

## Phase studies of mixed phosphated surfactants, n-hexane and water

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Mixtures of phosphated nonylphenoethoxylate (PNE), phosphated fatty alcohol ethoxylate (PFE) and n-hexane form 'oils' which may spontaneously emulsify when added to water. However, the degree of spontaneity and the stability of the resulting dispersions vary according to the constitution of the system. Studies of the equilibrium phase diagrams suggest that the anomalies may be attributed to the presence of liquid crystalline phases of different types which are formed in the presence of water.

The formulation of solubilized and emulsified systems has been widely investigated. The systems, which generally consist of mixtures of surfactants dissolved in an oil together with the active ingredient, often puzzled workers by the apparent complexity of changes brought about by alteration in the ratios of surface-active materials, oil and water. Only slight changes, for example, may produce profound alterations in the viscosity of the product or in its subsequent behaviour.

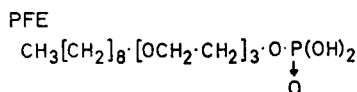
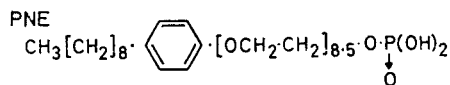
The particular concentration and temperature at which anomalies occur varies with the chemical nature and molecular weight of the surface-active agent selected as well as the nature and properties of the oil to be emulsified or solubilized. Studies in this area have been restricted to short chain hydrocarbon compounds because of the high viscosity and consequent difficulty of separating the constituent phases often encountered with the longer chain compounds. Only a limited range of solutes has been used with any one type of surface-active agent, and most results have been reported for compounds which may be regarded as polar solvents.

Self-emulsifying oils of the type used for the formulation of pesticides and herbicides are economically important materials which have previously received little systematic attention although there is a wealth of information which could be regarded as empirical (e.g. Ashworth, 1966). It is known, for example, that two surfactants are required for a formulation to successfully emulsify in water with little or no agitation. Although both of these materials must be soluble in the oil phase of the initial formulation, it is also widely recognized that one of them must be preferentially soluble in water and the other remain substantially in the oil phase when the system is added to an excess of water.

Investigation of the properties of phosphated nonylphenoethoxylate (PNE) and phosphated fatty alcohol ethoxylate (PFE) have already been reported by Groves,

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Mustafa & Carless (1972 and 1973 respectively) and the following structures were assigned to them:



During the continued investigation it was noted that these two surfactants appeared to possess many of the requirements for the formulation of spontaneous emulsions when dissolved in n-hexane and added to an excess of water. However, the ease with which emulsions could be formed (the spontaneity) and the stability of the resulting dispersions varied considerably according to the constitution of the mixture. The equilibrium constitution of mixtures was therefore investigated in order to explore the phases present and their relations, one to another. As the investigation proceeded it became clear that the proportion of water also played an important part in the formation of anomalous areas in the phase diagram and this was included.

The pattern of phase relations in surfactant-oil-water systems has been investigated by others for liquid oils and ionic surfactants which are soluble in both oil and water (McBain, Brock & others, 1938; Hyde, Langbridge & Lawrence, 1954; Dervichian, 1957; Lawrence, 1958; Mulley, 1961). Both binary (surfactant-water) and ternary (surfactant-oil-water) systems had similar anomalous regions and although there is less information for non-ionic surfactants, Lawrence & Mills (1954) suggested that they were much the same. The following anomalous regions can be identified in most of these systems (Mulley, 1961):

1. An area of single aqueous isotropic liquid  $L_1$ .
2. A similar area with the corresponding organic isotropic liquid phase,  $L_2$ .
3. A region in which the two liquid phases are in equilibrium (emulsion).
4. An area of one isotropic liquid phase in equilibrium with a liquid crystalline phase.
5. A corresponding area in which there is organic liquid phase in equilibrium with the liquid crystalline phase.
6. A three phase region in which the two isotropic liquids are in equilibrium with the liquid crystal phase.
7. A single phase of anisotropic liquid crystal.

All of these constituent phases could be identified in the systems containing PNE, PFE, n-hexane and water. It is the presence of two different anisotropic materials which appears to account for some of the differences observed when the oil-surfactant solution is added to water.

