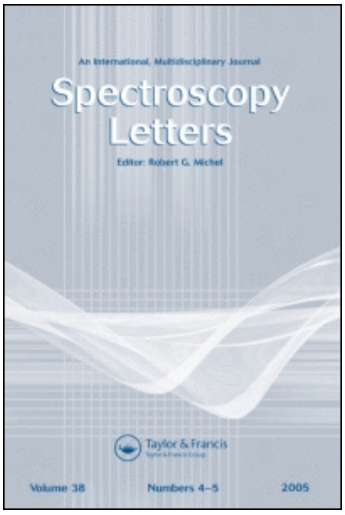

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The NMR and Viscosity Investigations of 1,3- and 1,4-Dioxanes in Binary Aqueous Solutions

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THE NMR AND VISCOSITY INVESTIGATIONS OF 1,3- AND 1,4-DIOXANES IN BINARY AQUEOUS SOLUTIONS

Key Words: 1,3-dioxane, 1,4-dioxane, aqueous mixtures, NMR spectroscopy, viscosimetry, hydration structure

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ABSTRACT

The measurements of ^1H NMR chemical shift and the shear viscosity as a function of temperature and concentration for 1,3-and 1,4-dioxane-water system were carried out. Our experimental results are consistent with data derived from other works. Both the chemical shift and viscosity data suggested the association processes between water and dioxane molecules.

INTRODUCTION

Hydration structures of simple, active organic solvants in aqueous solutions have received considerable attention. So far two models have been proposed [1-6]. The former is a hydrogen bond model which assumes that solvents form aggregates with water molecules and break down the network of water. The latter accepts that organic molecules are clathrated in interstics of the network and interactions with water are rather weak.

A notable example is 1,4-dioxane-water mixture which has been studied extensively. Both dioxane and water contain oxygen and can form hydrogen bonds but water molecules may act as proton acceptors and/or proton donors.

However, in the literature there is a long standing controversy regarding the effect of 1,4-dioxane on the three-dimensional network of water due to the difficulties involved in linking thermodynamic and spectroscopy data with a microscopic picture of intermolecular interactions on the molecular level [1-10].

It is well-known that many of the physical properties of the 1,4-dioxane solutions, when plotted versus the concentration, exhibit an extreme behaviour [2-5,8]. The association between dioxane and water molecules seems to attain a maximum when the molar ratio is close to 2:1 or 1:1 [1,4,7,8].

Unfortunately, there are very few data concerning the hydration structure of other polar dioxanes. Recently, Remerie [11,12] studied the aqueous solutions of 1,3- and 1,4-dioxanes by molecular dynamics methods and unexpected differences between both dioxanes mixtures were found.

In this paper the hydration structure of 1,3-dioxane was deduced by the indirect method. The temperature and concentration measurements of the ^1H NMR chemical shift, shear viscosity and density were carried out. We also undertook the temperature investigation of 1,4-dioxane-water systems in the broad range of temperature.

EXPERIMENTAL

The 1,4-dioxane(Fluka AG-purum) was further purified using the standard purification technique [14]. The 1,3-dioxane(Fluka AG-purum) was dried with sodium and twice fractionally distilled. The water was redistilled.

All ^1H NMR spectra were obtained on a Tesla BS 567 A FT spectrometer (100 MHz). The hexamethyldisiloxane (HMDS) as an external reference and deuterated N,N-dimethylformamide (DMF-d_7) for a spectrometer lock in a coaxial capillary were used. Chemical shifts were corrected for the sample bulk susceptibility [15].

The temperature was controlled with an accuracy 1 K. The shear viscosity was measured to an accuracy of 0.5 % using a modified Oswald viscometer with a suspended level of liquid described previously [16].

