

## **Turbidimetric Determination of the Molecular Weight of Micelles of Dihexyl Sodium Sulfosuccinate in Water**

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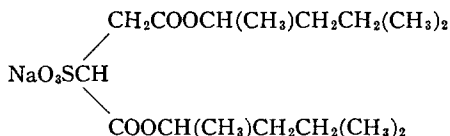
**T**HIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the first of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$4.00 per page) will not be made and no reprints will be furnished free.

### Turbidimetric Determination of the Molecular Weight of Micelles of Dihexyl Sodium Sulfosuccinate in Water

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January 14, 1948

**M**ANY papers concerned with the subject of micelle formation in solutions of colloidal electrolytes have appeared in the literature. The most recent of these have dealt with solubilization,<sup>1,2</sup> the use of dyes in locating the critical concentration necessary for micelle formation<sup>3</sup> (hereinafter designated by *c.m.c.*), and the structure of micelles as indicated by x-rays.<sup>4,5</sup> As yet, there has been no publication concerned with the evaluation of the molecular weight(s) of micelles by the turbidimetric method originated by Debye.<sup>6</sup>

We have used this method for determining the molecular weight of the micelles formed in water by the surface active agent dihexyl sodium sulfosuccinate (marketed by the American Cyanamid Company under the trade mark of "Aerosol" MA).



Molecular weight 388.5 just above the *c.m.c.* (about 0.024 g/cc or 0.0617 molar as determined here by the pinacyanol chloride method<sup>3</sup>).

The light scattering method requires the evaluation of the absolute turbidities of a series of solutions of different concentrations as well as the determination of the quantity  $\partial\mu/\partial c$  ( $\mu$  designates refractive index) for the solvent-solute pair being studied. The residual turbidity ( $\tau_2 = \tau_{\text{solution}} - \tau_{\text{solvent}}$ ) is given by

$$Hc/\tau_2 = 1/M_2 + 2Bc. \quad (1)^6$$

The constant  $H$  is equal to  $32\pi^3/3 \cdot 1/N\lambda^4 \cdot \mu_0^2 \cdot (\partial\mu/\partial c)^2$ . The turbidities were measured in a 90° instrument using RCA photo-multiplier tubes (931-A's). This turbidimeter measures a quantity proportional to the ratio of the in-

tensity of the light scattered at 90° to that of a small fraction of the light in the incident beam. Benzene, whose absolute turbidity is known,<sup>7</sup> was used as a standard. The solutions were filtered repeatedly into the turbidity cells through porous porcelain filter candles (porosity 0.3 with maximum pore size of 0.6 $\mu$  from Selas Corporation of America, Philadelphia 34, Pennsylvania) until free from motes. Three to five readings were made on each solution (at ca. 26°C) using approximately parallel light ( $\lambda 5461\text{\AA}$ ) from an H-3 mercury lamp. The values of  $(\partial\mu/\partial c)$  were determined for us by Mr. E. W. Anacker of the Department of Chemistry at Cornell University. Three pairs of solutions were studied at Cornell. These were: (1), 0 and 0.01 g/cc; (2), 0.05 and 0.06 g/cc; and (3), 0.09 and 0.10 g/cc. The values of  $\Delta\mu/\Delta c$  determined were: (1) 0.1201; (2) 0.1092 ( $\pm 0.001$ ); (3) 0.1113 ( $\pm 0.001$ ). The first value is to be suspected because 0.01 g/cc produces a cloudy solution which can be removed only by a fine porosity filter and which rendered indistinct the image of the slit in the differential refractometer. The values of  $H$  have been calculated in three ways: (I) assuming a straight line relationship between  $\Delta\mu/\Delta c$  and  $c$  for the solution pairs (2) and (3) with  $\Delta\mu/\Delta c$  equal to 0.1092 below 0.05 g/cc; (II) assuming a smooth curve relationship using all three points; and (III) assuming a sharp rise in  $\Delta\mu/\Delta c$  below *c.m.c.*

