Ultrasonic Absorption in Critical Binary Liquid Systems

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The results of ultrasonic absorption measurements for the systems heptane-nitrobenzene and aniline-cyclohexane are presented. Both of these systems have an upper critical solution temperature. A pulse reflection method was used for the measurements, which were carried out at frequencies from 3.4 to 50 Mc. The dependence of absorption on temperature and composition, as well as on frequency, was investigated. The experimental results were analyzed by means of a computer and are here compared with the results expected from a single relaxation time theory and from the theory presented by M. Fixman (*J. Chem. Phys.* **36** (1962) 1961). The latter theory is in reasonable agreement with the experimental results.

Previous investigations of ultrasonic absorption in binary liquid systems having a critical solution temperature [1-3] have shown a marked increase in absorption near the critical solution temperature. This increase is thought to be due to disturbance by the ultrasonic waves of the composition fluctuations which occur in the critical solution region.

Fixman [4,5] has developed a theory for ultrasonic absorption in the critical region by considering the interaction between variations in temperature and pressure caused by sound waves, and the long wavelength density fluctuations which are present in a system near its critical region. This paper presents new experimental data in this field.

EXPERIMENTAL

Electrical apparatus. The electrical apparatus used is shown schematically in Fig. 1. The equipment consisted of (1) a pulsed oscillator PG-650-C, (2) a precision attenuator ATT-693, (3) a tuned pre-amplifier PA-620 with a variable inductance in parallel, (4) a wide band amplifier WA-600-B, all from the Arenberg Ultrasonics Laboratory, (5) a standard signal generator MS-26 from Radiometer, and (6) a Tektronix 545A oscilloscope. A voltage stabilizer was necessary in order to eliminate variation in the gain of the amplifier due to line voltage fluctuations. The equipment was connected with 93 ohm cable.

Transducer. X-cut quartz crystals ground to give resonant frequencies around 3.4, 10 or 20 Mc were used as transducers. The crystals were glued onto pyrex glass cylinders
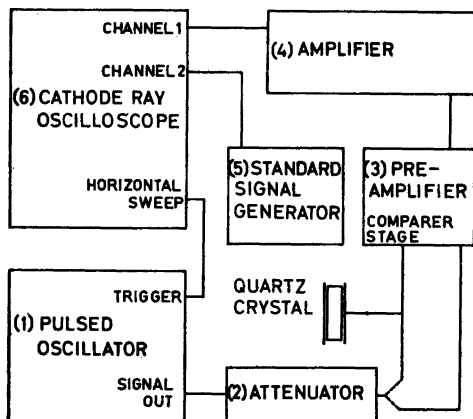
Fig. 1. Schematic diagram of the electrical apparatus.

with an epoxy resin, after the inner surface of the quartz plate had been silvered using Brashear's * process. A ring around the edge was left bare to prevent short-circuits. The outside of the cylinder and the crystal were then silvered using the same process, and the cylinder was glued into a brass mounting containing a cable connector. Contact to the inner surface was made by means of a strip of thin brass sheeting which acted as a gentle spring.

The crystal mounting was connected to the measuring cylinder and supply syringe as shown in Fig. 2. These were mounted by means of a brass ring in a perspex water thermostat which was set on a stand equipped with three levelling screws. The stand was set on a vibration-free shelf.

Measuring technique. Measurements were performed at frequencies around 3.4, 10, 17, 20, 23, 30, and 50 Mc. After varying the frequency locally to give maximum transducer efficiency, the pre-amplifier was tuned and the parallel inductance varied to give a maximum echo signal. The levelling screws on the stand were then adjusted to give the largest echo signals possible so as to make the crystal parallel to the surface of the liquid in the measuring tube.
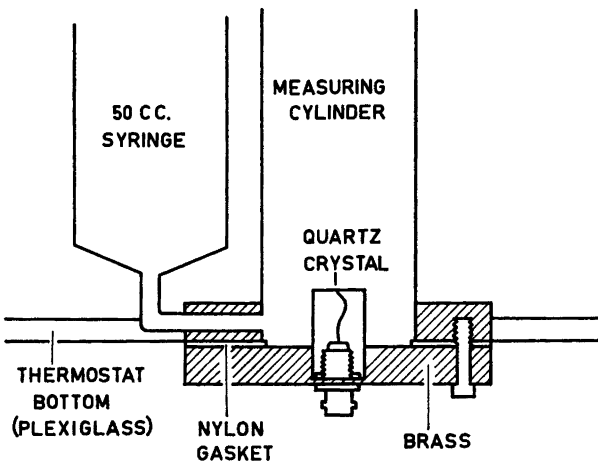

