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The Behavior of Aerosol OT in Organic Solvents

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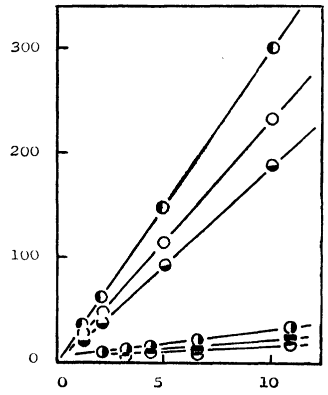
Synopsis. The parameters concerning the micelle formation of Aerosol OT in organic solvents were determined. In order to determine CMC, an apparatus was constructed for the measurement of the interfacial tension between mercury and organic media. The association numbers were estimated by vapor pressure depression measurements.

The behavior of oil-soluble surfactants in organic solvents has been studied from the stand-point of micelle formation,[1,2] but more data are needed for its elucidation as compared with the behavior of surfactants in water. We have carried out the following experiments on Aerosol OT (sodium 1,2-bis(2-ethylhexyloxycarbonyl)ethane-1-sulfonate, American Cyanamid Co., Ltd.) in benzene, cyclohexane, and carbon tetrachloride. In order to determine CMC, a new method and apparatus based on interfacial tension measurement between mercury and organic media were devised. The number average association numbers were estimated by vapor pressure depression measurements.



Concentration × 10^3 (mol kg^{-1})

Fig. 1. Thermister bridge reading (ΔR) *vs.* solute concentration in benzene.
◑: Aerosol OT as solute at 25 °C.
●: Aerosol OT as solute at 37 °C.
◓: Aerosol OT as solute at 45 °C.
◐: Triphehylmethane as solute at 25 °C.
○: Triphenylmethane as solute at 37 °C.
◒: Triphenylmethane as solute at 45 °C.

(1) Vapor Pressure Depression Measurement: For this a molecular weight apparatus (Hitachi-Perkin-Elmer, Type 115) was used. The thermister bridge reading, ΔR, which depends only on the vapor pressure, is plotted against the solute concentration in benzene in Fig. 1. The results for other solvents are similar to those shown in Fig. 1. In each measurement, triphenylmethane was used as a standard substance for calibration. The relationship of thermister bridge reading, ΔR, *vs.* solute concentration in benzene was linear above 1×10^{-3} mol kg^{-1}. As the ratio of the slope for Aerosol OT to that for reference, the number average association number was estimated to be 13. The values in other solvents are summarized in Table 1. The temperatue dependence of association numbers was small.

Table 1. CMC and association number (N) of Aerosol OT in organic solvents

		CMC (mol kg^{-1})	N
CCl_4	25 °C	1×10^{-4}	17
	30 °C	1.5×10^{-4}	17
	37 °C	2.5×10^{-4}	17
	45 °C		17
C_6H_6	25 °C		13
	37 °C	4×10^{-4}	13
	45 °C		13
C_6H_{12}	25 °C		17
	37 °C	5×10^{-4}	17
	45 °C		17

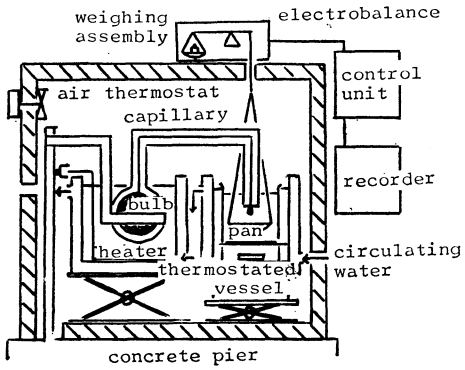


Fig. 2. The apparatus for the interfacial tension measurement between mercury and organic media.

(2) Interfacial Tension Measurements between Mercury and Organic Media: The measurements were carried out by the drop weight method. The apparatus is shown in Fig. 2. In order to drop mercury without vibration, the thermal expansion of mercury was employed according to the method of Sonntag and Strenge.[3] The bulb is heated just a little for the mercury to expand and fall into the platinum pan after a long interval. The weight of falling mercury drop in the organic media containing various amounts of Aerosol OT was measured *in situ* with the accuracy of $\pm 10^{-5}$ g by means of the load added to the electrobalance (Cahn RG Electrobalance, Cahn Instrument Co., Ltd.) holding the pan. The interfacial tension was calculated according to the method of Harkins and Brown.[4] The radius of the tip (0.045 cm) was obtained by calculation using the data[5] between mercury and

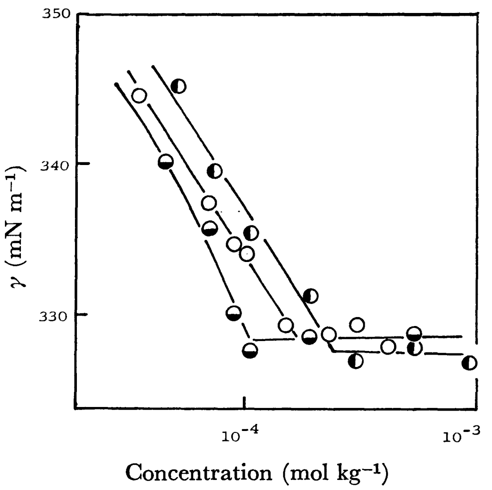


Fig. 3. Interfacial tension between mercury and carbon tetrachloride *vs.* solute concentration in logarithmic scale.
◒: at 25°C. ○: at 30°C. ◐: at 37°C.

benzene. As shown in Fig. 3, the plots of interfacial tension between mercury and carbon tetrachloride solution show a behavior similar to that of the surface or interfacial tension of aqueous solution of surfactant near CMC. From the equation of adsorption isotherm (Eq. 1), surface (or interfacial) tension against solute concentration in logarithmic scale breaks when the relationship between activity and concentration of surface active solute has a breaking point or CMC.

$$-\mathrm{d}\gamma = RT\Gamma \mathrm{d} \ln a_i \qquad (1)$$

Since the depression (Fig. 3) indicates the surface activity of solute to mercury/organic medium interface and relatively large association numbers were obtained (Table 1), we identified the breaking points in Fig. 3 as the CMC of Aerosol OT in carbon tetrachloride, also given in Table 1 with those in benzene and cyclohexane.

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