*CCA-1154*

# Association and Precipitation of Alkaline Earth Dodecyl Sulphate in Aqueous Media*

## *I. Krznarić, J. Božić, and N. Kallay*

*Laboratory of Physical Chemistry, Faculty of Science, University of Zagreb, Zagreb, Croatia, Yugoslavia, 41001 Zagreb POB 163*

The equilibrium in aqueous alkaline earth dodecyl sulphate solutions were examined by determining solubilities at different ratios of precipitation component amounts. The interpretation of the results indicates the formation of simple associates such as $Me(C_{12}H_{25}SO_4)_2$. The equilibrium constants of their formation were also determined. The logarithms of the equilibrium constants for the reaction:

$$Me^{2+} + 2\,C_{12}H_{25}SO_4^- \rightleftharpoons Me(C_{12}H_{25}SO_4)_2$$

were found to be 5 for $Mg^{2+}$ and $Ca^{2+}$, 5.2 for $Sr^{2+}$ and 6.4 for $Ba^{2+}$.

## INTRODUCTION

A recent review on aqueous detergent solutions reported by Fisher and Oakenfull has revealed a lack of experimental data on premicellar associates in solutions of ionic surfactants[1].

In our previous paper the precipitation diagrams of silver, copper (II) and lanthanum dodecyl sulphates were presented[2]. Such diagrams provide evidence of the equilibria in the solution, e. g. of the stability and composition of the species present.

The aim of this study was to examine the equilibria in aqueous solutions of alkaline earth dodecyl sulphates with special attention to association procesess. The investigations were done through the interpretation of the precipitation diagrams.

Bivalent dodecyl sulphate solubility and its temperature dependence were reported by Miyamoto[3], Hato and Shinoda[4] and Grebnev and Stefanovskaya[5].

## EXPERIMENTAL

*Procedure*

The precipitation-solubility curves (PS-curve) were obtained by mixing precipitating component solutions of the same volume (metal nitrate and sodium dodecyl sulphate). The presence of the precipitate could be seen 24 hours after mixing the components. To make sure that the systems were in equilibrium the observation was repeated one week later. No change in the results was found. The temperature was $(21 \pm 1)\,^0C$. The solutions were prepared by weighing and dissolving salts in redistilled water.

---

* Contribution No. 217 of the Laboratory of Physical Chemistry.

The origin of the salts was as follows: sodium dodecyl sulphate (BDH, England, specially pure), magnesium nitrate (Merck, Darmstadt, p. a.), calcium and strontium nitrates (Kemika, Zagreb, p. a.), and barium nitrate (Carlo Erba, Milano, p. a.).

<div align="center">RESULTS</div>

The experimental results are presented in Figure 1., which shows the precipitation-solubility curves (PS-curves) for different alkaline earth sulphates.

The PS-curve in the precipitation diagram (the coordinates are the logarithms of the initial (total) concentration of precipitation components) divides the concentration area where precipitation was observed, from the area where no precipitate could be detected. From now on dodecyl sulphate ion will be abbreviated as DS⁻.
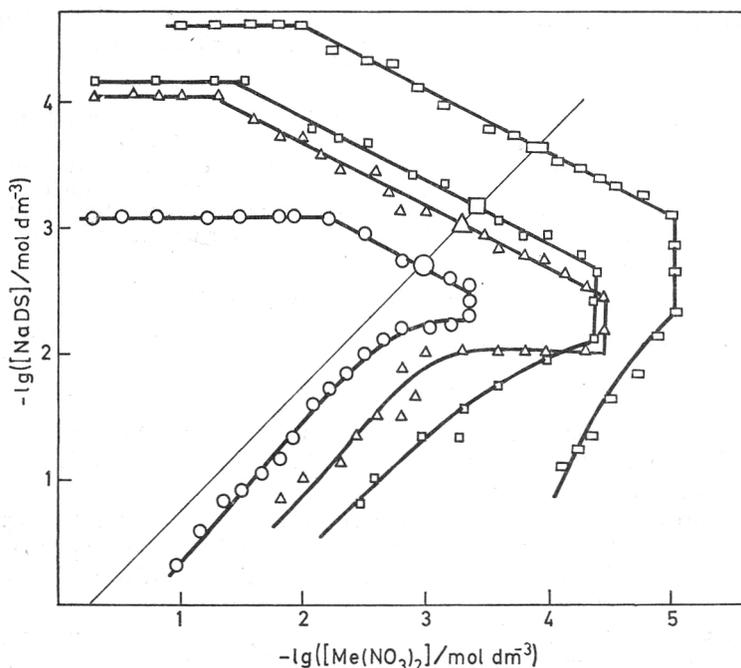


