May, 1993] © 1993 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 66, 1361—1365(1993) 1361

CMC of Alkylammonium Nitrate Determined by a Novel Method

Akira YAMAUCHI,* Minako INOUE, Hironori OHGI, and Takatoshi MITO
Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashi-ku, Fukuoka 812

(Received November 18, 1992)

A novel method for the determination of the critical concentration of a micelle formation based on the measurement of liquid junction potential was presented in this paper. The CMC values of the typical anionic and cationic surfactants and the new compounds, alkylammonium nitrates were obtained by using the method. The CMC values of the new compounds were confirmed by means of the conventional methods. In addition, the transport numbers of those compounds relating to the dynamic behavior in solution were estimated and the physical meaning was discussed.

So far, many methods to determine the critical concentration of a micelle formation (hereafter designated as CMC) have been reported.[1,2] Recently, the membrane electrodes selective to the several ionic surfactants have been developed and widely used to investigate the micellar solution.[3—11] In fact, the use of selective electrodes has provided us with more valuable information in the study of surfactant solutions. 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. In other words, it will be more convenient to get a new method common to various kinds of ionic substances.

Thus, we paid attention to the transport properties of the ionic substances in solution. The mobility of such a substance may change drastically owing to the formation of aggregated compound at certain concentration. The change in mobility might be reflected in the liquid junction potential generated at the interface between two solutions with different concentrations. This view is fascinating for the studies of micellar solutions or ionic substances in solution and it forces one to work into the materialization. Then, the liquid junction potentials at the interfaces formed by a glass sleeve were measured to finally obtain the transport numbers of two kinds of surfactants. This method does not only afford the CMC value easily, but also gives us the transport number of surfactant ion at least below CMC.[12] The transport number will be expected to supply new and dynamic information concerning the micellar solution.

On the other hand, there is a series of compounds which are known as alkylammonium nitrates.[13—15] The solution properties of the alkylammonium nitrates strongly depend upon the carbon numbers in alkyl chain. A preliminary study showed that the micelle formation is likely to begin from hexylammonium nitrate having 6 carbon numbers in alkyl chain.[16] In order to investigate the observation in detail, the liquid junction potentials were measured with respect to the alkylammonium nitrate solutions with three different alkyl chains.

Experimental

Materials: Two kinds of typical ionic surfactants, sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium bromide (DTAB) purchased from Tokyo Kasei Co., Ltd., were used without further purification. The CMC values have been confirmed by many studies and cited in the literature as 8.3×10^{-3} mol dm^{-3} and 1.6×10^{-2} mol dm^{-3}, respectively.[11,17] The alkylammonium nitrates used in this study were hexyl-, heptyl-, and octylammonium nitrates, and they were synthesized by neutralization reaction with the nitric acids and the corresponding amines in our laboratory.[13—16] According to the elemental analysis, the agreements between the calculated and found values of carbon and hydrogen were found within 0.3%.

Cell System: The cell for the liquid junction potential measurement was assembled as follows:[18]

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

where S denotes the sample solution, and the vertical double lines represent the liquid junction between sample solutions, S_1 and S_2. 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. NH_4NO_3 agars, which are inserted in (A) as the connecting electrolyte, possess the equal ionic mobilities. Hence, the liquid junction potentials at the interface can be regarded as zero. As a result, the total electromotive force (emf) represents only the potential at the liquid junction between S_1 and S_2.

In order to make sure of the CMC of alkylammonium nitrate solutions, the following electrochemical cell with the electrode selective to nitrate ion was prepared,

$$\mathrm{elcd.(NO_3) \mid S \mid elcd.(Ref.)}, \quad \text{(B)}$$

where S is the sample solution, elcd.(NO_3), the electrode selective to nitrate ion (Horiba, 8201-06T type) and elcd.(Ref.), the reference electrode (Orion, 90-02 type), respectively. The cell system (B) is the electrochemical cell without the liquid junction, and the emf (E) is given as a function of activity of the sample solution:

$$E = E^{\circ} + RT/F \ln a(\mathrm{NO_3}). \quad (1)$$

Provided the system (B) is calibrated by means of the electrolyte of a known activity such as $NaNO_3$, the standard potential, E° can be eliminated and then the activity of the sample solution, $a(\mathrm{NO_3})$ in S, can be obtained from the measurement of emf. In Eq. 1, R, T, and F are usual physical constants.

