

Measurement of the 'spontaneity' of self-emulsifiable oils

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Self-emulsifiable oils are solutions of surfactants in non-polar solvents which spontaneously form emulsions when added to water. Measurement of the degree of spontaneity has remained subjective. Accordingly, a method has been devised in which a small volume of the oil solution is injected into a flowing stream of water and carried across an intense beam of parallel light from a helium-neon laser. Light scattered from the beam by the dispersed oil droplets is collected by means of fibre optics onto an array of silicon photodiodes and the amplified output is integrated as a function of time. By varying the flow rate of the water stream it is possible to estimate the time required for an emulsifying system to come to its equilibrium state of dispersion under the conditions of the experiment, the 'spontaneity' of emulsion formation. Under the experimental conditions employed, systems comprising solutions of phosphated nonylphenoethoxylate (PNE) and phosphated fatty alcohol ethoxylate (PFE) in *n*-hexane came to equilibrium between 5 and 12 s, depending on the constitution. These times could be approximately correlated with the values for spontaneity estimated by the CPAC dilution test, although this latter test is somewhat subjective. The spontaneity appears to depend on the nature of the material existing within the phase diagram and the anomalous results obtained may be accounted for by the likely presence of a complex formed at the emulsion interface between the PNE, PFE and water during the dispersion process.

Emulsions, consisting of one immiscible liquid intimately dispersed in another liquid in the form of droplets (Becher, 1965) are thermodynamically unstable with a natural tendency for the two phases to separate. Most emulsion products are formulated to minimize these changes but in some circumstances it is neither practicable nor desirable to adopt the standard stabilizing measures. Thus, a pesticidal product may only require 1% or less of oil dispersed in water at the point of application as an emulsion, which is preferentially not stable. These specialized requirements have led to the introduction of anhydrous products which are added to an excess of water immediately before use, the so-called self-emulsifiable oils; also less accurately known as 'soluble oils'. These systems are required to form emulsions spontaneously or with a minimum of agitation and although the phenomenon of self-emulsification was first described by Gad in 1878 there have been surprisingly few fundamental investigations, despite the technological importance of the products. It would appear that certain 'rules' have been established for the successful formulation of pesticidal products but few attempts have been made to establish the underlying scientific reasons for the apparent validity of these rules. For example, to formulate DDT as a self-emulsifying

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oil in xylene both 'hydrophilic' (water soluble) and 'hydrophobic' (oil soluble) surfactants are required which must also be, at the same time, soluble in the oily solvent. The surfactants must also be in a definite ratio or balance with each other. In addition, factors such as the temperature of the dilution, the time of dilution and the concentration can all affect the state of the final dispersion as well as the ease of emulsion formation and stability of the final system.

We have attempted to clarify the mechanisms involved during the almost 'spontaneous' emulsification of a simplified model system. The main difficulty is that formation of the emulsion is extremely rapid following the addition of the 'oil' to water with considerable energies involved since there is a vast expansion of the oil-water interface in a brief time. With the more conventional type of emulsion the energy involved in emulsification is obtained from the homogenization process. In a self-emulsifying system the emulsification process takes place with little application of external energy so that the energy must be derived from internal molecular forces.

Methods for determining the degree of spontaneity have remained subjective, such as the standardized test accepted by the Collaborative Pesticides Analytical Committee of Europe (CPAC) and the United Nations Food and Agricultural Organisation (FAO). In this test a small volume of the 'oil' is added to an excess of water under standardized conditions, and the rate of emulsification is judged in terms of "good", "moderate" or "bad". Tests of this type have been criticized by Ashworth (1966) as being subjective with poor inter-laboratory reproducibility but they are, nevertheless, widely employed in the formulation and evaluation of commercial pesticidal emulsifiable oil products.

The 'spontaneous' emulsification is visualized as a dynamic process in which a large bulk of oil is broken down into a number of small globules over a finite period of time when added to a large excess of water. The process would come to rest when the globules achieve their optimum size, depending on the conditions of the experiment and the nature of the 'oil' constituents, both initially and at the equilibrium point. It is also suggested that the equilibrium particle size is a result of the disruptive and coalescence processes which occur simultaneously (Groves, 1970).

By injecting a fixed volume of the oil into a flowing stream of water, and taking measurements downstream of the mixing point it seemed possible that information on the time needed to reach equilibrium point might be obtained, i.e. the degree of 'spontaneity' expressed as a time which, while not ideal, should provide useful information.

