Effect of Inorganic Electrolytes on Dissolution Behavior of Mixed Anionic-Amphoteric Surfactant Systems

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The effects of some inorganic electrolytes on the dissolution behavior of anionic-amphoteric mixed surfactant systems have been studied in terms of dissolution temperature of a hydrated solid surfactant; these systems are sodium dodecyl sulfate (SDS) - N^{α}, N^{α}-dimethyl-N^{ϵ}-lauroyl lysine (DMLL), including different inorganic electrolytes (NaCl, NaSCN, or $CaCl_2$). The dissolution temperatures of mixed surfactant systems are lower than those of pure surfactant solutions and become less than 0 C at a certain mole fraction of surfactants. As the concentration of NaCl increases, the dissolution temperatures of systems at a DMLL mole fraction lower than 0.4 increase, while those of systems at a ratio higher than 0.9 remain almost the same. With increasing concentration of NaSCN, the dissolution temperatures of systems at a DMLL mole fraction lower than 0.4 increase, while those of systems at a ratio higher than 0.9 decrease. For $CaCl_2$ systems, there exists a maximum in the dissolution temperature at a certain composition, because addition compound formation between anionic and zwitterionic surfactants occurs due to the presence of calcium ions.

At present, surfactants are used widely in various fields. Recently, the effect on surface activity of a mixed surfactant system was found superior to that of a single surfactant system (1-3). Surfactants used in practical applications almost always consist of a mixture of surfactants. The investigation of mixed surfactant systems is also of great theoretical interest. For example, anionic-anionic (4-6), anionic-nonionic (7-12), anionic-cationic (13-15), anionic-amphoteric (16-19) and cationic-nonionic (20) mixed surfactant systems have been studied.

Amphoteric surfactants exhibit unique properties in aqueous solutions (21,22); for instance, the pH dependence of critical micelle concentration (CMC) (23,24). One of the most interesting properties of the amphoteric surfactants is a strong interaction and/or complex formation with anionic surfactants in aqueous solutions (25,26).

Recently, we have synthesized new amphoteric surfactants which were derived from lysine (27). One should note that these surfactants irritate the skin very little and exhibit good biodegradability. However, most of those surfactants are not soluble in water because of high Krafft points (27). It is important to lower the Krafft point for the practical uses of surfactants.

Addition of an inorganic electrolyte lowers the CMC and enhances the surface activity of a surfactant, but it elevates the Krafft point of the surfactant. It is then of great importance for practical uses of surfactants to find a compound which, when added, is able to lower the Krafft point. In line with this interest, some work (Ogino, K., M. Abe, Y. Sakama, M. Endo, H. Yokota, K. Sagawa, C. Eguchi and M. Takehara, unpublished) has been done on dissolution behaviors of anionic and amphoteric mixed surfactant systems: sodium alkyl sulfates (alkyl chain lengths: 12, 14 and 16); dodecyl benzene sulfonate; alpha-olefin sulfonates (alkyl chain lengths: 14 and 16); N^{α}, N^{α}-dimethyl-N^{ϵ}-lauroyl lysine (DMLL), N^{α}, N^{α}, N^{α}-trimethyl-N^{ϵ}-palmitoyl lysine (TMPL), and N,N-dimethyl-N-(carboxymethyl) lauroyl ammonium (DMCL). We found that mixing anionic surfactant with amphoteric surfactant will result in the Krafft point depression of surfactants.

In this paper, to elucidate the dissolution behavior of the mixed surfactant system, we report the effect of some inorganic electrolytes on the dissolution temperatures of anionic-amphoteric mixed surfactant systems.

EXPERIMENTAL

Materials: Anionic surfactant. Sodium dodecyl sulfate (SDS, $C_{12}H_{25}OSO_3Na$) was purchased from Wako Pure Chemical Industries, Ltd., Tokyo, Japan, and was more than 99.5% pure. It was extracted with ether and recrystallized from ethanol.

Amphoteric surfactant. N^{α},N^{α}-dimethyl-N^{ϵ}-lauroyl lysine (DMLL, $C_{11}H_{23}CONH(CH_2)_4\text{-}CH\ (N^{+}H(CH_3)_2)\ COO^{-}$) was supplied by the Central Research Laboratories of Ajinomoto Co., Inc. The synthesis and purification were described previously (27). It was dissolved in ethanol and deposited with acetone. The purities were ascertained by surface tension measurements.

