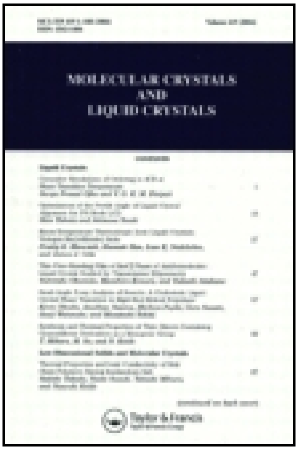

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Lyotropic Behaviour of Sheet-Like Chemical Compounds: Amphotropy of Phthalocyanine and Porphyrin Derivatives

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LYOTROPIC BEHAVIOUR OF SHEET-LIKE CHEMICAL COMPOUNDS: AMPHOTROPY OF PHTHALOCYANINE AND PORPHYRIN DERIVATIVES

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Abstract The data of the study of the lyotropic mesomorphism of several anionic, hydrophobic phthalocyanine and anionic porphyrin derivatives as well as of related metal complexes, obtained in our laboratory, have been summarised. The influence of structural changes of these compounds on the lyomesophase formation is discussed.

INTRODUCTION

A *columnar* type of the supramolecular packing in the liquid crystalline state, found for non-calamitic molecules by S. Chandrasekhar,[1] broadened the scope of liquid crystal research. Of late, we can see certain achievements in the investigation of the lyotropic mesomorphism of disc-like amphiphiles, e.g. derivatives[2–4] of triphenylene, phthalocyanine and porphyrin. The lyotropic behaviour of such compounds stem from the type of stacking of their flat molecules in columns which can display orientationally or two-dimensionally ordered phases (N- or M-chromonics[5] respectively). Up to now, nearly all investigations were connected to the lyotropic behaviour of such mesogens in *aqueous* solutions. Therefore, the lyomesomorphic porperties of differently structured *hydrophobic* compounds are more or less unexplored. To fill this gap, we studied the lyotropic mesomorphism of disc-/sheet-like compounds not only in aqueous solutions but also in organic solvents; some results are presented here.

MATERIALS AND METHODS

The synthesis of the anionic carboxylate and sulphonate derivatives of phthalocyanine and their metal complexes 1a–k and 2a–h (Tables 1 and 2)

TABLE 1 Carboxylate derivatives of the phthalocyanine metal complexes.

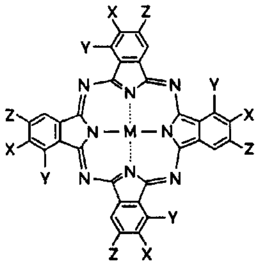
Structural formula	No.	Metal	Substituents			Mesogenic properties
			X	Y	Z	
	1a	Cu^{2+}	-COOH	-H	-H	+
	1b	Cu^{2+}	-COONa	-H	-H	+
	1c	Cu^{2+}	-COOH	-H	-H	+
	1d	Co^{2+}	-COOH	-H	-H	+
	1e	Co^{2+}	-H	-COOH	-H	-
	1f	Al^{3+}	-COOH	-H	-H	-
	1g	Al^{3+}	-H	-COOH	-H	-
	1h	Zn^{2+}	-COOH	-H	-COOH	+
	1i	Zn^{2+}	-COOH	-H	-H	+
	1j	$(2H^{+})$	-COOH	-H	-COOH	+
	1k	Cu^{2+}	-H	-COOH	-H	+

TABLE 2 Sulphonate derivatives of the phthalocyanine metal complexes.