MATERIALS AND METHODS

Materials

The model system consisted of solutions of phosphated nonylphenoethoxylate (PNE, Groves, Mustafa & Carless, 1972) and phosphated fatty alcohol ethoxylate (PFE, Groves, Mustafa & Carless, 1973) in n-hexane. Dilutions were in distilled water at 25°.

Methods

Spontaneous emulsification test. This is based on the CPAC test. A 1 ml bulb pipette was supported vertically with the tip 4 cm above the surface of water at the 100 ml graduation mark in a 100 ml measuring cylinder. Using the same apparatus

for each test, each 1 ml of system was allowed to fall freely into the water and the ease of emulsion formation expressed visually as "good," "moderate" or "bad".

Instrumental method

Theory. A beam of light passing through a cloud of randomly orientated small particles which are mainly spherical and mostly with diameters close to the wavelength of the incident light will be scattered by the particles in all directions. Measuring the light received at an angle normal to that of the concentric light beam will therefore be some indication of the size and number of the scattering particles.

Basic theories of light scattering have been discussed in detail by Van de Hulst (1957). The spectro-turbimetry of small oil droplets was considered by Goulden (1958, 1960, 1961) for cow's milk but, more recently, Walstra (1965) has pointed out that, whilst the scattering due to small particles has been rigorously considered in theory, the theory breaks down when considering a range of particle sizes, including the larger particles of around 1 μm diameter which are found in many emulsions.

The total energy scattered in all directions is equal to the energy of the incident light falling on an area of the dispersed materials less that energy absorbed by the particles. This means that the particle size, the number and the optical properties of the dispersed particles are all likely to influence the amount of energy received at a detection point (Van de Hulst, 1957). Intuitively we can write

$$\tau = K.a^2.n.\pi$$

where τ = measured turbidity, a is the particle radius, n is the number of particles and K is the efficiency factor which depends on the optical properties of the dispersion.

However, K will vary for each particle, depending on its properties and the relation between the size of the particle and the wavelength of the incident radiation. From the emulsification mechanism postulated earlier it would seem that the mean particle size decreases at the same time as the total number of particles increases. As there is no method available for separating these two processes, some indication of the time required for the process to come to equilibrium when it may be presumed that the disruption and coalescence processes have stabilized would be useful. At this point it would be probable that the overall turbidity of the system would remain constant. Hence any measurement of turbidity of the dispersion will only give an indication of the bulk changes within the system, and this is what is required.

The advantages of using the intense coherent monochromatic light of a laser beam when examining suspensions have been discussed by others (Woodward, 1963; George, Goldstein & others, 1965; Finnigan, Jacobs & Marsden, 1971; Isaksen, Williams & Heaps, 1971; Meric, 1972; Staffin, Ricci & Juels, 1972), but the main advantage is that the light is collimated with the result that apparatus design is greatly simplified and more flexible. Unlike the approach of Heyder, Roth & Stahlhofen (1972), no attempt was made to focus the beam and the detection system was designed to integrate as far as possible light scattered in a plane normally located to the incident beam at a point. This was achieved by using sampling ports aligned towards the centre of a tube along which the beam was passed. Light scattered onto the ports was detected by an array of phototransistors connected to a summing effect amplifier.

The apparatus (Fig. 1) consists of three main sections—the water supply, the analytical device and the light detectors.

