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THE ZETA POTENTIAL OF DROPLETS PREPARED FROM A SELF-EMULSIFYING OIL

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ABSTRACT

The zeta potential of droplets formed by the self emulsification of compositions of n-hexane, phosphated nonylphenol ethoxylate and phosphated fatty alcohol ethoxylate has been determined in water and aqueous electrolyte solutions over a pH range of 3-11. Anomalies may be noted as a function of the n-hexane concentration of the surfactant/oil composition added to water. This, it is suggested, may be related to the mesomorphic systems that occur in bulk composition/water mixtures and could form at the interface of the droplets in water.

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Effects on the electrophoretic/mobility observed in the presence of sodium, lithium, calcium or magnesium may be explained by the relative size of the sphere of hydration around the cation that controls the depth of penetration through the surface layers of the droplets.

Aluminum ions appear to react completely with the surfactant phosphate moiety, precipitating directly onto the droplet surface. The droplet surface charge always remains negative and below 30 mV except in the presence of aluminum ions. The maximum charge is obtained at the pH of 5.5 which approximates to the pKa_1 of the surfactant mixture.

INTRODUCTION

Spontaneous or self-emulsifying systems are widely employed for the delivery of biocidal chemicals. The spontaneous formation of an emulsion after the addition of an oil based solution of surfactant materials to water may occur over a variable time span, from seconds to months depending on the constitution of the system (1).

The properties of a simple model system consisting of n-hexane solutions of phosphated nonylphenol ethoxylate (PNE) and phosphated fatty alcohol ethyoxylate (PFE) have been explored previously in order to obtain more insight into this interesting process,(2) - (9). In summary, it has been possible to correlate the speed with which an emulsion forms with the formation in bulk mixtures of the oil/water/surfactant system of various mesomorpic phases. The suggestion has been made that the formation of the droplets and their subsequent stabilization against coalescence may be related to the formation of mesomorphic material at the interface of the droplet, (10).

Changing the amount of n-hexane in a 1:1 mixture by weight of the surfactants proved to be a simple method of moving across phase boundaries on the equilibrium ternary phase diagram. It was suggested (10) that this might result in changing the identity of the mesophase at droplet interfaces although direct evidence for this supposition has been difficult to obtain owing to the small size of the droplets.

Attention was accordingly turned to the measurement of electophoretic mobility since, by changing the pH or adding counter-ions, it might prove possible to provide some additional evidence of the interfacial identity of the droplets.

EXPERIMENTAL

Materials

Phosphated nonylphenol ethoxylate (PNE) - Phospholan PNP-9, Lankro Chemicals Ltd., Eccles, Manchester, used as described (2)

Phosphated fatty alcohol ethoxylate (PFE) - Phospholan PDE-3 Lankro Chemicals Ltd., used as received (3)

n-Hexane, Laboratory reagent grade, Fisons Scientific Apparatus Ltd., used as received

Water - double glass distilled. All other salts AnalaR grade, Hopkins and Williams Ltd.

Methods

Apparent pKa - the pKa of a 1:1 mixture by weight of PNE and PFE was determined by automatic titration of a solution containing 1.0 g dm^{-3} of the mixture in freshly boiled and cooled distilled water with 0.1 M sodium hydroxide under a nitrogen atmosphere. The titration curve had two inflection points corresponding to a $pKa_1 = 5.1$ and $pKa_2 = 9.1$.

Zeta potential - Electrophoritic mobility and the corresponding zeta potential were determined using a Zeta Meter (Zeta Meter, Inc., New York) in accordance with the operational procedures given in the manual. The average time for twelve particles to migrate one full-scale division was determined and the electrophoretic mobility (E), the velocity/unit voltage gradient, converted to the zeta potential by the Helmholtz-Smoluchowski equation

$$\zeta = E.\ 4\pi.\ Vt/Dt$$

Where Vt = viscosity of the medium (poise) and Dt is the dielectric constant of the medium at the temperature of measurement (25°C).

Preliminary experiments established that there was minimum fluctuation in the data when the concentration of the disperse phase was maintained at 0.001%. Plateau values were obtained in all cases at electrolyte concentrations of 0.001 M confirming the results of Riddick (11). Evolution of gas at a pH below 3 was observed and measurements were confined to the range of pH 3-11.

Preparation of the emulsions - The appropriate volume of the oil/surfactant system under evaluation was added to an excess of the diluent and the emulsion allowed to form in a closed container for 30 minutes. The container was then gently agitated before adding more diluent to the required volume. Because of the volatility of the oil, measurements were taken as rapidly as possible after completion of the emulsification stage.