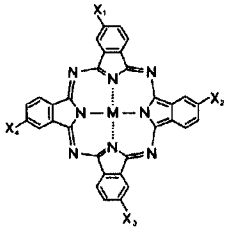
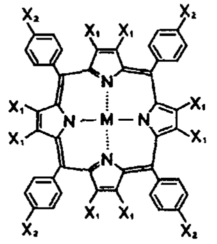
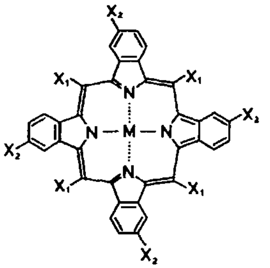
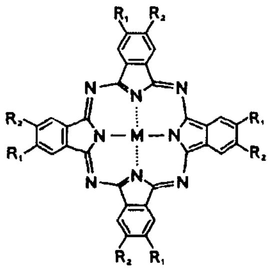
Structural formula	No.	Metal	Substituents				Mesogenic properties
			X_1	X_2	X_3	X_4	
	2a	$(2H^{+})$	$-SO_3H$	-H	-H	-H	-
	2b	$(2H^{+})$	$-SO_3R$	-H	-H	-H	-
	2c	Co^{3+}	$-SO_3H$	-H	$-SO_3H$	-H	-
	2d	Co^{3+}	$-SO_3H$	$-SO_3H$	$-SO_3H$	$-SO_3H$	-
	2e	Cu^{2+}	$-SO_3Na$	-H	$-SO_3Na$	-H	-
	2f	Cu^{2+}	$-SO_3H$	$-SO_3H$	$-SO_3H$	$-SO_3H$	+
	2g	Ni^{2+}	$-SO_3H$	$-SO_3H$	$-SO_3H$	$-SO_3H$	+
	2h	Fe^{2+}	$-SO_3H$	$-SO_3H$	$-SO_3H$	$-SO_3H$	+

TABLE 3 Anionic porphyrin derivatives and their metal complexes.

Structural formulas	No.	Metal	Substituents		Mesogenic properties
			X_1	X_2	
	3a	(2H$^+$)	-H	-SO$_3$H	+
	3b	Ni^{2+}	-H	-SO$_3$H	+
	3c	Cu^{2+}	-H	-SO$_3$H	+
	3d	Co^{3+}	-H	-SO$_3$H	-
	3e	(2H$^+$)	-H	-SO$_3$Na	+
	3f	Ni^{2+}	-H	-SO$_3$Na	+
	3g	Co^{3+}	-H	-SO$_3$Na	-
	3h	(2H$^+$)	-CH$_3$	-SO$_3$H	+
(3a)-O-(CH$_2$)$_4$-O-(3a)	3i	(4H$^+$)	-H	-SO$_3$H	-
	4a	(2H$^+$)	-H	-SO$_3$Na	+
	4b	Zn^{2+}	-H	-SO$_3$Na	+
	4c	Co^{2+}	-H	-SO$_3$Na	-



a: $R_1=R_2=C_{12}H_{25}O$,
$M=Cu^{2+}$;
b: $R_1=R_2=C_{12}H_{25}O$,
$M=Ni^{2+}$;
c: $R_1=C_{12}H_{25}S$, $R_2=H$
$M=Cu^{2+}$.

FIGURE 1 Molecular structures of the metal complexes **5a–c** of alkyloxy- alkylthiophthalocyanine derivatives.

are carried out according to B. Berezin.[6,7] The synthesis of the anionic porphyrin and hydrophobic phthalocyanine derivatives as well as of the related metal complexes 3a-i, 4a-c (Table 3), 5a-c (figure 1) were described elsewhere.[8-11]

The purity of all compounds was checked by tlc and elemental analysis. Organic solvents, e.g., linear alkanes, benzene and cyclohexane are commercially available and were used without purification.

Absorption spectra were recorded on a Specord UV VIS spectrophotometer and IR-spectra on a Specord 75 IR.

Phase transition data were obtained by polarizing microscopy. The lyotropic mesomorphism was investigated as described before.[12,13]

Polmicroscopic studies were carried out in a MIN-8 or in a Leitz Laborlux 12 Pol microscope using a hot stage Mettler FP 82 (heating rate 1-2 K min^{-1}). The texture photographs were made with a 24x36 mm microscope camera equipped with a photoautomat Wild MPS 51.