#### MATERIALS AND METHODS

##### *Materials*

PNE (as described by Groves & others, 1972); PFE (as described by Groves & others, 1973); n-hexane, laboratory grade (Fisons), used as received; water, triple-glass distilled.

##### *Methods*

##### *Construction of phase diagrams*

Ternary phase diagrams were constructed from solubility data expressed as weight of solute in total weight of solution. A mixture of either PNE and water or PFE and

n-hexane was prepared according to the specific points on the water-PNE or n-hexane-PFE axis. To these mixtures the third component was added gradually and allowed to equilibrate at the required temperature between each addition. Phase changes, if any, were observed after 3 h equilibration time. Occasionally a point not lying on either the water-PNE or the n-hexane-PFE axis had to be chosen to allow the phase boundary to be crossed normally to give a more definite phase transition.

In some areas of the system difficulty was experienced in separating the two isotropic liquids since viscous emulsions were formed. In these situations the triangular staggered walk technique of Boffey, Collison & Lawrence (1959) was adopted to enable the phase boundaries to be crossed normally.

Because of the volatility of n-hexane, all solubility measurements were made in ampoules sealed by fusion of the glass after first chilling in a solid carbon dioxide/acetone mixture. After sealing the ampoules were wiped dry, allowed to equilibrate and re-weighed. Any loss in weight was assumed to be due to n-hexane lost by evaporation and deducted from the weight of n-hexane originally present in the ampoule. Some solubility measurements were also made in ungreased glass-stoppered flasks.

All the containers were stored at the required temperature for periods of up to eight months to ensure that equilibration had been reached. However, very few changes were observed after the first 3 h period and all the results reported were observed at that time.

#### *Analytical methods*

Phase boundaries in some ternary systems were determined by analysis of the components of the phases isolated from equilibrated mixtures. The mixtures were prepared in graduated centrifuge tubes and, after equilibration, were centrifuged at the equilibration temperature in a thermostatically controlled centrifuge at 2500 rev min<sup>-1</sup>. After separation of the phases aliquots of the isotropic liquid phase were withdrawn and the surfactants differentially analysed.

PNE has two broad peaks at 277 and 226 nm, characteristic of phenolic and benzene moieties, whereas PFE is substantially featureless in the ultraviolet range. Examination of the spectra of mixtures of the two compounds in water showed that the PNE spectra were unchanged. The addition of quantities of PFE to PNE solutions produced no effect on the original spectrophotometric absorption, Fig. 1.

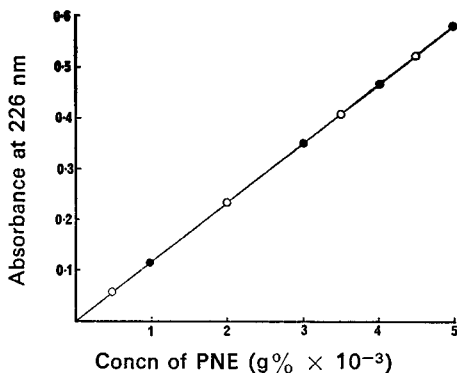


FIG. 1. Ultraviolet absorbance of aqueous solutions of PNE alone (○) and in combination with 0.001% w/v PFE (●).

The total amounts of PNE and PFE were determined by the basic (cationic) dye method of Jones (1945), as modified by Epton (1948) and Geyer (1964), using methylene blue and chloroform. The intensity of the blue colour in the chloroform layer was estimated with an EEL absorptiometer (Filter No. 605) and calibration curves were prepared for each component separately and together. Knowing the amount of PNE present in the mixture, the PFE could be determined by difference. Accuracy of the method was checked by preparing samples of known constitution and good agreement was obtained between theoretical and experimental results (Mustafa, 1973).

Water was determined by the Karl Fischer method.

Phase changes involving liquid crystals were examined in plane polarized light or viewed under a microscope using crossed polarizers. All the liquid crystalline phases were birefringent and, according to their position in the ternary or quaternary component diagrams, varied in consistency from fluid and just pourable to jelly-like or solid gels. Characterization of the liquid crystal type was by the visual microscope method of Rosevear (1968). All the isotropic phases were quite fluid and could be easily distinguished from the liquid crystalline or gels phases.

Good agreement between the synthetic and analytical methods was obtained in all cases.