RESULTS

By varying the amount of n-hexane added to a 1:1 mixture by weight of PNE:PFE it is possible to prepare compositions that should produce different mesomorphs when added to water (8). The effect this has on the zeta potential of the emulsion droplets dispersed at pH 3.0 is shown in Fig. 1. Similar anomalous results were noted at pH 5.0 and 9.0, suggesting that a more detained exploration of systems corresponding to various mesomorphic components might be of interest. Typical data for portions of the phase diagram corresponding to lamellar and hexagonal phase liquid crystals and for undifferentiated material are shown in Figs. 2-4.

It will be noted that, in general, inflections in charge occur at around pH 5.5 in the presence of most electrolytes. Aluminum ions caused a rapid drop in charge and a decreased stability of the emulsion systems, consistent with the charge being reduced below 30 mv (12).

DISCUSSION

Both PNE and PFE are anionic surfactants with ethylene oxide condensate moieties (2,3). The charge on the droplets arises mainly through ionization of the terminal phosphate group, with some absorption of specific ions from the solution. The results obtained show that the surface charge is generally electronegative, reaching an inflection point at around

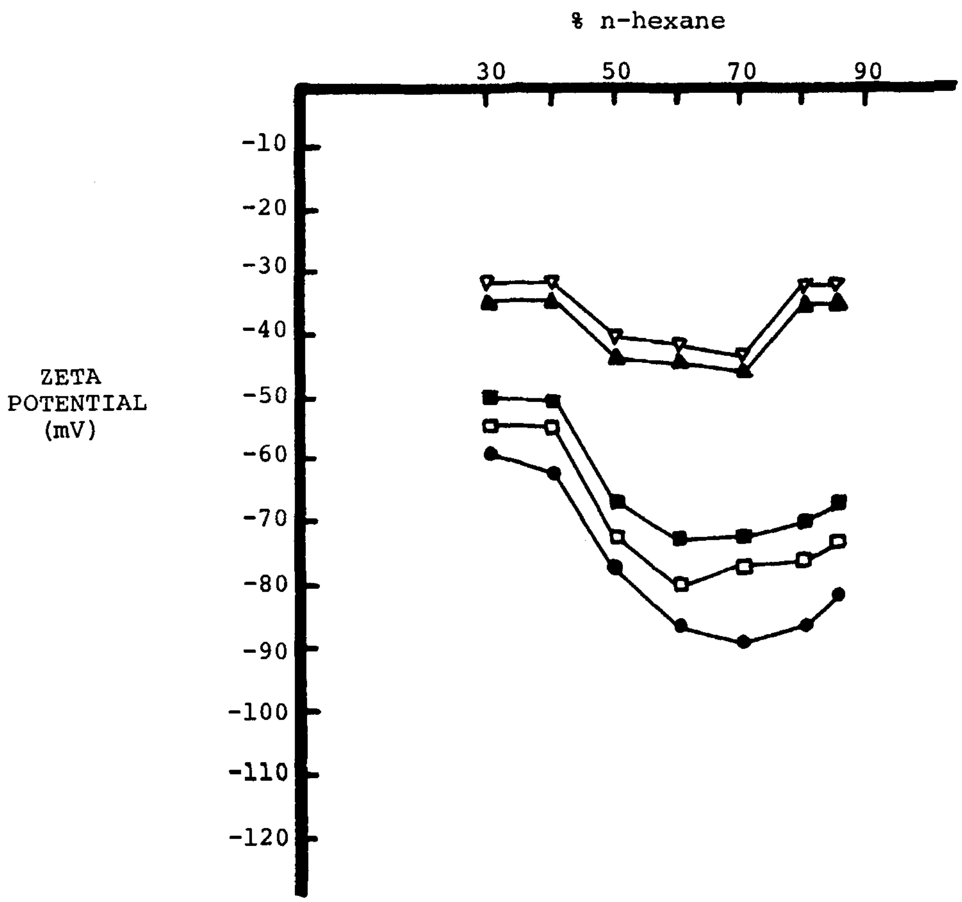

Fig. 1

The zeta potential of droplets formed from a mixture of 1:1 PNE: PFE in n-hexane, as a function of n-hexane concentration.