Inorganic electrolytes. Sodium chloride (NaCl), sodium thiocyanate (NaSCN), and calcium chloride dihydrate ($CaCl_2{\cdot}2H_2O$) were of reagent grade. Water used in this experiment was twice distilled and was deionized by an ion-exchange instrument (NANO pure D-1791 of Barnstead Co., Ltd.); its resistivity was about 18.0 megohm·cm and its pH was 6.7.

Methods: Dissolution temperature of the hydrated solid agent of surfactant. The dissolution temperatures (Td) of pure surfactants and their mixtures were estimated from the solution temperatures at 2.0×10^{-2} or 1.0×10^{-2} mol/l solutions on gradual heating (at most 1 C/min) up to 85 C in a water bath with vigorous stirring. The reproducibility of the measured dissolution temperatures was within 0.2 C. To obtain the hydrated solid agents equilibrated with their solutions, the surfactants were dissolved at high temperature and precipitated by cooling.

Preparation of addition compound and DMLL-Na^{+}. The addition compound is obtained by quick filtration of the crystalline agent precipitated under the

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following conditions: (concn. of surfactant, 2.0×10^{-2} mol/l; SDS:DMLL=1:1; concn. of $CaCl_2$, 2.5×10^{-2} mol/l) at a temperature below the dissolution temperature; the precipitate is then dried in vacuo after filtration. $DMLL^-Na^+$ is obtained by mixing DMLL with the alkaline solution of NaOH (pH = 13) and then evaporating the solvent.

IR. Infrared spectra were measured by using a 260-50 instrument of Hitachi Co., Ltd., Tokyo, with KBr tablet.

Determination of concentration of sodium ion and calcium ion. The instrument for the measurements of concentrations of sodium ion and calcium ion of supernatant solution after sedimenting the addition-compound was an atomic absorption spectrophotometer (Model 508, Hitachi Co., Ltd.).

Measurement of organic carbon dissolved in water. The concentration of the organic carbon of the supernatant solution after sedimenting the addition compound was determined with a total organic carbon analyzer, Model TOC-10B of Shimadzu Co., Ltd.

The concentration of Na^+, Ca^{2+} and organic carbon in the addition compound are obtained from the differences between the concentration in the total solution and in the supernatant solution.

RESULTS AND DISCUSSION

Effect of NaCl and NaSCN on dissolution temperature. The dissolution temperatures of SDS-DMLL mixed surfactant solutions at 2.0×10^{-2} mol/l (above CMC), for various concentrations of NaCl, are plotted against the mole fraction of DMLL in Figure 1. For the pure SDS and pure DMLL solutions, the dissolution temperatures are 17.1 and 40.0 C, respectively. By mixing those surfactants, the dissolution temperature begins to decrease, becoming less than 0 C at a certain composition region. As the concentration of NaCl increases, the dissolution temperatures of solutions below 0.4 mole fraction of DMLL increase, while those above 0.9 of mole fraction of DMLL remain almost the same.

Figure 2 shows the change of the dissolution temperatures of SDS-DMLL mixed surfactant solutions at 2.0×10^{-2} mol/l (above CMC) with the mole fraction of DMLL, for various concentrations of NaSCN. By adding those surfactants to the aqueous solutions including NaSCN, the dissolution temperature becomes less than 0 C at a certain composition region. The dissolution temperatures of solutions below 0.4 of mole fraction of DMLL increase with increasing concentration of NaSCN, while those above 0.9 of mole fraction of DMLL are lower than those of the salt-free system.

