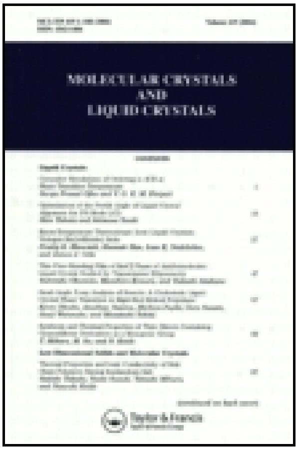

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Joseph F. Dyro [a] & Peter D. Edmonds [a]

[a] Department of Biomedical Engineering, Moore School of Electrical Engineering University of Pennysylvania, Philadelphia, Pennsylvania

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Ultrasonic Absorption and Dispersion at Phase Transition in Liquid Crystalline Systems: N-Octylamine-Water‡

JOSEPH F. DYRO and PETER D. EDMONDS

Department of Biomedical Engineering
Moore School of Electrical Engineering
University of Pennysylvania
Philadelphia, Pennysylvania

Abstract—A lyotropic liquid crystalline system, the amphiphile *n*-octylamine and water, has been studied to investigate the dependence of velocity and absorption of ultrasound on the mechanisms of isotropic-mesomorphic phase transition in the vicinity of the critical point, $C_c = 0.854$ mole fraction of water and $T_c = 35.8$ °C.

This work is the first ultrasonic study of a two-component lyotropic system in the region of an isotropic-mesomorphic transition. Measurements of ultrasonic absorption are reported over a frequency range from 10 MHz to 130 MHz and of velocity at 10 MHz. Relaxational processes controlled by a distribution of time constants greater than 10^{-8} sec (frequencies less then 30 MHz) are probable. Diffusion controlled processes may be inferred.

At 10 MHz the absorption in the critical region exhibits a maximum and the velocity undergoes a discontinuity. Such behavior is similar to that previously observed in thermotropic liquid crystals, binary liquids and gas-liquid systems at the critical point.

Measurements were also made over the full concentration range at three temperatures (31.1°, 36.85°, and 42.1 °C), corresponding to $(T - T_c)$ of $-4.75°$, $+1.0°$, $+6.25$ °C. At 36.85 °C a peak in the absorption was found at the critical concentration; at higher frequencies the maximum occurred at slightly lower concentrations of water. At 31.1 °C the isotherm intersects several phase boundaries and increased absorption, associated with increased viscosity, was observed in the mesomorphic phase.

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Introduction

The object of our current work is to study the lyotropic liquid crystalline system of *n*-octylamine and water. By the study of the amphiphile, octylamine, a prototype of the diols, phosphatides, and cerebrosides, we may be able to understand some properties of structurally more complex systems of biological importance. We also wish to explore the possibility of bridging the gap between the present theoretical understanding of critical phenomena in mixtures of simple liquids and the experimenal determination of the critical behavior of simplest lyotropic liquid crystalline systems. We observed similarities between the ultrasonic data obtained by us and those previously obtained by others for one component systems and binary liquid mixtures.

Previous ultrasonic work on transition phenomena has been performed on thermotropic systems, i.e., *p*-azoxyanisole and cholesteryl compounds.[1,2,3,4] In those systems studied, the absorption and velocity exhibit maxima and minima respectively at the isotropic-mesomorphic transition. Existing theories of gas-liquid and liquid-liquid transitions provide functional agreement with experimental data[5] and encourage the continuation of this study of liquid crystal phase transition phenomena.

To our knowledge this work is the first ultrasonic study of a lyotropic liquid crystalline system. We chose as a prototype of more complicated amphiphiles the eight-carbon alkylamine, *n*-octylamine. A large amount of water can be dissolved in octylamine but only a much smaller fraction of octylamine can be dissolved in water. Figure 1 shows the phase diagram of the *n*-octylamine-water system, determined by Ralston and coworkers.[6] Area 1 is isotropic solution. At MF 0.97 water and a temperature of 28 °C there is a consolute point, above which lies a two phase region, area 12, where octylamine and water exist as conjugate solutions. Areas 9 and 3 are two phase regions of isotropic solution and hydrated amine. Ralston *et al.* studied samples from Area 5 under polarized light; the presence of thread like lines prompted them to label this area the " nematic " phase. We shall describe it simply as the mesomorphic phase.

