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THE PHYSICAL-CHEMICAL PROPERTIES OF SURFACE-ACTIVE AGENTS IN LIQUEFIED HALOCARBON AEROSOL SYSTEMS*

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ABSTRACT

Surface-active agents may be used to enhance the properties of liquefied aerosol propellants or to diversify their applications. In order to minimize haphazard and empirical approaches to the use of surfactants, studies have been conducted to establish accurate methods for determining the relationships which exist between surfactants and aerosol systems.

The methods which were used in measuring solubilities, interfacial tensions and critical micelle concentrations of selected surfactants in liquefied propellants are presented. The correlations between these determinations and the results obtained with a cloud point technique are described. The value of this approach in measuring and predicting the required parameters of aerosol systems is also reviewed.

STATEMENT OF PROBLEMS

The increased interest in the utilization of surface-active agents in solving many problems in aerosol systems has been accompanied by an awareness of the need for the development of sound procedures for measuring the effects of surfactants in such systems.

The use of surface-active agents in preparing two-phase solutions, suspensions, emulsions or related aerosol products has been considered to be the most practical approach in circumventing many of the shortcomings inherent in the liquefied halocarbon propellants (1–3). However, most of the work accomplished with the aid of surfactants has been done on a rather

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haphazard and pragmatic basis, and reported studies in this area have been concerned with effects rather than causes. As a result, only generalized rules-of-thumb are available as guides when the use of surfactants in aerosols is contemplated (4).

Before surface-active agents may be employed in a system to modify the interfacial barrier and thus accomplish some specific task, certain fundamental characteristics of the surfactant in the system under study must be known. Among these are solubility, surface adsorption and critical micelle concentrations.

Measurement of these properties in aerosol propellants poses serious problems not normally encountered in nonpressure systems. It is therefore necessary that specialized instruments and techniques be developed when surfactants are studied in the liquefied halocarbon propellants.

In recognition of this need for more precise methods of measuring surfactant performance, a series of studies has been instituted for the purpose of developing these required procedures. The first in this series has been recently published (3). This report has described the use of a specially designed pressure tensiometer capable of accurately measuring surface and interfacial tensions under pressure. The pressure tensiometer has been used to establish relationships which exist between interfacial tensions of propellants and water in the presence of selected surfactants and the HLB values of the surfactants. The solvent properties of the propellants and the stability of emulsions prepared with these propellants were also shown to be interdependent. These relationships were established on the interfacial properties of individual propellants and other nonmiscible fluids.

This paper is the second in this series and presents additional specialized techniques in this area.

Critical Micelle Concentration Measurement

Knowledge of the critical micelle concentration (CMC) of a surfactant in any system is valuable in a variety of ways. Specifically, it is an indication of the concentration range in which surfactant ions or molecules begin to aggregate and form micelles. The point at which micelles form is also indicative of the minimum surfactant concentration required for the solubilization of insoluble substances into the system and the maximum detergency and foaming manifested by the surfactant (5).

At concentrations greater than the CMC value, the surface tension of the solution does not decrease further with an increase in surfactant concentration. This property is useful in determining the critical micelle concentration. The slope of the curve, depicting the lowering of surface or interfacial tension with increasing surfactant concentration, approaches zero, and this area of the curve represents the CMC region. A great many experimental points are required to estimate the CMC accurately and generally it is more convenient to utilize a semilog plot. A plot of surface tension *versus* the log of concentration approximates linearity, and the CMC is clearly discernible by a sharp break in the slope of the curve.

Since the formation of surfactant micelles in propellant/water systems has never been reported, it was decided to utilize the pressure tensiometer (3) to investigate the possibility of the existence of this phenomenon in such systems.

The nonionic surfactants known commercially as the Igepal CO®* series were chosen for these experiments. This homologous group of nonylphenoxypolyoxyethylenes is desirable for such studies since the members of the group differ from each other by known percentages of ethylene oxide. This alone modifies the surface activity of these compounds since the hydrophobic portion of the molecule is the same for each member of the series.

