ULTRASONIC VELOCITIES IN BINARY LIQUID MIXTURES NEAR THEIR CRITICAL SOLUTION TEMPERATURE

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Abstract

An investigation has been made of the variation of ultrasonic velocities and adiabatic compressibilities with temperature near the critical solution temperature of three binary liquid systems, *viz.*, water-isobutyric acid, phenol-water and aniline-cyclohexane. No anomalous change could be observed. Both velocity and adiabatic compressibility show a linear variation with temperature. Possible explanation for this behaviour is discussed.

1. Introduction

Certain binary liquid mixtures, *e.g.*, those of phenol and water, aniline and cyclohexane, etc., have the property of forming an one-phase system only above a particular temperature and exhibit a marked opalescence and turbidity in the vicinity of this temperature known as the critical solution temperature. The phenomenon of critical opalescence consists in an abnormally strong scattering of light. Measurements of ρ_h (the depolarisation of the transversely scattered light with the incident beam polarised in a horizontal plane) in these liquid mixtures show that ρ_h falls to values considerably less than unity as the critical solution temperature is approached (Krishnan, 1934). The phenomenon of critical mixing produces changes in the macrophysical properties like viscosity, magnetic and electric birefringence, etc. Recently ultrasonic velocity and absorption have been studied in binary liquid systems near the critical mixing point by Chynoweth and Schneider (1951) and Alfrey and Schneider (1953). No anomalous change in the velocity could be observed. On the other hand ultrasonic absorption showed a remarkable increase at the critical point. In view of the interesting results obtained in other physical properties and also in order to throw further light on the conditions existing in systems of two partially miscible liquids it was deemed of interest to measure ultrasonic velocities and compute adiabatic compressibilities therefrom, in some more systems exhibiting the phenomenon of critical mixing, *viz.*, water-isobutyric acid, phenol-water and aniline-cyclohexane.

2. Experimental Details

The present measurements of ultrasonic velocities were made with an ultrasonic interferometer of the fixed crystal moving reflector type employing a 1600 kc.

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crystal. Before starting the experiment the interferometer cell was thoroughly cleaned and to keep the temperature of the cell constant at any particular value water was circulated around the interferometer cell from a thermostatically controlled water-bath. In filling the interferometer the more dense component was first poured into the cell. This was immediately followed by the lighter phase. The liquid system was thoroughly stirred and allowed to reach thermal equilibrium. Bubbles found to collect under the reflector surface were removed by gentle manipulation of the stirrer. Between readings at two temperatures sufficient time was allowed for the system to reach temperature equilibrium. Temperatures were measured with a standard thermometer capable of reading correct to $0.1°$ C. attached to the inter-ferometer cell. The exact temperature at which the boundary between the two phases disappear could be observed since the interferometer cell and the water circulation jacket are of glass.

Readings of sound velocity were obtained in the following manner. The reflector was kept in position at a particular distance from the oscillating crystal so that the disturbing diffraction effects may not give rise to errors in the accurate measurement of the wavelength of sound. Measurements were started by keeping the temperature of the interferometer $15°$ C. above the critical mixing tempera-ture. As the reflector was moved through the nodal positions maxima were observed in the readings of the vacuum tube voltmeter measuring the output voltage of the quartz and the average distance through which the reflector was moved for fifty such maxima was taken for the measurement of sound wavelength. The experi-ment was repeated. The cell was kept closed so as to prevent evaporation of the components during the course of the experiment. Then the temperature was gradually reduced by adjusting the temperature of water circulating in the outer jacket and runs made at intervals of 1 or $2°$ C. down to the critical point. At least one hour was allowed with intermittent stirring for the system to attain tempe-rature equilibrium. The critical solution temperature was found to be unchanged at the end of the measurements.

The materials used were all very pure samples and they were redistilled before use. The concentrations are expressed as weight percentage of one of the compo-nents. Determinations of density were carried out with a specific gravity bottle suspended in a thermostatically controlled water-bath. Density determinations of Howell (1932) for phenol-water mixtures were used in the calculations.