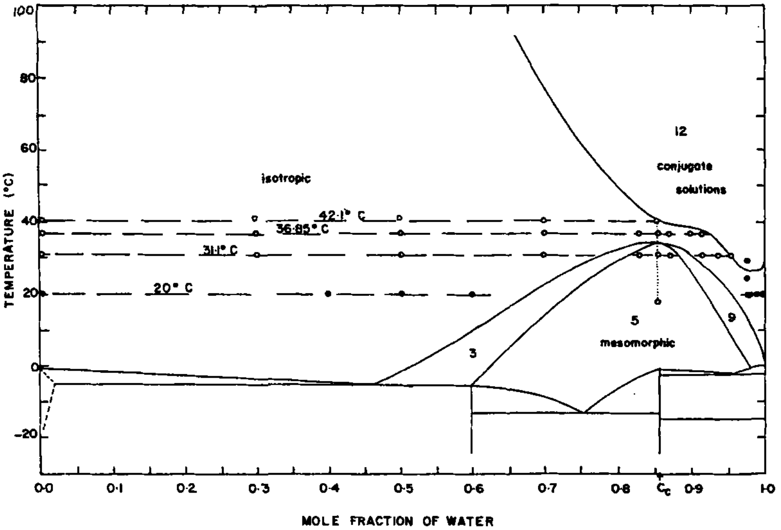

Figure 1. Phase diagram of the system *n*-octylamine–water (after Ralston *et al.* 1942) showing points on the phase diagram where ultrasonic measurements were made ○ this work, ● ref. 10).

Previous ultrasonic studies of monoatomic gases and binary liquid mixtures also revealed that the sound wave interacts most strongly with the system in the vicinity of its critical point.[5,7,8,9] We therefore focused our attention upon the vicinity of the critical point of the mesomorphic phase at $C_c = 0.854$ MF water and $T_c = 35.8$°C.

Table 1 lists the physical parameters relevant to sound wave propagation through a liquid medium. The sinusoidally varying pressure wave $P(x, t)$ is a solution to a plane wave equation, where P_0 is the sound pressure at the source, α is the spatial decay constant or the amplitude absorption coefficient, v is the phase velocity for propagation of a plane compressional wave and ω is the angular frequency. The two quantities available for measurement are the absorption coefficient α and the velocity v. The classical theory of sound propagation in isotropic liquids predicts that the attenuation parameter α/f^2 is a constant, which depends upon the shear viscosity η and density ρ of the medium and the

TABLE 1 Relevant Equations of Sound Wave Propagation

$$P(x, t) = P_0 e^{-\alpha x} e^{j\omega(t - x/v)}$$

$$\left(\frac{\alpha}{f^2}\right)_{\text{classical}} = \frac{8\pi^2\eta}{3\rho v^3} \ (\text{sec}^2\ \text{cm}^{-1})$$

$$v^2 = \frac{1}{\rho\beta_s} = \frac{\gamma}{\rho\beta_t}$$

$$\gamma = \frac{C_p}{C_v} \qquad \beta \equiv \text{compressibility}$$

velocity of propagation v through the medium. According to classical theory the absorption of sound can be attributed largely to the viscous resistance offered to the displacement of elemental volumes of fluid by the sound pressure wave. Additional contributions due to thermal conductivity and due to coupling of the energy of the sound wave with time dependent molecular processes may be significant in particular cases. The last is certainly of importance in the critical region where diffusion controlled processes occur.

In addition to these contributions to the attenuation, effective attenuation may also be introduced by inhomogeneities in the solution, which cause scattering of the sound wave.

The square of the phase velocity v may be expressed in terms of the density ρ, the adiabatic or isothermal compressibility, β_s or β_t, and the ratio of specific heats γ.

Figure 2 lists a number of systems, ranging from a one component monatomic fluid to a more complex lyotropic (binary) liquid crystalline system, such as n-octylamine and water. Shown here are typical behaviors of the density, shear viscosity, specific heat, thermal conductivity, adiabatic compressibility, ultrasonic absorption coefficient and phase velocity as a function of temperature (or density where indicated) in the critical region. Dashed lines indicate the critical temperature or density.