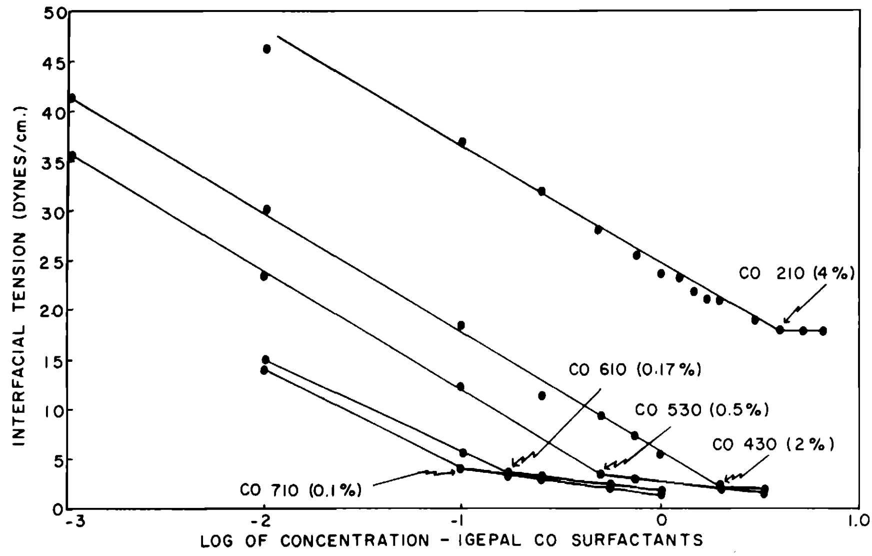

Figure 1.—Determination of critical micelle concentration by interfacial tension measurements. Igepal CO surfactants in propellant 11/water systems.

The results of interfacial tension readings obtained with the Igepals in Propellant 11/Water systems are shown in Fig. 1. The CMC for each surfactant is indicated and expressed as percentage (w/w). It can be noted that the CMC for each member of this surfactant family is related to its ethylene oxide content. The more hydrophilic members of the series form micelles at very low concentrations, while the more lipophilic members require higher concentrations and are not as effective in lowering interfacial

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* Igepal CO is a registered trademark of the General Aniline and Film Corp.

tension at equivalent concentrations. This relationship may be expressed in another manner by plotting the log of CMC against the ethylene oxide content of each surfactant. Figure 2 depicts this to be an approximate linear plot and illustrates the potential usefulness of these data. The surfactant properties of any other member of this series may be predicted in this system from its ethylene oxide content. A similar relationship may be established between the CMC of each surfactant and its HLB value as shown in Fig. 3.

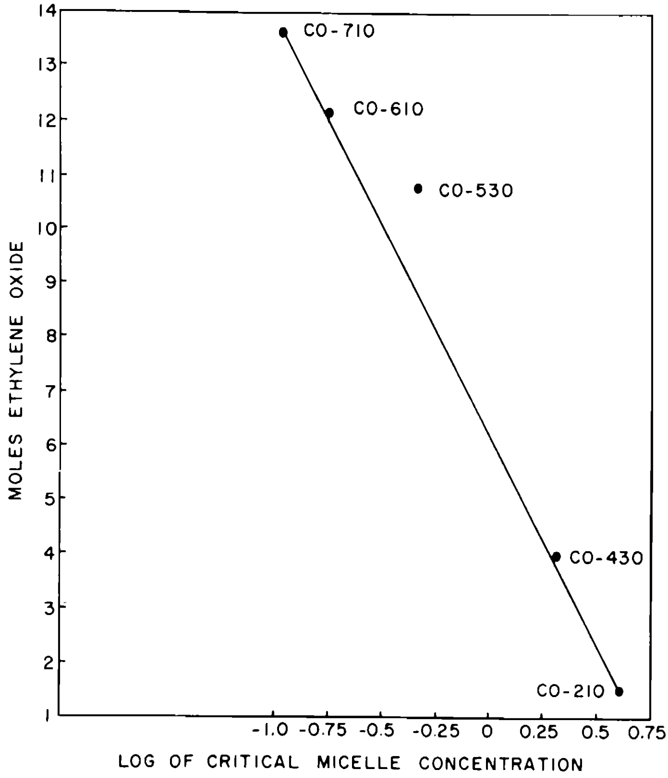

Figure 2.—CMC *vs.* ethylene oxide content of Igepal CO surfactants in propellant 11/water systems.

The measurement of the critical micelle concentration of these and other surface-active agents in systems containing water and Propellants 114, 12 or 113 have been accomplished in the pressure tensiometer as well. Results have been equivalent to those presented in this paper.