Measurements: The interface of the liquid junction was actually formed in a glass sleeve of a double junction type-reference electrode body (Orion, 90-02 type) which was the same as the reference electrode in cell system (B). The whole cell systems were placed in a water bath kept at a constant temperature of 25 °C throughout the experiments, and the emf's generated in the cell were measured by a digital ion analyzer (Orion, Model 901). The result with respect to NaCl solution was already described elsewhere[12] and it was shown that the cell system gives the reasonable transport numbers in the simple electrolyte solutions.[17] The emf of the cell system (B) was also detected by the digital ion analyzer as well. The electrical conductance measurement of hexylammonium nitrate was made as further verification of CMC.

Results and Discussion

SDS and DTAB: Firstly, the studies concerning surfactant solutions were performed. Figures 1(a) and 1(b) show the liquid junction potentials (E_L) produced by the anionic and cationic surfactants against the logarithm of surfactant concentrations in S_2. It should be noticed that there are two important results 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 obtained from the points were 8.3×10^{-3} mol dm^{-3} for SDS and 1.6×10^{-2} mol dm^{-3} for DTAB, respectively. The values were proved to correspond to the CMC from the comparison with the values in the literature.[11,17] Secondly, the relations between E_L and surfactant concentrations below CMC indicate the linearity. Taking account of the slope of the straight line, one can estimate the transport number of single dispersed surfactant ions. In general, the relation between E_L and the transport number of the ion, t^+ is given as the following equation:[19]

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

where C_I and C_{II}, respectively denote the surfactant concentrations in S_1 and S_2. Equation 2 informs that the linear relation in Fig. 1 leads to a constant transport number independent of surfactant concentration below CMC. The obtained values were given as 0.547 (t^-) for SDS and 0.234 (t^+) for DTAB in Table 1. The fact that t^- for SDS is larger than t^+ for DTAB suggests DS$^-$ ions in solution can move faster as compared with DTA$^+$ ions. One of the reasons would be attributed to the difference in structures between dodecyl chain and dodecyltrimethyl chain. As regards the curved portions above CMC, Eq. 2 can not easily be applied because a few aggregated species and single surfactant ions may coexist together in the solution. However, the tentative calculations were performed to get each value as the average of the transport numbers in micellar solutions. The values were summarized 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 owing to the high charge densities integrated by the micelle and the aggregated surfactant ions. Qualitatively speaking, the micelles with high charge densities may carry a large quantity of electric currents and then the transport number above CMC seems to be largely influenced by the charge number of micelle rather than the mobility. A more detailed and quantitative analysis will promise to characterize the properties of surfactant ions above CMC and it will be attractive target in the next study.

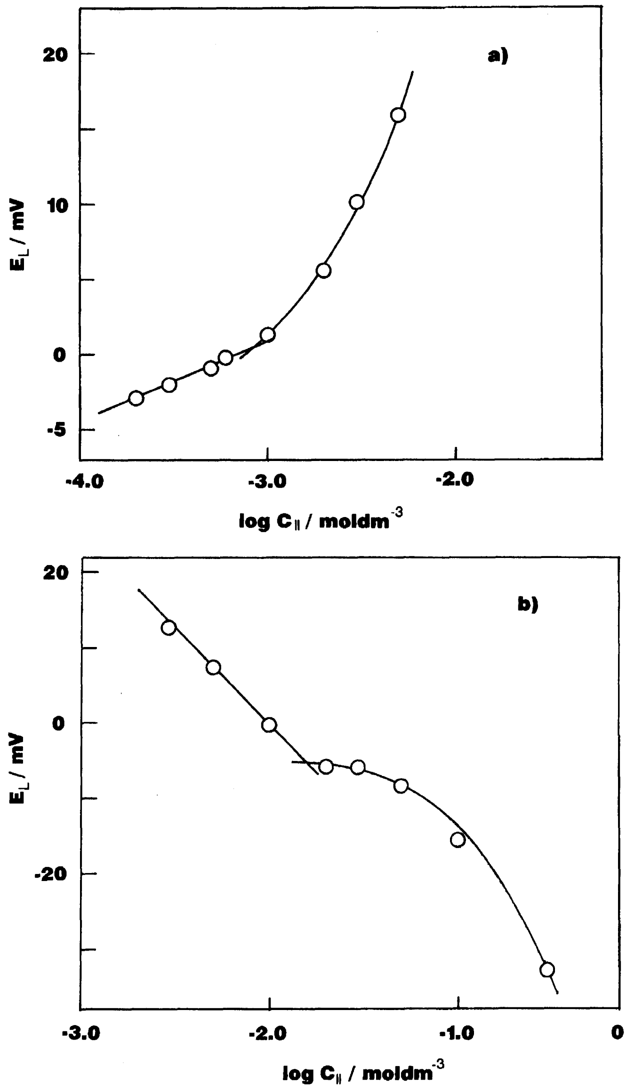

Fig. 1. Liquid junction potential, E_L vs. surfactant concentration, C_{II}. a) SDS, $C_I=6.0\times10^{-3}$ mol dm^{-3}, b) DTAB, $C_I=1.0\times10^{-2}$ mol dm^{-3}.