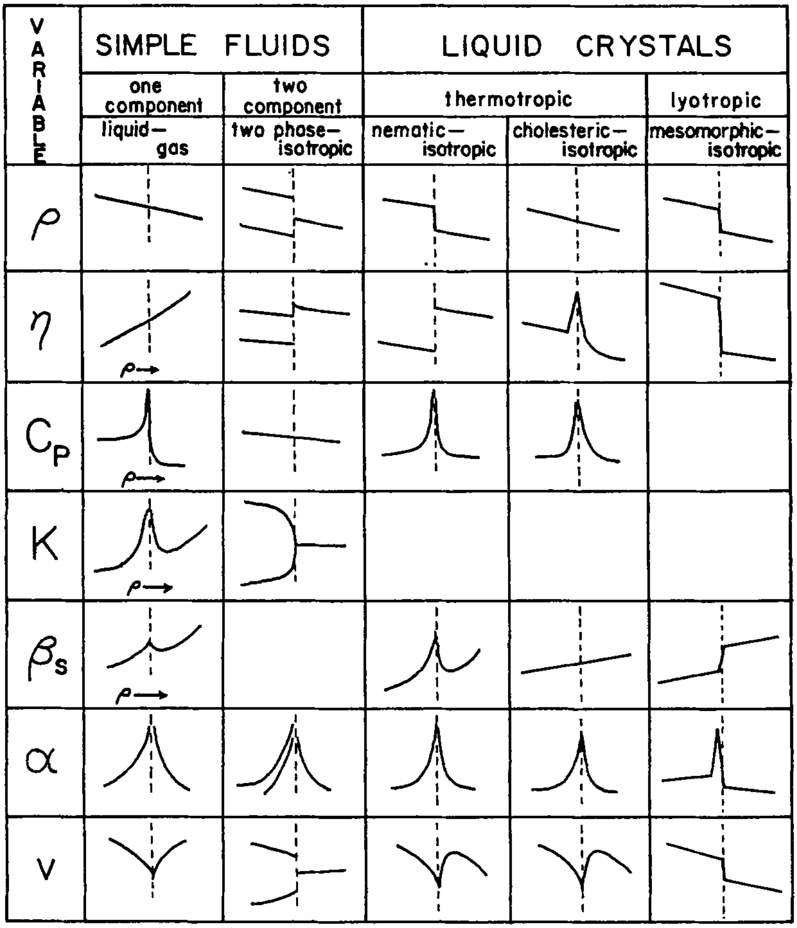

Figure 2. Dependence of various parameters on temperature (or density where indicated) in the critical region of fluids and liquid crystalline systems.

Measurements

Previous work in the vicinity of critical temperatures by other investigators has revealed an increase in α far greater than that expected from the classical theory of sound absorption.[5,7,8,9] We have now shown that such an anomalously large increase in α also occurs in the system n-octylamine-water‡ at the isotropic-mesomorphic critical point and that the velocity of sound suffers a step discontinuity.

CRITICAL REGION

Figure 1 shows the concentrations and temperatures at which our measurements were made. The dotted line indicates the locus of measurements beginning in the isotropic solution just below the two phase region and at a concentration $C_c = .854$ MF water. We then decreased the temperature passing successively through the isotropic phase, critical point, and into the viscous mesomorphic phase. Thermal stability ($\pm 0{\cdot}1$°C) was established at each temperature.

The results of this experiment are plotted in Figs. 3 and 4. Our measurements of α in the isotropic region were larger by a factor of 2 than those predicted by the classical theory alone. At temperatures within one degree of the critical temperature T_c the absorption increased sharply to a peak and then decreased rapidly. The explanation of the origin of the excess sound absorption near this critical point awaits future theoretical work. However, the similarity between this behavior and that of the less complex systems may make the formulation of a theory more general.

The step change in phase velocity finds its analogy in the velocity at the binary liquid critical point, which also suffers a step discontinuity. Figure 5 shows the behavior of the density at the

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‡ Aldrich #0-580–2 or Eastman #P7588 practical grade octylamine was distilled twice in a 47 cm packed column. Samples were prepared with glass-distilled water, pH7, immediately before measurement and were maintained in a nitrogen atmosphere.