Fig. 2. Diagram of the transducer and of the mounting for the measuring cylinder.
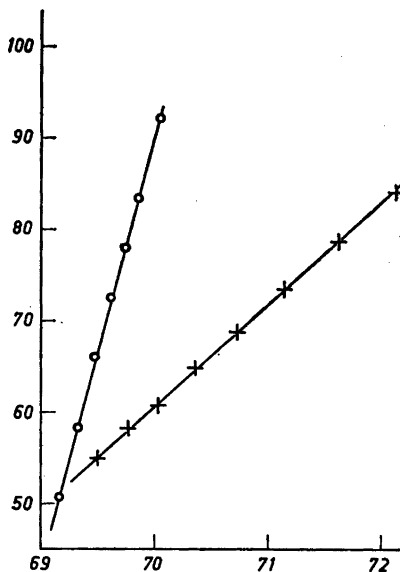
Fig. 3. Examples of attenaution curves.
Abscissa, relative distance of the surface
from the crystal (cm).
Ordinate, relative attenuation of the echo-
pulse signal (db).
  O, 64.4 % heptane; 20.0$_2$°C, 19.7$_7$ Mc.
  +, 60.9$_5$ % heptane; 31.0$_7$°C, 10.15 Mc.

Pulses about 5 μsec long, at a rate of 50 pulses per second, and varying from 1 to 30 V, depending on frequency and absorption, were applied to the crystal by way of the attenuator. The amplifier gain was then adjusted to obtain an echo signal of known size on the oscilloscope. After this the apparatus was re-connected so that the pulses were sent into the comparer stage of the preamplifier by way of the attenuator. The pulses were then again attenuated to be of the same size as the echo signal. This procedure was repeated for varying levels of liquid in the tube, the level being varied by means of the syringe, and its height being measured with a cathetometer.

By plotting the attenuation necessary to make the comparison signal equal to the echo signal (in db) against the cathetometer reading (in cm), values were obtained for the pressure absorption coefficient α in units of cm^{-1} (0.025 ln 10 times the slope of the attenuation *vs.* distance curve). Some examples of the graphs are shown in Fig. 3.

The scatter in the curves is most probably the result of (1) faulty parallelizing of the crystal and the liquid surfaces, (2) variation in amplifier gain due to overloading at short path lengths, and (3) inaccurate readings due to movement of the meniscus caused by mechanical vibrations or due to eye-strain.

No correction was made for the divergence of the beam, as no deviations from linearity except those within experimental error were observed in the graphs when the absorption was in the range from 1 to 3 cm^{-1}. In this range a precision of 0.5 % in determination of the slope of the attenuation *vs.* distance graph was possible, but towards the limits of the measurable range (0.2 and 7 cm^{-1}) the precision decreased to about 5 %. The upper absorption limit of the apparatus is due to the necessity for the amplifier to recover from the overload of the initial pulse before receiving the echo; this puts a lower limit to the length of the path through which a pulse must travel. At low absorption, the limit is due to the impossibility of making accurate measurements with the 1 db step attenuator at small attenuation differences.

Frequency measurements were made by connecting the standard signal generator to the second oscilloscope channel, adding the signal from it to the echo pulse signal, and varying the frequency to give zero beat frequency. This was repeated for as many harmonics as possible of the frequency in the pulse. No difference was noted between the frequency present in the echo and that in the initial pulse.

Materials. The system heptane-nitrobenzene was chosen because it has a convenient critical solution temperature of 19.4°C and because the pure substances have absorption

coefficients of the same order of magnitude. It was therefore expected that the effects on absorption in the system due to changes in efficiency of energy transfer through internal modes [7] would be small. Data are also presented on the systems aniline-cyclohexane, which has an upper critical solution temperature of 30.9°C.