Key	Substrate
▽	distilled water
▲	0.001 m lithium chloride
■	0.001 m sodium chloride
□	0.001 m magnesium chloride
●	0.001 m calcium chloride

At 25° the equilibrium ternary phase diagram of PNE: PFE: n-hexane in 50% w/w water contains hexagonal phase liquid crystal between 70 - 80% n-hexane, viscous isotropic liquid between 55 and 70% n-hexane and lamellar phase liquid crystal below 55% n-hexane, (6).

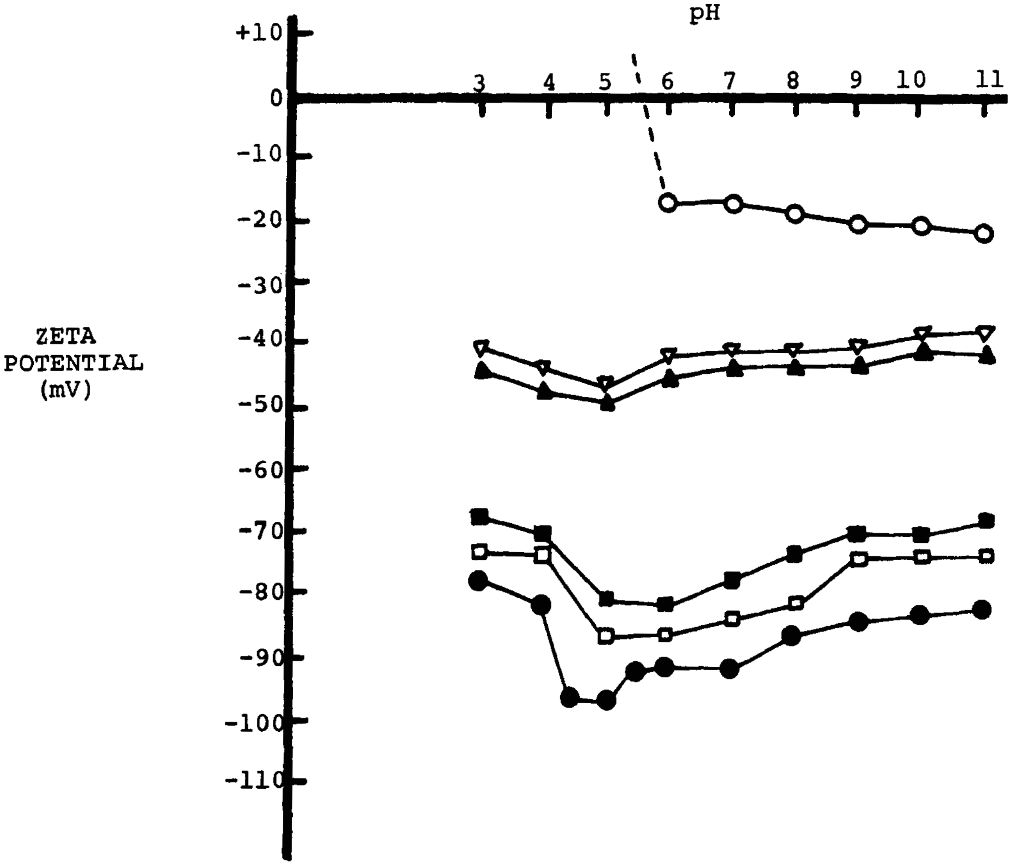

Fig. 2

The zeta potential of droplets prepared with the system PNE: PFE: n-hexane 25: 25: 50, equivalent to lamellar mesophase diagram in the presence of 50% water (6).

