# A Study of the Properties of Mixed Solutions of Sodium Dodecyl Sulfate and Dodecyl Alcohol

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A number of studies have reported on the effect of long-chain alcohols on such properties of solutions of surface active agents as their electrical conductivity and solubilizing power. Most of these studies have been made with solutions in which the additives have been dissolved completely by solubilization. However, it is also of importance to study the properties of those mixed solutions in which the amount of additives far exceeds that solubilized.

In previous papers[1-4] studying mixed solutions of sodium dodecyl sulfate and dodecyl alcohol, it was established that there exist some complexes composed of sodium dodecyl sulfate and dodecyl alcohol in the mixed solutions. Spectral experiment[2] on the mixed solutions indicated that the metachromatic color of toluidine blue changes abruptly to a normal color at a certain concentration of sodium dodecyl sulfate, the point depending on the amount of dodecyl alcohol. A similar color change has also been observed for the solution in the temperature 37~40°C range[2].

In the present paper electrical conductivity and viscosity measurements have been carried

1) I. Maruta, T. Sakai, F. Tokiwa and T. Saito, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 1512 (1961).

2) I. Maruta and F. Tokiwa, ibid., **82**, 1657 (1961).

3) I. Maruta and F. Tokiwa, ibid., **82**, 1660 (1961).

4) I. Maruta and F. Tokiwa, ibid., **83**, 732 (1962).

out in order to study the properties of the mixed solutions in further detail.

## Experimental

**Materials.**—Dodecyl alcohol (DA) was purified by repeated fractional distillation under reduced pressure. Gas chromatography failed to detect its homologues. The hydroxyl value of DA was found to be 301.0 (calcd. 301.1). Sodium dodecyl sulfate (SDS) was prepared from DA by the method of Dreger et al.[5] and was purified by repeated recrystallization from ethanol, followed by extraction with petroleum ether.

**Preparation of Mixed Solutions.**—A previously described method[1,2] was used for preparing the mixed solutions of SDS and DA. When a precipitate appeared in the stock solution during storage, it was heated to about 50°C before use, causing the precipitate to disappear.

**Electrical Conductivity and Viscosity Measurements.**—Electrical conductivity was measured with a conductance bridge, a Yanagimoto Model MY-7. The platinum electrodes were slightly platinized, and the cell constant was 0.482. The water used in preparing the solutions had a specific conductance of $1.0 \sim 1.5 \times 10^{-6}$ ohm$^{-1}$ cm$^{-1}$. The observed values were checked by measuring the equivalent conductances of potassium chloride solutions.

Viscosity was measured with an Ostwald-type viscometer, the flow time for water being 140.5 sec. The measurements were performed at varying temperatures ranging from 20 to 50°C with an accuracy of $\pm 0.01$°C.

## Results and Discussion

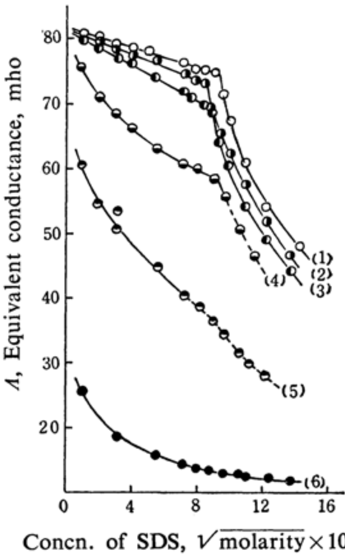



Fig. 1. The equivalent conductance plotted against the square root of the concentration of SDS with the addition of varying amount of DA at 30°C. The relative mole fractions of SDS and DA are; (1) 1.00 : 0.00, (2) 0.94 : 0.06, (3) 0.85 : 0.15, (4) 0.70 : 0.30, (5) 0.50 : 0.50, (6) 0.30 : 0.70.

