Determination of Cloud Points of Nonionic Surfactants

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Abstract

By use of a specially adapted fluorometer attached to a strip chart recorder, a spectrum or cloud-o-gram can be obtained from various types of ethylene oxide condensates (nonionic surfactants). A cloud-point reproducible to ±0.2C can be determined from the cloud-o-gram. The cloud-o-gram is unique for each classification, and differences can be detected within classifications.

Introduction

CLOUDPOINT, AS DEFINED by the AOCS Official Method Cc6-25, is that temperature at which a cloud is induced in a sample caused by the first stage of crystallization.

Several methods are described in the literature to determine this phenomenon (1,2). All of these methods are based on the visual detection of the first appearance or disappearance of cloud or turbidity. However, it was felt that such methods were too prone to human error. Therefore, a method was sought which would instrumentally record this phenomenon.

We found that by combining a specially adapted Turner G-111 Fluorometer and a strip chart recorder we could record the actual growth of the cloud. We called the recording or spectrum obtained a cloud-o-gram.

Experimental

Instrument

A standard Turner G-111 Fluorometer equipped with a Flow-thru cell door was attached to the 2.5 mv strip chart recorder of the Sargent Model XV Polarograph with a linear variable resistor in parallel with the output jacks of the fluorometer.

The resistor was set to match the output of the fluorometer to the recorder. (A 10 mv recorder would not require a resistor across the output jacks of the instrument.) A thermometer probe (YSI tele-thermometer model 43TC) was placed in the upper exit port, and a specially designed cell (Fig. 1) encased in a heating tape was attached to the intake and exit ports of the door by means of Swage-Lok fittings. The solutions were pumped through the system at a rate of 30 ml per minute by a peristaltic pump. Heating was controlled by a Variac and internal mixing in the cell obtained by a magnetic stirrer.

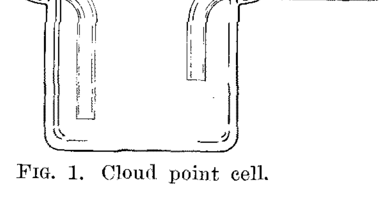

FIG. 1. Cloud point cell.

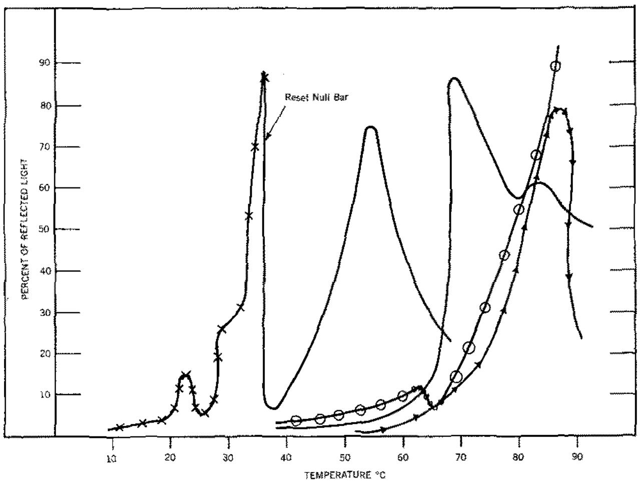

FIG. 2. Cloud-o-grams of surfactants containing varying moles EtO. Crosses, 8 moles; open circles, 10 moles; solid line, 15 moles; arrows, 30 moles.

The primary light source was filtered by a Corning 23A filter to allow only 570 μ or longer wave lengths to pass into the sample. This was done to prevent any possible source of error due to fluorescence of the aromatic portion of the nonionic compounds under study. The sensing portion of the fluorometer's optical system was attenuated by neutral density filters to keep the signal within the bounds of the recorder.

Sample Preparation

Most samples were prepared as 1% (w/v) in distilled water. However, it was found that some nonionics were either completely soluble or insoluble at all measurable temperatures. Those samples which were soluble at all measurable temperatures were prepared as 1% (w/v) in 10% sodium chloride while those that were insoluble were prepared as 1% (w/v) in 20–25% (v/v) isopropanol.

