[16d]); and is being adapted in work under the Hormel Foundation fatty acid project. The experiences of our colleagues have contributed to the progress reported here.

## Acknowledgments

It is our pleasant duty to thank D. M. Sand, who was in charge of the preparations of α-cyclodextrin. W. O. Lundberg, R. T. Holman, J. R. Chipault, and O. S. Privett provided numerous samples of lipides. Generous gifts of glycerides were obtained from Miss Audrey T. Gros, Southern Regional Research Laboratories, and F. H. Mattson, Procter and Gamble Company. The substances were of great value to us, and many of them have been listed here.

## Summary

Procedures for qualitative and quantitative paper chromatography of lipides have been described in detail, together with some practical applications.

With the monochain lipides it was found that one developing system serves universally. The long aliphatic chains essentially determine the chromatographic properties so that suitable conditions for chromatographing any lipide or lipide-like entity are predictable. For the same reason total analysis of natural mixtures cannot be done on one paper chromatogram due to superpositions.

For complete analysis of natural mixtures of fatty acids it is advisable at the present time to combine paper chromatography with some other separation method. Distillation supplements best but requires gram quantities of material while paper chromatography is applicable on gamma or milligram scale. Chain-length analysis by paper chromatography and low-temperature chromatography have been introduced and are promising methods to approach a completely micro method for analyzing complex mixtures.

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[Received December 6, 1956]

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# The Viscosities of Nonaqueous Solutions of Magnesium Caprate and Laurate

A. N. BOSE AND VIRENDRA K. DIXIT, Lucknow University, Lucknow, India

VISCOSITIES of nonaqueous solutions of sodium and potassium soaps were first studied by Mata Prasad (1). Ostwald and Riedel (2), Cawley, Carlie, King, and Kingman (3), and Wood, Nissan, and Garner (4) determined the viscosities of solutions of aluminum soaps in nonaqueous solvents. Alexander and Grey (5) made a critical study of the viscosity of aluminum soaps in benzene and studied the effect of the peptizer, cresol. They also tested the validity of an empirical equation given by Schulze and Blaschke (6) and later derived theoretically by Huggins (7).

In the present study the viscosities of magnesium caprate and magnesium laurate in aromatic hydrocarbons and aliphatic alcohols were determined at different temperatures and concentrations in an endeavor to determine whether the temperature affects the micelle size.

*Materials Used.* Capric and lauric acids (B.D.H.) were distilled under reduced pressure. Magnesium chloride (Merck Puriss) was used for the preparation of soaps.

Hydrocarbons were kept over calcium chloride for 15 days and then distilled and stored over sodium wire. They were again distilled at the time of preparation of solutions. The solvents had the following boiling points at atmospheric pressure:

| | B.P. |
|---|---|
| Benzene (B.D.H.) (Analar) | 79.5°C. |
| *o*-Xylene (Merck Puriss) | 143–144°C. |
| *p*-Xylene (Kodak) | 138.5°C. |
| Toluene (Thomas Tyrer) | 110.5°C. |
| *m*-Xylene (Merck Puriss) | 138°C. |

Alcohols were kept over potassium hydroxide for a week, then distilled and refluxed over 1% calcium for eight hours and again distilled. The distillates had the following boiling points at one atmospheric pressure:

| | B.P. |
|---|---|
| Butanol-1 (Merck Puriss) | 117–118°C. |
| 3-Methyl butanol-1 (Merck Puriss) | 129–130°C. |
| Hexanol-1 (B.D.H.) | 157–158°C. |
| Octanol-2 (Naarden) | 178°C. |

The magnesium soaps were prepared and analyzed by the same method as used by Pink (8) for magnesium oleate.

*Experimental Method.* As the solubility of these soaps at room temperature is low, their solutions were prepared at 70°C. in all solvents except benzene, which was used at 50°C. When these solutions were allowed to cool, soaps crystallized out. Therefore Ostwald's method for the determination of viscosity, which requires a knowledge of density of the solution, could not be applied. The viscosities of these solutions at different temperatures were determined by the modified method of Scarpa (9) which has been successfully used by Chatterji and Ram Gopal (10) and Chatterji and Bose (11) for the determination of viscosities of supersaturated solutions.

## Discussion

A straight line for oil solutions is obtained when log $\eta$ is plotted against 1/T (Figures 1 and 2). The viscosity data therefore fit Arrhenius' equation (12)

$$\eta = A\, e^{E_{vis}/RT}$$

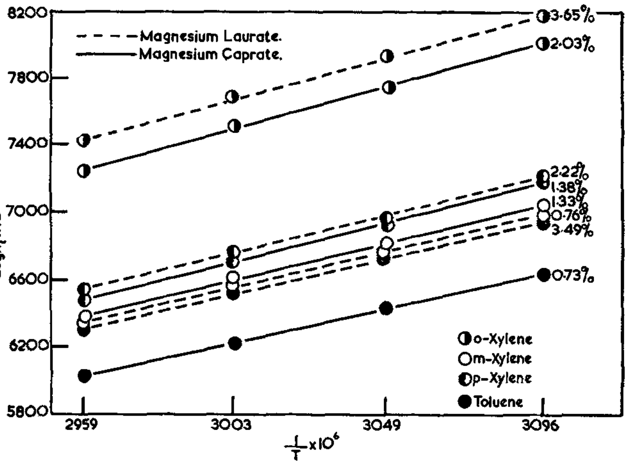

FIG. 1. Plot of log $\eta$ against 1/T for solutions of hydrocarbons.