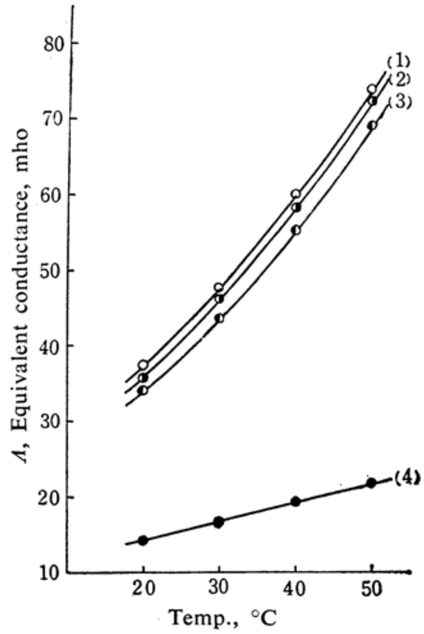
In Fig. 1 the equivalent conductance of an aqueous solution of SDS is plotted against the square root of the SDS concentration with the addition of varying amounts of DA at 30°C. In some cases, the conductance decreased slightly with time in the regions indicated by dotted lines in Fig. 1. Therefore, the reading was taken after the constant value had been attained, which required from 70 to 90 min. Most of the curves represent averages of at least two series of measurements. The addition of DA lowered the conductance, the degree of lowering increasing with an increasing amount of DA for a fixed concentration of SDS.

It has been shown in previous papers that SDS molecules or ions form a complex with DA molecules in the mixed solution, even in the region of a low concentration of SDS. Spectral studies[3,6], furthermore, have suggested that the ion-head of SDS is markedly affected by the hydroxyl group of DA in the complex formation. Therefore, one may explain the decrease in electrical conductance by the complex formation.

It can been seen in Fig. 1 that, in the mixed solutions, SDS exhibits a conductance behavior typical of ionic detergents up to a 0.3 mol. fraction of DA in SDS-DA. These curves exhibit a break point characteristic of critical concentration at a definite concentration of SDS. It is known that, when DA molecules are present in small amounts, they promote micelle formation and thus lower the critical concentration[7,8]. We can also observe a similar tendency in Fig. 1, though the effect there is not so distinct.

Previous investigation[2] has shown that the metachromatic color of toluidine blue in SDS-DA solutions returns abruptly to a normal color at a certain concentration of SDS, depending on the amount of DA present. The break point of the conductance concentration curve is considered to correspond to the point of this color change. In the present experiment, however, the effect of DA on the critical concentration seems to be not so marked.

5) E. E. Dreger et al., *Ind. Eng. Chem.*, **36**, 610 (1944).
6) I. Maruta, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **83**, 788 (1962).
7) B. D. Flockhart and A. R. Ubbelohde, *J. Colloid Sci.*, **8**, 428 (1953).
8) M. Miura and S. Arichi, *J. Sci. Hiroshima Univ., Sec. A*, **22**, 57 (1958).



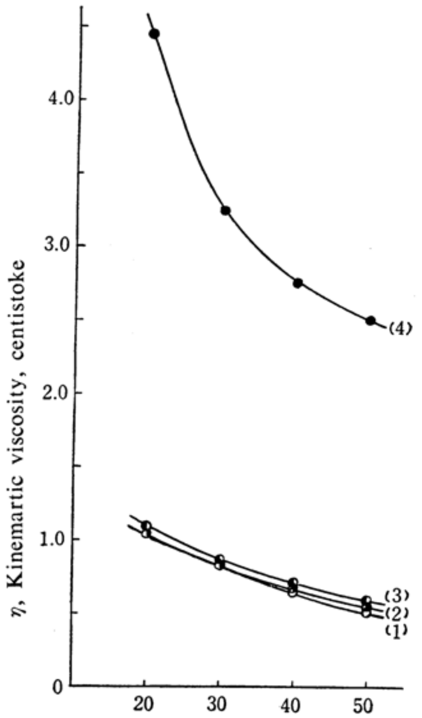




Fig. 2 and Fig. 3. The equivalent conductance and kinematic viscosity plotted against the temperature, for 0.02 molar SDS alone and with DA. The relative mole fractions of SDS and DA are; (1) 1.00 : 0.00, (2) 0.94 : 0.06, (3) 0.85 : 0.15, (4) 0.50 : 0.50.

