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Determination of CMC from Liquid Junction Potential Measurements

EDWARD J. WILLIAMS* and VICTOR F. SMOLEN▲

Abstract ☐ The CMC's of anionic and cationic surfactants were determined from diffusion potential measurements. The methodology used for the determinations is simple, capable of providing accurate results, and requires a minimum of very commonly available apparatus. The data also yield reliable transport number values for the surfactant ions.

Keyphrases ☐ CMC, surfactants—determined from diffusion potential measurements (liquid junction) ☐ Surfactants—determination of CMC using diffusion potential measurements (liquid junction) ☐ Transport numbers—determined using diffusion potential measurements (liquid junction), surfactants ☐ Diffusion potential measurements, liquid junction—determination of CMC surfactants, transport numbers

Surfactants are an important class of compounds with significant pharmaceutical applications as micellar solubilizing agents, stabilizers, antibacterials, *etc.* (1–6). One of the most important physical properties of a surfactant is its CMC. There are various methods of determining the CMC (7) which involve varying experimental difficulties and equipment requirements. The purpose of the present report is to describe a simple electrometric method for determining CMC values of ionic surfactants which requires a minimum of very commonly available apparatus. The method is demonstrated for two cationic detergents and an anionic detergent. In addition to CMC values, the transport number of the ions can be calculated from the data.

MATERIALS AND METHODS

Materials—Chromatographically pure dodecyltrimethylammonium bromide (I) was purchased[1]. Dodecylamine hydrochloride (II) was prepared from chromatographically pure dodecylamine in absolute ethanol and concentrated reagent grade hydrochloric acid using the procedure of Hutchinson and Winslow (8). Sodium lauryl sulfate (III) was also purchased[2]. Reagent grade potassium chloride was used to determine the conductivity apparatus cell constant. Double-distilled water was used to prepare all solutions.
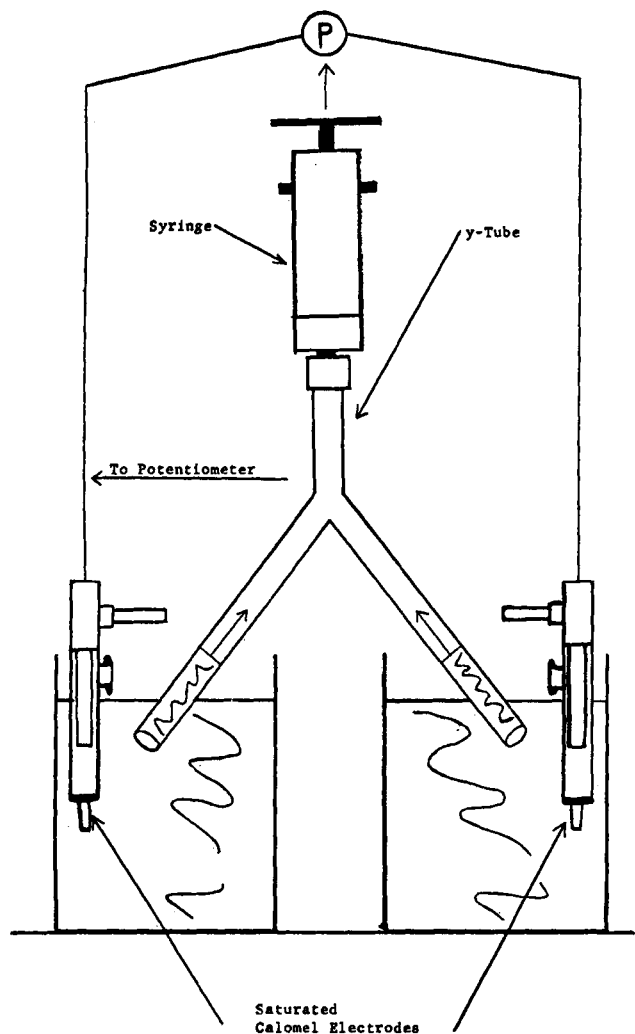
Liquid Junction Potential Measurements—The liquid junction cell, together with the electrodes, syringe, and 50-ml. beakers for containing the reference and sample solutions, is shown in Fig.1. The stem and arms of the Y-tube cell are each approximately 10 cm. in length with an inside diameter of 0.8 cm.; a 20-ml. syringe was employed. The electrodes are miniature saturated calomel electrodes (Corning) with fiber junctions. Potentials were recorded on a Sargent SR recorder. The different chart scales were utilized to achieve maximum precision for a given measurement on a given pair of solutions (reference and sample).