RESULTS AND DISCUSSION

It was observed that the signals of H(2), H(4,6) and H(5) protons of 1,3-dioxane moved down field with increasing water concentration (Fig.1). All methylene (CH_2) groups were shifted in the same manner about 0,4 ppm. The chemical shift of water protons both as a function of concentration and temperature changes more

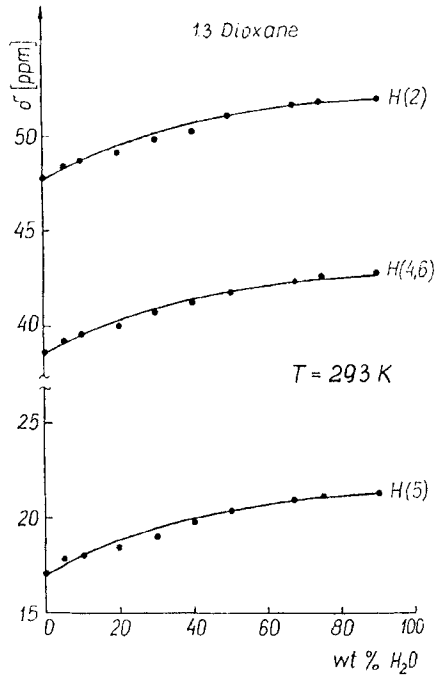

FIG. 1. Proton chemical shift of 1,3-dioxane as a function of water concentration.

distinctly. Since oxygen of 1,3-dioxane molecule may act as a proton acceptor, deshielding of protons suggests the formation water-dioxane aggregates by hydrogen bonds. It is worthy to be noticed that the proton chemical shifts of pure 1,3-dioxane are almost independent on temperature. The changes in chemical shifts are about 0,03 ppm in the whole region of the existence of that liquid, although its protons usually show extremely large changes δ when solvent is altered [13].

In order to obtain a more conclusive, experimental evidence on the interaction between water and dioxane

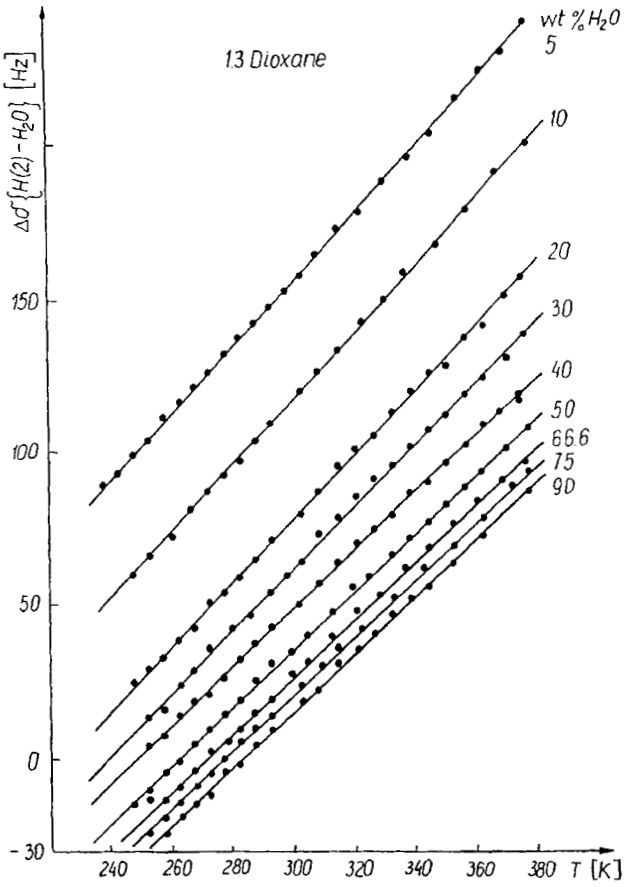

FIG. 2. Relative chemical shift of H(2) protons of 1,3-dioxane as a function of temperature for various weight % water.

molecules the difference in the chemical shift for H(2) and water protons $\Delta\delta$ [H(2)-H_2O] were plotted, as an example, in Fig. 2. The temperature dependence of $\Delta\delta$ [H_2O-Dx]for 1,4-dioxane-water mixtures was also shown in Fig. 3.