Thus it can be concluded that the size of the micelles in solution does not change with temperature. In the case of zinc soaps Martin and Pink (13) observed that the solubility of the soaps increased abruptly at a critical temperature. These workers pointed out that the increase in solubility is not caused by an alteration in the degree of aggregation of the soap molecules but is by a mesomorphic change in the solid soaps.

The values of $E_{vis}/R$, calculated according to the equation of Arrhenius for one concentration only, are given in Table I. Value of $E_{vis}/R$ has been given for only one concentration as it does not change much with concentration.

From the results given in Table I it is apparent that the values of $E_{vis}/R$ fall into two categories: a) for hydrocarbons it is between 1,000 and 1,320 and b) for alcohols it is between 2,300 and 2,950.

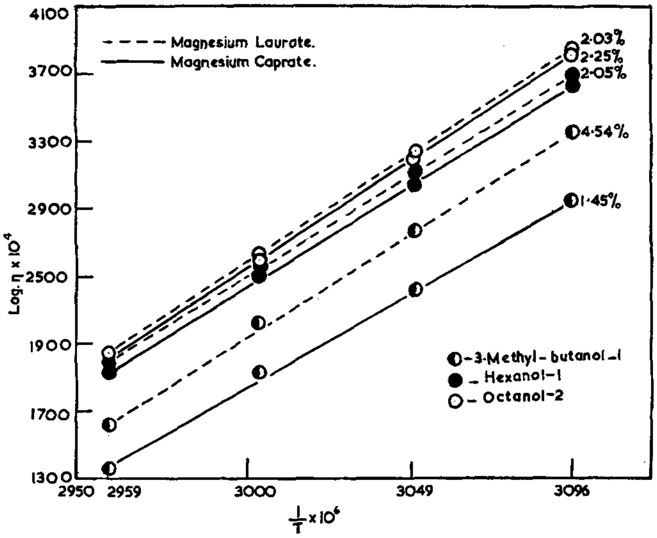

FIG. 2. Plot of log $\eta$ against 1/T for solutions of alcohols.

These values are not very different from the values for $E_{vis}/R$ of the pure solvents. Thus it can be concluded that there is not much interaction between the micelles and the solvent molecules. Furthermore in most cases the values of $E_{vis}/R$ for magnesium caprate and magnesium laurate for the same solvent are not much different from each other.

In Tables II and III the variation of relative viscosity with temperature is given. From these tables it is observed that the value of d/dt ($\eta$s/$\eta$o) decreased very slightly with the increase in temperature. These data further support the conclusion that there is very little interaction between the solvent molecules and the solute molecules, also that the degree of association of the soap molecules is not appreciably affected by temperature changes.

TABLE I

$E_{vis}/R$ Values for Magnesium Caprate and Laurate Solutions

| Solvent | $E_{vis}/R$ | Mg.–caprate | | Mg.–laurate | |
|---|---|---|---|---|---|
| | | Conc. g./100 g. solvent | $E_{vis}/R$ | Conc. g./100 g. solvent | $E_{vis}/R$ |
| Benzene | 1169 | 2.230 | 1320 | 1.936 | 1195 |
| Toluene | 1009 | 2.211 | 1159 | 2.259 | 1010 |
| *o*-Xylene | 1125 | 1.322 | 1169 | 2.056 | 1169 |
| *m*-Xylene | 1018 | 1.329 | 1115 | 2.210 | 1001 |
| *p*-Xylene | 1100 | 1.376 | 1164 | 1.553 | 1055 |
| Butanol-1 | 2304 | 1.395 | 2366 | 2.100 | 2378 |
| 3-Methyl butanol-1 | 2688 | 1.452 | 2911 | 1.486 | 2851 |
| Hexanol-1 | 2675 | 1.128 | 2758 | 2.046 | 2759 |
| Octanol-2 | 2896 | 1.160 | 2941 | 2.027 | 2988 |

(Note: The values of $E_{vis}/R$ have been calculated between the temperature 50°–60°C. for all the solutions except those in benzene for which it is between 40°–50°C.)