Based on this investigational evidence, it would appear that micellar formation is taking place in the propellant phase of the systems. The possibility of micelles forming in nonpolar liquids has been demonstrated in our laboratory in solubilization studies, and these data seem to be in agreement,

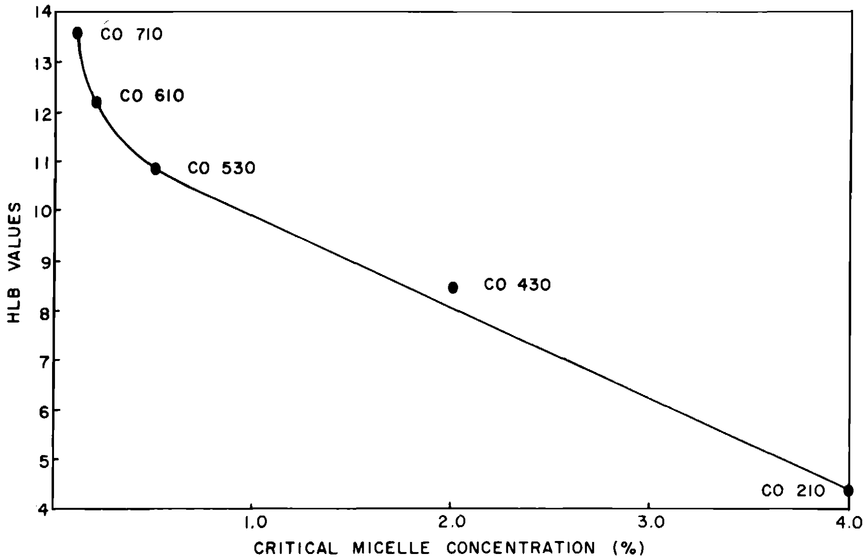

Figure 3.—CMC *vs.* HLB-Igepal CO surfactants in propellant 11/water systems.

INTERFACIAL TENSIONS OF PROPELLANT MIXTURES AND WATER SYSTEMS

The early work accomplished with the pressure tensiometer was carried out using individual halocarbon propellants. However, aerosol products usually contain mixtures of propellants, which are selected to achieve desirable pressures and other properties. Since the variety of propellant mixtures is infinite, it would be a difficult task to attempt to study all possible combinations. It was reasoned, therefore, that if meaningful data could be obtained with representative blends of propellants these data would be useful in predicting the properties of all other combinations of propellants within the ranges of the component members.

Five different blends of Propellants 11 and 12 were selected. The composition and some physical properties of these blends are listed in Table I.

TABLE I—CHEMICAL AND PHYSICAL PROPERTIES OF PROPELLANT 11/12 MIXTURES

Weight Per Cent Ratio of Propellant 11/12 Combinations	Liquid Density at 25°C, gm./cc.	Vapor Pressure at 25°C, psig.	Kauri-Butanol Value*
75:25	1.441	24	49.5
60:40	1.416	36	43.25
50:50	1.400	43	39
40:60	1.383	51	35
25:75	1.356	62	28.5

* Obtained by mathematical interpolation of known values for pure propellants.

The lowering of interfacial tensions between these propellant blends and water by the Igepal CO surfactants was measured in the pressure tensiometer. The role played by the composition of the propellant mixtures may be observed in Fig. 4. These curves were obtained with five different concentrations of the same surfactant, Igepal CO 520, and illustrate the fact that as the concentration increases the curve begins to approach linearity and the critical micelle concentration.

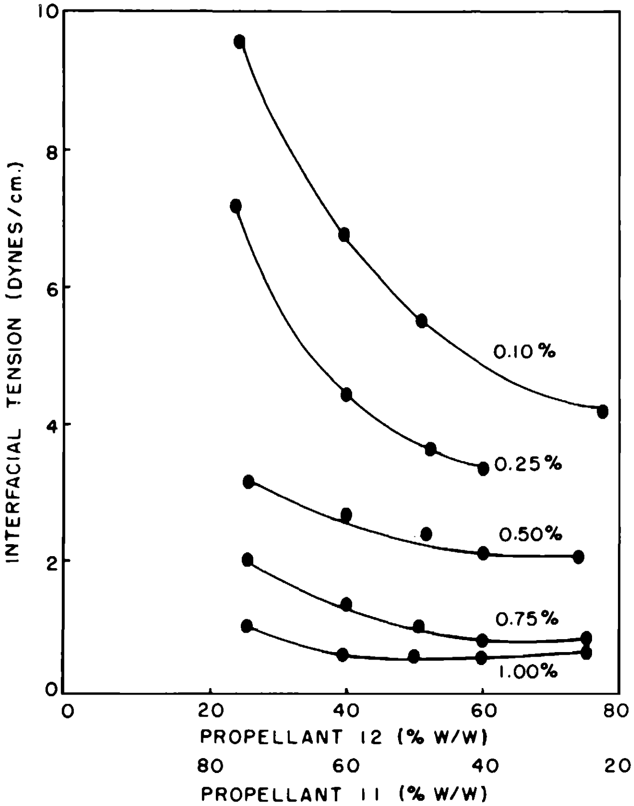

Figure 4.—Effect of concentration of Igepal CO 520 on interfacial tension of propellant 11/12 mixtures and water systems.