## RESULTS

The isothermal phase diagrams for both PNE and PFE in the presence of *n*-hexane and water, Figs 2 and 3, both show the typical areas described by Mulley (1961) and other workers. There are broad similarities between the two compounds in that both have areas of a pure liquid crystalline phase, identified as being of the 'neat liquid crystal' type. This is of interest since it has already been suggested that PNE behaves substantially as a non-ionic surfactant (Groves & others, 1972) whereas PFE has many properties associated with ionic surfactants (Groves & others, 1973).

Increase of the equilibrium temperature in both cases from 25 to 45° resulted in a decrease of the area of the liquid crystalline phase, possibly as a result of increased thermal motion. In the case of PNE there was also an extension of the isotropic  $L_1$  phase at the expense of the emulsion phase of  $L_1$  and  $L_2$  and this is clearly due to an increase of the water solubility of this material as the temperature is raised. In the

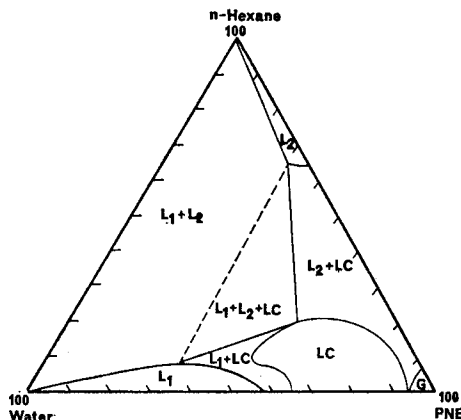


FIG. 2. Phase equilibrium diagram for a system containing PNE-water-*n*-hexane at 25°.  $L_1$  = isotropic aqueous liquid phase.  $L_2$  = isotropic organic liquid phase. LC = liquid crystalline phase. G = gel phase.

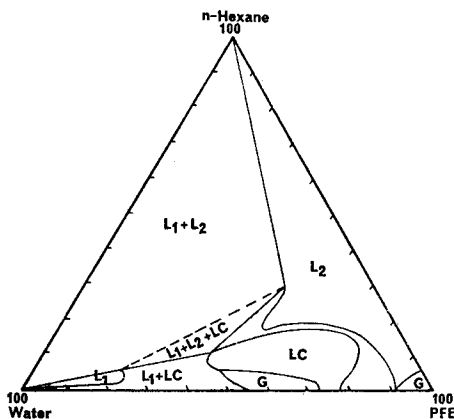


FIG. 3. Phase equilibrium diagram for a system containing PFE, water and n-hexane at 25°.  $L_1$  = isotropic aqueous liquid phase.  $L_2$  = isotropic organic liquid phase. LC = liquid crystalline phase. G = gel phase.

case of the substantially oil-soluble PFE it was the  $L_1L_2$  area which was increased at the expense of the liquid crystalline phase (Mustafa, 1973).

Equilibration in the presence of 0.05 M aqueous buffer systems had no effect on the phase relations for the PNE systems, probably because it is already substantially water soluble at acid pH. In the case of PFE which becomes more water soluble as the pH increases, the only noticeable change was a slight extension of the  $L_1$  phase into the  $L_1 + LC$  region.

However, the main interest of the investigation was in the properties of mixtures of the two surfactants since they stabilized emulsions of n-hexane in water in combination but not separately. The phase diagrams of PNE, PFE and either n-hexane or water were largely featureless (Fig. 4a, b), consisting of either isotropic liquid ( $L_2$ ) in the case of the n-hexane system or mainly neat liquid crystalline material in the case of the water-surfactant ternary system. These diagrams, together with Figs 2 and 3, represent the four faces of the quaternary phase diagram. During the formation of an emulsion by the addition of an oil solution of the two surfactants to an excess of water, it must be presumed that the equilibrium changes progressively in stages as the initially anhydrous oil solution is diluted out into the water phase. However, knowledge of the faces of the quaternary system diagram does not assist the under-

