SPECTROSCOPIC STUDY OF THE SOLUTE EFFECT ON THE STRUCTURE OF LIQUID WATER

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The effect of ten electrolytes and eight nonelectrolytes on the structure of liquid water in a H_2O--D_2O mixture was studied by near infrared spectroscopy. The results are interpreted in terms of the disturbing or promoting effect of solute on the cluster structure of water. The standard enthalpies of the hydrogen bond formation and the structure temperatures of the solutions were determined based on the temperature dependence of the absorbances.

The problem of the structure of liquid water and aqueous solutions has attracted considerable attention[1]. Experimentally is this problem frequently studied by absorption spectroscopy in the near infrared region, where the overtones and combination frequencies due to the —OH group vibrations appear[2-9]. In the interpretation of the results, basically two concepts have been applied: the mixture system concept and the continuum concept. In the former, described particularly in the works[10-14], liquid water is looked upon as consisting of two distinguishable species, *viz.* free water molecules and $(H_2O)_n$ clusters (n of the order of 10^1 to 10^2) in which the molecules are mutually hydrogen bonded. Of the various models, particularly significant is that of flickering clusters in which a dynamic equilibrium is assumed to be established between the free molecules and the clusters[10,11]. In the approach of the continuum concept, all water molecules are supposed to be hydrogen bonded, the energy of the hydrogen bonding varying smoothly across the liquid bulk[15,16]. The mixture system concept can well account for a great deal of the experimental results obtained, and recently it has received attention also from the theoretical point of view[17-19]. Also, there is available convincing experimental evidence supporting the mixture system model[2,20,21].

Measurements in near infrared are frequently performed on mixtures of water with deuterium oxide, in which the equilibrium

$$H_2O + D_2O \rightleftarrows HOD \qquad (A)$$

establishes rapidly. The components of the mixture give rise to absorption bands different in positions as well as intensities[2,4,7,21]. Their shape and intensity can vary appreciably on introducing solutes affecting the cluster structure of the system.

In the present work, solutions of a number of electrolytes and nonelectrolytes are examined from the point of view of their effect on the near infrared absorption spectrum of HOD, and the results obtained are interpreted in terms of the solute effect on the liquid water structure.

EXPERIMENTAL

The salts used were of reagent grade purity (Lachema, Brno). The liquids serving as solutes (acetonitrile, pyridine, acetone, dioxane, dimethylformamide, dimethyl sulphoxide, and tetra-hydrofuran) were distilled prior to use. The cyclic polyether 18-crown-6 was synthesized according to[22]; for $C_{12}H_{24}O_6$ calculated: 54.51% C, 9.16% H; found: 54.5% C, 8.9% H. Deuterium oxide (99.8 mol.%) was supplied by the Institute for the Manufacturing, Investigation, and Utilization of Radioisotopes (ÚVVVR) in Prague. The water system used as solvent was 6M-HOD.

The absorption spectra were scanned on an SF-8 double-beam grating spectrophotometer (LOMO, Leningrad) using D_2O as the reference medium. The cells were thermostated to within $\pm 0.1°C$ by means of the device described previously[23]. The solutions were set up and the spectra evaluated according to[2].

RESULTS AND DISCUSSION

The absorption bands of HOD at 1 416 nm (7 062 cm^{-1}) and 1 556 nm (6 427 cm^{-1}) are due[2] to vibrations of the free and hydrogen-bonded OH groups, respectively. In accordance with this assignment, the absorbance of the former band increases with temperature while that of the latter band decreases. The absorbance ratio
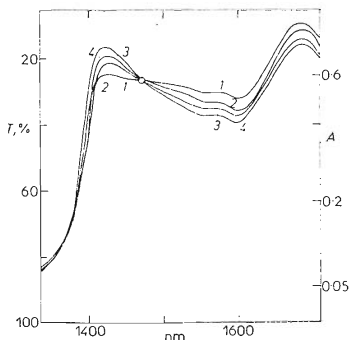

