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Microemulsion Polydispersion Due to Polymer Solubilization

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ABSTRAK

Hasil kajian mikroskop elektron sejuk-pecah menunjukkan bahawa mikroemulsi air-dalam-minyak mengalami politaburan teraruh dengan penambahan polimer larut-air.

ABSTRACT

Freeze-fracture electron microscopy results on water-in-oil microemulsion showed that significant polydispersion can be induced by adding water-soluble polymers.

Keywords: electron microscopy, microemulsion, polyethylene-oxide

INTRODUCTION

Freeze-fracture electron microscopy in aerosol-OT/water/alkane systems shows the fairly monodisperse globular structure of the L_2 phase (Jahn and Strey 1988). In this note we report two examples of polydispersion induced by solubilization of polyethylene oxide in an R = $[H_2O]/[\text{aerosol-OT}]$ = 65 microemulsion (L_2 phase).

MATERIALS AND METHODS

Aerosol-OT (from Sigma Co., USA) was first weighed in 10-ml flasks and dissolved in heptane. Aqueous polyethylene oxide (from Polymer Labs., Middlesex, England) solution was then added such that the total concentration of AOT was 0.1M and R = 65 was obtained. Two molecular weights were used, namely 12,300 and 105,000. The polymer to water weight ratio for both was 1/50. This was to ensure that the phase boundaries obtained at room temperature were relatively distant as well as to keep the number of polymer molecules small compared to the number of water droplets (known from previous studies using small-angle neutron scattering). Several drops of the samples were then transferred on to a dimpled stub, inverted and slammed on to a cold (liquid nitrogen temperature) copper block at a freezing rate of about 8000 K/s. The samples were then transferred to a Balzers 300 unit (kept at liquid nitrogen temperature and at 10^{-6} Torr) for fracturing and coating. No etching was made. The samples were then swirled in a warm acetone solution and the platinum-carbon replica fished out using a 200-mesh copper grid. Observations were made on the dried replica using a Philips EM300 transmission electron microscope.

RESULTS AND DISCUSSION

Plates 1 and *2* show the relatively polydisperse droplet structure of the polymer-containing microemulsions. Two populations of the microemulsion droplets were discernible: an unperturbed monodisperse droplet structure and larger polymer-containing droplets. For the polymer-containing droplets a simple model of polymer solubilization is hereby proposed:

Plate 1. Freeze-fracture electron micrograph of an aerosol-OT water-in-heptane microemulsion containing polyethylene oxide (mol. wt. = 105,000) at 55,000 magnification. Note the relatively small number of large droplets compared to a larger number of smaller droplets in the background

Let r be the radius of the polymer-solubilizing droplets and r_w that of the initially polymer-free droplets. Then,

$$4/3\ \pi r^3 = n\ 4/3 \pi {r_w}^3 + v_p \qquad (1)$$

where n is the required number of empty droplets to solubilize the polymer with microscopic volume v_p. Since the total area covered by the surfactant is roughly conserved, it follows that

$$r^2 = n{r_w}^2 \qquad (2)$$

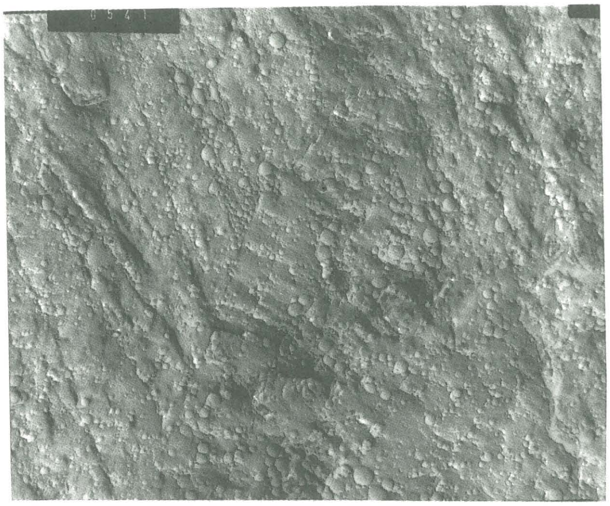

Plate 2. Freeze-fracture electron micrograph as in Plate 1 but for microemulsion containing polyethylene oxide of molecular weight = 12,300 at 27,000 magnification. The result is similar to Plate 1.

Mass and volume conservation also give

$$nN = N_w \quad \text{and} \quad V_p = Nv_p \tag{3}$$

where N and N_w are the total number of filled and empty droplets and V_p is the total polymer volume in the sample. Also,

$$V_w = N_w.4/3\pi r_w^3 \tag{4}$$

When (2-4) are substituted into (1) we obtain

$$4/3\pi r^3 = 4/3\pi r_w r^2 + 4/3\pi r_w r^2 V_p/V_w$$

which simplifies to

$$r = r_w(1 + V_p/V_w) \tag{5}$$

If the polymer randomly filled all the droplets this would suggest that the radius of the filled droplets would be larger by a small factor of roughly 1 + 1/50, which is not borne out by the micrographs seen in *Plates 1* and *2*. The fact that a bimodal distribution occurs suggests that $V_p/V_w \gg 1/50$ where V_w now refers not to the total volume of water but only to that corresponding to the filled droplets. This microscopic segregation of polyethylene oxide is probably due to the association of polyethylene oxide with Aerosol-OT similar to those observed in an independent study of this polymer in a sodium dodecyl sulphate solution (Cabane and Duplessix

1982). One would also suspect that the droplets would be Poisson distributed if the polymers were randomly distributed (which is not the case here) among the droplets (Rizzo 1986). Finally, it is expected that this process of droplet aggregation (e.g. by adding more polymers) will eventually lead to emulsification failure due to an average entropic loss.

CONCLUSION

We have shown evidence for a microscopic segregation of polyethylene oxide in water-in-oil microemulsion which leads to its polydispersion.

REFERENCES

CABANE, B. and J. DUPLESSIX. 1982. Small-angle neutron scattering studies of SDS-PEO complex. *J. Physique France* **43**: 1529-1541.

JAHN, W. and R. STREY. 1988. Microstructure of microemulsions by freeze-fracture electron microscopy *J. Phys. Chem.* **92**: 2292-2301.

RIZZO, V. 1986. Hydrophilic molecules solubilized in water-in-oil microemulsions. *J. Colloid and Int. Sci.* **110(1)**: 110-113.