The variation of the conductance with temperature is shown in Fig. 2 for 0.02 mol. SDS with varying amounts of DA. Figure 3 illustrates the variation of the viscosity for the same solutions. It may be seen in Figs. 2 and 3 that the presence of DA has little effect on the nature of the conductance and viscosity, except for the mixed solution containing a 0.5 mol. fraction of DA in SDS-DA.

In most aqueous solutions the change in conductance with the change in temperature is mainly caused by the change in viscosity, according to Walden's rule[9]. This is true insofar as the solution contains SDS alone, as is shown in Fig. 4, where the product of the conductance and of the viscosity is almost independent of the temperature. However, for mixed solutions with 0.06 and 0.15 mol. fractions of DA in SDS-DA, the product increases slightly with the increasing temperature. This may be explained either by an anomalous increase in conductance or by a decrease in viscosity with the increase in temperature. The results of the present experiment are consistent with the former explanation in that a change in the metachromatic color of toluidine blue in the mixed solutions occurs at relatively high temperatures (37~40°C)[2]. Since this

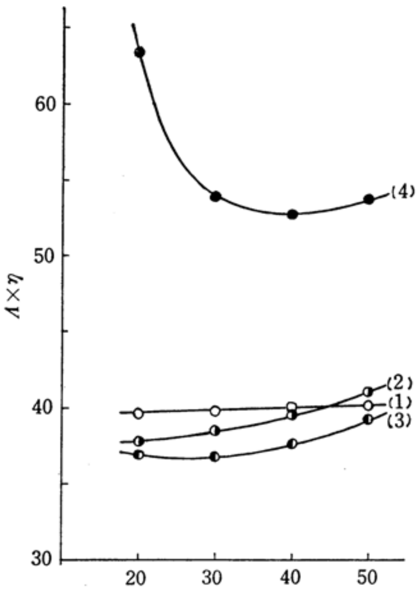



Fig. 4. The product of the equivalent conductance and the kinematic viscosity plotted against the temperature, for 0.02 molar SDS alone and with DA. The relative mole fractions of SDS and DA are; (1) 1.00 : 0.00, (2) 0.94 : 0.06, (3) 0.85 : 0.15, (4) 0.50 : 0.50.

9) A. F. Ward and A. G. Chitale, *Proc. 2nd. Int. Cong. Surface Activity*, **1**, 319 (1956).

observation of color change can be interpreted in terms of the decomposition of the SDS-DA complex into SDS and DA, the slight increase in the product may be explained as due to the decomposition of the complex. In the presence of 0.5 mol. fraction of DA, the viscosity behavior somewhat differs. The fact that at low temperatures the mixed solution is very viscous and still shows a relatively good conducting property is an indication of the formation of involved complexes through which the positive ions can easily move.

## Summary

Measurements have been made of the electrical conductivity and the viscosity of mixed solutions of sodium dodecyl sulfate (SDS) and dodecyl alcohol (DA). The addition of DA caused a lowering of the conductance, a phenomenon probably related to the formation of a complex composed of SDS and DA, but it did not essentially alter the form of the $\Lambda-\sqrt{c}$ curves up to 0.3 mol. fraction of DA in SDS-DA. The $\Lambda-\sqrt{c}$ curves of the mixed solution exhibit a break point which corresponds to a critical concentration of SDS, up to a 0.3 mol. fraction of DA in SDS-DA; the break point becomes obscure when the amount of DA present is larger than this value. The effect of the amount of DA on the critical concentration was not very large in this experiment.

The variation of the conductance and viscosity with the temperature was measured on the solution of SDS with varying concentrations of DA. For the solution of SDS without DA, the product of the conductance and the viscosity is almost independent of the temperature, while for the mixed solutions the product is dependent on the temperature, especially in the case of the mixed solution containing a considerable amount of DA.

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