The trends of the relative chemical shift for both dioxanes are similar but a few essential differences

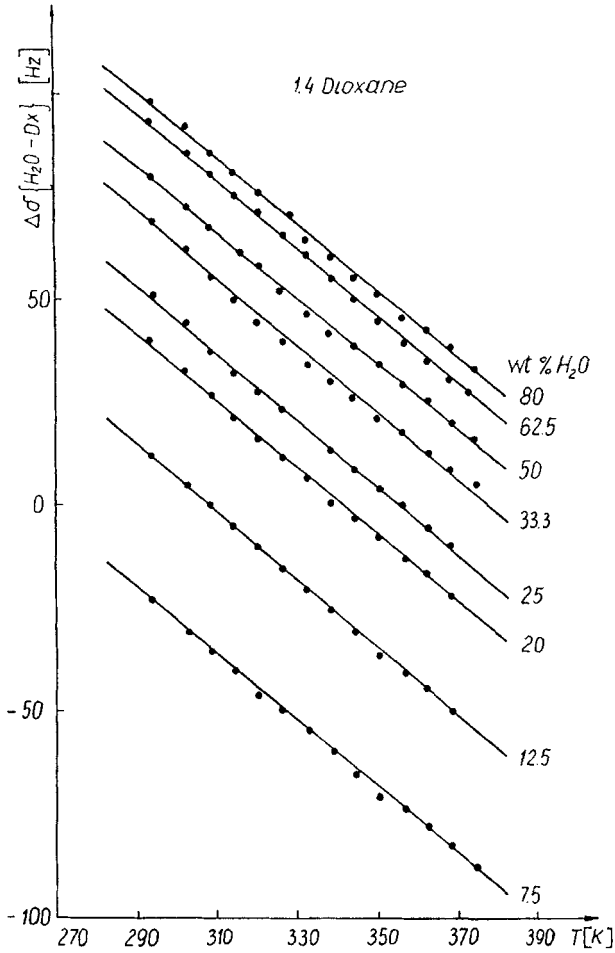

FIG. 3. Relative chemical shift of proton of 1,4-dioxane as a function of temperature for various weight % water.

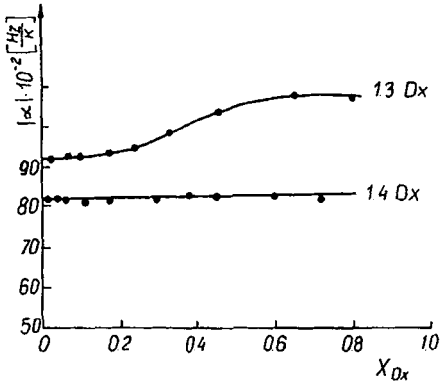

FIG. 4. Coefficients of slope α for plots from Fig. 2 and 3. as a function of dioxane concentration.

should be noted. Firstly, in Fig. 3 one can see that the slope of straight lines is the same in the whole concentration region, whereas in the case of 1,3-dioxane the slope changes with water concentration. It was also shown in Fig. 4 where the coefficients of slope α, obtained by a least-squared method, were plotted. From Fig. 2 it is evident that the temperature dependence of the chemical shifts of 1,3-dioxane changes the most effectively in the concentration region, where the strongest interactions between water and dioxane molecules are expected. This conclusion can be also derived from Fig. 4. There findings may indicate that interactions in 1,3-dioxane-water mixtures are stronger than 1,4-dioxane-water systems and confirm Remerie's suggestion [11, 12] that interactions between water and 1,4-dioxane molecules are weaker than solvent-solvent interactions independently on temperature.

Moreover, for curves in Fig. 2 and 3 the concentration dependence was also obtained (Fig. 5 and 6). In

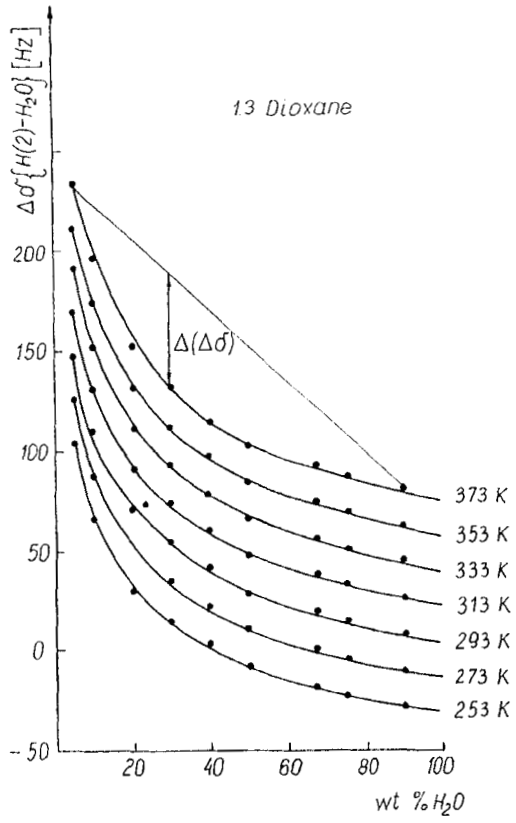

FIG. 5. Relative chemical shift of H(2) protons of 1,3-dioxane as a function of water concentration. The arrow shows the way of estimating values of $\Delta(\Delta\delta)$, according to Kinart [7].

