IR and NMR Studies of Hydrogen Bonding in Hexan-1-ol–Tetrabutylammonium Iodide Solutions in the Temperature Range 28–145 °C and in Tetrachloromethane

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IR spectra of (Bu_4NI)–hexan-1-ol solutions at 25, 55, 85, 115 and 145 °C in the OH stretching region have been investigated. The OH stretching spectra and the ^1H NMR chemical shifts of the hexanol OH-group were obtained from Bu_4NI–hexanol–CCl_4 solutions in the alcohol concentration range 3×10^{-3}–7.8 mol dm^{-3}. The relationship between absorbance and wavenumber is represented as the product of a Lorentzian and a Gaussian curve. Using this dependence deconvolution of the OH-band was carried out by the Simplex method. From these data, it was established that Bu_4NI is a structure-breaker at moderate temperatures and/or low concentrations of CCl_4. At higher temperatures or in very dilute solutions of Bu_4NI–hexanol in CCl_4, Bu_4NI is observed to be a structure-maker.

Based upon the statistical-mechanical theory of electrolyte solutions the square-mound potential $d_\pm/k_B T$ for some 1 : 1 electrolytes in alcohol solutions was calculated in our previous work.[1,2] The perturbation energy $d_\pm$ could be approached as the Gurney cosphere overlap Gibbs energy, and is the sum of many effects relating to the relative energies of interaction of the free ions and ion pairs with the surrounding solvent.[3,4] For most 1 : 1 electrolyte alcoholic solutions, especially those of higher alcohols, $d_\pm/k_B T$ increases with temperature[1] and corresponds to the energy gain of an ion in alcohol medium as compared with an ion-pair (without considering the Coulombic part of the interionic potential). From a comparison of the temperature dependences of square-mound potentials and the Gibbs energy of intermolecular interaction calculated using the theory of dielectric liquids, the sign and values of the temperature change of $d_\pm/k_B T$ are determined by the orientational correlations of dipoles of the solvent molecules. In alcoholic solutions the most important role is played by chain association units.

Starting from these conclusions, the purpose of the present paper may be formulated as follows: to investigate the influence of electrolyte on alcohol association over a wide temperature range by a direct experimental method. For this purpose the IR spectra of Bu_4NI–hexan-1-ol solutions at 25, 55, 85, 115 and 145 °C in the OH stretching region have been investigated. The OH stretching spectra and ^1H NMR chemical shifts of the hexan-1-ol (hexOH) OH-group were also obtained from Bu_4NI–hexOH–CCl_4 solutions in the concentration range 3×10^{-3}–7.8 mol dm^{-3} at room temperature. In contrast to lower homologues the relatively high boiling temperature of hexan-1-ol (157.1 °C) allows one to carry out the investigation at an elevated temperature without special instrumentation. Furthermore, the temperature range is in accord with our previous studies.[1,2] A literature overview has demonstrated that the majority of spectral investigations of alcohol solutions involve studies of lower alcohols at room or low temperatures.[5–11]

The use of Bu_4NI as an electrolyte enables us to simplify the interpretation of the spectra because of the absence of any influence of the Bu_4N^+ ion on the IR and NMR OH-group spectra.[12] The choice of this salt was dictated by its good solubility not only in hexOH, but also in the inert solvent CCl_4, which was used as an analogue of the effects of temperature on the alcohol self-association.

Experimental

Hexan-1-ol was dried for 10 days over freshly made K_2CO_3, then fractionally distilled under a pressure of 100 Pa. The water content in the alcohol was determined by the Karl–Fisher method and did not exceed 0.01%. The Bu_4NI used was of 'pure' grade and was recrystallizated six times from a benzene–hexane mixture. The final drying was performed at 55 °C and 1 Pa over P_2O_5. CCl_4 was boiled with P_2O_5 for 5 h and distilled. IR spectroscopic measurements were made on a double-beam Specord M80 spectrometer in NaCl, LiF and CaF_2 cells. CaF_2 cells were used at room temperature (28 °C) for pure hexOH and Bu_4NI–hexOH solutions, NaCl cells for measurements in CCl_4 medium. Our home-made LiF cell was used for multi-temperature investigations.

Nuclear magnetic resonance studies were made on a Tesla BS-487-B 80 MHz spectrometer at room temperature. ^1H chemical shifts were measured relative to hexamethyldisilane, which was added to samples in trace amounts. The following OH stretching spectra of hexOH were studied: (*a*) pure hexOH (I) and solutions of Bu_4NI in hexOH (II) (molality 0.56 mol kg^{-1}) at 28, 55, 85, 115 and 145 °C; (*b*) solutions of (I) in CCl_4 (III) and solutions of (II) in CCl_4 (IV) with a minimum concentration of alcohol of 4×10^{-3} mol dm^{-3}. All hexOH–Bu_4NI–CCl_4 solutions were made by dilution of (II) in pure CCl_4. This made it possible to keep the alcohol : electrolyte molar fraction constant (18 : 1) in all the solutions.