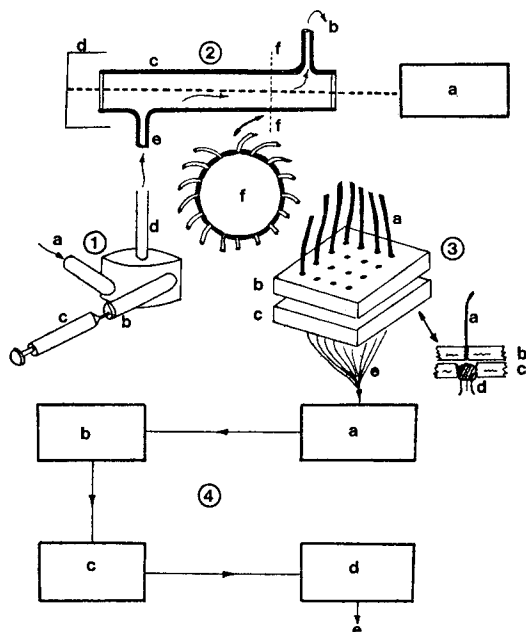


FIG. 1. Diagrammatic view of the apparatus used to measure emulsion spontaneity (not to scale). Section (1) Mixing section: (a) Water inlet from a 20 litre aspirator, constant level device and valves. (b) Rubber capped inlet. (c) Syringe containing material under investigation. (d) Outlet to analytical section. (2) Analytical section: (a) 3 mm helium-neon laser. (b) Outlet. (c) Brass tube with glass ends. (d) Light trap. (e) Inlet. (f-f) Position of 16 light guides inserted through wall of tube, shown in section in f. (3) Detector array: (a) Incoming steered light guides. (b) Perspex plate with holes to receive ends of light guides in 4×4 array. (c) Perspex plate with matching holes containing silicon photodiodes, (d). (e) Output leads from photodetectors. (4) Data acquisition section: (a) Summing effect amplifier. (b) A/D converter and magnetic tape logger. (c) Replay unit. (d) Teletype machine. (e) Output or computer interface.

The water supply is from a 20 litre aspirator connected via a constant level device and heating system to the inlet side of a mixing chamber. With the aid of adjustable valves the flow rate of water could be varied from 25 to 220 ml m^{-1} .

The mixing chamber, constructed of brass, has a water inlet and outlet together with a tangential rubber-capped injection port through which an emulsion system can be injected using an Agla syringe (Wellcome Foundation Ltd). This simple device enables rapid mixing to take place at a point where the water flow is turbulent.

The water stream is connected to the analytical section, consisting of a brass tube, 2.5 cm in diameter and 8.5 cm long. The inlet and outlet tubes are brazed onto the lower and upper surfaces respectively, as shown. The ends of the tube are closed with discs of optically flat glass, one cemented into place with epoxy resin, and the other held in place by a threaded cap and O-ring to facilitate removal, enabling the inside of the tube to be cleaned and polished as required.

Near the outlet tube are drilled, normal to the wall, 16 regularly spaced holes along the circumference of the tube, and through each hole is inserted the end of a 1 mm Crofon light guide (Du Pont/Rank Precision Instruments Ltd, Code No. 0040). Each guide is held in place with epoxy resin cement and thoroughly polished so that the end of the fibre is flush with the inside wall of the tube. The light guides are sleeved and brought to a flat Perspex plate in a 4×4 array, the length of the guides (30 cm) being chosen so as to avoid sharp bends which would otherwise affect the

efficiency of light transfer. The ends of the fibres projecting from the plate are also polished flat to minimize light losses. This plate is keyed to a second Perspex plate in which are embedded a corresponding array of silicon photodiodes, each phototransistor having its sensitive area exactly opposite the end of a light guide. The phototransistors (Fairchild, FPF 110) are of the NPN type and were selected for their sensitivity and response to red light, as well as their stability and design suitability. The phototransistors are connected in parallel to a summing effect amplifier, Fig. 2. By having point A at virtual ground and adjusting the output at Point d on test so that there is an output (V_o) of zero volts under dark conditions, it is possible to write

$$i_p = i_\Sigma = \text{sum of current from the phototransistors}$$

$$\text{Voltage output} = V_o = 10K \times i_\Sigma$$

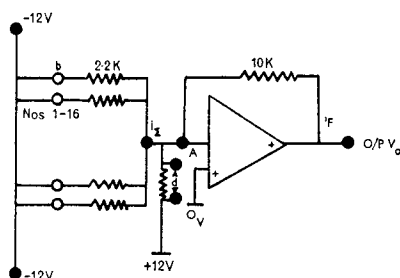


FIG. 2. Schematic diagram of the summing effect amplifier for amplifying output of the phototransistors Nos 1-16 in parallel.

The voltage output is converted from analogue to digital form and recorded on tape cassettes as a function of time using a Temple Electronics Data Logger Type D1. Data is recorded at 1 s intervals and printed out in digital form on an EMI teletype machine using the Temple Replay Unit, Type R2/T.

When exposed to daylight the array of phototransistors gave a maximum output of 5.5 V but when connected to the detection system the maximum output was of the order of 600 mV.

The detection system is mounted on an optical bench, together with a Scientifica-Cook Model B19/3 helium-neon gas laser producing a maximum power of 3 mW at 632.8 nm. The laser beam is passed down the principal axis of the detector tube into a black box, and the whole system is covered in a box to eliminate stray light.