The significance of the curves in Fig. 4 may be recognized by the fact that, once the interfacial tension reduction produced by various concentrations of a given surfactant is measured for a few propellant blends, then the interfacial tension for any other blend within the range may be calculated.

Figure 4 also illustrates a unique versatility afforded by the use of propellant blends. In nonpropellant liquids, changes in surface tension may be accomplished only by varying the concentration of a given surfactant. However, the added feature imparted to aerosol propellants stems from the change in solvent power which different blends produce. Thus, different interfacial tensions may be obtained with the same concentration of a surfactant by merely varying the ratio of the component propellants in the mixture. This effect is more markedly demonstrated in Fig. 5.

An additional interesting observation may be recorded at this point. Inspection of the interfacial tensions produced by the Igepals with Propellant 11/12 mixtures (Fig. 4) indicates that they approach zero with increased surfactant concentration. Evidence that solubilization of water in the propellant layer was occurring at these low points was manifested by an increase in volume of the lower propellant layer and a corresponding decrease in the upper water layer within the pressure tensiometer. These observations led to an additional study on the solubilization of water in the halocarbon propellants with the aid of surfactants. The results of this study will be the subject of a subsequent paper in the near future.

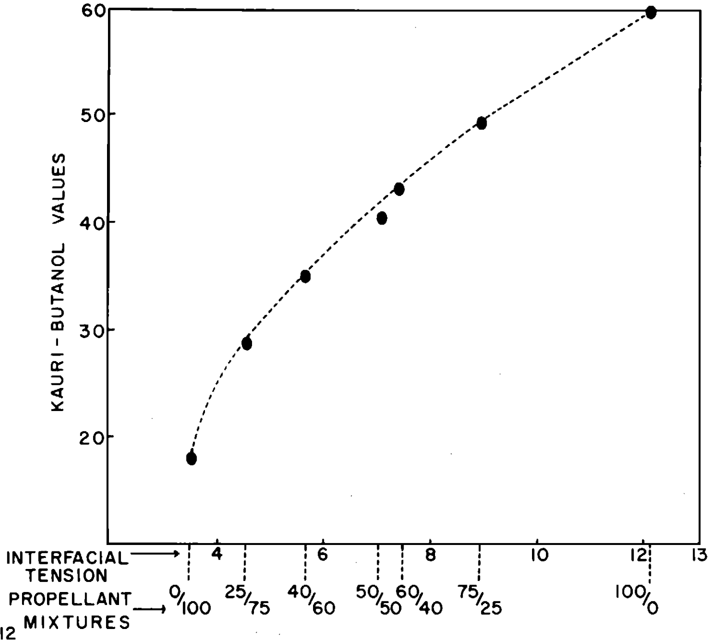

Figure 5.—Kauri-butanol values of propellant 11/12 mixtures compared to interfacial tensions of these propellant-water systems with 0.1% (w/w) CO 530 dissolved in the propellants.

Surfactant Solubility in Propellants

Published data on the solubility of a variety of substances in propellants are ill-defined, and the experimental methods used to determine solubility are often ill-designed. In most instances, quantitative data are lacking. Since a major part of this study depended on a knowledge of exact solubility data of the surfactants, an investigation was conducted to establish a simple but accurate method for determining solubility in the liquefied halocarbon propellants.

Previous attempts in our laboratory involved a method of withdrawing samples of "saturated" surfactant solutions in propellants which had been equilibrated at 25°C for 24 hours. The propellant was evaporated from an aliquot of the solution, and the residue represented the weight of the "dissolved" surfactant.

Certain inconsistencies in the results obtained by this method indicated that the aliquot samples were not true solutions but were actually very fine colloidal dispersions. Solutions which appeared to be clear to visual inspection demonstrated a Tyndall effect when viewed under a beam of light. This phenomenon had been reported by Becher and Clifton (6), who observed that aqueous solutions of nonionic surfactants manifested the same Tyndall effect. They attributed this to the heterogeneous nature of nonionic surfactants.

Attempts to circumvent this phenomenon were inconclusive. Ordinary methods of filtration were considered impractical due to the high volatility of the propellants, even if the undissolved surfactant could be held back by the usual filter media. Centrifugation at high speeds for 20 minutes failed to produce a concentration gradient within the samples, and this approach was discarded.

Since optical clarity could not be used as a criterion in solubility determinations, it was decided to employ a simple turbidometric technique to obtain a more accurate estimate of solubility. It was noted that, when accurately prepared solutions of known concentrations of surfactants in propellants were examined under a strong beam of light, the slight turbidity of these solutions remained constant until the concentration which exceeded the solubility was reached. The subsequent change in the polarization of the light beam was abrupt and occurred over an extremely narrow concentration range.