NMR spectra were obtained from systems (III and IV) at 28 °C.

Results and Discussion

Experimental spectra in the OH stretching region are shown in Fig. 1 and 2. Both for pure alcohol and for electrolyte solution the polymeric alcohol band shifted to higher wavenumbers and the intensity of the monomer band increased with temperature or CCl_4 concentration. In a qualitative sense these conclusions have long been known.[5–10,13–15] However, there are no quantitative descriptions of a simultaneous influence of higher temperature and electrolyte on the OH band profile resulting from alcohol self-association by hydrogen bonding.

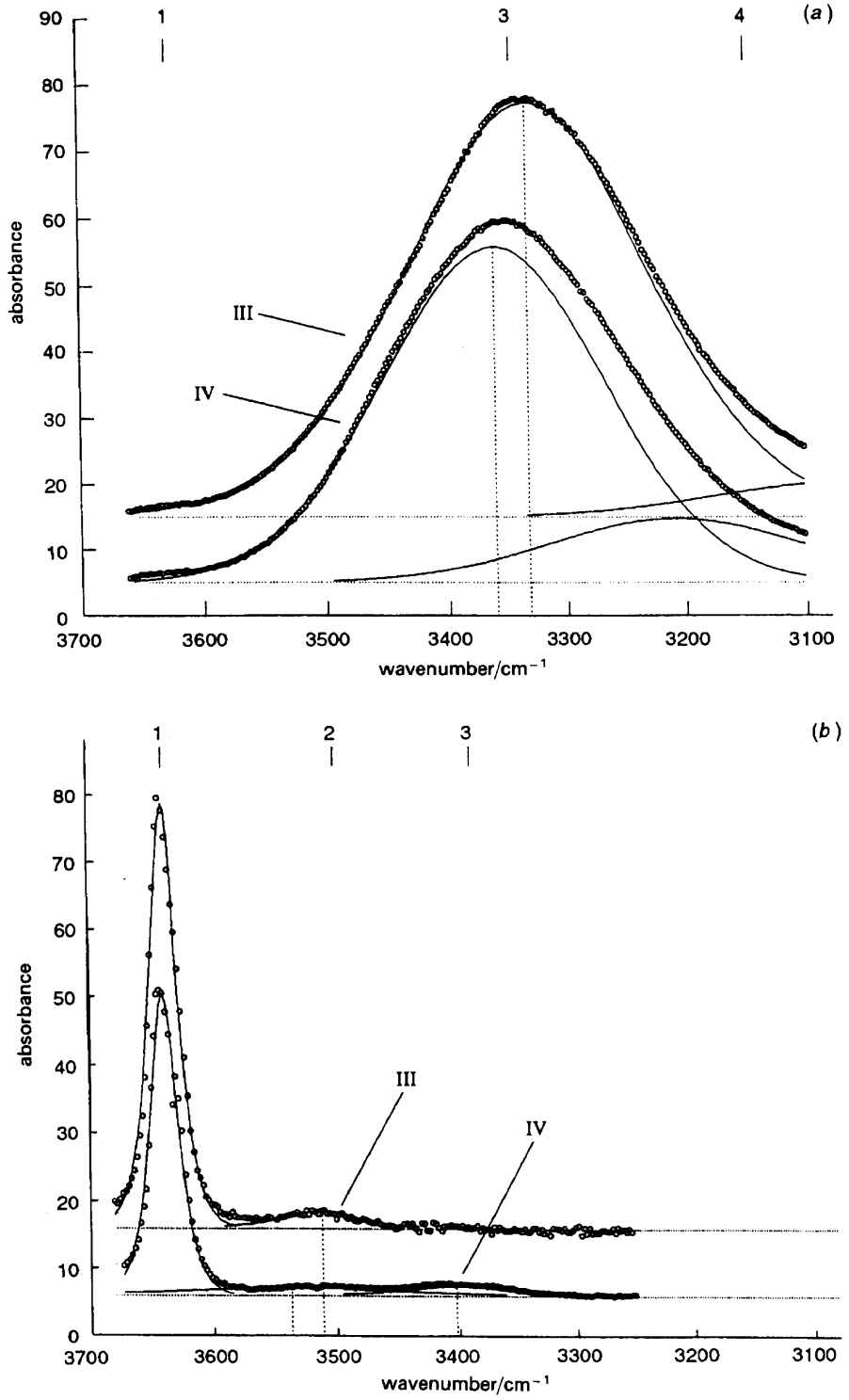


Fig. 1 Experimental (circles) and calculated (lines) IR spectra of hexOH–CCl_4 (III) and hexOH–Bu_4NI–CCl_4 (IV) solutions at 28 °C with alcohol concentrations of (*a*) 3.5 and (*b*) 0.015 mol dm^{-3}. The numbers on the top of each figure correspond to calculated bands.

