

Solubility and viscosity relations in the system ascorbic acid-water-polysorbate 80

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The solubility of ascorbic acid in dispersions of polysorbate 80 has been examined. Over a large region of the solubility range liquid crystal exists, bounded by isotropic liquid phases. Excess solubilizate separates out as crystalline material. The rheological properties are complex. Within the isotropic phases the viscosity is Newtonian, but as soon as liquid crystal is produced pseudoplastic or thixotropic flow occurs. In the centre of the liquid crystal region, there were concentrations exhibiting a "yield" value followed by relaxation before the usual thixotropic loop.

THE viscosity and stability of ascorbic acid in aqueous polysorbate 20 dispersions has recently been examined by Nixon & Chawla (1965). This system, because of its hydrophilic nature, produced no liquid crystalline phases. The viscosity of the system was Newtonian throughout and rose to a maximum in an ascorbic acid-saturated dispersion containing 68% w/w polysorbate 20.

The present system exhibited far more complex relationships between solubilization and viscosity; also, liquid crystal was present. Over large regions of the "viscosity map" non-Newtonian viscosity was observed.

Experimental

Ascorbic acid. Assay (iodometric) 99%, m.p. 190-192°, $[\alpha]_D^{20}$ 2% in water +22°, pH of 2% in water 2.5.

Polysorbate 80. (Tween, Honeywill-Atlas Ltd) complied with manufacturer's specification dated October, 1956.

Determination of viscosity. The Ferranti-Shirley cone and plate viscometer was used as previously described (Nixon & Chawla, 1965). Data obtained using this viscometer allowed the preparation of stress/strain diagrams which indicated the type of flow of the system. Viscosities were calculated from these curves.

Results and discussion

The solubility of ascorbic acid decreased slowly with increases in the polysorbate 80 concentrations and it was impossible to dissolve any ascorbic acid at polysorbate 80 concentrations above 97% w/w. Liquid crystalline gel showing birefringence under polarized light occurred over a wide region. Birefringence started at a concentration of 44% w/w polysorbate 80, no ascorbic acid being present. The smallest concentration of polysorbate 80 required to produce a system containing only liquid crystal was 37.5% w/w. This system contained 9.5% w/w ascorbic acid. With concentrations of ascorbic acid increasing above this there was a single liquid crystalline phase which required increasingly larger concentrations of polysorbate 80 for its existence. In a dispersion

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saturated with ascorbic acid, the single liquid crystalline gel phase occurred at a polysorbate concentration of 52.5% w/w. Below this single gel phase a region existed in which both liquid crystal and isotropic solution occurred.

The upper limit of the liquid crystalline phase was difficult to determine because of the very high viscosity. The system could not be separated into two phases by centrifugation and appeared to pass directly from a clear isotropic solution into a liquid crystalline gel exhibiting birefringence. This, according to Winsor, is an impossible transition and a region where liquid crystal is in equilibrium with isotropic solution should always occur (Winsor, 1954). At concentrations of ascorbic acid in excess of the solubility, crystalline ascorbic acid separates out.

Dispersions of ascorbic acid-polysorbate 80-water exhibited Newtonian or non-Newtonian flow depending upon the phases present. Within the region L_1 (Fig. 1) the viscosity was Newtonian. As soon as liquid crystal

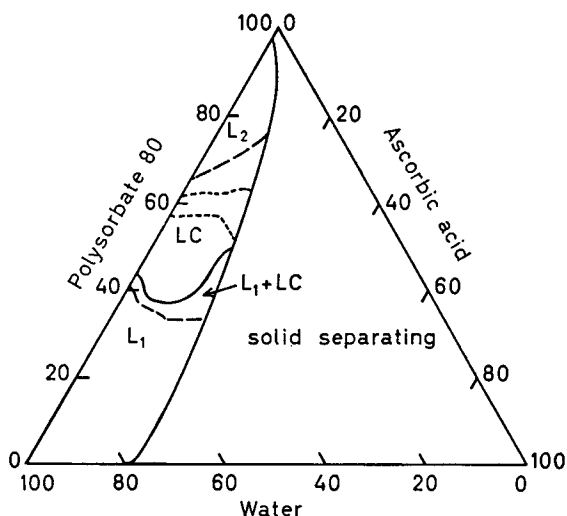


FIG. 1. The solubility of ascorbic acid in polysorbate 80 dispersions. L_1 and L_2 are isotropic liquid phases, and LC liquid crystal phases. Temperature $25^\circ \pm 0.1^\circ$; — — — upper and lower limit of existence for liquid crystal; — lower boundary of liquid crystal gel phase; - - - boundary of liquid crystal exhibiting yield/relaxation curve before thixotropic loop. All concentrations are % w/w.

existed in contact with the L_1 phase non-Newtonian flow occurred. At the boundary of the liquid crystalline region, pseudoplastic flow was exhibited. As the proportion of liquid crystal phase increased, this pseudoplastic behaviour became more pronounced and, immediately before the liquid crystal region, the dispersions began to exhibit thixotropy. When only liquid crystal existed, thixotropy was shown by all the systems examined. Finally on passing from the liquid crystal into the L_2 phase Newtonian viscosity once more occurred.

