appeared to melt, producing an isotropic single-liquid phase which caused the foam to disappear.

Further experiments were carried out by changing from diglycerol laurate (DGL) to diglycerol myristate (DGM), and this caused a drastic change in the stability of liquid paraffin, squalane, squalene and the TIO solvents. A further series of experiments was carried out in which foams were generated in diglycerol mono-myristate (DGMM)/olive oil, and this study was of more commercial interest since vegetable oils are widely applicable in food, cosmetic and toiletry formulations (40). Again, it was found that foam stability depended strongly on the fraction of fine particles in the dispersion; that is, 1 w% surfactant stabilized the foam for about 1 hour; 10 w% for months. For the DGML/olive oil system, it was shown that at 25°C, the foamability increases with increasing surfactant concentration from 1 to 3 w% and then decreased with further decrease in concentration, but the foam stability increases continuously with concentration.
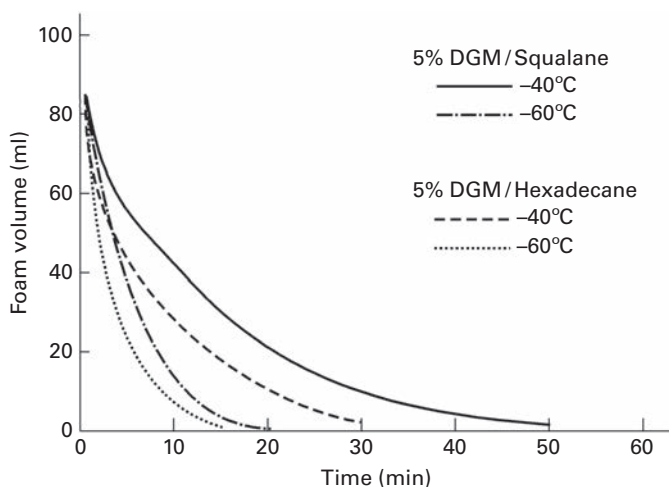
Fig. 9.9   Foam volume versus time for the 5 w% DGM/oil system at higher temperatures. From ref (40).
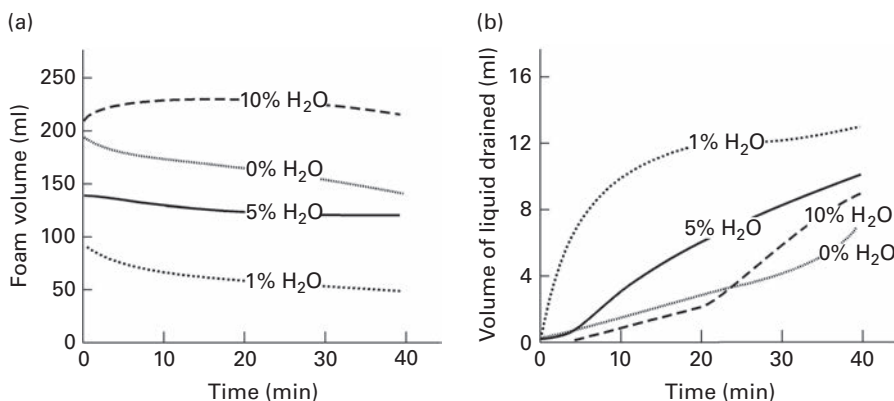
Fig. 9.10   The effect of added water on the 5 w% DGM/olive oil system: (a) foam volume versus time at different water and (b) corresponding volume of liquid drained versus time 25°C. From ref (41).

Foams were stable from a few minutes to several hours depending on the concentration. Temperature was also found to influence the foam stability of the DGM/squalane and DGM/hexadecane systems, and the results obtained at 40°C and 60°C are shown in Fig. 9.9. For these systems, the foam stability was reduced at higher temperatures and this reduction was attributed to the absence of L_β particles that stabilized the foam at lower temperatures.