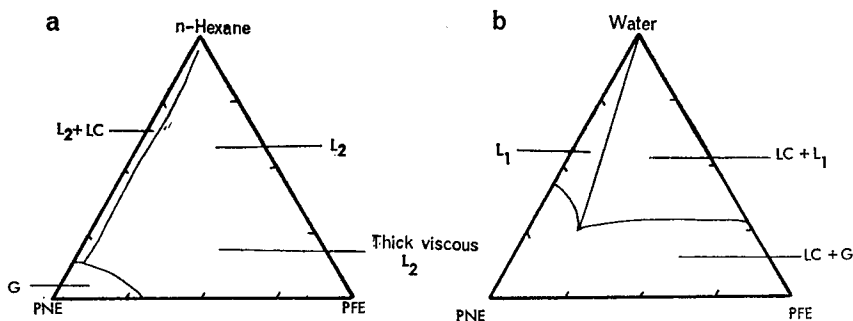


FIG. 4. Phase equilibria diagram at 25° for (a) PNE-PFE-n-hexane. (b) PNE-PFE-water.  $L_1$  = isotropic aqueous liquid phase.  $L_2$  = isotropic organic liquid phase. LC = liquid crystalline phase. G = gel phase.

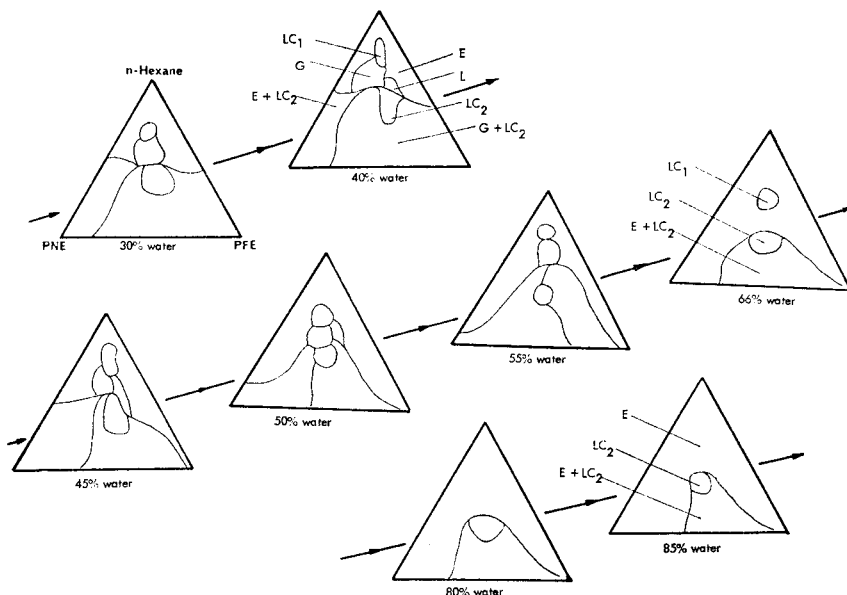


FIG. 5. Diagrammatic representation of the effect of progressively adding water to a mixture of PNE, PFE and n-hexane (Fig. 4a). L, Liquid. G, Gel. E, Emulsion.  $LC_1$ , Middle phase liquid crystal.  $LC_2$ , Neat phase liquid crystal.

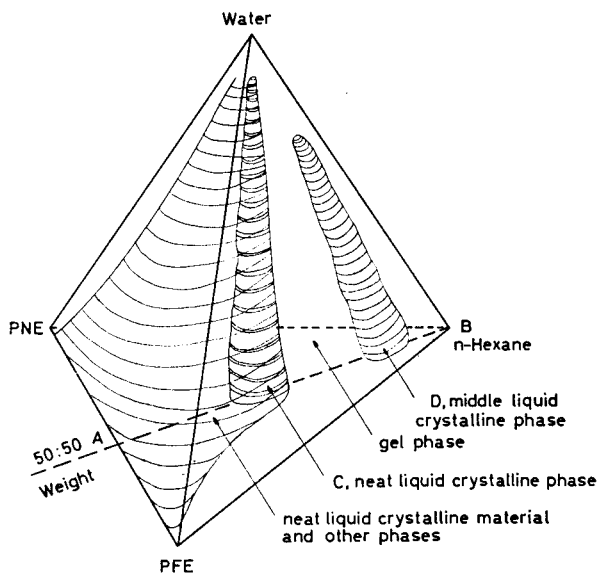


FIG. 6. Diagrammatic quaternary phase diagram for the system PNE-PFE-water-n-hexane at 25°.

standing of any changes which may occur during the dilution of an oil solution as it is diluted with an excess of water and moves towards its final equilibrium state.

