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# Determination of CMC Based on Measurement of Liquid Junction Potential

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A novel method for the determination of the critical concentration of a micelle formation(hereafter designated as CMC)based on the measurement of liquid junction potential was proposed in this study. In addition, the transport numbers of surfactant ions which express the dynamic behavior in surfactant solution were estimated.

It is well-known that there are many methods to determine the CMC.[1,2] Recently,the membrane electrodes selective to the several ionic surfactants have been developed and widely used to investigate the micellar solution.[3-7] The use of selective electrodes has provided us with more valuable information in the study of surfactant solutions.[8,9] In particular, the method is excellent to obtain the activities of surfactant ions in solution. However, it is not easy to find the materials suitable for the membrane electrodes.

Thus, we paid attention to the transport properties in the surfactant solution. The mobility of surfactant ions may change below and above CMC. The change in mobility might be reflected in the liquid junction potential $E_L$ generated at the interface between two surfactant solutions. According to the above-mentioned prediction, the experiments were enforced to detect the liquid junction potential at the interface formed by a glass sleeve and to obtain the transport number of surfactant ions. This method does not only afford the CMC value easily, but also gives us the transport number of surfactant ions at least below CMC. The transport number will be expected to present new and dynamic information concerning the micellar solution.

Two kinds of typical ionic surfactants, sodium dodecyl sulfate(SDS) and dodecyl trimethylammonium bromide(DTAB), were used without further purification in this study. CMC values have been confirmed by many studies and cited in the literature as 8 mM and 16 mM, respectively.[10]

As for the system measuring the liquid junction potentials, the following cell was assembled:[11)]

$$\mathrm{Ag}\,|\,\mathrm{AgCl}\,|\,\mathrm{KCl}\,|\,S_1\,\|\,S_2\,|\,\mathrm{NH_4NO_3}\,|\,\mathrm{KCl}\,|\,\mathrm{AgCl}\,|\,\mathrm{Ag} \quad , \qquad \text{(A)}$$

where S denotes the surfactant solution, and the vertical double lines represent the liquid junction between two surfactant solutions. In the cell system(A), the potentials for Ag | AgCl | KCl in both terminals are cancelled because the values are identical, but different in sign. As $NH_4NO_3$ agars, which are inserted in system(A) as the connecting electrolyte, possess the equal ionic mobilities, the liquid junction potentials at the interface can be regarded as zero. Therefore, the liquid junction potentials, except that at the double lines, may be neglected with high accuracy. In the case of SDS solution, KCl in the left side of system(A) was replaced with $NH_4NO_3$ in order to avoid the formation of potassium salt at the interface. Thus, the electromotive force(emf) represents only the potential at the liquid junction between $S_1$ and $S_2$. The interface of the liquid junction was actually formed in a glass sleeve of a double junction type-reference electrode body, which was purchased from the Orion Co., Ltd.

The whole cell systems were placed in a water bath kept at a constant temperature of $25^{\circ}C$ throughout the experiments, and the emf's generated in the cell were measured by means of a digital ion analyzer(Orion, Model 901).

Prior to the study of surfactant solution, the liquid junction potentials for aqueous NaCl solution were measured to examine whether the cell system gave a reasonable transport number or not. Then, the aqueous NaCl solutions were put into $S_1$ and $S_2$ of cell system(A) and the emf of the system was measured. In general, the relation between $E_L$ and the transport number of the ion $t^+$ is given as the following equation:[12)]

$$E_L = -(2t^+ - 1)RT/F \ln(C_{II}/C_I) \quad . \qquad (1)$$

The obtained value of $t^+_{Na}$ was 0.41 which agreed positively with that in the literature.[13)] From the result, the system presented was shown to give the correct transport numbers in the electrolyte solutions.