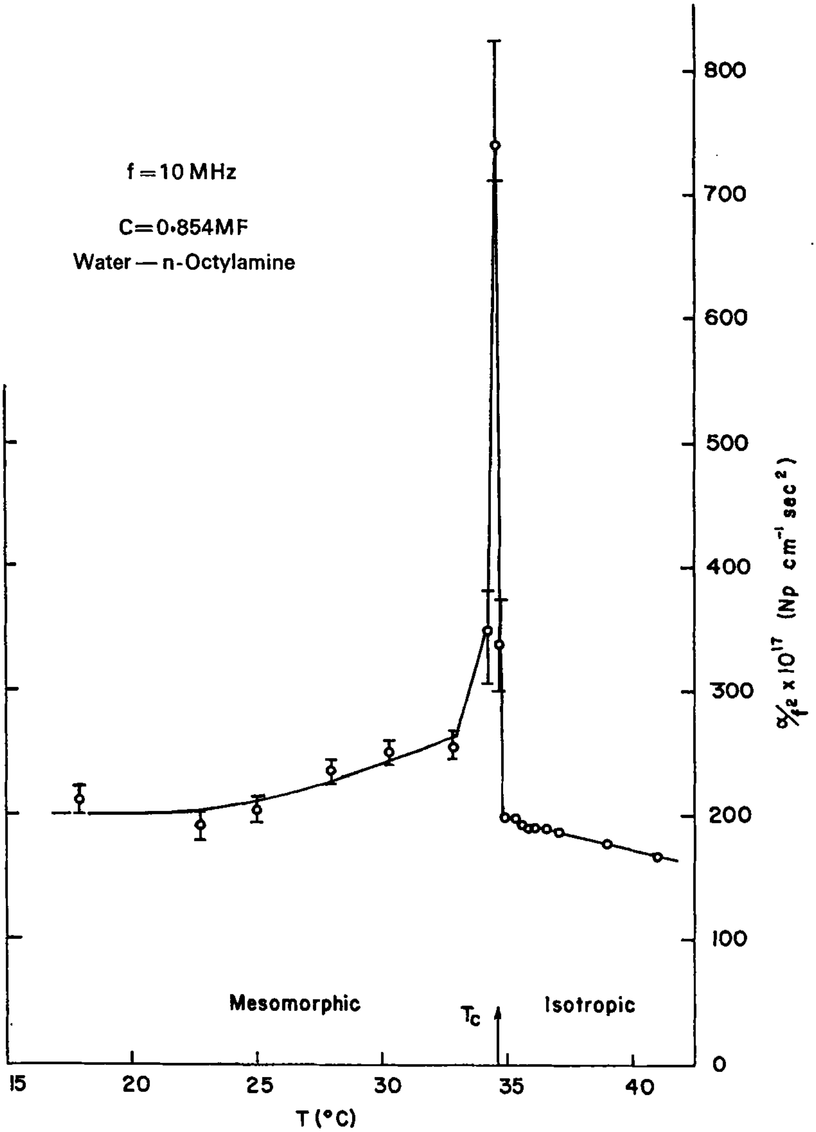

Figure 3. Temperature dependence of the absorption coefficient at the critical concentration.

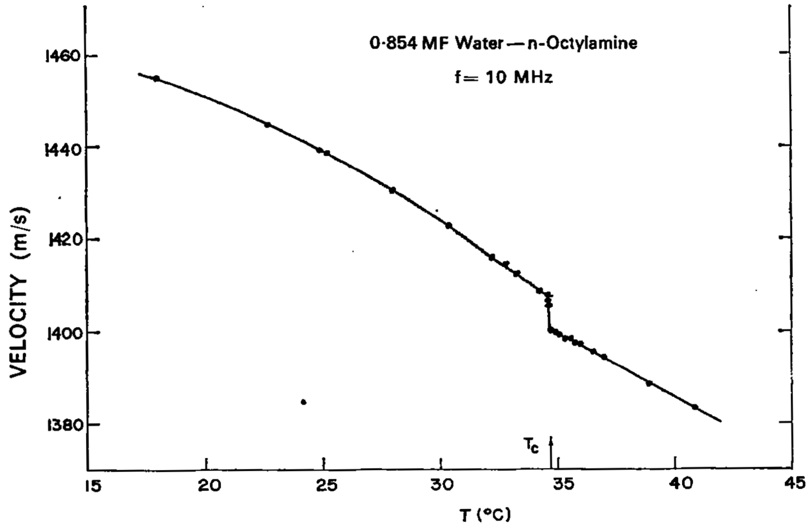

Figure 4. Temperature dependence of the velocity at the critical concentration.