The existence of micelles in these solutions was established by the method used by Singleterry and Arkin (14). Thus, when Rhodamine B was added to

TABLE II

The Variation of Relative Viscosity with Temperature of Nonaqueous Solutions of Magnesium Caprate

| Solvent | Conc. g./100 g. of solvent | Relative viscosity d/dt ($\eta$s/$\eta$o) | | |
|---|---|---|---|---|
| | | 50°C. | 60°C. | 70°C. |
| Toluene | 2.211 | 1.146 | 1.131 | 1.120 |
| *o*-Xylene | 1.322 | 1.100 | 1.096 | 1.086 |
| *p*-Xylene | 1.376 | 1.134 | 1.129 | 1.100 |
| *m*-Xylene | 1.329 | 1.120 | 1.119 | 1.106 |
| Butanol-1 | 1.395 | 1.059 | 1.053 | 1.035 |
| 3-Methyl butanol-1 | 1.452 | 1.084 | 1.077 | 1.050 |
| Hexanol-1 | 1.128 | 1.053 | 1.044 | 1.040 |
| Octanol-2 | 1.160 | 1.045 | 1.040 | 1.030 |

TABLE III

The Variation of Relative Viscosity with Temperature of Nonaqueous Solutions of Magnesium Laurate

| Solvent | Conc. g./100 g. of solvent | Relative viscosity d/dt($\eta s/\eta o$) | | |
|---|---|---|---|---|
| | | 50°C. | 60°C. | 70°C. |
| Toluene | 2.259 | 1.127 | 1.126 | 1.121 |
| *o*-Xylene | 2.056 | 1.118 | 1.113 | 1.095 |
| *p*-Xylene | 1.553 | 1.119 | 1.115 | 1.104 |
| *m*-Xylene | 2.210 | 1.141 | 1.142 | 1.136 |
| Butanol-1 | 2.106 | 1.073 | 1.066 | 1.050 |
| 3-Methyl butanol-1 | 1.486 | 1.090 | 1.070 | 1.050 |
| Hexanol-1 | 2.046 | 1.070 | 1.065 | 1.058 |
| Octanol-2 | 2.027 | 1.080 | 1.067 | 1.050 |

solutions of magnesium soaps, fluorescence was observed. This indicated the presence of micelles in the solutions. The formation of soap micelles is further supported by the fact that the solubility of water in these solvents is increased by magnesium soaps. Additional quantitative work is in progress in this laboratory. Pink and Martin (13) have determined by molecular weight measurements that each micelle contains 5 to 6 molecules of zinc soap and that the molecular weight of the micelle changes with the concentration of soap. Soyenkoff (15) has also detected particles of colloidal dimensions in solutions of iron and nickel soaps in benzene.

## Viscosity Concentration Relationship

The equation of Schulze and Blaschke (6)

$$\eta sp/c = (\eta sp/c)c = o\ (1 + k\,\eta sp)$$

has been applied to these solutions by plotting $c/\eta sp$ against the concentration. The graphs are smooth curves and not straight lines as had been obtained in the case of aluminum soaps by Alexander and Grey (5). This difference probably results from the change in the size of the micelles of magnesium soaps with the concentration.

The change in the size of the soap micelles with concentration is further evidenced by the fact that the value of log $(\eta s/\eta o)/c$ decreases with increasing concentration of the soaps, where $\eta s$ is the viscosity of the solution and $\eta o$ is the viscosity of the solvent. Kemp and Peters (16) as well as Alexander and Grey (5) pointed out that, if the size of the particles does not change with the concentration, the value of log $(\eta s/\eta n)/c$ should approach a constant value. In the case of aluminum soaps the value obtained by Alexander and Grey was 2.6, but for the solutions studied in the present communication no constant value for log $(\eta s/\eta o)/c$ was observed.

## Summary

The viscosities of nonaqueous solutions of magnesium caprate and magnesium laurate have been determined at different concentrations and temperatures. Because Arrhenius' equation was found to be applicable to these solutions, it has been concluded that the size of the micelles does not change with the increase in temperature.

The variation of relative viscosity with temperature was also calculated. The fact that the value of d/dt $(\eta s/\eta o)$ does not change much with temperature further supports the conclusion that the molecular aggregation of the soap molecules in the solvent is not affected by the temperature.

The equation of Schulze and Blaschke is not applicable to these solutions within the concentration range studied in the present work, probably because the size of the micelles changes with the increasing concentration of the soaps.

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[Received July 23, 1956]

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# Melting and Crystallization of Vegetable Waxes

RAUL DODSWORTH MACHADO, Instituto de Óleos, Rio de Janeiro, Brazil

PHENOMENA related to phase changes are most important in the analysis of waxes. Data are presented here which were obtained by a practical, rapid, and sufficiently accurate method (about 20 minutes for each sample). It is suggested that the following five tests be adopted as a routine procedure for waxes: a) odor, b) surface appearance, c) initial melting-point, d) melting point, e) crystallization point.

## Method

From the wax submitted for analysis a small part is taken with the necessary care to make it truly representative. The quantity taken must be sufficient to form a big drop on a half microscope slide, over a hot plate at 100–110°C. If the sample is dirty, a suitable method of purification, such as centrifugation of the melted wax, must be used (1). When the wax is being heated, its characteristic odor becomes stronger. The melted wax on the half-slide is well mixed with a glass rodlet (1 to 2 mm. in diameter), and a droplet is transferred to a circular cover slide (No. 1 thickness, 12-mm. in diameter). The droplet must be spread so as to form a thin layer.

The cover slide is rapidly transferred from the hot plate to a metal cooling block at room temperature to solidify the wax quickly. The surface of the droplet is then examined. This corresponds to the "spot melting test" (2). The surface may be dull (carnauba wax) or light-reflecting, varnish-like (licuri wax). The cover-slide with the droplet is then adapted to a