Figure 1. Precipitation — Solubility curve for alkaline earth dodecyl sulphate in aqueous media at (21±1) °C. The total concentrations of precipitating components are ploted on the axes.
○ Mg(DS)₂ · 6H₂O, △ Ca(DS)₂, □ Sr(DS)₂ □ Ba(DS)₂

<div align="center">INTERPRETATION OF EXPERIMENTAL DATA</div>

The interpretation of the results is based on the method described by Kratohvil, Težak and Vouk[6]. Its application to ionic surfactant systems was presented in our previous paper[2].

Here, it will be considered more critically because of special problems due to the application of the »mass action low« concept in the treatment of equilibria in ionic surfactant solutions[1].

The interpretation will be discussed on the case of barium dodecyl sulphate system and for this reason the precipitation diagram of the system Ba(NO₃)₂ — — NaDS is presented separately in Figure 2.
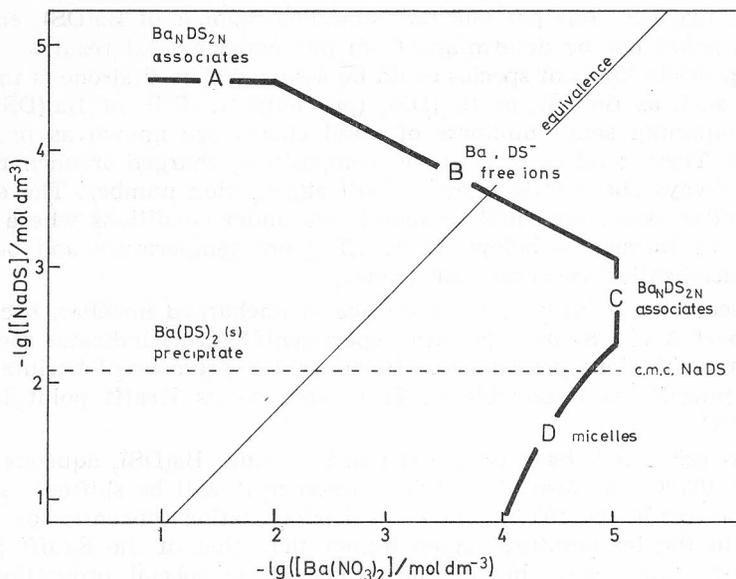
Figure 2. Precipitation diagram of the barium dodecyl sulphate system in aqueous media at (21±1) °C.

Four different parts of the PS-curve are shown. Part B was found to be linear with the slope —0.5 which points to the existence of free $Ba^{2+}$ and $DS^-$ ions. The following interpretation supports this statement. At limiting conditions of the PS-curve the ionic activities are related by the solubility product ($K_{so}^{\ominus}$)

$$K_{so}^{\ominus} = a_{Ba^{2+}} \; a_{DS^-}^2 \qquad (1)$$

($a$ = activity)

If electrolytes are completely dissociated

$$a_{Ba^{2+}} = y_{Ba^{2+}} [Ba(NO_3)_2]/mol \; dm^{-3} \qquad (2)$$

and

$$a_{DS^-} = y_{DS^-} [NaDS]/mol \; dm^{-3} \qquad (3)$$

($y$ = activity coefficient, $[Ba(NO_3)_2]$ and $[NaDS]$ are initial electrolyte concentrations) because at the PS-curve the amount of precipitate equals zero.