<u>Key</u> As for Fig. 1

○ 0.001 m aluminum chloride

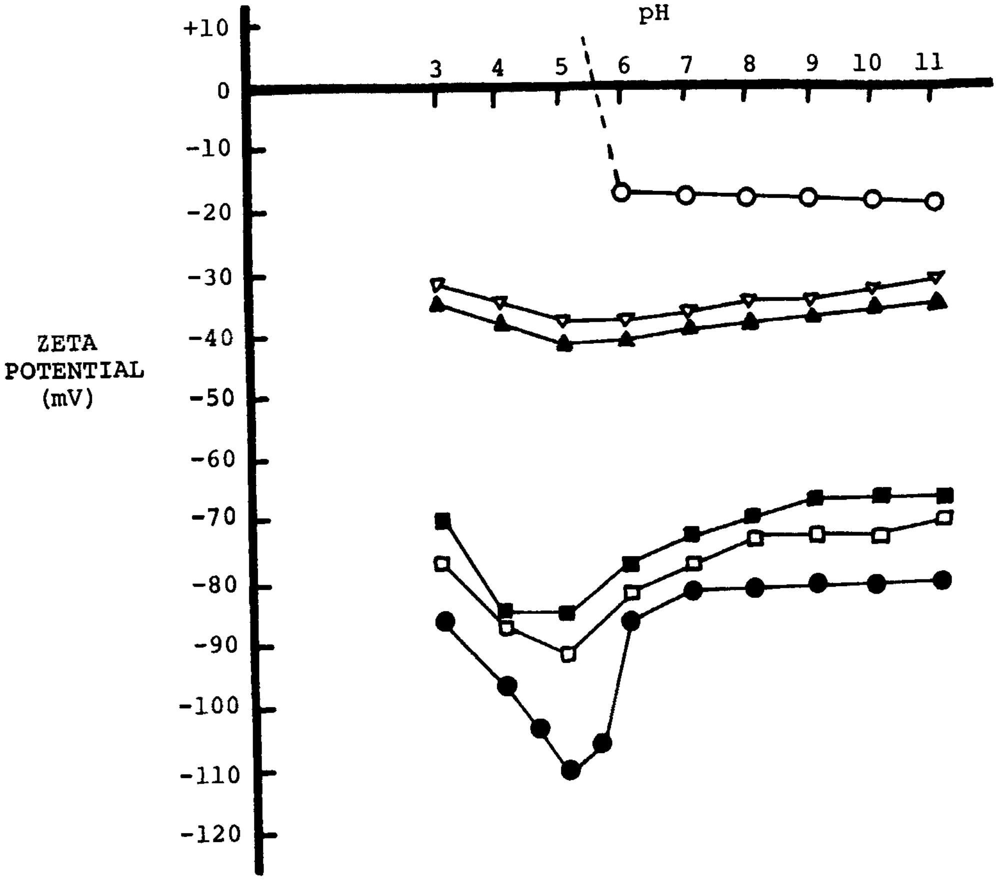

Fig. 3

As for Fig. 2, for the system PNE: PFE: n-hexane 10:10:80, equivalent to hexagonal mesophase on the equilibrium ternary phase diagram in the presence of 50% w/w water (6).

pH 5.5, approximately corresponding to the pKa_1 of the surfactant mixture. The different compositions corresponding to the various parts of the equilibrium phase diagram hve different behavior, depending on the pH of the environment. Those systems likely to contain hexagonal phase mesomorphs at their surfaces are more

