High pressure phase diagrams of two homologous series of Inotropics

A. J. Nicastro[a]; P. J. Bashus[a]; E. B. Tuska[a]

[a] Department of Physics, Bucknell University, Lewisburg, Pennsylvania, U.S.A.

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High pressure phase diagrams of two homologous series of lyotropics

by A. J. NICASTRO, P. J. BASHUS† and E. B. TUSKA‡

Department of Physics, Bucknell University, Lewisburg, Pennsylvania 17837, U.S.A.

The hexagonal–isotropic transition is studied in two homologous series of lyotropic liquid crystals. The high pressure phase diagrams are mapped up to 2 kbar for three homologues from each of the Triton X and Triton N series of non-ionic surfactants. We find that an interesting hexagonal–isotropic re-entrant phenomenon is a common feature of the transition lines of homologues in each series. For each homologue in each series, we report a systematic increase in the average value of dP/dT with decreasing concentration correlated with the presence of the re-entrant phenomenon.

1. Introduction

Amphiphilic molecules, having a hydrophilic head and a hydrophobic tail, in aqueous solutions can form micelles, giving rise to a wide class of lyotropic liquid crystal mesophases [1]. Among these mesophases, depending on the relative concentrations, temperatures, and pressures, one finds columnar hexagonal phases among a variety of phases with symmetries common to the more well-studied thermotropic materials. The appearance and properties of these liquid crystal phases in lyotropics have been examined in several experiments [2]. These systems exhibit anisotropic properties which are due to the orientational alignment of rod-like aggregates in solution which have a long-range order similar to thermotropic nematics. The size and shape distributions of the micelles, of course, are related to the microscopic properties of the system, but it is only at relatively high concentrations ($\gtrsim 20$ per cent) that the micelles can form anisotropic ordered phases.

In this paper, we examine the high pressure phase diagrams of two homologous series of lyotropic liquid crystals. Specifically, we report our results for hexagonal–isotropic transitions in aqueous solutions of octyl- and nonylphenol polyether alcohols, two homologous series of non-ionic surface active agents, more commonly known at Triton X and Triton N compounds [3]. A novel feature we report for the phase diagrams is the appearance of a disordered isotropic phase at pressures higher than those at which the hexagonal phase is found. A somewhat analogous phenomenon is manifested by thermotropic re-entrant nematics where the less well-ordered re-entrant nematic phase re-occurs at a lower temperature than the more well-ordered smectic A phase [4]. In our experiments, changes in pressure, rather than temperature, display the re-entrant phenomenon in the phase diagrams.

† Present address: Department of Physics, Lehigh University, Bethlehem, Pennsylvania 18015, U.S.A.

‡ Present address: Department of Physics, University of Delaware, Newark, Delaware 19716, U.S.A.

2.   Experimental methods

Our pressure studies examined three members from each of the Triton X and Triton N series of compounds. For completeness, some of the results of our previous investigation [5] of Triton X-100 are also reported here.

The two series of non-ionic surface active agents are prepared commercially by the reaction of octylphenol and nonylphenol with ethylene oxide. The products are alkylaryl polyether alcohols and are mixtures with respect to length of the polyoxyethylene chain. The table lists the materials studied, and the *n* values given in the table represent the average number of ethylene oxide units in the ether side-chain of each product. The distribution of various polyoxyethylene chain lengths in each of the surfactants follows a Poisson distribution [6]. While transitions in aqueous solutions of the surfactants are still well-demarcated, the effect of using mixtures rather than pure isomers is to broaden the transition slightly.

Materials studied. The average number of ethylene oxide units, *n*, in the ether side-chain is given for each material, as well as the cloud point temperature for a 1 per cent solution.