Fig. 1

Effect of sodium peroxodisulphate on the absorption spectrum of HOD; $c_{HOD} =$ = 6 mol dm^{-3}, temperature 25°C, cell thickness 1 cm, reference system: D_2O. Concentration of $Na_2S_2O_8$ (mol l^{-1}): *1* 0, *2* 0.5, *3* 1.0, *4* 1.5
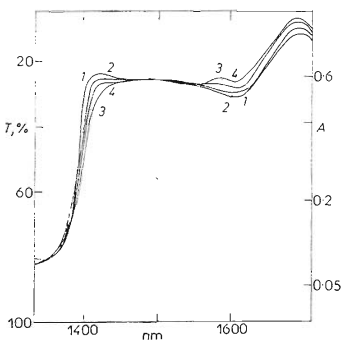
Fig. 2

Effect of dimethyl sulphoxide on the absorption spectrum of HOD; $c_{HOD} = 6$ mol . . dm^{-3}, temperature 25°C, cell thickness 1 cm, reference system: D_2O. Concentration of dimethyl sulphoxide (mol l^{-1}): *1* 0, *2* 1.0, *3* 2.0, *4* 4.0

$R = A_{1556}/A_{1416}$ can be looked upon as a measure of the structure of the solution under study. For HOD solutions in D_2O, the obtained average value of 30 measurements at $25.0°C$ was $\langle R_{HOD} \rangle = 0.876 \pm 0.006$. The inverse value of R_{HOD} served as a normalization factor by which the absorbance ratios were multiplied to obtain the normalized ratios R_N, whose values can be greater or less than unity according to whether the solute promotes or disturbs the cluster structure of water.

A typical example of the effect of solute on the absorption spectrum of HOD is shown in Fig. 1. Additions of peroxodisulphate caused the absorbance at 1 416 nm to increase and that at 1 556 nm to drop. The curves passed through an isosbestic point at 1 468 nm ($6\,812\ cm^{-1}$), similarly as those of pure 6M-HOD at different temperatures[2]. The occurrence of the isosbestic point is a direct consequence[24] of the two absorbing species, *viz*, the free and hydrogen-bonded HOD molecules, co-existing in a simple equilibrium

$$(HOD...HOD)_n \;\rightleftharpoons\; (HOD..HOD)_{n-m} + m\,HOD\,. \qquad (B)$$

Solutes disturbing the cluster structure of water cause the equilibrium to shift to the right side, those promoting the structure shift it to the left side. Among substances of the latter group is, for instance, dimethyl sulphoxide, which induces a marked absorbance decrease at 1 416 nm and increase at 1 556 nm (Fig. 2). Most of the

TABLE I

Normalized absorbance ratios R_N for electrolytes disturbing the cluster structure of water at 25°C

Electrolyte	c mol dm^{-3}	R_N
NaCl	1·0	0·944
	2·0	0·869
KCl	1·0	0·932
	2·0	0·869
NaN$_3$	1·0	0·939
	2·0	0·879
NaSCN	1·0	0·876
KSCN	1·0	0·878
NaClO$_4$	1·0	0·766
Na$_2$S$_2$O$_8$	0·5	0·840
	1·0	0·725
	1·5	0·625
K$_3$[Fe(CN)$_6$]	0·25	0·901
	0·5	0·800
	1·0	0·644

TABLE II

Normalized absorbance ratios R_N for electrolytes promoting the cluster structure of water at 25°C

Electrolyte	$\dfrac{c}{\text{mol dm}^{-3}}$	R_N
Li_2SO_4	1·0	1·016
	2·0	1·054
$(C_4H_9)_4NBr$	1·0	1·095
$MgSO_4$	1·0	1·109

TABLE III

Normalized absorbance ratios R_N for nonelectrolytes at 25°C

Substance	$\dfrac{c}{\text{mol dm}^{-3}}$	R_N
Urea	1·0	0·933[a]
Acetonitrile	1·0	0·981
	2·0	0·951
	4·0	0·892
Pyridine	1·0	1·019
	2·0	1·033
Acetone	1·0	1·013
	2·0	1·027
Dioxane	1·0	1·032
	2·0	1·060
Dimethylformamide	1·0	1·044
	2·0	1·076
Tetrahydrofuran	1·0	1·047
	2·0	1·080
Dimethyl sulphoxide	1·0	1·054
	2·0	1·123
	4·0	1·227
18-Crown-6	1·0	1·052

[a] The isosbestic point is shifted from 1 468 nm to 1 505 nm.