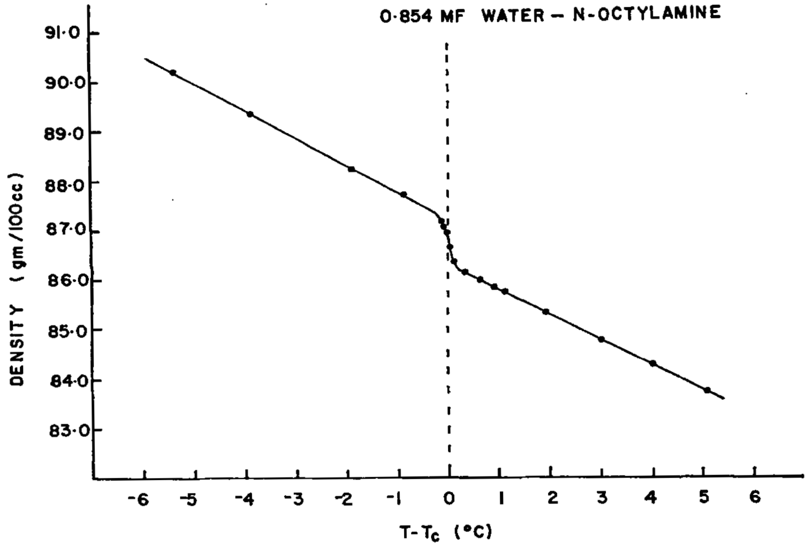

Figure 5. Temperature dependence of the density at the critical concentration.

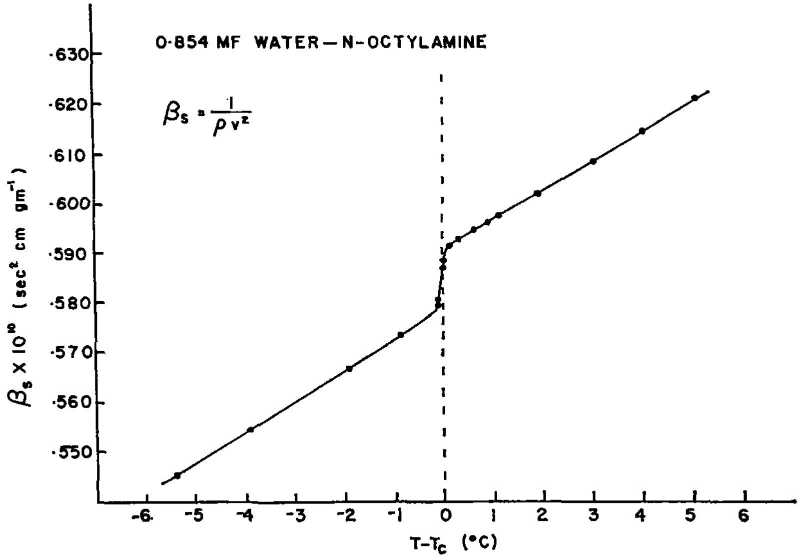

Figure 6. Temperature dependence of the adiabatic compressibility at the critical concentration.

critical concentration and at temperatures within 5 degrees of the transition. In going from the isotropic solution to the mesomorphic phase we observed a sharp increase in density of about 1 gm/100 cc. The change in density necessitates a contrary change in compressibility (Fig. 6) to account for the measured change in phase velocity. Such a velocity change might be expected to occur in a system that transforms from a less dense isotropic phase to a more tightly packed mesomorphic phase with a consequent change in the compressibility.

Isotropic Region

To obtain a better understanding of the acoustic behavior of our system we explored its composition and temperature range. Open circles on Fig. 1 represent points at which further measurements were made. Experiments reported in reference 10 are also included. The lines are four isotherms which are approximately 16 degrees and 5 degrees below the critical temperature and 1 and 6 degrees above the critical temperature respectively.

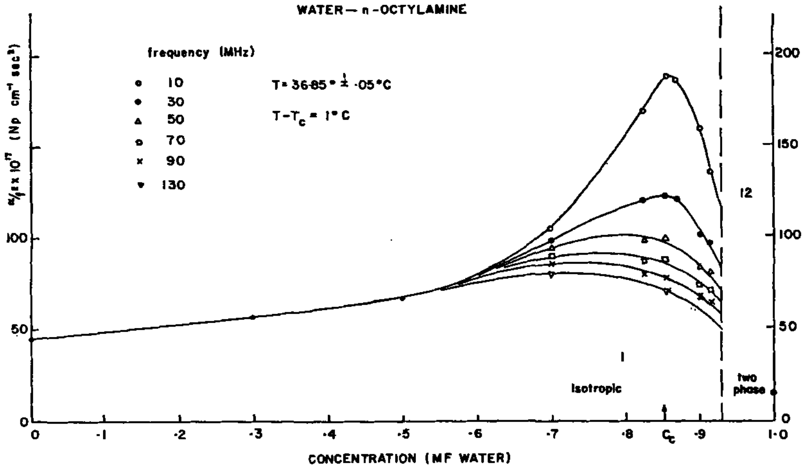

Figure 7. Concentration dependence of α/f^2 at 1 °C above the critical temperature.

