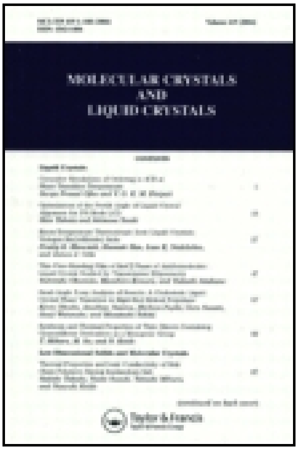

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Phase Diagrams of Lyotropics

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PHASE DIAGRAMS OF LYOTROPICS

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Abstract Principles of the interpretation of DSC data for binary systems are considered. The phase diagrams obtained must satisfy the requirements of the phase rule. DSC curves and the phase diagram for the dimethyloctylphosphine oxide - water system are given. The effect of the alkyl chain length upon the enthalpies of the hexagonal-isotropic and lamellar-isotropic transitions is discussed.

Phase diagrams[1-4] make the basis for the physico-chemical investigation of lyotropic liquid crystals. However, for some systems it is only the fact of the mesophase formation that is established; for other systems mesophases are identified, but their boundaries are not determined; heterogeneous regions are usually not studied, etc. The profoundity of our knowledge concerning the phase equilibria in 117 binary systems is discussed in a recent review[5]. Only few complete lyotropic diagrams of state are known.

Precise location of phase boundaries and extent of heterogeneous regions can be determined by means of DSC or DTA, the phases being identified by other techniques. In interpreting thermal analysis data an account should be taken of the specific features of the phase transitions occuring in binary and multicomponent systems.

According to the phase rule[6,7] invariant (isothermal) and monovariant (nonisothermal) phase transitions can take place in a binary system. An invariant process in this system is possible, besides transitions in pure components, either in the case of the transition temperature extremum or in the case of a three-phase equilibrium (eutectic, peritectic or incongruent melting). All the other phase processes in the system are monovariant. It may be difficult to detect the type of the process from a single DSC curve. One should compare DSC data for a number of compositions and evaluate the concentration dependence of the transition temperature.

The difference between these types of transitions is often not appreciated. For example, a heterogeneous region between a mesomorphic phase (Z) and an isotropic solution (I) is often represented in the way shown in Figure 1a. Thermodynamics requires maximum transition temperature to be an invariant point. In the course of the invariant process the Z phase transforms into the I phase of the same composition x_β at a single, precisely defined temperature (T_β , Figure 1b). In Figure 2a a phase diagram for a lipid-water system is shown. It is usually explained in terms of the gel (L_β) phase existence

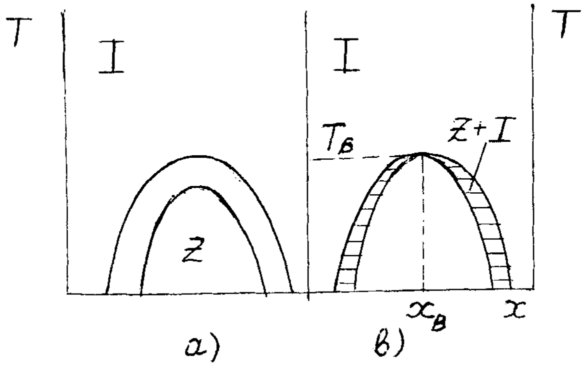

FIGURE 1. Maximum phase transition temperature

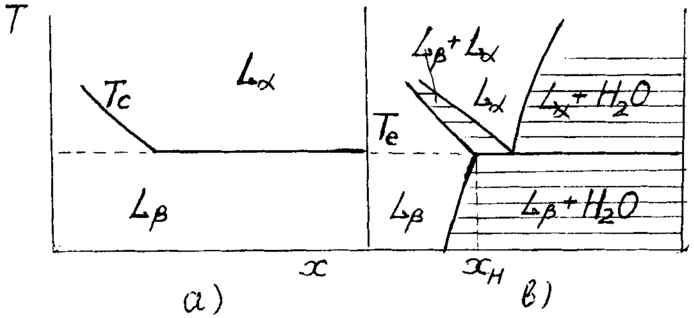

FIGURE 2.

at $T < T_c$, the lamellar (L_α) phase being present at $T > T_c$. However, according to the phase rule at $T > T_e$ the L_β and L_α phases must be separated by a heterogeneous region. As the T_c curve becomes parallel to the x axis, some three-phase equilibrium is to be observed at $T_c = T_e$. A possible version of a complete phase diagram is given in Figure 2b. At $x < x_H$ the $L_\beta - L_\alpha$ transition is monovariant. At $T = T_e$ the eutectic reaction $L_\beta + H_2O \rightleftarrows L_\alpha$ takes place.

