

# Dynamic Heat Capacity of Micellar Liquid Crystals

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## 1 . INTRODUCTION

The phase transitions of cesium perfluoro-octanoate (CsPFO,  $C_8F_{17}COOCs$ ) micelles in water have been studied using calorimetry,<sup>1)</sup> light-scattering and magnetic birefringence techniques.<sup>2)</sup> These micelles are disk shaped, and their size does not vary appreciably with temperature. Liquid crystal mesophases have been observed as a function of concentration and temperature,<sup>3-5)</sup> and aqueous CsPFO solutions provide a good opportunity to study the lyotropic nematic(N) - smectic A(SmA) and nematic(N) - isotropic(I) phase transitions. These transitions are second-order and weakly first-order, respectively. It is of interest to determine whether appreciable thermal fluctuation effects at these phase transitions. In order to clarify the thermodynamic nature of these transitions, we have carried out measurements using a high-resolution Joule-heating type AC calorimeter as described in elsewhere<sup>3)</sup> and also a differential scanning calorimeter (DSC) experiments on the same aqueous solutions for comparison.

## 2 . EXPERIMENTAL METHOD FOR MEASURING DYNAMIC HEAT CAPACITY

The samples of CsPFO using in this study were obtained from Dr. Rosenblatt in Massachusetts Institute of Technology, USA. These samples were synthesized according to the procedure given in Ref. 4 and were recrystallized from absolute ethanol.

The AC calorimeter used for these measurements has been described in Ref. 3 . The sample cell for CsPFO aqueous solutions shown in Fig. 1. The cell is a cup 10 mm in diameter and 1.2 mm deep pressed from 0.25 mm silver sheet. A lid of 0.075 mm silver foil is attached using a cold-welded indium seal. Ten short (2 mm) nickel rods were used for magnetic stirring. Runs were also made without stirring, in which case the Ni rods were replaced by a long coil of fine gold wire that greatly increased the effective internal thermal conductivity. The AC heat input was supplied at a frequency of 0.03 Hz by a thin-film resistance heater, and the resulting temperature oscillations ( $T_{ac}$ ) were measured with a microbead thermister. Then, the AC

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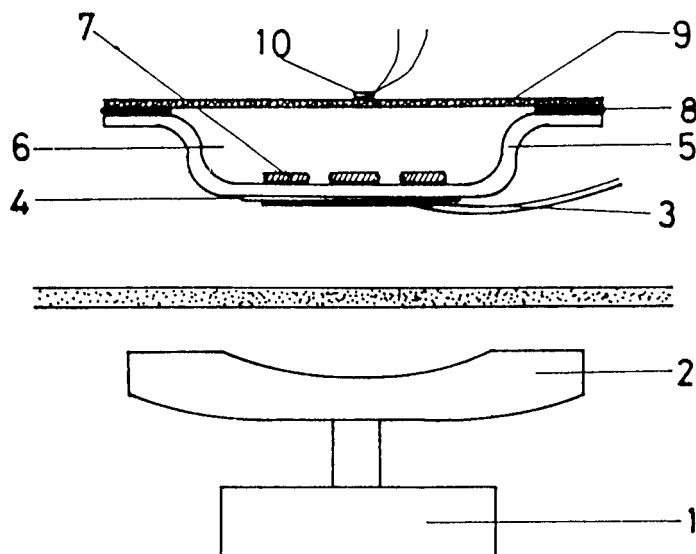


Fig.1 A sample cell used for the AC calorimetric measurement of CsPFO aqueous solutions with stirrers.

