Enthalpy of formation of crystalline surfactant molecular complexes

Nahoko Iimura, Kyoko Ikarashi, Hirotaka Hirata[*]

Niigata College of Pharmacy, 2-13-5 Kamishin'eicho, Niigata 950-2081, Japan

Abstract

The standard enthalpy of formation of novel chemical species — crystalline cationic surfactant molecular complexes — was studied to elucidate the bonding nature, serially scanning over the different surfactant chain-length homologs and various additive species. The enthalpy was not large, but was obviously dependent on the surfactant chain length and the chemical nature of the additive species. The typical complexes comprising long alkyl chain surfactants were formed endothermally, while in short alkyl chain homologs the process was exothermic. By examining the thermal aspect, it was suggested that the typical complexes of long alkyl-chain surfactants were derived not from attractive energetic force factors, but rather from entropic factors associated with the occurrence of severe disorder caused by heavy thermal agitation in the complex crystalline state. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Surfactant; Molecular complex; Enthalpy of dissolution

1. Introduction

It is commonly held that surfactants widely interact with various materials. The true nature of the interaction, however, is still unclear and there is a lack of any direct evidence, as for instance the stable isolation of the interacting entities; moreover, there is too much noncommittal knowledge without solid information which allows us to envisage clear details of the interaction. Under these circumstances, we have established, through X-ray crystallographical analysis, that the ionic surfactant species provides adequate stable molecular complexes in the crystalline state using a wide variety of aromatic substances [1–6].

In cationic surfactants, quaternary ammonium and pyridinium halides are especially pertinent in producing molecular complexes using various phenolics and aromatic basic substances as additives [1,2]. Anionic surfactants, such as alkyl sulfate salts, also produce favorable analogous molecular complexes with various phenolic materials [7]. To date, the number of surfactant complexes stably isolated has reached >200 species, and 50 or more have revealed their crystal structure through X-ray analysis. These surfactant molecular complexes are also very widely applicable through the alteration of the characteristics of complex substances, for instance the enhancement of solubility of medicinal drugs and subsequent reduction of dose and side effects, and the suppression of vapor pressure of volatile materials. In this respect, we succeeded in acquiring many kinds of medicinal drugs which were sparingly water soluble, by modifying them into easily water-soluble drugs [3].

[*] Corresponding author. Tel.: +81-025-268-1153; fax: +81-025-269-1157.
E-mail address: hirata@niigata-pharm.ac.jp (H. Hirata).

Thus, the abundant isolation of such complex species not only offers a material basis for the interaction between surfactants and those additive substances, but also the recognition of the universal existence of a series of novel chemical species as a group of new materials which we have so far failed to notice. This situation motivated a further exploration of the heat produced during complex formation to elucidate the origins of binding and the nature of the interaction between surfactants and additives. In the present study, we dealt with the enthalpy of formation of only the cationic surfactant molecular complexes, and did not examine the anionic surfactant complex species. The measurements extensively covered various additives from phenolics and aromatic basic materials to the non-polar substances, homologously scanning the surfactant chain length from C_{18} to C_6. Through these measurements it was revealed that the amount of heat produced was not so large, and that the typical surfactant molecular complexes with long alkyl chains (C_{18}–C_{12}) displayed endothermic formation of the complexes, while surfactants of shorter alkyl chain homologs showed exothermic complex formation.

2. Experimental

2.1. Materials

Surfactant molecular complexes were always newly prepared before thermal measurements through the normal method of solubilization in an aqueous medium for long alkyl-chain surfactants. For shorter chain homologs, appropriate solvent mixtures (water added with methanol or acetone) were often used. Surfactants and additives were commercially available and offered as materials for the complex preparation after several recrystallization treatment. Other details of the complex formation are described previously [1–3]. Each thermal specimen and solvent methanol for dissolution heat measurements were carefully treated in order to keep dry, although the effect of moisture was unexpectedly very small. KCl, necessary for calibration of the apparatus from its heat of dissolution to water, was of a super special grade from Wako (Osaka, Japan). It was dried at $120°$ for 3 h in a vacuum.

