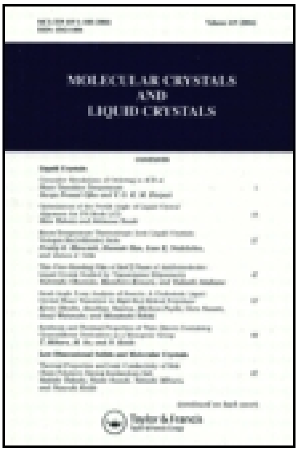

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Material Capture in the Surfactant Solid State

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MATERIAL CAPTURE IN THE SURFACTANT SOLID STATE

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Abstract An interesting behavior of gaseous capture of materials by solid surfactant matrices was examined in comparison with behaviors of other substances (other matrices) which possess long alkyl chain and supposedly similar crystal structure to the surfactant. Through this study it was revealed that the behavior of gaseous capture of materials was characteristic to the surfactant species. Of all surfactants cationic species was conspicuous followed by nonionics, while in anionics the behavior was very poor. Among cationics quaternary and tertiary species especially superior to any other class. For these cationic surfactant species the powder X-ray diffraction measurement disclosed that the gaseous capture of materials remarkably modified matrix surfactant crystal lattices, causing the surfactant molecular complex formation which had already been established by authors.

INTRODUCTION

We have already reported the wide formation of molecular complexes between surfactants and various materials as additives.[1-3] Irrespective of the surfactant species (ionics or nonionics) and of their chemical natures of additves the existence of the surfactant molecular complex formation has clearly been established through elementary analysis, uv spectroscopy etc.[2,3] Especially quaternary ammonium cationic surfactats easily provide many crystalline complexes.[2,3] Some of them have revealed the crystal structure of the surfactant molecular complexes by X-ray analyses.[4]

These surfactant molecular complex crystals are generally deposited from homogeneously solubilized solution systems when kept standing at a cooled condition after an attainment of the equilibrium of the solubilization conventionally treated in aqueous media.[2,3] The surfactant molecular complex crystals thus obtained are promptly dissolved when the solutions are warmed up after recovering all the solution characteristics and resulting the solubilized solution systems as they were.[2,3] It seems that these observations are full of suggestion to solve the problem of the "solubilization".[5]

On the other hand we have found some alternative methods to obtain those surfactant molecular complexes, e.g.,solid state mixing of both components and gaseous capture of the additive species to the solid surfactants etc.[6] Any of these is quite effective when the surfactants have potential to provide the molecular complexes in a pertinent pair of surfactants with additives. The complex formation is readily followed by the X-ray powder method, detecting the diffraction shift based on the lattice modification.

In this report we described the interesting behavior of the gaseous capture of materials to solid surfactants as main matrices, comparing the behaviors with other matrices which had long alkyl chains and polar groups such as higher alcohols, amines and fatty acids and others to know whether the analogous behaviors are commonly observable among those matrices. These substances selected for matrices are crystallographically well-known to be almost analogous to the surfactant, being in parallel arranged with the long alkyl chains in zigzag planar form to make layer structure with each other.[7,8]

Through these studies concerning the ability of the complex formation of those matrix substances with wide variety of captured materials such as phenols, amines, etc., we have acquired several knowledges that the ability to accept materials to form the molecular complexes is just specific to the surfactant species,i.e.,the higher alcohols, amines, fatty acids and others as matrices only apparently exhibit weight increase but substantially no responce to the gaseous capture of materials associated with their crystal lattice deformation, except for a special partner like an acid-base pair, and that the ability is the highest in cationic surfactant species and it follows in the order of nonionics and anionics. Among the ammonium cationics the quaternary and tertiary species had comparable high abilities and marked feasibilities to accept materials into their crystal lattices. The nonionic and anionic species followed the cationics but the latter was far inferior to the former and the lower classes of cationic ammoniums also showed almost none of effect to crystal lattice deformation by capturing materials. This trend well corresponds to the surfactant potential for the complex formation together with additive materials.

Although higher alcohols, amines and fatty acids exhibited a considerable acceptability to materials, their capturing behaviors seemed to be apparent. However these matrices obviously suggested some other interesting effects of an access of gaseous materials to cause intensified very sharp diffraction peaks with clear periodicity over a very wide 2 θ range. The change seems to be due to a gradual breaking of hydrogen bonds of those matrices by the access of gaseously captured materials so as to be resulted in an easily mobilized condition of matrix molecules and to form a stratified structure.

RESULTS AND DISCUSSION

Matrices of the gaseous material capture treated in this study are summarized in Table 1 together with their abbreviations.

TABLE 1 Matrices for the gaseous capture of materials.

Abbreviation	Matrix substance
CTAB	Cetyltrimethylammonium bromide
MTAB	Myristyltrimethylammonium bromide
LTAB	Lauryltrimethylammonium bromide
CDAB	Cetyldimethylammonium bromide
CMAB	Cetylmonomethylammonium bromide
CAB	Cethylammonium bromide
SLS	Sodium lauryl sulfate
SLBS	Sodium laurybenzenesulfonate
985	Polyoxyethylenenonylphenylether
C18OH	Steary alcohol
C18NH2	Stearyamine
C18COOH	Stearic acid
C18Na	Sodium stearate
PARA	Paraffin

As typical profiles the gaseous capture of *o*-bromophenol and *o*-toluidine at 55°C to surfactant matrices and to other matrix substances are illustrated in Figure 1 and 2. For the capture of *o*-bromophenol a cationic surfactant, CDAB, showed the highest ability followed by 985 (nonionic) and other cationic surfactants group. Stearylamine looks rather prominent but its ability to the phenols is due to the basic affinity to acidic substances. The similar result of acid-base relation is encountered in a stearic acid/*o*-toluidine system as seen in Figure 2. Among the matrices almost typical anionic surfactants like sodium stearate and sodium lauryl sulfate showed very little tendency to accept phenols like *o*-bromophenol and *p*-cresol. This tendency of the typical anionics is