The influence of small amounts of water on these systems was also systematically investigated, and in one study the foamability, foam stability and drainage rate were evaluated (41). From a fundamental viewpoint, this area of research is of interest since the addition of water is known to change the nature of the surfactant phase from the crystalline to the liquid crystalline state. The results obtained from the influence of added water (at three different concentration levels) on the 5 w% DGM/olive oil system are shown in Fig. 9.10.
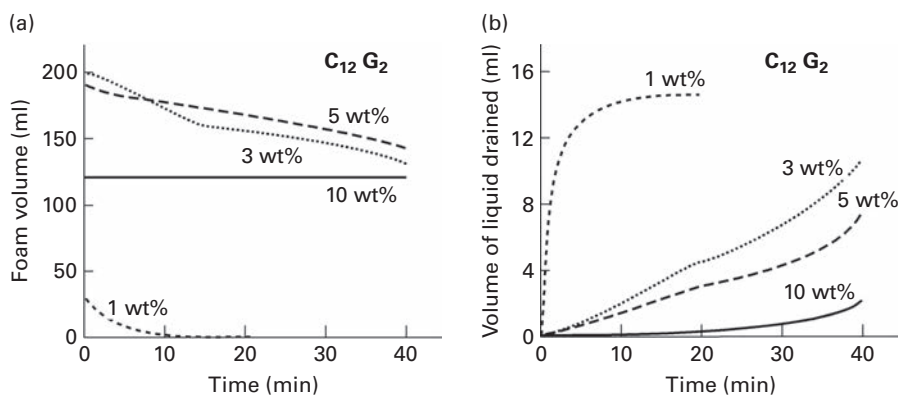
Fig. 9.11 (a) Foam volume and (b) volume of liquid drained for the $C_{12}G_2$/olive oil system at different compositions at 25°C. From ref (40).

These results indicate that both the foamability (foam volume) and the foam stability (volume of liquid drained) decreased upon adding water at 1 w% and 5 w%, but on further increasing the water content to the 10% level, the situation was reversed and the foam was reported to be stable for 4 hours. Also, the influence of the water additive level on the drainage characteristics of the foams was studied and the results are shown in Fig. 9.10(b). This plot indicates that the volume of foam drained initially increased up to the 1 w% but then decreased as the water content increased to the 5 w% and 10 w% level.

In addition, the influence of the surfactant concentration on the foamability, foam stability and drainage was studied for the DGM/olive oil system, and the results are shown in Fig. 9.11. At 1 w%, it was found that the breakdown of foam began immediately with high drainage and the foam totally collapsed after 20 mins, as shown in Fig. 9.11(a); but with an increase in surfactant concentration, the foam stability increased and the foams produced at the 10 w% level were stable for more than 6 hours. From Fig. 9.11(b), it can also be inferred that the liquid drainage was decreased with increasing surfactant concentration and around 95 w% of liquid was drained off within 10 mins in the 1 w% DGM system, but it took about 30 mins for 50% liquid to drain off at the 3 w% level. Interestingly no liquid drained off within 20 mins in the 10 w% surfactant system. This indicates the liquid-holding capacity of the foams was increased following the increase in surfactant concentration.

The foaming of dispersed lipid crystals (hydrogels or oleogels based on lipid materials) in oil was investigated at different temperatures by Fameau and coworkers (42). At high temperatures above the melting point of the crystals, foams could no longer be produced, but below the melting point, the foams were stable for months due to the crystals stabilizing the bubble interface. Differential scanning calorimetery measurements revealed that the formation of the lipid crystals in the oils was temperature dependent, and crystals could be reversibly formed and melted at different temperatures. This enabled a thermo-responsive non-aqueous foam system to be designed.