From (1), (2) and (3)

$$— lg \, ([NaDS]/mol \; dm^{-3}) = — 1/2 \, lg \, K_{so}^{\ominus} + lg \, y_{DS^-} + 1/2 \, lg \, y_{Ba^{2+}} +$$

$$+ 1/2 \, lg \, ([Ba(NO_3)_2]/mol \; dm^{-3}) \qquad (4)$$

Under these conditions (part B of PS-curve) the activity coefficients could be calculated by using the Debye-Hückel theory. However, at low ionic strength their influence on the result is negligible.

Figure 2. shows slope —0.5 in this region which means that these assumptions are justified.

Part A of the PS-curve (Figure 2.) indicates associatia. The parallelism with the X axis means that associates contains equivalent amounts of $Ba^{2+}$ and $DS^-$
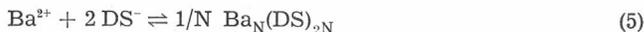
ions, e. g., two DS⁻ ions per one $Ba^{2+}$ ion. The number of $Ba(DS)_2$ entities in associates could not be determined from our experimental results.

Two possible kinds of species could be assumed. The first one is the simple associate, such as $Ba(DS)_2$ or $Ba_2(DS)_4$ (probably $Ba_3(DS)_6$ or $Ba_4(DS)_8$). Such species containing small numbers of alkyl chains are known as premicellar associates[1]. They could be of different composition, charged or uncharged, but they are always characterized by a small aggregation number. The existance of premicellar associates could be found also under conditions where micelles could not be formed — below the Krafft point temperature and below the critical micellization concentration (c.m.c.).

The second possibility is the presence of uncharged micelles, because the slope of part A of PS-curve (within experimental error) indicates the composition of two DS⁻ ions per $Ba^{2+}$ ion. However, the presence of barium dodecyl sulphate micelles is impossible at 21 °C because its Krafft point is higher than[3] 100 °C.

It was estimated that the Krafft point for pure $Ba(DS)_2$ aqueous solution lies about 105 °C. Because of $Ba(NO_3)_2$ presence it will be shifted[7,8] somehow to temperatures above 105 °C. The critical micellization concentration could be observed in the temperature region higher than that of the Krafft point. In the concentration region higher than c.m.c. some special properties of the detergent solution could be observed (surface activity, solubilization etc.) being the consequence of micelle existence. It has been reported[1] that ionic surfactant micelles contain from 10 to 100 alkyle chains. The bivalent dodecyl sulphate micelles contain about 100 alkyl chains[9].

As barium dodecyl sulphate micelle cannot exist at 21 °C, we conclude that part A of the PS-curve (Figure 2.) corresponds to small associates. Their formation could be represented by

$$Ba^{2+} + 2\,DS^- \rightleftharpoons 1/N\ Ba_N(DS)_{2N} \tag{5}$$

($Ba_N(DS)_{2N}$ means associate containing $N$ $Ba^{2+}$ and $2\,N$ dodecyl sulphate ions, the most simple case is $N = 1$ and consequently the associate is $Ba(DS)_2$, but $N$ could be somewhat higher 2 or 3).

The relevant equilibrium constant is

$$K^{\ominus}_{ass} = \frac{a^{1/N}_{Ba_N(DS)_{2N}}}{a_{Ba^{2+}}\, a^2_{DS^-}} \tag{6}$$

The interpretation of part A of the PS-curve (Figure 2.) includes the following statements. Practically all of the DS⁻ ions from NaDS are in the form of associates because of a high $Ba^{2+}$ excess and the absence of precipitate. At the limiting conditions of the PS-curve the activities of $Ba^{2+}$ and DS⁻ ions are related by the solubility product ($K^{\ominus}_{so}$). The associate activity coefficient is unity because of its zero charge. The possible compositions $BaDS^+$, or $Ba_2(DS)_3^-$ or similar will give a slope significantly different from those obtained. It follows that

$$-\lg\ ([NaDS]/mol\ dm^{-3}) = -N \lg K^{\ominus}_{ass} - N \lg K^{\ominus}_{so} - \lg 2N \tag{7}$$