The investigation of the thermodynamic properties of the dissolution was carried out by adiabatic scanning calorimetry (DASM-4) with a cell volume of 0,5 mm^3 at a sensitivity of 0,625 μW; the scanning rates were 1 K min^{-1} (heating) or 0,5 K min^{-1} (cooling).

RESULTS AND DISCUSSION

The first information on the *thermotropic* phase behaviour of phthalocyanine derivatives and related compounds were published more than ten years ago.[14,15] Further research established that their mesomorphism is determined by the number and length of the side alkyl chains.[16-19] It seems that more than four parafinic side chains of definite length are necessary to stabilize the discotic structure, the adequate number being related to the overal size of the central rigid core.[15]

Usually, the search of the discotic *lyotropic* mesogens is connected with substances, possessing a flat rigid core and a long side symmetrical substituents.[2,20] In contrast, we investigated the lyotropic phase behaviour of anionic substances *without* long parafinic chains. The first steps in the developing of this idea have been made by S. Gaspard et al.[21]: a lyotropic mesophase of a phthalocyanine substituted with four carboxylate groups. However, this time the structure of this lyomesophase was not established and in the ternary systems with the sulphonate derivatives a lyotropic phase behaviour was not found.

The hydrophilic compounds, investigated by us are: carboxylate derivatives of the phthalocyanine and their metal complexes (Table 1, "+" marked their mesogenity in polar solvents); sulphonate derivatives of phthalocynine and their metal complexes (Table 2); sulphonate derivatives of the tetraphenylporphine and tetra-2,3-pyridine-porphyrazine (Table 3). We found that the lyomesogens of these groups have a tendency to the plane-to-plane association. They form columnar mesophases (stack-of-coins type); their structures were identified as N- or M-phases of the chromonic[22-24] type by polarizing microscopy and X-ray diffraction.

Characteristic for all these studied compounds is, that a strong tendency to the lyomesomorphism is shown by the metal complexes of the bivalent metals. The trivalent metal complexes form the oxodimers, which are not capable for forming the columnes in the solvents.[27,28]

The presence of one or two polar substituents is not enough for such molecules in order to form the lyomesophases. The substitution of every "X" or "X" and "Z" position (Table 1) of the benzene rings of the macrocycles favoured the lyomesophase formation. The substitution of position "Y" suppresses the lyomesomorphic properties of anionic phthalocyanine derivatives.[27,28]

It was surprising for us that tetrasulphophenylporphin with the movable phenyl fragments (3a-c,e,f) form the lyomesophases similar to coplanar molecules.[8,9,29] Besides, additional substitution of 3h by a methyl group does not suppress the lyomesomorphic properties of this compound.

We started our investigation on the influence of dimerization on the preservation of the lyomesogenity in the range of tetraphenylporphins. The first investigated compound (3i, bridging group = $-O-(CH_2)_4-O)$ does not form any lyomesophase, although the monomer 3a does form it. Probably, this may be connected with the length of the bridging group, which leads to the rotation of the porphyrin units in the solution.

The temperature-concentration region for the lyomesophase existence depends on the character of lateral substituents and pH value of the solvents. For example, carboxyderivatives of phthalocyanine form lyomesophases starting with the mesogen concentration in the compositions at 3-4 wt% and mainly at a pH between 9 and 11. Sulphonate derivatives at concentrations between 13 and 30 wt% and a pH between 6 and 13.[30]

As we described before,[27] the formation of the supramolecular columns of such compounds is connected with the two processes: the π-π interactions between the macrocycles and the hydrogen bond formation by the lateral substituents. In order to study the influence of the different polar groups on the formation of the supramolecular aggregates, we investigated the thermodynamic of dissolution of the phthalocyanine copper complexes 1a and 2f which differ only in their lateral substituents (Tables 1 and 2). On the basis of the experimental data we calculated the heats of the dissolutions for each complex. The heat capacity of the solutions at any case is lower than that of water. The solutions with the concentration of the compounds 1 wt% have curves of the heat capacity repeating the form of the water ones. The phase transition N_{chr}-> I was found in the aqueous system of 1a at 3 wt% of the mesogene. At this concentration the characteristic of the heat capacity curve of 1a is more steep compared with 2f. This shows a better capability of 1a to form the hydrogen bonds, and for their destruction by the increasing of the temperature (figure 2).