- |                           |                   |                       |
|---------------------------|-------------------|-----------------------|
| 1 . Synchronous motor,    | 2 . Magnetic bar, | 3 . Microfilm heater, |
| 4 . Varnish layer,        | 5 . Silver cup,   | 6 . Sample,           |
| 7 . Nickel stirring rods, | 8 . Indium seal,  | 9 . Silver lid,       |
| 10 . Bead thermister.     |                   |                       |

temperature and the phase are approximately given by

$$T_{ac}(L) = Q_0 / 2 C_p \times [1 + (1/\omega^2 \tau_s^2) + \omega^2 \tau_{int}^2 + (2L/3R_1)]^{-1/2} \times e^{i(\omega t - \phi)}, \quad (1)$$

$$\phi = \arcsin < [1 - (4/\omega^2 \tau_{int}^2/3) + (L/3R_1)] / [1 + (1/\omega^2 \tau_s^2) + \omega^2 \tau_{int}^2 + (2L/3R_1)] >, \quad (2)$$

where  $Q_0$  is the amplitude of the AC power input from the microfilm heater,  $\omega = 2\pi f$  and  $T_{ac}$  are the frequency and the AC amplitude of the resulting temperature oscillations, respectively.<sup>3)</sup> In these expressions,  $\tau_s$  is the sample-to-bath relaxation time,  $\tau_{int}$  is the relaxation time for thermal equilibrium in the sample and  $C_p$  is the heat capacity of the sample. When  $\omega$  is chosen so that  $1/\omega \tau_s \ll \omega \tau_{int}$ , the frequency-dependent term in Eq. (1) is expressed by

$$C_p = Q_0 / T_{ac}(L), \quad (3)$$

$$\phi = \arcsin < [1 - (4/\omega^2 \tau_{int}^2/3) + (L/3R_1)] / [1 + \omega^2 \tau_{int}^2 + (2L/3R_1)] >. \quad (4)$$

Therefore, the heat capacity is inversely proportional to the amplitude of the AC temperature.

The DSC curves were obtained using a Seiko Electronics Type SSC/560U differential scanning calorimeter connected to a Hewlett-Packard 85 computer. For this instrument, the

scanning rate can be varied from 0.01 to 5.0 K/min, the total volume of the sample pan is approximately 70  $\mu\text{l}$ , the inaccuracy caused by baseline noise is less than  $\pm 10 \mu\text{J/K}$ , and the accuracy of the absolute temperature determination is better than  $\pm 0.1 \text{ K}$ . The present measurements were carried out on samples of about 50 mg mass in a furnace surrounded by dry nitrogen gas supplied at a flow rate of 50 ml/min. The heating rate was used 0.5 K/min, which is moderately slow compared with scanning rate of 2 - 5 K/min often used for DSC studies of liquid crystals.

### 3 . RESULTS AND DISCUSSION

The upper curve in Fig.2 shows the total heat capacity of a CsPFO aqueous solution and the silver cell, and the lower curve shows the heat capacity for the empty cell. It is seen from this figure that the heat capacity peaks associated with these SmA - N and N - I transitions are very small but clearly observable. The peak  $C_p$  values are only about 2% greater than the background value. The observed  $C_p$  values,  $C_p(\text{obs})$ , correspond to the total heat capacity of a sealed cell weighing about 650 mg, in which 140 - 150 mg is weight of the CsPFO solutions. The values of the heat capacity per gram of CsPFO are determined from

$$C_p = [C_p(\text{obs}) - C_p(\text{empty})]/W, \quad (5)$$

Where  $C_p(\text{obs})$  is the heat capacity obtained for a filled cell,  $C_p(\text{empty})$  is the measured heat capacity of the same cell empty, and  $W$  is the weight of CsPFO in the aqueous solution. The empty cell data are well described by an empirical straight line

$$C_p(\text{empty}) = 0.1120 \times 10^{-3} \cdot T + 0.1009 \text{ (J/K)}, \quad (6)$$

Which was obtained by a least-squares fit to 437 points over the 312 - 357 K temperature range. By using Eqs.5 and 6, one can convert the observed data points, such as those shown in Fig.2, into the heat capacity per gram of CsPFO.

