

# ULTRACENTRIFUGAL STABILITY OF NONAQUEOUS EMULSIONS

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It has been shown earlier<sup>1-3</sup> that in addition to normal O/W and W/O emulsions, it is possible to prepare a new third type of oil-in-oil emulsion (nonaqueous system) with two nonaqueous immiscible liquids as internal and external phases and surfactant as emulsifier.

Breaking of emulsions is generally considered to take place in two steps<sup>4</sup>: flocculation in which droplets of the dispersed phase form aggregates (this step is reversible) and coalescence which results in the ultimate separation of dispersed droplets as a bulk phase. Ultracentrifugation<sup>5</sup> is found to offer a means for accomplishing the flocculation step very rapidly and thus producing a highly concentrated emulsion before appreciable coalescence can occur. The coalescence process then could be studied independently. In this paper emulsion stability is used exclusively to refer to the rate of coalescence.

In the present communication the stability of nonaqueous emulsions prepared with benzene and ethylene glycol as two nonaqueous phases and sodium dioctylsulphosuccinate as emulsifier has been determined quantitatively employing an ultracentrifuge at 25,980 r.p.m.

A series of nonaqueous emulsions of benzene (BDH) in ethylene glycol (BDH) was prepared with various concentrations of emulsifier. A 1:1 phase ratio by volume was used and the concentration of sodium dioctylsulphosuccinate (BDH) was varied from 1 to 5% (w/v % of ethylene glycol). The heterogeneous mixtures of benzene and ethylene glycol containing anionic surfactant were emulsified with the help of Braun emulsator for final making of the O/O emulsions.

A Beckman Spinco Model E analytical ultracentrifuge was used in this work with a 12 mm light path and a 4 degree sector angle standard cell having a capacity of about 0.8 ml. Immediately after preparation of an oil-in-oil emulsion, 0.7 ml of the emulsion was injected into the ultracentrifuge cell through a hypodermic needle. The cell was then placed in an analytical rotor and subsequently centrifuged in the ultracentrifuge at 25,980 r.p.m. The time required for acceleration to this constant speed was 2 min and 45 sec  $\pm$  15 sec. Zero time in the experiments were taken as the time at which constant speed was reached. All runs were made at 30°  $\pm$  0.1° C.

During centrifugation three layers develop in the cell: transparent layer of benzene, the remain-

ing opaque, concentrated stable emulsion and the transparent layer of ethylene glycol. Photographic records were made of the cell at regular time intervals during the experiment. The layers give sharp boundaries on a photographic plate which change position with time as more benzene is separated from the emulsion. Determination of the positions of the boundaries on a series of such plates taken at successive time intervals permits calculation of the rate of separation of benzene from the emulsion. Measurements were made with a travelling microscope determining the distance from the top of the cell to the benzene-emulsion and emulsion-ethylene glycol interfaces, and to the bottom of the cell.

The volume,  $V$ , corresponding to a length,  $l$ , in the 4° sector angle standard cell is given by

$$V = \frac{4}{360} \pi l [(d + l)^2 - d^2] \\ = \frac{\pi l}{90} (2d + l)$$

where  $d$  is the distance from the centre of rotation to the top of the cell and  $l$  is the thickness of the cell. A graph was plotted of the volume as a function of the measured value of  $l$  from the top of the cell using an optical enlargement of 2.03. The plot was then used to determine the volume from the differences between the measured distances to the different interfaces.

The per cent of the initially emulsified benzene which has separated at any given time is determined by dividing the volume of the benzene layer by the sum of the volumes of the benzene layer and the creamed emulsion. Figure 1 is the characteristic of the curves