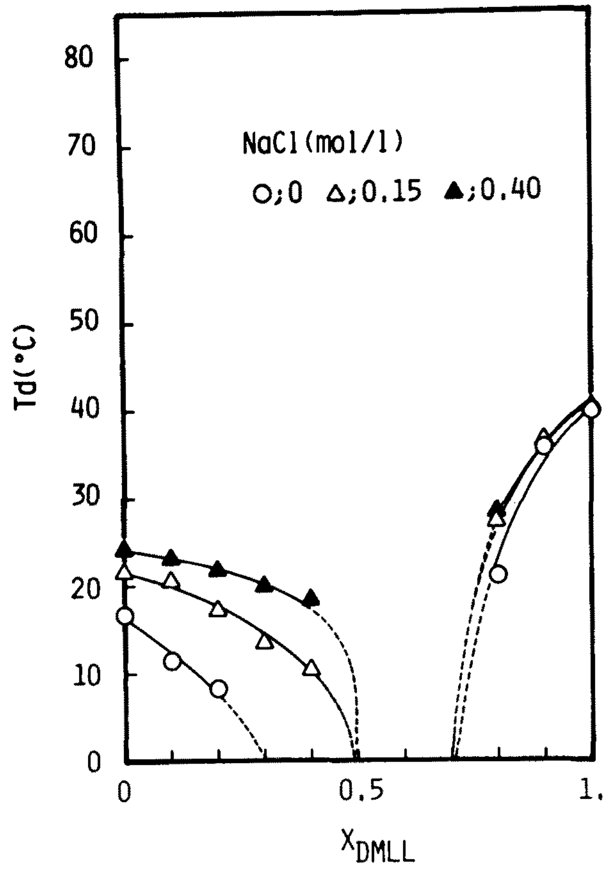

FIG. 1. Effect of NaCl on dissolution temperature (Td) in SDS/DMLL system. Concn. of surfactant: 2.0×10^{-2} mol/l.

TABLE 1.

Difference between effect of NaCl and of NaSCN on dissolution temperature in DSD/DMLL system.

Salt / ^{x}DMLL	0.15 (mol/l)		0.40 (mol/l)	
	NaCl	NaSCN	NaCl	NaSCN
0	22.0(°C)	21.9(°C)	24.6(°C)	24.0(°C)
0.1	20.9(°C)	19.7(°C)	23.4(°C)	23.6(°C)
0.2	17.6(°C)	18.0(°C)	22.2(°C)	22.3(°C)
0.3	14.0(°C)	13.1(°C)	20.3(°C)	19.6(°C)
0.4	10.7(°C)	8.4(°C)	18.7(°C)	15.6(°C)
0.9	36.8(°C)	29.0(°C)	36.7(°C)	20.3(°C)
1.0	40.0(°C)	32.2(°C)	40.0(°C)	31.0(°C)

Table 1 depicts the dissolution temperatures in added NaCl systems and/or NaSCN systems, which are obtained from Figures 1 and 2. In the lower molar region of DMLL (below 0.4), each dissolution temperature in NaCl systems is almost the same as that in NaSCN systems, at constant mole fraction of DMLL and concentration of an electrolyte. This means that the dissolution temperature in those systems does not depend on the kind of anion in the electrolyte molecule. This may be attributed to the fact that the CMC of SDS as an anionic surfactant is dependent on only the counter ion (positive ion), not on the same ion (negative ion) as the surfactant ion. At mole fraction above 0.9 of DMLL, the dissolution temperature of the system with 0.15 mol/l NaCl added was almost equal to that with 0.40 mol/l NaCl added, while that of the system with 0.40 mol/l NaSCN added is lower than that for 0.15 mol/l NaSCN. With respect to this matter, Tsujii et al. (28) have suggested that the pow-

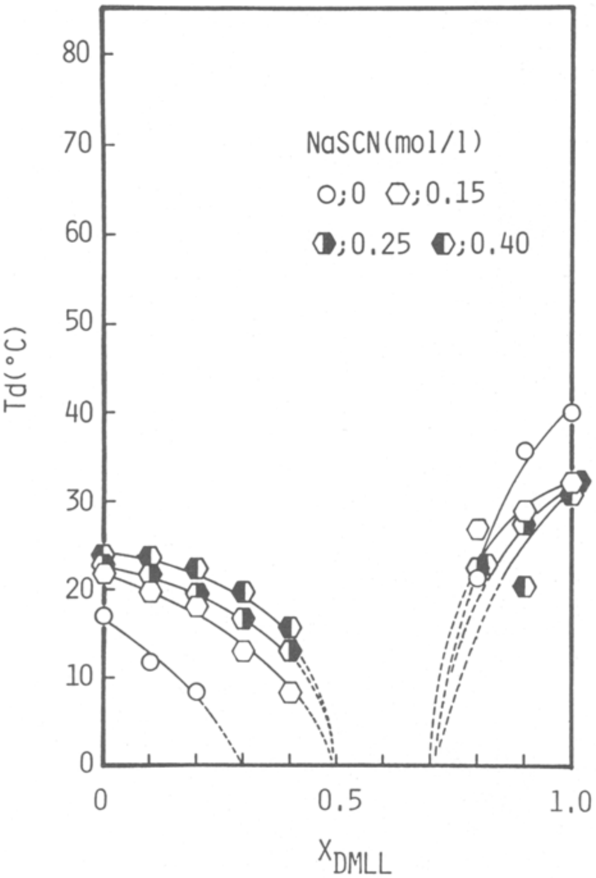

FIG. 2. Relationship between dissolution temperature (Td) and mole fraction of DMLL in SDS/DMLL including NaSCN. Concn. of surfactant: 2.0×10^{-2} mol/l.

