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Thermal Behavior of Alkylamine-Zinc Bromide Adducts

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The thermal behavior of alkylamine-zinc bromide adducts, $(RNH_2)_2 ZnBr_2$, has been studied by differential scanning calorimetry, powder X-ray diffractometry, and broad-line ^1H NMR spectrometry. An enantiotropic mesophase is observed for the adducts of heptylamine and higher homologous members. Enthalpy change at the transition into an isotropic liquid located between 136 to 156°C is as small as 2 to 3 kJ mol^{-1}. The X-ray diffraction pattern of the mesophase is of the unstructured smectic type. The layer spacing (d/nm) measured just above the melting point is approximated by $d = 0.186\,n + 0.597$, where n is the number of carbon atoms in the alkyl group R, suggesting a bilayer structure. The second moment of the resonance spectrum in the mesophase is 0.1 to 0.3 G^2, indicating almost liquid-like characteristics. Equilibrium relations were determined for a number of binary systems composed of the adducts and aromatic compounds. Phenanthrene and acenaphthene dissolve into the mesophase of the octadecylamine adducts as much as 50 mol% but substantially less when the alkyl group is shorter.

Keywords: Layer compounds; alkylamine; zinc bromide; smectic layer; solubilization

INTRODUCTION

Since Vacatello and Corradini studied some layer compounds of general formula $(RNH_3)_2 MX_4$, the attention of numerous scientists has been extensively paid to them [1–9]. The crystal structures consist of layers of corner-sharing MX_6 octahedra with a divalent metal ion in their center, alternating with compact layers formed out of alkylammonium ions. These ordered layers are known to be transformed into various disordered smectic layers in

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successive phase transitions prior to melting. Although works on the above-mentioned compounds were followed by those on non-ionic alkylamine metal halide adducts, $(RNH_2)_2MCl_2$, where M = Zn or Cu, by the same research group [10, 11], to the best knowledge of the present authors, no further study has been published on the thermal behavior of compounds of the latter type.

The zinc chloride adducts, where the number of carbon atoms in the alkyl group (n) is 6,8,...16, were made by Salerno *et al.* [10]. All the compounds show solid-solid phase transitions at temperatures lower than 100°C and melt between 131 and 167°C into a mesophase which is recognizable only in a short range of the temperature. The thermograms indicate a large broad endothermic change superposed upon clearing. The authors reported no temperature for this transition. The copper chloride adducts with alkylamine of $n = 10$, 12,...18 were found by Busico *et al.*, to melt with decomposition even though the melting point is lower than that of the corresponding zinc chloride adduct. It was not made clear whether a mesophase is formed by these copper chloride adducts or not [11]. We prepared a new series of the adducts employing zinc bromide instead of the chloride and succeeded in generating a mesophase stable up to the clearing point. Accordingly, a detailed study on the mesomorphic behavior of compounds of the type $(RNH_2)_2MX_2$ could be carried out for the first time.

EXPERIMENTAL

The desired compounds were formed as white precipitates when alkylamine or its hot methanolic solution was added to zinc bromide dissolved in the same solvent in a mole ratio of 2 : 1. The precipitates were filtered and recrystallized three times from ethanol ($4 \leqslant n \leqslant 7$), hexane-ethanol mixtures ($8 \leqslant n \leqslant 11$), or hexane ($12 \leqslant n \leqslant 18$). Only fresh samples were employed for the physical measurements because the adduct loses gradually the amine, even at room temperature if $n \leqslant 15$. Found: C, 48.49; H, 9.16; N, 4.74; Br, 26.80%. Calcd for $(C_{12}H_{25}NH_2)_2ZnBr_2$: C, 48.37; H, 9.13; N, 4.70; Br, 26.82%. Calorimetric curves were obtained by a Rigaku Denki differential scanning calorimeter, Model 8001 SL/C, at a heating rate of 5°C min^{-1}. The phase diagrams were determined by calorimetry using mostly 10 mol% incremental mixtures. X-Ray measurements on powdered samples were made with a Toshiba recording diffractometer, Model ADG 301, using filtered copper radiation. The temperature of the sample holder was controlled as described in our previous papers [12]. ^1H MNR spectra were recorded as the first derivatives at

40 MHz, using a JEOL model JES-ME-3X spectrometer with a broad-line NMR attachment, Model JES-BE-1, which employs a crossed-coil system. Second moments were calculated for both halves of the derivative curve and corrected for modulation broadening.