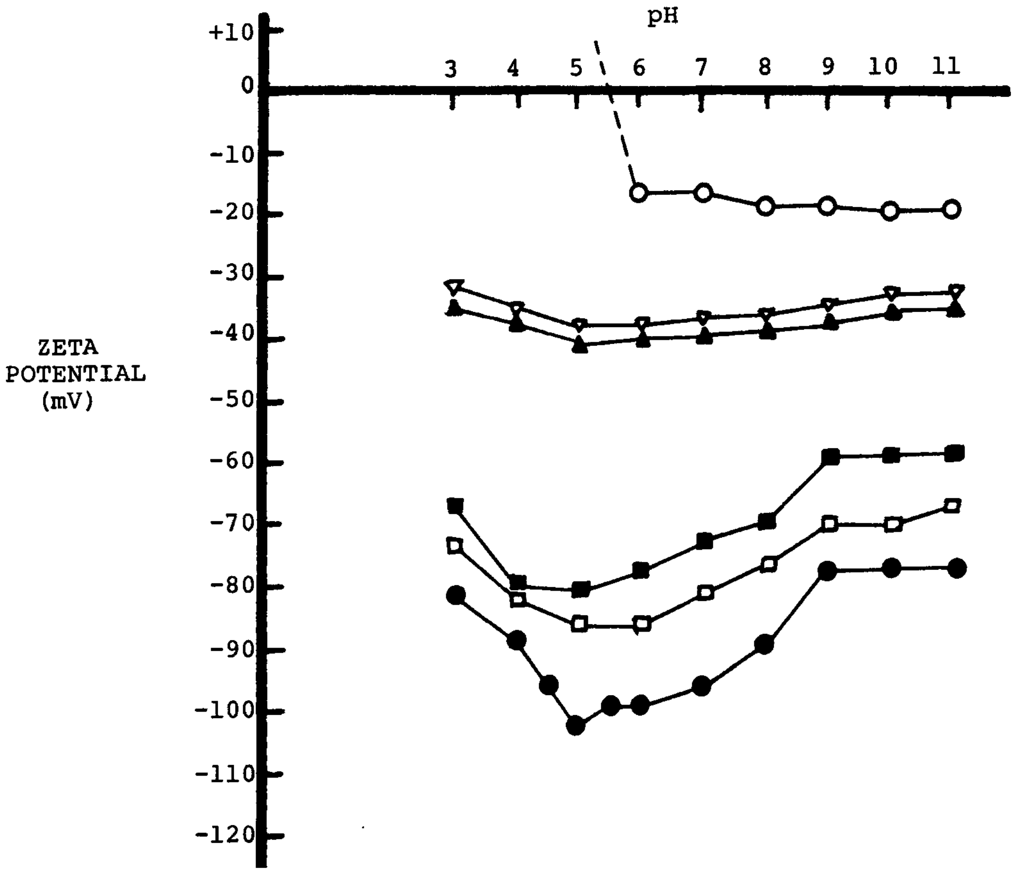

Fig. 4

As for Fig. 2, for the system PNE: PFE: n-hexane 7.5: 7.5:85, equivalent to the phase boundary between hexagonal mesophase and undifferentiated material on the ternary phase diagram in the presence of 50% w/w water (6).

electro negative than their corresponding lamellar phase systems under acid (pH 3-5) conditions where the surfactant molecules themselves are only partially ionized. These differences may arise from structural differences between interfacial mesomorphic material. For example, the hexagonal material may be visualized as having the lipophilic portions of the molecules projecting towards the inner part of the surface, with the hydrophilic groups projecting outward into the surrounding water (13-16). On the other hand, the lamellar phase structure is more closely packed and ordered with a coherent double layer of surfactant molecules and ions separated by water (13). The observed differences in zeta potential are consistent with the changes in the postulated degree of order at the interface. These differences persist even at a high pH where it is most likely that the phosphate terminal groups are completely ionized, suggesting that the overall structural identity is retained.

Zeta potential values obtained in water become depressed when sodium ions are introduced. Napper (18) suggested that this effect is due to penetration of the Stern layer by the sodium ions, allowing adsorption of the counter-ions and compression of the diffuse part of the double layer. Under the same conditions, lithium ions produced less depression of the charge although, from a structural point of view, lithium has a smaller atomic radius and would be anticipated to penetrate more readily. This suggests that the lithium ion is more hydrated (17). The hydrated lithium ions have a reduced ability to destroy local structure rather than strucure-breaking characteristics.

Divalent cations reduce the charge on the droplets more than 1:1 valency cations and there were only slight differences between acid and alkaline environments. Magnesium ions depressed the charge more effectively than calcium, probably because they penetrated to the surface more readily. Inorganic phosphates do not bind Ca^{++} (21) and phosphates in general depress Ca^{++}

adsorption (22). In the case of Mg^{++} the diffuse layer is not so compressed and it is unlikely that Ca^{++} will adsorb onto the surface because of competition between water molecules and the hydrated shells around the Ca^{++}. Calcium ions behave as indifferent electrolyties, at least at that concentration. This may also result from steric repulsion from the polyoxyethylene chains on the surfactant molecules (24, 25).

Zeta potential in the presence of aluminum was lowered considerably and Al^{+++} is considered to destroy the protective layers of charge around suspended particles by suppressing the thickness of the outer part of the electrical double layer (26). The surface charge of phosphate tended to become more electronegative in the presence of Al^{+++} at high pH, the opposite effect being observed with Ca^{++} (27, 28).

The adsorption of Al^{+++} is more likely to involve more than a simpler exchange reaction, (29). Those authors suggested that ions may be precipitated by hydrolysis of $Al\ (OH)^{++}$ and $Al\ (OH)_2^{+}$. Amorphous aluminum hydroxide surfaces are known to absorb and precipitate phosphates from solution as $Al(OH)_2, H_2PO_4$. This may explain the initial coagulation of the phosphate surfactant stabilized emulsions by Al^{+++} which is then followed by precipitation. No differences consistent with the postulated interfacial structures of the emulsion droplets can be detected when the zeta potential is measured at alkaline pH in the presence of aluminum ions.

In summary, the surface of droplets prepared from a self-emulsifying system carries a charge that appears to be influenced in magnitude by the composition of the system. These changes are consistent with structures postulated to be formed on the surface of the droplets during the emulsification process (10).

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