Experimental method

All measurements were made with the water stream at a temperature of 25°. The water velocity was adjusted to the required value using the inlet valves and, after recording the base voltage output of the system with clean water passing through the detector tube, an appropriate volume of the oil was injected rapidly into the mixing chamber inlet. Over a period of a few minutes the voltage output rose to a maximum value (Fig. 3) and then decayed to the original base line value. The recorded data were printed out and the area under the curve determined as a measure of the total number and size of the particles passing through the detection zone of the apparatus. Since the volume of the water between the mixing chamber and the plane of the sensing zone in the detector tube could be measured and the flow rate was known, the time

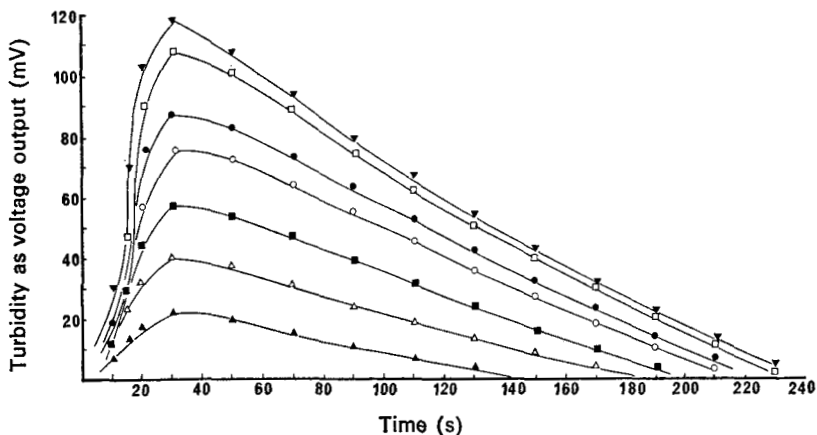


FIG. 3. The turbidity as voltage output vs time curves for increasing volumes of homogenized milk injected at a flow rate of 100 ml min^{-1} at 25° . ▲, 0.2 ml. △, 0.4 ml. ■, 0.6 ml. ○, 0.8 ml. ●, 1.0 ml. □, 1.2 ml. ▼, 1.4 ml.

required for a particle to leave the mixing chamber and enter the sensing zone could be easily determined, assuming no inertial or drag effects on the particles.

RESULTS

The effect of emulsion concentration

Following the theoretical considerations it was anticipated that there would be a linear relation between the concentration of an emulsion system and the total turbidity or, in this case, the output voltage of the detector.

From a sample of homogenized cow's milk as a model increasing volumes of milk were injected using a standardized technique with a water flow rate of 100 ml min^{-1} . Voltage output vs time curves are shown in Fig. 3 and the integrated output values in Fig. 4.

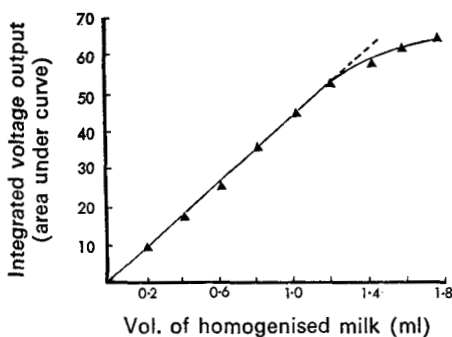


FIG. 4. Integrated voltage output vs volume of homogenized milk from Fig. 3, showing the characteristic inflection point.

It will be seen that the relation is linear up to a point, suggesting that Beer's Law is obeyed until, presumably, the emulsion is too concentrated and internal scattering takes place within the dispersion. The experiment was repeated using a self-emulsifiable oil and the same effect was noted.

Since there appeared to be a rational basis for the use of the device, calibration curves were prepared for each of the systems to enable all subsequent measurements to be taken at a concentration below the inflection point shown in Fig. 4.

The effect of water velocity

Using the homogenized milk as an example of an emulsion system already at its equilibrium, the apparatus was tested by injecting 0.1 ml volumes at different water velocities. The results are shown in Fig. 5 and it will be noted that there is no evidence of an inflection point over the whole of the water velocity range, suggesting that the instrument is unaffected by these environmental changes.