Accordingly, starting with the anhydrous system (Fig. 4a), a series of dilutions were made with different quantities of water and this gave the situation summarized in Fig. 5. In diagrammatic form, much simplified, the quaternary diagram is shown in Fig. 6 to give an indication of the relations of the two liquid crystalline phases.

The main feature of these systems is the formation of liquid crystalline material immediately water is added to the anhydrous mixture, in particular, the formation of a separate type of liquid crystal isolated from the smectic neat phase and identified by microscope examination as 'middle phase' liquid crystal. One other notable feature is the fact that, as the water concentration is increased, the middle phase material disappears into the  $L_1$  phase followed, presumably, at a later stage, by the neat phase.

#### DISCUSSION

The diagrammatic quaternary phase diagram (Fig. 6) is helpful in the consideration of the changes brought about in the properties of the oil-surfactant mixtures when diluted in water.

As discussed by Sherman (1968), there is adequate evidence in the literature to suggest that surfactants and other materials such as aliphatic alcohols or acids form molecular complexes as liquid crystalline structures in aqueous systems. Many of these data have been obtained from aqueous systems without a dispersed oil phase. In addition, all three of the main types of surfactant (anionic, cationic and non-ionic) form liquid crystals in aqueous systems regardless of whether they are complexed with a long chain polar compound (Winsor, 1954, 1968).

Ionic surface-active agents with short alkyl chains may not form a separate liquid crystalline phase until the concentration reaches 20–30% but, as the chain length increases, the concentration at which the liquid crystalline structures form decreases rapidly (Lawrence, 1961). When the hydrocarbon chain length reaches eighteen carbon atoms the liquid crystals may form at concentrations as low as 1–2% (Mulley, 1964). In aqueous systems containing a surfactant-long chain fatty alcohol or acid complex, the liquid crystalline structures form much more readily, possibly because the repulsive forces between the ionized heads of the surfactant have been reduced by the presence of the alcohol or acid molecules allowing closer packing of the molecules (Mulley, 1964). Ekwall, Mandell & Fontell (1969) have indicated that mesomorphic phases may be formed below the critical micelle concentration in systems containing surfactants and polar compounds, a suggestion reinforced by Lawrence & Hyde (1960) investigating the effect of organic materials on the conductivity curves of ionic surfactants.

However, when the third component of a ternary system is a non-polar liquid, the formation of liquid crystalline material is only likely at high concentrations of the surfactant since the non-polar material may not aid in the orientation of the molecular complex. For example, Mulley (1964) visualized that the addition of water-insoluble compounds to aqueous solutions of surfactants containing Hartley micelles would only gradually change the micelle structure until the liquid crystalline phase separated out. This concept has been discussed and amplified by Winsor (1954, 1968).

The fact that the liquid crystalline phases can be separated out of a PNE-PFE system with apparent facility suggests that the system may be aberrant in some way and this is also substantiated by the manner in which the same proportion of surfactants can form either neat or middle phase liquid crystals depending upon the amount of hexane present in the initial mixture. In fact, there is some evidence (Groves, Mustafa & Carless, 1974) that the two surfactants are capable of complexing together in a 1:1 ratio, the approximate position of the midline marked A–B on Fig. 6 which coincides with the centres of the liquid crystalline phases of the quaternary system.

We are therefore in a better position to understand the anomalous behaviour of mixtures of the surfactants when dissolved in oil and poured into an excess of water if we postulate that the behaviour observed is not that of the surfactants, oil and water but rather the constituent phases which are formed initially when these components are mixed.

Thus, if an equal mixture of PNE and PFE is diluted with n-hexane the position of any particular mixture along the midline A-B (Fig. 6) will be determined by the amount of n-hexane in the system. When the mixture is added to an excess of water the water will dilute the oil solution and a new system will form according to the position of the original mixture on the midline. Starting at point C, for example, will result in pure neat liquid crystal forming, and at point D pure middle liquid crystal. Once the first quantities of water have penetrated into the oil solution the subsequent ease of penetration will depend entirely on the properties of the respective liquid crystal. For starting points outside the midline it will be clear that the subsequent behaviour will again depend on the type of material which is formed in the presence of water.

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