3. RESULTS

The water-isobutyric acid system.—According to the depolarisation measure-ments of Krishnan (1935) the critical solution temperature is at $25.5°$ C. for the critical concentration of the mixture containing 50% by weight of the acid. The components were weighed and poured carefully inside the interferometer cell and the ultrasonic velocity was measured from 40 to $25.5°$ C. A number of readings were taken near the critical solution temperature and the average value of sound velocity was calculated. The velocity and density do not show any anomalous change in the critical region. The velocity increases linearly from 1326 met./se c

at 40° C. to 1334 met./sec. at 25·5° C. The compressibility-temperature curve is also smooth, linear and continuous (Fig. 1).
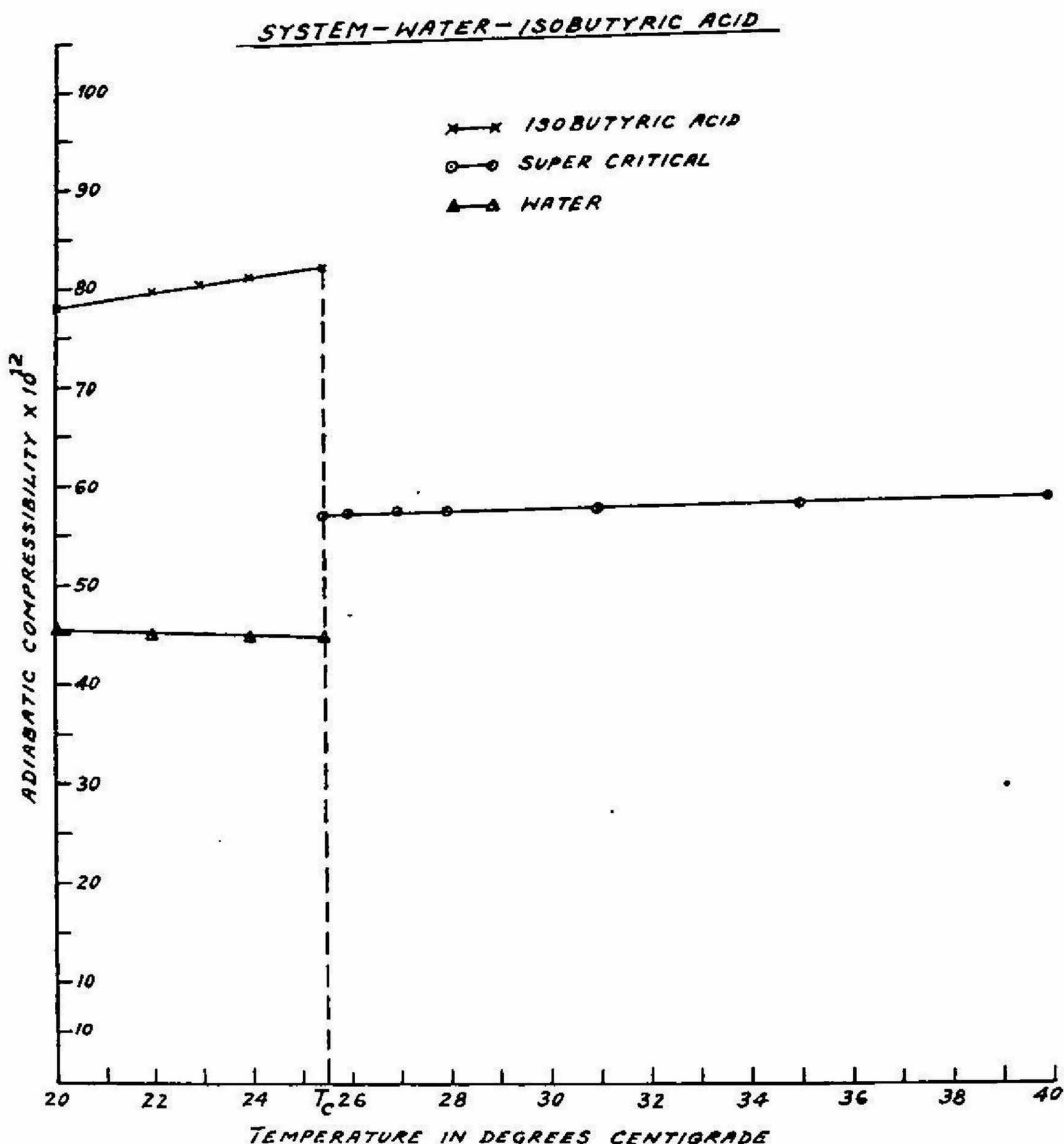
FIG. 1

