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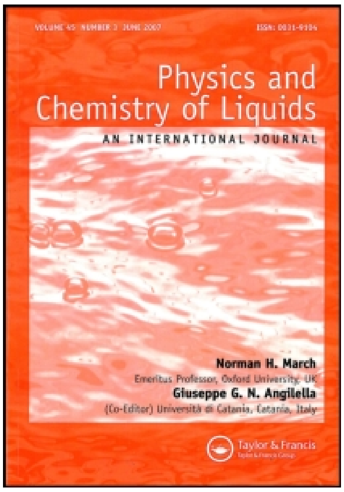

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DYNAMICAL EVIDENCE OF AGGREGATES IN ISOMERIC ALCOHOLS MIXTURES BY O—H STRETCHING BAND ANALYSIS

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Polarized and depolarized Raman data in mixed isomeric alcohols *n*-Pentanol and 2-Methyl-2-Butanol are presented. The spectra, obtained as a function of temperature and concentration, have been performed in the intramolecular O—H stretching region. The analysis of the spectral features of the deconvoluted bands, center frequency, percentage intensity and halfwidth, performed in the frame of a previous investigation on the pure components, shows that the aggregative processes, present in these H-bonded liquids, reflect themselves also on this spectral region furnishing evidence that, as evidenciated by other techniques, in the 2M-2BuOH rich region, the formation of hetero-structures, determining a strengthened respect to the more "fragile" pure tertiary alcohol, is present.

KEY WORDS: Associated liquids, vibrational spectroscopy

1 GENERAL CONSIDERATIONS

The physical and chemical properties of associated systems have been extensively studied from a theoretical and experimental point of view[1,2,3].

It is commonly accepted that the existence of the highly directional hydrogen bond, whose energy value ranges between 2 and 6 Kcal/mol, strongly influences the kinds of inter-molecular arrangements present in H-bond liquids. Being the mean life time of this peculiar bond in the psec time scale, these systems can be considered as "transient" ones in dynamical equilibrium, with time steps triggered by the breaking and the reforming of the bonds.

The investigation of isomeric alcohols like *n*-Pentanol (*n*-PeOH) and 2-Methyl-2-Butanol (2M-2BuOH) allows to obtain a better insight into the complex nature of the O—H bond. Owing to the difference between the lengths, the degree of branching of the alkyl chain and to the position of the O—H group, these two isomers exhibit different aggregative properties. In particular Raman[4,5], IR[5], static dielectric and viscosity[6] measurements indicate for the linear alcohol (*n*-PeOH) the existence of monomers, dimers and oligomers with an aggregation degree higher than two having a structural arrangement similar to a zig-zag chain[7]; in 2M-2BuOH, instead, because of its intrinsic steric hindrance, only the presence of monomers and dimers (open and cyclic) is revealed.

Moreover ultrasonic, hypersonic, viscosity and dielectric measurements[8,9] suggest that a unique mechanism, the making and breaking of the intermolecular H-bond, triggers a structural relaxation (at low frequency) and a shear relaxation (at high frequency). In the case of 2M-2BuOH also a coupling between internal rotations and structural changes has to be considered for explaining the acoustic relaxation.

The mixing of the two alcohols shows a clear departure from the ideal mixing behaviour as confirmed by volumetric and thermodynamic studies[10]. More precisely, a volume contraction phenomenon, in the *n*-PeOH poor region, has been observed. Furthermore the molar excess heat capacity shows a S-shape behaviour with the minimum in the *n*-PeOH rich region and the maximum in the opposite mixture concentration one. Maldestam–Brillouin measurements[11] as a function of scattering angle, temperature and concentration, in the mixture, reveal the existence of a shear relaxation phenomenon, similar to the one detected in the two pure alcohols, whose activation enthalpy closely remembers the behaviour, as function of concentration, of the molar excess heat capacity. In addition the excess dilution enthalpy exhibits an esothermic effect when the linear alcohol is added to the more sterically hindered component. Such an experimental evidence suggests that the adding of *n*-PeOH to the more molecular tertiary alcohol, favours the formation of new hetero-alcoholic aggregates.

On the other hand in the more associated *n*-PeOH rich region the presence of 2M-2BuOH gives rise to a destructuring effect in the original connectivity of the pure linear alcohol.

The molar refractivity as a function of mixture composition and temperature[12] indicates that the hetero-structures present in the 2M-2BuOH rich region are more polarized than the cyclic dimers of the tertiary alcohol.