the case of apolar dioxane values of the chemical shift are constant above 80 weight. % of water. These results are also supported by other experimental [9,10] and molecular dynamics data [11,12].

It was stated that at low concentration, the small apolar organic molecules may even enhance the structure of

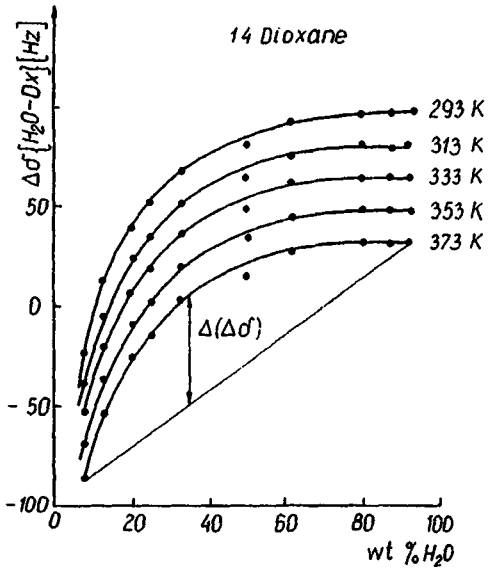

FIG. 6. Relative chemical shift of protons of 1,4-dioxane as a function of water concentration for various temperatures.

water by hydrophobic contributions and interactions with water are rather weak. On the other hand, in aqueous solutions of 1,3-dioxane, where stronger interactions due to its large dipole moment, are expected, values of $\Delta\delta$[H(2)-H_2O] change in the whole concentration region.

Thus, using the data for the concentration dependence of the relative chemical shifts their derivation from additive properties viz. the $\Delta(\Delta\delta)$ values [7] were obtained, in the way shown in Fig. 5.

Since the temperature dependence of $\Delta(\Delta\delta)$ is very weak, only results for room temperature were shown in Fig. 7. The broad maxima obtained from the plot $\Delta(\Delta\delta)$

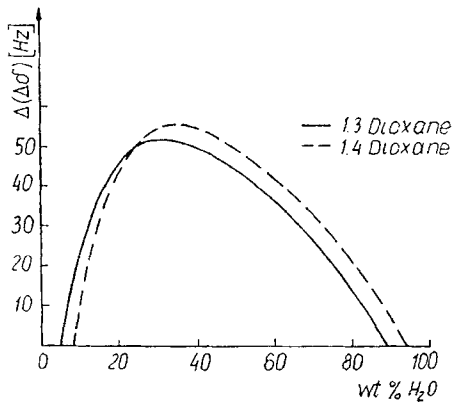

FIG. 7. Derivations from additive properties $\Delta(\Delta\delta)$ as a function of water concentration.

versus concentration are very similar for both dioxane mixtures. Furthermore, in Fig. 4 one can see that the change of coefficients of slope for 1,3-dioxane occurs at the same concentration region.

An example of the temperature dependence of the shear viscosity of 1,3-dioxane water mixtures was shown in Fig. 8. All solutions display temperature changes according to the Arrhenius equation :

$$\eta(t) = \eta_o \exp[E_a / RT]$$

Coefficients E_o and η_o calculated on the basis of experimental data were listed in Table 1. The changes of the activation energy as a function of concentration can be observed.

