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**The Viscosity of Water-Propanol Mixtures and Their
Behaviour in N.M.R.**

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Fisica. — *The Viscosity of Water-Propanol Mixtures and Their Behaviour in N.M.R.* Nota di PIETRO LUIGI INDOVINA ^(*), presentata ^(**) dal Corrisp. M. AGENO.

RIASSUNTO. — Allo scopo di sottoporre ad ulteriori controlli sperimentali il modello collettivo del legame a idrogeno, proposto da M. Ageno è stato eseguito un accurato studio sia con misure di viscosità, che con la R.M.N. di miscele acqua-propanolo, in funzione della concentrazione. Viene messo in evidenza uno stretto legame tra il campo di risonanza degli ossidrili ed il massimo della viscosità. Si discute un quadro interpretativo in pieno accordo con le previsioni del modello collettivo del legame a idrogeno e con i risultati delle precedenti esperienze.

A new, collective type, model has recently been proposed [1] for the hydrogen bond, according to which each individual bond cannot be localized between any specific pair of atoms, but consists of a correlated system of bridges.

According to this model, a molecule of water can take part in only two independent hydrogen bonds, while a molecule of a primary alcohol can take part in only one such bond.

The proposed model has made it possible to interpret, in a simple and brilliant manner, the viscosity maxima [2] of systems consisting of a primary alcohol (methanol, ethanol) and water. These viscosity maxima have so far not been adequately understood in the light of the existing theories of the hydrogen bond [3].

There is a surprisingly good agreement between the average chain length of the molecules [2] in water, as a function of the temperature, obtained from viscosity measurements, and that obtained in a manner completely independent of the heats of vaporization of water at various temperatures.

A further confirmation [4] of the validity of the model, based on predictions from it, was obtained from high resolution Nuclear Magnetic Resonance (N.M.R.) measurements on the protons in a water-ethanol system. The dependence, at a given temperature T , of the concentration of the protons from the hydroxyl groups of both water and ethanol agrees perfectly with the viscosity measurements and is easily explained by the proposed model.

To test the general validity of the model we have gone on to study the behaviour of a water-propanol mixture both from a viscosity and a N.M.R. point of view. The experimental results of the viscosity measurements as a function of the concentration, are given in fig. 1. The measurements were made using an Ubbelohode viscosimeter at 30°C. A thermostated bath was used to maintain a constant temperature within 0.01°C.

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(**) Nella seduta del 14 gennaio 1967.

The behaviour is of the same type as observed with a system composed of water and a primary alcohol and is clearly different from the behaviour of a water-secondary alcohol type system [2].

The heat of hydration of propanol is 12.76 KJ per mole of solute at infinite solution [5], which is higher than the heats of hydration of both methanol and ethanol, which are 8.37 and 10.63 KJ, respectively. This heat

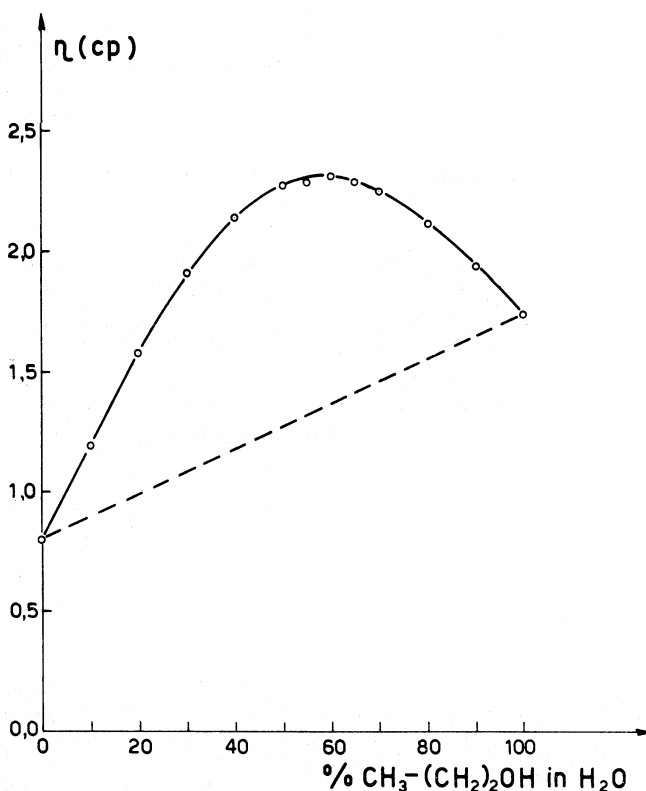


Fig. 1.

of hydration is sufficiently high to suppose that each molecule of alcohol in the mixture is bound to one or more molecules of water, at least when the percentage of alcohol is not too high.