Surfactant	*n*	Cloud point
Octylphenol series		
Triton X-114	7·5	22°C
Triton X-100	9·5	65°C
Triton X-102	12·5	88°C
Nonylphenol series		
Triton N-101	9·5	54°C
Triton N-111	11·0	72°C
Triton N-150	15·0	95°C

Our experiments examined the hexagonal–isotropic phase transitions in aqueous solutions of the compounds shown in the table. The water solubility (and surface activity) of non-ionic surface-active agents are dependent on the hydrophilic nature of the ether linkages in the polyoxyethylene chain. These ether linkages are readily hydrated at room temperature, and the water solubility of the products at room temperature and above is dependent on the number of these hydrated linkages. Each of the compounds used in our experiments is completely soluble in water. Triton compounds with polyoxyethylene chain lengths shorter than those we have used are not soluble, but merely dispersible or even insoluble.

An increase in temperature reduces the forces of hydration, and the surfactants then become less soluble in water. The non-ionics therefore normally exhibit a cloud point, which is the temperature above which all but very dilute aqueous solutions become turbid and eventually form two phases [7]. The cloud point for each of the systems investigated is given in the table. The relatively low cloud point for Triton X-114 limited some of our high pressure measurements.

The columnar hexagonal phase was exhibited by the six Triton compounds roughly between the concentrations of 40 per cent to 60 per cent by weight for these materials. The pressure–temperature measurements, which mapped the hexagonal–isotropic transition, were made using a Daniels optical microscope pressure cell. The systems to be studied were encapsulated in an arrangement consisting of a cylindrical shell of fluoran tubing with *c* axis cut sapphire windows at the ends. The capsule containing the sample was placed in the optical pressure cell whose temperature could

be controlled to better than 0·04°C. The pressures were generated using a reciprocating hand pump with a mixture of hydraulic jack oil and heptane as the pressure fluid. A calibrated thermistor was used to measure temperatures, and pressures were read from a Heise bourdon gauge accurate to 5 bar. Typically, however, random errors in locating a point on a transition line exceeded by about a factor of 4 the limit at which the pressure gauge could be read and the level at which the temperature could be controlled.

The phase transitions were observed by examining the sample between the crossed polarizers of a microscope; the presence of the columnar hexagonal phase was easily discernible by the appearance of birefringent aggregates of the hexagonal phase. A point on the transition line was located by first setting the pressure and, starting from the condensed phase, scanning slowly in temperature until the sample melted. For the 60 per cent Triton X-100 and 58 per cent Triton N-111 systems, we found no significant difference between the transition lines determined by the above method and the transition lines traced by holding temperature fixed and scanning in pressure. Due to the relatively large values of dP/dT for these systems, we found holding pressure fixed while varying temperature to be the most expedient method for delineating a transition line.

During the course of an experiment to trace out a transition line in the $P–T$ plane, continual cycling in temperature and pressure could perhaps lead to the contamination of the sample by the pressure fluid. When collecting data for a particular transition line, we periodically re-checked the clearing point at some lower 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. Contamination and deterioration were rarely problems, but these measures ensure that the data presented in figures 1 (a)–(f) are reproducible and represent true equilibrium phase transitions.

Points on the lines in figures 1 (a)–(f) are the average of three to six measurements. Mean absolute deviations were typically less than 0·1°C when scanning in temperature and less than 20 bar in the infrequent times when pressure was varied.

3. Results and discussion

The hexagonal–isotropic transition lines for various concentrations of the compounds listed in the table are shown in figures 1 (a)–(f). One feature common to the phase diagrams of both homologous series that was noted in our past study [5] of Triton X-100 is the markedly high values of the average slope, $\langle dP/dT \rangle$, for transition lines of these systems, at least a factor of two greater than in clearing transitions in other systems of lyotropics or thermotropics. Moreover, it is clear from the phase diagrams that $\langle dP/dT \rangle$ for each transition line is a strong function of concentration for any particular homologue. Specifically, $\langle dP/dT \rangle$, as determined by a least squares linear fit, increases rapidly with decreasing concentration, becoming infinite for certain concentrations of Triton X-100 and X-102 and for Triton N-101 (see figure 2). A point on a transition line where dP/dT is infinite is due to ΔV vanishing in the Clausius–Clapeyron equation.