9.6   Bulk viscosity

Many studies orientated toward understanding foaming in oil wells have stressed the importance of adsorption of surface-active additives on rocks and the build-up of surfactant multilayers at the gas/liquid interface (43). The important role of surface viscosity and elasticity in the mechanism of stability has also been emphasized. However, a number of researchers have highlighted the role of bulk viscosity, and this property is related to the drainage of interstitial fluid in the foam. In many cases, the relationships between the bulk viscosity and foaming were based on empirical data, but the situation is complex since it is well known that the bulk viscosity of a crude oil depends on the composition and varies according to the location of the wells, the age of the oil, the composition and also impurities such as water, and particles such as sand, clay, aggregates, paraffin crystals, precipitated asphaltenes, etc. Most of these parameters appear to influence the bulk viscosity and foaming performance to some extent. Poindexter and coworkers (44) reported that bulk viscosity, density, the interfacial tension, molecular weight, concentration of asphaltenes, etc. influenced the foaming of crude oils. Callaghan (8) concluded that the average lifetime of crude oil foams is almost linearly dependent on bulk viscosity, although, in addition, the surface rheological properties such as shear and dilational viscosities had a pronounced effect on foaming performance. Viscosity has also been shown to be important for other different types of oils. For example, Negishi and coworkers (45) related the tendency of frying oils to generate foam to an empirical triglyceride index which suggested the foaming was related to the drainage or viscosity of the oil.

It is also well known that the high viscosity of non-aqueous liquid dispersion containing colloidal particles produces stable foams. Ottewill and coworkers (33) generated stable foams from a commercial grade hydrocarbon oil which contained colloidal-sized calcium carbonate particles stabilized by alkyl benzene sulfonate. The increase in bulk viscosity of the dispersion with the solid content could be expressed by the equation

$$\eta_d = \eta_o(1 + k_1\varphi_s + k_2\varphi_s^2 \ldots \ldots)^\varphi \tag{9.1}$$

where η_o is the viscosity of the liquid matrix, η_d is the viscosity of the dispersion and ϕ_s is the volume of the dispersed solids. It can be presumed that the increase in stability was caused by the decrease in drainage rate of the liquid dispersion occurring between the thin lamellae films. It was also suggested that increase in bulk dispersion viscosity caused a damping effect of the ripples at the lamellar surface produced by thermal fluctuations which further enhanced the stability. However, there was a strong possibility that some of the particles were partially hydrophobic and became attached to the bubble interface, as highlighted in Chapter 10.

9.7   Inorganic electrolytes in non-aqueous liquids

Henry and Craig (5) showed that inorganic electrolytes have an important influence on the stability of bubbles under dynamic conditions in organic solvents. Studies were

reported for swarms of bubbles which were generated by passing air through a frit in a glass column, and the stability was evaluated by measuring the turbidity. Both single and binary non-aqueous solvents were used in the experiments. Initially, methanol, formamide, propylene carbonate (PC) and dimethylsulfoxide (DMSO) were selected as the non-aqueous liquids, and a series of different inorganic electrolytes (NH_4SCN, $MgCl_2$ H_2SO_4, $NaClO_4$, NaCl, HCl) were chosen as the solutes. The influence of the different types of inorganic electrolytes on inhibiting the coalescence of bubbles in each of the organic solutes was determined and the results compared to the ion-specific effects previously reported by Craig and Nineham (46), which was used to explain the inhibition of bubble coalescence in aqueous electrolyte solutions.

Overall, it was found that several different inorganic electrolytes inhibited the coalescence process to some extent (in a similar way to that observed in the aqueous systems), but lower concentrations of inorganic electrolytes (0.01 M to 0.1 M) were required. Interestingly, it was also found that formamide showed ion-specific salt effects which were dependent upon ion combinations in a similar way to the combining rules observed in the aqueous systems, as discussed in Chapter 6, Section 6.5. However, in the case of PC, although the results were found to be consistent with the ion-combining rules, the ion assignment differed from those for water. For methanol and DMSO, all the salts used were found to inhibit bubble coalescence. From these studies, the authors suggested that the stability of the bubbles against coalescence in the non-aqueous electrolyte solutions was mainly determined by the drainage of the liquid between the thin films separating the bubbles. Dynamic thinning and rupture of the liquid film are known to be dependent on the hydrodynamics boundary condition (which may vary from slip to non-slip), and it was proposed that thinning dominated the coalescence process and surface forces play a less important role. It was also speculated that the particular arrangement of ions (anions and cations) in the interfacial region could define the ion gradient and interfacial tension, which influence interfacial drainage rates and film thinning.