More complex phase equilibria can be discovered in lipid-water systems, whereas preliminary investigation gives schematic diagrams of the kind shown in Figure 2a. A peritectic reaction and two eutectic reactions were found[8] in dipalmitoylphosphatidylcholine-water system. A complete phase diagram was obtained due to the application of a sensible DSC instrument and the use of small scanning rates (V = 0.1 K/min).

Thermodynamic relations for the heat capacity (C_p) of heterogeneous systems making the basis of the interpretation of DSC and DTA data for binary and multicomponent systems were previously considered.[9,10] Theoretical C_p values and DSC curves for the phase diagrams of different types were given.

In this work DSC results for the dimethyloctylphosphine oxide (C_8PO) - water system are presented. Liquid crystalline hexagonal (H_1) and lamellar (L_α) phases were found[11] in this system with the help of polarizing microscope. Other homologues of the phosphine oxide series were previously studied: phase diagrams and concentration dependence of the enthalpies of the lyomesophase-isotropic transitions were obtained for the $C_{10}PO$-water and $C_{12}PO$-water systems;[12,13]

heat capacity of the L_α and I phases in the $C_{12}PO$-water system was determined.[14]

EXPERIMENTAL

Measurements were carried out with the help of a Setaram DSC-111 instrument. Twice-distilled water and purified by sublimation C_8PO were used. Samples were prepared by weight and sealed in steel cells. DSC traces were recorded from -5 to 70°C (V = 1 K/min) for 26 mixtures, the composition of the samples ranging from $x = 0.4$ to $x = 1$ (x - weight fraction of C_8PO). Phase transitions were studied with scanning rates of 0.5, 0.25 and 0.1 K/min. The temperature intervals of the transitions were found by extrapolation of the peak width to zero heating rate.

RESULTS AND DISCUSSION

Typical DSC curves and the phase diagram for the C_8PO-water system are given in Figures 3 and 4 (3a: V = 0.1 K/min; 3b: V = 0.5 K/min). Compositions of the mixtures in Figure 4 are marked with the same numbers as the DSC curves in Figure 3. The peaks in curves 1-3 correspond to the H_1-I transition; in curve 4 the peak of the L_α -I transition is observed. Well-defined narrow peaks at $T_e = 3.9$°C ($x = 0.793 \div 0.975$) indicate the eutectic reaction $L_\alpha + C \rightleftarrows I$ (C - crystals). Curve 5 is a DSC trace for the mixture of the eutectic composition $x_e = 0.796$. At $x > x_e$ the two-phase regions become apparent in