The nitrobenzene used in the measurements was Fluka purissimum grade. The value of the pressure absorption coefficient α divided by the square of the frequency was 71.7×10^{-17} cm^{-1}sec^2, at 20 mc and 25°C. This agrees well with the values of Heasell and Lamb [8] $(74 \times 10^{-17}$ at 100 Mc, 24°C) and Pellam and Galt [9] $(79 \times 10^{-17}$ at 15 Mc, 24°C).

Fluka purum grade (better than 99 % pure) heptane was used. The value of α/f^2 was 43.6×10^{-17} at 25°C and 20 Mc. A sample of Phillips pure grade heptane had an α/f^2 of 46.7×10^{-17} at 25°C, 20 Mc. These values do not agree well with that of Pellam and Galt [9] $(80 \times 10^{-17}$ at 15 Mc, 22°C). The purity of the heptane was therefore checked by gas chromatography. The chromatography curves show the presence of impurities which were estimated to be of the order of at most 0.2 %.

Freshly opened Merck analyse grade aniline and Fluka purum grade cyclohexane were used for the second system.

Results. The results of the absorption measurements are shown in Figs. 4—10. The phase diagram obtained for the system heptane-nitrobenzene is also shown in Fig. 4 for use as a reference. The points for this curve were obtained by noting the lowest temperatures at which the system continued to be in one phase for at least 15 min after reaching the temperature.

Care was taken to ensure thermal equilibrium; near the critical solution temperature, the system was kept at the desired temperature for at least 2.5 h before measurement.

The effect on the absorption of likely impurities was negligible. Addition of a drop of acetone (the cleaning agent for the measuring tube) or water (the thermostat fluid) to a system near the critical region did not measurably alter the absorption. Consistent values for absorption were obtained with crystals of different surface areas.
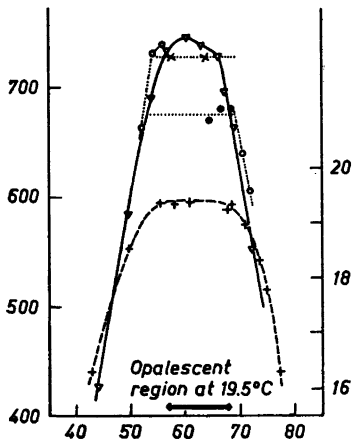

Fig. 4. Phase diagram and absorption in the system heptane-nitrobenzene.
Abscissa, per cent by volume heptane.
Left ordinate, α/f^2 (cm^{-1}sec^2 × 10^{-17}).
Right ordinate, temperature (degrees C).
    ∇ 19.5$_2$°C, 19.6$_2$ Mc,
    O   19.3$_6$°C, 19.6$_2$ Mc,
    ●   upper phase,
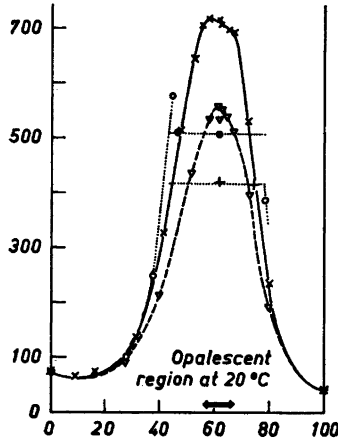   ×   lower phase,
    +   points on the phase diagram.

Fig. 5. Absorption in the system heptane-nitrobenzene.
Abscissa, per cent by volume heptane.
Ordinate, α/f^2 (cm^{-1}sec^2 × 10^{-17}).
    ×   20.0$_2$°C, 19.7$_7$ Mc,
    ∇ 25.0$_5$°C, 19.7 Mc,
    O   16.3$_1$°C, 19.1$_0$ Mc, + upper phase,
    ●   lower phase.

DISCUSSION

Composition dependence. The flat top of the phase diagram in Fig. 4, and the good agreement between the experimental critical solution temperature $(19.3_8°C)$ and that listed in Ref. 10 $(19.4_8°C)$ again suggest that the materials used were of relatively good purity.

