

## Ultraviolet Absorption Study of Aqueous Mixtures of Monohydric Alcohols: Water Structural Effects.

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**Summary.** — The ultraviolet absorption spectra of aqueous mixtures of methanol, ethanol, 1- and 2-propanol in the spectral region (190 ÷ 210) nm were measured as a function of alcohol concentration in the entire cosolvent mole fraction. The ultraviolet absorption coefficient exhibits, for all the systems investigated, an anomalous behaviour which occurs in the water-rich region (mole fraction of cosolvent  $x_2 < 0.1$ ) and which for each alcohol shows the existence of a solvent composition,  $x_2^*$ , corresponding to which the association state of the alcohol molecules changes. This behaviour is in line with the prediction of a liquid-clathrate-hydrate model and with the conclusions drawn from recent results on compressibility data.

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### 1. - Introduction.

It is well known that alcohol-water mixtures show unusual properties in the water-rich region which have been attributed to an initial structuring of the water induced by the solute molecules followed by destruction of this structure as the mole fraction of cosolvent increases<sup>(1,2)</sup>.

The actual mechanism of this structure-forming action is uncertain. One of the proposed models, the liquid clathrate one, is of particular interest<sup>(2)</sup>. X-ray

(1) F. FRANKS and D. J. IVES: *Q. Rev. Chem. Soc.*, **20**, 1 (1966).

(2) F. FRANKS and D. J. REID: in *Water a Comprehensive Treatise*, Vol. 2, edited by F. FRANKS (Plenum Press, New York, N. Y., 1973), p. 323.

diffraction studies of water suggest that water has a long-range order structure, having numerous cavities which can accommodate another species. In the liquid-clathrate model it is assumed that, on entering water, alcohol molecules accumulate in the void volume in the water and become accommodated in cavities similar to those found for guest molecules in clathrate hydrates<sup>(3)</sup>. In so doing, the hydroxyl group hydrogen bonds into the water lattice forming the cavity wall, the hydrophobic alkyl group being the guest in the cavity, stabilizing it but not specially interacting with the water. With increasing cosolvent mole fraction, a point is reached,  $X_2 = X_2^*$ , where there is insufficient water to accommodate the cosolvent in a clathratelike structure. At this mole fraction interference between solvent cospheres produces a structure-breaking action.

Although no simple clathrate-containing alcohols are known, this may be a valid description of the actual system which has already been used for explaining, in a qualitative manner, the fact that some of the physical properties of alcohol-water mixtures show extrema at some intermediate composition of the mixture<sup>(4-8)</sup>. For instance, the existence of time-average clathratehydratelike structure of ethanol-17H<sub>2</sub>O-type ( $X_2^* = 1/18$ ) in ethanol-water mixtures has been proposed by Glew<sup>(4)</sup> to account for an anomalous molar volume at about 0.06 mole fraction of ethanol in aqueous ethanol solutions; further support for this hypothesis has recently come from compressibility measurements on ethanol-water mixtures performed in our laboratory. This study<sup>(9)</sup> contains a large number of data in the water-rich region that allow accurate quantitative analysis; the observed compressibility behaviour suggests that ethanol molecules are isolated from one another initially ( $X_2 < X_2^*$ ) and only come into contact when there is no longer sufficient water to provide clathrate cavities for all the ethanol molecules. These suggestions seem very reasonable, thus it is important to have further experimental data in the dilute-alcohol region in order to lend further support to this description.

Although most of the properties of alcohol-water mixtures have been closely investigated, little attention has been paid to their ultraviolet absorption spectra. It is known that saturated alcohols in the gas phase begin to absorb near 200 nm with the maximum of the first band near 185 nm<sup>(10)</sup>. This band has

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<sup>(3)</sup> D. W. DAVIDSON: in *Water a Comprehensive Treatise*, Vol. 2, edited by F. FRANKS (Plenum Press, New York, N. Y., 1973), p. 115.

<sup>(4)</sup> D. N. GLEW: *Nature (London)*, **195**, 698 (1962).

<sup>(5)</sup> E. K. BAUMGARTNER and G. ATKINSON: *J. Phys. Chem.*, **75**, 2336 (1971).

