

A note on the interaction between two phosphated surfactants

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Evidence of an interaction between the water-soluble phosphated nonylphenoethoxylate (PNE) and the oil-soluble phosphated fatty alcohol ethoxylate (PFE) could not be obtained when the two compounds were mixed in the anhydrous state. However, measurements of refractive index, interfacial tension, density and viscosity of aqueous solutions of the two surfactants showed anomalies which were at a maximum when they were present in an approximately equal ratio by weight.

Thin-layer chromatography confirmed the anomalous properties of mixtures of the two compounds and it is suggested that these result from the formation of a complex material involving PNE, PFE and water.

The fact that molecules of surfactants can associate to form micelles and liquid crystals is well established (Friberg & Wilton, 1970; Friberg, 1971). Both phosphated nonylphenoethoxylate (PNE) (Groves, Mustafa & Carless, 1972) and phosphated fatty alcohol ethoxylate (PFE) (Groves, Mustafa & Carless, 1973) are unexceptional in this respect. However, emulsions of n-hexane in water could not be obtained with either compound alone whereas mixtures of the two dissolved in n-hexane readily produced 'spontaneous' emulsions when added to water. In addition, the quaternary phase diagrams of PNE, PFE, n-hexane and water showed several anomalies (Groves, Mustafa & Carless, 1974), which included well-defined areas of liquid crystalline material of different types.

Thin-layer chromatographic examination of mixtures of the two compounds suggested that there was anomalous behaviour resulting from some type of interaction between PNE and PFE, and the properties of mixtures were therefore investigated further by other methods.

MATERIALS AND METHODS

Materials

PNE-phosphated nonylphenoethoxylate-Phospholan PNP-9 (Lankro Chemicals Ltd), used as received (Groves & others, 1972). PFE-phosphated fatty alcohol ethoxylate-Phospholan PDB-3 (Lankro Chemicals Ltd), used as received (Groves & others, 1973). n-Hexane, laboratory grade (Fisons), used as received. Water: triple-glass distilled.

Methods

Thin-layer chromatography. The method is based on those used by Patterson,

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Hunt & Tucker (1966) and Mansfield & Locke (1964) for the determination of mixtures of surface-active materials. Silica gel (Kieselgel G.E. Merck A.G., Darmstadt) was spread on 20 × 20 cm glass plates to a thickness of 0.25 mm. Using a 5 μ l pipette, 30 μ l volumes of surfactant solutions in chloroform were applied to the plates which were then developed with a mixture of equal parts of butanol, glacial acetic acid and water. After development and drying, the organic materials on the plates were identified by exposure to iodine vapour and drying, spraying with sulphuric acid and heating or by spraying with the Burger's reagent as modified by Patterson & others (1966). Similar results were obtained using the three methods of detection.

Infrared absorbance. Spectra were determined with a Unicam SP 200 spectrophotometer, using a thin film on potassium bromide discs.

Ultraviolet absorbance. Spectra were determined on aqueous or non-aqueous solutions using a Unicam SP 800 spectrophotometer.

Viscosity measurements were made at 25° using a calibrated Ubbelohde viscometer following the method in the British Standard No. 188 (1957).

Densities of aqueous solutions were measured at 25° using a 10 cm³ specific gravity bottle according to British Standards Nos. 733 (1965) and 1797 (1968).

Refractive index was determined using an Abbé refractometer connected to a thermostated water bath at 25°.

Interfacial tensions between n-hexane and water solutions were measured using a Du Nouy tensiometer, as described by Groves & others (1972).

RESULTS

Direct evidence of complexation was sought by carrying out infrared absorption spectral analysis of anhydrous mixtures of the two materials compressed into KBr discs but the results were inconclusive, so too were the ultraviolet findings.

It seemed possible that the t.l.c. method might throw light on any interaction between the two materials. That a mixture of the surfactants produced only one spot when run on a plate under carefully standardized conditions was not unexpected when considered in the light of the additional evidence of complexation; what was unexpected was the fact that not only did the 50:50 mixture of these materials produce a single spot with an R_F value intermediate between those of the components, but as the proportion was varied, an additional spot could be produced with a R_F corresponding to whichever component was in excess. Some results of this t.l.c. investigation are shown in Table 1, but additional evidence indicates that the liquid crystalline

Table 1. *Thin-layer chromatography of PNE, PFE and a mixture on silica gel, developed with butanol-glacial acetic acid-water (equal parts).*

Sample	R_F (mean of 7)	R_{ST}^*	Observation
PNE	0.66	92.9	Single spot
PNE	0.75	105.6	Single spot
PNE:PFE:50:50	0.71	100	Single spot

* Due to Ganshirt (1969).

$$R_{ST} = \frac{\text{distance of sample spot from origin} \times 100}{\text{distance of reference material from origin}}$$

phases noted in the quaternary phase diagram themselves also behave in an anomalous fashion consistent with them having properties quite separate from the starting materials (Groves & Mustafa, 1974).

Assarson & Eirich (1968) suggested that molecular association between two materials could be detected by deviation from anticipated measurements when determining physical properties such as density or viscosity.

Refractive index measurements of anhydrous mixtures of the PNE and PFE, and mixtures of the compounds in *n*-hexane showed no deviation from the anticipated behaviour (Fig. 1), suggesting that there is no interaction in the absence of water.