Fresh reference and sample solutions were prepared before each run. The surfactant concentration in the reference solutions for all of the surfactants was 0.0010 *M*. Surfactant concentrations in the sample solutions ranged from 0.0020 to 0.050 *M*. Approximately 50 ml. of a reference solution and 50 ml. of a sample solution were placed in the appropriate beakers (Fig. 1); the electrodes were placed into the solutions followed by the insertion of the arms of the Y-tube. The syringe was used to draw the two solutions into the arms of the Y-tube. When the two solutions came in contact to form a liquid junction at the Y-tube intersection, the ensuing liquid junction potential was recorded on the moving chart. Fresh reference solutions were used with each sample solution to minimize contamination effects due to cumulative leakage of potassium chloride through the reference electrode fiber junction. All potentials were corrected for small electrode asymmetry potentials, which were measured for each pair of solutions. The measurements were made at room temperature (25 ± 1°).

Conductometric Method—Conductivity measurements were made with a conductance bridge (Serfass), operating at a frequency of 1000 Hz., used in conjunction with a Washburn-type conductivity cell with platinized electrodes. A specific conductance value of 0.0129 ohm^{-1} cm.$^{-1}$ for 0.100 molal KCl at 25° (9) was used to calculate the cell constant (2.15 × 10^{-7} cm.). Solutions were pre-
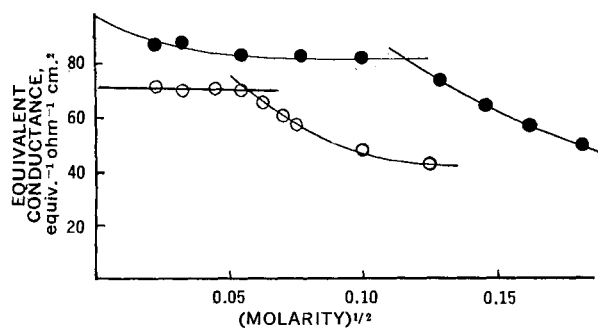
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[1] Lachat Chemical Co.

[2] Mann Chemical Co.

Figure 3—*Equivalent conductance of dodecylammonium chloride* (O) *at 25°. The discontinuity in the curve indicates the CMC.*

RESULTS AND DISCUSSION

Equivalent conductance results for I and III are plotted in Fig. 2; similar data for II are shown in Fig. 3. Figures 4 and 5 present similar results of liquid junction potential measurements. The relationship between the liquid junction potential and the ratio of the sample (C_S) solution to reference (C_R) solution concentrations is defined by Eq. 1, where R = 8.31 J./°K, F = 96,500 C., T = 298°K, and Δt represents the difference between the anion and cation transport numbers, $\Delta t = (t_- - t_+)$ or $(1 - 2t_+)$, for cationic surfactants or the difference between the cation and anion transport numbers, $(t_+ - t_-)$ or $(1 - 2t_-)$, for anionic surfactants:

$$E_{LJ} = \frac{RT}{F} \Delta t \ln \frac{C_S}{C_R} = 0.059 \ \Delta t \ \log \frac{C_S}{C_R} \qquad (\text{Eq. 1})$$

The value of Δt changes abruptly at the CMC of ionic surfactants (10). Because of this behavior, plots such as those presented in Figs. 4 and 5 provide a good estimate of CMC values for a variety of ionic surfactants. Liquid junction potential data at surfactant concentrations below the CMC can be used to provide transport number values for the involved surfactant ions because the slopes of the lines below the CMC's in Figs. 4 and 5 are equal to Δt. Equation 2 can be used to calculate the transport numbers of the cations of cationic surfactants or the anions of anionic surfactants:

$$t_+ \text{ or } t_- = (1 - \text{slope})/2 \qquad (\text{Eq. 2})$$

By assuming that the surfactants behave as ideal univalent strong electrolytes at concentrations below their CMC's (11), the transport numbers calculated using Eq. 2 are good approximations of the respective transport numbers at infinite dilution. Such values are required for the implementation of the bioelectrometric technique (12–14) being used in the author's laboratory to study the *in vivo* interaction behavior of the surfactants with tissue surfaces.

CMC values calculated from both the equivalent conductivity data and the liquid junction potential data are presented in Table I for comparison. The agreement between the results of the two modes of measurement is quite satisfactory. These CMC values are also in agreement with the literature values listed in Table I. CMC values for I and II agree closely with the corresponding literature values. However, low values for the CMC of III are not uncommon. Most
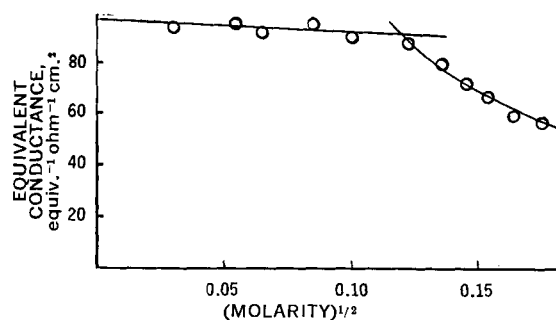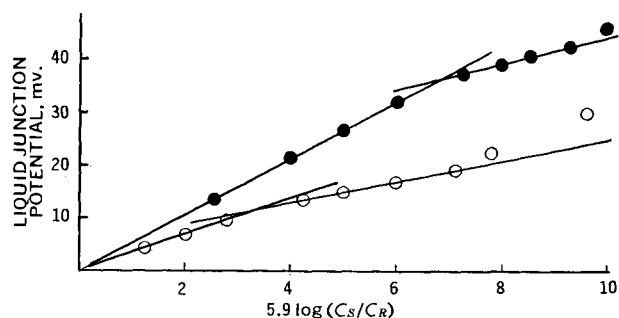