Table 1. Transport Numbers of Surfactants

Surfactants	t below CMC	t above CMC[a]
DS$^-$	0.547	0.61 (0.01—0.05)
DTA$^+$	0.234	0.34 (0.02—0.30)

a) Values were averaged over several results and the concentration ranges were indicated in parentheses in mol dm^{-3} unit.

Alkylammonium Nitrates: Alkylammonium nitrates having the carbon numbers of 6,7, and 8 in the alkyl chain were examined in this section. For the sake of simplicity, they were designated as C_6AN, C_7AN, and C_8AN, respectively. The liquid junction potentials of the aqueous alkylammonium nitrate solutions, E_L's were measured against the various concentrations and given against the logarithmic concentrations in Fig. 2. It should be noticed that the results were shifted one another by 10 mV in Fig. 2. The result showed that each relation consists of two portions, the straight relation and curved one as well as the cases of surfactant solutions. Obviously the intersection between the two portions can be considered as the CMC values. The values were 4.20×10^{-1} mol dm^{-3} for C_6AN, 3.43×10^{-1} mol dm^{-3} for C_7AN, and 1.66×10^{-1} mol dm^{-3} for C_8AN, respectively, and resulted in somewhat greater CMC value in contrast with the typical surfactants. This implies that these substances are stable and soluble as single species in the solution. The straight lines for the three species showed almost the same slopes and the results calculated by Eq. 2 were summarized in Table 2. The transport numbers, t^+'s were approximately 0.35 and the difference between them could not be appreciably recognized. With comparison to t^- for SDS and t^+ for DTAB, the present value was positioned in the intermediate. As the transport number reflects the relative movement of cation and anion in solution, the values in different solutions can not be compared quantitatively each other. However, it can be positively said that in the case of DTAB and C_nAN, the difference is caused by the alkyl chain length. Here, to represent abovementioned matters by the numerical values, we tried to use a limiting equivalent conductivity of ion. As seen in Figs. 1 and 2, the experimental results below CMC showed the linear relations against logarithmic concentrations. These facts mean that the present transport numbers are independent of the concentration and can be regarded as the limiting quantities. Thus, using $\lambda^\circ(Na^+)$, $\lambda^\circ(Br^-)$, and $\lambda^\circ(NO_3^-)$ in literature,[20] the limiting equivalent conductivities of DS^-, DTA^+, and C_nA^+ were estimated and given as follows: $\lambda^\circ(DS^-)$: 60.50, $\lambda^\circ(DTA^+)$: 23.87, $\lambda^\circ(C_6A^+)$: 39.33, $\lambda^\circ(C_7A^+)$: 38.65, and $\lambda^\circ(C_8A^+)$: 37.31 cm^2 S mol^{-1}. As expected, the results for cationic species exhibited the dependence upon the alkyl chain length while in the case of DS^- ion, it was presumed that sulfate group in DS^- ion gave a strong influence to transport process in solution.[20] The transport numbers from the curved portions were given as averaged values in Table 2. The discrepancy with those below CMC was not so large. This may suggest that the number of aggregated molecules are few, but further mention was avoided owing to the same reason described in the part of surfactant.