Equation (7) shows that the parallelism of part A of the PS-curve with the X-axis means no change in the composition of the associate; no change in the

$N$ value and two DS⁻ ions per one $Ba^{2+}$ ion. A similar treatment of part C of the PS-curve (Figure 2.), which lies in the DS⁻ ions excess, gives

$$- \lg ([Ba(NO_3)_2]/mol\ dm^{-3}) = -N\ \lg K^\ominus_{ass} - N\ \lg K^\ominus_{so} - \lg N \qquad (8)$$

Knowing the $N$ value (e. g. 1, 2 or 3) it is possible, by using eqs. (7) and (8), to evaluate from the precipitation diagram the equilibrium constant of assotiation reaction (5).

Part D of the PS-curve lies in the region of micelle presence. The. c.m.c. for NaDS[10] is $8 \times 10^{-3}$ mol dm⁻³ and its Krafft point temperature is 8 °C.

Figure 1 shows the results for $Mg(DS)_2$, $Ca(DS)_2$, $Sr(DS)_2$ and $Ba(DS)_2$ systems. For all systems part D starts from $[NaDS] \approx 8 \times 10^{-3}$ mol dm⁻³.

The interpretation of part D should include ion exchange and will not be considered here.

Table I presents the data evaluated from precipitation diagrams.

TABLE I

| Substance | Solubility product $- \lg K^\ominus_{so}$ | Equilibrium constant of association $\lg K^\ominus_{ass}$ | | | | | |
|---|---|---|---|---|---|---|---|
| | | excess of DS⁻ | | | excess of Me²⁺ | | |
| | | $N = 1$ | $N = 2$ | $N = 3$ | $N = 1$ | $N = 2$ | $N = 3$ |
| $Mg\ (DS)_2 \cdot 6\ H_2O$ | 8.4 | 5.0 | 6.6 | 7.1 | 5.0 | 6.6 | 7.1 |
| $Ca\ (DS)_2$ | 9.3 | 5.0 | 7.0 | 7.7 | 4.9 | 7.0 | 7.7 |
| $Sr(DS)_2$ | 9.6 | 5.2 | 7.2 | 8.0 | 5.3 | 7.3 | 8.0 |
| $Ba(DS)_2$ | 12.0 | 6.4 | 8.7 | 9.5 | 6.3 | 8.6 | 9.5 |

The solubility product ($K^\ominus_{so}$), equilibrium constant of association ($K^\ominus_{ass}$) for alkaline earth dodecyl sulphates in aqueous media at $(21\pm1)°C$. The $K^\ominus_{ass}$ values were calculated from the data obtained at excess of cation ($Me^{2+}$) and also at excess of DS⁻ ions. The values were calculated by assuming $N=1$, $N=2$ and $N=3$, i. e. formation of associates: $Me(DS)_2$, $Me_2(DS)_4$ and $Me_3(DS)_6$, respectively. The error, estimated as the maximum deviation from the mean value, is $\pm0.3$ for $\lg K^\ominus_{so}$ and $\pm0.4$ for $\lg K^\ominus_{ass}$ values, respectively.

### DISCUSSION

The results of this study indicate the formation of small associates in the aqueous solutions of earth dodecyl sulphates. The composition of associates was found to be $Me_N(DS)_{2N}$ and the $N$ value was assumed to be small in relation to those of micelles. The formation of such associates was not described in the literature before.

The method used in this study was based on the interpretation of the solubility and its disadvantage lies in the low accuracy of data. However, this method is characterized by a clear physico-chemical treatment based on the statement that at limiting conditions corresponding to the precipitation-solubility curve the amount of precipitate equals zero, but the activities of ions are still related by the solubility product.

