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 × 10^{-3} h^{-1} at 30°, 6·86 × 10^{-3} h^{-1} at 35° and 45·5 × 10^{-3} 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° ± 1°, 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.

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Viscoelastic and continuous shear properties of Carbopol gels

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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°, 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} cm^2 and 2·3 to 5·1 × 10^8 poise (Carbopol 940) and 40 to 4·0 × 10^{-4} dyne^{-1} cm^2 and 0·70–44 × 10^7 poise (Carbopol 941) respectively. Plots of log compliance *vs* concentration and 1/T° 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.

Table 1.   Model analysis for 3% w/w Carbopol 940 and 941 Systems.

	Jo $\times 10^{-4}$	Jl $\times 10^{-5}$	η1 $\times 10^{7}$	τl $\times 10^{2}$	J2 $\times 10^{-5}$	η2 10^{6}	τ2 $\times 10$	J3 $\times 10^{-5}$	η3 $\times 10^{5}$	τ3 $\times 10$	ηo $\times 10^{8}$
940 N	1·4	1·0	10	11	1·0	17	14	1·5	12	1·8	3·0
U	2·0	1·3	2·8	3·6	1·2	1·5	1·8	—	—	—	3·8
941 N	10	41	·25	10	13	1·1	14	40	·41	1·7	·01
U	9·7	14	·40	5·4	16	·22	3·6	—	—	—	·52

N = Neutralized,   U = Unneutralized,   J = Compliance,   dyne^{-1} cm^2. η = Viscosity   poise
τ = Retardation time, s.

Unneutralized Carbopol 940 and 941. Flow curves were similar but showed a marked decrease in consistency compared with neutralised systems. Carbopol 941 gels increased in hysteresis with increase in concentration. The creep curves approached Hookean behaviour and calculated parameters were of the same order as those derived from neutralized gels. This indicates that in their rheological ground state the neutralized and unneutralized systems are similar, but when tested at high shear rates differences in structure become apparent (i.e. strong electrostatic repulsion between ionized carboxy groups and weak hydrogen bonding between undissociated carboxy groups).

Subjective differences at tertiary level (Sherman, 1971)–940 gels were creamy and viscous, 941 preparations were sticky and elastic.

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The influence of alcohol chain length on the structure and rheology of emulsions stabilized by cetomacrogol/long chain alcohols

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Previous studies showed that alcohol structure markedly affects the consistencies of o/w emulsions stabilized by ionic surfactant/long chain alcohol mixed emulsifiers (Eccleston & Barry, 1973). This present work investigates the influence of alcohol chain length and homologue composition on the rheological stability of non-ionic cetomacrogol emulsions.

Liquid paraffin emulsions prepared with cetomacrogol and alcohols tetradecanol (A), hexadecanol (B), octadecanol (C) and cetostearyl alcohol (D) were examined by microscopical, particle size analytical and rheological (continuous shear, small strain creep and oscillation) techniques at 25° as they aged over 30 days.

The particle sizes of the emulsions were similar, and did not increase with age. Thus, as in previous work, rheological stabilities were not correlated with particle size distributions, but rather with viscoelastic networks formed in the continuous phases when non-ionic mixed emulsifiers interact with water (Barry & Eccleston, 1973).

The rheological properties of emulsions A and B differed from C. Emulsion D, of mixed homologue composition, showed properties of all three emulsions prepared with the pure alcohols. A and B were semisolid immediately after preparation and of a similar consistency. This was shown in oscillation by the similar values for amplitude ratios and phase lags throughout the frequency range $25 \times 10^{-3} - 25$ Hz and in creep by similar total compliances. Continuous shear data, however, indicated that A was more resistant to breakdown at high shear rates. The apparent viscosities derived for a standardized shearing cycle were considerably greater for A. Emulsion C was so mobile after preparation that initial oscillatory and creep data were not derived. Apparent viscosities were considerably below those of A and B.