Experiments were extended to a binary mixture of non-aqueous liquid composed of DMSO and PC which were highly miscible. The influence of the composition of the binary solvent on the inhibition of bubble coalescence in the presence of LiBr, KSCN and HCl was studied. These electrolytes were highly soluble in the binary solvent. From the experiments, all these electrolytes were found to inhibit coalescence more effectively in the binary solvent than in the single solvents, but it was also found that the mixture of DMSO and PC did not exhibit strong bubble coalescence inhibition over the whole range of solvent compositions. In fact, a slight minimum in bubble coalescence occurred in PC at the 25% v/v level, but this could not be satisfactorily explained by the surface elasticity mechanisms. In this case it was suggested that the stability was caused by the formation and adsorption of complexes (between DSMSO and PC) at the interface, which modified the surface viscosity. In addition, thin film drainage studies were carried out and the resistance to rupture of the thin films produced between air and the non-aqueous solution was evaluated using the thin film micro-interferometry technique, as described in Chapter 3. It was found that the inhibiting electrolyte decreased the thin-film drainage rate. It was also observed that the film reached a lower thickness before

rupturing. This behavior contrasted with that for non-inhibiting electrolytes, where the effects on the drainage were negligible These results appear to suggest that both the thin-film drainage and rupture processes are affected by the electrolyte, but a complete explanation of the ion-specific effects and the physico-chemical mechanisms underlying different types of electrolytes is yet to appear.

9.8   Interfacial charge in non-aqueous systems

According to the double layer theory, one of the major parameters controlling the magnitude of the electrostatic interfacial charge is the dielectric constant of the liquid (ε_r), and for many hydrocarbons with low ε_r, such as lubricating oils with values of as low as 2 to 4, the dissociation of solubilized chemical additives is restricted since the counterions have limited solubility in the solvent. This has led many investigators to assume that it is difficult to build up charge in extremely low ionizing solvents, since the mechanism of charge separation cannot function, and until recently it was believed that the mechanism of electrostatic repulsion caused by overlapping double layers could not act to stabilize liquid lamella. However, it is also important to consider the fact that the ε_r values of organic liquids cover a range of values, and although some hydrocarbons have low values, others have values in the intermediate range. For example, several ketones have ε_r values in the range of about of 20, and certain types of amides have higher values. Since the Debye length ($1/\kappa$) is inversely proportional to the square root of ε_r and the electrostatic double could possibly extend a considerable length, under these circumstances a repulsive interaction could be achieved.

In more recent years it has been shown that repulsive forces can exist between charged surfaces in non-polar liquids, and Briscoe and Horn (7) detected a very weak and long-range repulsive force in *n*-decane containing sodium di-2 ethylhexylsulfosuccinate (AOT) surfactant (in the millimolar concentration range) using the modified surface force apparatus with mica substrates. This force was about 10 times weaker than the double-layer force in distilled water. A model was derived in which only counterions enter the calculation in the absence of a reservoir of ions in the solvent. Measurement of the force under different conditions showed that it was very sensitive to trace amounts of water that are inevitably present in surfactant aggregates of AOT in the organic liquids. It is also well recognized that charge separation can occur by mechanisms other than electrolytic dissociation, such as acid/base exchange processes. These involve acidic polymeric dispersants adsorbing to basic interfacial sites or vice versa, followed by proton transfer and subsequent desorption of the charged species into the organic media (47). This occurs with common oil-soluble dispersants in neutral hydrocarbons which are basic amines or nitrogen bases (polyisobutene types that have a basic anchoring group) while acidic-type dispersants that adsorb on basic sites include partial esters of phosphoric acid and poly(12-hydroxy stearic acid). Since many of the dispersants such as poly-isobutene and the poly-hydroxy stearic acid types are short-chain polymers with molecular weight in the range of 2000 to 3000, there is also the possibility that they act to some extent as steric stabilizers as well as charge stabilizers in organic liquids.