In Table I the values of solubility products are listed. Our results are in accord with the results obtained by Miyamoto[3] and Grebnev and Stefanov-

skaya[5] presented in Table II together with some other properties of alkaline earth dodecyl-sulphate aqueous solutions.
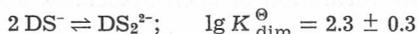
It was concluded that alkaline earth dodecyl sulphate associates contain equivalent amounts of cations and anions, so that their composition can be described as $Me_N(DS)_{2N}$. There is no doubt concerning this result because any other composition would give quite a different slope of part A of the precipitation-solubility curve (Figure 2.). The analyses show that the slope equals x for any N value of the associate composition described as $Me_{N-x}(DS)_{2N}$. The x value could be only an integer number so the possible slopes are —1, 0, 1, 2, 3 etc. Within experimental error the slope could be $0 \pm 0.2$ and consequently associates are uncharged species with $Me_N(DS)_{2N}$ composition. The N value cannot be evaluated from the presented experimental data. It could be obtained from the associate formation curve, but there are great difficulties in providing such experiments. Potentiometric measurements by using the ion-selective electrodes or $DS^- \,|\, Hg_2(DS)_2 \,|\, Hg$ electrode could not give satisfactory data. The temperature at which the systems are investigated (21 $^0$C) was below the corresponding Krafft temperatures for all of the investigated systems (Table II).
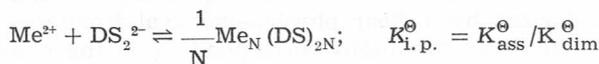
TABLE II

*Results on Alkaline Earth Dodecyl Sulphates Found in the Literature The Relevant References are Given in Brackets. The* $K_{50}^{\ominus}$ *Values were Calculated from Solubilities.*

| Composition of Substance | Solubility product $-\lg K_{so}^{\ominus}$ | | Critical micellization molality | Krafft point temperature | | Micel. aggreg. number |
|---|---|---|---|---|---|---|
| Mg $(DS)_2 \cdot 6\,H_2O$ [3, 9] | 8.45 | [3] | $8.80 \cdot 10^{-4}$ mol/kg at 25 $^0$C   [3, 4] | 25 $^0$C | [3] | 99 [9] |
| Ca $(DS)_2$   [3] | 9.41<br>9.29 | [3]<br>[5] | $1.18 \cdot 10^{-3}$ mol/kg at 50 $^0$C    [4] | 50 $^0$C<br>50 $^0$C | [3]<br>[4] | |
| Sr $(DS)_2$   [3] | 9.58<br>9.29 | [3]<br>[5] | $1.10 \cdot 10^{-3}$ mol/kg at 67 $^0$C   [3, 4] | 64 $^0$C | [3] | |
| Ba $(DS)_2$   [3] | 11.2<br>11.5 | [3]<br>[5] | | 100 $^0$C<br>105 $^0$C | [3]<br>[4] | |

It means that there is no possibility of micelle existence, so the N value should be as small as 1, 2, 3. In order to estimate the N value, i. e. the number of $Me(DS)_2$ entities comprising an associate molecule, the results on dimerisation equilibrium constant obtained by Mukerjee, Mysels and Dulin[11] can be used:

$$2\,DS^- \rightleftharpoons DS_2^{2-}; \quad \lg K_{dim}^{\ominus} = 2.3 \pm 0.3$$

A comparison of the association reaction with the dimerisation one will give:

$$Me^{2+} + DS_2^{2-} \rightleftharpoons \frac{1}{N} Me_N(DS)_{2N}; \quad K_{i.\,p.}^{\ominus} = K_{ass}^{\ominus}/K_{dim}^{\ominus}$$

This ion pairing reaction could be compared to another ion pairing reaction between divalent ions. In Table III the $K_{i.\,p.}^{\ominus}$ for different N values are presented. The right column shows the equilibrium constants for ion pairing of

TABLE III

The Equilibrium Constants of Ion Pairing Reaction: $Me^{2+} + DS_2^{2-} \rightleftharpoons \dfrac{1}{N}$