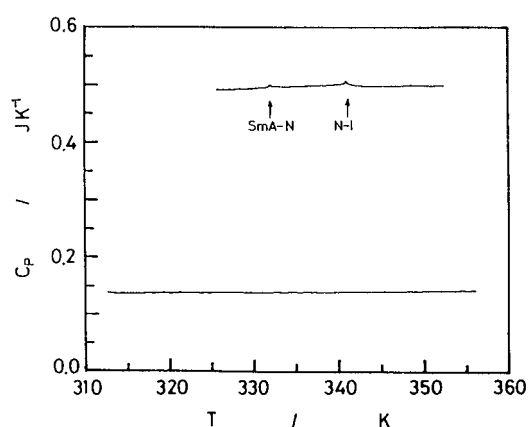


Fig.2 Heat capacity of a filled cell containing 0.1496 g of CsPFO aqueous solution containing 65 wt% CsPFO (upper curve, scanned at 0.86 K/h with continuous stirring) and the empty cell (lower curve).

Measurements were carried out with and without stirring on solutions containing 41 wt% CsPFO and 65 wt% CsPFO. No important differences were observed in the character of the temperature dependence of  $C_p$  data obtained near the transition with and without stirring. Furthermore, there was no qualitative difference in the behavior of the specific heat capacity peaks for 41 wt% solutions and 65 wt% solutions, as shown in Fig.3 and 4.

A DSC study was also carried out for the aqueous solution containing 41 wt% CsPFO, and a typical DSC scan is shown in Fig.5. Comparison of Figs.4 and 5 shows that there is a systematic difference of approximately 10 percent in the absolute heat capacity values. However, the uncertainty in the absolute value of  $C_p$  is estimated to be 5-10% for the AC method and 12-15% for the DSC method.

Figure 6 gives a direct comparison of the DSC measurements and AC calorimetric measurements of heat capacity in the transition region for the 41 wt% sample. In order to compensate for the systematic difference in the absolute heat capacities for these two data sets, the DSC curve has been shifted up by small constant amount (0.26  $J/Kg$ ). As shown in Fig.6, the heat capacity peaks determined by AC calorimetry agree quite well with the DSC peaks associated with the phase transitions. Furthermore, the AC calorimetric data do not exhibit any shifts in the phase of the  $T_{ac}(\ )$  oscillation signal or any anomalous changes in the  $T_{ac}$  amplitude at either of the transitions. These observations indicate that the latent heat at the nematic-isotropic transition be small. From the DSC method, the total enthalpy  $H + H_0$ .  $H_0$  is any first-order latent and  $H$  is the pretransitional contribution  $\int C_p dT$ , where  $C_p$  is any excess heat capacity associated with the transition. The AC method measures the pretransitional heat capacity (and thus  $C_p$ ) but not the latent heat. The presence of first-order phase coexistence can,

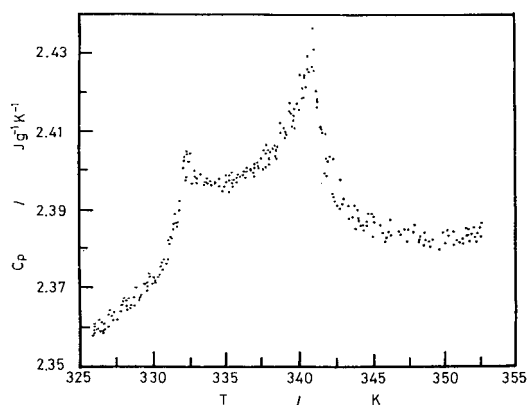


Fig.3 Specific heat capacity of an aqueous solution containing 65 wt% CsPFO. These data were obtained from the run shown in Fig.2 which was carried out with continuous stirring.