We used an algorithm suggested by Symons[6] to compute the approximate band shape:

$$A_{calc} = \left[B + \sum_{i=1}^{m} A_i(\nu)\right] \log e \quad (1)$$

$$A_i(\nu) = A_{0,i} L_i(\nu) G_i(\nu) \quad (2)$$

$$L_i(\nu) = \frac{1}{1 + (2^{1-\beta})(\nu_{max,i} - \nu)^2/\sigma_i^2} \quad (3)$$

$$G_i(\nu) = \exp\left(-\beta \ln(2) \frac{(\nu_{max,i} - \nu)^2}{\sigma_i^2}\right) \quad (4)$$

In eqn. (1)–(4) A_{calc} is the calculated intensity, A_i is the absorbance of each unit, B is the base line, $A_{0,i}$ is the band height, L_i and G_i are Lorentzian and Gaussian terms, respectively, ν_{max} is the band position in abscissa units, σ is the half-bandwidth at half-height, m is the number of bands producing the overall envelope, β is a Gaussian contribution, ν is the abscissa value at which the absorbance is to be calculated.

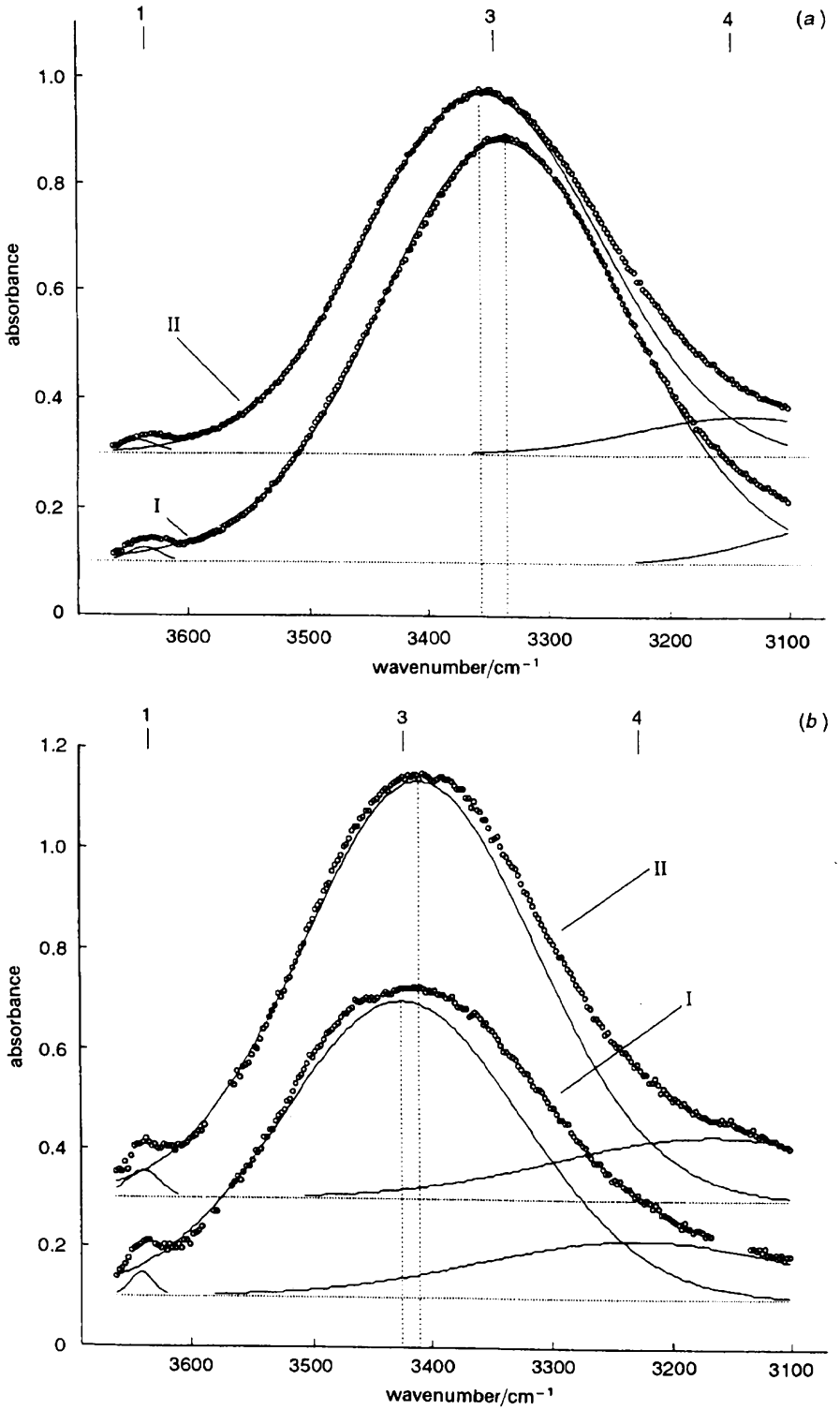


Fig. 2 Experimental (circles) and calculated (lines) IR spectra of pure hexOH (I) and hexOH–Bu_4NI (II) solutions at (*a*) 55 and (*b*) 115 °C