Figure 1—*Experimental arrangement for the determination of the CMC of ionic surfactants by the measurement of liquid junction potentials. The experimental solution (containing varying concentrations of the surfactant) and the reference surfactant solutions are drawn up by the syringe to form a liquid junction within the Y-tube. The liquid junction potential is measured with a potentiometric device used in conjunction with the saturated calomel electrodes.*

pared volumetrically from fresh stock surfactant solutions and were run immediately, the most dilute solution being run first. The cell was rinsed thoroughly before each measurement. All measurements were made at a temperature of 25 ± 1°, and each specific conductance value was corrected for the small specific conductance of the double-distilled water used as the solvent.

Figure 2—*Equivalent conductance of sodium lauryl sulfate* (O) *and dodecyltrimethylammonium bromide* (●) *at 25°. The discontinuities in the curves indicate the CMC's.*

Figure 4—*Liquid junction potential results for sodium lauryl sulfate* (O) *and dodecyltrimethylammonium bromide* (●). *The discontinuities in the curves indicate the CMC's.*
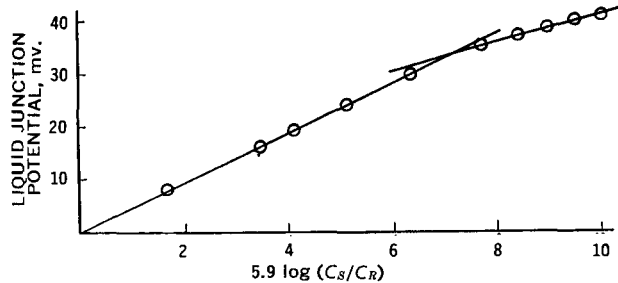
Figure 5—*Liquid junction potential results for dodecylammonium chloride* (O). *The discontinuity in the curve indicates the CMC.*

commercial samples of III contain a small amount of lauryl alcohol, which may form mixed micelles and lower the CMC.

Table II lists the values of the surfactant ion transport numbers calculated from the data presented in Figs. 4 and 5. Inspection of Table II reveals that the transport numbers calculated from the liquid junction potentials are in excellent agreement with transport numbers obtained from the conductometric results. The agreement with literature values is also satisfactory.

That the liquid junction potential method can provide reliable transport number values was confirmed by results for the drug carbamylcholine hydrochloride. The equivalent conductance of this quaternary ammonium compound in aqueous solution at 25° is approximately 110 ohm^{-1}-cm./equivalent, which yields a value of 0.31 for the transport number of the carbamylcholine cation. The transport number value for this cation from liquid junction potential measurements was also found to be 0.31.

SUMMARY AND CONCLUSIONS

A liquid junction potential method was developed and tested for determination of the CMC of ionic surfactants by comparison to the established conductometric technique most commonly employed. The liquid junction potential method was found to be quite sensitive and to yield accurate, reliable results rapidly from a single determination. Furthermore, this method requires a minimum of very commonly available equipment which, besides minor glassware, includes only a potentiometric measuring device (*e.g.*, pH meter, potentiometer, or recorder) and two saturated calomel electrodes such as are supplied with pH meters.

Table I—CMC Values

| | Experimental CMC (Molar) | | |
| | Liquid Junction Potential Method | Conducto-metric Method | Litera-ture[a] Values |
Surfactant			
Sodium lauryl sulfate	0.0037	0.0035	0.0080
Dodecylamine hydrochloride	0.013	0.014	0.013
Dodecyltrimethylammonium bromide	0.014	0.014	0.015

[a] *Reference 15.*

Table II—Surfactant Ion Transport Numbers

Surfactant Ion	Experimental Values[a]	Literature Values[b]
Lauryl sulfate	0.32 (0.31)	0.30, 0.33
Dodecylammonium	0.25 (0.21)	0.24, 0.22
Dodecyltrimethylammonium	0.23 (0.21)	0.22

[a] The values in parentheses were calculated from the equivalent conductivity data in Figs. 2 and 3. The other values were calculated from the liquid junction potential results in Figs. 4 and 5. [b] These values were calculated from equivalent conductivity data reported in *References 16–19.*

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