<sup>(6)</sup> M. J. BLANDAMER, N. J. HIDDEN and M. C. R. SYMONS: *Trans. Faraday Soc.*, **66**, 316 (1970).

<sup>(7)</sup> N. V. CHEKALIN and M. I. SHAKHPERONOV: *Sov. Phys. Acoust.*, **17**, 147 (1971).

<sup>(8)</sup> N. ITO, T. FUJIYAMA and Y. UDAGAWA: *Bull. Chem. Soc. Jpn.*, **56**, 379 (1983).

<sup>(9)</sup> G. ONORI: *Nuovo Cimento D*, **8**, 465 (1986).

<sup>(10)</sup> A. J. HARRISON, B. J. CEDERHOLM and M. A. TERWILLIGER: *J. Chem. Phys.*, **30**, 355 (1959).

usually ascribed to a  $n \rightarrow \sigma^*$  <sup>(11)</sup> transition, *i.e.* absorption of a photon in this spectral region results in the excitation of a nonbonding electron of the hydroxyl oxygen to an antibonding  $\sigma^*$  orbital of the alcohol.

The involvement of the oxygen-unshared pairs of electrons in hydrogen bonding exerts a great influence on the absorption spectrum <sup>(12)</sup>. The alcohol absorbance in the range (185 ÷ 200) nm is, therefore, a sensitive probe of solute-solute and solute-solvent interactions and as such provides a useful parameter for elucidating the structural interactions in the water-alcohol mixture.

In the present investigation the ultraviolet absorption spectra of aqueous methanol (at 20 °C), ethanol (at 20, 50, 60 °C), 1- and 2-propanol (at 20 °C) in the spectral region (190 ÷ 210) nm were measured as a function of alcohol concentration in the entire cosolvent mole fraction region.

The main object of the present investigation is to check the prediction inherent in the liquid-clathrate-hydrate model, also supported by the adiabatic compressibility data, of the existence for each of the investigated alcohols of one critical concentration in the water-rich region corresponding to which the state of association of the alcohol molecules changes.

## 2. - Materials and methods.

Absorption spectra were recorded with a Mod. 369 Shimadzu spectrophotometer, the cell housing compartment of which was kept at  $(20.0 \pm 0.1)^\circ\text{C}$  with water circulating from a thermostatted bath; quartz cells 1 cm or 0.1 cm long were used.

The alcohols (J. T. Beker, spectrophotometric grade) were used without any further purification. The water used was distilled and all mixtures studied were prepared by weighing the components.

Water is designated as component 1 and the cosolvent as component 2. Thus in the water-alcohol mixture,  $X_1$  is the mole fraction of water and  $X_2 = 1 - X_1$  is the mole fraction of alcohol. The molar extinction coefficient  $\epsilon$  of alcohol in water was calculated using the usual expression

$$\epsilon = A/c_2 d ,$$

where  $A$  is the absorbance of the mixture,  $c_2$  the alcohol concentration in moles per litre and  $d$  the cell depth in centimetres. The densities used to calculate  $c_2$  from  $X_2$  were taken from the literature <sup>(13)</sup>.

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<sup>(11)</sup> H. TSUMBOMURA, K. KIMURA, K. KAYA, J. TANAKE and S. NAGAKURA: *Bull. Chem. Soc. Jpn.*, **37**, 417 (1964).

<sup>(12)</sup> M. ITO: *J. Mol. Spectrosc.*, **4**, 106 (1960).

<sup>(13)</sup> R. F. BRUNEL and K. VAN BIBBER: *International Critical Tables* (McGraw-Hill Book Company, New York, N. Y., 1928).

### 3. - Results and discussion.

The electronic spectra of aqueous alcohols lie mostly in the vacuum ultraviolet<sup>(1)</sup> beyond the region of available measurement of a normal spectrophotometer. Probably, for this reason they have received relatively little attention from investigators.

Figure 1 shows the molar extinction coefficient,  $\epsilon$ , of ethanol in water, as a function of wavelength in the range (190 ÷ 210) nm at various ethanol concentrations. The observed spectra do not display any absorption maxima, but show structureless end absorption. In this spectral region the absorption coefficient of water is negligible in comparison with that of alcohols.