Figure 7 shows the results of the measurements in the isotropic region along the isotherm that is 1° above the critical temperature. The attenuation increases linearly and slowly with an increase in the concentration of water. Six frequencies from 10 to 130 MHz were used and the absorption increased to a maximum upon approaching the critical composition. For 10 and 30 MHz the maximum value of α/f^2 occurred at the critical concentration. As the measurement frequency increased we observed an apparent shift in the location of the peak toward lower concentrations of water. The significance of the shift in the peak is found in the relaxational behavior of molecular diffusion processes.

The quantity α/f^2 is a constant if only contributions from the shear viscosity are considered and viscous relaxation does not occur. However, if a time dependent molecular process occurs in the solution, the pressure and temperature perturbations introduced by the sound waves may interact with the process; the maximum interaction takes place at a characteristic frequency f_c and a relaxation curve (Fig. 8) will result described by the equation $\alpha/f^2 = A/[1 + (f/f_c)^2] + B$. If more than one molecular process

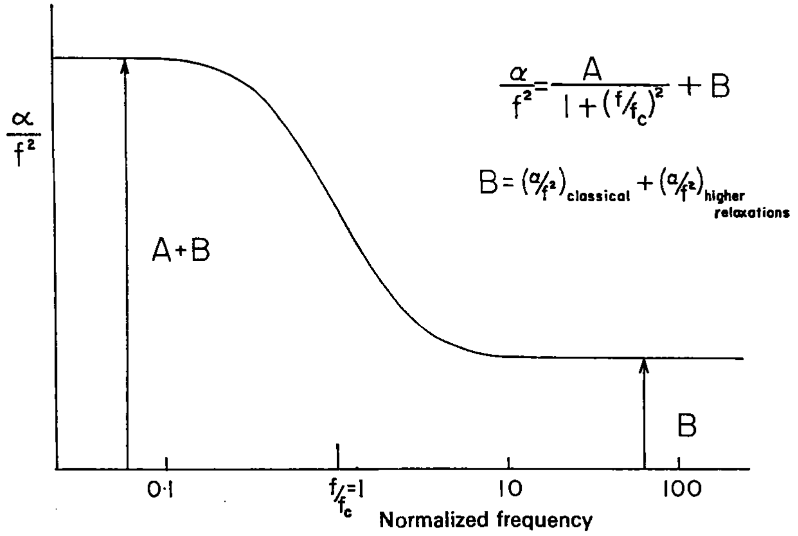

Figure 8. Frequency dependence of α/f^2 for a single relaxation process.

occurs, each characterized by a different frequency, then summation occurs and the combined effect will be a broadening of the relaxation curve or appearance of separate relaxational regions: $\alpha/f^2 = \sum[A_i/1 + (f/f_{ci})^2] + B$.
Measurements at the critical concentration (Figs. 8, 9) show several examples of such broadening of the relaxation curve. It appears that the characteristic frequencies of the molecular processes occurring in the region of phase transition are below 30 MHz and the time constants of these processes are longer than 10^{-8} seconds.

An explanation of the shifting of the maximum seen in Fig. 7 and Fig. 10 can be attempted now. We assume that relaxational behavior (such as that discussed in references 11, 12, and 13), characterized by frequencies greater than 30 MHz and occurring at concentrations greater than 0.5 MF water, is taking place. This may be molecular association of water and octylamine by hydrogen bonding, but the details of the mechanism do not concern us in the present phenomenological considerations. The contribution of the phase transition processes to the total