2.2. Apparatus

A heat conduction-type twin calorimeter (Model MMC-5111, Tokyo Riko, Tokyo, Japan) was used. It was assured that the apparatus had the sensitivity of heat detection of ca. 0.12 μV/μW, a thermistor sensitivity of 52 mV/°C, a base line sensitivity of ±0.5 μV/ 10°C for 24 h and thermostat stability of 3×10^{-3}°C, respectively. In comparing the heat quantity derived from the apparatus used with the authorized value of the dissolution heat [8] of carefully treated KCl crystals to water, the error was within 0.5%. The error in the heat of dissolution of all specimens (sole additives, sole surfactants and complexes) examined was similar, being within a few percents. In the present study, the heat quantity was always evaluated graphically through the thermistor voltage–time trace drawn by a recorder (Servocorder SR6221 Graphtec, Yokohama, Japan).

3. Results

The surfactant molecular complexes dealt with in this study appear in Table 1, together with the necessary molecular data for the heat evaluation. All these surfactant molecular complexes are produced and isolated in the crystalline state [1–3]. As already mentioned, these surfactant molecular complexes are quite stable and it is very easy to determine their molar composition, for instance by UV spectrometry or elementary analysis [1–3]. X-ray crystallography is the most direct and reliable method because well defined crystals are available. The values of the molar composition ratios are important to evaluate each molar standard enthalpy of formation of the complex species at 298.15 K.

In Fig. 1, typical structures, and in Table 2, several crystal findings of the cationic surfactant molecular complexes related to this subject are listed [3–6]. In all cationic surfactant species, irrespective of the difference of the surfactant chain length and the variety of the additive chemical nature, the complex structures shown here are quite common at such points that the additive molecules are always accommodated between the heads and tails of the surfactant molecules in the mother surfactant crystal matrix. The consequence of this accommodation of the additive

Table 1
Surfactant molecular complexes dealt with in this study

Complex surfactant/additive	Molar composition ratio surfactant/additive
STAB[a]/2-naphthol	1/1
STAB/p-phenylphenol	2/1
CTAB[b]/2-naphthol	1/1
CTAB/p-phenylphenol	2/1
CTAB/diphenylamine	2/1
CTAB/indole	3/2
CTAB/diphenyl	2/1
MTAB[c]/2-naphthol	1/1
MTAB/p-phenylphenol	2/1
MTAB/diphenylamine	2/1
MTAB/indole	3/2
LTAB[d]/2-naphthol	1/1
LTAB/p-phenylphenol	2/1
LTAB/diphenylamine	2/1
LTAB/indole	3/2
DTAB[e]/2-naphthol	1/1
DTAB/p-phenylphenol	1/1
DTAB/diphenylamine	3/2
DTAB/indole	3/2
OTAB[f]/2-naphthol	1/1
OTAB/p-phenylphenol	1/1
OTAB/diphenylamine	3/2
OTAB/indole	3/2
HTAB[g]/2-naphthol	1/1
HTAB/p-phenylphenol	1/1
HTAB/diphenylamine	3/2
HTAB/indole	3/2

[a] Stearyltrimethylammonium bromide.
[b] Cetyltrimethylammonium bromide.
[c] Myristyltrimethylammonium bromide.
[d] Lauryltrimethylammonium bromide.
[e] Decyltrimethylammonium bromide.
[f] Octyltrimethylammonium bromide.
[g] Hexyltrimethylammonium bromide.

molecules causes lattice elongation along the longest direction of the mother surfactant unit cell [3–6]. This generality in the complex structure might infer that the diversity of the thermal characteristics observed in various surfactant complexes should directly reflect the molecular interaction between surfactants and additives, but not simply be dependent on the packing style of molecules in the complex crystals.

The standard enthalpy of formation ($\Delta H_f^{\ominus}$) of the surfactant molecular complexes was derived from measurements of the standard heat of dissolution of the respective materials, S (surfactant), A (additive) and $S_m A_n$ (complex of *m–n* molar ratio), to any commonly dissolvable medium. For such a medium we used methanol throughout. The scheme of the heat estimation involved in the surfactant complex formation is depicted in Fig. 2 as the enthalpy cycle together with necessary notations in each passage. The notations S(MeOH), etc. express the dissolution state of the surfactant, etc. in methanol and $\Delta H_1^{\ominus}$, $\Delta H_2^{\ominus}$, $\Delta H_3^{\ominus}$, and $\Delta H_5^{\ominus}$, signify respective molar heats of dissolution of S, A and $S_m A_n$ to methanol, and of S to methanol solution which contains corresponding quantities of molar A necessary to comprise the complex species. The relation between $\Delta H_6^{\ominus}$ and $\Delta H_5^{\ominus}$ is the reverse. $\Delta H_4^{\ominus}$ implies the molar heat of the reaction between A and S in methanol. This heat was not examined in this study, because it was assumed to be very small.