The absorption *vs.* composition curves seem to flatten off in the opalescent regions (Figs. 4—6). The curve for heptane-nitrobenzene has a negative slope
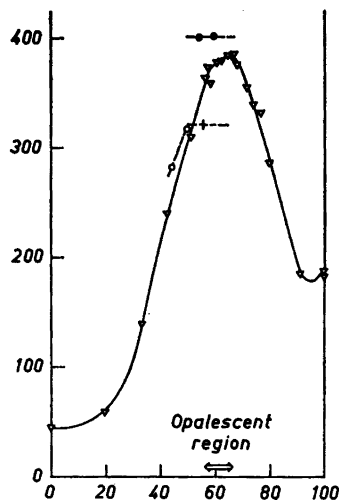
Fig. 6. Absorption in the system aniline-
cyclohexane.
Abscissa, per cent by volume cyclohexane.
Ordinate, α/f^2 $(cm^{-1}sec^2 \times 10^{-17})$.
O $31.2_0°C$, 19.6_2 Mc,
△ $29.8_1°C$, 19.6_2 Mc,   ● upper phase,
    + lower phase.

in this region, while cyclohexane-aniline has a positive slope. On separation into two phases at a lower temperature, the denser phase (smaller percentage of heptane) has a higher absorption coefficient in the first system; the lighter phase (greater percentage of cyclohexane) has the higher absorption coefficient in the second system. The absorption in these regions may be the sum of the volume times the specific absorption of two phases present in the form of the small droplets.[11]

In Fig. 5 (the curve for $16.3_1°C$, 44.4 % heptane) and Fig. 4 (the curve for $19.3_6°C$, 56.3 % heptane), values for the absorption are obtained which are higher than those in either phase of the two-phase regions. Assuming that the system was in thermal equilibrium during the measurements, this suggests the possibility of the existence of a meta-stable one-phase system in the two-phase region.

The curves in Fig. 7 show that the extra absorption at low concentrations of nitrobenzene in heptane is proportional to the fourth power of the concentration with good accuracy.

Temperature dependence. The curve of absorption *vs.* temperature, Fig. 8, is of the same form as those for similar systems; aniline-hexane at 600 kc [1] and nitrobenzene-hexane near 20 Mc.[3] The theory presented by Fixman [5] predicts that at constant frequency and composition the absorption per wave-length
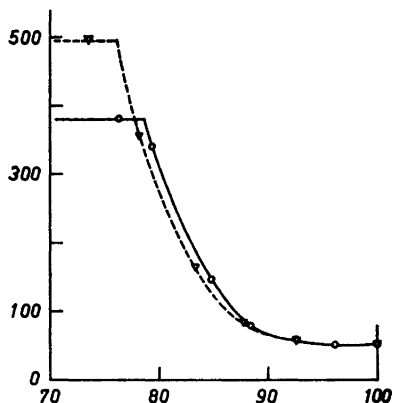
Fig. 7. Absorption in the system heptane-
nitrobenzene.
Abscissa, per cent by volume heptane.
Ordinate, α/f^2 (cm^{-1}sec^2 $\times$ 10^{-17}).
∇ 17.5$_6$°C, 19.8$_3$ Mc, upper phase,
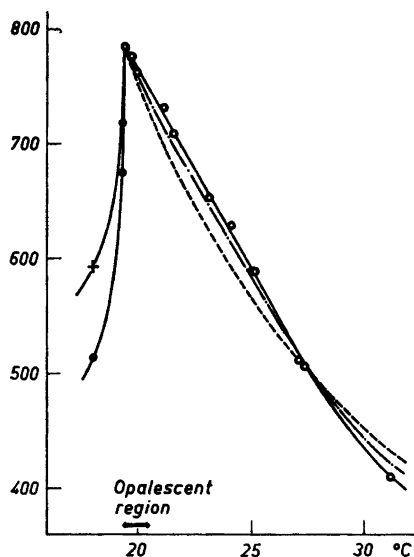O 15.7$_3$°C, 19.8$_3$ Mc, upper phase.