Deconvolution of the experimental band shape was carried out by minimizing the sum of square deviation Q for k experimental points:

$$Q = Q[B, \beta, (A_{0,i}, \nu_{\max,i}, \sigma_i)_{i=1,m}] = \sum_{j=1}^{k} (A_{j,\text{exp}} - A_{j,\text{calc}})^2 \quad (5)$$

The individual band parameters ($A_{0,i}$, $\nu_{\max,i}$, σ_i) and the common parameters β and B were altered until a good fit with the experimental band was obtained. Eqn. (5) was minimized by the Simplex method.[16] As a statistical evaluation of fitted parameters the diagonal elements of the covariation matrix were used:

$$\Delta X_i = (\text{cov } X)_{ii} = \sqrt{[s^2(H^{-1})_{ii}]} \quad (6)$$

$$s^2 = \frac{Q}{m-n} \quad (7)$$

where H is the matrix of the second derivatives of Q with respect to X and s is the approximation dispersion.

The results of data handling by the algorithm outlined above are presented in Table 1 (for III and IV) and Table 2

Table 1 IR spectra of OH-group vibration in hexOH–CCl_4 (III) and hexOH–CCl_4–Bu_4NI (IV) solutions at 28 °C

	n^a	band height	band width	band position
III				
$c = 0.004$,[b] $\beta = 0.05$, $s = 0.017$	1	154 ± 2	11.7 ± 0.2	3639(±9 × 10^{-4})
$c = 0.02$, $\beta = 0.17$, $s = 0.005$	1	145 ± 5	12.7 ± 0.5	3639(±2 × 10^{-4})
	2	5.9 ± 0.6	37 ± 5	3511(±1 × 10^{-6})
$c = 0.04$, $\beta = 0.16$, $s = 0.025$	1	140 ± 5	13.1 ± 0.5	3639(±1 × 10^{-3})
	2	13.2 ± 0.7	51 ± 5	3520(±1 × 10^{-5})
	3	4.9 ± 0.5	70 ± 11	3377(±5 × 10^{-6})
$c = 0.07$, $\beta = 0.29$, $s = 0.086$	1	121 ± 16	13 ± 1	3639(±3 × 10^{-3})
	2	15 ± 3	49 ± 6	3509(±9 × 10^{-5})
	3	10 ± 2	102 ± 15	3366(±3 × 10^{-5})
$c = 0.97$, $\beta = 0.53$, $s = 0.002$	1	22 ± 2	13 ± 2	3636(±5 × 10^{-6})
	3	241 ± 21	119 ± 8	3343(±2 × 10^{-6})
	4	17 ± 58	69 ± 16	3055(±2 × 10^{-6})
$c = 3.42$, $\beta = 0.65$, $s = 0.003$	1	6.0 ± 0.5	15 ± 2	3636(±4 × 10^{-6})
	3	180 ± 12	120 ± 6	3338(±1 × 10^{-5})
	4	15 ± 14	76 ± 9	3068(±9 × 10^{-6})
$c = 6.68$, $\beta = 0.68$, $s = 0.03$	1	2.4 ± 0.3	15 ± 2	3637(±4 × 10^{-6})
	3	133 ± 8	120 ± 5	3335(±3 × 10^{-5})
	4	12 ± 6	106 ± 11	3056(±1 × 10^{-5})
$c = 7.98$, $\beta = 0.66$, $s = 0.005$	3	144 ± 7	119 ± 4	3331(±8 × 10^{-5})
	4	12 ± 4	126 ± 16	3067(±1 × 10^{-5})
IV				
$c = 0.0036$, $\beta = 0.14$, $s = 0.011$	1	119 ± 6	12.8 ± 0.6	3639(±4 × 10^{-4})
	3	0.5 ± 1	106 ± 347	3422(±1 × 10^{-7})
$c = 0.01$, $\beta = 0.19$, $s = 0.14$	1	103 ± 11	13 ± 1	3639(±5 × 10^{-3})
	2	2.7 ± 0.6	99 ± 106	3536(±1 × 10^{-5})
	3	3 ± 2	49 ± 21	3402(±3 × 10^{-5})
$c = 0.03$, $\beta = 0.21$, $s = 0.017$	1	109 ± 8	12.7 ± 0.8	3639(±5 × 10^{-3})
	2	6.1 ± 0.8	51 ± 9	3536(±1 × 10^{-5})
	3	7 ± 1	63 ± 9	3402(±3 × 10^{-5})
$c = 0.06$, $\beta = 0.29$, $s = 0.059$	1	9991 ± 11	13 ± 1	3639(±2 × 10^{-3})
	2	9 ± 1	38 ± 5	3508(±5 × 10^{-5})
	3	14 ± 2	62 ± 6	3392(±5 × 10^{-5})
$c = 1.16$, $\beta = 1.00$, $s = 0.00006$	1	17 ± 1	16 ± 1	3636(±1 × 10^{-6})
	3	192 ± 16	119 ± 7	3361(±3 × 10^{-6})
	4	18 ± 64	106 ± 23	3076(±1 × 10^{-6})
$c = 3.71$, $\beta = 1.00$, $s = 0.001$	1	5.7 ± 0.2	18.8 ± 0.9	3635(±2 × 10^{-6})
	3	155 ± 3	113 ± 1	3354(±3 × 10^{-5})
	4	16 ± 4	107 ± 7	3139(±2 × 10^{-6})
$c = 7.45$, $\beta = 1.00$, $s = 0.005$	3	117 ± 26	109 ± 12	3360(±5 × 10^{-4})
	4	22 ± 19	126 ± 29	3209(±1 × 10^{-4})