In Fig. 1 are given two curves: (1),  $\tau_2$  vs.  $c$  showing the break between 0.02 and 0.03 g/cc; and (2),  $Hc/\tau_2$  vs.  $c$  using  $H$  values according to (I). Proceeding from high to low concentrations, curve (2) exhibits a marked rise in ordinate value at a concentration which lies to the high side of the *c.m.c.* determined by the pinacyanol chloride method. This rise continues on the low side of the *c.m.c.*, suggesting that the low concentration branch might climb to give an ordinate intercept equal to the reciprocal of the molecular weight of the single molecules. In the data presented here, this does not happen; instead, the curve starts descending. This is probably caused by the inaccuracy of the turbidity data at the two lowest concentrations studies. (Those acquainted with this method will realize that it is not easy to evaluate turbidities as low as  $1 \times 10^{-6} \text{ cm}^{-1}$ .) The high concentration branch of curve

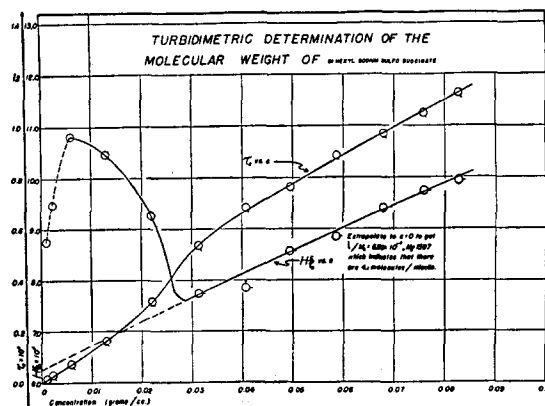


FIG. 1.

(2) has been extrapolated to  $c=0$  in order to get  $1/M_2 = 6.26 \times 10^{-4}$ , which means that  $M_2$  is 1597 and that the aggregation number is  $1597/388.5 = \sim 4$  (actually 4.11) molecules per micelle in this fairly narrow concentration range. According to Vetter<sup>8</sup> the aggregation number is 23.6. If  $H$  values are calculated according to (III), the same answer is obtained for  $M_2$ . If (II) is used,  $M_2$  comes out 1430 and the aggregation number is 3.7. All three methods of treating the  $\Delta\mu/\Delta c$  data produce a sharp break in the  $Hc/\tau_2$  curve in the vicinity of *c.m.c.* We are attempting to establish the  $\Delta\mu/\Delta c$  vs.  $c$  relationship on the concentration range (0 to 0.09 g/cc) with a greater degree of certainty. It is anticipated that this will again lead to an aggregation number of 4 in agreement with this preliminary result.

The *c.m.c.* for the substance under investigation has been determined by other methods<sup>9</sup> which indicate that this concentration occurs in the vicinity of 0.055 molar (0.021 g/cc). The turbidity curve would lead one to believe that the *c.m.c.* cannot be specified sharply but that the change to micelles is accomplished over the range 0.02–0.03 g/cc. For this particular substance, this is in agreement with all other methods which show the effect.

Upon being informed of these results Professor Debye told us that Mr. E. W. Anacker and he had used the turbidimetric method for determining molecular weights of micelles of cationic soaps. The micelles of the substances which they investigated had molecular weights about ten times as great as that found for the substance with which the present note is concerned. Professor Debye also told us of his method of working up the data in the special case of colloidal electrolytes. This method requires that  $\tau_2$  vanish below the *c.m.c.* In the case presented here this does not happen, and so the data have been treated in the usual manner. (Professor Debye and Mr. Anacker communicated their results to the Rubber Reserve on October 30th and 31st, 1947.)