Fig. 8. Absorption in the system heptane-
nitrobenzene.
Abscissa, temperature (degrees C).
Ordinate, α/f^2 (cm^{-1}sec^2 $\times$ 10^{-17}).
O 61 % heptane, 19.10 Mc, + upper
   phase, ● lower phase,
– – – – theoretical curve,
       $B = 45 \times 10^{-17}$
–·–·– theoretical curve,
       $B = 200 \times 10^{-17}$.

will be proportional to a function $g(d)$ given in Fig. 1 in Ref. 5. If the velocity is independent of temperature, then the contribution to α/f^2 from the absorption due to critical phenomena is also proportional to $g(d)$ at constant frequency. The variable a and the function which determines the absolute theoretical value of the absorption are both functions of the thermodynamic constants of the system, the frequency, and two parameters. When the system is at the critical composition, d is also proportional to $(T-T_c)$.

The contribution to α/f^2 not due to the critical phenomena, B, was estimated from Fig. 5 as 45×10^{-17} cm^{-1} sec^2. This estimate was made assuming that in the absence of the critical phenomena, the composition dependence of the absorption would be of the same form as that in binary liquid systems where no association occurs and where the pure components have absorption coefficients of the same order of magnitude.[7]

Both the vertical and the horizontal scales of the curve of $g(d)$ vs. d were adjusted by fitting this curve at two points to the curve of (α/f^2-B) vs. T. The shapes of the two curves obtained in this way are seen to be quite similar, but within the limits of the approximation and experimental error, the curves do not overlap.
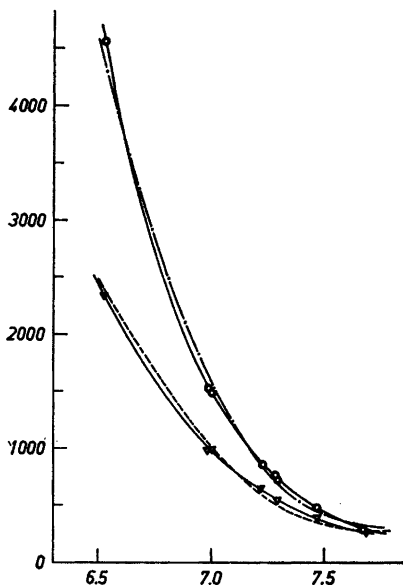
Fig. 9. Absorption in the system heptane-
nitrobenzene.
Abscissa, $\log_{10}$ frequency (Mc).
Ordinate, $\alpha/f^2 (\text{cm}^{-1}\text{sec}^2 \times 10^{-17})$.
O 61 % heptane, 20.0_3°C,
— · — curve fitted from equation (1).
▽ 61 % heptane, 25.0_5°C,
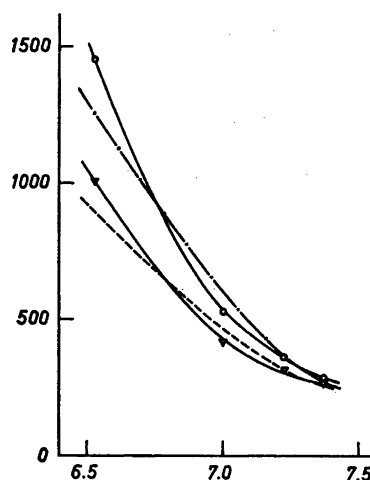— — — — curve fitted from eqn. (1).

Fig. 10. Absorption in the system heptane-
nitrobenzene.
Abscissa, $\log_{10}$ frequency (Mc).
Ordinate, α/f^2 ($\text{cm}^{-1}\text{sec}^2 \times 10^{-17}$)
O 62.5 % cyclohexane, 31.1_6°C,
— · — curve fitted from eqn. (1),
▽ 62.5 % cyclohexane, 34.8_9°C,
— — — curve fitted from eqn. (1).

When B is increased to 200, as suggested by the order of magnitude of the iterated values of B in columns 3 and 11 of Table 1, then the agreement between the calculated and the experimental values is improved. The velocity falls by about 1.5 % on lowering the temperature from $T_c + 5$ to T_c in a similar system but at a lower frequency.[1] Using this as an estimate of the error due to the above velocity approximation, then the experimental and the theoretical curves can be said to overlap within experimental error. It should be noted that in this way a total of three parameters are actually adjusted.