[a] Band number. [b] Concentration in mol dm^{-3}.

(for I and II). Typical resolutions of IR spectra for all of these systems is shown in Fig. 1 and 2. The resolved bands are labelled 1, 2 *etc.* from the high-frequency end. The band labels correspond to the band number in Tables 1 and 2.

We now focus on the bands matched to the condition of the hexanol OH-group in (I–IV). Band 1, with ν_{max} at *ca.* 3640 cm^{-1}, is the typical band of the fundamental vibration of the monomeric alcohol OH-group.[14] At ambient temperatures its intensity is vanishingly small in samples containing pure alcohol or in Bu_4NI–hexOH solutions. Only at higher temperature, and particularly in dilute CCl_4 solutions, is this band very much more pronounced (see Fig. 1 and 2 and Tables 1 and 2).

Furthermore, following Symons' results for methanol,[6] we suggest that band 2 at *ca.* 3570–3540 cm^{-1} corresponds to the fundamental vibration of the OH-group in terminal hexOH molecules in polymeric or dimeric association units. It may be represented by equilibria (i) and (ii), where S_n denotes a solvent that forms n hydrogen bonds.

The wide low-frequency band in system (I), according to our calculations, can be reconstructed with minimum of two symmetrical bands, as indicated in Fig. 1 and 2, with ν_{max} at *ca.* 3330–3430 cm^{-1} (labelled 3) and *ca.* 3045–3270 cm^{-1} (labelled 4). It should be pointed out that the hydrogen bonds for average doubly bonded hexOH molecules (S_2) are stronger than those formed by terminal molecules (S_1) in polymer or dimer units because of the reinforcing effect of the bond to oxygen. We assume that absorption band 3 in the fundamental (ν_{OH}) is due to doubly bonded hexOH molecules [see (ii)].

Except for chain association units, alcohol molecules form branched or 'bush' (group) associated units where triply bonded molecules (S_3) are necessarily present [Scheme 1 (iii)].[17]

For these molecules the reinforcing effect will naturally be much more than for S_2. Since the shift to low frequency is approximately proportional to the hydrogen-bond strength, we conclude that band 4 corresponds to vibration of the OH-groups of the S_3 molecules.