At 30°C the viscosity of water is 0.80 cp and that of propanol is 1.74 cp.

If a small amount of water is added to the propanol, a mixture is obtained the viscosity of which is higher than that of either component. This is in agreement with the previously proposed interpretation [2] according to which the addition of a primary alcohol partly prevents the resonance transfer of water molecules from one aggregate to another. The situation at maximum viscosity is one in which the molecules of alcohol reduce to a minimum the possibility of molecular exchange between the various aggregates present. It should however be noted that this is true only when the two

components A and B, of a given solution, between which there is a possibility of hydrogen bond formation, do not have very different viscosities.

If, however, we are faced with a situation in which the two components have very different viscosities, as in the case of the water-propanol system,

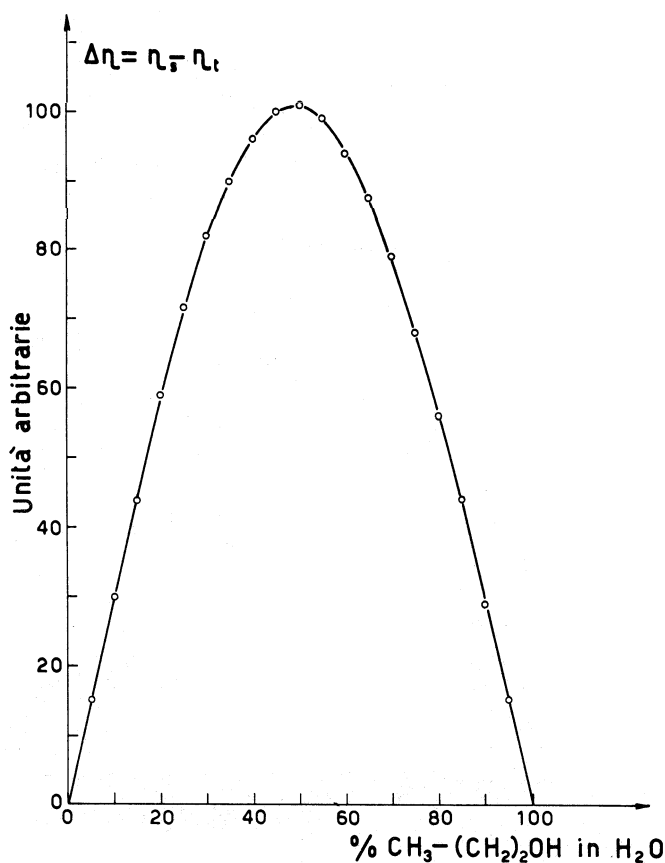


Fig. 2.

then the really significant quantity is the deviation of the experimental value obtained for the viscosity from a linear dependence of the type:

$$\eta_{AB} = p\eta_A + q\eta_B$$

where η_A , η_B and η_{AB} are the viscosities of the components A and B and of the solution AB, respectively, and p and q are the percentage weights of the two components.

The diagram in fig. 2 gives the difference between the measured viscosity η_s and the value η_{AB} which in fig. 1 is indicated by a broken line. Thus a curve is obtained with a maximum at a concentration of about 50% of propanol molecules in water.

The average length of the chains in water at 30°C [2], calculated from the heats of vaporization, is 4.57, which is in excellent agreement with the value of 50% obtained for the maximum deviation from ideal behaviour.

The encouraging results obtained thus far led us to test the validity of the proposed model still further, this time from the point of view of the N.M.R., which we had already done for water-ethanol solutions.

