POTENTIOMETRIC MEASUREMENTS IN SOLUTIONS OF NON-IONIC SURFACTANTS

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Potentiometric measurements made in deionized cetomacrogol solutions show that the surfactant does not affect the pH values of sodium hydroxide solution or hydrochloric acid. The pH in buffer solutions containing cetomacrogol is changed to an extent which depends on the buffer acid. Possible mechanisms of this action are discussed and analytical applications indicated.

Though electrochemical methods have been widely applied to solutions of cationic and anionic surfactants, there is a comparative paucity of literature dealing with the application of such methods to solutions of non-ionic surfactants (Moillet, Collie and Black, 1961).

The present introductory paper is concerned with the possibility of applying potentiometric techniques to investigations of the properties of non-ionic surfactant solutions.

No detailed studies of the behaviour of the glass electrode in the presence of surfactants are available, although potentiometric measurements have been made in the presence of surfactants and no fundamental difficulties reported (Sexsmith, 1959; Veis, 1960). The pH values measured in such solutions might differ from those measured in water because of change in asymmetry potential of the glass electrode or modification of the activity coefficients of the ions present.

Experimental

Cetomacrogol, B.P.C. (Evans Medical, Ltd.) was found to contain small traces of alkaline impurities. It was therefore deionised by passage through columns of ion-exchange resins (B.D.H., analytical grade, I.R.-120 and I.R.A.-120), a method of purification first applied to non-ionic surfactants by Ginn (1959). After regeneration, the resins were washed with distilled water till the washings were neutral. The purified cetomacrogol solution obtained from the column was collected under nitrogen. Physico-chemical data on the characteristics of the cetomacrogol used will be reported later.

All solutions were prepared from carbon dioxide-free distilled water. During pH measurements it was not possible to pass nitrogen into the solutions, to prevent contamination by carbon dioxide, because of foaming; nitrogen was therefore passed over the solution.

The concentration of cetomacrogol in the effluent solution obtained from the ion-exchange column was checked by measurement of refractive index which varied linearly with concentrations of cetomacrogol solutions between 1 and 20 per cent w/v. Both the titration cell used for the pH

measurements and the refractometer were thermostatically controlled to 25° ±0·1°.

The electrodes used for pH measurements were: reference-Cambridge saturated calomel; indicator E.I.L. GH533. Two pH meters were used: the Pye Dynacap (accuracy ±0·02 pH) and the E.I.L. Vibron Electrometer with unit 33B attached (accuracy ±0·002 pH under optimum conditions). The pH scale was standardised as usual on *aqueous* potassium hydrogen phthalate solution (0·05M), and the electrode response checked on this buffer after each run; no changes were observed after use with cetomacrogol solution. Periodic checks on linearity of response were made using borax buffer solution (0·01 M).

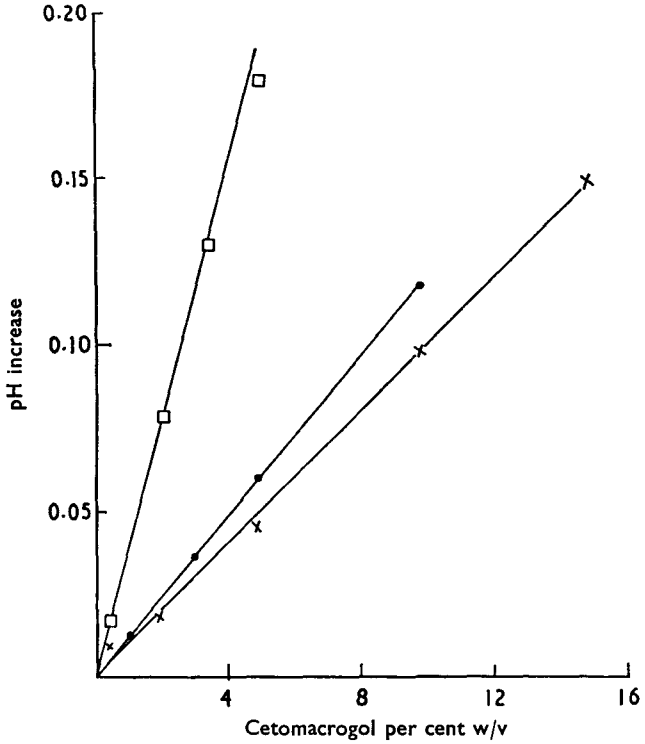

FIG. 1. Effect of cetomacrogol on buffer solutions.
□—□ Potassium hydrogen phthalate (0·05 M).
●—● Borax (0·05 M).
×—× Citric acid-sodium phosphate (McIlvaine buffer) pH 4·00.