RESULTS AND DISCUSSION

Table I summarizes transition temperatures. Figure 1 provides plots of the temperatures against the number of carbon atoms in the alkyl group. Here, K, M, and I stand for crystal, mesophase, and isotropic liquid, respectively. The enthalpy changes associated with the $K_2 - K_1$ and $K_1 - M_2$ or $K_1 - M_1$ transitions for an individual member ($n = 6$ to 18) agree nearly with each other: they are 16 kJ mol^{-1} for both the transitions in the hexylamine adduct and increase up to 34 and 29 kJ mol^{-1}, respectively as the series is ascended. The changes associated with the $M_2 - M_1$ and $M_1 - I$ transitions are as small as 2 to 3 kJ mol^{-1}, supporting the above-mentioned phase assignment.

The X-ray diffraction pattern is indicative of a layer structure. The layer spacing (d/nm) in the crystalline state measured at room temperature is approximated by $d = 0.173\ n + 0.532$. The increment per methylene group is longer than 0.125 nm expected for a fully-extended configuration but undoubtedly shorter than 2×0.125 nm. Therefore, it is likely that the alkyl chains form a bilayer structure and are inclined with respect to the layer

TABLE I Transition Temperatures (°C) of Alkylamine-Zinc Bromide Adducts

n^a	K_2	K_1	M_2	M_1	I
4	. 79	.119			.
5	. 66	.132			.
6	. 81	.144		[.142][b]	.
7	. 93	.135		.149	.
8	. 96	.124		.156	.
9	.102	.116		.155	.
10	.101	.115		.155	.
11	.102	.110		.155	.
12		. 99	.107	.153	.
13	. 50	. 84	. 92	.152	.
14		. 98		.146	.
15	. 66	. 90	. 97	.145	.
16	. 65	. 95	.105	.139	.
17	. 76	.100	.104	.139	.
18	. 74	. 96	.102	.136	.

a. The number of carbon atoms in the alkyl group.
b. Monotropic transition.

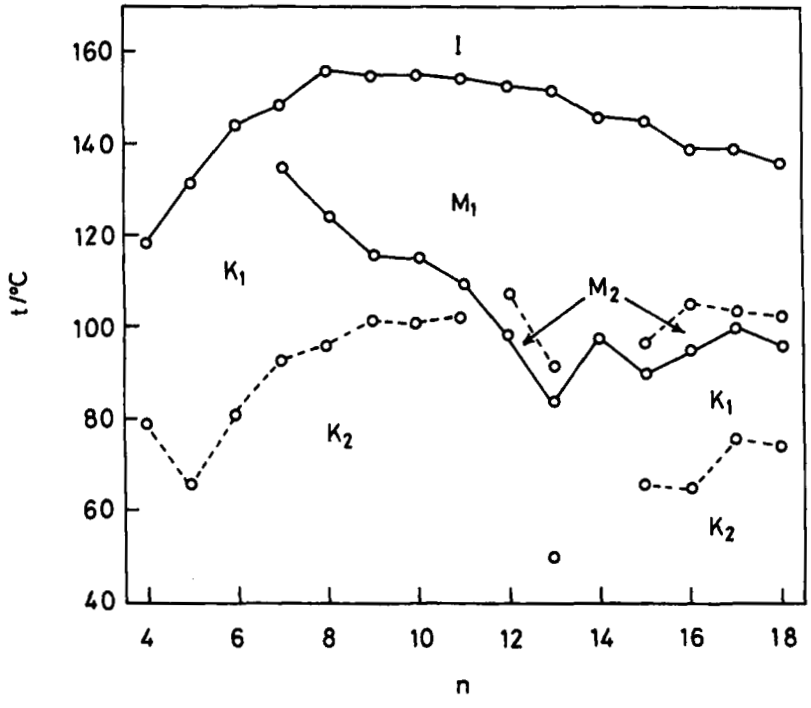

FIGURE 1 Plots of the transition temperatures against the number of carbon atoms in the alkyl group.

normal by 46° provided that they are fully-extended. Similar structure but with smaller tilt angles has been proposed for the zinc chloride and copper chloride adducts [10, 11]. The layer spacing in the former adducts at 107°C is given by $d = 0.225\ n + 0.567$ and that in the latter at room temperature by $d = 0.211\ n + 0.642$, suggesting tilt angles of 26° and 32° respectively.

