LETTERS TO THE EDITOR

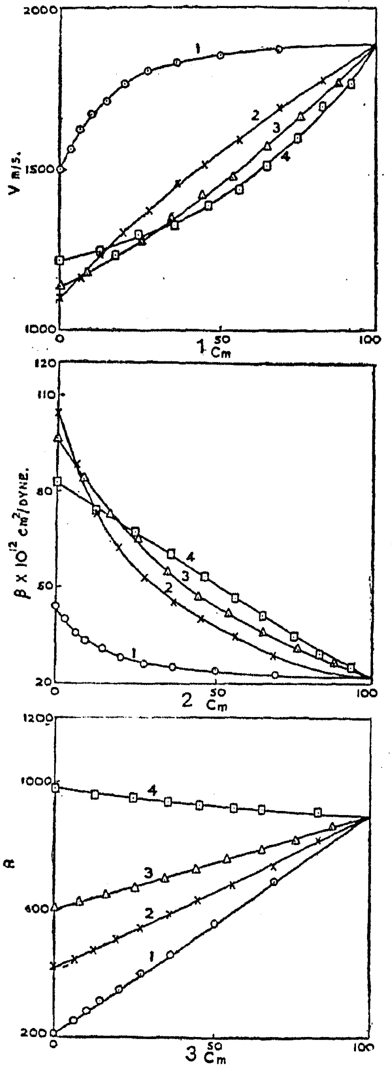
ULTRASONIC STUDIES IN GLYCEROL-ALCOHOL MIXTURES

Nomoto[1] reviewed the available data on liquid mixtures and showed that even though properties like ultrasonic velocity and adiabatic compressibility show deviations from the ideal linear behaviour, the molar sound velocity and the molar compressibility vary linearly with molar concentration. In the present investigation the variation of ultrasonic velocity in (1) Glycerol-Water; (2) Glycerol-Methyl alcohol; (3) Glycerol-Ethyl alcohol and (4) Glycerol-*n*-butyl alcohol is measured with a view to study the nature of variation of adiabatic compressibility and molar sound velocity with concentration. The ultrasonic velocity is determined up to an accuracy of 0·1% by using the interferometer method.[2]

Figures 1, 2 and 3 represent the nature of variation of ultrasonic velocity (V), adiabatic compressibility (β) and molar sound velocity (R) respectively, with molar concentration for all the liquid mixtures investigated. All these measurements were made at room temperature 30° C.

All the four mixtures have a common constituent glycerol which is a highly associated liquid. The other component liquids are also of the same type due to the presence of active (OH) dipoles. For the first mixture it will be seen from Fig. 1, that the velocity of the mixtures rises very rapidly with the addition of glycerol at lower concentrations and slowly above 50% concentration. This rapid rise of velocity is attributed to the breaking up of molecular associations of the two component liquids. The compressibility curve in Fig. 2 shows the exact opposite behaviour in that the adiabatic compressibility first falls off very rapidly at lower concentrations of glycerol and then slowly at higher concentrations. Here glycerol is a liquid containing (OH) groups and the interaction of the glycerol molecules with water molecules is greater than the interaction among themselves. This results in breaking up of associations of water molecules when the cohesive energies locked up in different associations will be released. As the molecules all round will now knit up more closely due to freed dipoles, the cohesive energy increases thereby decreasing the compressibility. Thus this effect results in a rapid decrease of adiabatic compressibility at lower concentrations of glycerol. After the process of breaking up of associations ceases the compressibility falls less rapidly reaching finally the value of glycerol. It is interesting to note that the variation of molar sound velocity R, shown in **Fig. 3**, is perfectly linear as expected in spite of the peculiar nature of variation of velocity and adiabatic compressibility.

In the next mixture glycerol-methyl alcohol the deviation of velocity variation from linear law is less as can be seen from Fig. 1. The



FIGS. 1-3. Fig. 1. Variation of ultrasonic velocity (V) in (1) glycerol-water, (2) glycerol-methyl alcohol, (3) glycerol-ethyl alcohol and (4) glycerol-*n*-butyl alcohol mixtures with molar concentration C_m of glycerol. Fig. 2. Variation of adiabatic compressibility β in (1) glycerol-water, (2) glycerol-methyl alcohol, (3) glycerol-ethyl alcohol and (4) glycerol-*n*-butyl alcohol mixtures with molar concentration C_m of glycerol. Fig. 3. Variation of molar sound velocity R in (1) glycerol water, (2) glycerol-methyl alcohol, (3) glycerol-ethyl alcohol and (4) glycerol-*n*-butyl alcohol mixtures with molar concentration C_m of glycerol.

compressibility concentration curve is less steep than in the previous case. Again the variation of molar sound velocity is found to be linear as can be seen from Fig. 3. The data for glycerol and ethyl alcohol mixture do not show any prominent deviation from ideal linear behaviour. The velocity *versus* concentration curve falls slightly below the ideal linear variation curve unlike the two previous cases. The compressibility variation is less non-linear than those for the two previous mixtures. In the case of glycerol and *n*-butyl alcohol mixtures, though the velocity *versus* concentration is more curved towards the same side as the third mixture, the compressibility curve is nearly linear. The molar sound velocity concentration curve on the other hand shows a slight deviation from linearity as can be seen from Fig. 3.

An interesting feature that can be generalised for these four mixtures is that the large curvature of the compressibility concentration curve for glycerol-water mixture progressively decreases until the last mixture. Similar general change in the shape of the curve is noticed for the velocity-concentration graph. An important conclusion from this is that water has the maximum effect on the glycerol molecules and that the breaking up of associations is maximum for this case. For methyl alcohol and other higher alcohols the effect progressively decreases.

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