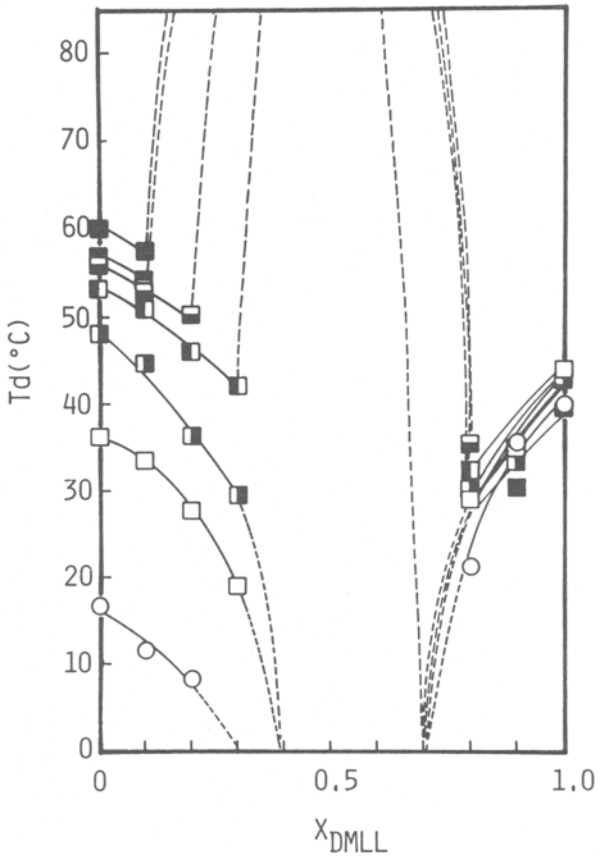

FIG. 3. Dissolution temperature (Td) of SDS/DMLL including $CaCl_2$ (concn. of surfactant: 2.0×10^{-2} mol/l) as a function of mole fraction of DMLL. $CaCl_2$ (mol/l); ○, 0; □, 2.5×10^{-3}; ◨, 5.0×10^{-3}; ◧, 1.0×10^{-2}; ⬓, 2.5×10^{-2}; ⬒, 5.0×10^{-2}; ■, 2.5×10^{-1}.

er of the negative ion, which causes the Krafft point depression, decreases in the order of $SCN^- > I^- > NO_3^- > Cl^-$: the so-called lyotropic series. In this study, the difference in dissolution temperature depression in the presence of NaSCN or of NaCl seems also to be attributable to the difference in the lyotropic series.

Effect of $CaCl_2$ on dissolution temperature. Figure 3 represents the change in the dissolution temperature of SDS-DMLL mixed surfactants at 2.0×10^{-2} (above CMC) with the mole fraction of DMLL, for various concentrations of $CaCl_2$. In the case of the concentration region lower than 5.0×10^{-3} mol/l of $CaCl_2$, the dissolution temperatures of SDS-DMLL mixed surfactant solutions become less than 0 C between 0.4-0.7 mole fraction DMLL. However, at the concentration region higher than 1.0×10^{-2} mol/l of $CaCl_2$, the dissolution temperatures increase up to 85 C or more. The composition region where the surfactant mole does not dissolve extends with increasing concentration of $CaCl_2$.

Tsujii et al. (29) reported that the Krafft points of binary mixtures of anionic and amphoteric surfactants showed a maximum at a certain composition. They suggested that the appearance of a maximum in Krafft point vs composition curves could be attributed to the addition compound (or intermolecular compound) formation between anionic and amphoteric surfactants in the solid phases. An addition compound apparently is formed between SDS and DMLL in the solid phases because the dissolution temperature vs mole fraction curves have a maximum. However, the dissolution temperature vs mole fraction curves do not have a maximum in NaCl systems, so an addition compound is not formed between SDS and DMLL. This means that the formation of the addition compound is closely related to the existence of calcium ions.

Figure 4 exhibits the change in dissolution temperature of SDS-DMLL mixed surfactant solutions at 1.0×10^{-2} mol/l (above CMC) with the mole fraction of DMLL, for various concentrations of $CaCl_2$. At concentrations lower than 2.5×10^{-3} mol/l $CaCl_2$, the dissolution temperatures of SDS-DMLL mixed surfactant solutions become less than 0 C at a certain molar region. For the case of 5.0×10^{-3} mol/l of $CaCl_2$, the dissolution temperature is 85 C at a molar ratio of 0.5. Regarding this, Tsujii et al. (29) have suggested that the composition of the addition compound (anionic and zwitterionic surfactants) is that of the Krafft point maximum. Therefore, this may imply that the mole fraction of dodecyl sulfate ion/DMLL complex is 1 to 1.