Within the liquid crystalline phase the degree of thixotropy, as measured by the area of the thixotropic loop, increased proportionately to the

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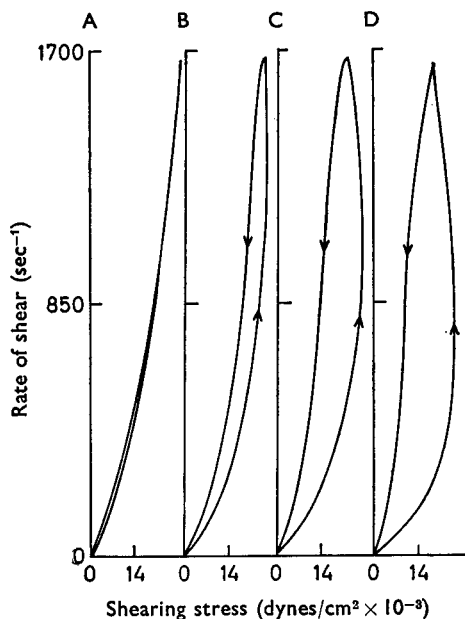


FIG. 2. The effect of ascorbic acid concentration on the degree of thixotropy. Concentration of polysorbate 80, 46% w/w; concentrations of ascorbic acid % w/w: A. 0. B. 5.2. C. 10.4. D. 14.8. Temperature $25^\circ \pm 0.1^\circ$. Cone size 2 cm. Sweep 120 sec.

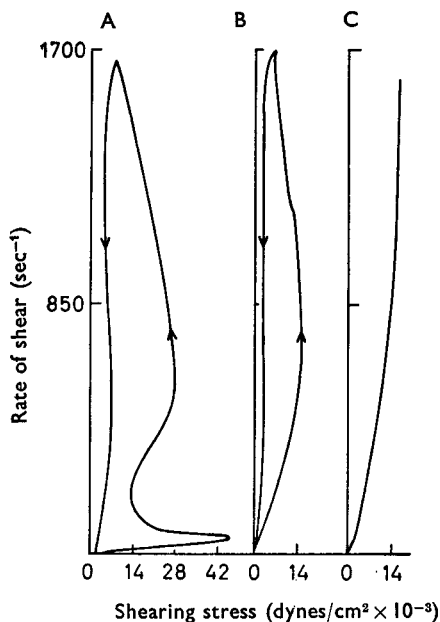


FIG. 3. Yield value before normal thixotropic loop and the effect of recycling on the liquid crystal systems. Polysorbate 80 concentration % w/w 53, ascorbic acid concentration % w/w 15. Temperature $25^\circ \pm 0.1^\circ$. A. Original system. B. Recycled once. C. Fifth recycle. Cone size 2 cm. Sweep 120 sec.

ascorbic acid present (Fig. 2). On recycling the system the thixotropic properties disappeared and pseudoplastic flow occurred. In very thixotropic dispersions, the system had to be recycled a number of times before complete pseudoplasticity was produced. This thixotropic behaviour returned on standing but the degree of thixotropy, as measured by the area of the loop, was reduced.

A centre of anomalous rheological behaviour was found within the liquid crystalline region (Fig. 1). Within this small region the thixotropic curve exhibited a preliminary "yield" value (Fig. 3). A dispersion containing 60.5% w/w polysorbate 80 and 10.8% w/w ascorbic acid showed further divergencies from the normal liquid crystal thixotropic loop. After the yield value and relaxation shown by systems within this region the hysteresis curve crossed over itself and was particularly narrow. The degree of thixotropy, as measured by the area within the thixotropic loop, decreased as the boundary between the L_2 and LC phases was approached. Once the boundary had been passed the L_2 phase exhibited Newtonian viscosity although the consistency of the dispersions was gel-like.