N.M.R. at high resolution makes it possible to estimate the electron density in the vicinity of the nuclei, by measuring the chemical shift of the nuclei (and of the protons in particular). Every phenomenon which disturbs this density, particularly molecular interactions of the hydrogen bond type,

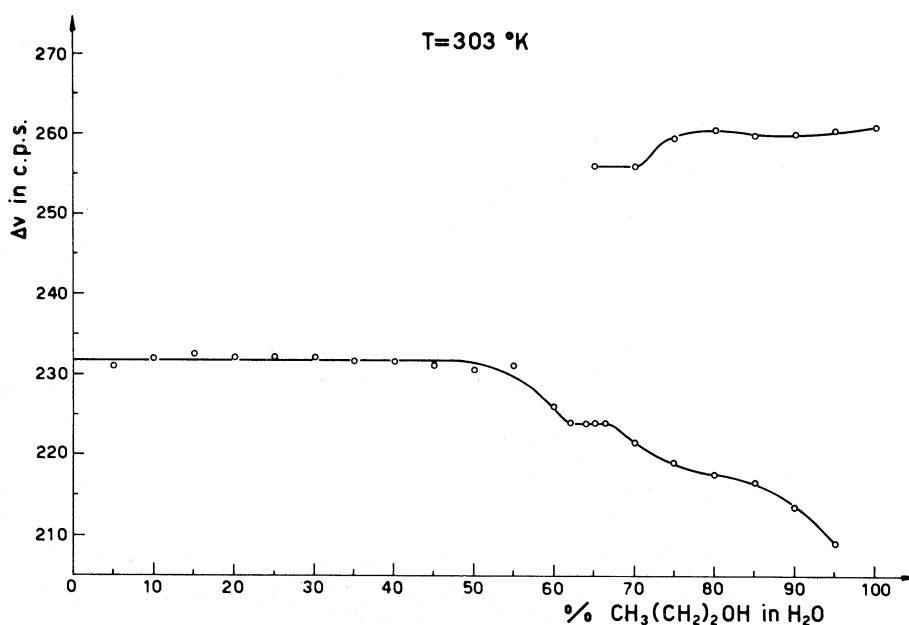


Fig. 3.

causes changes in the chemical shift. These changes are a function of quantities such as concentration temperature, pressure and the frequency of N.M.R. measurements.

Measurements, in water-propanol solutions, as a function of the concentration were carried out 1957 by Zimmerman and Foster. They measured at 40 Mc/s the resonance field of the protons of the hydroxyl groups as a function of the concentrations, using the resonance signal of the CH₃ group as a reference. Their results show step-like changes of the resonance field of the hydroxyl group as a function of the concentration, with sudden variations corresponding to molecular ratios of alcohol to water of 6 : 1, 2 : 1, 1 : 1, 1 : 2.

The results of our chemical shift measurements as a function of the concentration for the water-propanol system at 30°C, are given in fig. 3.

We have also used the methyl group as a reference for calculating the resonance fields of the hydroxyls.

The first observation that can be made is that the dependence of the resonance field of the hydroxyls does not show the step-like changes with sudden variations as do the measurements of Zimmerman and Foster. In addition, a general trend is obtained as a function of the concentration, which is of the same type as that found for the water-ethanol solutions [4]: only one signal whose resonance field does not depend on the concentration, up to a propanol concentration in water of 50%, and two separate signals for higher concentrations (the measurements of Zimmerman and Foster give no evidence of the second signal). Of the two signals present at higher concentrations, that which is observed at higher fields, that is, nearer to the