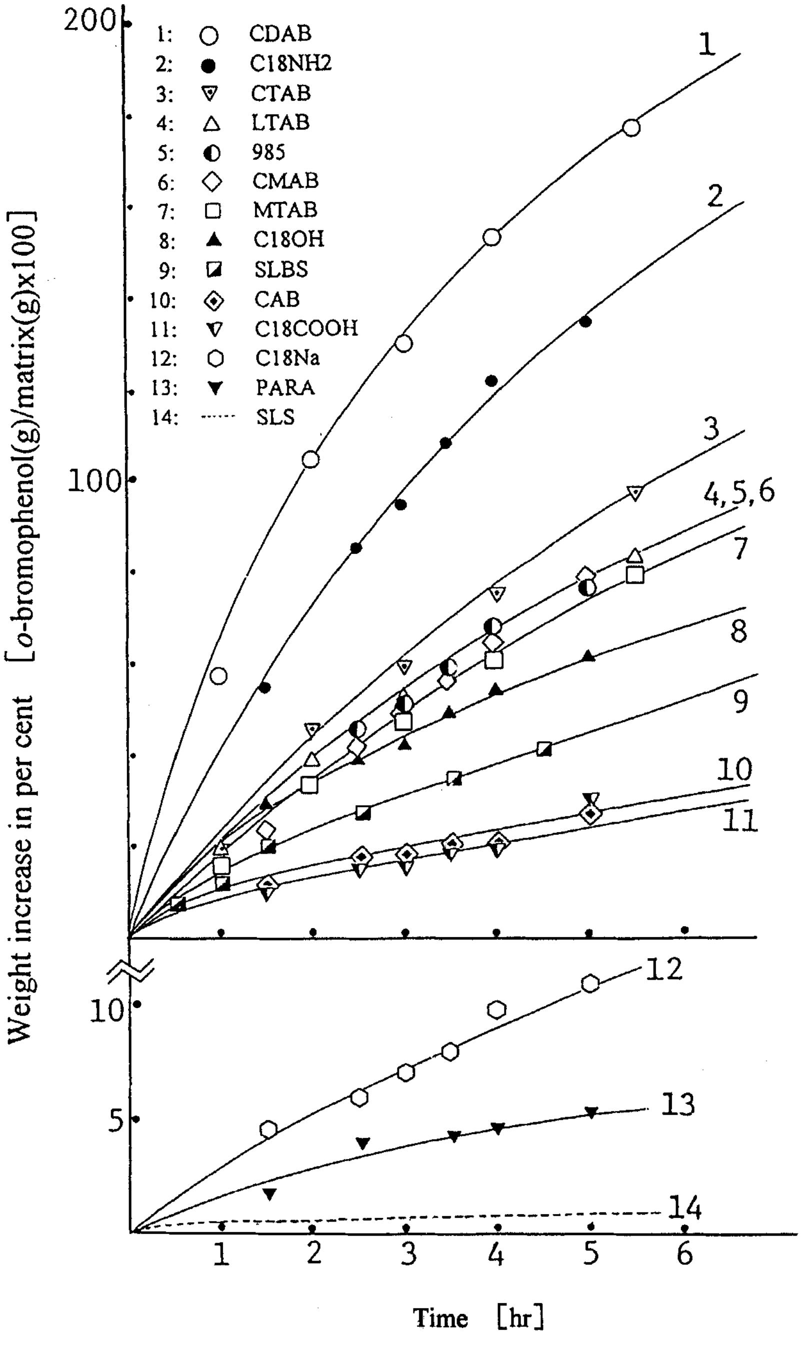

FIGURE 1 Profiles of gaseous *o*-bromophenol capture to various matrices at 55°C

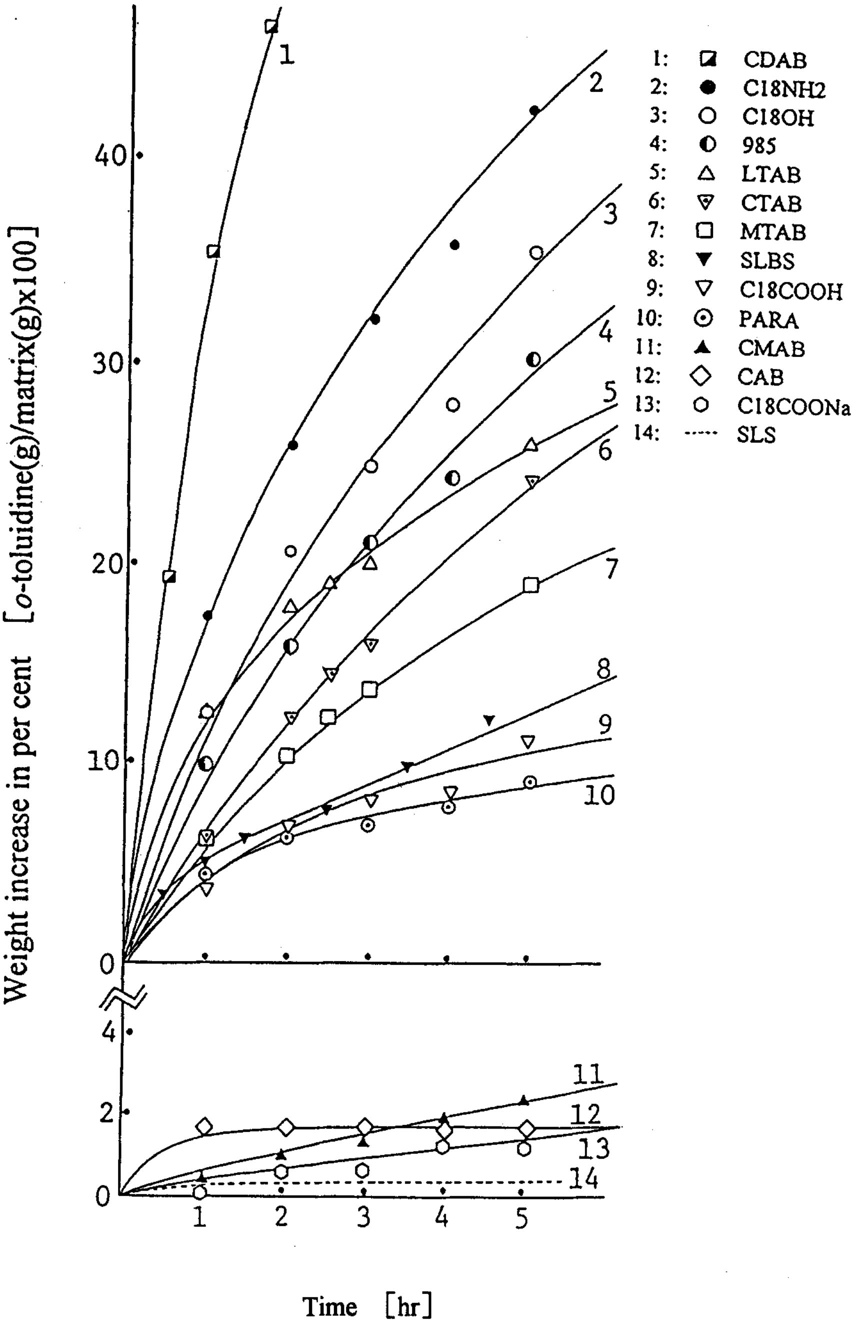

FIGURE 2 Profiles of gaseous *o*-toluidine capture to various matrices at 55°C

very common also to accept basic substances like *o*-toluidine. For a weak anionic surfactant like SLBS the ability was medium. Of the other matrices the long alkyl chain substances containing paraffin are also not so effective to the phenols. The weight increase exhibited in these species especially in paraffin seems to be an apparent result associated to the vapor condensation in the crystal crevices or on the surface areas.