It is evident from fig. 1 that the molar absorption coefficient of ethanol in water is markedly dependent on alcohol concentration, that is, the absorbance of ethanol in water does not obey Beer's law

$$A = \epsilon_2 c_2 d ,$$

where  $\epsilon_2$  is the molar extinction coefficient of the pure component. Methanol, 1- and 2-propanol have been found to have similar spectral properties.

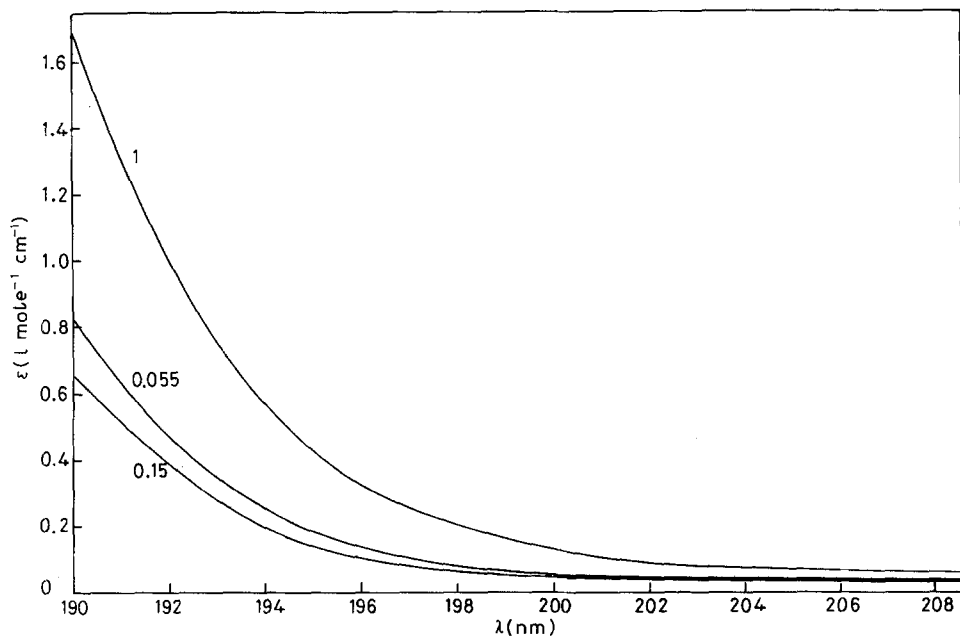


Fig. 1. - Molar extinction coefficient,  $\epsilon$ , of aqueous ethanol as a function of wavelength at various ethanol mole fractions.

Since we must compare measurements performed at different temperatures, it is convenient to express the alcohol concentration in terms of its molar fraction:

$$X_2 = c_2 / (c_1 + c_2) .$$

Figure 2 shows the quantity  $\epsilon X_2$  as a function of ethanol mole fraction  $X_2$  at various temperatures for the mixture. It is evident that there is a deviation from an ideal behaviour that is more marked at higher temperatures (see also inset to fig. 2). Moreover, there is evidence in the extremely dilute region of a concentration  $X_2^*$  corresponding to which we observe a decrease in the molar extinction coefficient.

Note that  $X_2^*$  diminishes slightly when the temperature increases, assuming values near 0.05 similar to those which characterize a solid clathrate hydrate of type II having the composition ethanol-17H<sub>2</sub>O. Our spectrophotometric data strongly suggest that this type-II ethanol hydrate is present in the extremely dilute region of aqueous ethanol solutions.

The other mixtures investigated show a behaviour similar to that of the ethanol-water system (see fig. 3-5). In all the systems investigated the quantity  $\epsilon X_2$  increases linearly with  $X_2$  up to a concentration  $X_2^*$  peculiar to each alcohol. For  $X_2 > X_2^*$  the molar extinction coefficient decreases. The  $X_2^*$  concentration