The phenol-water system.—From his measurements on density, Howell (1932) finds the critical solution concentration as 34·6% by weight of phenol and the critical temperature as 66·4° C. Acoustic velocities for a mixture containing 34·6% by weight of phenol was measured from 75° C. down to 66·4° C. at intervals of 1° C. Velocity shows a linear decrease from 1502 met./sec. at 75° C. to 1495 met./sec. at 66·4° C. As in the previous case a smooth, linear and continuous variation of adiabatic compressibility is noticed (Fig. 2).
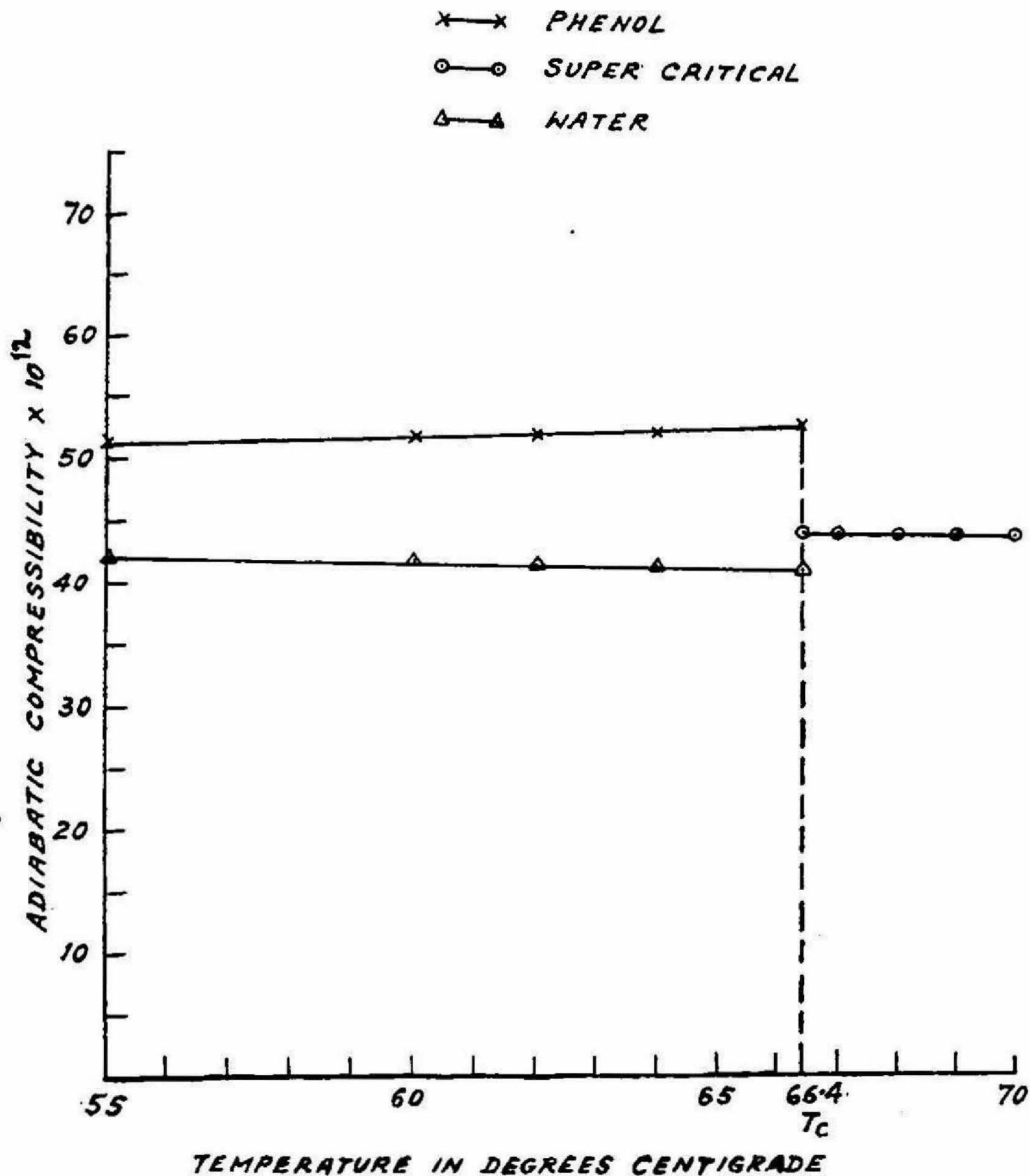
FIG. 2