For the final assessment of the standard heat of the complex formation we needed to determine at least the four values of the standard heat of dissolution of the crystalline materials to methanol (either $\Delta H_1^{\ominus}$ or, $\Delta H_2^{\ominus}$, and $\Delta H_3^{\ominus}$, and either $\Delta H_5^{\ominus}$ or $\Delta H_6^{\ominus}$ according to the selection of either $\Delta H_1^{\ominus}$ or, $\Delta H_2^{\ominus}$). With regard to the selection of either $\Delta H_5^{\ominus}$ or $\Delta H_6^{\ominus}$, the latter heat of dissolution appeared to be more preferable than the former, because the amount of the latter was much larger than that of the former. Accordingly, the necessary values for the final evaluation of $\Delta H_f^{\ominus}$ are limited to those of three passages. These values should be, of course, the ones obtained in the pertinent concentration range without further effect of dilution (see Fig. 3). The findings of the averaged values of heat of dissolution in each passage are summarized in Tables 3–5. The typical profiles of each species of dissolution relative to methanol are depicted in Fig. 3. Over the very wide range of the molar ratio of methanol to dissolved species, almost no drift of the heat values implies that each species is in a state of almost no interaction within this range; therefore, it appears that there is no effect of dilution on each species at any selected point within this range. As depicted in Fig. 3, it is likely that very little interaction exists between surfactant and additive in methanol, i.e. $\Delta H_4^{\ominus}$ must be rather small, since the molar heat of dissolution of the complex was very close to the sum of those of two moles of surfactant and one mole of the additive. (Note that, in this exemplified case, the complex was
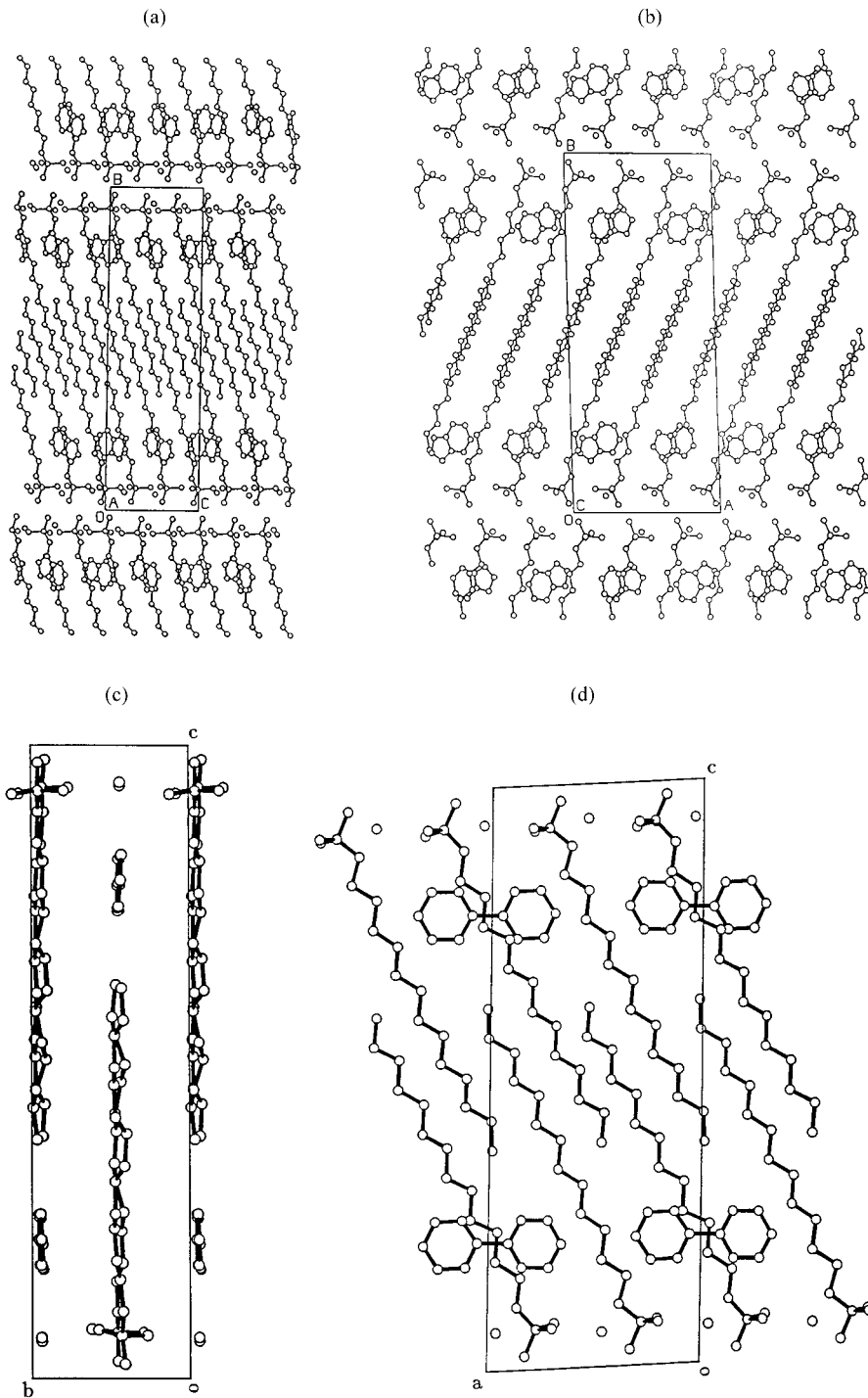
(a)