The increase in $\langle dP/dT \rangle$ with decreasing concentration, perhaps diverging about some concentration X_0, gives some information regarding the volume change across the transition. From the Clausius–Clapeyron equation, $\langle dP/dT \rangle \propto 1/\langle \Delta V \rangle$.

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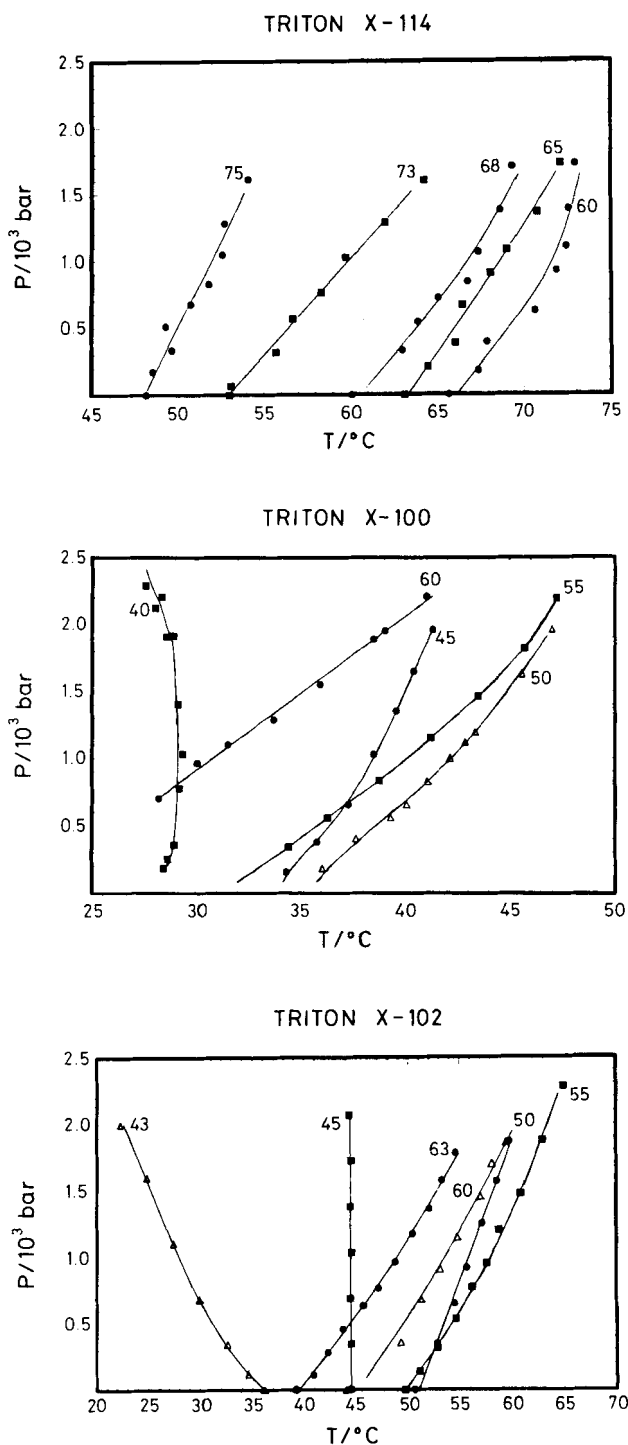
TRITON N-101