$Me_N (DS)_{2N}$ at 21 °C in aqueous media.

| Cation | lg $K^{\ominus}_{i.p.}$ | | | Equilibrium constant for MeSO₄ ion pair* formation lg $K^{\ominus}$ |
|--------|---------|---------|---------|---------|
|        | $N = 1$ | $N = 2$ | $N = 3$ |         |
| $Mg^{2+}$ | 2.7 | 4.3 | 4.8 | 2.1 to 2.3 |
| $Ca^{2+}$ | 2.7 | 4.7 | 5.4 | 2   to 2.57 |
| $Sr^{2+}$ | 2.9 | 4.9 | 5.7 | 2.1 to 2.55 |
| $Ba^{2+}$ | 4.1 | 6.4 | 7.2 | 2.3 |

* Different equilibrium constants of the reaction: $Me^{2+} + SO_4^{2-} \rightleftharpoons MeSO_4$ have been reported in the literature[12,13], and the region of its dispersion is indicated in the table. The error, estimated as the maximum deviation from the mean value, is $\pm 0.7$ for $K^{\ominus}_{i.p.}$ values.

alkaline earth with $SO_4^{2-}$ ions found in the literature[12,13]. A comparison of the equilibrium constants presented in Table III permits the conclusion that the $N=1$ value is the most probable. Higher $N$ values would result in high $K^{\ominus}_{i.p.}$ values which are in disagreement with other similar ion pairing equilibrium constants.

REFERENCES

1. L. R. Fisher and D. G. Oakenfull, Chem. Soc. Rev. 6 (1977) 25.
2. J. Božić, I. Krznarić, and N. Kallay, Colloid Polym. Sci. 257 (1979) 201.
3. S. Miyamoto, Bull. Chem. Soc. Japan 33 (1960) 371.
4. H. Hato and K. Shinoda, Bull. Chem. Soc. Japan 46 (1973) 3889.
5. A. N. Grebnev and L. K. Stefanovskaya, Zh. Fiz. Khim. 41 (1967) 1343.
6. J. Kratohvil, B. Težak, and V. Vouk, Arhiv Kem. (Zagreb) 26 (1954) 191.
7. H. Nakayama and K. Shinoda, Bull. Chem. Soc. Japan 40 (1967) 1797.
8. M. J. Schwuger, Kolloid-Z. u Z. Polymere 233 (1969) 979.
9. I. Satake, I. Iwamatsu, S. Hosokawa, and R. Matuura, Bull. Chem. Soc. Japan 36 (1963) 204.
10. H. H. Lange and M. J. Schwuger, Kolloid Z. - Z. Polym. 223 (1968) 145.
11. P. Mukerjee, K. J. Mysels, and C. I. Dulin, J. Phys. Chem. 62 (1958) 1390.
12. L. G. Sillen and A. E. Martell, Stability Constants, Special Publication, No. 17, London, The Chemical Society, Burlington House, W. 1, 1964.
13. L. G. Sillen and A. E. Martell, Stability Constants, Special Publication, No. 25, Supplement No. 1, London, The Chemical Society, Burlington House, W. 1, 1964.

SAŽETAK

Asocijacija i taloženje zemno-alkalnih dodecil sulfata u vodenoj sredini

I. Krznarić, J. Božić i N. Kallay

Ispitivana je ravnoteža u otopinama zemno-alkalnih dodecil sulfata. Ispitivana je topljivost pri različitim omjerima precipitacijskih komponenti. Interpretacija rezultata ukazuje na postojanje jednostavnih asocijata kao npr. $Me(C_{12}H_{25}SO_4)_2$. Određivane su konstante ravnoteže. Logaritam konstante ravnoteže za reakciju $Me^{2+} + 2 C_{12}H_{25}SO_4^- \rightleftharpoons Me (C_{12}H_{25}SO_4)_2$ iznosi 5 za $Mg^{2+}$ i $Ca^{2+}$, 5,2 za $Sr^{2+}$ i 6,4 za $Ba^{2+}$.