(b)

(c)

(d)

Fig. 1. Some crystal structures of surfactant molecular complexes which appear in this study. Projection of complex, CTAB/indole, (a) on the b–c plane; and (b) on the a–b plane, respectively. Projection of complex, MTAB/diphenyl (c) on the b–c plane; and (d) on the a–c plane, respectively.

Table 2
Crystal data of cationic surfactant molecular complexes related to this study

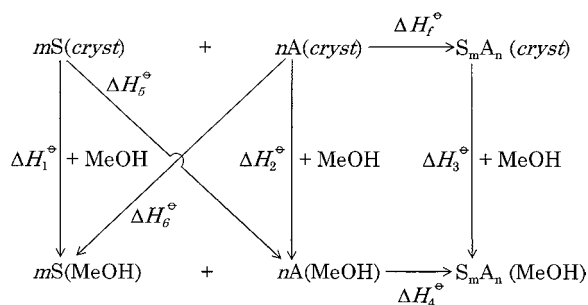| Complex (surfactant/additive)	CTAB/indole	CTAB/diphenyl	MTAB/diphenyl	LTAB/p-phenylphenol
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1$	$P2_1$	$P2_1$
a (Å)	13.250 (8)	11.10 (3)	11.100 (1)	11.10 (1)
b (Å)	32.161 (5)	7.47 (3)	7.456 (1)	7.406 (2)
c (Å)	9.230 (1)	31.9 (1)	29.71 (1)	27.19 (1)
α (°)	88.91 (1)			
β (°)	92.55 (3)	91.8 (3)	94.21 (1)	95.50 (6)
γ (°)	91.38 (3)			
V (Å^3)	3927	2641	2452	2227
Z	2	2	2	2

Fig. 2. Enthalpy cycle for the evaluation of the standard heat of formation of the surfactant molecular complex.

composed of S_2A in its molar ratio). This finding is consistent with those of other measurements observed in vapor pressure osmometry in which the complex species appeared to be entirely dissociated into components in the methanol medium [9].