According to Westmeier [17] additional information on the processes occurring in the system can be obtained by analyzing the temperature coefficient of viscosity :

$$\beta = \frac{d\eta}{dT}$$

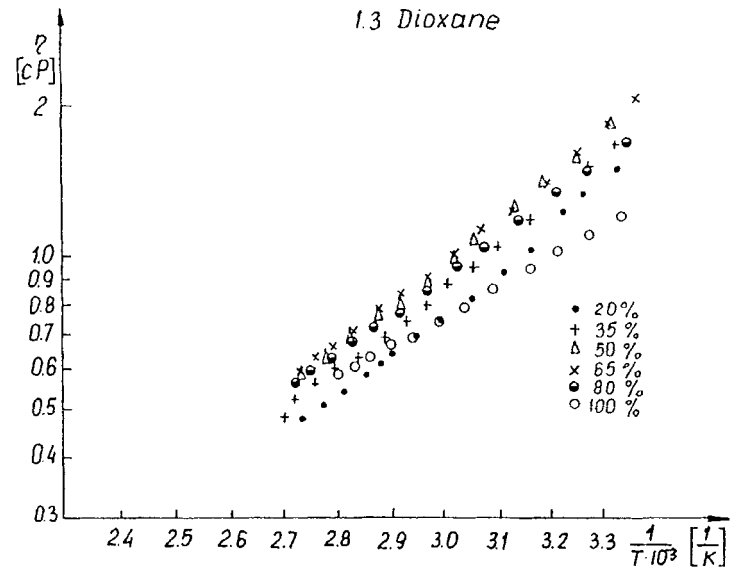

FIG. 8. Shear viscosity of 1,3-dioxane as a function of 1/T for various weight % water.

TABLE 1

Activation energies E and pre-exponetial coefficients

wtg%H_2O	1,3-Dx + H_2O		1,4-Dx + H_2O	
	E_a [kJ/mol]	$\eta_o \cdot 10^3$ [cP]	E_a [kJ/mol]	$\eta_o \cdot 10^3$ [cP]
0	11,20	13,0	11,90	18,0
0,20	14,70	4,5	15,64	3,5
0,35	16,65	2,6	16,89	2,4
0,50	16,10	2,9	17,32	2,0
0,65	16,57	2,2	17,02	1,9
0,80	16,68	2,9	15,66	2,6

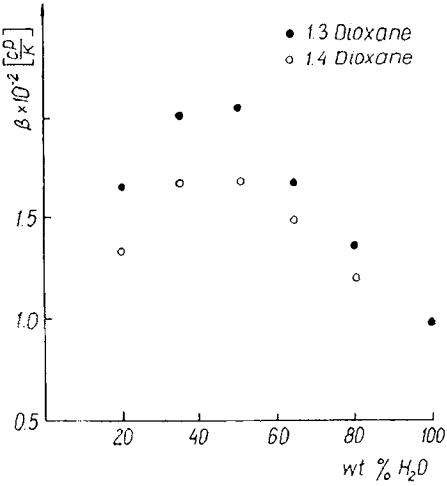

FIG. 9. The temperature coefficients β as a function of water concentration.

Fig. 9 shows the concentration dependence of β. For both dioxane mixtures maxima of the β coefficient versus water concentration were obtained. The maxima for 1,3- and 1,4-dioxane solutions occur in the same concentration region as for chemical shifts.

The existence of maxima in Fig. 7 and 9, as it was suggested [2-5, 8], should be connected with aggregation processes in those solutions. The association between dioxane and water molecules seems to attain maximum when the molar ratio is closed to 1:2.

As mentioned above, from the molecular dynamics study [11, 12], it was concluded that for 1,3-dioxane-water mixtures, water molecules became more strongly bound by the solute with increasing temperature. In the case of 1,4-dioxane-water mixtures this effect is not observed and solvent-solvent interactions dominate sol-

vent-solute ones. Results of our study did not fully confirm that suggestion.

CONCLUSIONS

The present work on dioxane-water mixtures shows that measurements of ^1H NMR chemical shifts and viscosity may be also used to study the structure of simple liquid mixtures. Both the chemical shifts and viscosity data suggest the existence of a weak complex in aqueous dioxane mixtures.

Although our results not fully confirm Remerie's suggestion on differences in the structure of both dioxane mixtures with increasing temperature some distinctions have been obtained.

Moreover, it would be interesting to compare our experimental data, especially for 1,3-dioxane, with other results obtain, for instance, from NMR measurements of the relaxation times, Xe chemical shifts or dielectric relaxation.

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