In the group of cationics quaternary ammonium salts (CTAB etc.) showed a considerable excellence compared with other ammonium matrices. It has already been established that they have an outstanding ability to accept many phenols to provide highly stable crystalline molecular complexes[2,3] and that the lower classes (secondary and primary) ammoniums have no ability to accept phenols into their crystal lattices as estimated by X-ray diffraction diagrams shown later, though CMAB apparently shows a high acceptability to the phenol. As for those quaternary ammoniums it appeared that at low temperatures the shorter the alkyl chain in the homolog was the more preferable to accept materials, while the order was reversed at higher temperature. However, this observation is well recognized through an estimation of the apparent activation energy necessary to be taken up into the surfactant crystal lattice to generate the complex species. The estimated values of the apparent activation energy in referred to their alkyl chain length in the homologs are listed in Table 2 showing that those ammoniums have much preferable affinity to phenols than to amines with less values to the former than to the latter.

The quaternary ammonium cationic surfactants widely exhibit the ability to accept aromatic amines as well as phenols to provide crystalline molecular complexes.[3] Some of these were X-ray crystallographically analysed.[4] In this study of the gaseous capture the ability was observed as shown in Figure 2. The cationic surfactant, CDAB, is also superior to any other substance, followed by higher amine and alcohol and other cationics. Thus, the fact that quaternary ammoniums (CTAB etc.) are grouped in a significant class with high ability to accept amines and also effective to provide the molecular complexes with these amines are well supported by the shift of the X-ray diffraction patterns of the powder method.

TABLE 2 Apparent activation energy for material intrusion to the matrix crystal lattice of quaternary ammonium surfactants through gaseous capture.

Captured material/Surfactant	Activation energy (kJ /mol)
o-Bromophenol/CTAB	58.9
/MTAB	34.5
/LTAB	14.0
o-Toluidine/CTAB	108.6
/MTAB	76.2
/LTAB	101.5

The other materials tried to be captured by the surfactant matrices such as aldehydes and ketones etc., showed almost very poor effect although the data were omitted here. For these materials nonionic and cationic surfactant matrices also appear to have some potentials. The X-ray studies, however, denied the ability to accept those materials to the surfactant crystal lattices, deducing a presumable condensation on the surface or to the crystal crevice.

As stated above *o*-bromophenol and *p*-cresol are unambiguously established to provide molecular complexes together with quaternary ammonium cationic surfactants such as CTAB.[2] Many of these groups have afforded us informations as to their crystal structures through the X-ray crystallography.[4] In relation to these facts some clear modifications of the surfactant crystal lattices observed in the course of capturing phenols are presented in Figure 3 through 7. In the Figures the lowest angle diffraction of CTAB etc. alone which is due to almost stretched hydrocarbon chain in trans-zigzag form is, for instance in CTAB (Figure 3), shifted to much lower angle side to such extent as to disappear out of the Figure. This evidences an elongation of surfactant crystal lattices involved by the intrusion of materials through the gaseous capture. The fact of the lattice expansion is quite consistent with the surfactant molecular complex formation already established through their structural analyses.[4] The similar effect of expansion of the surfactant crystal lattices is also observed in other systems which provide surfactant molecular complexes containing CDAB system as seen in Figure 4 through 7.

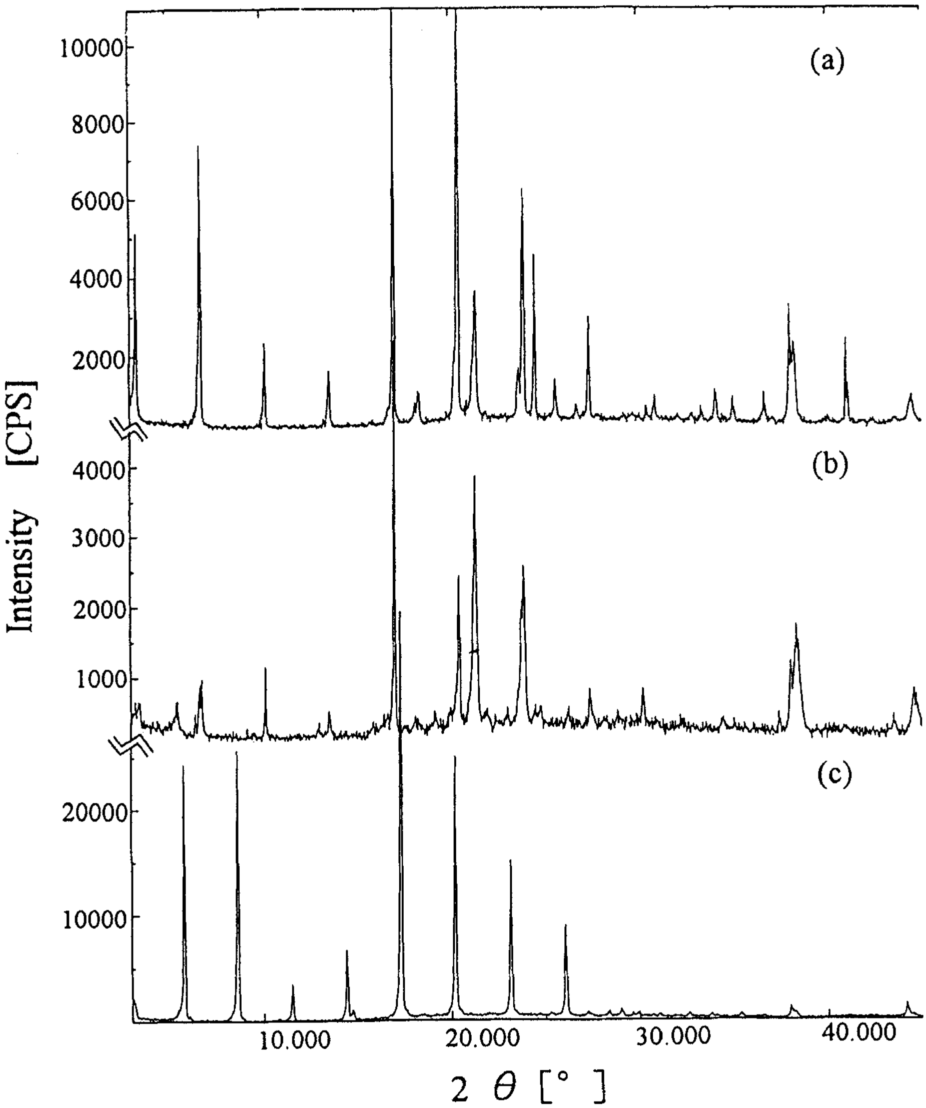

FIGURE 3 X-ray diffractions of powder specimens resulted by gaseous capture to CTAB matrix, a) 0, b) 15, and c) 80 molar per cent capture of *p*-cresol in the ratio of *p*-cresol/CTAB, respectively.