Development of Cloud-o-grams and Cloud Point

The sample was placed in the cell and pumped through the system prior to heating to insure freedom from bubbles or foam which would cause erroneous readings on the recording chart. When the solution was free from bubbles or foam, heat was applied at a constant rate. A change in reflected light oc-

TABLE I

Effect of Moles EtO on Cloud Point

Theoretical moles EtO[a]	Sample	Cloud point C.		Moles EtO by NMR	Moles EtO by NIR
		Intersept	1st Max.		
10	1	60.0	60.5	11.3	11.0
	2	57.8	59.3	10.6	10.7
	3	57.2	58.7	10.1	10.1
8	1	22.8	26.0	9.2	9.0
	2	21.3	22.5	8.5	8.8
	3	19.8	22.2	8.1	8.2
15	1	63.9	68.8	15.8	
	2	63.8	68.2	15.6	
	3	63.7	68.0	15.2	
30	1	85.0	88.0	34.9	
	2	80.1	84.5	27.9	
	3	77.5	81.0	26.8	

[a] The 8 and 10 mole samples were run as 1% aqueous solutions. The 15 and 30 mole samples were run as 1% in 10% NaCl solutions.

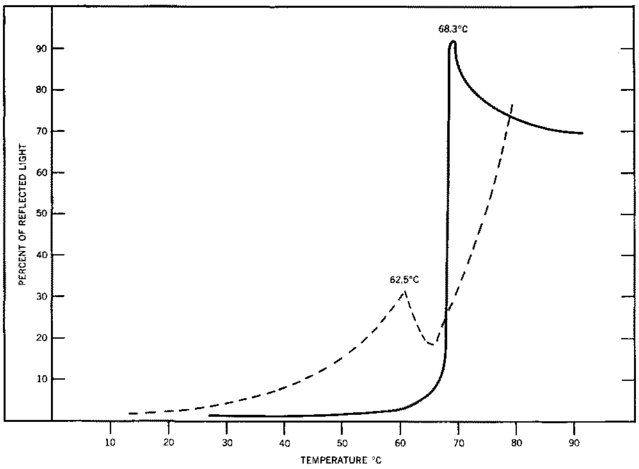

FIG. 3. Cloud-o-grams of surfactants containing 10 moles EtO.

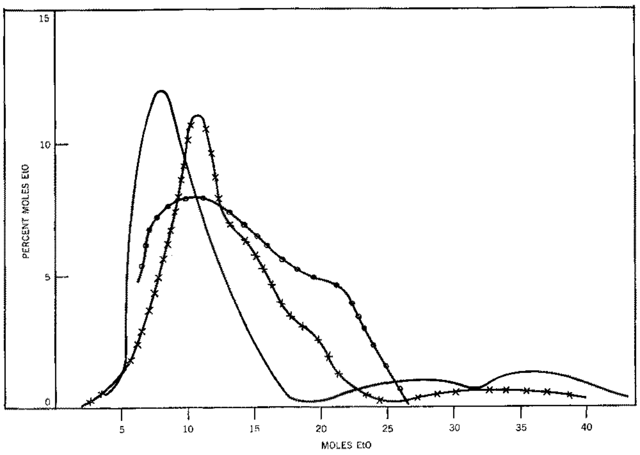

FIG. 5. Poisson distribution of various combinations of moles EtO. Solid line, 8–30 moles 5–1 ratio, 11.7 moles EtO aver. Open circles, 8–15 moles 1–1 ratio, 11.5 moles EtO aver. Crosses, mixture of solid lines and open circle 1–1 ratio, 11.5 aver.

curred as turbidity or cloud developed and was automatically recorded on the strip chart recorder. The temperature was manually recorded at 1C intervals at the appropriate points as the spectrum developed. The percentages of reflected light were then plotted against their respective temperatures on arithmetic graph paper, and a unique curve developed. This we called a cloud-o-gram. Different average moles of ethylene oxide condensate gave different cloud-o-grams and these cloud-o-grams were unique for each classification (Fig. 2). It was also noted that there were some variations in cloud-o-grams within samples of the same average moles of ethylene oxide (Fig 3).