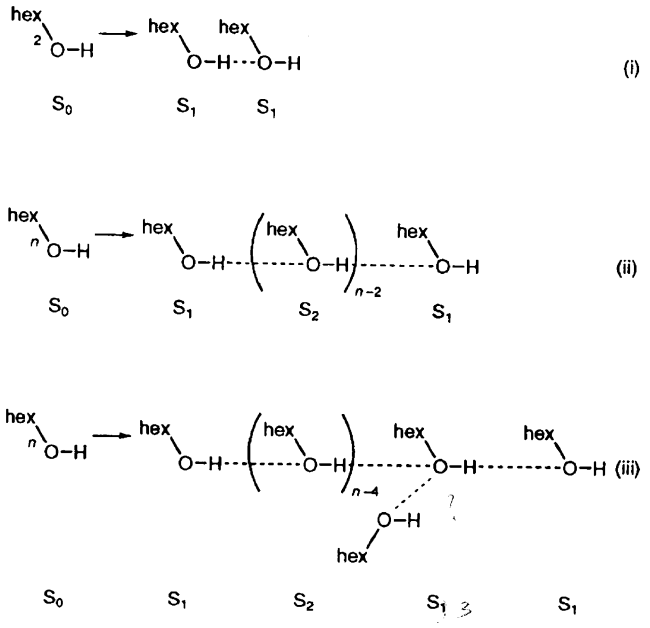
It has been determined from dielectric measurements[17] that chain-type association is dominant for normal higher alcohols. This fact is responsible for the greater intensity of band 3 as compared with band 4. The results of dielectric investigations[17] make it possible to establish that, in spite of the relatively long length of the hydrocarbon chain, the mean level of association of hexanol at 25 °C is as great as 11 [*i.e.* $n = 11$ in eqn. (ii)–(iii)]. These two factors complicate the detection of terminal molecules in spectra of pure hexOH. In this case, the spectra are reconstructed with two (at low temperatures) or three bands, 1, 3 and 4.

Note that ν_{max} for bands 2–4 is dependent on the presence

Table 2 IR spectra of OH-group vibration in pure hexOH (I) and hexOH–Bu_4NI (II) solutions at various temperatures

	n^a	band height	band width	band position
I				
$t = 28$,[b] $\beta = 0.66$, $s = 0.0052$	3	144 ± 7	119 ± 4	3331($\pm 9 \times 10^{-5}$)
	4	12 ± 4	126 ± 16	3067($\pm 2 \times 10^{-5}$)
$t = 55$, $\beta = 0.78$, $s = 0.0009$	1	0.8 ± 0.1	11 ± 2	3638($\pm 2 \times 10^{-6}$)
	3	409 ± 4	122 ± 9	3350($\pm 9 \times 10^{-6}$)
	4	5 ± 10	134 ± 29	3046($\pm 5 \times 10^{-5}$)
$t = 85$, $\beta = 1.00$, $s = 0.0009$	1	1.3 ± 0.2	11 ± 2	3640($\pm 2 \times 10^{-6}$)
	3	32 ± 5	126 ± 10	3378($\pm 2 \times 10^{-5}$)
	4	5 ± 15	185 ± 11	3055($\pm 6 \times 10^{-6}$)
$t = 115$, $\beta = 1.00$, $s = 0.0013$	1	2.4 ± 0.4	11 ± 2	3641($\pm 5 \times 10^{-6}$)
	2	30 ± 7	119 ± 12	3425($\pm 3 \times 10^{-5}$)
	3	6 ± 19	157 ± 51	3228($\pm 8 \times 10^{-6}$)
$t = 145$, $\beta = 1.00$, $s = 0.0003$	1	1.5 ± 0.9	16 ± 6	3443($\pm 8 \times 10^{-7}$)
	3	7 ± 3	109 ± 51	3506($\pm 8 \times 10^{-6}$)
	4	4 ± 4	133 ± 43	3270($\pm 8 \times 10^{-6}$)
	5	6 ± 74	97 ± 69	3084($\pm 8 \times 10^{-6}$)
II				
$t = 28$, $\beta = 1.00$, $s = 0.0052$	3	117 ± 26	109 ± 12	3360($\pm 5 \times 10^{-4}$)
	4	22 ± 19	126 ± 29	3206($\pm 1 \times 10^{-4}$)
$t = 55$, $\beta = 1.0$, $s = 0.001$	1	1.4 ± 0.1	27 ± 3	3644($\pm 8 \times 10^{-7}$)
	3	32 ± 3	108 ± 3	3397($\pm 2 \times 10^{-5}$)
	4	7 ± 7	153 ± 22	3209($\pm 6 \times 10^{-6}$)
$t = 85$, $\beta = 1.0$, $s = 0.0004$	1	1.4 ± 0.1	27 ± 3	3644($\pm 8 \times 10^{-7}$)
	3	32 ± 3	108 ± 3	3397($\pm 2 \times 10^{-5}$)
	4	7 ± 7	153 ± 22	3209($\pm 6 \times 10^{-6}$)
$t = 155$, $\beta = 1.00$, $s = 0.0009$	1	2.7 ± 0.1	15.6 ± 0.9	3639($\pm 6 \times 10^{-6}$)
	3	41 ± 1	115 ± 1	3423($\pm 2 \times 10^{-5}$)
	4	6 ± 2	154 ± 20	3164($\pm 2 \times 10^{-6}$)
$t = 145$, $\beta = 1.00$, $s = 0.001$	1	4.0 ± 0.2	12.1 ± 0.5	3639($\pm 6 \times 10^{-6}$)
	3	46.1 ± 0.7	113.7 ± 0.5	3423($\pm 2 \times 10^{-5}$)
	4	8 ± 1	147 ± 12	3164($\pm 2 \times 10^{-6}$)

[a] Band number. [b] Temperature in °C.