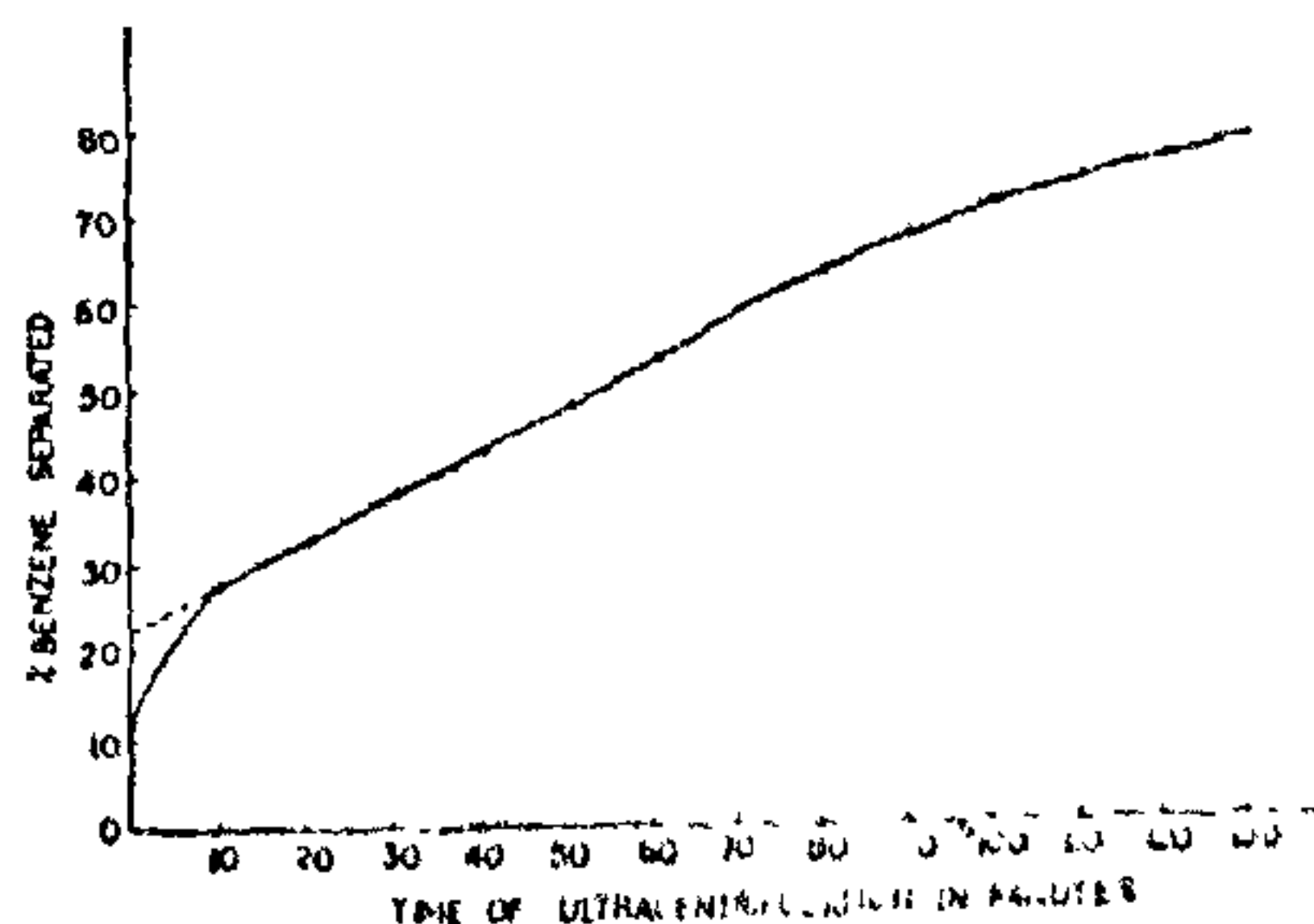


FIG. 1. Rate of separation of benzene from a 50% v benzene - 50% v ethylene glycol - 1.0% w sodium dioctyl-sulphosuccinate nonaqueous emulsion.

of per cent benzene separated vs. time of ultracentrifugation. In this case the nonaqueous emulsion of 50% v benzene in 50% v ethylene glycol is stabilized with 1% w sodium dioctylsulphosuccinate. The rate of separation at the known speed is determined from the slope of the linear portion of the curve. The slope of the line, i.e., the rate of separation of benzene in per cent per min, is termed the ultracentrifugal stability and its extrapolated intercept on the axis at zero time is the per cent benzene separated at zero time.