Mixtures of surfactants in propellants were prepared initially in increments of 10% (w/w) concentration and then in 1% (w/w) increments. After rotation for 24 hours at 25°C, these mixtures were examined under a beam of light. The percentage strength of that solution which just preceded the one which demonstrated the marked change in polarization of the Tyndall beam was considered to be the solubility of the surfactant in the given propellant or blend.

This method was found to be reproducible to within 1% when several determinations were made on different surfactant-propellant solutions. The Igepal CO surfactants with HLB values up to 10.8 were found to be soluble in all proportions in Propellant 11 and Propellant 11/12 mixtures. The solubility of the surfactants with higher HLB values decreased with an increase in Propellant 12 concentration. The solubility data obtained in this manner are in excellent qualitative agreement with predictions made on the basis of the Kauri-butanol values of the propellants and the HLB of the surfactants. It was noted that the higher the Kauri-butanol value of a mixture the greater the solubility of a surfactant and *vice versa*. An increase in the HLB value of a surfactant resulted in a corresponding decrease in solubility in any given propellant mixture. Table II is an example of data obtained in this manner.

TABLE II—PER CENT SOLUBILITY (w/w) OF IGEPAL CO SURFACTANTS

Propellant	Igepal, CO 210	Igepal, CO 430	Igepal, CO 520	Igepal, CO 530	Igepal, CO 630
11	S*	S	S	S	S
11/12 (75:25)	S	S	S	S	37
11/12 (60:40)	S	S	S	S	35
11/12 (50:50)	S	S	S	S	30
11/12 (40:60)	S	S	S	S	20
11/12 (25:75)	S	S	S	S	10
12	4	3	2	1	0.1

* S = Greater than 50% solubility.

CLOUD POINT DETERMINATIONS RELATED TO SURFACE PROPERTIES

Cloud point determinations have been utilized to establish relative degrees of association between surfactants and their solvents. The general technique involved has been to heat slowly a 1 or 2% solution of a nonionic surfactant in water and then to note the temperature at which the solution becomes cloudy. The more hydrophilic a surfactant the higher its cloud point in water. This index indirectly indicates the HLB value of the surfactant, and this method has been used to categorize groups of surfactants.

The cloud point method is limited, however, because extremely hydrophilic surfactants may not precipitate from water at temperatures approaching its boiling point, while the more lipophilic surfactants are insoluble in water even at room temperature.

Due to these limitations, another technique for establishing relative degrees of surfactant-solvent association has been developed. This technique is essentially a "salting-out" phenomenon and, because the endpoint is the production of a cloudy precipitate, it has also been called a cloud point method. Greenwald and co-workers (7) have shown that a dioxane-benzene solution of an oil or surfactant may be titrated with water to a cloud point value which is related to the HLB character of the oil or surfactant.

A similar cloud point technique is used to estimate the solvent power of organic solvents, including the liquefied aerosol propellants. Kauri-butanol values for solvents are obtained by titrating a standard solution of Kauri gum dissolved in butyl alcohol at 77°F with the liquid under consideration. The endpoint is reached when the turbidity produced due to precipitation of the gum prevents reading 10 point type through the Erlenmeyer titration flask (8).

It was reasoned that this technique conducted in an apparatus capable of maintaining the integrity of a pressure-producing system could provide useful information on surfactant performance in aerosol propellants. It was further reasoned that, since there is an interdependence of the HLB and the solubility of a surfactant with interfacial tension reduction, it was conceivable that a cloud point technique would be a rapid and accurate means of predicting surface activity in aerosol systems.