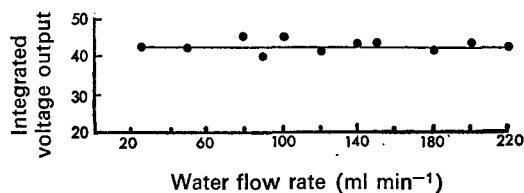


FIG. 5. The effect of water flow rate at 25° on the integrated voltage output when 0.1 ml homogenized milk is injected.

However, when the experiment was repeated with a self-emulsifiable oil, results similar to those shown in Fig. 6 were obtained, a marked inflection point being apparent in accordance with the theoretical predictions. Estimation of this inflection point and therefore the equilibration time required for the system under investigation appeared to be reasonably precise since it involved interpolation of two linear curves.

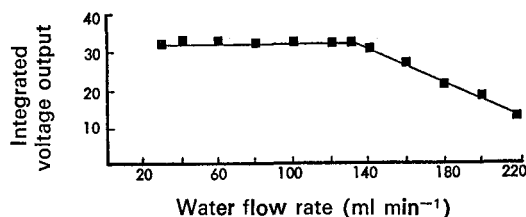


FIG. 6. The effect of injecting 0.1 ml of a system containing PNE 35, PFE 35 and n-hexane 30 at different water flow rates at 25°, showing the inflection point used for estimating the spontaneity time.

Repeatability of the experiments

Using a fixed volume of 0.1 ml of an oil at a water velocity of 100 ml min⁻¹, the apparatus was tested by repeating the experiment 16 times. The results (Table 1) suggest that, apart from the first few seconds of the experiment where the voltage output is low, the reproducibility of the experiment was high, of the order of ±1%.

Measurement of the equilibration times

Not all the PNE-PFE-n-hexane systems previously reported (Groves, Mustafa & Carless, 1974) could be investigated using this apparatus since the mixtures were too viscous to allow the rapid injection required in this technique. However, some of the systems were investigated by first determining the concentration range over which

Beer's Law was obeyed and then measuring the equilibration time or degree of spontaneity. Results are shown in Table 2, together with the results obtained from the subjective method.

DISCUSSION

Results using the laser apparatus, Table 2, suggest that there are relatively few differences between the different samples since the results only range between 5 and

Table 1. *Reproducibility of 16 experimental runs using 0.1 ml of a system containing PNE, PFE and n-hexane (25:25:50), at a water velocity of 100 ml min⁻¹.*

Time intervals (s)	Mean voltage (mV)	Standard error	Standard error as % of mean
3	2.00	0.24	12.0
5	4.60	0.18	3.94
10	15.81	0.32	2.03
20	63.94	0.72	1.12
31	80.70	0.08	0.10
40	70.12	0.09	0.12
60	45.90	0.12	0.26
80	27.31	0.11	0.40
100	15.0	—	—
120	10.0	—	—
140	6.0	—	—
160	4.0	—	—

Table 2. *Subjective spontaneity and time to reach equilibrium for a number of PNE-PFE-n-hexane systems at 25°.*

PNE	Constitution (% w/w)		CPAC spontaneity g = good; m = moderate; b = bad	Time (s) to reach equilibrium
	PFE	n-Hexane		
35	35	30	b	7.85
7	63	30	b	12.0
63	7	30	b	11.8
30	30	40	b	7.7
54	6	40	b	11.3
6	54	40	b	11.4
25	25	50	b	6.37
45	5	50	b	10.8
5	45	50	b	10.8
22.5	22.5	55	m	6.5
20	20	60	m	6.8
36	4	60	b	10.2
4	36	60	b	10.2
17.5	17.5	65	m	6.5
15	15	70	g	5.66
27	3	70	m	9.6
3	27	70	m	9.5
12.5	12.5	75	g	5.66
10	10	80	g	5.9
18	2	80	b	8.4
2	18	80	b	8.5
7.5	7.5	85	m	6.37
5	5	90	m	6.5
2	8	90	b	7.4
8	2	90	b	7.6

12 s. It is therefore necessary to first consider the validity of the experiment in order to ascertain whether these small differences are significant.

