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Influence of the Size of Rare Earth Ions on the Surface Crystallization of Complexes

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π-A isotherms of $RE(TTA)_3Phen$ (RE = La, Sm, Eu, Gd, Tb and Y; TTA = thenoyltrifluoroacetone; Phen = 1,10-phenanthroline) mixing with arachidic acid (AA) in molar ratio of 1:1 and influence of rare earth ions in complexes on the surface crystallization of monolayers were studied in this paper.

Keywords: rare earth complex; crystallization; monolayer

INTRODUCTION

The luminescent enhancement and intermolecular energy transfer in Langmuir-Blodgett (LB) films of $Eu(TTA)_3Phen$ with its complexes of energy donors mixing with AA in molar ratio of 1:1 have been studied[1-3]. However, the properties of these complexes at air/liquid interface have not been reported. In this work, the features of monolayers of $RE(TTA)_3Phen$ and $Eu(TTA)_3Phen$ with $La(TTA)_3Phen$ or $Y(TTA)_3Phen$ in different molar percentages mixing with AA in molar ratio of 1:1 are approached. The influence of rare earth ions

on the monolayers was studied and the relation of the size of ions and the crystallization was obtained.

EXPERIMENTAL SECTION

Syntheses of $RE(TTA)_3Phen$ and drawing of surface pressure-area (π-A) curves were carried out as previously described[3]. The compositions of monolayers were listed in Table I.

TABLE I The compositions of monolayers and some parameters

L	Film-forming materials	π (mN/m)	R_{RE}^{3+}(Å)[4]
1	$La(TTA)_3Phen$:AA=1:1	4.0	1.06
2	$Sm(TTA)_3Phen$:AA=1:1	7.0	0.96
3	$Eu(TTA)_3Phen$:AA=1:1	8.0	0.95
4	$Gd(TTA)_3Phen$:AA=1:1	8.0	0.94
5	$Tb(TTA)_3Phen$:AA=1:1	8.8	0.92
6	$Y(TTA)_3Phen$:AA=1:1	9.0	0.88
7	[30%$Eu(TTA)_3Phen$+70%$La(TTA)_3Phen$]:AA=1:1 (in molar percentage)		
8	[50%$Eu(TTA)_3Phen$+50%$La(TTA)_3Phen$]:AA=1:1		
9	[80%$Eu(TTA)_3Phen$+20%$La(TTA)_3Phen$]:AA=1:1		
10	[30%$Eu(TTA)_3Phen$+70%$Y(TTA)_3Phen$]:AA=1:1		
11	[50%$Eu(TTA)_3Phen$+50%$Y(TTA)_3Phen$]:AA=1:1		
12	[80%$La(TTA)_3Phen$+20%$Y(TTA)_3Phen$]:AA=1:1		

RESULTS AND DISCUSSION

π-A Curves of $RE(TTA)_3Phen$ and the Size of Rare Earth Ions

The isotherms of L1-6 are shown in Fig.1. These curves have a same shape. They include a long plateau, which indicates a very slow change in surface pressure. According to electron diffraction (ED) pattern of L11 at π = 9 mN/m

in Fig.2, hexagonal diffraction spots illustrate that there are microcrystal particles in the monolayer. Therefore, the plateau on π-A curves corresponds to a crystallization. A difference in the curves to each complex is the pressure which the plateau appears. Among them $Y(TTA)_3Phen$ has the highest pressure and $La(TTA)_3Phen$ has the lowest one.

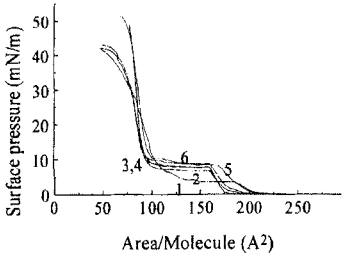

FIGURE 1 π-A curves for L1~6.

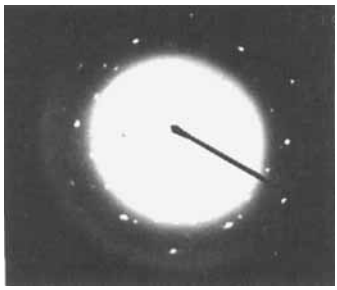

FIGURE 2 ED pattern for L11.

For searching the internal relations of the phenomenon, the radii of the rare earth ions are considered. The surface pressures of plateaus and the radii of the rare earth ions are all listed in Table I. It can be seen that the less the radius is, the higher the plateau pressure of the complex has. It also explains that the difference in size of rare earth ions in the complexes affects the space size of the complex. Therefore, when the complexes have a same structure[3], it is helpful to use the method to determine the radius of a central ion.

π-A Curves of $Eu(TTA)_3Phen$ with $La(TTA)_3Phen$ or $Y(TTA)_3Phen$

To the further research on the monolayers, the experiments of mixing $Eu(TTA)_3Phen$ with $La(TTA)_3Phen$ or $Y(TTA)_3Phen$ in different molar percentages have been done. Fig.3 shows the π-A curves for L7-9 and Fig.4 shows those for L10-12. Because of the low pressure of $La(TTA)_3Phen$, π of

plateau is raised, as the molar percentage of $Eu(TTA)_3Phen$ increases. Conversely, to $Y(TTA)_3Phen$ it is lowered. From Fig.3 and Fig.4, there is a long plateau, not a ladder, on each curve. It may be an even mix to the complexes because of the similar structure. The result is equal to forming a new complex. Moreover, it may apply to control the crystallization of monolayer of complexes at air/liquid interface artificially.

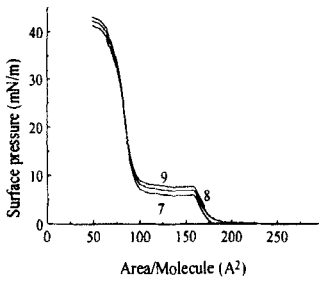

FIGURE 3 π-A curves for L7~9.

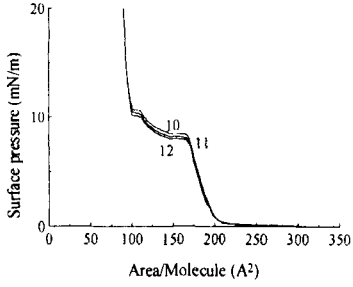

FIGURE 4 π-A curves for L10~12.

CONCLUSIONS

We have studied the surface crystallization of rare earth complexes when they were compressed. The radii of the ions concern the surface pressures of plateaus on π-A curves. $Y(TTA)_3Phen$ has the highest π and $La(TTA)_3Phen$ has the lowest one. When a high π complex is mixed with a low π one, a plateau of an intermediate π can be gotten.

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