Scheme 1

of Bu_4NI, the CCL_4 concentration and the temperatures, unlike ν_{max} for monomeric band 1. This derives from the fact that, in effect, these bands are the sum of individual closely related bands due to the energetic states of the OH-group. That is, the influence of temperature and inert solvent leads to the distribution of the molecules amongst the possible conformations in the polymer, which is reflected in the intensities of the corresponding OH bands. As a result, the positions of the polymer bands change. This serves as a basis for the known empirical rule:[11,14,18]

$$\Delta H_{\text{H-bond}} = C(\nu_{\text{max, monomer}} - \nu_{\text{max, polymer}})^{1/2} \quad (8)$$

where C is a constant, *i.e.* the enthalpy change, ΔH, of H-bond formation depends upon the polymer band shift. Note that $\Delta H_{\text{H-bond}}$ can result from (*a*) a change in the energy (strength) of a fixed number of hydrogen bonds; (*b*) a change in the extent of hydrogen bonding with a fixed energy. For this reason, in our opinion, it is more proper to discuss ν_{max} in terms of structure-making and structure-breaking effects.

Taking into account eqn. (8), the position of polymer band 3 has been chosen as the quantitative characteristic of self-association of hexanol by hydrogen bonding.

Our results (Fig. 3 and Tables 1 and 2) indicate that there is no need for the introduction of an additional band that corresponds to the OH-group H-bonded with I^- ion in any of the spectra (large Bu_4N^+ ions are unlikely to form hydrogen bonds with alcohol molecules and do not greatly modify the total hydrogen bonding in alcohols[6,12]). The experimental overlapping curve may be represented by as many bands as for pure hexOH without any essential difference in dispersion (Table 1, 2). Moreover, as shown in Fig. 3, within the standard deviation, the width of band 3 does not depend on the presence of electrolyte. That is, the bands 3 and 4 in systems with and without Bu_4NI are the same.

Summarizing, we can contend that the influence of temperature, inert solvent and electrolyte on the state (strength) of hydrogen bonds in liquid hexanol can be described with the aid of a single qualitative characteristic, namely, the position of the polymer band 3 (ν_{max}) (at least for an electrolyte such as Bu_4NI).

There is another important reason for this conclusion. As follows from quantum-chemical calculations[11] of the hydrogen-bonded complex of ethanol with Br^-, the alcohol

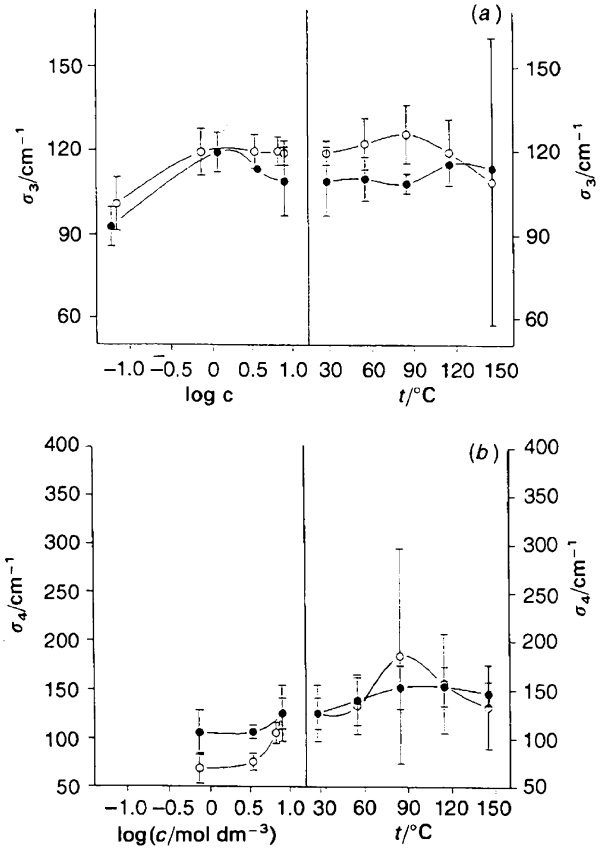


Fig. 3 Width of (*a*) polymer band 3 and (*b*) polymer band 4 of OH-group at various temperatures (on the right: ○, I; ●, II) and alcohol concentrations (on the left: ○, II; ●, IV)