RESULTS

Potentiometric curves of N/2,000 hydrochloric acid with N/300 sodium hydroxide solution and of the same hydrochloric acid containing 2, 4 and 10 per cent w/v cetomacrogol with the same sodium hydroxide solution were superimposable between pH 3 and 10, i.e. over the whole range of the titration.

The pH values of some common buffers in the presence of varying cetomacrogol concentrations were measured (Fig. 1). Increases in pH values were detected and in all instances the pH change appeared to be a linear function of the cetomacrogol concentration. The change in pH was greatest for the least water-soluble acid used, i.e. phthalic acid. This warranted further investigation into the effect of cetomacrogol upon such acids. As more information could be obtained from titration curves than from measurements on buffers, a series of titrations of varying concentrations of sodium benzoate (in the presence of cetomacrogol) with hydrochloric acid were performed. Some of the curves so obtained are shown in Figs. 2, 3 and 4. For comparison, similar titration curves of sodium benzoate in the absence of cetomacrogol are shown.

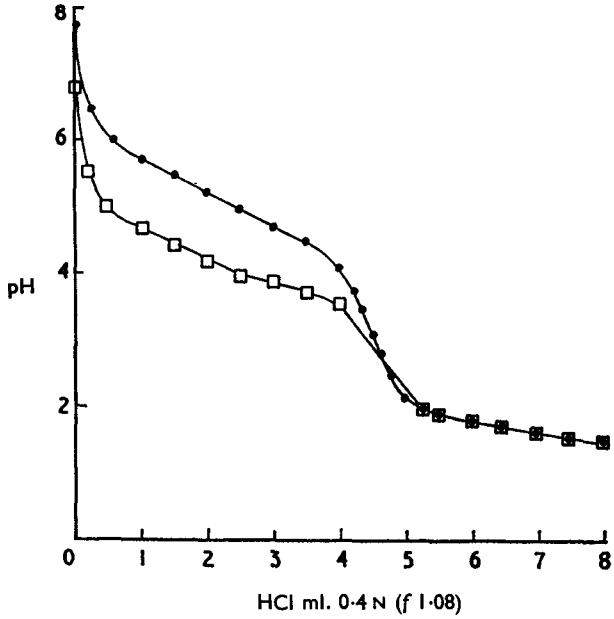

FIG. 2. Titration of sodium benzoate (77·8 mM) with hydrochloric acid (*f* 1·08) (25 ml. of solution containing 1·95 × 10^{-3} mole sodium benzoate).
●—● 20 per cent w/v cetomacrogol present.
□—□ No cetomacrogol present, precipitation occurred at about 2·5 ml.

DISCUSSION

Behaviour of Glass Electrode in Cetomacrogol Solution

The fact that the titration curves of hydrochloric acid against sodium hydroxide and of hydrochloric acid plus cetomacrogol against sodium hydroxide were superimposable, shows that the standard pH scale may be used in the presence of cetomacrogol (and probably equivalent amounts of other non-ionic surfactants). Thus the difference ($E_{cell}^{x} - E_{cell}^{s}$) between the measured cell e.m.f. values in the standard buffer solution, s, and any given hydrochloric acid/sodium hydroxide

mixture, x, is independent of the cetomacrogol concentration between pH 3 and 10. The pH values measured in cetomacrogol solution may therefore be described by the equation

$$pH_x = pH_s + \frac{E_{cell}^x - E_{cell}^s}{2{\cdot}303\ RT/F}$$

where pH_s is the pH value allocated to the standard *aqueous* buffer solution. Any pH value so described may be theoretically interpreted as for aqueous solutions, subject to evaluation of the correct activity coefficients. These appear to be very near unity in the hydrochloric acid/sodium hydroxide solutions.

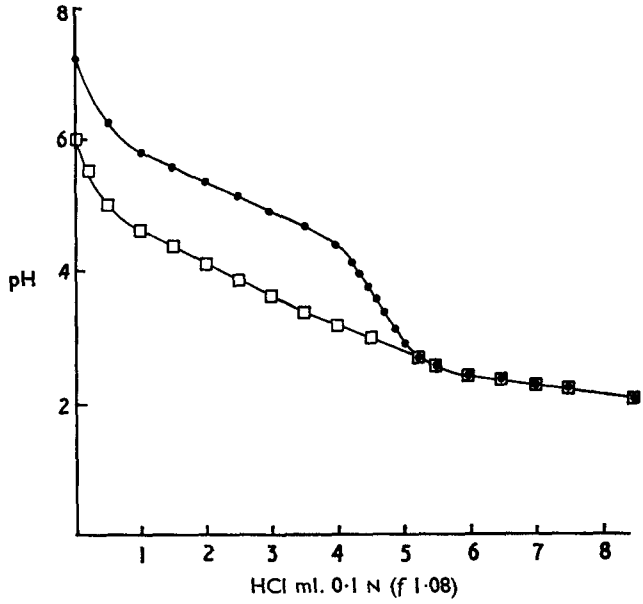

FIG. 3. Titration of sodium benzoate (19·46 mM) with hydrochloric acid (f 1·08) (25 ml. of solution containing 0·487 × 10^{-3} mole sodium benzoate).

