

PHASE EQUILIBRIA IN SYSTEMS CONTAINING COMMERCIAL NON-IONIC SURFACE-ACTIVE AGENTS AND BENZENE

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IN recent years attempts have been made to describe solubilised systems by phase rule diagrams to establish the phenomena on a general basis. This approach should help to rationalise the often complicated solution behaviour of surface-active agents, and provides a firmer foundation for comparison between systems, since only solubility limits showing the same type of phase transitions should be compared when attempting to explain solubilities on a molecular or micellar basis.

Lawrence (1958) has published papers elucidating many features common to the various solubilised systems, giving the results in the form of ternary phase diagrams. Other workers have made isolated reports of similar phase diagrams. Most of this work was with anionic materials, usually at one temperature. A few cationic materials were also used. For many pharmaceutical purposes non-ionic surface-active agents are more useful, and have therefore been chosen for a comprehensive study of their solubilising properties. A preliminary account of part of this work has been given recently (Mulley, 1961), for some solutes and pure synthetic non-ionic agents of the alkyl polyether type (Mulley, 1958, 1960). The present paper gives uncompleted results obtained with three commercial surface-active agents, using benzene as the material to be solubilised.

The binary and ternary phase diagrams (Fig. 1) were obtained by visual examination of selected mixtures of the non-ionic surface-active agents with water and benzene, and by observing the effect of temperature on the phases present. Three commercial surface-active agents were used (Honeywill and Stein Ltd., London, W.1). They were Brij 30, Brij 35,

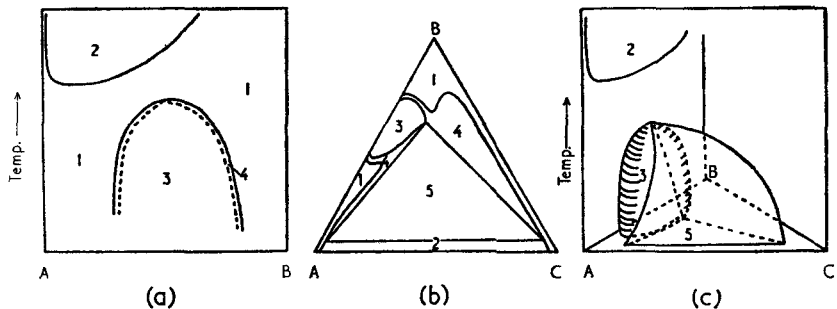


FIG. 1. Diagrammatic phase equilibrium drawings for binary and ternary systems containing non-ionic surface-active agents, benzene and water. (a) Binary diagram for the surface-active agents and water. (b) Ternary diagram at room temperature. (c) Ternary diagram showing the effect of temperature on regions 3 and 5. A, B and C = 100 per cent of water, surface-active agent and benzene respectively.

and Tween 60 and had the following (HLB) numbers respectively, 9.5, 16.9, and 14.9. The first two are polyoxyethylene lauryl ether derivatives with about 3.5 and 21 ethylene oxide units per molecule (calculated from the HLB values), and the other is a polyoxyethylene sorbitan monostearate. Temperatures between 5° and 100° were investigated in the binary systems, but only up to about 70° in the ternary systems owing to the lower boiling point when benzene is present.

In the binary mixtures the following regions and associated phases were found (excluding solid phases): region 1, a single isotropic liquid phase; region 2, two isotropic liquid phases; region 3, one anisotropic liquid crystalline phase; region 4, one isotropic liquid and one liquid crystalline phase. In the ternary systems containing benzene a fifth region is found where three phases are in equilibrium, two being isotropic liquids and the other liquid crystal. Diagrammatic representation of the relative positions of these regions is shown in Fig. 1. The phase boundaries are not accurately known in some regions. The liquid crystal phase existed up to the following temperatures in the binary systems, Brij 30, 72°; Brij 35, 56°; Tween 60, 77°. In the ternary systems it disappeared at lower temperatures in the Brij 30 and 35 mixtures, but continued above the boiling point in the Tween 60 system.

The pattern of phase behaviour found is remarkably similar to that described by Lawrence (1958) and agrees also with the few other diagrams in the literature. Although the concentrations and temperatures at which particular phases exist in different systems vary, the general arrangement of the regions for anionic, cationic and non-ionic surface-active agents and a number of different additives follows a common pattern, a fuller account of which has been given recently (Mulley, 1961).

The use of such phase diagrams in the formulation of solubilised products has already been pointed out by O'Malley, Pennati and Martin (1958). In addition, phase equilibria at very low concentrations of surface-active agents are important in the study of the mechanism of detergency (Lawrence, 1959; Mulley and Metcalf, *J. Colloid Sci.*, to be published). Moreover, changes in the nature of the phases present in emulsified systems, due to variation in temperature, are probably responsible, at least in part, for changes in their rheological properties and possibly for emulsion breakdown. The effect is marked with emulgents of the non-ionic type.

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