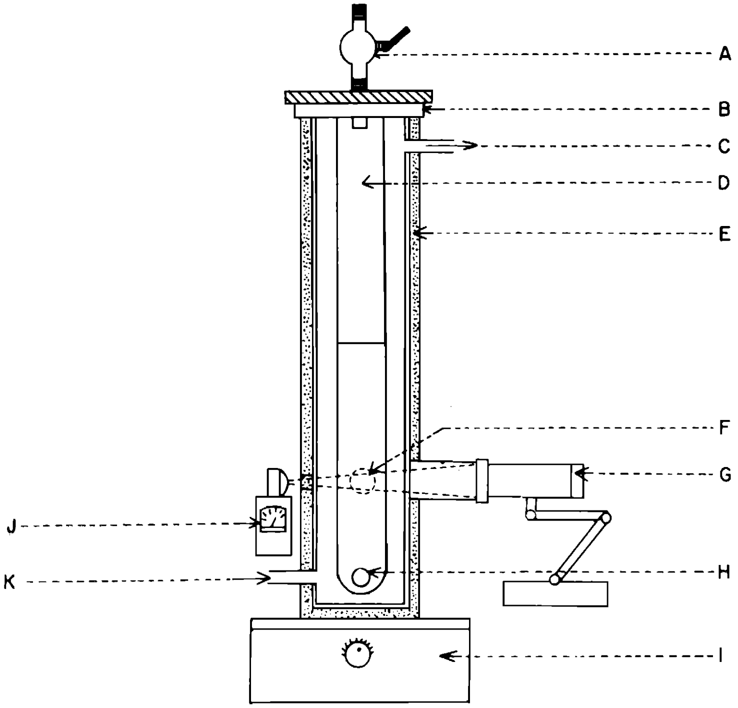

Figure 6.—Schematic representation of apparatus for the determination of cloud points of propellant-surfactant mixtures.

The five blends of Propellants 11 and 12 described in Table I were employed as the solvents for the Igepal CO surfactants. It was decided to titrate these solutions with Propellant 114. Any other combinations of propellants may be used, provided that the surfactants are soluble in one and less soluble in the other (titrating) propellant.

Description of Apparatus: The plexiglass safety tube for a three-ounce Fischer and Porter aerosol compatibility tube was modified to convert it into a constant temperature jacket for the apparatus (Fig. 6). The jacket was fitted with inlet and outlet tubes to permit the circulation of water which maintained a constant temperature in the apparatus. The circulating water was maintained at 25°C and was pumped into the jacket at inlet tube (K) and back into the constant temperature bath from the outlet tube (C).

To minimize subjective errors in arriving at a sharp and reproducible endpoint, a photoelectric cell and a light beam were positioned on both sides of the tube so as to permit the fixed beam of light to pass through the contents of the tube and then register on the photoelectric cell at the opposite side. The light beam was generated by a small but powerful spotlight (G) mounted on an adjustable base. The Plexiglass jacket was completely covered with black Velcro* fastener tape (E) to prevent any incident or reflected light from entering the tube and thus interfering with the reading of the light beam intensity. Velcro tape was selected as the lightproof cover since it could be removed and reapplied to the apparatus many times without losing its ability to adhere. A strip of the female portion of the tape was cut away to permit reading of the millimeter reference scale on the glass tube. During each determination this was covered with a corresponding male strip.

Small holes were also cut into the Velcro tape to permit the beam of light to enter the tube and to emerge at a point on the opposite wall where it registered on the photoelectric cell. A view of the contents at right angles to the beam of light was provided by another small opening in the tape (F).

The photoelectric cell utilized in this apparatus was a Model S Brockway Exposure Meter** (J). The light scale on the photometer permitted reading of the endpoint directly in each cloud point determination. The intensity of the light beam passing through the clear solution of surfactant at the start of each determination was adjusted to produce a reading of 250 footcandles on the photometer scale. The endpoint was read when a cloud was produced which scattered the beam of light sufficiently to register only 5 footcandles on the scale.

A cloud point determination was carried out by first accurately weighing 4.0 g. of the surface-active agent in the glass tube (D). A magnetic ball stirrer (H) was placed in the tube. The tube was sealed with a stainless steel adaptor to which was fitted a toggle valve (A). The adaptor was

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* Velcro Corporation, 681 Fifth Avenue, New York, N. Y. 10022.

** Brockway Camera Corp., New York, N. Y. 10038.

secured in place by means of the nylon packing and aluminum packing nut (B) normally used to hold a standard 1 in. aerosol can valve in the mouth of the compatibility tube. As an additional measure against leakage of propellants, the adaptor was constructed with an "O" ring and a rubber gasket.

This assembly was then placed on a magnetic stir plate (I) and connected by means of a flexible pressure hose attached to the valve (A) to a Foresman Liquid Gas Manipulator* which in turn was connected to a propellant supply tank. The propellant mixture under investigation was then pressure-filled into the apparatus. A quantity of propellant just short of the calculated amount was introduced into the tube. This was permitted to reach a temperature of 25°C, and then the volume was carefully adjusted by adding more propellant. The millimeter reference scale on the glass compatibility tube had been calibrated so as to enable the conversion of propellant volume to weight. The final adjustment was made in the volume of the contents to produce a total of 20 g. of solution. Thus, every determination was carried out on a 20% (w/w) solution of a surfactant in a propellant mixture.

With the light shield (E), spot light (G) and photometer (J) in position, the valve (A) was then regulated to admit Propellant 114 into the tube. When the vapor pressure of the propellant mixtures in the tube was higher than the vapor pressure of Propellant 114, the Foresman apparatus was used to provide a positive pressure to Propellant 114, and this permitted the addition of the propellant in controlled quantities. As Propellant 114 was slowly added to the surfactant solution in the tube, the rotation of the magnetic stirrer was adjusted to provide thorough mixing and to maintain the precipitate which ultimately formed in a state of moderate agitation.