This problem was originally suggested by one of us (J. K. Dixon). The experimental turbidity measurements and calculations were carried out by R. F. Stamm. The electronic circuits, as well as other contributions, were made by T. Mariner. After the turbidities were measured, the concentrations were determined in duplicate by Mr. Norman Woodberry (wt. percent solids) and Dr. John W. Berry (percent Na). Mr. John J. Whalen made up all the solutions and performed the dye experiments. We wish to thank Professor Debye for his help and Mr. Anacker for determining the  $\Delta\mu/\Delta c$  values. These experiments are being continued.

<sup>1</sup> J. W. McBain and K. E. Johnson, *J. Am. Chem. Soc.* **66**, 9–13 (1944).

<sup>2</sup> R. S. Stearns, H. Oppenheimer, E. Simon, and W. D. Harkins, *J. Chem. Phys.* **15**, 496–507 (1947).

<sup>3</sup> M. L. Corrin, H. B. Kleven, and W. D. Harkins, *J. Chem. Phys.* **14**, 480–486 (1946).

<sup>4</sup> W. D. Harkins, R. W. Mattoon, and M. L. Corrin, *J. Am. Chem. Soc.* **68**, 220–228 (1946).

<sup>5</sup> S. Ross and J. W. McBain, *J. Am. Chem. Soc.* **68**, 296–299 (1946).

<sup>6</sup> P. Debye, *J. Phys. and Colloid Chem.* **51**, 18–32 (1947).

<sup>7</sup> Jean Cabanes, *La Diffusion Moléculaire de la Lumière* (Paris, 1929), p. 197.

<sup>8</sup> R. J. Vetter, *J. Phys. and Colloid Chem.* **51**, 262–277 (1947).

<sup>9</sup> A. P. Brady and D. J. Salley, *J. Am. Chem. Soc.* (in press).

## Product Distribution in the Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen

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February 13, 1948

ONE of the interesting features of the Fischer-Tropsch synthesis which has aroused considerable speculation since its discovery<sup>1</sup> is the peculiar distribution of the reaction products according to carbon content.<sup>2</sup> The dashed curve in Fig. 1 taken from Underwood<sup>3</sup> is illustrative of the distribution obtained experimentally with cobalt catalysts at atmospheric pressure and 190–200°C. The relatively small production of  $C_2$ ,  $C_3$ , and  $C_4$  hydrocarbons is noteworthy. Some investigators have attributed the apparent deficit of these hydrocarbons to consumption in the process and hence have considered them in the role of reaction intermediates. It is significant, however, that Craxford<sup>4</sup> has observed a somewhat similar product distribution in the hydrogenation-cracking of high molecular weight Fischer-Tropsch wax. In Craxford's view, the product distribution is a result of the operation of some "polymerization-depolymerization equilibrium in the last stages of the process" which, he indicates, may involve paraffin hydrocarbons. The purpose of this preliminary communication is to point out that thermodynamic equilibrium among the *n*-paraffins yields a distribution which is qualitatively similar to that observed experimentally.

A simplified modification of the Brinkley method<sup>5</sup> was employed for the equilibrium calculations. Carbon formation was neglected and consideration was limited to the

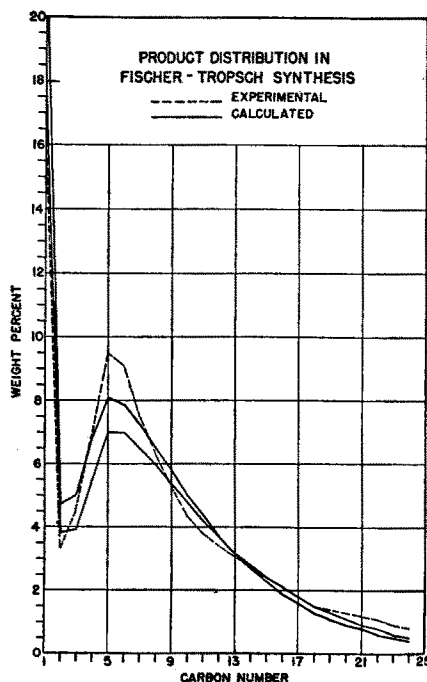


FIG. 1.