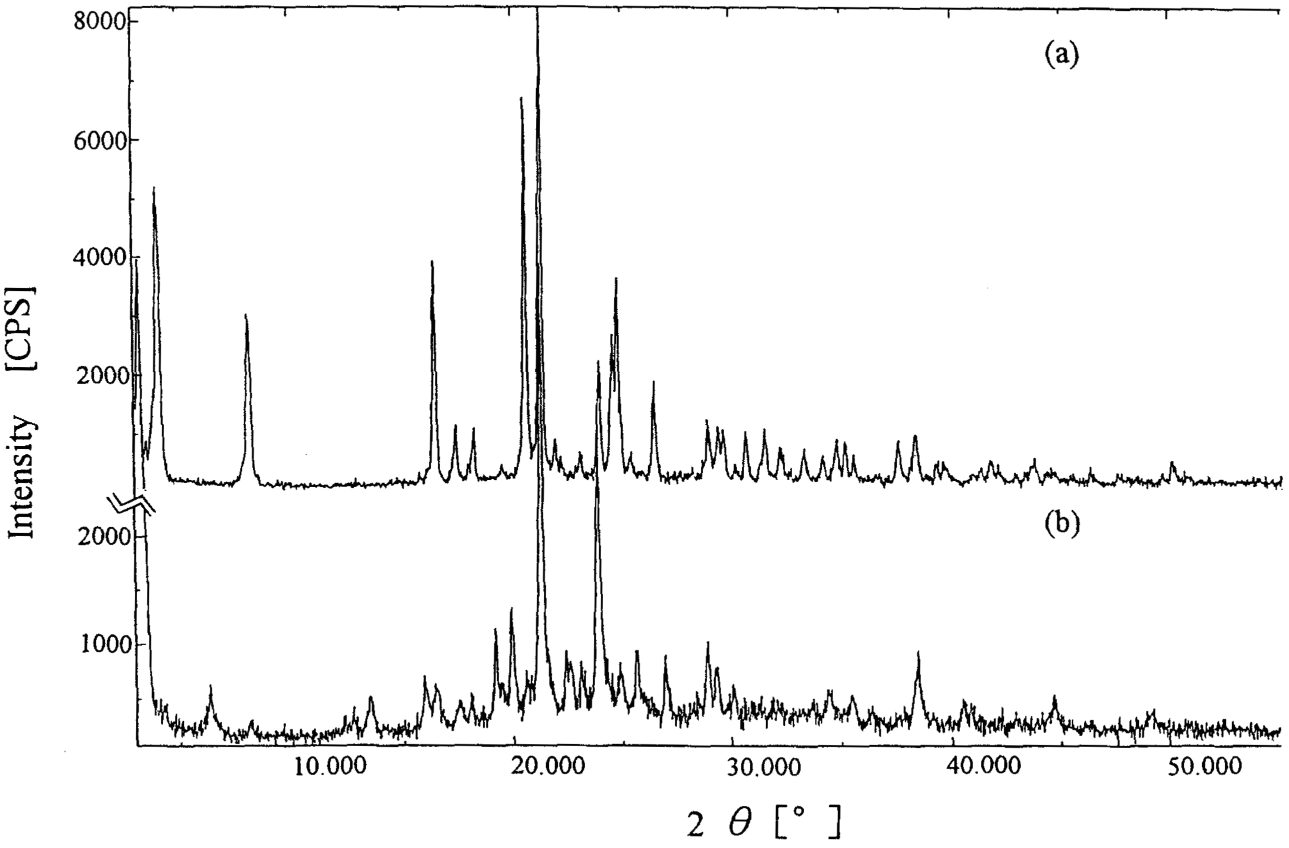

FIGURE 4 X-ray diffractions of powder specimens resulted by gaseous capture to LTAB matrix, a) 0, b) 11, and c) 28 molar per cent capture of *p*-cresol in the ratio of *p*-cresol/LTAB, respectively.