Titration with Propellant 114 was continued until the first appearance of a precipitate of the surfactant. Simultaneously, the indicating needle in the photometer registered a decrease in the light intensity. At this point the addition of Propellant 114 was discontinued, and in most instances the initial precipitate slowly redissolved while the photometer reading again approached 250 footcandles. The contents of the tube were permitted to reach 25°C, and then Propellant 114 was added slowly until the photometer reading was decreased to 5.

A reading was made again after a short interval to insure temperature equilibration, and adjustments were made when necessary. A constant photometer value of 5 was construed to indicate that none of the precipitate had redissolved and that the endpoint had been reached. The male Velcro strip was then removed to permit a reading of the final volume of the contents of the tube on the reference scale. The difference between the original and final volumes was used to calculate the weight of the Propellant 114 which had been required to produce the cloud point.

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* Robert A. Foresman, Jr., 1690 Margaret St., Philadelphia 24, Pa.

This procedure was found to be reproducible when several determinations, carried out with the same surfactants, produced cloud point values which varied only in the first decimal point.

The results of some cloud point determinations are depicted in Fig. 7. It is apparent that, as the amount of Propellant 12 increases the cloud point for any single surfactant is lowered, or, conversely, as the percentage of Propellant 11 increases, a correspondingly larger amount of Propellant 114 is required to produce the cloud point for a given surfactant. This is in agreement with solubility relationships discussed earlier.

Fig. 8 shows the correlation existing between the log of cloud points and the ethylene oxide content of the Igepal CO surfactants in the different propellant mixtures.

These two plots (Figs. 7 and 8) clearly indicate that the cloud point of a surfactant obtained by this technique is related to the solvent power of the propellant mixture and the HLB index of the surfactant.

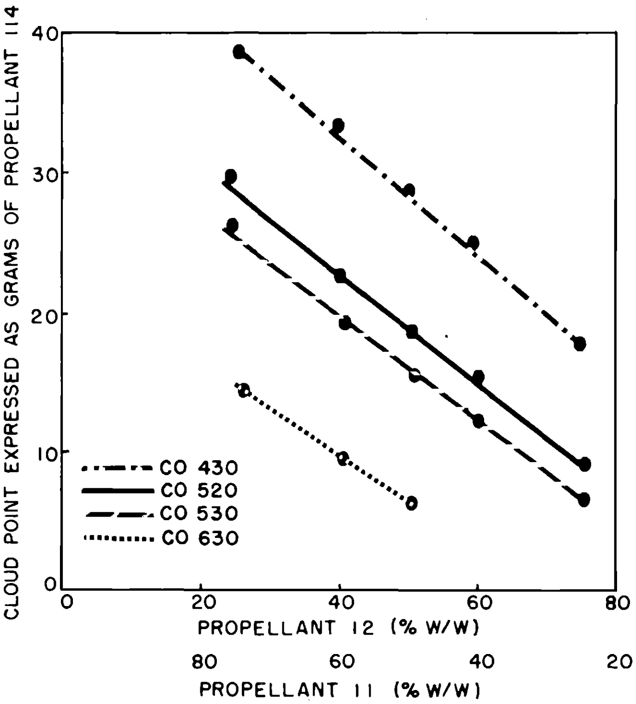

Figure 7.—Cloud points of Igepal CO surfactants in propellant 11/12 mixtures.

Cloud points for these surfactant-propellant systems were then compared with the interfacial tensions they manifested against water in the pressure tensiometer. The relationship for different concentrations of four different

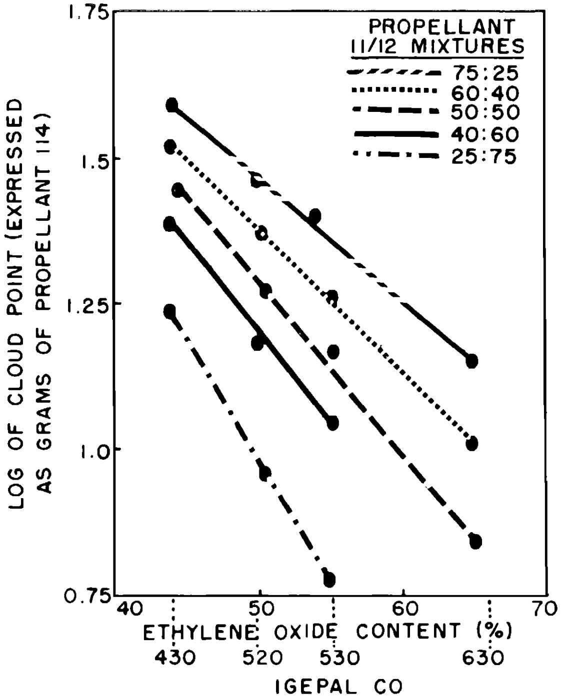

Figure 8.—Relationship of ethylene oxide content of Igepal CO surfactants with their cloud points in propellant 11/12 mixtures.

surfactants in the same propellant mixtures is shown in Fig. 9. This indicates that cloud point values may be directly correlated with interfacial tension data for the same solutions. In view of these results the cloud point technique is not only more rapid but apparently more sensitive than the interfacial tension method for differentiation of HLB characteristics.

