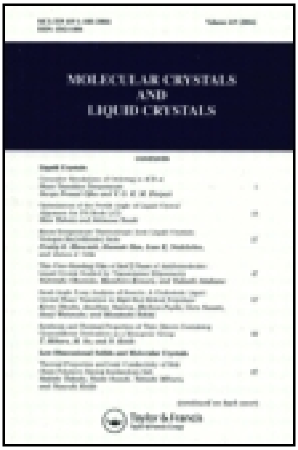

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The Middle Soap-Isotropic Transition at High Pressures in OPE_{10}/Water

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The Middle Soap-Isotropic Transition at High Pressures in OPE_{10}/Water

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The middle soap-isotropic phase transition in p, t-octylphenoxynonaethoxyethanol (OPE_{10}) and water systems is examined at high pressures. It is found that the melting curves in the P-T plane share some characteristics with transitions in thermotropics but are generally much steeper than in other liquid crystalline systems. The strong curvature of the melting line for one concentration allows transitions from isotropic to condensed to isotropic phases when changing pressure at a fixed temperature. The effect of increasing pressure on the peak in transition temperature as a function of concentration is to move it toward higher concentrations.

INTRODUCTION

Pressure studies have demonstrated their utility in exploring the nature of the intermolecular forces responsible for the existence of the liquid crystalline state. Changes in pressure and, consequently, in density ultimately represent changes in mean molecular distance, one of the most fundamental types of parameter variation. Such studies provide information on pressure derivatives and functional dependencies of the order parameter and mean-field potential.

Most investigations of the effects of pressure on liquid crystals have examined the phase diagrams of thermotropic materials;[1] not nearly as much attention has been devoted to lyotropic systems. Moreover, recent pressure studies of lyotropics have concentrated on phospholipids,[2-7] with relatively little attention given to soap systems that have been well-studied in other contexts. In this article, we examine the middle soap-isotropic transition in OPE_{10}/water systems up to 2500 bars, extending the range of previous measurements with lyotropics.

EXPERIMENTAL METHODS

OPE_{10} (p, t-octylphenoxynonaethoxyethanol) is an anhydrous, nonionic surface active agent. The phase structures, water binding, and molecular dynamics have been previously studied.[8-13] Our investigations examined systems of OPE_{10} and water at concentrations (in weight percent of OPE_{10}) between 40% and 60%. In this range OPE_{10}/water exhibits a hexagonal middle phase. At higher concentrations, a (lamellar) neat phase is found. The complete temperature-concentration phase diagram at atmospheric pressure is shown in Figure 1.[14] The material used in our experiments was obtained from Eastman Organic Chemicals.[15] The water used in making the solutions was triply filtered to remove organics and metals, doubly distilled, and deionized.

The systems to be studied were encapsulated in an arrangement consisting of a cylinder of fluran tubing with two closely spaced windows at the ends. The capsule containing the sample was placed in a high pressure optical cell whose temperature could be controlled to better than 0.02°C. The pressures were generated using a reciprocating hand pump with a mixture of hydraulic jack oil and heptane as the pressure fluid. Tem-

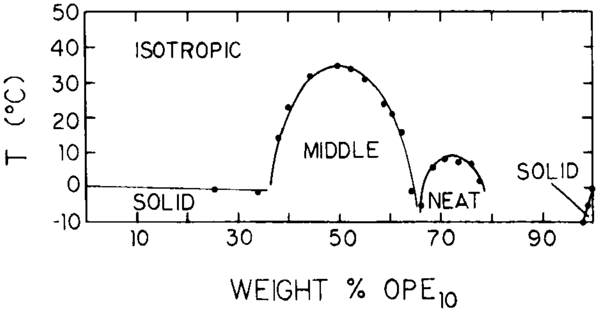

FIGURE 1 The phase diagram of OPE_{10}/water at atmospheric pressure.[14] The concentration is in weight percent of OPE_{10}.

peratures were measured with a calibrated thermistor, and pressures were read from a Heise bourdon gauge accurate to 5 bar.

The phase transitions were observed by examining the sample between the crossed polarizers of a microscope. A point on the transition line was determined by first setting the temperature and allowing the high pressure cell and jacket to come to thermal equilibrium. The sample was pressurized until the condensed phase was reached, and then the pressure was gradually lowered until the entire sample melted. Due to the strong first-order character of this transition, the pressure at which the condensed phase first appeared was typically 1 kbar higher than where melting occurred on lowering the pressure. The data, of course, represent transitions from the condensed phase to the isotropic phase.

The one exception to delineating the melting lines by examining transitions from the liquid crystalline state to the isotropic occurs with the 40% concentration curve. As can be seen from Figure 2, this concentration possesses an isotropic phase at pressures greater than where the liquid crystalline phase occurs. At a particular temperature for the 40% mixture,