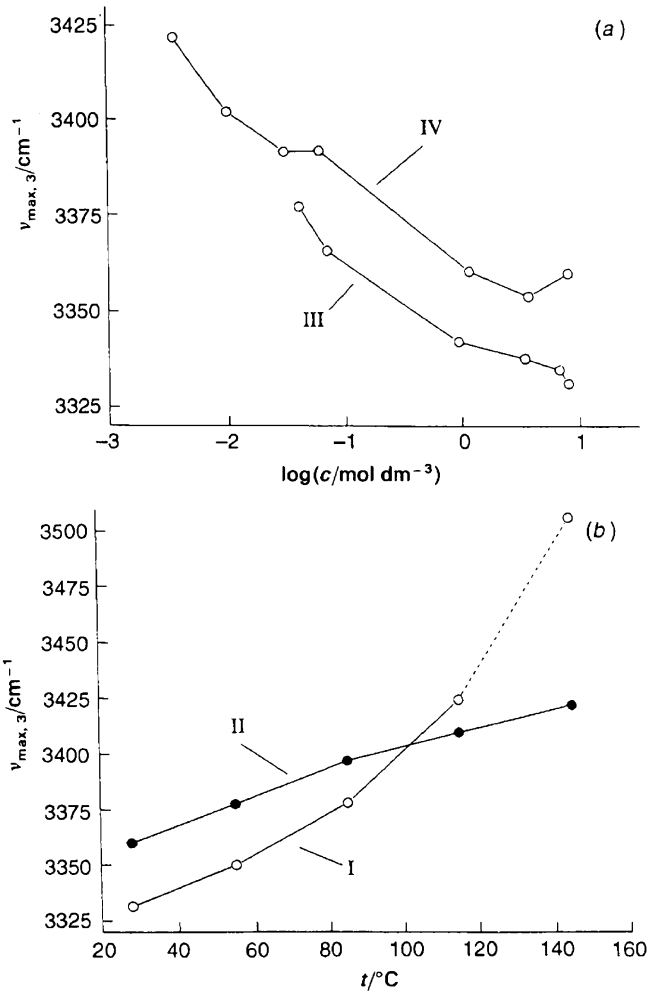


Fig. 4 Polymer band 3 position *vs.* concentration of alcohol (*a*) for hexOH–CCl_4 (II) and hexOH–Bu_4NI–CCl_4 (IV) solutions and *vs.* temperature (*b*) for pure hexOH (I) and hexOH–Bu_4NI (II) solutions

molecule is brought into the strong negative field of the anion. As this takes place, about 10% of the negative electrostatic potential of Br^- is retained at a range of three intervals between the hydrogen of the alcohol molecule and the Br^- ion (1.0–1.5 nm). In the condensed phase we conclude that the magnitude of this field offers the possibility of a large influence of the anion on reformation of hydrogen bonds between alcohol molecules at long distances from the anion. This deduction correlates well with the appreciable change in ν_{max} of band 3 in spite of the low content of electrolyte molecules (1 : 18). For example, at 28 °C ν_{max} of band 3 for pure hexOH is 3331 cm^{-1} and that for Bu_4NI solution is 3360 cm^{-1}; this corresponds to an increase of temperature of 50 °C for pure hexOH.

The main results of this work may be represented by the dependence of polymer band position (ν_{max}) *vs.* concentration of an inert solvent [CCl_4, Fig. 4(*a*)] or temperature [Fig. 4(*b*)] for all solutions investigated (I–IV).

Conclusions

When the intrinsic structure of the solvent is clearly defined (low temperature, low inert solvent concentration) an electrolyte, such as Bu_4NI, plays a structure-making role.

In contrast, if some conditions (higher temperature, near the boiling point, very dilute solutions in the inert solvent) led to significant destruction of the set of hydrogen-bonds in alcohol, the electrolyte (even one such as Bu_4NI) could act as a structure-maker, that is it could lead to the reinforcement of hydrogen bonds in the solvent.

This result is supported by the results of NMR investigations (Table 3). It is known[13] that hydrogen-bond formation leads to a downfield shift of the hydroxy proton chemical shift. The hydroxy proton peak for hexOH in Bu_4NI solutions (IV) is upfield compared with systems without electrolyte, *i.e.* δ(III) > δ(IV), whereas in dilute solutions δ(III) < δ(IV) (Table 3). This difference corresponds to an alcohol concentration of *ca.* 0.06 mol dm^{-3} (*cf.* 0.04 mol dm^{-3} from IR measurements).

Table 3 ^1H Chemical shifts (δ) of hexOH OH-group for hexOH–CCl_4 (III) and hexOH–CCl_4–Bu_4NI (IV) solutions at 28 °C as a function of alcohol concentration (*c*)

c/mol dm^{-3}	δ
III	
0.005	0.931
0.009	1.288
0.018	2.000
0.048	3.188
0.094	3.863
0.191	4.344
0.492	4.813
0.741	5.044
1.000	5.200
IV	
0.005	1.013
0.010	1.388
0.018	2.150
0.051	3.250
0.096	3.848
0.187	4.225
0.483	4.650

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