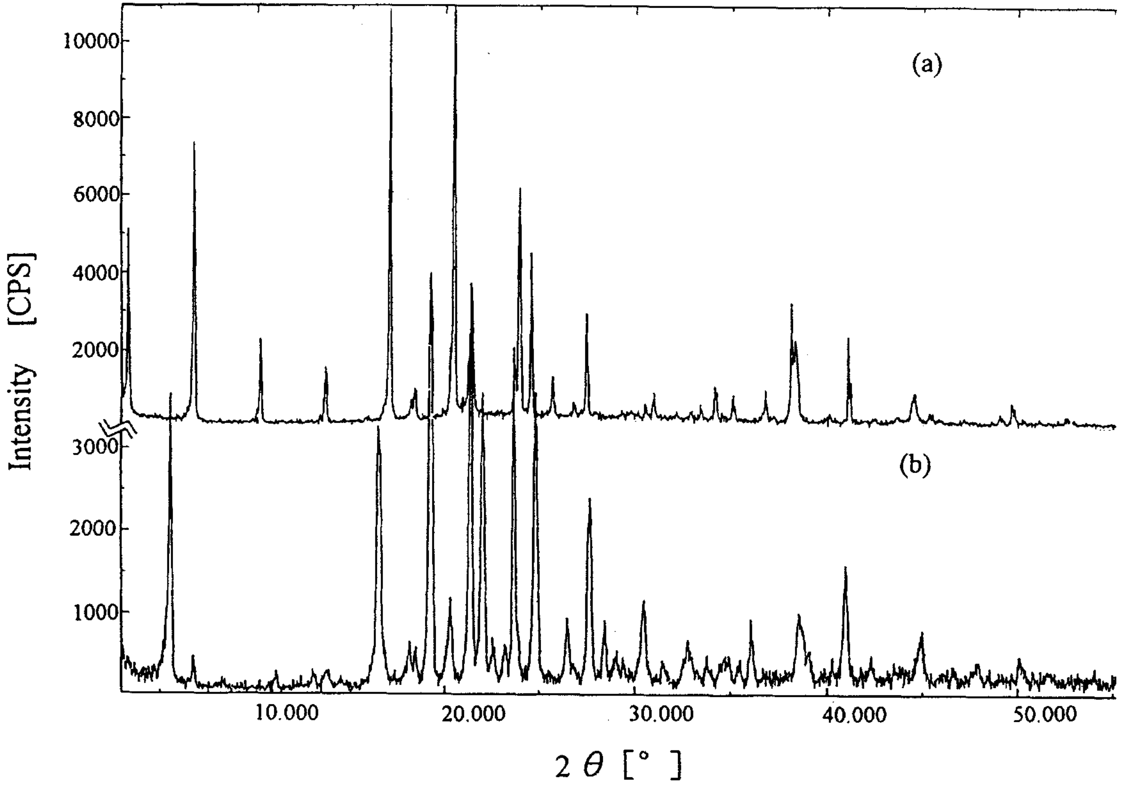

FIGURE 5 X-ray diffractions of powder specimens resulted by gaseous capture to CTAB matrix, a) 0, b) 12, and c) 36 molar per cent capture of *o*-toluidine in the ratio of *o*-toluidine/CTAB, respectively.

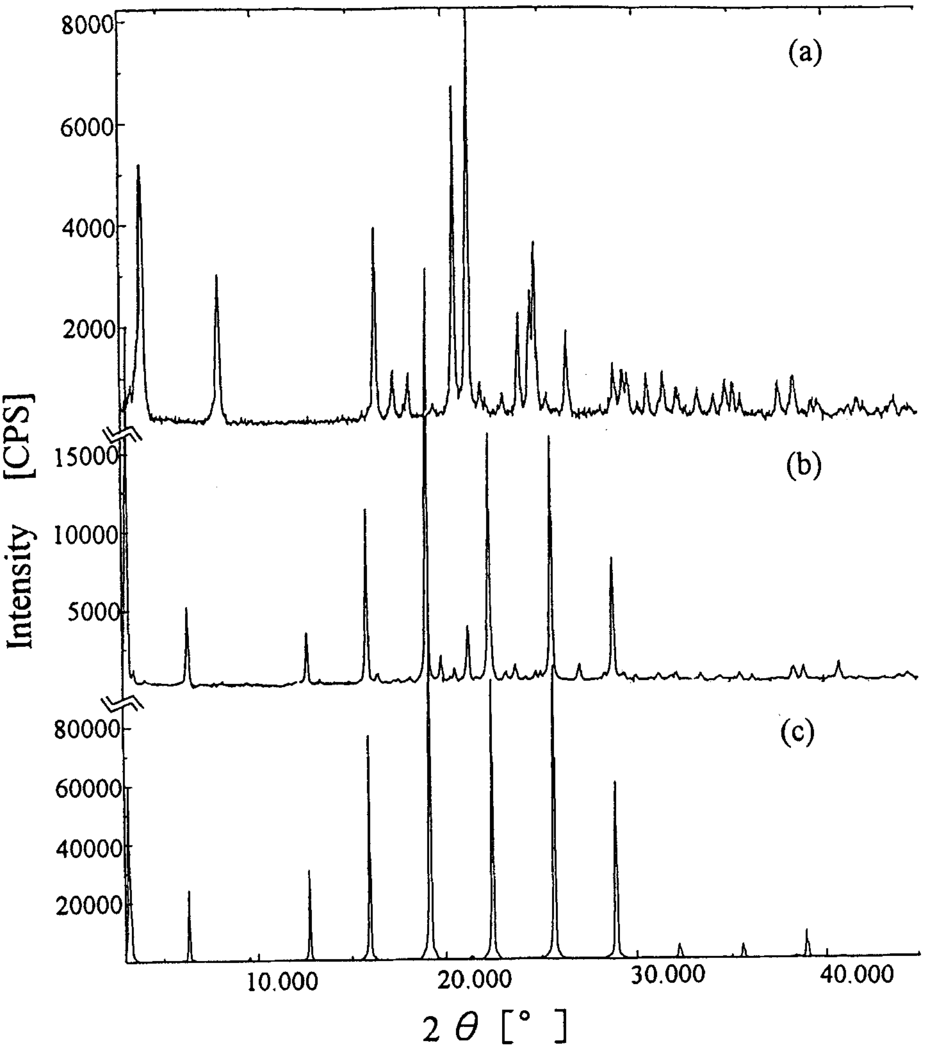

FIGURE 6 X-ray diffractions of powder specimens resulted by gaseous capture to LTAB matrix, a) 0, b) 20, and c) 30 molar per cent capture of *o*-toluidine in the ratio of *o*-toluidine/LTAB, respectively.

