

Solubilization and rheology of the system ascorbic acid-water-polysorbate 80: temperature effects

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Changes induced by temperature in the relative position and extent of the isotropic and liquid crystal phases present in the ascorbic acid-water-polysorbate 80 system have been recorded. Increases in temperature reduce the size of the liquid crystal phase. This phase is pseudoplastic, but a small central region also shows thixotropic hysteresis loops. On recycling, most systems show Newtonian behaviour. In the isotropic regions, an increase in temperature results in a fall in log of viscosity proportionate to $1/T_{abs}$, but in the liquid crystal region an increase in temperature may cause a similar fall or, because of a change in the relative position of the system within the liquid crystal region, an increase.

In previous papers the authors have reported on the solubility and rheology, at 25°, of ascorbic acid-water systems containing polysorbate 20 and polysorbate 80 (Nixon & Chawla, 1965, 1967). In the systems containing polysorbate 20, no anisotropic liquid crystal phase existed and the viscosity was Newtonian throughout all the single phase systems. In similar systems using polysorbate 80 as the solubilizer a far more complex picture was found. A large band of viscous anisotropic liquid crystal phase occurred. The rheological behaviour within this region was pseudoplastic when only small amounts of liquid crystal were present, but revealed complex thixotropic properties when liquid crystal was the only phase present. The present work reports on the changes produced by temperature on the solubility and rheological properties of ascorbic acid-water-polysorbate 80 systems.

EXPERIMENTAL

Ascorbic acid, polysorbate 80 and water complied with the specifications given previously (Nixon & Chawla, 1967).

Determination of viscosity. The Ferranti-Shirley cone and plate viscometer was used as described by Nixon & Chawla (1965). Stress-strain diagrams showing the rheological properties of the systems were prepared.

Determination of solubility. Solubility was taken as the average between an under and over saturated solution containing a difference of 10 mg ascorbic acid per 5 ml solution. In the viscous liquid crystal regions the dispersion was first warmed to 60° to speed equilibration. The end point was determined after storage at the desired temperature for 24 h.

RESULTS AND DISCUSSION

The solubility of ascorbic acid in polysorbate 80-water systems showed a negligible change at temperatures between 25° and 40° (Fig. 1). In no case could ascorbic acid

be dissolved in concentrations of polysorbate 80 above 97% w/w. The highest concentration of dissolved ascorbic acid was found in the absence of polysorbate 80, but even here the increase in solubility was only from 20.75% w/w at 25° to 22.1% w/w at 40°. As the concentration of polysorbate 80 increased, the solubility of ascorbic acid in the system fell.

The principal effect of temperature was on the type and position of the micellar phases present. At 25°, in the absence of ascorbic acid, birefringence commenced at 41% w/w polysorbate 80 and continued up to a concentration of 64% w/w. Pure liquid crystal appeared to be present from about 44% w/w polysorbate 80. The upper limit of the liquid crystal phase was imprecise and difficult to determine. At higher temperatures the width of this liquid crystal band was very much smaller as shown by Fig. 1 and Table 1.

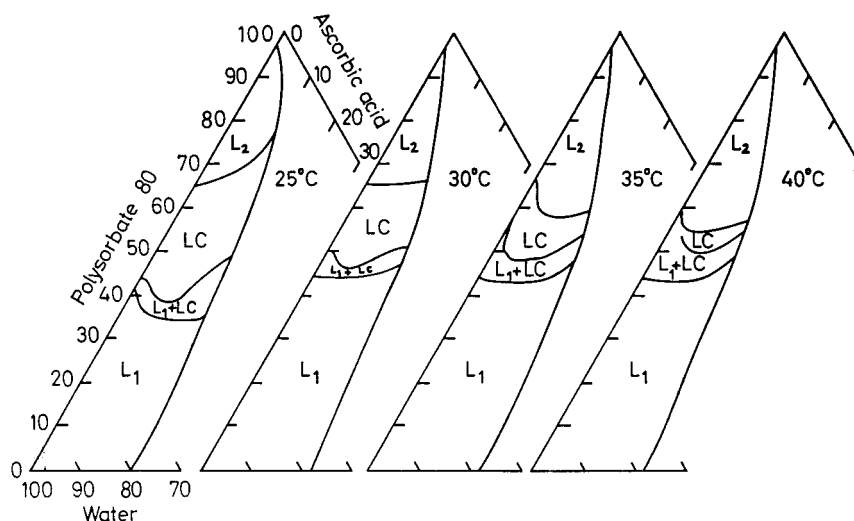


FIG. 1. Solubility of ascorbic acid in polysorbate 80-water systems: effect of temperature on phases present. L_1 and L_2 , isotropic phases; LC, liquid crystal.