The dissolution of all crystalline materials to methanol proceeded endothermally. From these heats of dissolution, the standard enthalpy of formation ($\Delta H_f^\ominus$) of the surfactant molecular complexes was calculated as the follows:

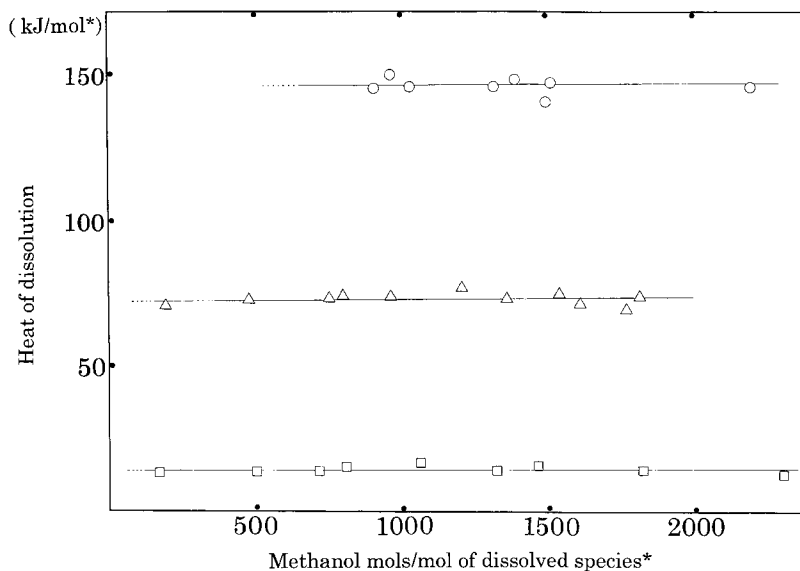$$\Delta H_f^\ominus = \Delta H_2^\ominus + \Delta H_5^\ominus - \Delta H_3^\ominus \tag{1}$$

Fig. 3. Typical heat profile of dissolution of additive *p*-phenylphenol (□); surfacant, CTAB (△); and their molecular complex, CTAB/*p*-phenylphenol (○) to solvent methanol at each molar ratio in methanol to dissolved species. (*) In case the dissolved species is complex, the species and the moles in the diagram imply component surfactants and their number of moles.

Table 3
Standard heat of dissolution of surfactants (ΔH_1) and that of additives (ΔH_2) to methanol

	ΔH_1	ΔH_2 (kJ/mol)$^{-1}$
STAB	76.75±1.31	
CTAB	72.90±1.16	
MTAB	68.24±1.62	
LTAB	51.39±0.35	
DTAB	40.11±1.12	
OTAB	24.72±0.27	
HTAB	21.11±0.50	
2-Naphthol		9.74±0.25
p-Phenylphenol		14.38±0.17
Diphenylamine		14.01±0.13
Indole		8.58±0.10
Diphenyl		13.05±0.19

Thus, we obtained the standard enthalpy of formation of the surfactant molecular complexes in the crystalline state as compiled in Table 6, with various additive species and surfactant alkyl-chain length variations.

4. Discussion

As mentioned previously, at present we have no thermal information on the surfactant complexation, which can be appropriately compared with each other, since these surfactant molecular complexes which have provided a series of thermal findings are novel materials that have received little attention to date. Looking at Table 6, however, it can be recognized that the standard enthalpies of formation ($\Delta H_f^{\ominus}$) of the typical surfactant molecular complexes which are composed of higher surfactant homologs and various additives are positive, although they are not so large in absolute value. As a consequence, the process of complex formation proceeds endothermally when the surfactants have alkyl chains longer than twelve and exhibit the typical characteristics of surfactants. As shown in Table 6, at a specified surfactant (CTAB) the amount of endotherm is clearly dependent upon the nature of the additive species, i.e. it is largest in phenolics (2-naphthol and *p*-phenylphenol) successively followed by the basic substances (diphenyla-

Table 4
Standard heat of dissolution (ΔH_3) of surfactant molecular complex homologs to methanol

	ΔH_3 (kJ/mol)$^{-1}$				
	p-Phenylphenol	2-Naphthol	Diphenylamine	Indole	Diphenyl
STAB	81.37±0.87	75.70±1.72			
CTAB	73.31±0.39	69.39±1.00	75.46±0.31	71.43±0.55	77.50±0.32
MTAB	67.38±0.94	59.51±0.60	66.73±0.17	62.07±0.40	
LTAB	57.57±1.27	51.71±2.02	58.28±0.40	51.40±0.39	
DTAB	50.55±0.64	52.37±0.75	51.00±0.52	45.03±0.23	
OTAB	45.89±1.50	52.06±0.13	47.12±0.26	40.46±0.34	
HTAB	46.36±1.21	46.93±0.21	43.05±0.59	35.92±0.38	

Table 5
Standard heat of dissolution of surfactants to methanol which contain each additive in its molar ratio so as to correspond to the complex formation (ΔH_5)