The cloud-point temperature was determined from the cloud-o-gram as the intersect of two lines, one drawn along the base line A and one drawn along the rising reflected light line B (Fig. 4). This point coincided with what was generally agreed upon as the first visible detection of cloud or turbidity. Repeated runs of duplicate samples of the same material did not vary any more than ±0.2C. The point of the first maximum ("C," Fig. 4) also did not vary any more than that.

Table I illustrates cloud points obtained by this method on predetermined average moles of ethylene oxide. The averages were determined by nuclear magnetic resonance (NMR) and NIR where applicable.

Discussion

The profile of the cloud-o-gram may be explained as the dehydration of the ethylene oxide chain to form insoluble particles followed by the coalescence of the particles. As the number of these reflecting particles increase, it follows that the amount of reflecting light also increases, causing a positive slope. Next these particles once more coalesce with each other to form reflection aggregates of large size, but of much smaller number, thus causing a negative slope. The return to the positive slope may be explained by one or both of the following:

1) As the temperature increases the molecules containing the higher moles of ethylene oxide dehydrate to form aggregates of nearly equal size as those already in solution. The resulting increase in the number of these particles once more causes an increase in reflected light.

2) The acceleration of the particles by the increasing temperature may cause fragmentation, thus increasing their number. When either an equilibrium is set up between the particles forming and those breaking apart, or when all of the molecules have been dehydrated and the end of the process is therefore reached, the cloud-o-gram should level off. Although not reported here, such a leveling process was obtained in this laboratory.

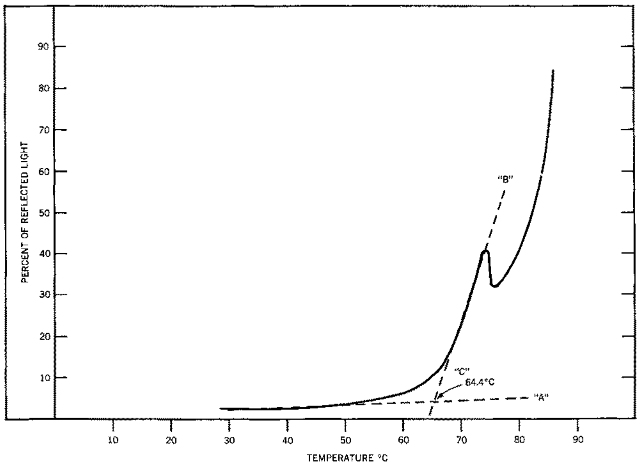

FIG. 4. Method for determining cloud point. 10 moles EtO.

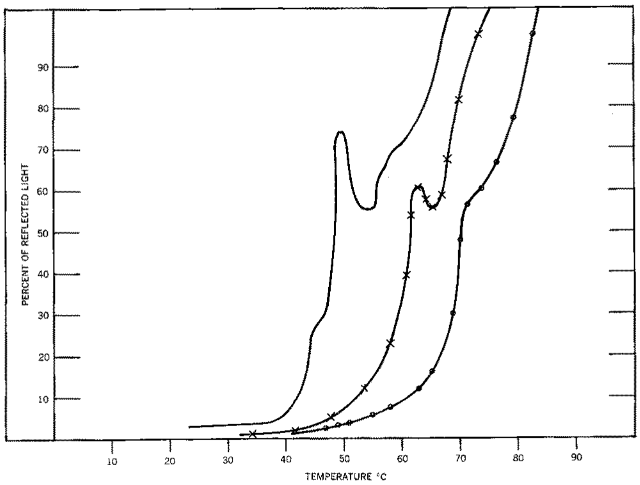

FIG. 6. Cloud-o-grams of synthetic mixtures of surfactants.

We thought that the differences noted in the cloud-o-grams and cloud points of the materials containing the same average moles of ethylene oxide might lie in the distribution of moles around the average. Therefore, samples were made by combining samples of different average moles to contain an average of 11.5 ±0.2 moles of ethylene oxide and were processed through this procedure. Figure 5 is a graphic representation of the distribution of the moles of ethylene oxide of these combinations based on the Poisson Distribution of each component. Figure 6 illustrates the cloud-o-grams and cloud points obtained from these combinations.

