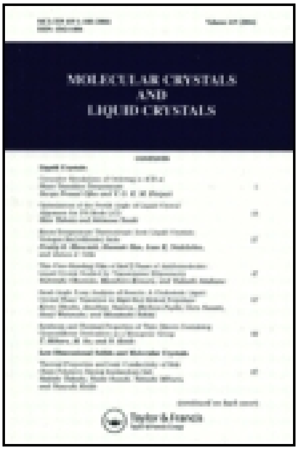

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Differential Enthalpy and Entropy Effects of Dissolution of Phases for a Nonionic Surfactant-Water System

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DIFFERENTIAL ENTHALPY AND ENTROPY EFFECTS OF DISSOLUTION OF PHASES FOR A NONIONIC SURFACTANT-WATER SYSTEM

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Abstract Heat capacity jumps (ΔC_p) at the transitions of a system from a one-phase to a two-phase state and transition enthalpies (ΔH) are measured for the lyotropic liquid crystal dimethyldodecylphosphine oxide-water system by means of DSC. Differential enthalpy and entropy effects of dissolution of one phase in another are calculated for the hexagonal (Hex)/liquid (I), lamellar (Lam)/I, crystals (C)/Lam and C/I phase transitions.

The differential enthalpy and entropy effects of dissolution of a phase j in a phase i, $Q(i|j)$ and $S(i|j)$, $Q(i|j)=TS(i|j)$, make thermodynamic characteristics of a transition at a constant temperature, while the transition enthalpies characterize it at a constant gross concentration. According to the procedure described elsewhere[1,2], the differential effects can be found using ΔC data for non-isothermal phase transitions[3] and using ΔH data for isothermal phase processes.

The measurements of ΔC_p,ΔH and temperatures of phase transitions were performed with the help of a Setaram DSC 111 instrument. A fragment of the phase diagram of the dimethyldodecylphosphine oxide (abbreviated $C_{12}PO$) - water system is presented in Fig. 1. In Fig. 2 an example of the heat capacity data is given. The values of ΔC_p strongly depend upon the temperature, concentration and the nature of phases taking part in the transition. When compared at

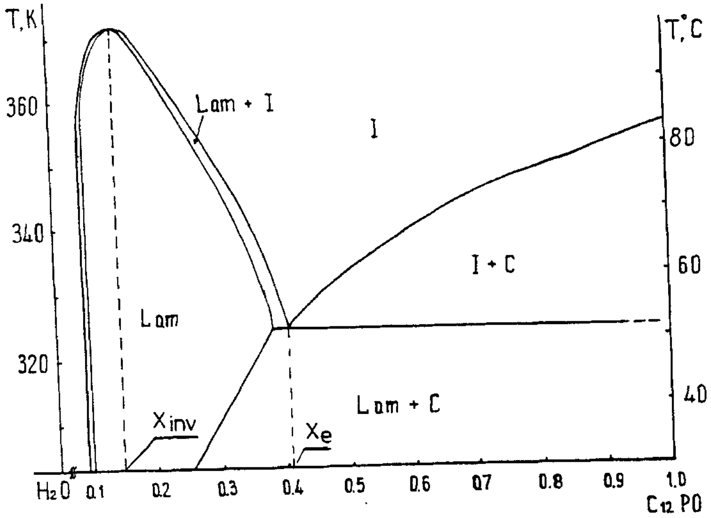

FIGURE 1 A fragment of the phase diagram of $C_{12}PO$-water system. C - crystals, Lam - liquid crystalline lamellar phase, I - isotropic liquid.

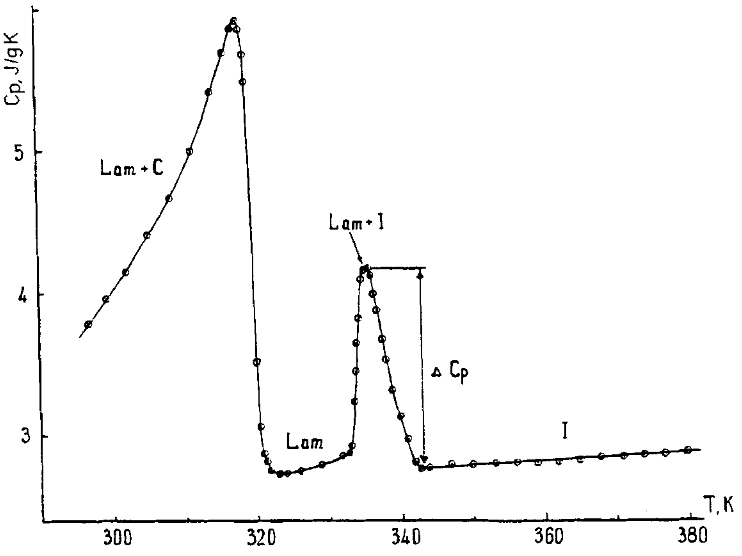

FIGURE 2 The temperature dependence of the heat capacity of $C_{12}PO$-water system at x=0.352. Scanning rate 1 K/min. ΔC_p - heat capacity jump at the Lam+I→I transition.

constant temperature, the heat capacity jumps at the lyomesophase/liquid phase transition are in the majority of cases lower than those of the transformations of crystals into isotropic liquid or lamellar phase:

$$\Delta C_p(Lam+I\rightarrow I)<\Delta C_p(Lam+C\rightarrow Lam)<\Delta C_p(I+C\rightarrow I)$$

The values of ΔC_p for the Lam/I transition at low surfactant content are by the order of magnitude lower than those at high surfactant content.