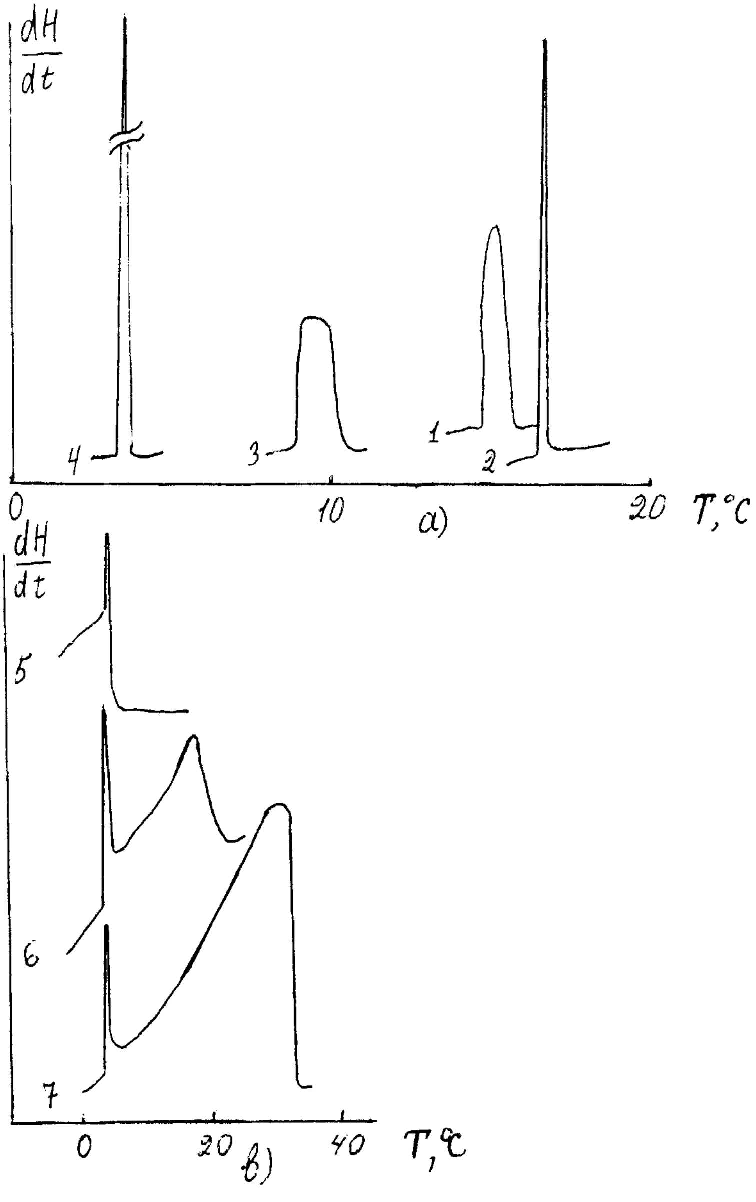

FIGURE 3. DSC curves for the C_8PO-H_2O system

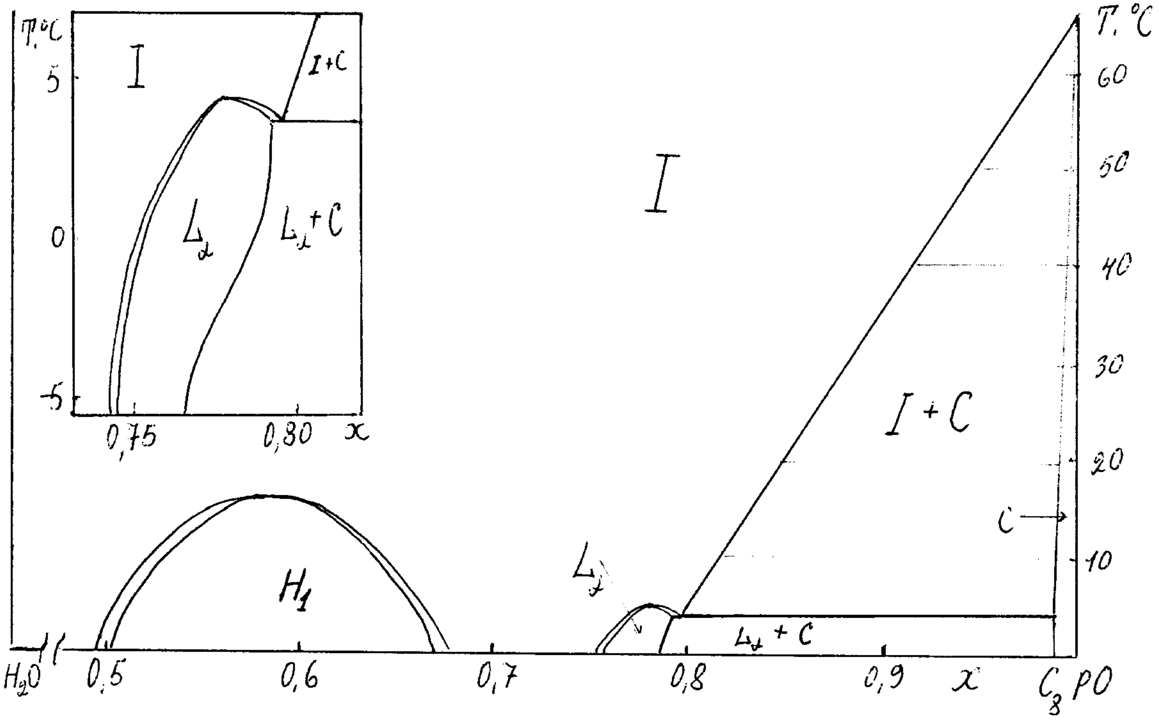

FIGURE 4. Phase diagram for the dimethyloctylphosphine oxide-water system

in curves 6 and 7: at $T < T_e$ the phases L_α and C are in equilibrium, while at $T > T_e$ the phases I and C coexist. Finite jumps of the heat capacity of the system[9,10] at the transition from the heterogeneous region I+C to the one-phase region I can be clearly seen in this curves.