The aniline-cyclohexane system.—According to Krishnan (1935) the critical solution temperature for this mixture is 30° C. and the consolute concentration 46% by weight of aniline. Runs of the interferometer were commenced from 50 to 30° C. in a mixture of aniline and cyclohexane containing 46% by weight of aniline. There is a linear decrease of ultrasonic velocity with increasing temperature from 1320 met./sec. at 30° C. to 1240 met./sec. at 50° C. The adiabatic compressibility shows a smooth and linear variation with temperature (Fig. 3).
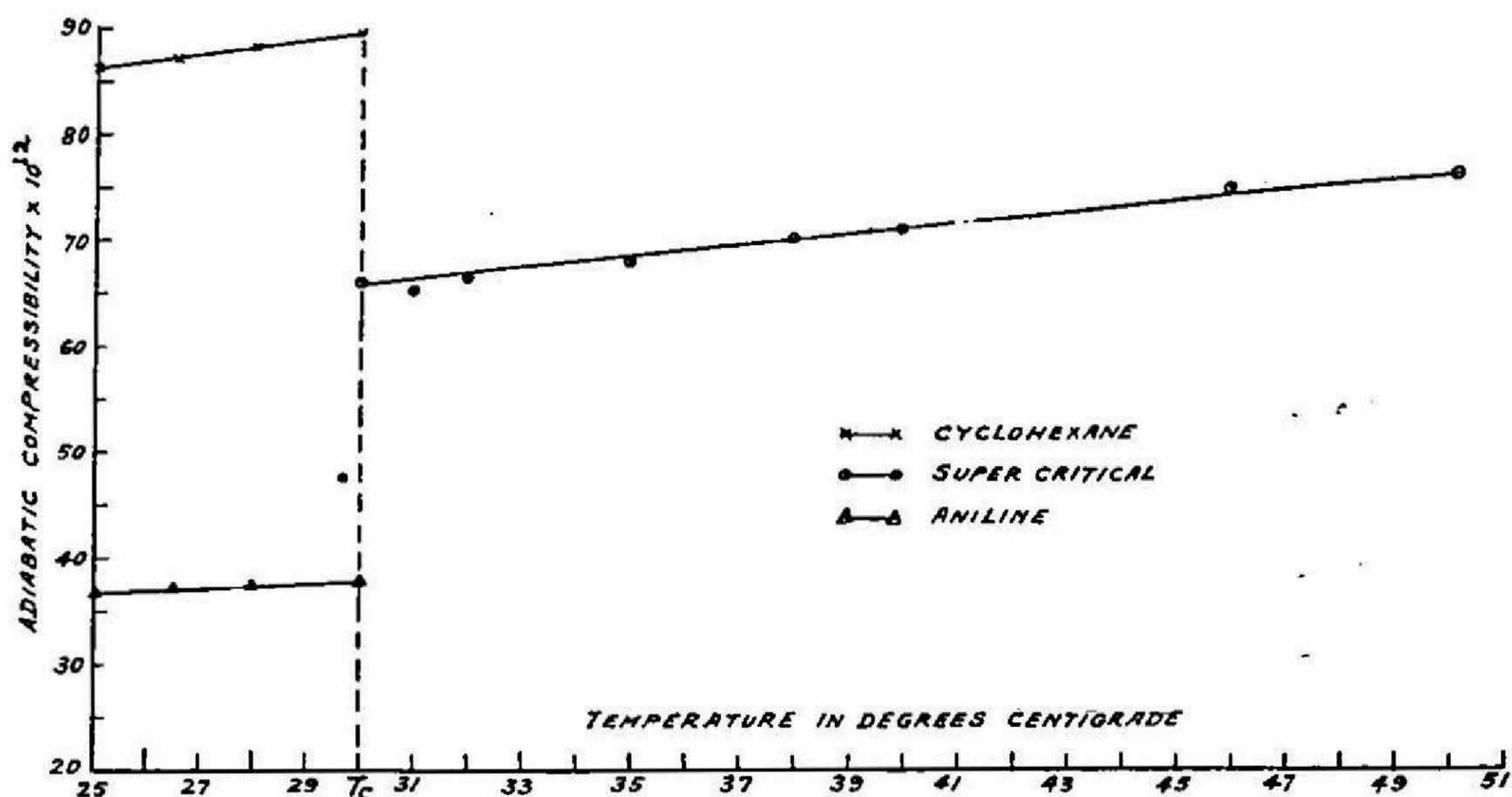
FIG. 3