Evidence for charging of particles and surfaces often comes from electrokinetic studies, for example, zeta potentials of between –25 and –125 mv have been observed for various types of particles dispersed by a chemical dispersing agent in non-polar media of low conductivity (32). Also, with some detergent-type surfactants, ions are solubilized in non-polar liquids, as detected by conductivity, and this has been explained by an acid/base mechanism. This was also established from experiments in other systems. Where dispersants are not present in the solution, particles with basic surface sites demonstrate positive zeta potential when dispersed in acidic organic solvents (chloroform, or methylene chloride), while particles with acidic surface sites show negative zeta potentials when dispersed in basic organic solvents (ketone or ethers). Solvents such as nitriles have both acidic and basic functionality, and when powders are dispersed in acetonitrile, the particles may show a positive or negative charge depending on the predominant acidity or basicity of the powder surface (48). Solvents such as methylisobutylketone and methanol show similar behavior. It has also been shown that inverse micellar soaps or sulfonates of polyvalent metals such as calcium, barium and zinc ions also act as dispersants. In addition, oil-soluble high molecular weight lauryl sulfonate anions are weak bases, whereas the calcium and zinc ions are weak acids. Barium and calcium sulfonates react with hydroxide surfaces, providing basic species that can confer a high negative charge (49). More recent studies using ATR-FTIR analysis have shown that cationic surfactants such as dialkyl dimethyl ammonium bromide can adsorb and desorb from silica in toluene solution, and the process is extremely sensitive to small amounts of water (50).

9.9 Defoaming in non-aqueous solutions

In addition to generating foam, PDMS and perfluoro polymers are known to act as antifoamers in non-aqueous liquids, and their effectiveness is determined by their solubility in the liquid phase. Typically these polymers have a higher degree of solubility in hydrocarbons than in water (PMS in crude oil $< 10^{-3}$ gdm^{-3} and in water 10^{-6} gdm^{-3}) and PMS, and when they are present at concentrations below the solubility limit they act as pro-foamers for hydrocarbons. Studies by Fraga and workers (51) have shown that the defoaming of crude oil by neat antifoam involved a bridging mechanism characterized by a negative spreading coefficient and positive bridging coefficient. It was also shown that the antifoam performance of various alkoxylated PDMS in crude oil could be increased as the solubility is reduced by incorporating alkoxyl groups in PDMS chain.

9.10 Thin film studies with non-aqueous and ionic liquids

Early drainage studies with thin films prepared with benzene and chlorobenzene were reported by Scheludko (52), but the films were found to be unstable and no long-range electrostatic repulsive forces were detected, suggesting the interface was uncharged. The drainage, rupture thickness and lifetime of thin liquid films between

air bubbles in diesel fuel were reported by McKendrick and coworkers (53); it was found that with a fluorosilicone surfactant the interface was highly rigid but ruptured at high film pressures. It was also shown that the surfactant could act as an anti- or pro-foamer depending on bubble size. Thin film studies have also been documented with ionic liquids which are usually considered to be salts with weak crystal lattice energies. They frequently remain in the liquid state at room temperatures and have high viscosities. In the literature many studies have been reported in which attempts have been made to correlate the structure and the physico-chemical properties of ionic liquids to specific applications. They can be easily tuned by changing the chain length of the cation or by changing the type of anion. Ionic liquids can be modified to act as surface-active agents and, with different degrees of hydrophobicity, they have potential applications as both foam boosters and defoamers. Law and Watson (54) reported surface tension rates for $[C_nmim][X]$, where C_nmim represents the $1-C_nH_{2n+1}$-3-methylimidazolium cation, where n = 4 [bmim], 8 [omim] and 12 [C_{12}mim] and X = PF_6^-, BF_4^-, Cl^- of Br and found a wide range of values from 45 to 24 mN/m at 336 K. Martino and coworkers (55) measured the surface tension of salts based on the pairing of cations such as 1-ethyl-3-methylimidazolium with different types of anions. Phosphonium-based ionic liquids produced by Cytec Industries, USA, have been shown to be versatile defoamers (56).