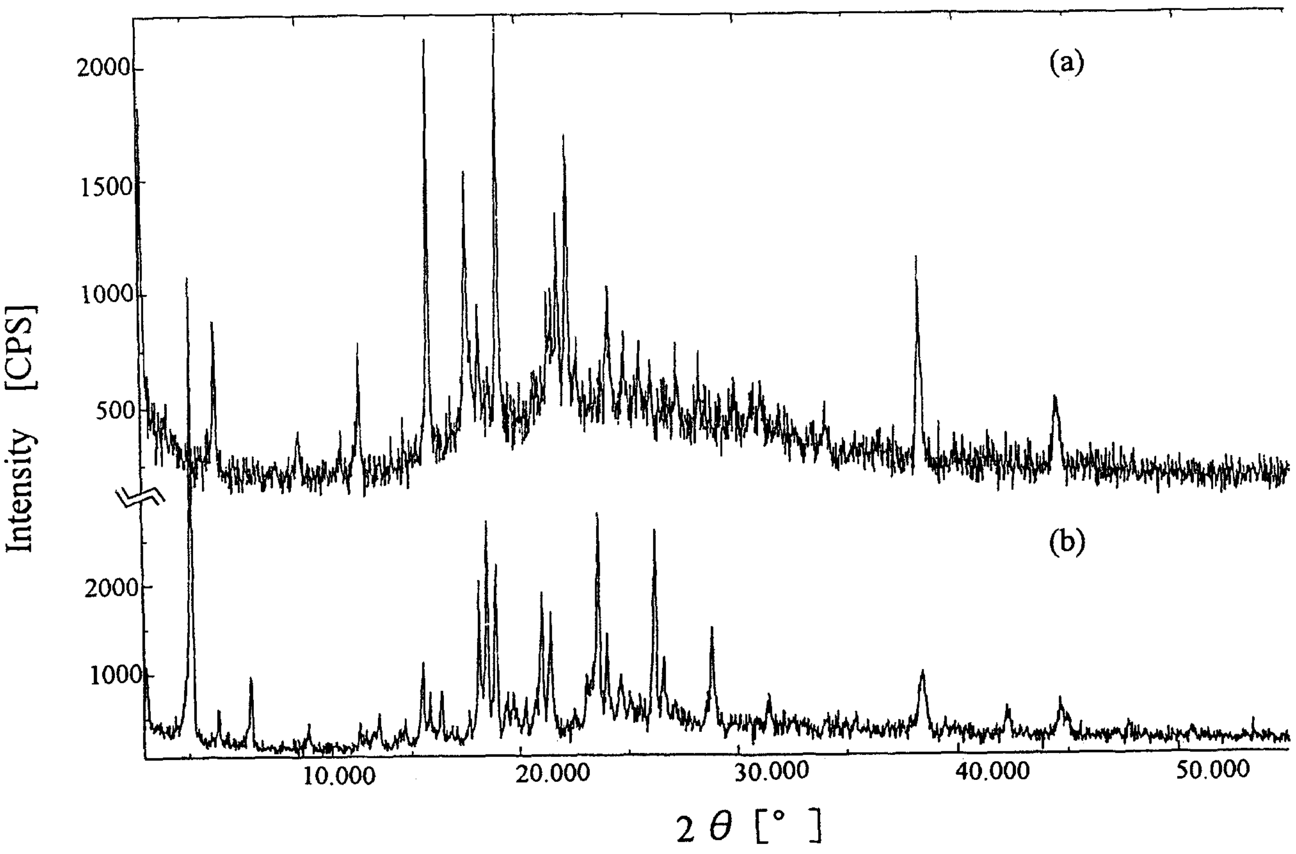

FIGURE 7 X-ray diffractions of powder specimens resulted by gaseous capture to CDAB matrix, a) 0, b) 48, and c) 130 molar per cent capture of *p*-cresol in the ratio of *p*-cresol/CDAB, respectively.

Matrix groups of weakly or little effective to gaseous capture, with almost no shift of diffraction, however, revealed another aspect that some small peaks concealed in rather noisy background become sharper and far more eminent with increase of the intensity and that they were scattered in perfectly equalized distance over a very wide 2 θ range. The strict periodicity of the peak distance enable us to evaluate the Bragg angle of much lower side below 3 degree. Most matrices dealt with in this study have the longest spacings in such very low angle regions resigned by the machine limit. An estimated d value for C18OH, for instance, was obtained to be 41.2Å. The value is quite appropriate assuming that two molecules of the alcohol with each extended hydrocarbon chains are dimerized through composing hydrogen bonds.[7,8]

These aspects predict an occurrence of stratified structure aroused by an intrusion of gaseously captured materials into matrix lattices. Such a structure seems to be inherent to molecules which have long alkyl chain and polar head group moieties and behave themselves like mesogens. Therefore no such effects of the stratum inducement were observed in solid paraffin which just consisted of hydrocarbon chain without any polar head group. It seems that presumably the gaseously captured materials access the matrix surface and cause gradual disruption of hydrogen bonds of the higher alcohols, amines, aliphatic acids etc., and a subsequent enhancement of the well ordered array of these molecules. As typical examples in Figure 8 through 10 profiles of such stratum lattice inducing systems containing low class ammoniums and a higher alcohol are presented. The structure encountered here might be supposed to a kind of crystal form transient to that of smectic stratums in which the array of molecules were actually believed to be much more disturbed.[9,10] In contrast to such smectic structures these gaseously captured systems, of course, yet persists in the crystalline lattices as directly indicated by the diffraction peak sharpness.

Thus the relationship between the acceptability of the gaseous material to the surfactant matrix and their lattice modification to cause the molecular complex formation detected by the powder X-ray diffraction has been clarified. In accordance with these observations the thermogravimetry of specimens of different capturing characteristics offered results which showed the stability of the captured materials in various matrices. Figure 11 illustrates profiles of the weight decrease with temperature in CTAB/*o*-

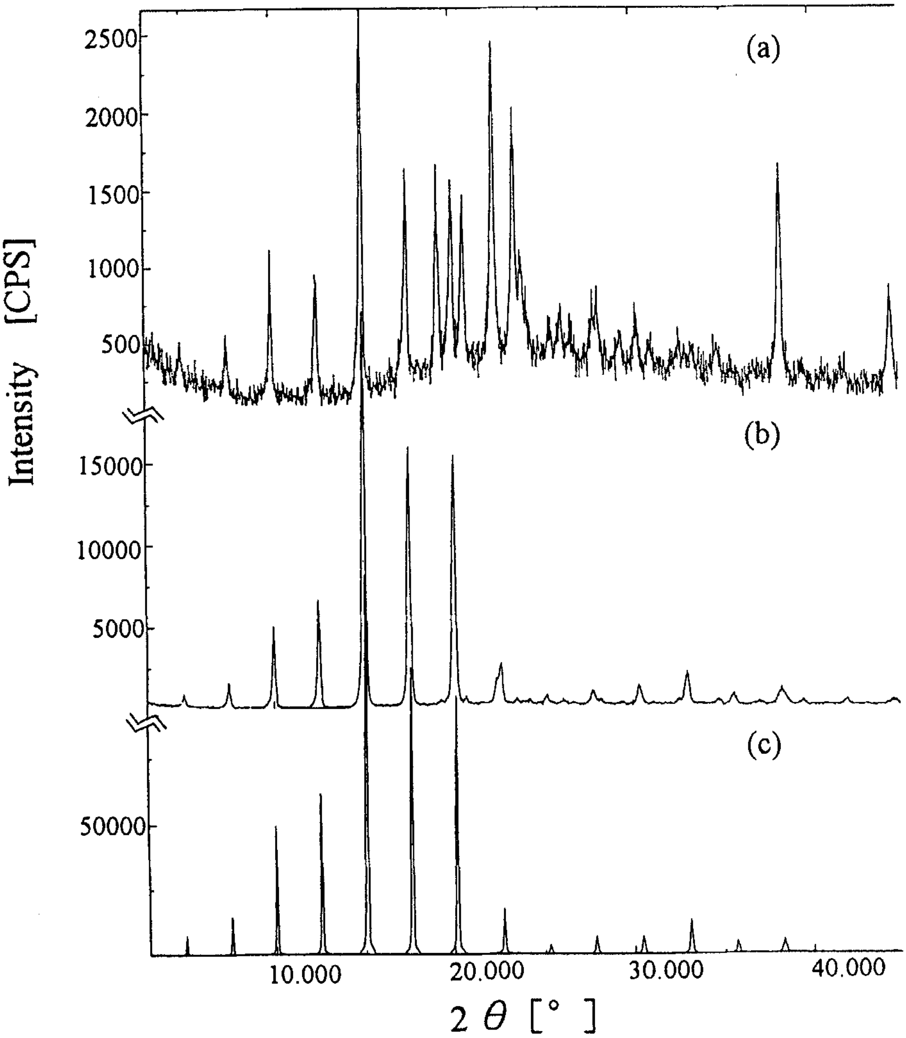

FIGURE 8 X-ray diffractions of powder specimens resulted by gaseous capture to CMAB matrix, a) 0, b) 10, and c) 41 molar per cent capture of *p*-cresol in the ratio of *p*-cresol/CMAB, respectively.