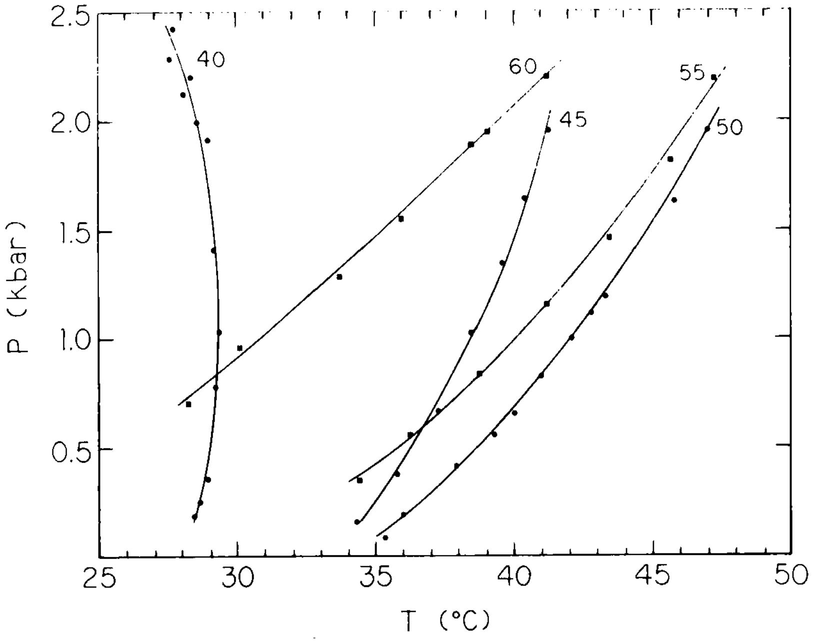

FIGURE 2 The high pressure phase diagram of OPE_{10}/water. The melting lines for the middle soap-isotropic phase transition are shown for various concentrations where the middle phase is exhibited.

data on the upper half of the curve represent transitions from the isotropic to the middle phase; data on the lower half mark transitions from the liquid crystalline state to the isotropic phase. The location of the one data point near where dP/dT becomes infinite ($P \sim 1$ kbar) was determined by fixing the pressure and then increasing temperature until the transition was reached.

Continual cycling in pressure could perhaps lead to the contamination of the sample by the pressure fluid. A sensitive measure of the integrity of the sample is the amount by which the temperature and pressure coordinate of a point on the transition line has changed. When collecting data for the phase diagrams, we periodically rechecked the clearing point at some low pressure where we had previously observed the transition. A deviation of the new clearing point from the previously measured portion of the transition line was taken as an indication that the sample had been contaminated or had deteriorated. Data taken subsequent to finding that the sample was contaminated were disregarded. These measures insure that the data presented in Figure 2 are reproducible and represent true equilibrium phase transitions.

EXPERIMENTAL RESULTS AND DISCUSSION

The middle-isotropic transition lines for various concentrations of OPE_{10}/water are shown in Figure 2. All the transition lines exhibit a curvature toward the pressure axis that is typical of most melting transitions. One notable feature of the curves is their steepness. In pressure studies of both thermotropics[1,16] and other lyotropics[7] to date, the melting transition was found to rise at a rate of between 25 and 50 bars/°C. In no case is the rate smaller than 120 bars/°C for the transition lines in Figure 2.

The tendency for the transition line to curve toward the pressure axis is extreme in the case of the 40% concentration line. At low pressures the slope is large and positive. With increasing pressure dP/dT becomes infinite, and, with further increases in pressure, eventually develops a large negative slope. An infinite value for dP/dT is due to Δv vanishing in the Clausius-Clapeyron equation. The negative slope is particularly interesting, because along this portion of the phase boundary the isotropic phase is more dense than the middle phase.

The peculiar shape of the 40% curve allows a kind of "reentrant" behavior. That is, it is possible to start at a fixed temperature with the sample initially in the isotropic phase, increase pressure until the condensed phase is formed, and increase the pressure further and enter the isotropic phase again. This is actually observed. Is the high pressure isotropic phase identical to the one found at lower pressures? We suspect that at elevated pressures, the higher concentration curves will display a behavior similar to the 40% line. The 45% curve is already suggesting this.

The ultimate effect of the increasing steepness of the melting curves with decreasing concentration (culminating in a sign change in dP/dT for the 40% line) can be seen from a plot of T vs X for increasing pressures (see Figure 3). It can be seen that the peak in transition temperature at atmospheric pressure at a concentration of 50% shifts toward higher concentrations. From the qualitative graph in Figure 3, the shift is about 1% per kbar.

CONCLUSION

The middle-isotropic transitions in OPE_{10}/water systems have features similar to melting transitions in thermotropics and other lyotropics studied to date. Notable differences are found. The transition lines are generally steeper than melting curves normally encountered in other liquid crystalline systems, with at least one example of a sign reversal in the slope. This permits a type of "reentrant" behavior on changing pressure allowing transitions from isotropic to condensed to isotropic phases. The effect of

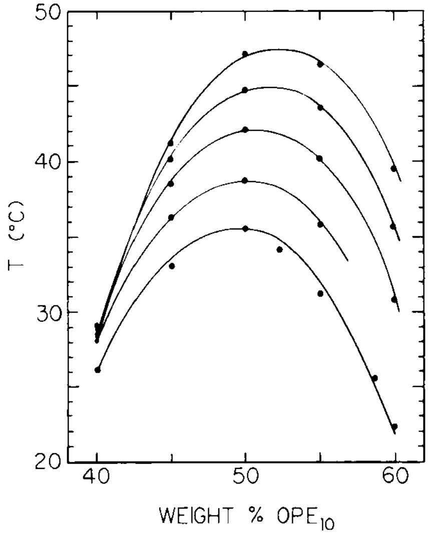

FIGURE 3 The phase diagrams of OPE_{10}/water at various pressures beginning at atmospheric pressure and subsequently being incremented by 500 bar.

increasing pressure on the peak in transition temperature as a function of concentration is to shift it toward higher concentrations.

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