	ΔH_5 (kJ/mol)$^{-1}$				
	p-Phenylphenol	2-Naphthol	Diphenylamine	Indole	Diphenyl
STAB	78.91±0.25	78.77±0.43			
CTAB	71.64±0.88	72.16±1.98	69.30±0.17	71.84±0.25	68.86±0.17
MTAB	60.12±1.72	63.23±1.14	59.96±0.70	56.47±0.50	
LTAB	48.53±0.17	51.23±0.35	46.78±0.41	47.01±0.56	
DTAB	37.58±0.24	36.95±1.12	35.84±0.21	36.65±0.02	
OTAB	28.02±0.20	25.01±0.24	29.83±0.23	28.09±0.38	
HTAB	22.11±0.23	17.30±0.10	21.06±0.18	21.52±0.12	

Table 6
Standard heat of formation(ΔH_f) of crystalline surfactant molecular complexes

Surfactant/ additive	2-Naphthol	*p*-Phenylphenol	Diphenylamine	Indole	Diphenyl
	ΔH_f (kJ/mol)$^{-1}$				
STAB	12.81±0.28	11.92±0.27			
CTAB	12.51±0.30	12.71±0.32	8.45±0.20	8.99±0.10	4.41±0.12
MTAB	13.46±0.28	7.12±0.17	7.84±0.91	2.98±0.13	
LTAB	9.26±0.61	5.34±0.40	3.11±0.10	4.19±0.14	
DTAB	−5.68±0.34	1.41±0.06	0.55±0.09	0.42±0.13	
OTAB	7.31±0.56	−3.49±0.78	−3.08±0.08	−3.79±0.20	
HTAB	−19.89±0.23	−9.87±0.60	−7.98±0.35	−5.82±0.40	

mine and indole) and the non-polar substance (diphenyl). This trend is maintained in the other surfactant homologs. These systems of complexes containing CTAB as the main partner with various additives exhibit remarkable viscoelasticity in aqueous solutions [10–13], where enormously elongated gigantic micelles were observed through an electron microscope [14]. Thus, it is interesting that in the system which implies markedly strong interactions between surfactants and additives, the heat produced by the complex formation is endothermic. This endothermic aspect gradually shifts toward exothermic, in accordance with the decrease in the surfactant alkyl chain length. This feature is also very common in every examined system as seen in Table 6 with each specified additive material. The enthalpy of the surfactant complex formation is thus more endothermic as the alkyl chain in surfactants becomes longer, while it is more exothermic as the alkyl chain becomes shorter. This trend is also quite general irrespective of the chemical nature of the coupled additive materials with surfactant species.

From physicochemical viewpoints of the surfactant, these trends parallel the ease of acquisition of the complex species in the aqueous medium [1–3]. Thus, the ease of acquisition of these surfactant molecular complexes from aqueous solution systems becomes higher in the longer alkyl-chain homologs which are normally categorized as genuine surfactants and truly appreciated in their performance, for instance as a dispersant in solubilization or emulsification. In reality, in this thermal measurement, the utilized surfactant molecular complex specimens of all higher homologs are obtained rather readily through the conventional treatment of solubilization in aqueous

media. In contrast, shorter alkyl-chain homologs of complex species are only available in a non-aqueous system, since these shorter alkyl-chain surfactants can exhibit a very poor ability to solubilize any additive material in aqueous systems [15,16], because of their inferiority of association [17,18,19]. In such shorter chain length regions the enthalpy of the complex formation is exothermic.

The consequence of the endothermic formation of the typical surfactant molecular complexes with long alkyl-chain homologs implies that the equilibrium of the surfactant complex formation shown in Eq. (2) more preferably declines toward

$$\text{surfactant} + \text{additive} \rightleftharpoons \text{complex} \tag{2}$$
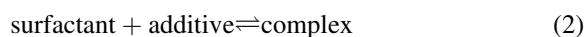
the complex formation side even at high temperatures. This implication corresponds well with the finding that the significantly high stability of the complex additive species is retained at a considerably high temperature in the state of occlusion in the complex crystal structures as shown by thermogravimetric analysis [3,20]. This effect led us to attempt the storage and the shelf-life extension for thermally fragile drugs [3,20].