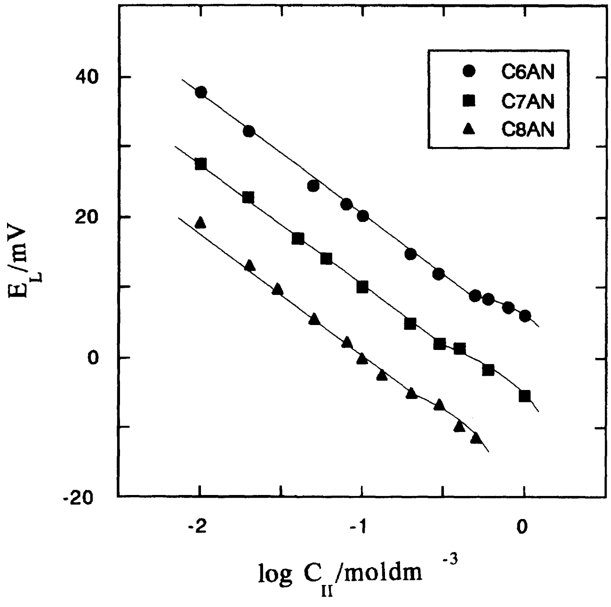

Fig. 2. Liquid junction potential, E_L vs. C_nAN concentration, C_{II}. The fixed concentrations for all C_nAN is $C_I=1.0\times10^{-1}$ mol dm^{-3}. The E_L's for C_6AN and C_7AN are shifted by 20 mV and 10 mV upward, respectively. Notations are inserted in the figure.

Table 2. Transport Numbers of C_nAN

$CnAN$	t^+ below CMC	t^+ above CMC[a]
C_6A^+	0.355	0.37 (0.5—1.0)
C_7A^+	0.351	0.37 (0.4—1.0)
C_8A^+	0.343	0.37 (0.2—0.5)

a) Values were averaged over several results and the concentration ranges were indicated in parentheses in mol dm^{-3} unit.

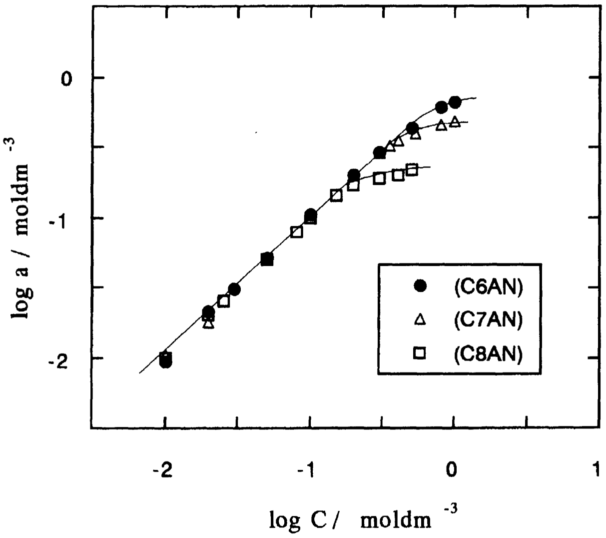

Fig. 3. Activities of nitrate ions, log a vs. C_nAN concentration, log C. Activity was obtained from Eq. 1. Notations are inserted in the figure.

The conventional measurement which is the alternative method to know the micelle formation in C_nAN system, was made to ascertain the CMC. The electrode selective to nitrate ion can electrochemically response only the concentration of nitrate ion as described in experimental section. If the C_nAN in aqueous solution forms the micelle, the activity of the counter ion, nitrate ion may also change below and above CMC. In Fig. 3 the change of activities of nitrate ions were plotted against the logarithms of C_nAN concentrations. One can see the obvious changes of the activities around the concentration corresponding to CMC. The concentrations at the inflection points were satisfactorily in agreement with those from the liquid junction potential and thus, the values were recognized as CMC. These results represent that even C_6AN with the short alkyl chain can form the micelle although the aggregation number is expected to be quite small. We should be careful with respect to the results of C_nAN because C_6 AN especially is regarded as the limit in micelle formation. Hence, the electrical conductances of C_6AN solution were examined as a function of the concentration and given in Fig. 4. The result gave the same inflection point as in Figs. 2 and 3 and supported the formation of aggregated species at least. The dependence of CMC on carbon number was given in Fig. 5. From the results, one can see the low slope compared with the case of typical surfactants.[2,21,22] This means that the free energy of transfer per one methylene group into the micelle is small and the aggregation number is also small.

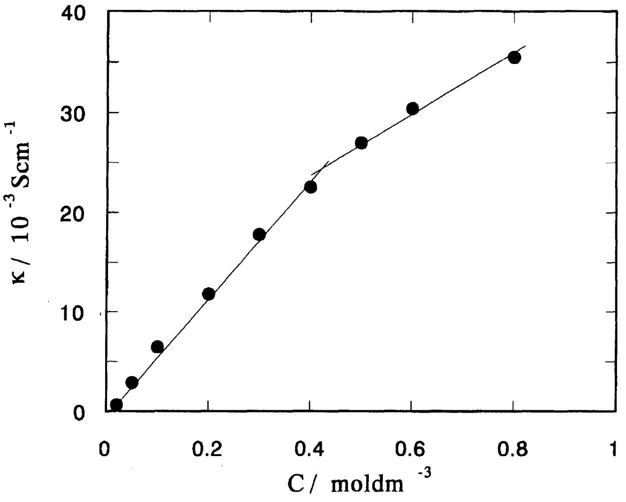

Fig. 4. Relation between conductivities, κ and C_6AN concentrations, C.