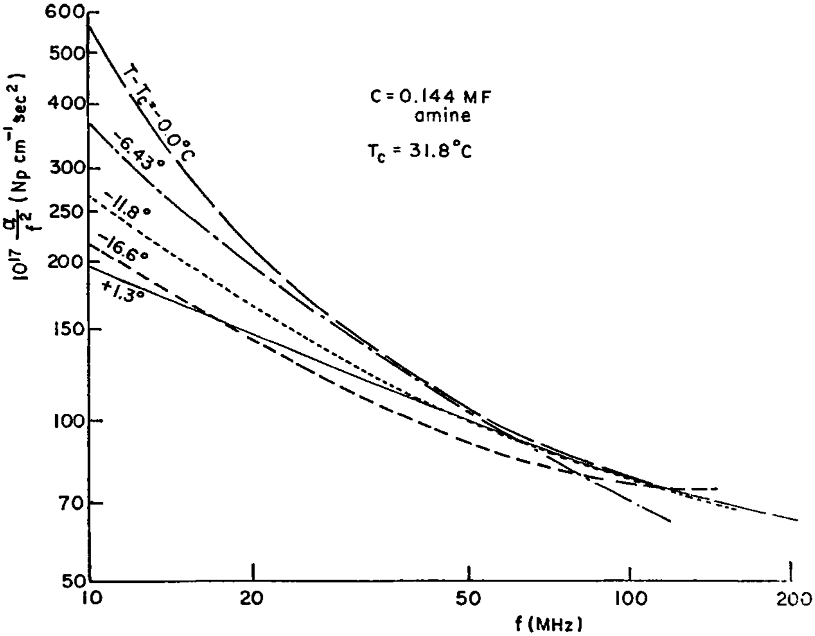

Figure 9. Frequency dependence of α/f^2 for *n*-octylamine–water, corresponding to more than a single relaxation process. (For this inadequately purified sample, $T_c = 31.8$°C)

absorption is not sensed at the higher frequencies since this condition of measurement is at the tail end of the phase transition relaxation curve. However, as the measurement frequencies are lowered and approach those that interact most strongly with the molecular diffusion mechanisms an increase in α/f^2 occurs. The shift in the peak reflects the relative magnitudes of the contributions from molecular diffusion and molecular association processes. Figure 10 is a diagrammatic representation of the surface α/f^2 vs. concentration and frequency.

At high concentrations of water (greater than 0.97 MF) a single relaxation process has been reported.[10,12] This was characterized by one time constant corresponding to a frequency of about 25 MHz in the temperature range, 20° to 30 °C. The reaction taking place here may be related to the formation of micelles (critical

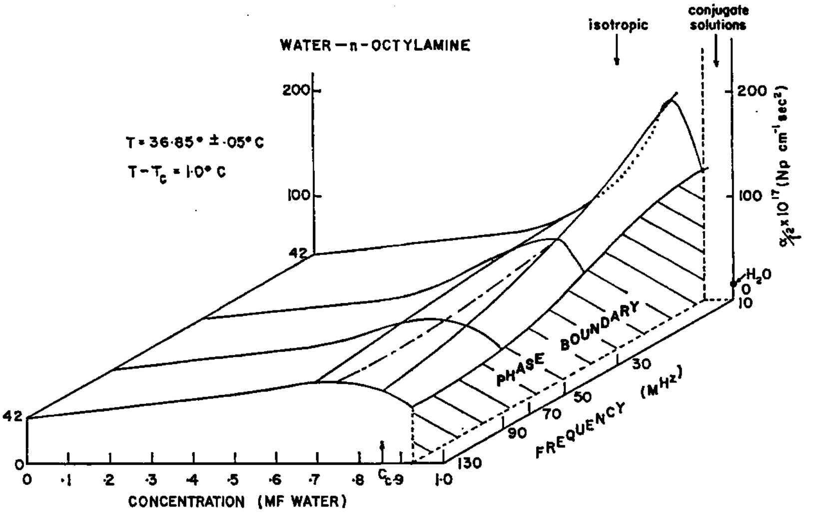

Figure 10. Surface representing the dependence of α/f^2 on concentration and frequency.

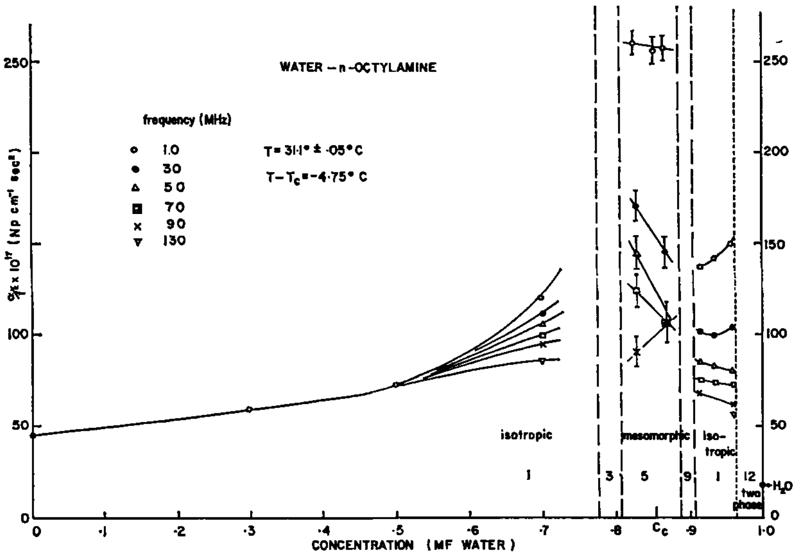

Figure 11. Concentration dependence of α/f^2 at 4.75 °C below the critical temperature.