These cloud point data demonstrate the utility of the method with aerosol propellants. Cloud point values are related both to the composition of the propellant mixtures and to the hydrophile-lipophile character of the surfactant. The technique may be used in predicting cloud point-dependent properties of either surfactants or propellants or their blends.

Summary and Conclusions

More exact and meaningful data have been made possible by means of special techniques developed for pressure systems. The use of a pressure tensiometer has demonstrated that critical micelle concentrations of nonionic surfactants may be measured in liquefied halocarbon propellant/water systems and related to the properties of the surfactants. Similar relationships may be shown by means of the pressure tensiometer to exist between interfacial tension measurements of propellant mixtures and water in the presence of selected surfactants.

A method is reported which may be used to obtain more precise solubility values for nonionic surfactants in propellants and their blends.

A cloud point technique utilizing aerosol propellants has been shown to offer a rapid and accurate method for screening and predicting surfactant behavior in these systems. This method is considered to be significant in determining the hydrophile-lipophile character of a surfactant in a propellant mixture.

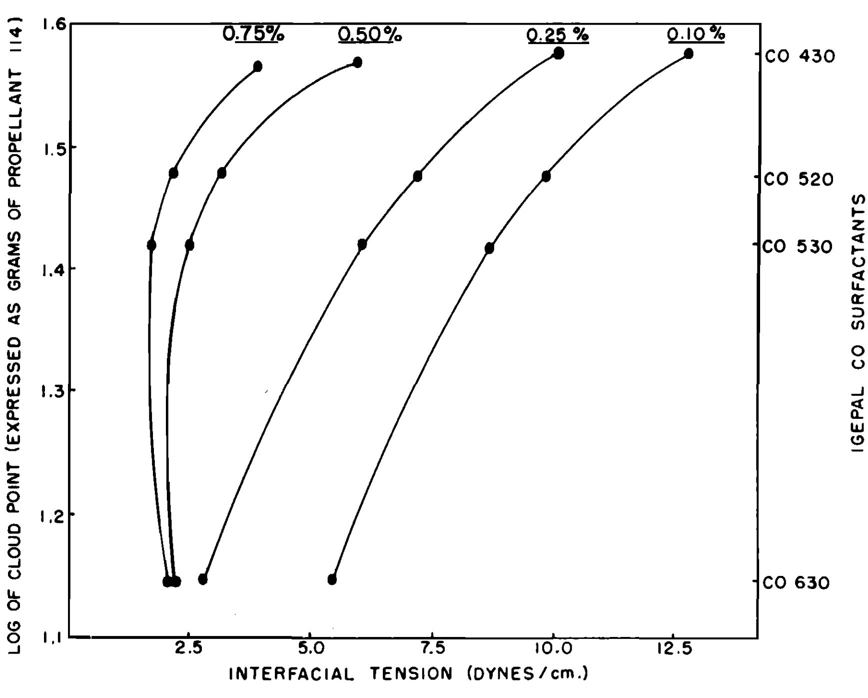

Figure 9.—Relationship between log of cloud points of selected Igepal CO surfactants and interfacial tensions of propellant 11/12 (75:25)-water systems.

Evidence has been obtained to indicate that the nonpolar nature of the halocarbon propellants may be sufficiently modified by surfactants to enable them to dissolve polar compounds. The methods reported in this study may be utilized to establish the required relationships to accomplish this and to determine other effects dependent on surface activity on a more valid basis than was heretofore possible.

Acknowledgments: The authors are grateful to Dr. Milo Gibaldi for his assistance during the conduct of this study.

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1. Freon Propellants from E.I. du Pont de Nemours Co., Inc., Freon Products Division, Wilmington, Del.
2. Aerosol valves from the Risdon Manufacturing Co., Naugatuck, Conn.
3. Aerosol plastic coated bottles from the Wheaton Plasti-Cote Company, Mays Landing, N. J.
4. Igepal surface-active agents from Antara Chemicals Division of General Aniline & Film Corp., New York.

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