In Figure 2, the temperature dependence of spacing is exemplified by even members of the series. When $n \leqslant 13$, the spacing increases abruptly at a temperature appreciably lower than the solid-solid transition temperature revealed by calorimetry; namely, between 50 and 75°C depending upon the alkyl chain length, and then decreases suddenly at the melting point (see plots a and b). The melting point shown by X-ray diffractometry is also lower than that found by calorimetry when the alkyl chain is short; for example, by about 20°C for the decylamine adduct, but good agreement is found for the octadecylamine adduct. The nonconformity in melting point of the lower homologous members may arise from loss of the amine as the powdered

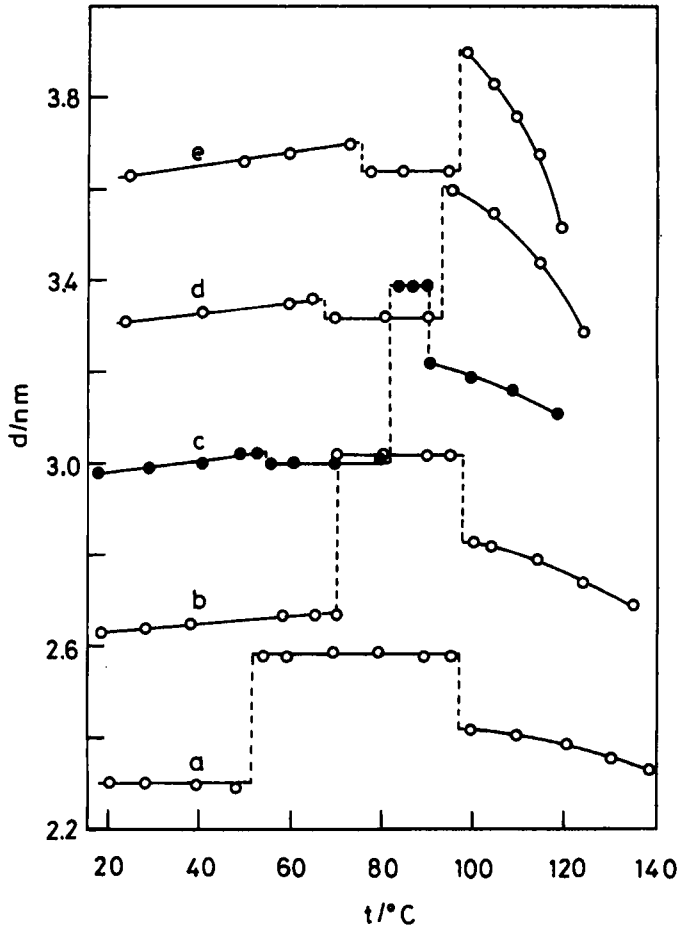

FIGURE 2 Temperature dependence of the layer spacing of (a) the decylamine adduct, (b) the dodecylamine adduct, (c) the tetradecylamine adduct, (d) the hexadecylamine adduct, and (e) the octadecylamine adduct.

sample was spread over an aluminum plate maintained continuously at high temperatures; however, the large difference in the solid-solid transition temperature cannot be explained in the same way and is left to be clarified. When $n \geqslant 15$, the spacing decreases slightly at the solid-solid transition temperature revealed by calorimetry and increases sharply at melting point (see plots d and e in Fig. 2). In the case of the tetradecylamine adduct, the spacing contracts a little at the solid-solid transition as the higher members do. By further

heating it increases abruptly, here too no endothermic peak being detected in the calorimetric curve, and then decreases discontinuously by melting. Thus, this particular adduct behaves like a higher member of the homologous series when the temperature is low and like a lower member when the temperature is high. Note that the M_2 phase observed for the homologous members with $n \geqslant 12$ is missing in this member. As depicted in Figure 3, the spacing in the high-temperature solid phase appearing in members with $n \leqslant 14$ is approximated by $d = 0.196\,n + 0.640$ and that appearing in members with $n \geqslant 14$ is essentially the same as the spacing recorded at room temperature (see lines b and b′ in Fig. 3). A small shrinkage of the layer spacing observed for the higher homologous members is ascribed to the thermal expansion of spacing in the low-temperature phase by raising the temperature to this solid-solid transition.