TRITON N-111

TRITON N-150
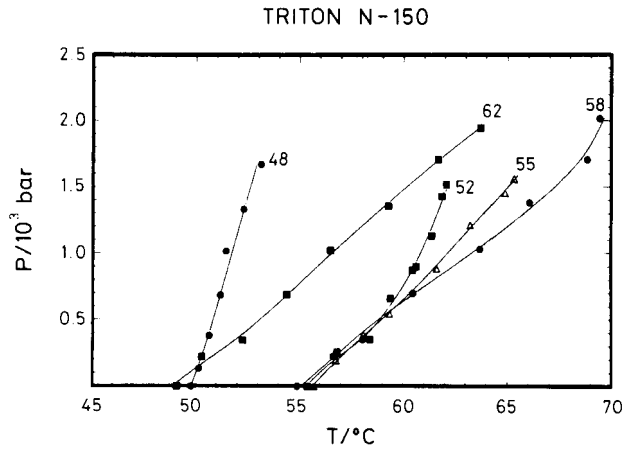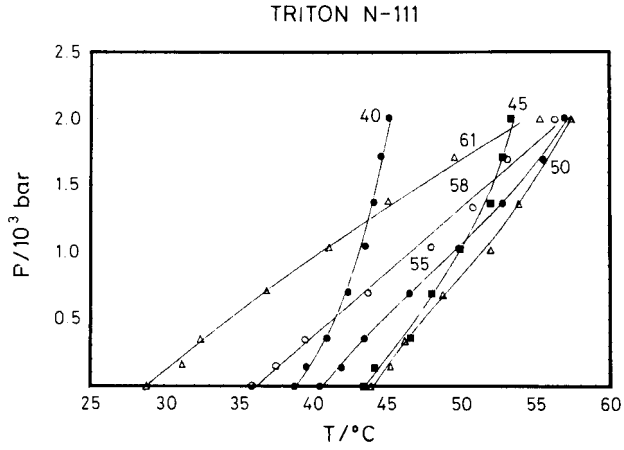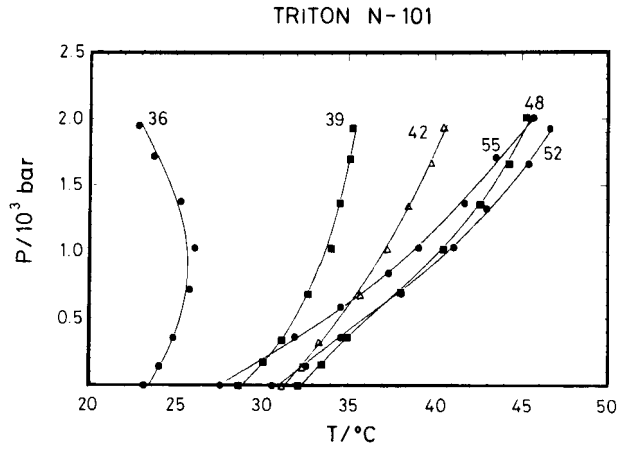
Figure 1. The hexagonal–isotropic transition lines for various concentrations of six homologues in the Triton X and Triton N series. The concentrations (in weight per cent) are shown next to the corresponding transition lines.
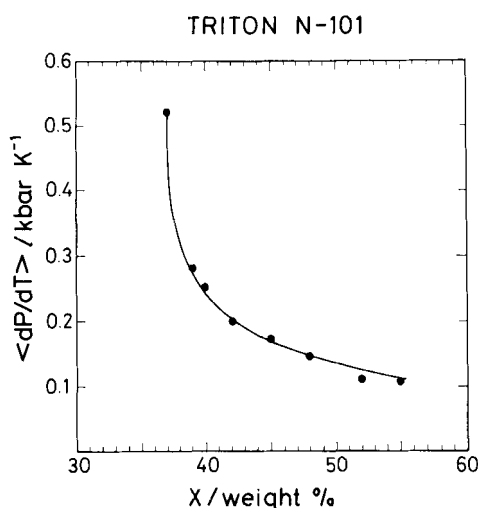
TRITON N-101

Figure 2. The average value of dP/dT (as determined by a linear least squares fit) as a function of concentration for transition lines of Triton N-101.

Consequently, our results imply that $\Delta X = X - X_0$ should be proportional to $\langle \Delta V \rangle$ (but not necessarily directly proportional) assuming that the system is not near a critical point and that the latent heat of the transition does not behave anomalously. X_0 may be accessible in the sense that the homologue may in fact have a hexagonal mesophase at X_0, as in the case of Triton X-100, X-102, and N-101, or may be fiducial with the system not possessing a mesophase at X_0. When X is near X_0, $\langle dP/dT \rangle$ becomes infinite due to the vanishing of ΔV. Volumetric measurements or a calorimetric determination would be quite useful in verifying the link between ΔX and ΔV.