It is important to consider these results in the knowledge that the various parameters involved in measuring the spontaneity can be determined with reasonable precision. For example, the total liquid throughput of the apparatus is collected during the experiment over a period of time determined with a stopwatch so that the reported flow rate is likely to be precise to within 1%. The voltage output is recorded with an accuracy of $\pm 0.1\%$ and replicate readings suggest a high degree of reproducibility (Table 1). It would therefore seem not unreasonable to attribute an accuracy of better than $\pm 5\%$ to each point on the integrated voltage output vs flow rate curves. Moreover, estimates of the spontaneity are based on measuring the flow rate above which the emulsification process is not complete before the dispersing system is carried past the sampling point. This critical flow rate is determined by interpolation of two linear curves, both of which are precise in meaning and self-consistent. Hence it must be concluded that the times are significant under the conditions of the experiment, and are significant enough for a realistic comparison of one emulsion system with another.

Inspection of Table 2 shows that, although the constitution of the self-emulsifiable oil appears to affect the degree of spontaneity, there is also an approximate correlation with the results obtained from the subjective CPAC test. Systems which take 7 s or more to come to equilibrium appear to be classified as having "bad" spontaneity whereas those emulsifying in less than 6 s are described as "good", intermediate values being "moderate".

As noted by Groves, Mustafa & Carless (1974a), mixtures of PNE, PFE and n-hexane exist together in an involved type of phase system containing, in the presence of water, at least two types of liquid crystal, a transparent gel and various multiphase components. In addition it has been demonstrated (Groves, Mustafa & Carless, 1974b) that, in the presence of water, PNE and PFE form a complex in approximately equal parts by weight.

Examination of the results in Table 2 suggested that there were differences in the ease of emulsification between various mixtures selected from various parts of the equilibrium phase diagram. There appeared to be an approximate correlation between the results from samples containing 9:1 or 1:9 ratios of PNE:PFE, and also the amount of n-hexane in the sample. When treated in this fashion the results obtained in Fig. 7 were obtained.

From Fig. 7, results obtained with mixtures of materials selected from either side of the mid-line of the phase diagram appeared to be superimposable and the time required for equilibration declines in a regular fashion as the n-hexane concentration is increased. No immediate explanation for this effect can be offered but it may simply lie in the fact that the viscosity of the 'oil' plays a part in the ease with which the droplets are dispersed in water.

However, the results obtained for the mixtures in which the PNE and PFE are in equal weights are completely anomalous, confirming previous indications that the complex between the two compounds plays a significant part in promoting emulsification. The distinct differences at various points along this line provide a subject for further speculation and investigation.

It is suggested that there is a correlation between the formation of liquid crystalline material in the sample as it is diluted with water and the time required for the system

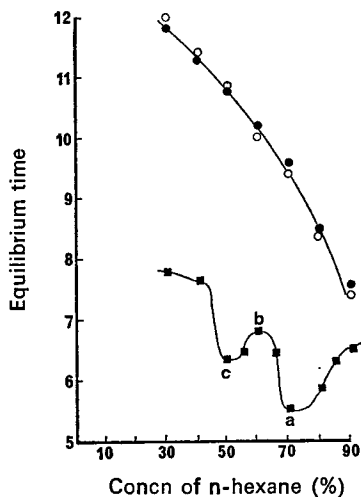


FIG. 7. The effect of changing the n-hexane concentration on the emulsion equilibrium time for systems containing different proportions of PNE and PFE: ●, system containing 9:1 PNE:PFE. ○, system containing 1:9 PNE:PFE. ■, system containing 1:1 PNE:PFE. (a) mixture consists of middle phase liquid crystal. (b) mixture consists of gel phase. (c) mixture consists of neat phase liquid crystal.

to come to equilibrium. The phase relationships have been explored by Groves & others (1974a) and it is clear that as the system is diluted with water and the n-hexane concentration is reduced, transitions from one phase to the other will occur. Thus, moving from right to left (Fig. 7), middle phase liquid crystal (a) is followed by the transitional gel phase (b) and the neat phase liquid crystal (c). This might account for the anomalous behaviour since presumably a drop of the PNE-PFE-n-hexane system added to water will change in constitution as the water penetrates into the drop. A system in which the middle type of liquid crystal predominated during the initial stage of dilution and dispersion, i.e. corresponding to (a), would appear to disperse more rapidly than one containing predominantly neat liquid crystal (c). As a tentative explanation it is suggested that this may be due to the relative difference in hydrophilicity between the two types of liquid crystal (Groves & Mustafa, 1974) and the ease with which water molecules can penetrate, thereby expanding the interface. Rapid expansion of the interface will clearly produce an unstable situation, resulting in disruption of the oil-water surface and breakdown in the droplet size, manifested by the formation of a 'spontaneous emulsion.'

Acknowledgements

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