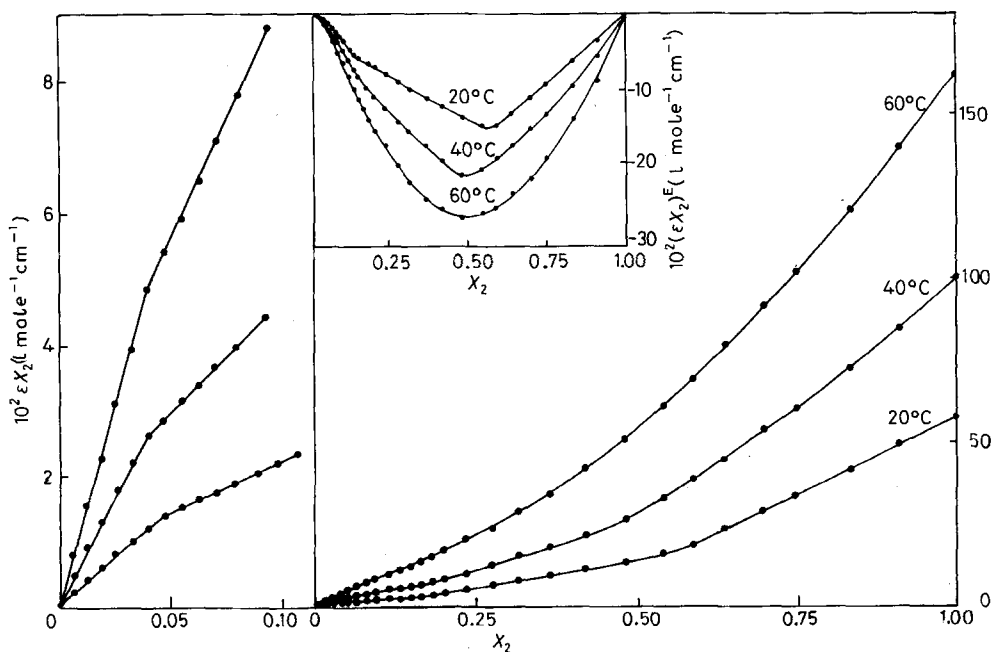


Fig. 2. - The quantity  $\epsilon X_2$  at 194 nm for aqueous ethanol as a function of mole fraction of alcohol,  $X_2$ , at various temperatures. The excess quantity  $(\epsilon X_2)^E$ , plotted against  $X_2$  in the inset, gives the deviation of  $\epsilon X_2$  from a linear dependence on mole fraction.

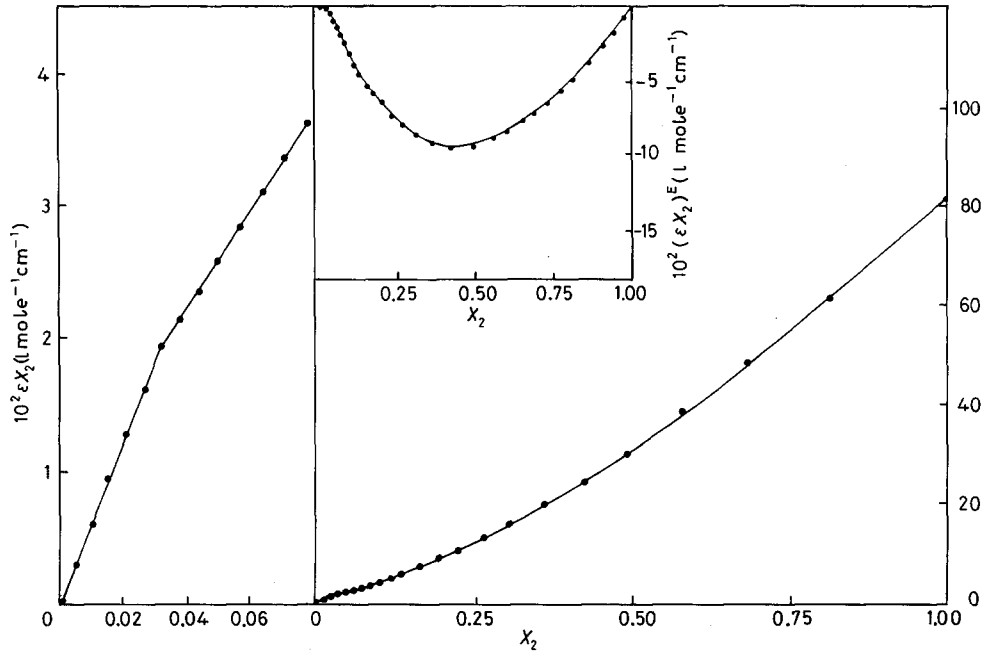


Fig. 3. - The quantities  $\epsilon X_2$  and  $(\epsilon X_2)^E$  (see inset) at 194 nm for aqueous methanol as a function of mole fraction of alcohol at 20 °C.