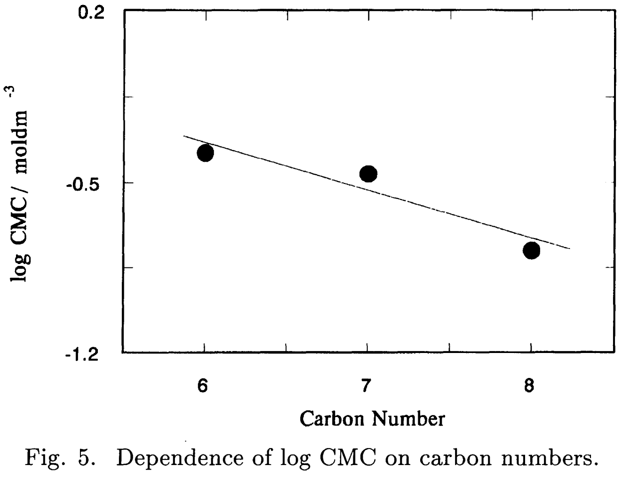

Fig. 5. Dependence of log CMC on carbon numbers.

As a concluding remark, it can be said that the method due to the liquid junction potential is simple and convenient to determine CMC. It is basically applicable to all the ionic surfactants. The transport numbers of single dispersed surfactant ions below CMC were also estimated and the CMC of alkylammonium nitrates were presented as new physicochemical quantities.

Authors acknowledge financial support from The Salt Science Research Foundation, No. 92009.

References

1) R. Zana, "Surfactant Solution," Marcel Dekker, New York (1986).

2) K. Shinoda, T. Nakagawa, and T. Isemura, "Colloidal Surfactant," Academic Press, New York (1963).

3) C. Gavach and P. Seta, *Anal. Chim. Acta*, **50**, 407 (1970).

4) B. J. Birch and D. E. Clarke, *Anal. Chim. Acta*, **61**, 159 (1972).

5) T. Sasaki, M. Hattori, J. Sasaki, and K. Nukina, *Bull. Chem. Soc. Jpn.*, **48**, 1397 (1975).

6) A. Matsubara and K. Nomura, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **10**, 77 (1976).

7) A. Yamauchi, T. Kunisaki, T. Minematsu, Y. Tomokiyo, T. Yamaguchi, and H. Kimizuka, *Bull. Chem. Soc. Jpn.*, **51**, 2791 (1978).

8) A. Yamauchi, H. Tokunaga, S. Matsuno, and H. Kimizuka, *Nippon Kagaku Kaishi*, **3**, 388 (1980).

9) T. Sasaki, *Yukagaku*, **24**, 207 (1975).

10) I. Satake, S. Noda, and T. Maeda, *Bull. Chem. Soc. Jpn.*, **56**, 2581 (1983).

11) P. Mukerjee and K. J. Mysels, *Nat. Stand. Ref. Data Ser.*, (*U. S., Nat. Bur. Stand.*), **36**, 51 (1971).

12) A. Yamauchi and M. Inoue, *Chem. Lett.*, **1992**, 1619.

13) D. F. Evans, S. H. Chen, G. W. Schriver, and E. M. Arnett, *J. Am. Chem. Soc.*, **103**, 481 (1981).

14) D. F. Evans, A. Yamauchi, R. Roman, and E. Z. Casassa, *J. Colloid Interface Sci.*, **88**, 89 (1982).

15) D. F. Evans, A. Yamauchi, G. J. Jason, and V. A. Bloomfield, *J. Phys. Chem.*, **87**, 3573 (1983).

16) T. Mito, Thesis of Master Degree, Kyushu University, 1990.

17) "Kagaku Benran," ed by the Chemical Society of Japan, Maruzen, Tokyo (1975).

18) B. M. Braun and H. Weingartner, *J. Solution Chem.*, **14**, 675 (1985).

19) S. G. Schultz, "Basic Principles of Membrane Transport," Cambridge Univ. Press, Cambridge (1980).

20) R. A. Robinson and R. H. Stokes, "Electrolyte Solution," Butterworths, London (1959).

21) C. Tanford, "The Hydrophobic Effect: Formation of Micelles and Biological Membranes," John Wiley & Sons, New York (1973).

22) Y. Moroi, "Micelles," Plenum Press, New York and London (1992).