According to thermodynamic equations [1], the heat capacity jump in a binary system tends to infinity as $x\rightarrow 1$ and when the point of the extremum of a transition temperature is approached; at the eutectic point ΔC_p is discontinuous because of the intersection of two different liquid curves. The values of ΔC_p for the system considered are in agreement with the theoretical requirements: $\Delta C_p(I+C\rightarrow I)$ grows as $x\rightarrow 1$, $\Delta C_p(Lam+I\rightarrow I)$ increases as the invariant point ($x_{inv.}$) of the Lam/I transition is approached, and $\Delta C_p(I+C\rightarrow I)$ and $\Delta C_p(Lam+I\rightarrow I)$ tend to different limiting values as the eutectic point (x_e) is approached (Fig. 3).

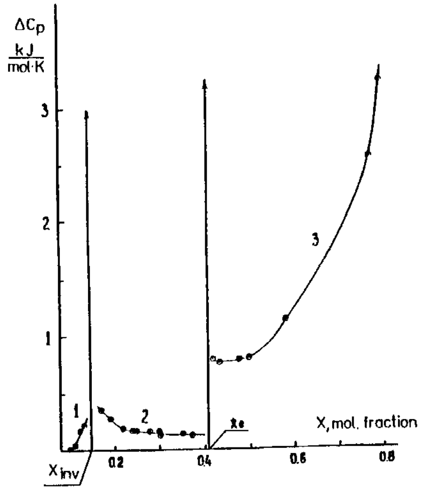

FIGURE 3 Concentration dependence of the heat capacity jumps in the $C_{12}PO$-water system at the transitions Lam+I→I (curves 1 and 2) and C+I→I (curve 3).

TABLE I Differential enthalpy (Q(i|j)) and entropy (S(i|j)) effects of dissolution of phase j in phase i, i,j=I,Lam,C, in C_{12}PO-water system. x - C_{12}PO content. Q(i|j) in kJ per mole of mixture.

x, mol.fract.	Transition		Q(i|j), kJ/mole		S(i|j), J/mole K
0.059	I+Hex→Hex	Q(Hex|I)	-0.007	S(Hex|I)	-0.02 ±0.01
0.061			-0.016		-0.06 ±0.02
0.073			-0.02		-0.06 ±0.02
0.059	Hex+I→I	Q(I|Hex)	0.009	S(I|Hex)	0.03 ±0.02
0.061			0.013		0.04 ±0.02
0.075	Hex/I	ΔH(Hex/I)	0.027	ΔS(Hex/I)	0.090±0.003
0.148	Lam/I	ΔH(Lam/I)	0.15	ΔS(Lam/I)	0.40 ±0.01
0.162	I+Lam→Lam	Q(Lam|I)	-0.19	S(Lam|I)	-0.5 ±0.2
0.224			-0.54		-1.5 ±0.2
0.260			-0.62		-1.8 ±0.2
0.276			-0.65		-1.9 ±0.2
0.352			-0.64		-1.9 ±0.2
0.192	Lam+I→I	Q(I|Lam)	0.35	S(I|Lam)	1.0 ±0.2
0.225			0.38		1.1 ±0.2
0.240			0.43		1.2 ±0.2
0.290			0.61		1.7 ±0.2
0.410		Q_e(I|Lam)	0.65	S_e(I|Lam)	2.0 ±0.3
0.231	C+Lam→Lam	Q(Lam|C)	18	S(Lam|C)	60 ±10
0.280			21		70 ±10
0.410		Q_e(I|C)	29	S_e(I|C)	90 ±10
0.468	C+I→I	Q(I|C)	29	S(I|C)	90 ±20
0.590			23		70 ±20
0.795			24		70 ±20
1.0		ΔH(C/I)	50	ΔS(C/I)	140 ±10

The differential effects of dissolution of a lyomesophase in a liquid phase are by two or three orders of magnitude lower than those effects for the crystal+liquid ⟶ liquid phase transition:

$$Q(I|Lam)<<Q(I|C)$$

The behaviour of the heat capacity jumps and of the differential effects in the $C_{12}PO$-water system has much in common with the tendencies observed for these values in the aqeous solution of dimethyldecylphosphine oxide.[2] Here some new results were obtained: ΔC_p for the hexagonal/liquid phase transition, which made it possible to calculate $Q(I|Hex)$ and $Q(Hex|I)$. As can be seen, these values are usually lower than the differential effects of the Lam/I transition:

$$Q(I|Hex)<Q(I|Lam).$$

The enthalpy of invariant transitions can be measured with great accuracy. At the point of the extremum of the phase transition temperature $Q(i|j)=\Delta H(j/i)$. Differential effects obtained from ΔC_p data (which are less accurate) can be compared to the effects for the invariant transitions in a data consistency test [2]. As can be seen from Table I, $Q(I|Hex)$ for monovariant transitions is not inconsistent with the value of $\Delta H(Hex|I)$, and the values of $Q(I|Lam)$ obtained from ΔC_p data are in agreement with the magnitude of $\Delta H(Lam/I)$, on one hand, and of $Q_e(I|Lam)$, on the other hand.

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