micelle concentration $\cong$ 0.007 MF octylamine[14]). However the reported conditions of measurement in the isotropic phase at 30 °C are incompatible with Fig. 1. New data shown on Fig. 11 indicate an increase of α/f^2 at 10 and 30 MHz on approaching the boundary between phases 1 and 12 along the 31.1 °C isotherm. This behavior is compatible with the occurrence of a maximum in absorption in isotropic regions in the vicinity of consolute points which has been observed previously in binary mixtures of water and tertiary aliphatic amines.[8,11] However, previous data for *n*-octylamine-water[10] show a decrease in α/f^2 on approaching the consolute point from the isotropic region at constant concentration, $C_c = 0.975$ MF water. Hence, inadequate data is currently available to specify the absorption profiles in this region.

MESOMORPHIC REGION

The parameter α/f^2 increases substantially in the mesomorphic region at the lower frequencies of measurement (10 and 30 MHz). No regular trends in either concentration or frequency have been identified.

Ancillary measurements of viscosity were carried out at temperatures between 35° and 37 °C with a Hoeppler rolling ball viscometer for the mesomorphic phase and with an Ostwald-Cannon-Fenske viscometer for the isotropic phase. An increase in viscosity by a factor of 30 to 40 was found in the mesomorphic phase relative to that of the isotropic phase. The increase would correspond to a rise to $(\alpha/f^2)_{\text{classical}} \cong 3000 - 4000 \times 10^{-17}$ Np. cm^{-1}s^2 in the absorption parameter. Since no measured values of α/f^2 at 10 MHz exceed this lower estimate of $(\alpha/f^2)_{\text{classical}}$, we conclude that either the effective viscosity at frequencies $f > 10$ MHz is less than the static value (due to relaxation of the viscosity mechanism) or that the measurements of viscosity with the rolling ball were substantially in error. Since viscosity measured on the first pass of the ball was $\cong$ 25% less than the value attained after several passes, the history of the mesomorphic phase was clearly of importance and it is not clear that a value of $(\alpha/f^2)_{\text{classical}}$ can be uniquely specified for this anisotropic phase.

Conclusion

In summary we have observed an anomalously large value of the absorption of sound at the mesomorphic-isotropic transition similar to that which has been observed in less complex one-component and two-component systems. Future interest attaches particularly to a determination of the profile of the absorption maximum shown in Fig. 3. We have also made preliminary studies over the full composition range in an attempt to understand which interactions are actually taking place between amphiphile and water.

The importance of making measurements over a large composition, temperature and frequency range cannot be overemphasized. In a complex system one finds a number of molecular processes each contributing their share to the total absorption.

REFERENCES

1. Hoyer, W. A. and Nolle, A. W., *Journal of Chemical Physics* **24**, 803 (1956).
2. Gabrielli, I. and Verdini, L., *Nuovo Cim.* (series 10) **2**, 426 (1955).
3. Zvereva, G. E. and Kapustin, A. P., *Soviet Physics* (*Acoustics*) **10**, 97 (1964).
4. Zvereva, G. E., *Soviet Physics* (*Acoustics*) **11**, 212 (1965).
5. Anantaraman, A. V., Walters, A. B., Edmonds, P. D. and Pings, C. J., *J. Chem. Phys.* **44**, 2651 (1966).
6. Ralston, A. W., Hoerr, C. W. and Hoffman, E. J., *J. Amer. Chem. Soc.* **64**, 1516 (1942).
7. Chynoweth, A. G. and Schneider, W. G., *J. Chem. Phys.* **20**, 1777 (1952).
8. Chynoweth, A. G. and Schneider, W. G., *J. Chem. Phys.* **19**, 1566 (1951).
9. D'Arrigo, G. and Sette, D., *Proc. of Fifth Int. Cong. on Acoustics*, Liege, Art. No. D54 (1965).
10. Edmonds, P. D., Pearce, V. F., Andreae, J. H., *Brit. J. Appl. Phys.* **13**, 551 (1966).
11. McKellar, J. F., and Andreae, J. H., *Nature* **195**, 778–780 (1962).
12. Andreae, J. H., Edmonds, P. D. and McKellar, J. F., *Acustica* **15**, 74 (1965).
13. Barfield, R. N. and Schneider, W. G., *J. Chem. Phys.* **31**, 488 (1959).
14. McKellar, J. F. and Andreae, J. H., *Nature* **195**, 865 (1962).