The X-ray diffraction pattern of the mesophase is of the unstructured smectic type. The layer spacing measured just above the melting point is expressed by $d = 0.186\,n + 0.597$ (see line c in Fig. 3), suggesting that the phase is of the C type. Although the values recorded at high temperatures must be

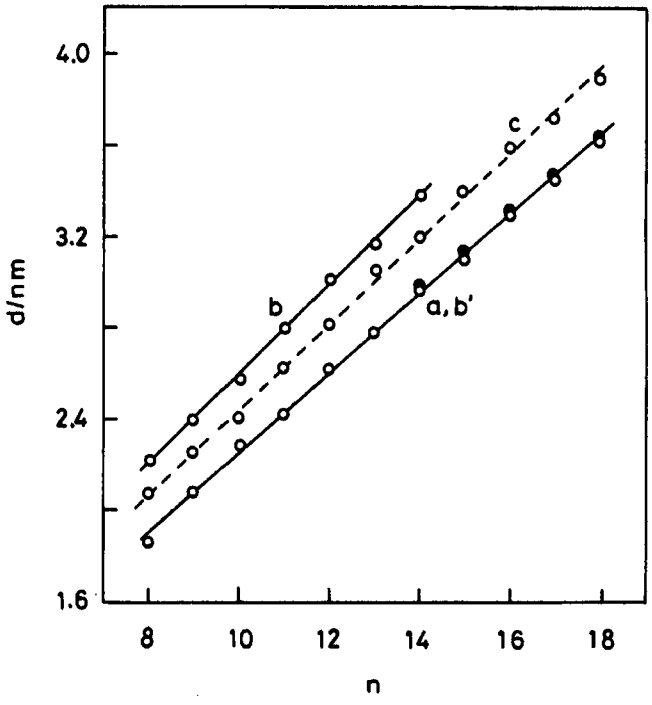

FIGURE 3 Plots of the layer spacing against the number of carbon atoms in the alkyl group: (a) solid at room temperature, (b) and (b′) high-temperature solid phase, and (c) mesophase.

considered to be only approximate because of partial thermal decomposition, they fit reasonably well in the line. It must be noted that the M_1 and M_2 phases are not differentiated by this quantity. The alkyl chains in mesophase are postulated to be far from the all-trans conformation [13]. The introduction of a small amount of gauche-trans-gauche conformations into the chains pretilted to the layer normal in the crystalline phases may result in an decrease in the average tilt angle and contribute to some expansion of the layer spacing. However, a large amount of such conformations may account for a rapid decrease of the spacing in the mesophase by raising the temperature.

The binary system consisting of hexadecylamine and octadecylamine adducts forms a continuous solution for each of the M_1, M_2, K_1, and K_2 phases. The layer spacing in solid solutions measured at room temperature is longer than that expected from the linear relationship, whereas that of the mesophase measured just above the melting point deviates in the opposite direction as depicted in Figure 4. The deviation is as large as 0.1 nm in the range rich with the higher homologous member in the crystalline phase, in which the alkyl chains are supposed to be fully extended, and also in the range rich with the lower homologous member in the mesophase, in which the chains are highly

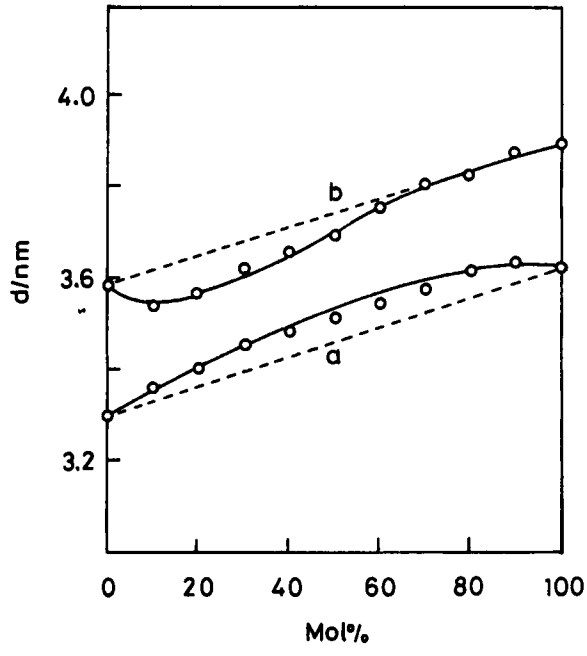

FIGURE 4 Composition dependence of the layer spacing in the system consisting of the hexadecylamine and octadecylamine adducts: (a) solid solution at room temperature and (b) mesophase.