As illustrated, we have a preponderance of low molecular weight material (8 moles) but enough of the higher weights to average out at the desired level. However, the cloud points obtained are not what one expects of 11.5 mole material, but more like that of a 9 or 10 mole material. Although the average moles are nearly equal, the cloud-o-grams reflect the differences in the distribution around the average.

Additional confirmation of the effect of the mole distribution around the average was obtained by plotting the data of Mayhew and Hyatt (3) on arithmetical probability paper.

REFERENCES

1. American Society of Testing Materials, ASTM Designation D97-57 (1957).
2. Official and Tentative Methods of the American Oil Chemists' Society, Sampling and Analysis of Commercial Fats and Oils, Official Method Dc 6-25.
3. Mayhew, R. L. and R. C. Hyatt, JAOCS *29*, 357 (1961).

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Solidification of Unsaturated/Saturated Fatty Acid Mixtures and Its Relationship to Chilling Sensitivity in Plants

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Abstract

Freezing points of mixtures of palmitic and linoleic, or palmitic and linolenic acids, the predominant fatty acids in plants, decrease slowly as the unsaturated fatty acid is increased to 60 mole %. Beyond this per cent the freezing point is depressed quite markedly by each addition of unsaturated fatty acid. Linoleic and linolenic acids have similar effects on the freezing points of the mixtures until about 82 mole % unsaturated fatty acid. Differences of less than 5% in the amount of unsaturated fatty acid have a marked effect on the freezing point of mixtures at the approximate composition of fatty acid in plant membrane lipids.

Introduction

LIPIDS MAY PLAY an important role in chilling injury of plants (injury which occurs in some plant species at temperatures below about 10C but above freezing) (4,6,7); however, it has not been possible to relate lipid composition to the basic cause of chilling injury until concepts were reported relating the role of lipids in membrane systems at a subcellular level (2). Recent work (6) has demonstrated a relationship between fatty acid composition of mitochondrial membranes and sensitivity toward chilling of species from which the mitochondria were derived. In general, species which were sensitive to chilling temperatures possessed mitochondria with a higher amount of saturated fatty acids in their mitochondrial membranes than chilling-resistant species. In the work of Wheaton (12), fatty acid compositions of phospholipids extracted from root tissues of a number of plant species were surveyed and a tendency toward the sensitive species having the greater amount of saturation existed. Correlation of sensitivity to chilling and fatty acid composition was not precise, and it appeared that taxonomic relationships were equally important. A relationship of the amount of unsaturation of fatty acids in mitochondrial membranes to cold sensitivity was more clearly demonstrated in animal studies where it has been shown that mitochondria derived from warm-blooded animals possessed more saturated fatty acids than those derived from cold-blooded animals (8,9). These studies indicated that the mitochondria from warm-blooded animals with the more saturated fatty acids could not maintain their flexibility at lower temperatures, implying a disruption of metabolism and energy supply, while those from cold-blooded animals with more unsaturated fatty acids could maintain their flexibility at lower temperatures.

In evaluating the physical characteristics of fatty acids in relationship to their influence on membrane properties, it is known that chain length, number of double bonds, and position of the double bonds, all play a role in determining the physical properties of the lipid. The predominant fatty acids in nongreen plant tissues are palmitic (28%), linoleic (40%), and linolenic (21%), with lesser amounts of stearic (3%) and oleic (5%), and others in trace amounts (12). Assessment of the role of these fatty acids in relation to the physical properties of membrane lipid raises the question as to whether the difference between two double bonds in linoleic and three double bonds in linolenic can significantly alter the freezing point or solidification of the membrane lipid. Since the double bond index (the summation of weight % of each acid in a mixture multiplied by the number of double bonds it contains per molecule, divided by 100) has been used to classify the degree of unsaturation in a lipid, it is important to evaluate this point critically, because a small change in the distribution of either linoleic or linolenic can markedly alter the double bond index. A freezing point curve for mixtures of palmitic (the saturated fatty acid of major importance in plant material) and oleic is available in the literature (10). It seemed of importance to prepare diagrams for palmitic and linoleic, or palmitic and linolenic so that the role of these mixtures may be adequately considered.