●—● 20 per cent w/v cetomacrogol present.
□—□ No cetomacrogol present.

Mechanism of Surfactant-acid Interaction

It is apparent from Figs. 1 to 4 that the surfactant has reduced the activity of the various acid components of the solutions studied. The possibility that this is due to uptake of hydronium (H_3O^+) ions or of protons by the surfactant is remote, as no such effect was discernable in the hydrochloric acid/sodium hydroxide titrations. Were the pH changes due to alterations in asymmetry potential, such changes would have to be a linear function of cetomacrogol concentration with a different slope for each buffer; this is most unlikely.

The aqueous concentration of the buffers will change with cetomacrogol concentration if the micelles are considered as a separate phase. This

would not affect the buffer pH values to the extent found, as only the activity coefficients are modified and the calculated effect appears to be small.

It must therefore be concluded that the pH changes observed in the buffer solutions and in the sodium benzoate titration must arise from some other cause. Solubilisation studies by Dyer (1959), have shown that the ionised (or salt) form of a weak acid is not solubilised by surfactants and his results indicate that the pK_a values of such acids are not affected by the presence of surfactants. Although Dyer's results were obtained using ionic surfactants there seems no reason to anticipate that the same conclusions are not valid for non-ionic surfactants. Thus it would appear that the pH changes are due to selective solubilisation of the various acids present in the surfactant solutions.

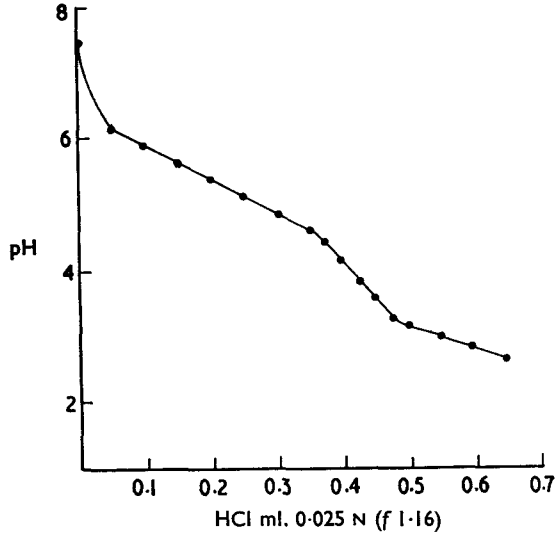

FIG. 4. Titration of sodium benzoate (4·87 mM) with hydrochloric acid (f 1·16) (25 ml. of solution containing $0{\cdot}1218 \times 10^{-3}$ mole sodium benzoate); 20 per cent w/v cetomacrogol present.

There are a number of possible mechanisms by which such solubilisation may occur. Ahsan (1960) and Barr (1957), have postulated complex formation between non-ionic surfactants and a variety of substances, and this may be involved in the case of the more water-soluble acids.

Alternatively, the acids may be adsorbed on to the surface of the micelle or dissolved in the palisade or central regions of the micelle. Solubilisation has been explained by a number of workers in terms of partition between two phases (McBain and Hutchinson, 1955, and Riegelman, 1958).

Pharmaceutical and Analytical Applications

Clearly the use of the usual phthalate standardising buffer solutions in the presence of cetomacrogol leads to error (e.g., if 5 per cent w/v cetomacrogol is present, the electrode standardisation will be 0·18 of a pH unit high). Small errors will also be introduced if citrate or borax buffers are used in the presence of cetomacrogol.

The formulation of buffered preparations containing surfactants may be more complicated than would at first appear, because of the possibility of preferential solubilisation of one of the constituents of the buffer system by the surfactant. The results obtained are consistent with observations by other workers on the reduction of activity of drugs and bactericides in systems containing surfactants (Allawala, 1953; Bean, 1950, 1951; Woodward, 1962).

The titration curves of sodium benzoate in the presence of cetomacrogol lie well above the curves for aqueous sodium benzoate up to the end-point, after which they coincide. This results in a sharper inflection being obtained at the end-point. The equivalence point may be determined potentiometrically in cetomacrogol solutions in very low concentrations of sodium benzoate (e.g. 1 mM), and good agreement is obtained with the present lengthy and somewhat cumbersome official method (B.P. 1958). Similar pH changes have been obtained in the titration of solutions of sodium salicylate and a number of other substances. Further details of analytical applications and the mechanism of solubilisation will be reported later.

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