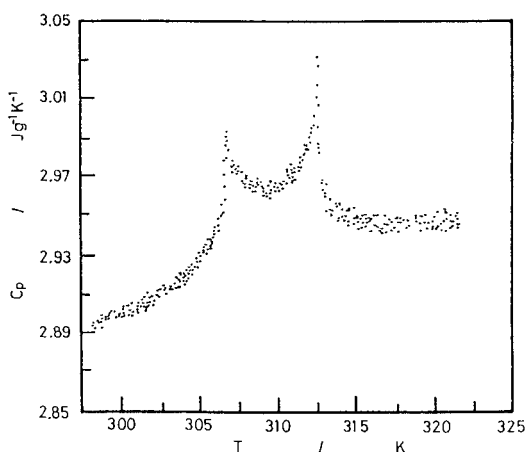


Fig.4 Specific heat capacity of an aqueous solution containing 41 wt% CsPFO. This run was carried out at a scan rate of 0.84 K/h without stirring.

however, be detected qualitatively by characteristic phase shifts and unusually high values of  $C_p$ .<sup>5)</sup> For first-order transitions which exhibit both a latent heat and pretransitional enthalpy, the area under the DSC curve will exceed  $H$  as determined by AC calorimetry and phase shifts in the  $T_{ac}$  signal will be observed over the region of two-phase coexistence.

Neither of these features occur in the present system. Thus our data support the conclusion, based on optical studies,<sup>2)</sup> that

the CsPFO nematic-isotropic transition is very close to second order. However, no systematic change with composition was detected in the N-SmA heat capacity peak in spite of the fact that the transition is reported to change from second-order at 41 wt% to tricritical near 65 wt%.

A quantitative comparison of the enthalpies obtained from AC calorimetry and DSC is given in Table 1. These values were obtained by measuring the area of the excess heat capacity peaks. The AC values agree with preliminary results cited by Ching et al.<sup>6)</sup> Since the  $C_p(N-I)$  and  $C_p(N-SmA)$  peaks are very small and lie close to each other in temperature, it is difficult to separate them accurately and no analysis of the data terms of critical exponents is possible.

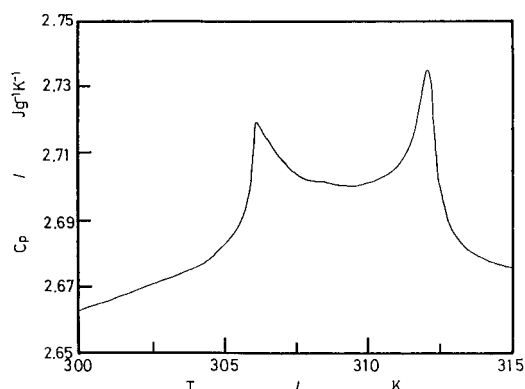


Fig.5 Specific heat capacity of a solution containing 41 wt% CsPFO as measured by DSC. The heating rate was 0.5 K/min.

Table 1

The thermal properties of CsPFO at the phase transitions. The transition enthalpy values are given in Joule per gram of CsPFO. The estimated uncertainty in the AC enthalpy values is  $\pm 0.04$  J/g

		Concentration 65%			Concentration 65%		
		SmA-N	N-I	Total	SmA-N	N-I	Total
AC Calorimetry	Transition Temperature	332.53K		341.40K	306.42K		312.12K
	Enthalpy	~ 0.18	~ 0.24	0.42	~ 0.08	~ 0.24	0.32
DSC	Transition Temperature				306.2K		312.1K