disordered. Thus, the layer spacing in the K_2 phase observed for the octadecylamine adduct is not affected by the addition of 10 to 20 mol% of the hexadecylamine adduct and is decreased only when 30 mol% or more of the lower homologous member are added. In the latter composition range the octadecyl chain has to be shortened by conformational disordering.

In the phase diagram of a binary system consisting of dodecylamine and octadecylamine adducts, the presence of a eutectic (transition between the M_2 and K_1 phases) at 90°C and about 35 mol% of octadecylamine adduct is unquestionable evidence that the high-temperature solid phases are not completely miscible, reflecting the dissimilar thermal behavior in layer spacing of these two phases. Although the difference in spacing between the dodecylamine and octadecylamine adducts is large, the deviation from linearity like the above-mentioned could be noted.

In Figure 5, the second moments of broad-line ^1H NMR spectra measured for the decyl, dodecyl and tetradecylamine adducts are presented as a function of the temperature. It is interesting to note that the arrows indicating the temperature at which the layer spacing expands abruptly are located in the range where the second moment decreases appreciably. The shoulder found around 100°C for the decylamine adduct (see plot a) may correspond to the $K_2 - K_1$ and $K_1 - M_1$ transitions.

The second moments of NMR spectra of the hexadecylamine and octadecylamine adducts are shown in Figure 6. The $K_2 - K_1$ and $K_1 - M_2$ transitions are accompanied by sharp and large decreases in the moment, by about 8 G^2 and 3 G^2 ($1G = 10^{-4}$ T) respectively. The observed moments in the K_2 phase, about 5 G^2, are smaller (almost by a factor of two) than those found for the high-temperature phase of $(C_{10}H_{21}NH_3)_2CdCl_4$ in which the existence of "alkyl chain melting" was proposed by Kind *et al.* [4]. The moments in the present M_1 and M_2 phases in the order of $0.1G^2$ may imply that the alkyl chains are essentially in a liquid-like state. The octadecylamine adduct shows moments larger than those of the hexadecylamine adduct throughout the examined temperature range. While the 50 mol% mixture (see plot c) exhibits moments intermediate between those of the two component compounds below −40°C, the moment becomes smaller than those of the lower homologous member above this temperature. Besides, it falls off without exhibiting distinct stepwise change at the $K_2 - K_1$ and $K_1 - M_2$ transitions, reinforcing the view that the alkyl chains are conformationally disordered by mixing, even in the K_2 and K_1 phases.

The bilayer found in the mesophase of the present adducts may bear some resemblance to lamellar structures of micelles. It is well-known that solubilization