Table 1. *Boundary of liquid crystal regions (% w/w polysorbate 80)*

Temperature °C	Absence of ascorbic acid			5% w/w ascorbic acid			10% w/w ascorbic acid			Solubility limit of ascorbic acid		
	a	b	c	a	b	c	a	b	c	a	b	c
25	41	44	64	36	39	67	34.5	40	—	34	49	76
30	44	50	66	44	46	65	44	48	66	47	51	66.5
35	44	57	66	43	48	59	43	48.5	58	48	54	59
40	44	—	59	43	—	54	43	50	55	48	55	56

(a) Lower limit of liquid crystal + L_1 ; (b) lower limit of liquid crystal only; (c) upper limit of liquid crystal + L_2 .

In the presence of ascorbic acid an increase in temperature between 30° and 40° made little difference in the polysorbate concentration at which liquid crystal first appeared, but between 25° and 30° an appreciable increase in the concentration was necessary to produce liquid crystal. At the higher temperatures the concentration of polysorbate 80 producing liquid crystal showed only a slight dependence on ascorbic

acid concentration until the acid solubility limit was approached, then the polysorbate concentration required rose slightly.

Greater changes, than in the lower boundary, occurred in the concentration of polysorbate 80 required to maintain liquid crystal. At 25° this concentration rose gradually as the solubility limit was approached. There was little effect between 25° and 35° on the limiting concentration of polysorbate required to maintain liquid crystal, but at 40° it fell. With ascorbic acid present the necessary concentration of polysorbate 80 fell with increasing temperature, but it was virtually independent of the ascorbic acid concentration at any individual temperature, except that it rose slightly as the solubility limit was approached.

It is a thermodynamic necessity that between the liquid crystal region and the single isotropic phase there should be a region where the two micellar types coexist. In the present system it was impossible to distinguish this at the upper limit of liquid crystal's existence, possibly because the band was too narrow to distinguish by the technique of solubility determination. At the lower limit for liquid crystal formation, the co-existent phase, liquid crystal plus isotropic liquid, was readily distinguishable as an opaque dispersion contrasting with the clear yellow of both the isotropic liquid and liquid crystal phases on their own.

This band of liquid crystal plus isotropic liquid tends to a minimum width between 5 and 10% w/w ascorbic acid. At 40° at low acid concentrations the band extends the full width of the liquid crystal region.

The rheological properties of the system under consideration may conveniently be divided into two sections. In the isotropic liquid phases the viscosity was Newtonian, whilst in those regions where liquid crystal was present, far more complex non-Newtonian rheological properties were shown.

Andrade (1930), Sheppard (1930) and Sheppard & Houck (1930) have shown that to a first approximation Newtonian fluids obey the temperature dependent relation $\eta = Ae^{-\epsilon/kT}$ where ϵ is the potential energy of adjacent molecules and k is the Boltzmann constant. From this expression it is possible to derive the following expression $\log \eta = \log A + B/T \log e$ where B is ϵ/k and A is a constant. A plot of $\log \eta$ against $1/T$ will be a straight line. Typical data for both isotropic liquid phases are shown in Fig. 2 where it is apparent that in these regions of the solubility diagram a normal viscosity–temperature relation holds.

Systems containing liquid crystal exhibited non-Newtonian rheological properties. At the first appearance of liquid crystal, pseudoplastic flow occurred, but when the liquid crystal only phase was reached, thixotropic hysteresis loops occurred. These hysteresis loops were frequently accompanied by a “spur” value as reported previously (Nixon & Chawla, 1967) and also observed by others (Barry & Shotton, 1967).