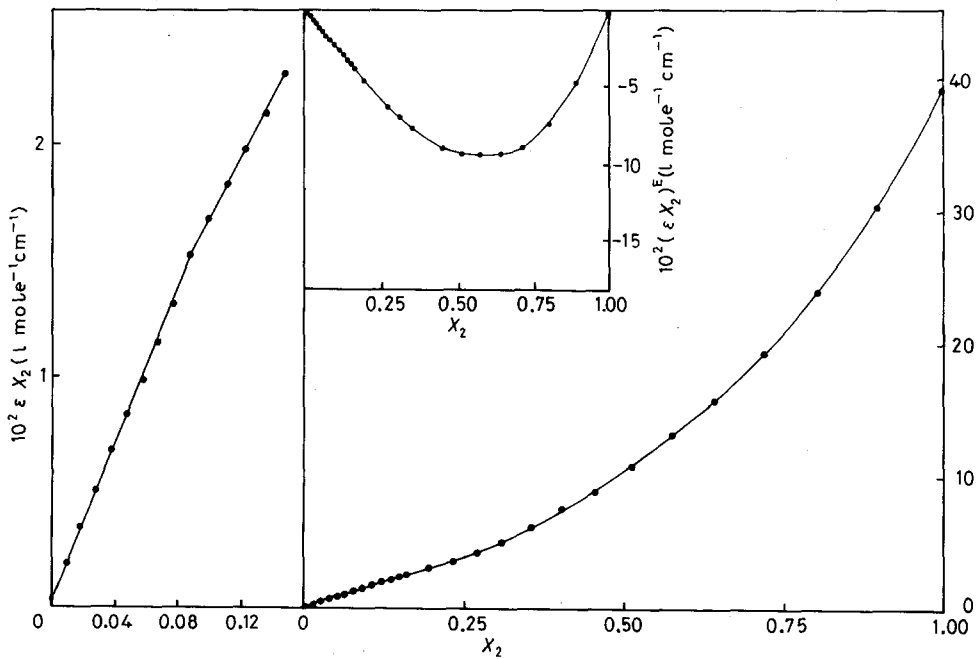


Fig. 4. - The quantities  $\epsilon X_2$  and  $(\epsilon X_2)^E$  (see inset) at 194 nm for aqueous 1-propanol as a function of mole fraction of alcohol at 20 °C.