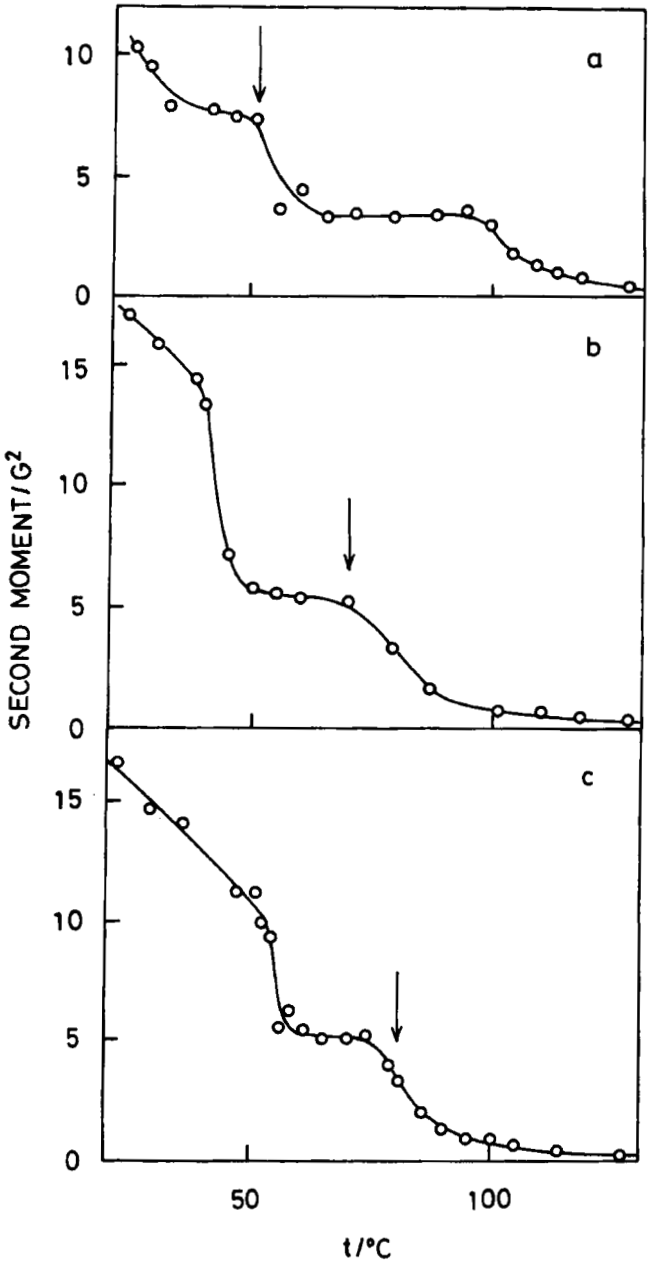

FIGURE 5 Second moments of broad-line ^1H NMR spectrum: (a) the decylamine adduct, (b) the dodecylamine adduct, and (c) the tetradecylamine adduct. The vertical arrow indicates the temperature where the layer expands abruptly.

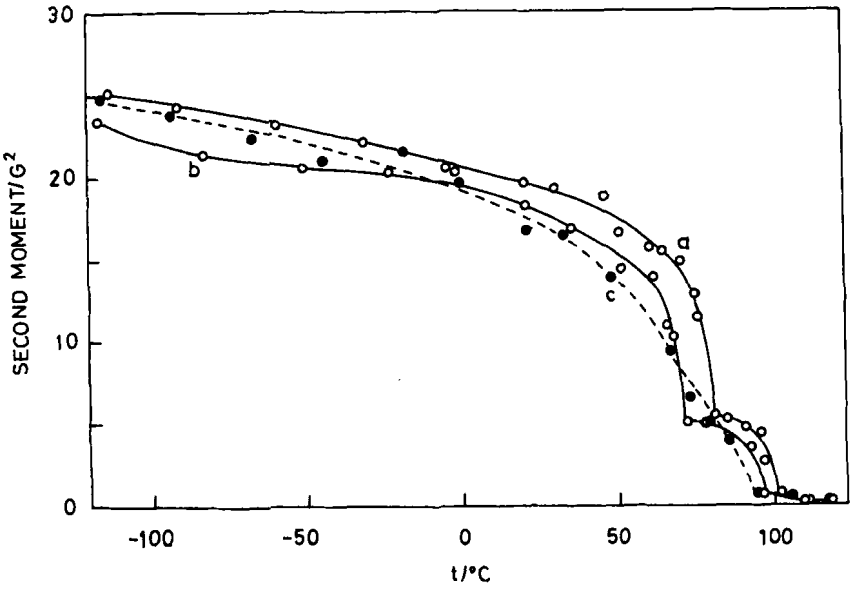

FIGURE 6 Second moments of broad-line ^1H NMR spectrum: (a) the octadecylamine adduct, (b) the hexadecylamine adduct, and (c) 50 mol% mixture thereof.

