

decrease in cmc with the non ionic SAA's as ethylene oxide chain length increases, this is unexpected and is contrary to the results found by El Eini, Barry & Rhodes (1973) but agrees with results reported by Carless, Challis & Mulley (1964). The differences between the results found here and those reported in former work are presently being investigated. Possible explanations include the presence of impurities (Elworthy, Gyane & Macfarlane, 1969), surface ageing and the decreasing solubility of the ethylene oxide portion with increasing molecular weight (Schick, Atlas & Eirich, 1962). The adsorption of surfactant onto the glassware, which only occurs in small quantities, does not affect the cmc values.

Intrinsic viscosity values for the non-ionics compare favourably with the results reported by El Eini & others (1973).

Hydrophobic interactions are being investigated by the addition of small quantities of organic additives (alkyl ureas and alcohols) to the SAA solutions. The addition of aliphatic alcohols to C12TAB solutions causes a decrease in cmc, the effect increasing as alcohol chain length increases; the corresponding $[\eta]$ values follow a similar pattern, these results can be attributed to the effect of alcohols on water structure.

However for a given concentration of alcohol $[\eta]$ increases with increasing alcohol chain length. This can be explained by the different alcohols altering the shape of the micelle such that the axial ratio a/b , and consequently $[\eta]$, are affected.

REFERENCES

- CARLESS, J. E., CHALLIS, R. A. & MULLEY, B. A. (1964). *J. Colloid Sci.*, **19**, 201-212.
EL EINI, D. I. D., BARRY, B. W. & RHODES, C. T. (1973). *J. Pharm. Pharmac.*, **25**, 166P.
ELWORTHY, P. H., GYANE, D. O. and MACFARLANE, C. B. (1969). *Ibid.*, **21**, 617-618.
NEMETHY, G. (1967). *Angewandte Chemie International Edition* **6**, 195-206.
SCHICK, M. J., ATLAS, S. M., EIRICH, F. R. (1962). *J. Phys. Chem.*, **66**, 1326-1333.
WEIBULL, B. (1960). Third International Congress on Surface Active Compounds, 121-124.

Correlation of phase inversion temperature with stability of oil-in-water emulsions stabilized by (polyoxyethylene)₄ cetyl ether

R. P. ENEVER

Department of Pharmaceutics, The School of Pharmacy, University of London, Brunswick Square, London WC1N 1AX, U.K.

Oil-in-water emulsions containing 30% w/w liquid paraffin, 3% w/w (polyoxyethylene)₄ cetyl ether (Texofor A4), and from 0.1% w/w to 10.0% w/w sodium chloride have been examined.

Phase inversion temperatures (P.I.T.) of the emulsions were determined by the programmed temperature rise viscometric technique described previously (Sunderland & Enever, 1972), and also by monitoring their conductivity-temperature relations whilst heating them under the same programmed temperature conditions.

Emulsion stability was assessed by measurement of globule coalescence rates. The number of globules per ml of emulsion was determined at various times by a photomicrographic method, and linear relations were obtained when the logarithm of globule count was plotted against time. Stability was also determined by long term storage of the emulsions.

The P.I.T. values of the emulsions ranged from 53.5° (0.1% w/w sodium chloride) to 30.5° (10.0% w/w sodium chloride), and the relation between P.I.T. and sodium chloride concentration was curvilinear. The P.I.T. values determined by the conductivity method agreed well with those obtained by the viscometric technique.

The apparent viscosity-temperature relations of the emulsions containing from 0.1 to 6.0% w/w sodium chloride also showed an additional discontinuity at approximately 35°. Microscopic examination and ultra-centrifugation studies showed that this was due to the

disappearance of a liquid crystalline phase from the aqueous medium. The globule coalescence data obtained at various temperatures showed that there was a rapid decrease in emulsion stability upon disappearance of this liquid crystalline phase. For example, for the emulsion containing 2.0% w/w sodium chloride, the values for globule coalescence rate were $3.03 \times 10^{-3} \text{ h}^{-1}$ at 30°, $6.86 \times 10^{-3} \text{ h}^{-1}$ at 35° and $45.5 \times 10^{-3} \text{ h}^{-1}$ at 37°.

In the present work a correlation has been found between the P.I.T. values of the emulsion series and their globule coalescence rates at constant temperature. There was also a correlation between creaming rates and their P.I.T. values. For example, after 100 days storage at $20^\circ \pm 1^\circ$, the proportion of clear aqueous phase in the emulsion containing 0.1% w/w sodium chloride was 0.5% whereas for the emulsion containing 10.0% w/w sodium chloride the proportion was 25%. After 200 days storage, cracking was only evident in the emulsions containing from 8 to 10% w/w sodium chloride, and the proportion of oil separated was from 4 to 6%.

Parkinson & Sherman (1972) have examined the use of P.I.T. as an accelerated method for evaluating emulsion stability and, according to Shinoda & Saito (1969), non-ionic stabilized emulsions should be satisfactorily stable provided their P.I.T. values are from 25° to 70° above storage temperature. Since the P.I.T. values obtained in the present work were very low in comparison with those examined by these workers, one might have expected the emulsions to be highly unstable. However, the presence of the liquid crystalline phase below 35° greatly enhanced stability.

REFERENCES

- PARKINSON, C. & SHERMAN, P. (1972). *J. Colloid Inter. Sci.*, **41**, 328-330.
 SHINODA, K. & SAITO, H. (1969). *Ibid.*, **30**, 258-263.
 SUNDERLAND, V. B. & ENEVER, R. P. (1972). *J. Pharm. Pharmac.*, **24**, 804-814.

Viscoelastic and continuous shear properties of Carbopol gels

B. W. BARRY AND M. C. MEYER

School of Pharmacy, Portsmouth Polytechnic, U.K.

Aqueous Carbopol gels are widely used, yet little is known of their fundamental rheological properties which depend on carboxyvinyl polymer networks. This work investigates the continuous shear (Ferranti-Shirley cone/plate viscometer) and viscoelastic (concentric cylinder creep viscometer, parallel plate Weissenberg Rheogoniometer) properties of such gels as functions of concentration and temperature. Some comparisons with unneutralized systems are made.

Neutralized (triethanolamine) Carbopol 940 and 941. For 1-10% w/w gels pseudoplastic or plastic flow curves, with negligible hysteresis, were obtained. Spur points occurred above 5% w/w. Apparent viscosities (derived from apex of rheograms) varied exponentially with concentration and $1/T^\circ$, the latter providing apparent activation energies for flow in the region of 2 kcal mol⁻¹. This rather low value indicates the stability of the gels with respect to temperature. In creep both systems behaved as highly elastic semisolids (model analysis of Voigt units in series with a Maxwell unit—Table 1 shows representative systems). With total compliances (after 50 min) and residual viscosities varying from 2.4 to 0.76×10^{-4} dyne⁻¹ cm² and 2.3 to 5.1×10^8 poise (Carbopol 940) and 40 to 4.0×10^{-4} dyne⁻¹ cm² and 0.70 – 44×10^7 poise (Carbopol 941) respectively. Plots of log compliance vs concentration and $1/T^\circ$ approached linearity for Carbopol 940 but deviated for Carbopol 941. Oscillatory data further illustrated the dominant elastic nature of the gels with phase lags around 2° for Carbopol 940 and 20° for Carbopol 941.