Secondly, the endothermic process, as seen in the long alkyl-chain homologs, suggests that such typical surfactant molecular complex formations are predominantly promoted by the entropy factor rather than the energy factor, taking into account the following energetic considerations based on Eq. (3). Thus, these surfactant

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} \tag{3}$$

molecular complexes might be anticipated to possess high values of entropy in the standard state. The

anticipation is supported by several appearances: (i) every complex crystal is mechanically very soft to the touch compared with both components, surfactants and additive species (especially with the mother surfactant); (ii) significantly high dielectric coefficient in its crystalline state at a far lower temperature before any transition, suggesting heavy thermal motion of the complex additive species in the complex crystals [21]; and (iii) above all, by the finding that in the structural studies by X-ray the work is always inevitably troubled by rather high values of the *R*-factor, almost all of which come from disorder of hydrocarbon chains in these complex crystals even at a considerably low temperature of $-50°C$ [4–6]. These facts suggest that the surfactant molecular complex crystals are structured at random and the components, especially additive species, are subjected to severe thermal agitation in the crystal matrices in agreement with the above opinion that the complexes must be in a state of high entropy. The argument that these surfactant molecular complexes are very pliant in their hydrocarbon moiety even in the crystalline state might be extended to the common aspect regarding micelle characteristics in the aqueous solution, where the micelle core is likely to be very close to the state of fused hydrocarbon [22–24].

The formation of the crystalline surfactant molecular complex is realized in a very wide variety of additive species coupled with cationic surfactants [3]. Generally, there appears to be no preference in the choice of additive material in the complex formation for cationic surfactants, which range from polars, such as phenolics and aromatic basics, to non-polar materials such as biphenyl [3,6]. With regard to polar additives, phenolics, such as 2-naphthol and *p*-phenylphenol, are rather acidic while diphenylamine and indole studied here are rather basic in nature. Thus, these additives chemically belong to a reverse group with each other, although both species are, from their attractive viewpoints, so commonly supplied just with donor hydrogen necessary to interact with surfactants as to result in complex formations by hydrogen bonding. Biphenyl, however, which is classified as a non-polar substance and is still one of the important and pertinent materials used as an additive, carries no such donor hydrogen or other marked sources to cause an attracting effect with cationic surfactants, which leaves only a slight possibility of a CH–π interaction [6].

It appears, therefore, unreasonable to seek the basis of the complexation by the attractive nature between these surfactants and additives. Moreover, in the case where the complexation is due to attractive forces, the resultant heat must be exothermic. In contrast, the typically generated long alkyl-chain surfactant complexes were all endothermic, i.e. the complexation in this situation must be a heat-absorbing process. Therefore, it can be concluded that the major source in the typical complexation of long alkyl-chain surfactants should be attributed to non-energetic factors which substitute the attractive force effect between components for increasing entropy of the system involved in complex formation, converting heat balance from negative to positive. However, in shorter chain surfactants the heat of complex formation is exothermic. In this process, attractive force between surfactants and additives might be predominant in the molecular complex formation.

5. Conclusion

The standard heat of formation of crystalline cationic surfactant molecular complexes, the almost universal existence of which has recently been established through X-ray crystallography [4–6], was measured to elucidate the nature of the complex formation. The heat of the complex formation was not so large, but it was significantly dependent on the surfactant chain length, i.e. in long alkyl-chain homologs the heat was endothermic, while it was exothermic in short-chain homologs. With regard to the additive species at a specified surfactant, it was revealed that the standard enthalpy of formation of the surfactant molecular complex is largest in phenolics, showing ≈ 10 kJ/mol, followed by several basic materials and then by non-polar substances in which the values were the smallest. The thermal feature found corresponded well with the ease of acquisition of the surfactant molecular complexes from an aqueous medium, which was also parallel to the surfactant's ability to solubilize various materials.

From the present findings it was suggested that, in the formation of typical surfactant molecular complexes of long alkyl-chain surfactants and additives, the process was not promoted by energetic factors, which is simply due to attractive forces between

component materials, but rather by entropic factors which gave rise to the gradual occurrence of a heavy thermal agitation state during complex formation, since the process in question was clearly endothermic. However, the complex formation using shorter chain surfactant homologs might be due to attractive forces between surfactants and additive species, since the process was exothermic.

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