Frequency dependence. Parts of the relaxation curves for the critical compositions at different temperatures were obtained for the two systems (Figs. 9 and 10).

The equation for absorption due to a single relaxation frequency f_c[12] is

$$\frac{\alpha}{f^2} = \frac{A}{(1 + f^2/f_c^2)} + B \tag{1}$$

when the velocity is assumed to be independent of frequency. Velocity measurements made by the authors indicate that this assumption is valid within the accuracy considered. The data from Figs. 9 and 10 were fitted to this equation

using the method of least squares to determine the values of the parameters A, B, and f_c. As seen in Figs. 9 and 10, the fit is in no case within the range of the experimental error. This indicates that there exists more than one relaxation frequency, as suggested by previous workers.[2,13] Table 1 shows the values obtained for A, B, f_c and the root mean square deviation relative to unity, σ.

Using eqns. (25) and (27) of Ref. 5, and again assuming the velocity independent of frequency, then

$$\alpha/f^2 = C\,f^{-M} + B \qquad (2)$$

The value for M suggested by Fixman is 1.25. The data from Figs. 9 and 10 were again used in another least-squares computer program which adjusted the parameters C, B, and M to give the best fit to the experimental points. The values obtained for C, B, M, and σ are also listed in Table 1.

Table 1. Values of f_c are listed in Mc, A and B in $cm^{-1}sec^2 \times 10^{-17}$, and C in corresponding units.

System (1) — 61 % heptane, 20.0_2°C.
System (2) — 61 % heptane, 25.0_5°C.
System (3) — 62.5 % cyclohexane, 31.1_6°C.
System (4) — 62.5 % cyclohexane, 34.8_9°C.

Sys-tem	Eqn. (1)				Eqn. (2)				Eqn. (2), M fixed				B from Fig. 5—6
	$A \times 10^{-3}$	B	f_c	σ	$C \times 10^{-3}$	B	M	σ	$C \times 10^{-3}$	B	M	σ	
(1)	5.51	243	5.76	0.076	16.3	6	1.04	0.009	23.0	134	1.25	0.067	45
(2)	2.78	252	6.13	0.076	6.38	1	0.81	0.020	11.7	215	1.25	0.121	45
(3)	1.35	159	7.07	0.013	4.91	123	1.08	0.014	6.0	179	1.25	0.030	90
(4)	0.89	177	7.07	0.087	3.61	163	1.09	0.011	3.7	197	1.25	0.022	90

The values of σ are consistently lower when eqn. (2) is used. Even when M is fixed at 1.25 and the number of parameters is lowered to two, the values of σ using eqn. (2) are still of the same order of magnitude as those obtained using eqn. (1). The parameters in eqn. (2) are placed in such a way, however, that in this frequency region they make eqn. (2) more flexible than eqn. (1).

It should be noted that when the data are fitted by a single relaxation equation, the values of B obtained from the least-squares iterations are higher than those estimated by linear interpolation from the curves in Figs. 5 and 6. A higher value of B also gives better agreement in the comparison of the theoretical and the experimental temperature dependence of the absorption. This suggests that part of the absorption may be due to presence of processes in the system, other than those present for the pure components, which do not relax in this frequency region, but at higher frequencies.

CONCLUSIONS

The data presented here, indicate that accurate ultrasonic absorption measurements are useful in locating the critical point, as well as in clarifying other phenomena related to structural and kinetic effects in liquid systems which have a critical solution temperature.

The only quantitative theory for absorption in the critical region available at the present time [4,5] seems to give reasonable agreement with the experimental data when the parameters in it are adjusted. Measurements in a wider range of frequencies and on a greater variety of systems would be of interest, however, for a better evaluation of this theory.

Low frequency measurements would be especially useful in extending the range of data available for the iteration schemes, thus making the values obtained from them more reliable. High frequency measurements would be useful in obtaining an experimental value for B, thus fixing one parameter.

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