Table 2 shows the dissolution temperatures of SDS-

DMLL mixed surfactant solutions at 1.0 × 10^{-2} mol/l and 2.0 × 10^{-2} mol/l (above CMC) in $CaCl_2$ systems. At the same concentration of $CaCl_2$, the dissolution temperatures at 1.0 × 10^{-2} mol/l of surfactant are higher than those at 2.0 × 10^{-2} mol/l of surfactant. At the same ratio of surfactant to $CaCl_2$ concentrations (2:1 and 5:1), the dissolution temperatures are almost the same. As mentioned above, the dissolution temperature is independent of the anion species in the electrolyte molecule.

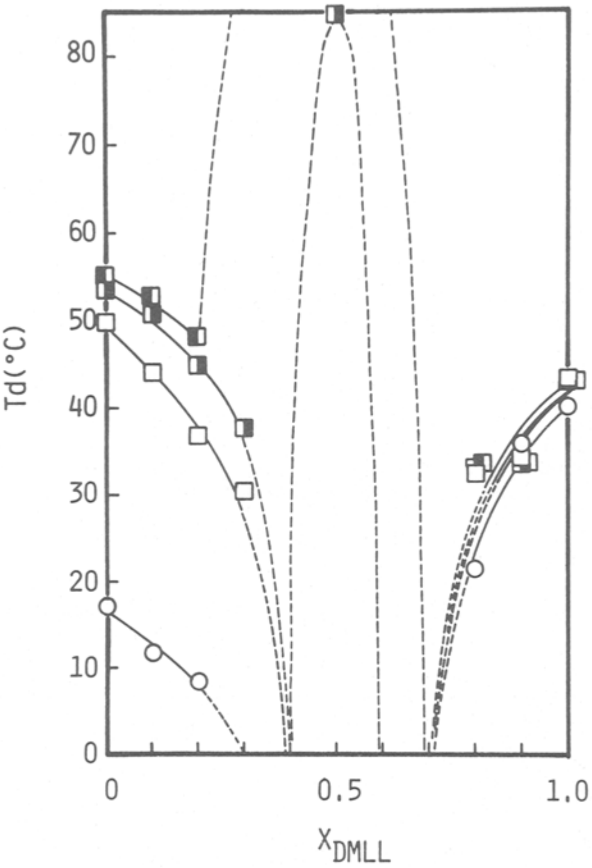

FIG. 4. Effect of $CaCl_2$ on dissolution temperature (Td) in DSD/DMLL system. $CaCl_2$ (mol/l); ○, 0; □, 2.5 × 10^{-3}; ◨, 5.0 × 10^{-3}; ◧, 1.0 × 10^{-2}. Concn. of surfactant: 1.0 × 10^{-2} mol/l.

TABLE 2.

Effects of surfactant and $CaCl_2$ concentrations on dissolution temperature in SDS/DMLL system.

Surfactant	1.0 × 10^{-2} (mol/l)		2.0 × 10^{-2} (mol/l)	
$CaCl_2$ (mol/l)	2.5 × 10^{-3}	5.0 × 10^{-3}	5.0 × 10^{-3}	1.0 × 10^{-2}
X_{DMLL};0	49.9(°C)	53.5(°C)	48.3(°C)	53.5(°C)
0.1	44.1(°C)	50.7(°C)	44.8(°C)	51.1(°C)
0.2	36.9(°C)	44.9(°C)	36.6(°C)	46.2(°C)
0.3	30.5(°C)	37.6(°C)	29.7(°C)	42.3(°C)

The dissolution temperature below a mole fraction of 0.3 appears to be dependent on the ratio of surfactant and calcium ion concentrations.

Structure and composition of the addition compound in $CaCl_2$ system. Figure 5 shows the infrared absorption (IR) spectra of SDS, $DMLL^-Na^+$, and the addition-compound in $CaCl_2$ system. SDS exhibits the characteristic absorption bands of a sulfate at 1210 and 1250 cm^{-1}. $DMLL^-Na^+$ has the characteristic absorption bands of a carboxylate at 1600 cm^{-1}. The absorption bands of the addition compound are at 1210, 1250 and 1600 cm^{-1}. This means that the addition compound contains a sulfate group due to SDS and a carboxylate group due to DMLL. The composition of the addition compound can, therefore, be estimated by determining the concentration of Na^+, Ca^{2+} and total organic carbon.