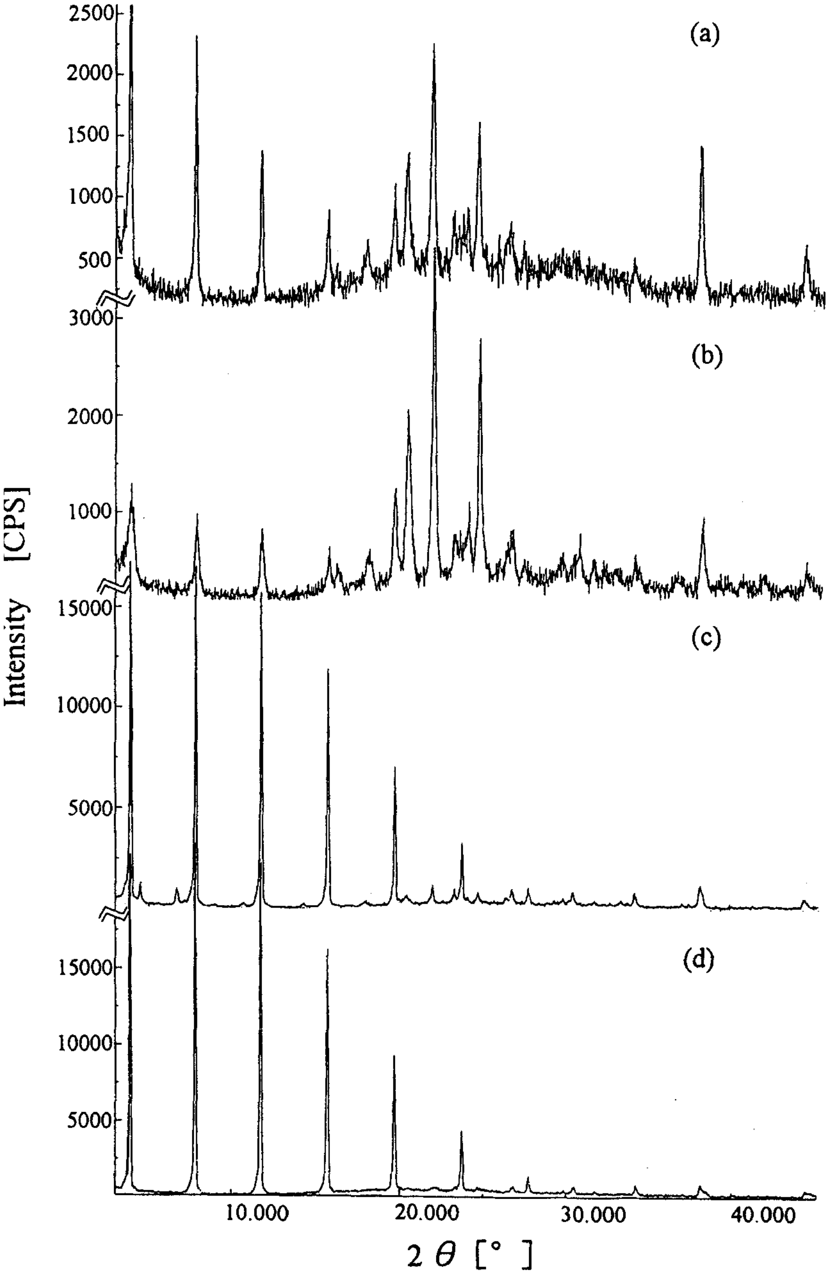

FIGURE 9 X-ray diffractions of powder specimens resulted by gaseous capture to CAB matrix, a) 0, b) 4, and c) 55 molar per cent capture of *p*-cresol in the ratio of *p*-cresol/CAB, respectively.

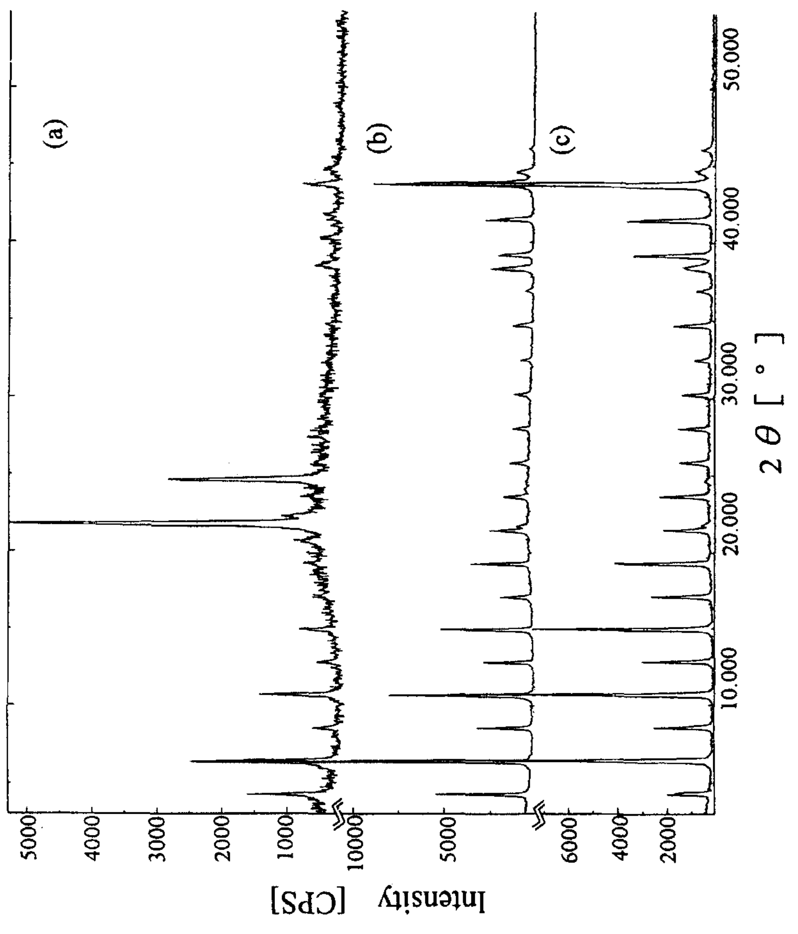

FIGURE 10 X-ray diffractions of powder specimens resulted by gaseous capture to C18OH matrix, a) 0, b) 85 molar per cent of *p*-cresol in the ratio of *p*-cresol/C18OH, and c) 45 molar per cent *o*-toluidine in the ratio of *o*-toluidine/C18OH, respectively.