Moreover, the Kirkwood correlation factor behaviour as a function of concentration suggests the presence of cyclic dimers ($g_k < 1$) in the pure 2M-2BuOH and the formation of open dimers (homo and hetero) ($g_k > 1$) by increasing the *n*-PeOH content. Finally viscosity data[11,12] evidenciate a maximum of the 2M-2BuOH rich region that has been attributed to hindered hetero-structures.

The present work represents a part of an extensive study that our group have carried out on isomeric alcohols and on their mixtures by means of several spectroscopic techniques[4,5,9,11]. The aim of this paper is to show that the aggregative processes present in such mixtures reflect themselves on the O—H stretching region of the Raman spectra.

It's well known that the study of this spectral region, yields information about the vibrational dynamics. The original narrow O—H band centered at $\sim 3600\ \mathrm{cm}^{-1}$ in the gas phase presents a low wave-number shift, a broadening of the shape and an intensity variation going towards the liquid phase. Furthermore, the study of the evolution of this band furnishes information about the different aggregative forms of intermolecular arrangements and about their relative population.

The polarized spectral components were deconvoluted in symmetrical bands whose center frequency, half-width at half maximum (HWHM) and intensity, when concentration and temperature change, allow to clarify the evolution of the different conformational arrangements of the mixtures in their not ideal mixing process.

2 EXPERIMENTAL SET-UP AND DATA ANALYSIS

The liquid samples were prepared starting from high-purity *n*-PeOH and 2M-2BuOH (certified grade quality products), purified as previously described[8,10,12]. The alcoholic mixtures were prepared by weight and filtered in order to remove physical impurities. The preparation was performed inside an Ar-filled dry-box to avoid water contamination. The resulting samples showed a water content less than 0.01 ± 0.001 as measured by vapor phase chromatography. The investigated molar fraction values [*n*-PeOH]/[2M-2BuOH] were: 1.1180, 0.2056, 0.4616 and 0.7081. Deuterated pure *n*-PeOD and 2M-2BuOD alcohols and their mixtures were also considered to evaluate the C—H contribution that overlaps with its wing to the O—H one.

We used a 90° scattering geometry with a fully computerized SPEX RAMALOG 5 triple monochromator equipped with a CD2A compudrive using the 4880 Å line of a unimode SPECTRA PHYSICS Ar^+ laser, working at ~500 mW, as exciting source. The measurements were performed in the spectral range of 2500 ÷ 4000 cm^{-1}

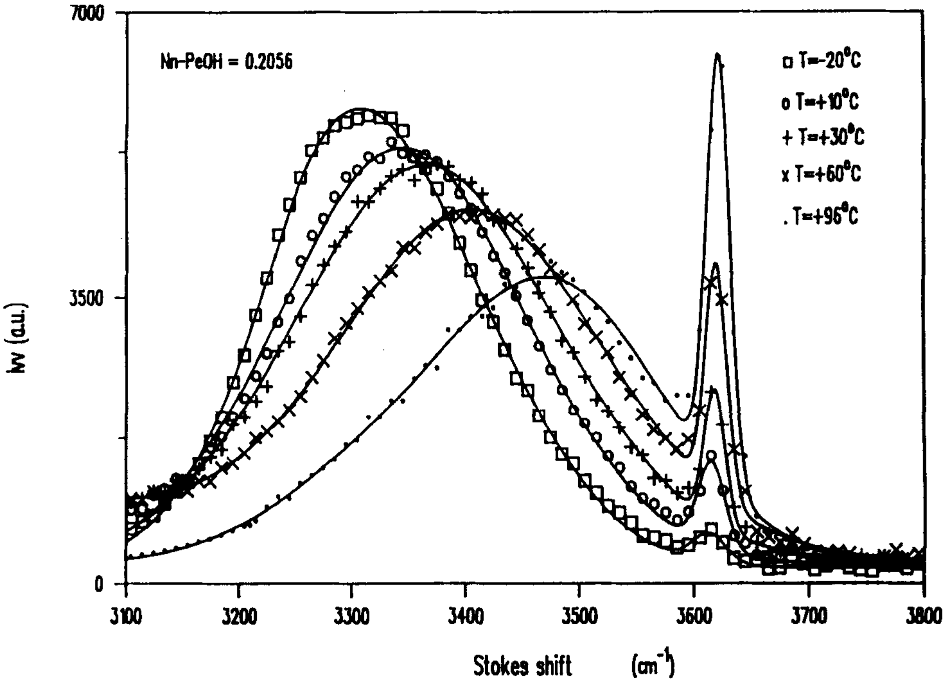

Figure 1 Raman spectra in the VV polarization geometry for the molar fraction value of 0.2056 at different temperatures. Squares, circles, crosses, stars and dots: experimental data; continuous lines: theoretical fits.

of the Stokes shift with a resolution of 5 cm^{-1} in the VV and VH polarization geometries in the temperature region from −20°C to 110°C. In particular for the temperatures of −20°C, 10°C, 30°C and 60°C we used a Harney–Miller thermostat, whereas for $T = 60°\text{C}$, 90°C and 110°C an especially designed optical thermostat with a temperature stability better than 0.1°C, in the whole range investigated.