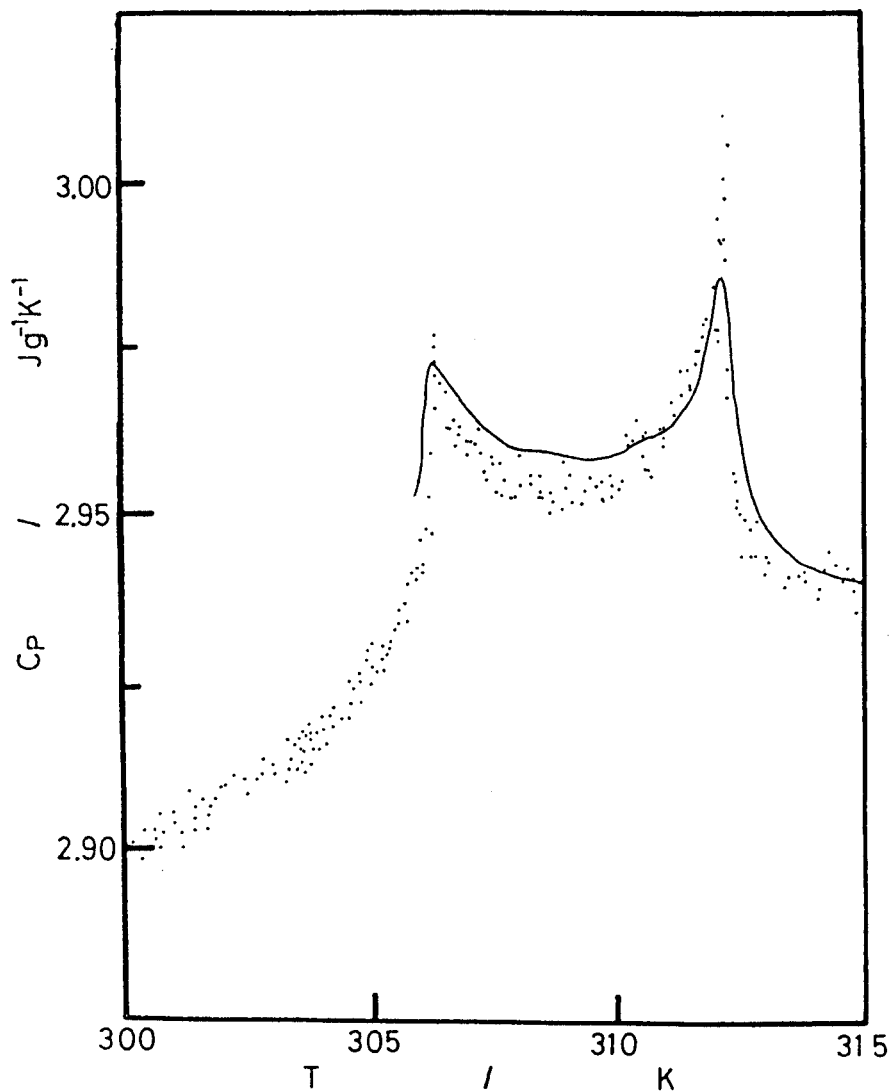


Fig.6 Comparison of the temperature dependence of the specific heat capacities for the 41 wt% CsPFO solution, as determined from AC calorimetry (data points) and DSC (solid curve, shifted up by 0.26 J/Kg).

#### 4 . CONCLUSIONS

We have carried out a study of the phase transition of cesium perfluoro-octanoate (CsPFO) micelles in water using high-resolution AC calorimetric techniques and differential scanning calorimetry(DSC). Aqueous solutions of CsPFO undergo two order-disorder phase transitions : a second-order nematic-smectic A (or lamellar) transition and a very weakly first-order nematic-isotropic transition. Small excess heat capacity peaks associated with each of these transitions

have been observed for solutions with 41 wt% CsPFO and 65 wt% CsPFO. The integrated transition enthalpy  $\int C_p dT$  for the N-SmA transition is about 0.14 J/g (Joule per gram of CsPFO solute) at 65 wt% and about 0.10 J/g at 41 wt%. No qualitative difference was observed in these  $C_p$  (N-SmA) divergences, in spite of expected behavior in the second order transition at 41 wt% to tricritical transition near 65 wt%. The integrated transition enthalpy was larger for the N-I transition : about 0.23 J/g at 65 wt% and about 0.27 J/g at 41 wt%.

Recently further study has been followed. Shin and Kumar<sup>7)</sup> have reported the quantitative analysis of the specific heat at the phase transition in a lyotropic liquid crystal. According to their explanation, the specific heat amplitude ratio and value of the specific heat exponent at the N-SmA transition suggest 3D XY-type behavior. A decrease in the latent heat and coexistence range with decreasing concentration, such as observed at the N-I transition, suggest an approach to a Landau point.

## References

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