At temperatures below 30° a small region in the liquid crystal phase gave anomalous rheological flow curves. In these systems a spur value occurred above which pseudoplastic flow was noted until a rate of shear of 850 s⁻¹ was reached. Above this value a slight dilatant flow curve was found. After the shear rate was allowed to decay, the curve showed a slight hysteresis loop to the left at all shear rates, the width of this loop being small over the dilatant portion of the curve. At temperatures above 30° this anomalous behaviour at high shear rates disappeared along with the “spur” on the curves. A thixotropic hysteresis loop was found in only one system studied (53% polysorbate 80–8% ascorbic acid–39% water) at temperatures above 30°. At the

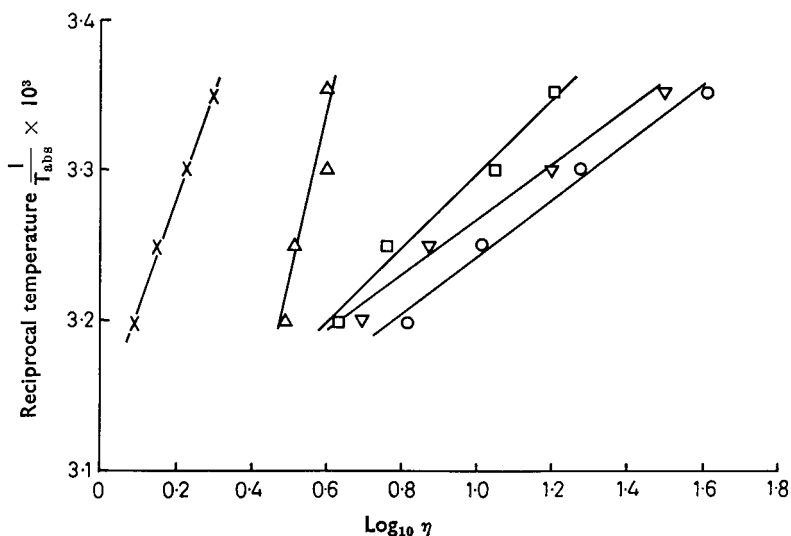


FIG. 2. Effect of temperature on the viscosity of isotropic dispersions of ascorbic acid-water-polysorbate 80.

% w/w Composition:	Ascorbic acid	Polysorbate 80	Water
×	0	9.36	90.64
△	19.17	11.14	69.69
□	4.86	80.76	14.38
▽	0	70.99	29.01
○	19.19	71.09	9.72

Abscissa in centipoises for ×, △: poises for □, ▽, ○.

higher temperatures the flow behaviour was pseudoplastic throughout the liquid crystal region.

Recycling of the systems resulted in the destruction of this hysteresis loop in all cases and the substitution of pseudoplastic flow, which on continuous recycling (more than 5 cycles) approached Newtonian behaviour. Where the original liquid crystal system had exhibited pseudoplasticity, recycling produced Newtonian viscosity. This occurred usually after two recycles at temperatures above 35° but occasionally required as many as 5 recycles at lower temperatures. On allowing the system to stand for up to 1 h, the original rheological behaviour tended to be re-established, particularly when this had been pseudoplastic. The thixotropic hysteresis loops did not, after this time, return to their full width.

As suggested by Barry & Shotton (1967) it would appear that systems such as those described do not exhibit true thixotropy, in that the area occupied by the hysteresis loop does not return to its full value even after prolonged standing. The findings suggest that the structural breakdown occurring at higher rates of shear does not completely reform on standing. The dilatent behaviour exhibited by certain systems at high rates of shear suggests that the structural breakdown has proceeded to the extent of "squeezing" water out of the liquid crystal gel and thus producing shear thickening. That this water is not taken back into the liquid crystal system in the same way is shown by the slight hysteresis loop produced on reducing the shear rate.

The spur values which have been noted on certain liquid crystal systems are a fairly frequent occurrence in rheograms (De Butts, Hudy & Elliott, 1957; Martin, Banker & Chun, 1964; Boylan, 1966; Barry & Shotton, 1967). They have been explained as

indicating the presence of three-dimensional gel structures. In the present system this would be formed by chains of liquid crystal micelles. As suggested by Barry & Shotton (1967), the resistance of these threads would have to be broken down before deformation could occur. Because of this breakdown of structure the spur does not show on subsequent recycling.

With these non-Newtonian systems it is not possible to give more than an "apparent" viscosity (Table 2) at a definite rate of shear (850 s^{-1}). Plots of apparent viscosity

Table 2. *Changes in the flow characteristics with temperature for representative systems*