The addition of a small amount of water to the mixture of the two surfactants produced a marked deviation in the expected behaviour of the refractive index measurements, seen in Fig. 1, a maximum being reached at a point corresponding to a 50:50 mixture by weight of the two compounds. This observation was therefore extended by examining other physical properties and these results are shown in Figs 2 and 3. They again confirm the influence of water on the interaction between PNE and PFE which, in all cases, appears to reach a maximum when the two compounds are in approximately equal proportions by weight.

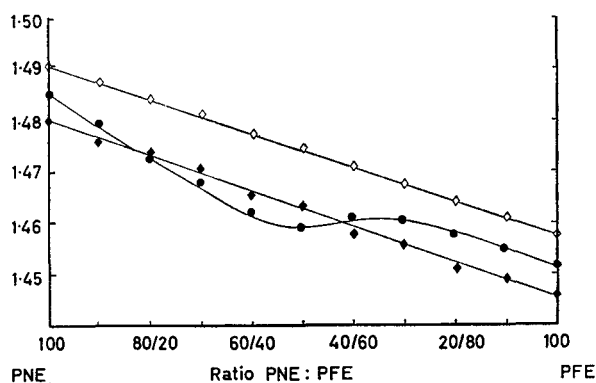


FIG. 1. The refractive index of different ratio mixtures of PNE:PFE. \diamond Anhydrous mixture. \blacklozenge *n*-Hexane, 10% w/w, added to mixture. \bullet Water, 10% w/w, added to mixture.

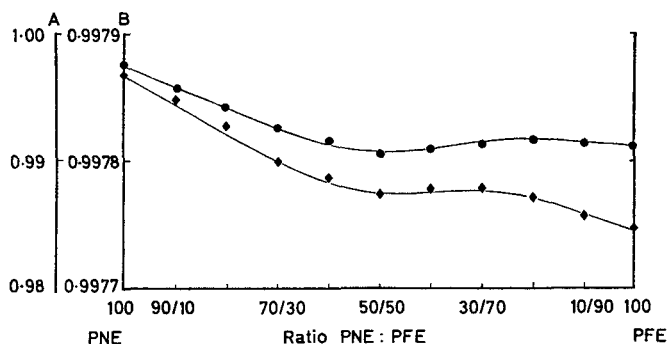


FIG. 2. Density and viscosity measurement, on aqueous solution containing different ratios of PNE:PFE in a total of 10% w/v. A, viscosity cP (\blacklozenge). B, density (\bullet).

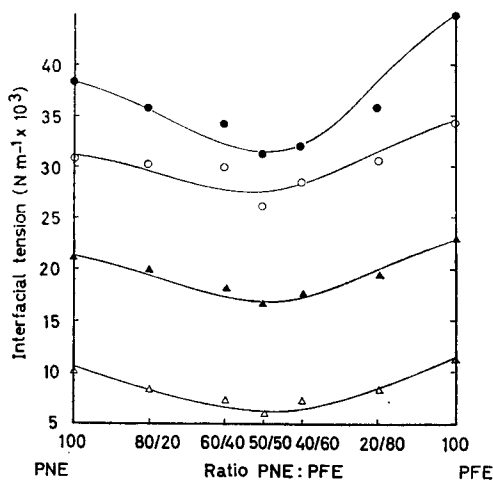


FIG. 3. Anomalies in interfacial tension measurements of aqueous solutions containing different ratios of PNE:PFE. A total weight of: ●, 0.00001%; ○, 0.0001%; ▲, 0.001%; △, 0.01%.

DISCUSSION

The evidence in Figs 1–3 suggests that PNE and PFE are capable of reacting together to form a definite and definable complex molecule in the presence of water. Little direct information could be obtained about this complex but, since the molecular weight assigned to PNE is 677 and PFE 353 (Groves & others, 1972, 1973), it would appear that the 50:50 ratio by weight corresponds to one molecule of PNE reacting with two molecules of PFE, the water being required to promote the formation of hydrogen bonds as suggested by Ekwall, Mandell & Fontell (1969).

It is therefore tempting to draw an analogy with the Schulman & Cockbain (1940) theory of the formation of interfacial complexes between hydrophylic and hydrophobic surface active materials. Both PNE and PFE are anionic surfactants with ethylene oxide condensate residues and neither would be regarded as a hydrophobic material. However, of the two, PFE has a shorter ethylene oxide chain and behaves substantially as if it were an anionic surfactant so, in relative terms, it is less hydrophilic than PNE. In a practical situation at the interface of an oil-in-water system it is probable that the PFE would remain substantially in the oil phase, whereas the PNE would pass into the aqueous phase. Hence, any complex formation between the two is most likely to occur at the oil-water interface. This reasoning has led Friberg (1971), amongst others, to justify the extrapolation of measured properties of bulk materials to the solution existing at an interface. Any attempt to correlate the bulk properties of a system such as those measured in the previous paper (Groves & others, 1974) with the interfacial properties of an emulsion system must therefore take into account the behaviour of anomalous areas of the phase diagram or the properties of any complex materials formed as a result of interaction between any of the components of the system.

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