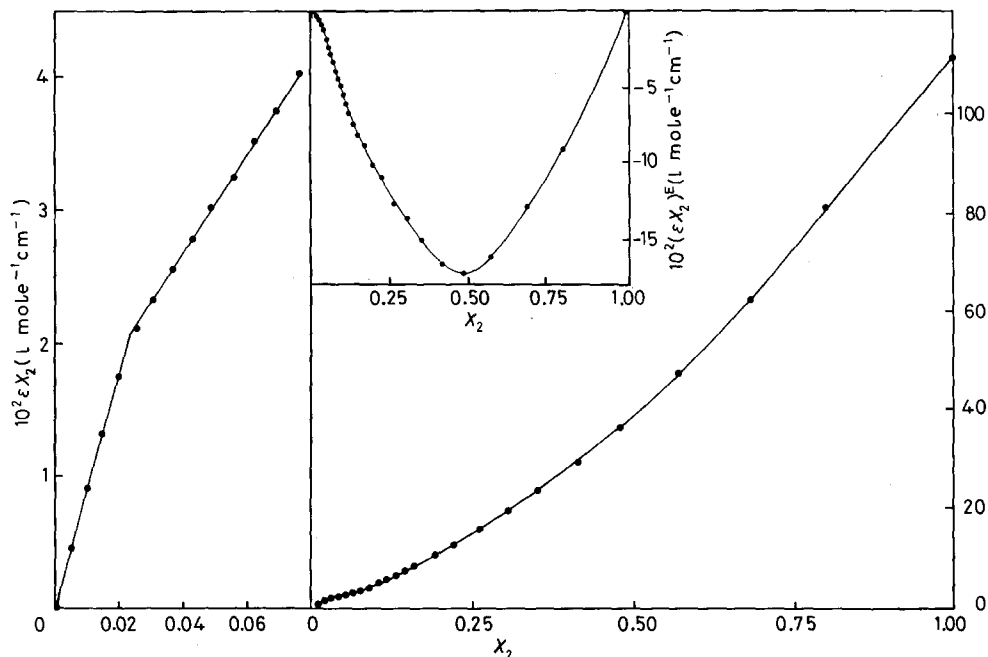


Fig. 5. - The quantities  $\epsilon X_2$  and  $(\epsilon X_2)^E$  (see inset) at 194 nm for aqueous 2-propanol as a function of mole fraction of alcohol at 20 °C.

shifts to lower values for increasing of alkyl group size and we find the values 0.09, 0.05, 0.03 and 0.03, respectively, for the methanol, ethanol, 1- and 2-propanol at 20 °C.

A similar dependence on the alkyl group size has been seen in other solution properties; thus the values found for  $X_2^*$  are nearly the same as those at which an anomalous behaviour of the adiabatic compressibility occurs<sup>(14)</sup> and are close to (but slightly smaller than) those at which a minimum in the partial molar volume of the nonaqueous component occurs for the same systems<sup>(15)</sup>. Similar patterns of behaviour to those shown are observed for all wavelengths in the spectral range explored ((190 ÷ 210) nm).

Deviations of  $\epsilon X_2$  from a linear dependence on mole fraction were calculated using the relation

$$(\epsilon X_2)^E = \epsilon X_2 - \epsilon_2 X_2 .$$

The excess quantity  $(\epsilon X_2)^E$  is plotted against  $X_2$  in the inserts of fig. 2-5.

This quantity is negative for all compositions for all the systems examined. The data for the ethanol-water system (fig. 2) show that the dependence of  $(\epsilon X_2)^E$

<sup>(14)</sup> S. BENEVENTI: Degree Thesis, University of Perugia, Italy (1986).

<sup>(15)</sup> K. NAKANISHI: *Bull. Chem. Soc. Jpn.*, 33, 793 (1960).

on  $X_2$  changes greatly with temperature at  $X_2 > X_2^*$  but not at  $X_2 < X_2^*$ . The curve at 60 °C is nearly symmetrical about  $X_2 = 0.5$  but, on decreasing the temperature, the curve shows a fairly complex shape and a second point of inflection at about 0.16 appears besides that already found at 0.05. At the same time the minimum shifts to higher alcohol concentrations. Note that the molar concentration of 0.16 corresponds well to the observed maximum viscosity enhancement in supercooled aqueous solutions of ethanol<sup>(16)</sup>.

In the absence of a detailed theoretical structural model only a few inferences can be drawn from the experimental data. The dependence of  $\epsilon X_2$  and  $(\epsilon X_2)^E$  on  $X_2$  as well as the effect of temperature can be interpreted in terms of the degree of hydrogen bonding present. The presence of such bonds lowers the transition probability of the optical electrons. In fact, the absorbance of alcohols is much lower in the neat liquid<sup>(11)</sup> than in the gas phase<sup>(10)</sup> and, besides, in the liquid the absorbance increases strikingly on raising the temperature (see fig. 2). When alcohols are added to water, some hydrogen bonds must be broken and new hydrogen bonds between water and alcohol should be formed. Thus the negative value of  $(\epsilon X_2)^E$  indicates the existence in the water-alcohol mixture of a greater number of hydrogen bonds, where the hydroxyl groups are involved, with respect to that expected for an ideal behaviour.

The anomalous behaviour observed in the water-rich region, in agreement with what is suggested by compressibility measurements, may reflect the change in the state of association at  $X_2 > X_2^*$  due to H bonding between alcohol molecules. In this interpretative framework,  $X_2^*$  would, therefore, correspond to the concentration of alcohol favouring a maximum induced structure, but the concentration at the minimum in  $(\epsilon X_2)^E$  corresponds to that favouring maximum alcohol-alcohol and alcohol-water interactions.