Table 3 shows the concentration of Na^+, Ca^{2+} and carbon in the addition-compound. We found that the addition compound consisted of 0% of Na^+, 15.6% of Ca^{2+} and 98.7% of organic carbon. As mentioned above, the mole fraction of dodecyl sulfate ion/DMLL is 1 to 1. Therefore, the composition of the addition compound is estimated to be dodecyl sulfate ion: DMLL:Ca^{2+} = 5:5:2. If we consider the neutralization of the electric charge in the addition compound, the composition of the addition compound may consist of dodecyl sulfate ion:DMLL:Ca^{2+} = 4:4:2. The experimental value is consistent with the calculated value. Thus, the dissolution temperatures of the hydrated solid agents in SDS-DMLL systems including salt are dependent on both the mixing radio of surfactants

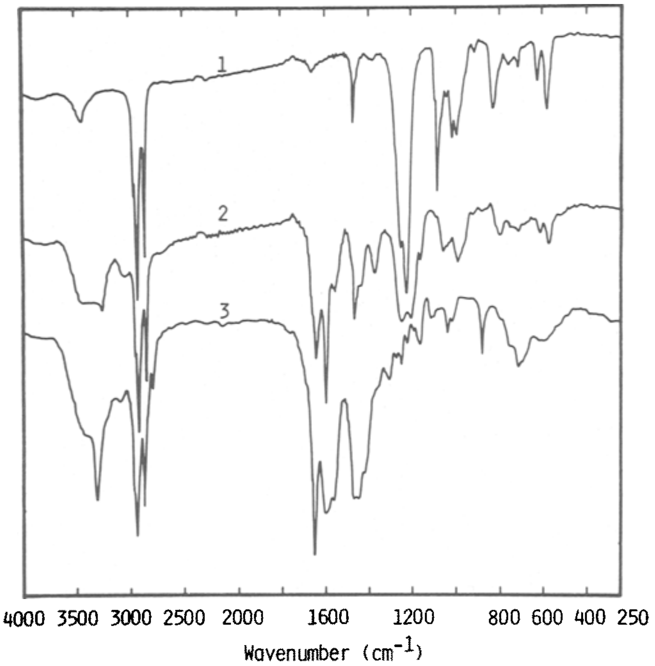

FIG. 5. Infrared spectra for SDS, addition-compound, and $DMLL^-Na^+$ suspended in KBr. 1, SDS; 2, addition-compound; 3, $DMLL^-Na^+$.

TABLE 3.

Composition of the addition-compound formed in SDS/DMLL/$CaCl_2$ system.

	Na		Ca		C	
	(mol/l)	(%)	(mol/l)	(%)	(mg/l)	(%)
Supernatant solution	1.00×10^{-2}	100	2.11×10^{-2}	84.4	50.8	1.32
Addition-compound	0	0	3.90×10^{-3}	15.6	3.84×10^{3}	98.7

and the kinds of salt. One should note that as the concentration of $CaCl_2$ becomes larger than a certain value, the dissolution temperature rapidly increases. This may be attributed to the fact that the addition compound formation between dodecyl sulfate ion and DMLL is caused by the presence of calcium ions.

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ERRATUM

The wrong figure was inadvertently published as Fig. 5 in "Preparation of Geometrical Isomers of Linolenic Acid" by A. Grandgirard, F. Julliard, J. Prevost and J.L. Sebedio in *JAOCS 64*:1434 (October 1987). The correct figure and figure caption are published below.

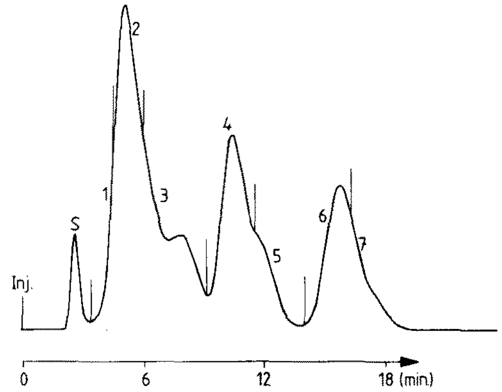

FIG. 5. Preparative HPLC fractionation of a mixture of FAMEs isolated from a heated linseed oil (275 C, 12 hr, under nitrogen, same HPLC conditions as in Fig. 2).