takes place in alkyl chain lamella of the micelle when organic compounds such as heptane, octanol, benzene, phenol, and aniline are added [14]. We studied earlier the addition of alcohol or alkylamine to the layer compounds made of nickel cyanide and alkylamines, $Ni(CN)_2(RNH_2)_2$, measuring changes in layer spacing by X-ray diffractometry because the endothermic peaks due to phase transitions were too broad to analyze any change in thermograms [12]. The peaks observed for $(RNH_2)_2ZnBr_2$ are sharp enough so that the dissolution of additives can be examined by differential scanning calorimetry. Consequently, we undertook preparation of phase diagrams of binary systems employing the present layer compounds. In order to compare with solubilization data reported by Klevens [14], the following aromatic hydrocarbons were selected as the second components; phenanthrene, acenaphthene, fluoranthene, and pyrene. Typical diagrams are presented in Figures 7 and 8. These fairly complicated diagrams were drawn referring to those of mixed crystal systems systematized by Roozeboom [15]. The maximum amount of phenanthrene dissolved into the M_1 phase of the decylamine adduct is represented by point a, 25 mol% at 100°C, that into the K_1 phase by point b, 28 mol% at 83°C, and that into the K_2 phase by point c, less than 20 mol% at 73°C (see Fig. 7a). Although the solubility of an additive into a particular phase

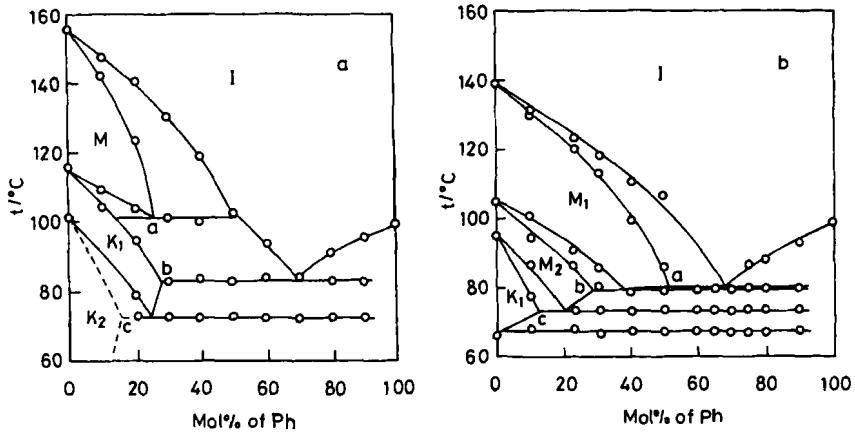

FIGURE 7 Phase diagram of the binary system consisting of (a) the decylamine adduct and phenanthrene (Ph) and (b) the hexadecylamine adduct and the same hydrocarbon.

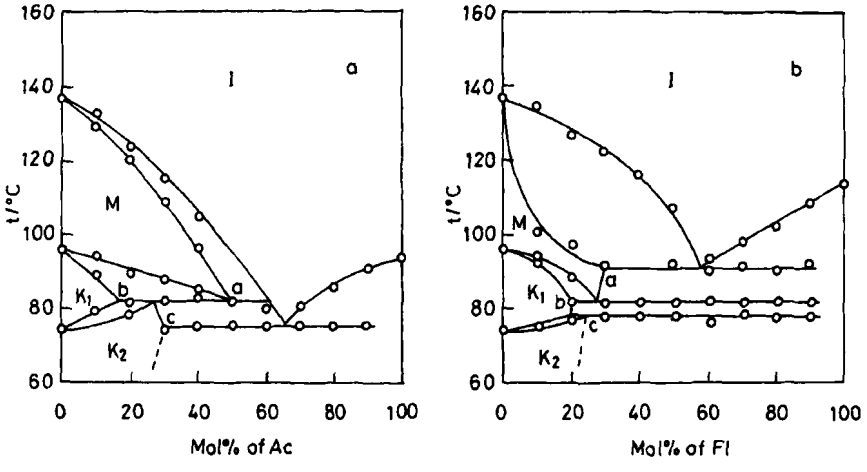

FIGURE 8 Phase diagram of the binary system consisting of (a) the octadecylamine adduct and acenaphthene (Ac) and (b) the same adduct and fluoranthene (Fl).

of alkylamine adduct is greatly influenced by the type of diagram, the hydrocarbon tends to dissolve more into the mesophase of the higher homologous members. For instance, phenanthrene dissolves into the M_1 phase of the hexadecylamine adduct up to 50 mol% at 80°C (see point a in Fig. 7b), into the M_2 phase up to 28 mol% at 80°C (point b), and into the K_1 phase

up to only 12 mol% at 73°C (point c). The higher solubility into the M_1 phase may be partly attributed to remarkable narrowing of the width of the field where the M_1 phase and an isotropic liquid phase coexist, only 15 mol% at 80°C in the hexadecylamine adduct compared to 24 mol% at 100°C in the decylamine adduct.