electrolytes affected the absorption spectrum in a way labelling them as the cluster structure disturbing substances, whereas only few of them exerted an opposite effect. The normalized absorbance ratios for the two groups of electrolytes and for the investigated nonelectrolytes are given in Tables I, II, and III, respectively. The shift of the isosbestic point observed in the case of urea is obviously due to complex interactions between water molecules and this solute[25]. Still, the R_N value classes urea among substances disturbing the liquid water structure, which is in accordance with the conclusions of the work[26]. Of interest is the considerable disturbing effect of peroxodisulphate and hexacyanoferrate(III) ions. As the data of Table I indicate, their effect exceeds that of sodium perchlorate, considered as typical active substance in this respect[2,20,21,27]. As to the organic compounds, all of them except urea and acetonitrile are substances favouring the cluster structure of water, the effect being most pronounced in the case of dimethyl sulphoxide and the cyclic polyether, 1-crown--6. One of the conceivable mechanisms that may bring about an increase in the number of hydrogen bonds is formation of 1 : 1 or 1 : 2 complexes with water, proved to take place with acetone, dioxane, dimethyl sulphoxide, and some other organic compounds[6,8,9,28]. The complex formation, however, cannot be the sole phenomenon governing the number of hydrogen bonds, as it occurs, for instance, also in aqueous solutions of acetonitrile[9], which is among the cluster structure disturbing substances (Table III).

The temperature dependence of the absorbance ratio obeys van't Hoff's reaction isotherm

$$\ln R = -\Delta H^0/RT + B \, , \tag{1}$$

TABLE IV

Standard enthalpies of hydrogen bond formation ΔH^0 and structure temperatures T_{str} of electrolyte solutions; concentration 1 mol dm^{-3}, experimental temperature 298·1 K

Electrolyte	$-\Delta H^0$ kJ mol^{-1}	T_{str} K
NaSCN	9·5	307·7
NaClO$_4$	9·1	319·0
K$_3$Fe(CN)$_6$	7·5	321·7
Na$_2$S$_2$O$_8$	8·3	322·2
MgSO$_4$	9·3	291·4
(C$_4$H$_9$)$_4$NBr	11·5	292·1

where ΔH^0 is the standard enthalpy of the hydrogen bond formation. The dependence of $\ln R$ on $1/T$ was in all cases linear over the region of $13-45°C$, which made it possible to determine the ΔH^0 value and, in the sense of their definition[29], also the structure temperatures of the substances concerned (Table IV). For the pure 6M-HOD solution in D_2O, $\Delta H^0 = -10.4 \pm 0.3$ kJ mol^{-1}, which agrees well with the published values of -9.92, -11.7, and -14.2 kJ mol^{-1} (refs[2,30,31], respectively).

Some conclusions concerning the relations between the nature of the solute and its effect on the structure of water can be drawn based on the R_N values measured and the results of other works dealing with this topic. Apparent is particularly the effect of the hydrophobic part of the molecule or ion, similarly as was the case with quaternary ammonium salts[2,32]. When the organic (hydrophobic) part is bulky enough, the substance has a marked promoting effect on the cluster structure of water. If, on the contrary, atoms capable of hydrogen bond formation are present in the molecule or ion, the structure disturbing effect occurs. This view is supported by the well-known effect of perchlorate ions as well as by the presented pronounced disturbing effect of peroxodisulphate and hexacyanoferrate(III) ions. Hydrogen bond formation between HOD molecules and the solute anions disturbs the stability of the $(HOD)_n$ aggregations. If both hydrophobic groups and atoms capable of hydrogen bond formation are present in a molecule or ion, the influence on the cluster structure is governed primarily by the size of the hydrophobic part. The data of Table III are consistent with this assumption: except for acetonitrile and urea, in which the hydrophobic part of the molecule is small in size, all of the organic compounds are among the liquid water structure promoting substances, although each of them contains oxygen or nitrogen atoms. In terms of this concept it is not possible to interpret the structure promoting effect of sulphate (Table II), in the case of magnesium sulphate even exceeding that of the tetrabutylammonium ion. This fact calls for additional experimental investigation. In the light of the results achieved, the division of solutes into the two groups of structure promoting or disturbing substances based solely on the size of the molecule (ion) and its charge[27] appears to be too crude. Another conclusion arrived at is that the solutes can affect the cluster structure of water to an appreciable extent only if present in a sufficiently high concentration.

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