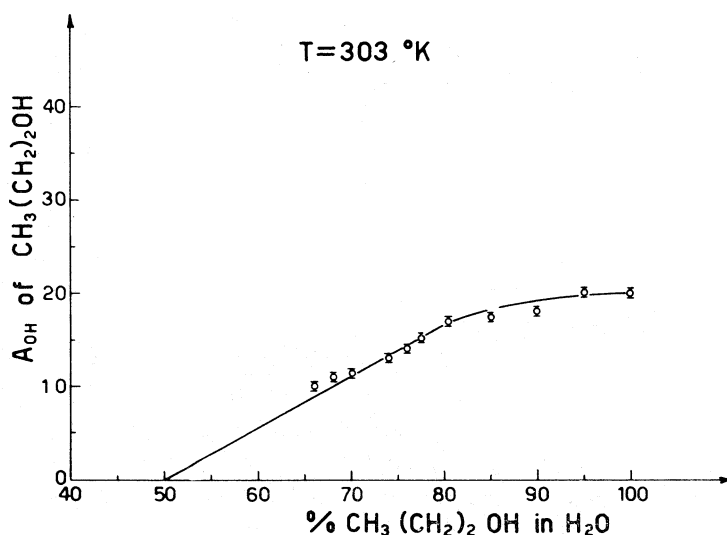


Fig. 4.

signal of the methyl group, clearly shows its continuity with the only signal present at low concentrations. From the point where the signal divides, the resonance field of the methyl group becomes displaced with increasing concentration and its total area decreases to zero as the percentage of water in the mixture tends towards zero. The second signal, which appears at a propanol concentration higher than 50%, at first has a very small total area which increases with the concentration and gradually joins the signals of the hydroxyls of pure propanol.

We next determined with the maximum possible precision the concentration at which the signal of the propanol hydroxyl groups appears. This was done by drawing a graph (fig. 4) in which the area of this signal was plotted on the ordinate and the percentage composition was plotted on the abscissa. Extrapolating to zero area, a concentration of about 50% is obtained.

This concentration is in good agreement with that at which there is a maximum deviation of the water-propanol solution from ideal behaviour, at 30°C.

To estimate the errors associated with each experimental point, the same criterion as described in detail in a previous paper [4] was used. The characteristics of the dependence of the chemical shift of the hydroxyl groups on concentrations, shown in fig. 3, can be interpreted without any difficulty and fall within the framework of the proposed model for the hydrogen bond [1].

As long as the concentration of propanol in water is lower than that at which there is a maximum deviation of the viscosity of the solution from linear behaviour, all the alcohol molecules are linked to water, saturating the hydrogen bonds available in the polymolecular bonds of water. Consequently, all the protons of the hydroxyls occupy the same molecular positions because they all take part in the hydrogen bridges which join two oxygen atoms. In actual fact, the terminal protons of each chain of water molecules occupy slightly different molecular positions. In non-saturated bonds, the terminal protons actually give rise to constant exchanges and each proton assumes a terminal position for a very brief period. The resonance field of the protons of the terminal hydroxyls is probably only slightly different from that of the others. This difference is most probably responsible for the asymmetry of the signal, which can be observed by slowly changing the magnetic field through the conditions of resonance.

When all the hydrogen bonds available in water are saturated with molecules of alcohol, an excess of alcohol can give rise to single molecules or to dimers which mix with the molecular aggregates present without becoming bound to them. Thus, on the one hand, the viscosity of the solution begins to decrease, and, on the other, a second signal appears, whose area gradually increases due to the protons of the alcohol hydroxyl groups.

Two facts remain to be clarified. The first one (see fig. 3) relates to the resonance field of the protons belonging to the hydroxyls of the water molecules which are saturated with alcohol molecules and their dependence to a marked degree on the concentration when the latter is higher than 60%. In addition, the reason for which the area of the signal of the alcohol, shown in fig. 4, tends to saturation with increasing concentration must be explained.

Both these facts can be explained by noting that when a considerable excess of alcohol is present in the mixture, above the amount needed to saturate the bonds available in water, the average structure of the polymolecular aggregates of water molecules is undoubtedly affected. First of all, the average length of the chains undoubtedly decreases and an ever increasing number of alcohol molecules become hydrated. It must not be forgotten that hydrogen bonds are relatively weak and that thermal motion is sufficient to produce the conditions in which every now and then a few are broken. When this occurs in the presence of an excess of alcohol, the two parts of the broken chain have a high probability of becoming saturated, thus form-

ing two shorter chains from a longer one. Secondly, with an increase in the alcohol concentration, more complex aggregates can undoubtedly be formed, containing different numbers of molecules, with an ever-increasing prevalence of alcohol molecules.

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