Ionic liquids also dissolve many different types of surfactants, and Bu and coworkers (57) showed that it was possible to prepare foam films with an ionic liquid solvent (1-ethyl-3-methyl-imidazolium tetrafluoroborate [EMIM] [BF_4]) stabilized by a non-ionic surfactant. Initially, the thin foam films were prepared by immersing a wire frame in a solution of polyethylene oxide (PEO)-based surfactant consisting of a dodecyl chain linked to 23 ethylene oxide units (Brij-35).The thin films were carefully lifted out of the frame and allowed to stand for over 1 hour. Gradually, during drainage, the film exhibited bright irridescent colors (as similarly observed with aqueous films), and after a period of time the viscous film was transferred onto a porous copper substrate (constructed with microns square holes) and allowed to stand for one day. Following this time period, the layer thinned down spontaneously to a Newton Black Film (NBF) structure consisting of a reversed bilayer solvated with the ionic liquid remaining in the holes. This process is illustrated in Fig. 9.12. From confocal Raman spectroscopy, XPS and X-ray analysis, the presence of a solvated [EMIM] [BF_4] structure was evident in the central part of the holes, and the excess ionic liquid and the Brij-35 migrated to the edge of the holes. From the data it was concluded that Brij-35 surfactant produced NBFs solvated with a triple molar quantity of [EMIM] [BF_4]. It was proposed that the inside of Brij-35 film must be filled with highly entangled PEO moieties and the surface, mainly occupied by dodecyl chains and also the imidazolium cation, has a suitable size to be encircled by 8 ethylene oxide units of PEO. NBFs were also produced with octadecyl chain linked to 20 (Brij-78) and 100 ethylene oxide units (Brij-700), respectively, with the same ionic liquid.

It was shown that the films can exist at temperatures much higher than the melting point of Brij-35, but the origins of thermal stability were not clear. Also smooth films were produced using a difunctional block polymer copolymer composed of one hydrophobic polypropylene oxide (PPO) part and two hydrophilic PEO parts (Pluronic F127). Although
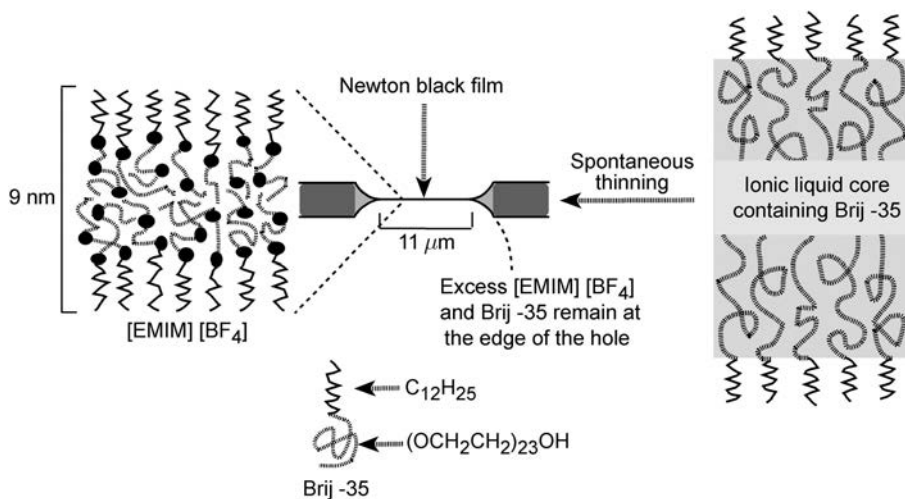
Fig. 9.12   Formation of a Newton Black Film solvated with (EMIM) (BF_6) consisting of a reverse bilayer using a film transfer technique. From ref (57).

these films were similar to the Brij-35 films, the thickness was considerably greater (19 nm), possibly due to incomplete drainage. It was suggested that the ionic liquid (EMIM) (BF_4) acts to screen the double-layer repulsion so that the main stabilizing mechanism was steric repulsion. The incomplete drainage of (EMIM)(BF_4) in these films implies high affinity between the PEO chains and (EMIM)(BF_4). The obtained films exhibited superior thermal stability when compared to that of the aqueous systems. At the present time no foaming studies have yet been carried out with these types of ionic liquids.

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