In addition to the increase in $\langle dP/dT \rangle$ with decreasing concentration, evident in the transition lines for a particular homologue is the trend toward increasing curvature with decreasing concentration. While the trend is not as clear as the increase in $\langle dP/dT \rangle$ with decreasing concentration, the two effects together produce an interesting re-entrant phenomenon for two homologues. For the 36 per cent Triton N-101 system and the 40 per cent Triton X-100 system, a hexagonal–isotropic re-entrant phenomenon is exhibited. For these systems, it is possible to start at a fixed temperature, with the sample initially in the isotropic phase, increase pressure until the ordered phase is formed, and increase pressure further and enter an isotropic phase again. The portions of these transition lines with negative slope are particularly interesting since along this portion of the phase boundary, the isotropic phase is more dense than the lyotropic nematic phase. This is also the case with the 43 per cent Triton X-102 system. Normally in phase transitions, the higher pressure phase is more well ordered than the lower pressure phase. While not a law of thermodynamics, it is counter-intuitive and is reminiscent of the re-entrant nematic phase in thermotropic materials. For $P–T$ phase diagrams of re-entrant thermotropics, the re-entrant phenomenon is exhibited along a line of constant pressure and involves the nematic and smectic A phases [4]. Our systems exhibit a re-entrant phenomenon involving the columnar hexagonal and isotropic phases along lines of constant temperature. The origins of the re-entrant phase in thermotropics, however, are probably different to those of the lyotropic re-entrant phase. In the case of thermotropics, steric effects due to either molecular pair formation or the mixing of dissimilar molecules seem to be

responsible for the re-entrant behaviour. The same mechanism cannot be operative in the soap systems which we investigated. Curiously, the re-entrant nematic phase in thermotropics disappears at higher pressures.

The re-entrant phenomenon which we report here is difficult to explain within the framework of existing theories of lyotropics. In discussions of the phase changes in mixtures of anisotropic particles [8, 9], the transition is usually explained in terms of a competition between orientational and packing entropy. Increasing pressure, which is equivalent in many respects to increasing the total monomer concentration, crowds the constituent aggregates. When the pressure (or concentration) gets high enough, the aggregates align to form rods, which decreases the orientational entropy. To partially offset this loss in orientational entropy, the system reorganizes into larger rods. Theories [10, 11] of micellar self-assembly treat each different size and shape aggregate as a separate species, but to explain the re-entrant phenomenon we report here, it must be that the species are linked by equations of chemical equilibrium between the monomer and aggregate particles. Otherwise, if the packing and orientational entropies were the only portions of the free energy affecting rod size, the micelles would continue to contribute to rod growth with increasing pressure and an isotropic phase would not be reached. Perhaps a limiting mechanism in the form of a mixing entropy is operative which favours a large number of small aggregates rather than a small number of large ones, providing a negative feedback against continued rod growth with increasing pressure, and so producing the re-entrant effect.

4. Summary

Our high pressure study of the hexagonal–isotropic phase transition examined two homologous series of non-ionic surfactants. While the phase diagrams of the systems show similarities to those of thermotropics and other lyotropics, notable differences are found. The average values of dP/dT for the transition lines are large and strongly increasing with decreasing concentration. The curvature of the transition lines also increases with decreasing concentration. These two effects together give rise to a novel type of hexagonal–isotropic re-entrant phenomenon. Our phase diagrams indicate that this re-entrant phenomenon is a general feature of our systems and may be prevalent in other lyotropic systems. Volumetric experiments are now needed to verify the decrease in ΔV with increasing pressure for these systems which exhibit re-entrant phases and also to verify that for a fixed pressure, the volume change across the transition increases with increasing concentration differences from a concentration about which $\langle dP/dT \rangle$ diverges.

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