Comparison of DSC data for a number of compositions allows the types of the phase processes to be determined. The transition temperatures are maximum at $x = 0.58$ for the H_1-I transition (T=16.5°C, curve 2) and at $x = 0.773$ for the L_α-I transition (T=4.2°C, curve 4); with a sufficient accuracy these processes can be considered invariant. Except the transitions mentioned and the eutectic reaction all the other phase processes in the concentration and temperature range studied are monovariant. The peaks of invariant and monovariant transitions in the DSC traces obtained with the same heating rate differ in shape and width. With sufficiently small scanning rates (V = 0.1 K/min) narrow sharp well-defined peaks correspond to the invariant phase processes, the peak width tending to zero as $V \rightarrow 0$ (e.g. curves 2, 4 and 5-7). Wide peaks appear in the DSC traces for the monovariant processes; non-zero values of the transition temperature intervals are obtained as $V \rightarrow 0$ (e.g. curves 1 and 3).

The temperature range of the mesophase stability is maximum at the compositions corresponding to the invariant points (molar ratio $H_2O:C_8PO$

is 8 for the H_1 phase and 3 for the L_α phase). The heterogeneous regions H_1+I and L_α +I (in contrast to the regions L_α +C and I+C) are very narrow: the temperature interval is less than 2°C and the node width does not exceed 0.015.

The area in the phase diagram occupied by the lyomesophases is much less in this system than in those containing $C_{10}PO$ and $C_{12}PO$.[12-14] The area of the H_1 phase is greater than that of the L_α phase for a short-chain surfactant and vice versa for the $C_{10}PO$-water and $C_{12}PO$-water systems.

The enthalpies of the H_1-I and L_α -I invariant transitions were measured, which allowed us to compare the enthalpies and the entropies of the invariant processes in the phosphine oxide series system:

	H_1-I transition		L_α -I transition	
System	ΔH, j/mole*	ΔS, j/(mole* K)	ΔH, j/mole*	ΔS, j/(mole* K)
C_8PO+H_2O	71	0.25	95	0.34
$C_{10}PO+H_2O$	43	0.14	129	0.39
$C_{12}PO+H_2O$	27	0.09	148	0.40

* Mole of mixture

The values of the enthalpies of the transitions from lyomesophases to isotropic solution are by 2-3 orders less than enthalpies of solid-liquid transitions. As the alkyl chain grows the enthalpy of the H_1-I transition increases and that of the L_α –I decreases. The entropy of the transitions changes in the same way.

The experimental data obtained are useful for the comparison of thermodynamic properties of hexagonal and lamellar phases in systems containing surfactants of different chain length.

REFERENCES

1. P. Ekwall, Adv. Liquid Cryst., 1, 1 (1975).
2. R. G. Laughlin, ibid., 3, 41 (1978).
3. R. G. Laughlin, ibid., 3, 99 (1978).
4. G. J. T. Tiddy, Phys. Rep., 57, 1 (1980).
5. A. G. Morachevsky, T. G. Churyusova, E. P. Sokolova and G. G. Chernik, in Chemistry and Thermodynamics of Solutions, edited by A. G. Morachevsky and L. S. Lilich (Leningrad University, Leningrad, 1986) 6, pp. 121-167 (in Russian).
6. V. Anosov, M. Ozerova and Y. Fialkov, Foundations of Physico-chemical Analysis (Nauka, Moscow, 1976, in Russian).
7. J. E. Ricci, The Phase Rule and Heterogeneous Equilibrium (D. Van Nostrand, Toronto, 1951).
8. C. Grabielle-Madelmont and R. Perron, J. Colloid Interface Sci., 95, 471 (1983).
9. G. G. Chernik and V. K. Filippov, Vestn. Leningr. Univ., 18, 50 (1980).
10. V. K. Filippov and G. G. Chernik, Thermochim. acta, 101, 65 (1986).
11. K. W. Hermann, J. G. Brushmiller and W. L. Courchene, J. Phys. Chem., 70, 2909 (1966)
12. G. G. Chernik, E. P. Sokolova and A. G. Morachevsky, Vestn. Leningr. Univ., ser.1, iss.4, 50 (1986).
13. G. G. Chernik, in Liquid Crystals and Their Practical Application Abstr. 5 All-Union conf. (Ivanovo, 1985) 2, p.216.
14. G. G. Chernik and A. M. Starodubtzev, dep. ONIITA Khim (Cherkassy, 1984) N716XP -D84. 6 pp, (in Russian).