

# Reflectance measurements on gels and emulsions containing cetrимide and cetostearyl alcohol—a preliminary investigation

R. C. ROWE\* AND H. K. PATEL

*ICI Pharmaceuticals Division, Alderley Park, Macclesfield, Cheshire SK10 2TG, UK.*

Various light scattering properties—the reflectivity, contrast ratio and scattering index of a series of gels and emulsions containing cetrимide, cetostearyl alcohol, water and liquid paraffin have been examined using reflectance measurements made at 560 nm using a four-filter, tristimulus colorimeter. The scattering properties of both systems were dependent on the total interfacial surface area of either the dispersed unreacted cetostearyl alcohol and/or the dispersed droplets of liquid paraffin, and hence increased with increasing concentration of both ingredients. For the emulsion containing liquid paraffin, the scattering properties increased linearly with the concentration of liquid paraffin but with the ternary gel system the scattering properties were not directly related to cetostearyl alcohol concentration. This was confirmed by microscopy as due to the changes in the size of the dispersed unreacted cetostearyl alcohol. The results illustrate the potential of this simple, reproducible non-destructive technique in the study of the structure of such systems.

The mixed emulsifier system of cetrимide and cetostearyl alcohol is frequently used in the formulation of antiseptic creams and much work has been done in an attempt to define the structure of these creams (Barry & Saunders 1970; Eccleston 1975). The creams have been invariably described, somewhat subjectively, as shiny, white semi-solids but any further work to quantify this appearance has tended to be ignored despite the fact that, in as early as 1936, optical techniques in the form of reflectance measurements had already been shown to be of use in assessing the opacity of simple oil-in-water emulsions (Morse 1936). More recent work by Langlois et al (1954) using transmission measurements and Lloyd (1959) using reflectance measurements have also demonstrated the applicability of optical techniques in the study of both coloured and white emulsions. In this paper we report the use of reflectance measurements to determine the scattering properties of gels and emulsions containing cetrимide and cetostearyl alcohol with specific emphasis on defining the relations between the results and the proposed structure of these systems.

## *Theory*

The optical properties of a dispersed system, be it an emulsion or suspension, are dependent upon light reflection and refraction at the various interfaces, light absorption by the various phases, and light scattering by the dispersed phase. While the laws of

reflection and refraction at plane boundaries are well established, the laws of scattering are complex, especially where the intensity of the incident light is much diminished by passage through the system as occurs with an opaque emulsion and other intensely light scattering systems. In the analysis of such a system, it is always assumed that only one side of the sample is illuminated and that, for reflectance measurements, the other side is in intimate contact with a defined backing reflecting the transmitted light in a defined manner. In the assessment of the system as a whole, three measurements can be easily made: firstly, the measurement of the reflectance of the sample with a highly reflecting white backing (designated  $R_w$ ); secondly, the measurement of the reflectance of the sample with a highly absorbing black backing (designated  $R_B$ ), and thirdly the measurement of the reflectance of a sample so thick that any further increase in thickness has no significant effect (designated  $R_\infty$  commonly known as the reflectivity or reflectance at infinite thickness). From these measurements, a simple approach to the assessment of the opacity of the sample can be made in terms of the contrast ratio (usually expressed as a percentage) equivalent to the ratio of  $R_B$  to  $R_w$  at some defined thickness.

However, if data of a more fundamental nature are required, then it is necessary to apply the Kubelka-Munk theory (Kubelka & Munk 1931). In this theory two more constants are needed to define the optical properties of the system, viz  $S$ , the scattering coefficient, a measure of the total light

\* Correspondence.



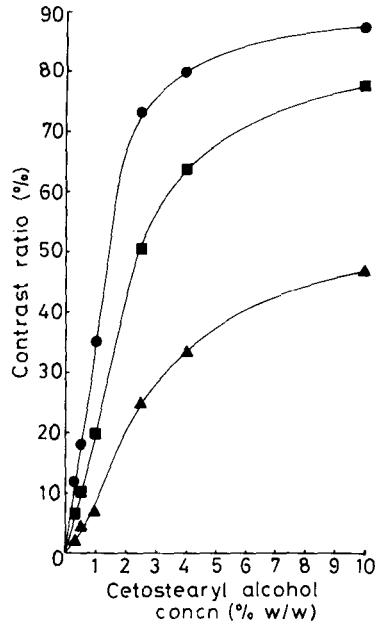


FIG. 1. The effect of cetostearyl alcohol concentration on the contrast ratio at three thicknesses for the ternary gel formulation. ● 5.33 mm ■ 3.53 mm ▲ 1.78 mm.

and thus provides a statistical estimate of its precision. These results can be put in perspective by comparison with data for scattering coefficients obtained for tablet film coatings containing titanium dioxide; 50–200 mm<sup>-1</sup> (Rowe 1984).