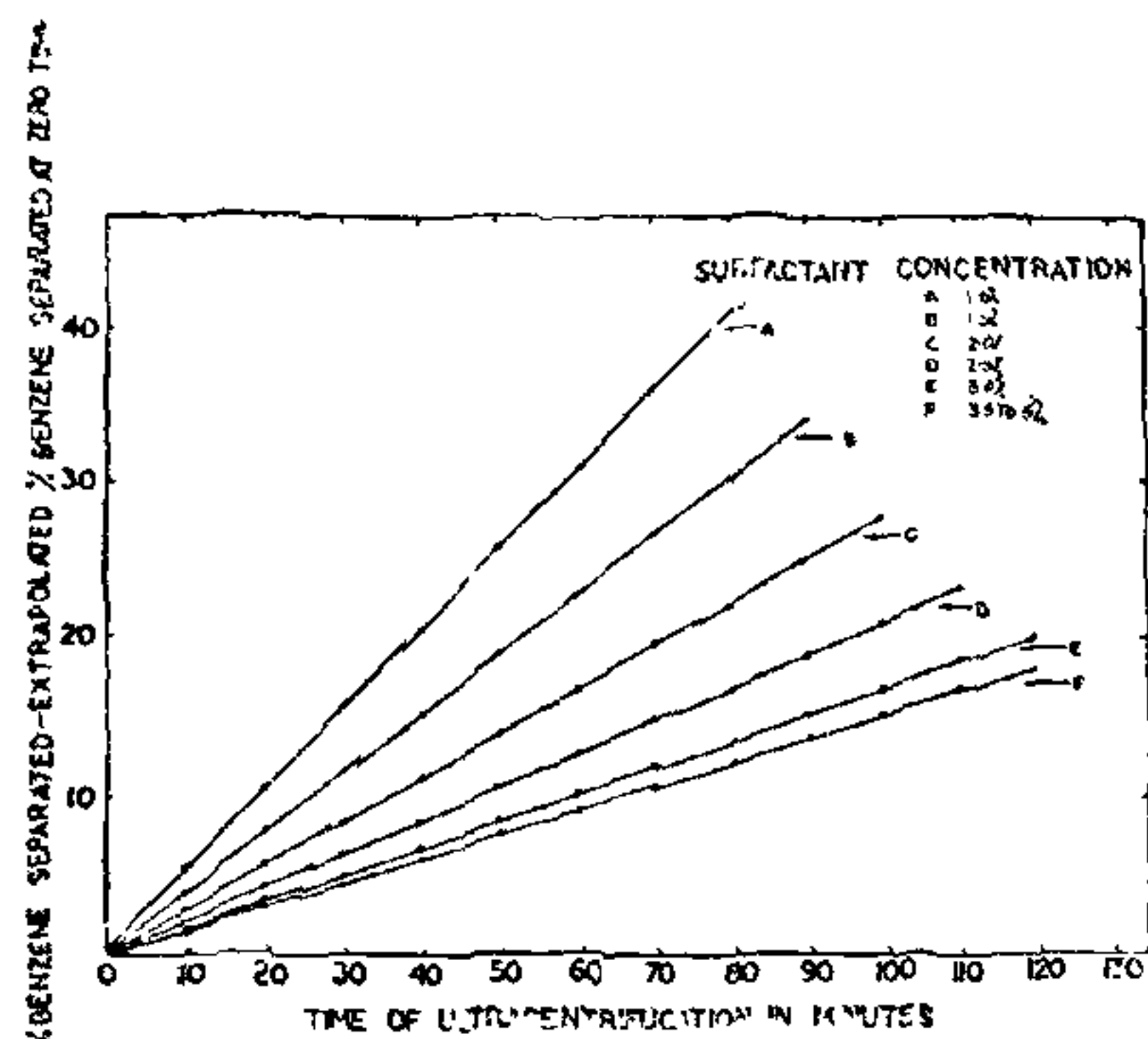


FIG. 2. Effect of initial surfactant concentration on the rate of separation of benzene from nonaqueous emulsions centrifuged at 25,980 r.p.m.

Figure 2 shows the effect of concentration of emulsifier on the rate of separation of benzene from the emulsions in the ultracentrifuge. Increasing the concentration of surfactant at first decreases the rate of separation of benzene from the emulsion and also the amount of benzene which is separated rapidly on initial centrifugation before the steady state rate is reached. At higher concentrations the rate becomes independent of the initial concentration of emulsifier, as is strikingly shown in Fig. 2, all emulsions prepared with surfactant concentration between 3.5 and 5% separating benzene at the same rate.

The results of the ultracentrifugal experiments indicate that the rate of coalescence of non aqueous

emulsion droplets decreases with an increase in initial surfactant concentration until an optimum surfactant concentration is reached and thereafter is independent of concentration.

During ultracentrifugal studies, the benzene droplets in oil-in-oil emulsions have been forced by centrifugation into very closely packed arrays which can be described as aggregated emulsions. The resistance of the aggregated droplets to coalescence arises from the existence of emulsifier adsorbed on the particle surfaces. No change observed in stability of nonaqueous emulsions to centrifugation when the emulsifier concentration exceeds an optimum value, is believed to be associated with the density of packing of adsorbed emulsifier on the particle surface. As the emulsifier concentration is raised, the amount of emulsifier adsorbed on the emulsion particle increases and the area of the particle surface per adsorbed emulsifier molecule decreases. Thus the amount of adsorption at the interface increases, with resultant decrease in the rate of separation of benzene from the emulsion. At the optimum concentration of the emulsifier, the density of packing is at its highest value with the area per adsorbed emulsifier molecule approaching the actual molecular cross section. At this point, the mechanical stability of the adsorbed emulsifier layer can reasonably be expected to be greatest. The addition of emulsifier in excess of the optimum concentration should only increase the number of molecules in the ethylene glycol phase without appreciable effect on the density of packing of the adsorbed emulsifier and consequently beyond this point the ultracentrifugal stability should no longer be dependent on the concentration of surfactant.

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