In Figures 8a and 8b are represented the equilibrium relations for the acenaphthene- and fluoranthene-octadecylamine adduct systems. The two mesophases appearing in the pure adduct could not be separated in these diagrams. The mesophase at 82°C may contain acenaphthene up to 50 mol% (point a in Fig. 8a), the K_1 phase at the same temperature up to 17 mol% (point b), and the K_2 phase at 75°C up to 30 mol% (point c). On the other hand, the maximum solubility of fluoranthene into the M_1 phase is 28 mol% at 90°C (point a in Fig. 8b), into the K_1 phase 19 mol% (point b), and into the K_2 phase more than 20 mol% at 78°C (point c). The coexistence field of the mesophase and the isotropic liquid phase is in quite a different shape; that is, it extends over merely 11 mol% at 82°C or less in the acenaphthene-adduct system but is as wide as 28 mol% at 90°C or more, say, 40 mol% around 100°C, in the fluoranthene-adduct system. These two diagrams belong to the type different from those given in Figure 7; therefore, the solubility of the hydrocarbon into the low-temperature solid phase ought to be higher than that into the high-temperature solid phase. The pyrene-octadecylamine adduct system produces a diagram essentially the same as that given in Figure 8b, point a being located at 24 mol% and 95°C.

The solubilities of hydrocarbons into a 0.5 M aqueous potassium dodecanoate solution at 25°C reported by Klevens are as follows; 6.65×10^{-3} moles of phenanthrene per liter, 6.48×10^{-3} moles of acenaphthene per liter, 2.86×10^{-3} moles of fluoranthene per liter, and 2.24×10^{-3} moles of pyrene per liter [15]. The number of hydrocaron molecules solubilized into a micelle was estimated to be 2.0 in the case of phenanthrene and acenaphthene and 0.90 and 0.71 in the case of fluoranthene and pyrene respectively. Our experiments and Klevens' are under so contrasting conditions that the numerical values differ in many orders of magnitude; nonetheless, the solubilities obtained by the present equilibrium relations appear to be in conformity with the order of Klevens'.

It may be worthwhile to mention the binary system composed of the adduct and mesogenic compounds. Azoxydianisole (K 117.5 N 135 I) and *N*-(4-phenylbenzylidene)-4-(ethoxycarbonyl) aniline (K 121.6 S_A 131 I) were employed for this purpose because the temperature ranges covered by their mesophases are well matched to those of the adducts [16]. The mesophases of

TABLE II Transition Temperatures (°C) of Alkylamine-Zinc Iodide Adducts

n^a	K_2	K_1	M	I
12	51	74	118	
14	60	80	117	
16	69	89	115	
18	78	93	111	

a. The number of carbon atoms in the alkyl group.

the hexadecylamine adduct and these mesogenic compounds are not of the same type and were found to be not completely miscible as predicted. The maximum solubility of these compounds into the mesophase of the adduct is markedly smaller than that of phenanthrene and acenaphthene; that is, 19 mol% at 108°C in the case of the nematogen and 16 mol% at 98°C in the case of the smectogen.

Lowering of the melting point as much as 23 to 41°C by replacement of zinc chloride with zinc bromide may acount for the emergence of thermodynamically stable mesophase. If a larger anion is employed, the cohesive energy in the inorganic layer may be more reduced and the melting point may be depressed; therefore, some zinc iodide adducts have been examined. As listed in Table II, not only the melting point but also the clearing point are lower than those of the corresponding zinc bromide adduct. As a result, the temperature range covered by the mesophase is diminished: 18°C for the octadecylamine-zinc iodide compared to 40°C for the zinc bromide analog. Unlike the behavior of alkylamine-zinc bromide adduct, the layer spacing expands at both the $K_2 - K_1$ and $K_1 - M$ transitions. For example, the hexadecylamine adduct gives 2.61 nm in the K_2 phase, 2.88 nm in the K_1 phase, and 3.19 nm in the M phase.

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