The measurements of surfactant solution were carried out to obtain the transport numbers of surfactant ions. Figure 1 shows the $E_L$'s with regard to anionic and cationic surfactants against the concentration in $S_2$. Two important results should be emphasized in Fig.1. In the first result the inflections take place clearly in the relations of $E_L$ vs. the surfactant concentrations for the two kinds of surfactants. The values at the points were $8.3 \times 10^{-3}$ mol·dm$^{-3}$ for SDS and $1.6 \times 10^{-2}$ mol·dm$^{-3}$ for DTAB, respectively. It can be concluded that the values correspond to the CMC from the

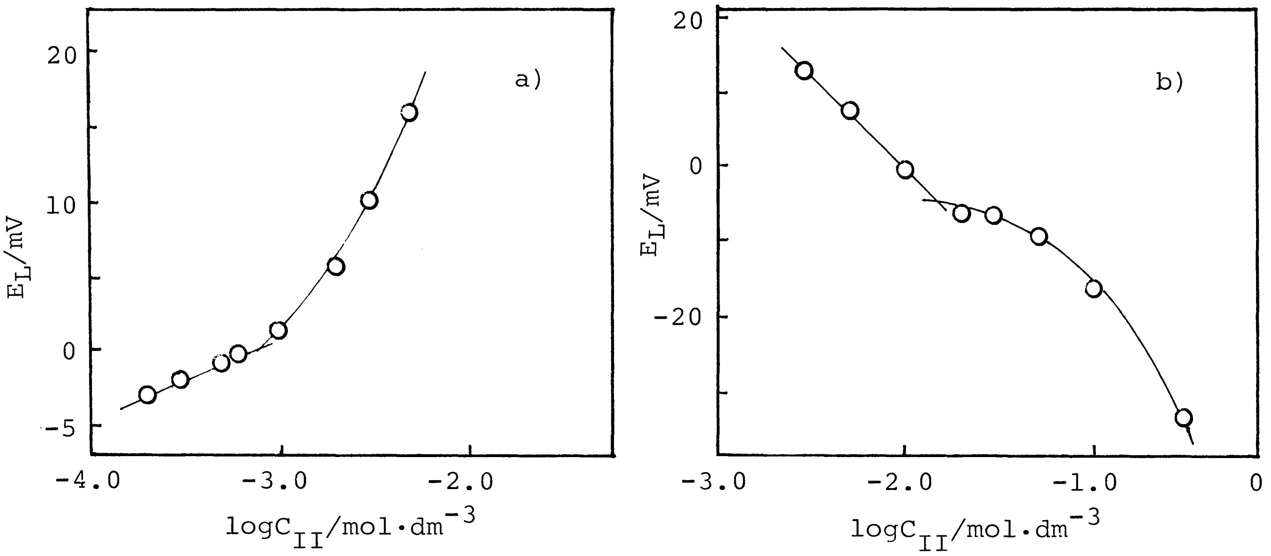

Fig.1. Liquid junction potential, $E_L$ vs. concentration of surfactant, $C_{II}$. a) SDS, $C_I = 6.0 \times 10^{-3}$ mol·dm$^{-3}$, b) DTAB, $C_I = 1.0 \times 10^{-2}$ mol·dm$^{-3}$. CMC values determined from the inflection points in the figures were $8.3 \times 10^{-3}$ mol·dm$^{-3}$ for SDS and $1.6 \times 10^{-2}$ mol·dm$^{-3}$ for DTAB.

comparison with the values in the literature.[10)] Secondly, the relations between $E_L$ and surfactant concentrations below CMC indicate linearity. Taking notice of the slope of the straight line, one can estimate the transport number of single dispersed surfactant ions. The values were given as 0.547($t^-$) for SDS and 0.234($t^+$) for DTAB, respectively in Table 1. As regards the curved portions above CMC, Eq.1 can not easily be applied because a few aggregated species and single surfactant ions may coexist there. However, the tentative calculations were performed to get each value as the average of the transport numbers in micellar solutions. The values are indicated in Table 1 together with those below CMC. The values of transport numbers above CMC turned out to be greater than those below CMC. This result may be attributed to the high charge densities caused by the micelle

Table 1. Transport numbers below and above CMC

| Surfactants | t below CMC | t above CMC[a)] |
|---|---|---|
| SDS | 0.547($t^-$) | 0.608($t^-$) |
| DTAB | 0.234($t^+$) | 0.341($t^+$) |

a) Values were averaged over several results.

and the aggregated surfactant ions. A more detailed analysis will promise to characterize the properties of surfactant ions above CMC and it will be an attractive target in the next study.

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