bromophenol, /*o*-toluidine, CAB/*o*-bromophenol, /*o*-toluidine, and stearyl alcohol/*o*-toluidine systems. The former two systems are grouped in a class of tight capture of materials to the surfactant matrices and the latter three are in another class of apparent capture. The former systems draw slowly decreasing curves with temperature which imply the tight occlusion of the phenol and the amine in the molecular complex crystal lattices presumably yielded in these systems, whereas in the latter systems the apparent capture induces extremely rapid decrease in weight. The difference between two systems is very conspicuous especially in two CAB systems with quite varied aspect.

In the diagram an added behavior of the weight decrease of CTAB/*p*-cresol complex system is quite useful to compare with those of the others. The nearly similar decreasing behavior found in CTAB/*o*-bromophenol suggest an existence of strong interaction between them causing the surfactant molecular complex formation. Some clear difference observed in CTAB/*o*-bromophenol and CTAB/*o*-toluidine might be referred to the grade of the affinity of acidic and basic materials to CTAB matrix. The affinity difference of these materials seems also to be reflected on the clear difference of the activation energy necessary for each material to be accepted in the CTAB etc. matrix crystal lattices.(see Table 2)

EXPERIMENTAL

The amount of the gaseous capture of materials (*p*-cresol, *o*-bromophenol and *o*-toluidine) to various matrices was followed by the weight increase of the matrices which were exposed to the vapor of the above materials at a definte temperature for a designated time period. X-ray diffraction measurements by Cuk α beam were relied on a GEIGER FLEX RAD-2B of Rigaku Denki Co.,Ltd. (Tokyo) operated at a 40kV, 30mA condition. Thermogravimetry was carried out by using Rigaku THERMOFLEX TAS 300 TG 8101D at a heating rate of 10°C/min.

CONCLUSION

Through the studies it was clarified that the ability of the gaseous capture of materials to surfactant matrices and other substances as matrices which had long alkyl chain and

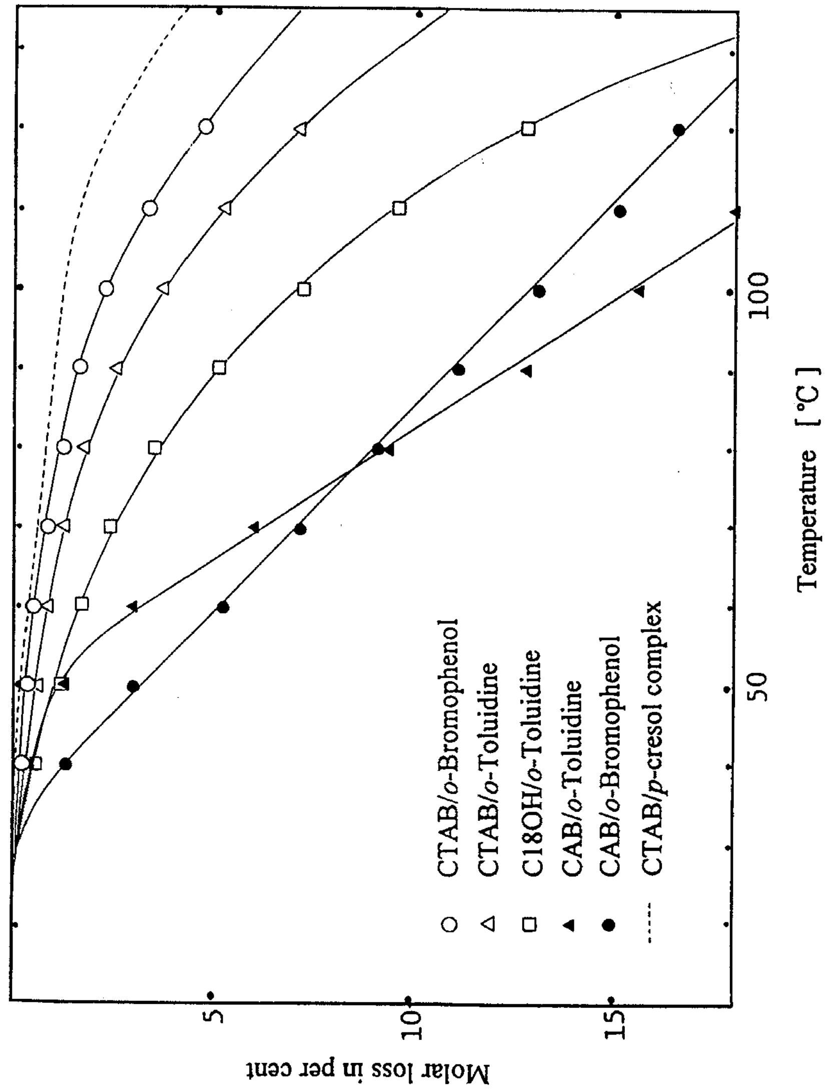

FIGURE 11 Thermogravimetry of specimens resulted by gaseous capture of various materials in CTAB matrix.

analogous crystal structure were compared with each other. As to matrices for the gaseous capture of several materials such as phenols, aromatic amines, aldehyde and ketones, the acceptability of the surfactant species excelled to any other matrix. Among surfactant matrices cationics exhibited the most excellent ability followed by the nonionic species with considerable excellence and by very poor anionics. Of the cationic species the quaternary and tertiary ammonium salts were always prominent in the acceptability of the gaseous capture of various materials, while the lower classes ammoniums showed only very poor acceptability. These ability were supported through X-ray studies which showed the shift of the diffraction peaks. The peak shift positively proved crystal lattice modifications of the surfactant matrices involved by the gaseous capture of materials into the surfactant crystal. The tendency of the acceptability of materials were directly associated with the availability of the surfactant complexes and also deeply correlated to the solubilizing power of those surfactant species for those materials. On the other hand, it is very interesting to note that the matrices group which shows no shift of diffractions in the course of the gaseous capture of various materials and no tendency of molecular complex formation with matrix substances is deeply associated with an occurrence of very remarkable stratified structures induced by an intrusion of a small amount of materials. It appears that those gaseously captured materials improved the arrangement of molecules in the original matrix crystal lattice to a well ordered stratum array involved by a disruption of hydrogen bonds.

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