#### 4. - Conclusions.

The present experimental results, in line with the prediction of a clathrate-hydrate model and with the conclusions drawn from the results of compressibility data, show the existence in dilute aqueous alcohol mixtures of a cosolvent concentration value  $X_2^*$  in correspondence with which the association state of alcohol molecule changes. The  $X_2^*$  value decreases on going from methyl alcohol to propyl alcohol.

These results were interpreted by assuming that cavities in the framework of the water structure are gradually filled up by alcohol molecules up to a concentration  $X_2^*$ . Accordingly, water appears able to accommodate more molecules of solute as its bulk decreases. Besides this, on raising the temperature the amount of cosolvent which can be accommodated in this way decreases,

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<sup>(16)</sup> B. L. HALFPAP and C. M. SORENSEN: *J. Chem. Phys.*, **77**, 466 (1982).



*i.e.*  $X_2^*$  decreases. In agreement with what is suggested by compressibility data, one can assume that in the  $X_2 < X_2^*$  region the alcohol molecules are kept apart by the formation of hydration cages around each of them and only come into contact when there is no longer sufficient water to provide clathrate cavities for all the alcohol molecules.

The results described in this paper are of interest, not only for themselves, but also for their relevance to the effects of solvent perturbation on the conformational stability of biological macromolecules and on the equilibria and rates of chemical reactions. Recent investigations have stressed the importance of the contribution from structural changes of the solvent for this kind of problem<sup>(17)</sup>. Work is in progress in our laboratory to prove the existence of a precise correlation between certain effects of alcohols on various chemical and biochemical systems and the observed changes in the solvent structure<sup>(18,19)</sup>.

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<sup>(17)</sup> D. EAGLAND: in *Water a Comprehensive Treatise*, Vol. 4, edited by F. FRANKS (Plenum Press, New York, N. Y., 1975), p. 305.

<sup>(18)</sup> G. BALDINI, H. FU-HUA, G. VARANI, L. CORDONE, S. L. FORNILI and G. ONORI: *Nuovo Cimento D*, **6**, 618 (1985).

<sup>(19)</sup> S. BENEVENTI and G. ONORI: *Biophys. Chem.*, **25**, 181 (1986).

## ● RIASSUNTO

È stato misurato lo spettro di assorbimento di soluzioni acquose di metanolo, etanolo, 1- e 2-propanolo, nell'intervallo spettrale (190 ÷ 210) nm, in funzione della temperatura e della frazione molare,  $x_2$ , di cosolvente. L'assorbanza delle miscele esaminate mostra un comportamento anomalo nella regione ricca in acqua ( $x_2 < 0.1$ ). In questo modo si individua, per ciascun alcool, un valore  $x_2^*$  della frazione molare in corrispondenza del quale cambia lo stato di associazione delle molecole di alcool. Tale comportamento è in accordo con le conclusioni tratte da un recente studio sulla compressibilità di miscele acqua-alcool etilico e con l'ipotesi dell'esistenza nelle miscele esaminate di strutture locali simili a quelle di un clatrato idrato.

## Исследование поглощения ультрафиолетового излучения в водных растворах моногидридных спиртов: структурные эффекты воды.

**Резюме (\*).** — Измеряются ультрафиолетовые спектры поглощения в водных смесях метанола, этанола, 1- и 2-пропанола в спектральной области (190 ÷ 210) нм, как функция температуры и молярной доли,  $x_2$ , соразвителя. Коэффициент ультрафиолетового поглощения для всех исследованных систем обнаруживает аномальное поведение, которое имеет место в области с большим содержанием воды (молярная доля соразвителя  $x_2 < 0.1$ ) и которое для каждого из спиртов указывает на существование значения молярной доли  $x_2^*$  растворителя, при котором происходит изменение состояния связи молекул спирта. Это поведение согласуется с предсказаниями о существовании локальной структуры в исследованных смесях и с выводами из недавних исследований сжимаемости водных смесей спиртов.

(\*) *Переведено редакцией.*