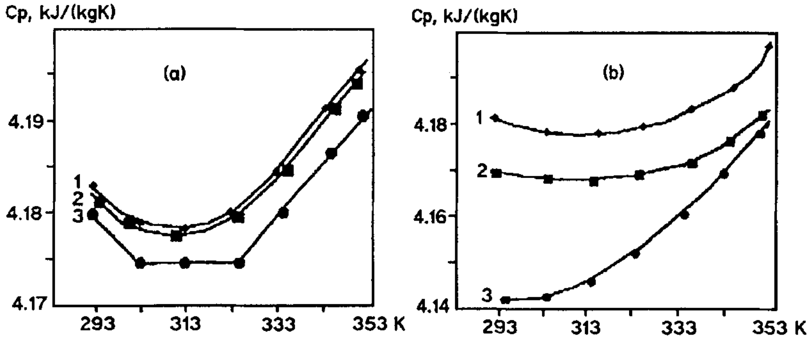


FIGURE 2 Curves of the heat capacity of tetracarboxylate (1a) and tetrasulphonate (2f) phthalocyanine copper complexes in aqueous systems, ph 10.0, c = 1 wt% (a) and 3 wt% (b). 1: H_2O; 2: 2f/NH_4OH/H_2O system.

The same idea is proved by the characteristics of the enthalpy of dissolution curves.[31] Thereby, the obtained results prove the high probability of the hydrogen bonds formation in the aqueous systems of **1** in comparison with **2**. The kind of the effect may be one of the reasons of the considerable difference in concentrations of the lyomesophase formation of **1** and **2**.

In order to compare the intermolecular interactions between the *hydrophobic* and *hydrophilic* phthalocyanine derivatives in solution, we studied the lyotropic mesomorphism of a copper and nickel complex of octadodecyloxyphthalocyanine (**5a** and **b** in figure 1) as well as of a copper complex of tetradecylthiophthalocyanine (**5c**). **5a** and **5b** show thermotropic mesomorphism.[10,32] An X-ray analysis showed the columnar hexagonal order in their thermotropic mesophase. A thermotropic phase behaviour between 328 and 573 K was found for **5c**, further heating leads to decomposition of the sample. With organic solvents, e.g., benzene, cyclohexane and alkanes, these compounds form lyomesophases.[33] On the basis of a textural characteristic (figure 3) these mesophases may be similar to N- or M-phases of the chromonic type.

FIGURE 3 Textures of a contact preparation of the tetraalkylthiophthalocyanine copper complex (**5c**) with pentadecane, showing the Schlieren-texture in the upper and the herring-bone structure in the lower part, T = 329 K (on cooling), magnification x 320. **See Color Plate VII.**

The binary system **5a**/pentadecane was studied in more detail. Its phase diagram is characteristic for chromonic mesogens[5] as well as for anionic phthalocyanines.[30] The concentrational dependence of the lyomesophase formation resembles that of the sulphonate derivatives,[30] but in this case the area of the lyomesophases exist at higher concentrations of the lyomesogen. Probably, this may be connected with the fact, that π-π interactions between macrocycles and the electrostatic forces play a dominant role in the supramolecular aggregate formation. The influence ofside chains on molecular interactions is relatively small. The similarity of the supramolecular packing of sheet-like mesogens in aqueous solutions or in organic solvents makes the development of a new nomenclature necessary.

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