The opacity or intensity of light scattering in any dispersed system, be it an emulsion or a suspension, is dependent upon the following:

(a) The complex index of refraction of the dispersed phase relative to that of the continuous phase,  $m$ , defined by the equation of Mie (1908):

$$n = (n_d/n_c) (1 - ik) \tag{5}$$

where  $n_d$  and  $n_c$  are the refractive indices of the dispersed phase and the continuous phase respectively,  $k$  is the absorption coefficient of the dispersed phase and  $i$  is the square root of  $-1$ . For the white opaque system used in this study  $k$  will be negligible and hence the opacity will be dependent solely upon the value of the ratio  $n_d/n_c$ . In fact, in the case of paint films, it has been shown that there is a rectilinear relationship between relative opacity and the function

$$\left[ \frac{(n_d/n_c)^2 - 1}{(n_d/n_c)^2 + 2} \right]^2 \quad \text{Mitton (1973)}$$

(b) the interfacial surface area, which is factor dependent not only upon the dispersed phase vol-

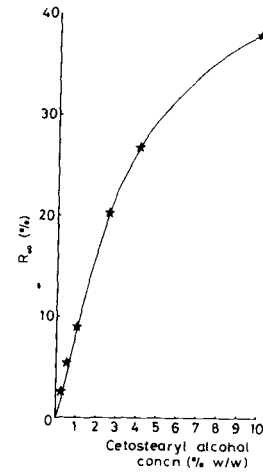


FIG. 2. The effect of cetostearyl alcohol concentration on the  $R_{\infty}$  value for the ternary gel formulations.

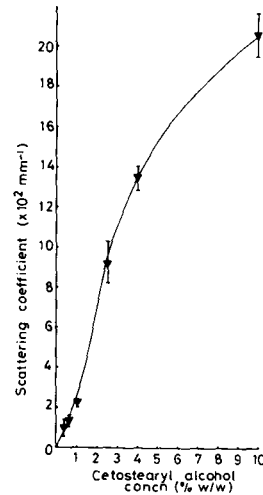


FIG. 3. The effect of cetostearyl alcohol concentration on the scattering coefficient for the ternary gel formulation.

ume but also on the size and distribution of the dispersed phase. It has been shown, for instance, that for a coloured oil-in-water emulsion  $R_{\infty}$  is directly related to the interfacial surface area raised to a power (Lloyd 1959). However, Langlois et al (1954) have shown a direct relation between the interfacial surface area and the relative light transmission (defined as the ratio of the light intensity transmitted by the clear liquid to that transmitted by the emulsion of which it is in the external phase, i.e. a measure of the opacity) for white emulsions, the proportionality constant being a function of the ratio  $n_d/n_c$ .

Despite the fact that in the system studied here the

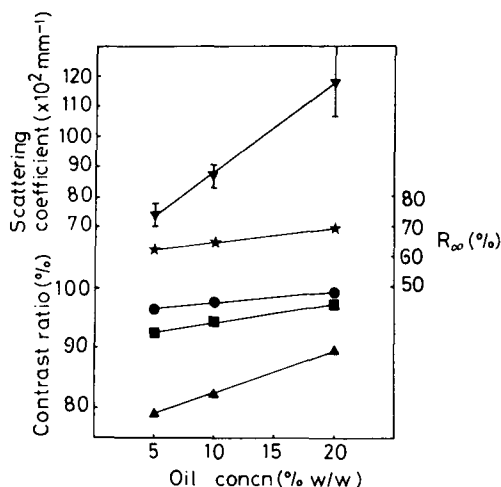


Fig. 4. The effect of the concentration of liquid paraffin on the contrast ratios at three thicknesses (● 5.33 mm ■ 3.53 mm ▲ 1.78 mm), the  $R_\infty$  value ★, and the scattering coefficient ▼ for the emulsion formulation.

continuous phase is not simply water, as used by previous workers, but consists of water entrapped in a continuous lyotropic liquid crystalline network produced by the interaction of cetostearyl alcohol and the cetrimide (Eccleston 1975), and that the dispersed phase is either liquid paraffin and/or unreacted particles of cetostearyl alcohol, the light scattering data do conform to the concepts discussed above. Firstly, the opacities of the emulsions are generally higher than those of the ternary gels, as indeed they should be, since the refractive index of the liquid paraffin is 1.48 compared with 1.43 for the refractive index of cetostearyl alcohol, and secondly, there is a direct relation between the opacity and the oil concentration in the emulsion studied (microscopical examination confirmed that there was no significant difference in the size distribution of the oil droplets with increasing oil concentration).

The opacity change on the addition of increasing amounts of cetostearyl alcohol in the ternary gel is due primarily to the amount and size of the excess cetostearyl alcohol particles present. At concentrations below 1% cetostearyl alcohol there is little light scattering since there is no unreacted alcohol—a result confirmed microscopically. Above this concentration there is a rapid increase in scattering due to increasing amounts of unreacted cetostearyl

alcohol, but the increase is not linear as would be expected. Microscopical examination of these systems revealed that at concentrations above 4% cetostearyl alcohol there was a gradual increase in the overall size of the unreacted particles. This would lead to a lower than expected interfacial surface area and hence a lower opacity.

These results have a particular relevance when considering the applicability of reflectance measurements as a quality control technique. In all the systems studied, great care was taken to avoid air entrapment on cooling. However, on one occasion in the manufacture of a ternary gel containing 10% cetostearyl alcohol, air entrapment did take place. Subsequent reflectance measurements showed that the aerated system had an  $R_\infty$  of 54.54% (cf. 38.11% non-aerated) and a scattering index of  $0.5356 \pm 0.0332$  (cf.  $0.2070 \pm 0.0120$  non-aerated). Aeration had increased the apparent dispersed phase volume and hence the total interfacial surface area.

The results certainly show that differences in the scattering properties of these systems can be highlighted by this method and illustrate its potential in the study of their structure and in the optimization of the formulation and processing conditions during product development. The technique is simple, reproducible, rapid and, above all, non-destructive.

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