4. DISCUSSION

Our measurements of ultrasonic velocities and adiabatic compressibilities in these liquid systems near and above the critical solution temperature show that there is no anomalous change in velocity and compressibility in this region. Even the scatter of the individual points in the velocity curves cannot be taken as indicative of a definite variation since the measurement of velocity at the critical point is rather difficult because of the excessive sound absorption, and the scatter of the points is of the order of the experimental error.

To explain this behaviour we have at the very outset to take into account of the existence of molecular clusters, in the neighbourhood of the temperature of critical mixing. In fact the existence of such clusters is rendered highly plausible by the extensive observations on light scattering and critical opalescence. It has also been possible on the basis of such studies to give an estimate of the diameter of the clusters, which is of the order of the wavelength of the visible light (Krishnan, 1934). Not only is the tendency for the formation of molecular clusters is greatest for the critical composition of the mixture but that the size of the clusters formed is a maximum for this mixture is seen from the depolarization measurements of Krishnan (1936).

Now, the ultrasonic absorption studies of Alfrey and Schneider (1953) indicate, however, that the greater part of the excess absorption is atrributable to a relaxation mechanism. This is because the absorption due to viscosity and scattering of the sound beam due to molecular clusters acting as scatterers are not able to account for the excessive absorption, in spite of the fact that near the critical solution temperature the number of scattering centres must be considerably larger.

Further. the evidence regarding the formation of molecular clusters renders it highly probable that the relaxation mechanism is of the structural type. A typical instance of such a type of relaxation process is that usually regarded as responsible for the excess absorption in water, as explained by Hall (1948).

Following Hall, we can assume the existence of two states in the mixture between which molecular transitions are effected by the passage of the acoustic wave. In this case the compressibility can be regarded as consisting of two components, one the " instantaneous compressibility " b_∞ (which is probably comparable with that of the pure liquids) and other a relaxational compressibility b_t. In such a case the effective compressibility for any frequency ω is given by

$$b = b_\infty + \frac{b_t}{1 + j\omega T},$$

where T is the relaxation time. The complex velocity (following Hall) is given by

$$\frac{1}{c^2} = b\rho.$$

Separating this into real and imaginary parts we get for the propagation velocity

$$\frac{1}{|c|^2} = b'\rho = b_0\rho - b_t\,\omega^2 T^2 \rho . \frac{b_\infty}{b_0},$$

where b_0 is the effective compressibility $(b_\infty + b_i)$, neglecting terms of the higher order other than the second. It is seen from this equation that the expected velocity change is small, being of the second order in $(\omega T)^2$ and has probably escaped observation either because the relaxation frequency is far above the experimental frequencies in which case ωT is far less than unity, so that the second factor is very small or the relaxation compressibility b_t is very small. In either case the departures of the curve giving the temperature variation of velocity (or adiabatic compressibility) from a smooth and continuous course are but slight, probably below experimental errors. The effect is probably observable only in the neighbourhood of the relaxation frequency, the determination of which involves experiments on velocity and absorption over a wide frequency range.

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