System % w/w		Temperature °C	Original flow properties	Flow after 5 recycles	Viscosity or apparent viscosity (at shear rate 850 s^{-1}) after recycling poises
Ascorbic acid	Polysorbate 80				
19.17	11.14	25	Newtonian	Newtonian	0.0396
		30	Newtonian	Newtonian	0.0396
		35	Newtonian	Newtonian	0.0321
		40	Newtonian	Newtonian	0.0309
15.0	51.5	25	Thixotropic	Pseudoplastic	14
		27	Pseudoplastic	Newtonian	15.09
		35	Pseudoplastic	Newtonian	16.97
		40	Pseudoplastic	Newtonian	17.92
10.39	45.86	25	Thixotropic	Pseudoplastic	13.41
		27 (a)	Thixotropic	Pseudoplastic	13.44
		27 (b)	Thixotropic	Pseudoplastic	13.23
		30	Pseudoplastic	Newtonian	11.06
		35	Pseudoplastic	Newtonian	7.54
		40	Pseudoplastic	Newtonian	6.13
0.0	45.57	25	Slightly thixotropic	Pseudoplastic	11.73
		30	Pseudoplastic	Newtonian	10.37
		34	Pseudoplastic	Newtonian	10.83
		35	Pseudoplastic	Newtonian	9.90
		38	Pseudoplastic	Newtonian	9.28
		40	Pseudoplastic	Newtonian	7.07
0.0	60.93	25	Thixotropic	—	—
		27	Thixotropic	Pseudoplastic	24.47
		30	Thixotropic	Pseudoplastic	32.06
		31	Thixotropic	Pseudoplastic	23.22
		35	Thixotropic	Newtonian	13.68
		40	Newtonian	Newtonian	8.96
8.0	81.0	25	Newtonian	Newtonian	35.20
		30	Newtonian	Newtonian	17.91
		35	Newtonian	Newtonian	9.67
		40	Newtonian	Newtonian	6.60
4.86	80.76	25	Newtonian	Newtonian	16.20
		30	Newtonian	Newtonian	10.37
		35	Newtonian	Newtonian	5.66
		40	Newtonian	Newtonian	4.24

against temperature after 5 recycles were treated in a similar manner to the isotropic liquid phase and specimen curves are shown in Fig. 3. Not only is the apparent viscosity of these systems affected by the non-Newtonian flow, but also by differences in relative position within a solubilized phase brought about by temperature changes. Thus it is possible for a system exhibiting thixotropic properties at low temperatures, to pass through a pseudoplastic phase into Newtonian viscosity at high temperature,

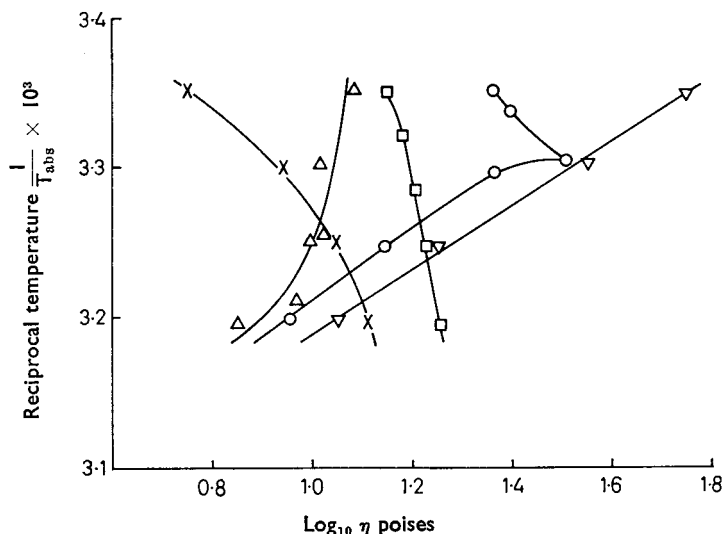


FIG. 3. Effect of temperature on the apparent viscosity after recycling of anisotropic dispersions of ascorbic acid-water-polysorbate 80. Shear rate at measurement 850 s^{-1} . Number of recycles 5.

% w/w Composition:	Ascorbic acid	Polysorbate 80	Water
×	15.5	48.5	36.0
△	0	45.6	54.4
□	15.0	51.5	33.5
▽	11.5	68.0	20.5
○	0	60.9	39.1

corresponding to a change from a system containing liquid crystal micelles to one containing small spherical micelles. Certain of these systems, again depending on the change in their relative position within the liquid crystal region, show higher apparent viscosities (measured at a shear rate of 850 s^{-1}) with increase in temperature. When the system becomes isotropic the Newtonian viscosity now exhibited falls in a similar manner to the other isotropic systems.

It is therefore apparent that examination of the rheological behaviour of solubilized systems, requires that not only temperature effects on the individual system be considered, but also the effect of changes in the relative position of the phases present within the solubilization diagram.

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