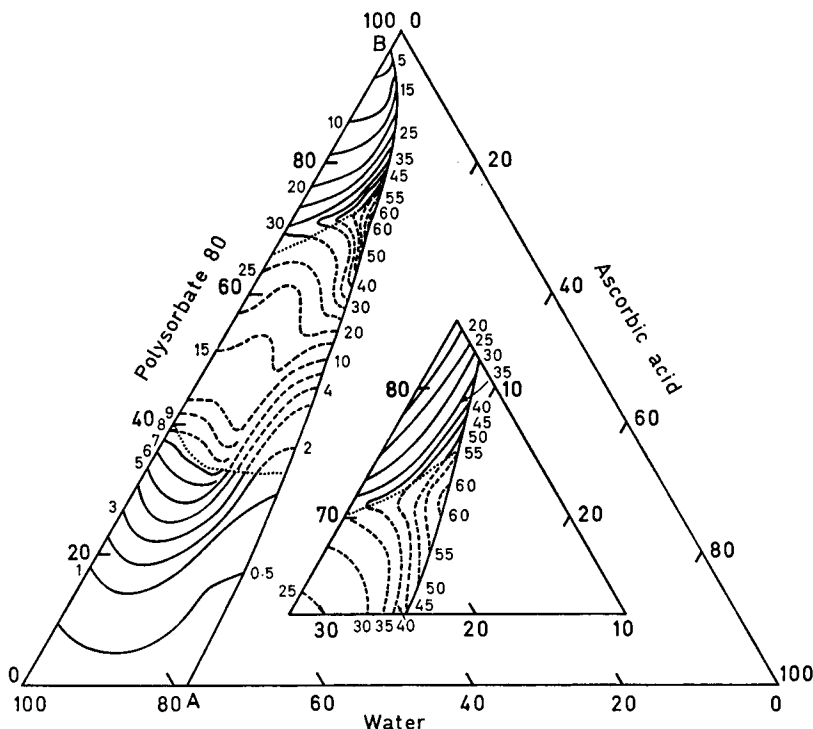


FIG. 4. Viscosity relationships in the system polysorbate 80-ascorbic acid-water. Line A-B is the solubility curve of ascorbic acid. — Newtonian viscosity in isotropic L_1 and L_2 phases. --- Derived apparent viscosity from recycling anisotropic $L_1 + LC$ and LC phases. All viscosity measurements in poises. Temperature $25^\circ \pm 0.1^\circ$. Concentrations % w/w.

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A viscosity co-ordinate map (Fig. 4) was prepared as previously (Nixon & Chawla, 1965). Within the L_1 and L_2 phases, where the viscosity was Newtonian, the contours represent regions of true viscosity, but within the LC and LC + L_1 phases, where non-Newtonian flow occurred, only "apparent" viscosities could be recorded. These "apparent" viscosities are calculated from the slope of the straight line portion of the pseudo-plastic curve or the linear portion obtained by recycling the thixotropic liquid crystalline gel. This viscosity map was far more complex than the one found for the system using polysorbate 20. The viscosity, particularly in the liquid crystalline and L_2 phases, was particularly high when compared with polysorbate 20 systems. Even in the isotropic L_1 phase, where in the previous system the addition of ascorbic acid resulted in an increase in viscosity, the contours did not show a simple pattern. Within this region the initial addition of the acid caused an increase in viscosity but subsequent additions, as the solubility limit was approached, resulted in a fall. This fall in viscosity was accompanied by a slight fall in pH. Angelescu & Popescu (1930), Angelescu & Ciortan (1939) and Angelescu & Manolescu (1941) have reported similar phenomena. They found that the addition of phenol or cresol to soap solutions produced an initial rise in viscosity which they attributed to an increase in the colloidal nature and solvation of the solute. The fall in viscosity on the further addition of solute was attributed to true molecular dispersion of the solute. Conductivity measurements indicated the presence of only small micelles in the less viscous systems. Bose (1952), studying the effect of added alcohol on sodium oleate solutions, also noted the existence of these viscosity maxima. In the present systems the viscosity contours in the L_1 phase appear to be amenable to the above explanation. The initial addition of ascorbic acid to an L_1 non-ionic surface-active agent solution probably results in most of the acid being taken up by the micelles. Once these are saturated, corresponding to the maximum viscosity, further additions of acid are dissolved in the water pseudo-phase.

Hyde, Langbridge & Lawrence (1954) have reported the change in viscosity on the addition of an octanoic acid to 36% Teepol solutions. At 25° the viscosity increased to a maximum in the liquid crystal region when a unimolecular ratio of additive to soap was present. This peak viscosity fell rapidly towards the end of the liquid crystal phase and the system was fluid again before all the liquid crystal had gone. These authors also found that as the chain length of the additive increased so did the size of the peak. Collison & Lawrence (1959) made a similar study of the system dodecyl sulphate-water-n-octylamine. They studied the effect of addition of the latter compound on 16.7% aqueous solutions of the soap. The viscosity maximum in the liquid crystal region at 25° was too large to measure with their viscometer. Both these studies used a rising column capillary viscometer and there is no indication whether the viscosity was Newtonian throughout or whether non-Newtonian viscosity occurred in the presence of liquid crystalline phases.

In the liquid crystal and liquid crystal + L_1 regions of the system ascorbic acid-water-polysorbate 80, non-Newtonian flow properties were

observed. Dervichian, Joly & Titchen (1954) have plotted portions of a viscosity contour diagram for the system potassium laurate-water-potassium carbonate and found the regions of viscosity and regions defined by streaming birefringence corresponded. Newtonian viscosity only occurred where birefringence was absent, as in the present system. Dervichian explained the viscosity changes within the phases of his system by suggesting they were caused by "transformations of higher order." It was suggested that these changes of state were "homogeneous" and only indicated by abrupt changes in thermodynamic properties such as entropy or compressibility. Winsor (1954) explained the phenomena in terms of the relative stability of emulsions of his S and G phases. In certain regions, the rate of shear could exert a big influence on the ratio and constitution of the phases present. This is evident from the changes in the rheological curves of the present ascorbic acid systems on recycling. Here, the thixotropic liquid crystal phase is broken down to give an emulsion of liquid crystal and isotropic solution, which at low rates of shear exhibits pseudoplastic flow properties. At high rates of shear the linearity of the stress/strain curves indicates that organized gel structure is absent.

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