The signal detection and the normalization of the recorded Raman signals were controlled by a compatible IBM PC/XT computer connected with the spectrometer[13]. By using a motor-driven polarizer, it was possible, for each step time of the instrument, to monitor simultaneously the contribution I_{VV} and I_{VH} of the spectra.

Moreover, the simultaneous normalization of the signal with the exciting laser light allows to avoid the effect of the unwanted laser line instability.

Figure 1 represents, as an example, the Raman spectra in the VV polarization geometry for the molar fraction value of 0.2056 at different temperatures. The C—H stretching vibrational band, that spreads over the 2800 ÷ 3200 cm^{-1} range and is convoluted with the O—H stretching, has been removed by means of a comparison with the deuterated mixtures[14]. As it can be seen, the O—H stretching contribution covers a wide spectral region (~800 cm^{-1}) indicating that these modes are induced by the presence of an intermolecular connectivity. Concerning the OH stretching mode deconvolution it is well known that a suitable procedure can be obtained by using Voigt profiles. However, in order to compare the present data with the ones

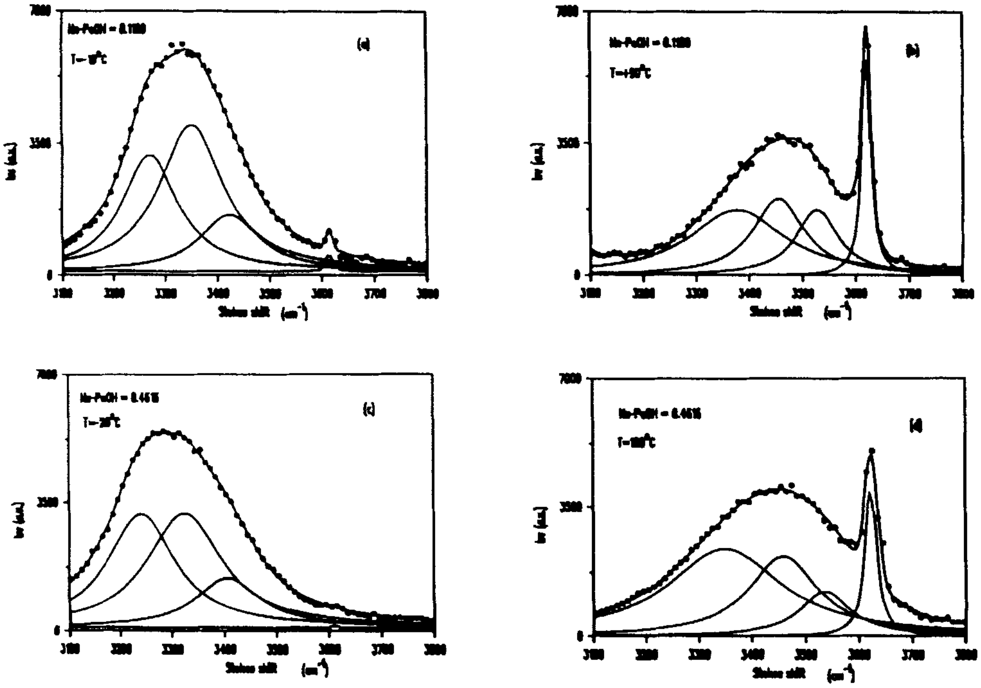

Figure 2 Resuls of the spectral deconvolution in four symmetric sub-bands of the polarized spectra. Circles: experimental data; continuous lines: theoretical fits. Molar fraction values: (a) and (b) 0.1180, (c) and (d) 0.4616.

obtained in the pure components[4,5] we used the minimum number of symmetrical bands (three plus one of the free OH stretching mode) (see Figure 2). In particular the fits have been performed, by means of a Minuit procedure, by taking into account at the extreme mixture concentration region the parameters obtained in the pure alcohols.

3 DISCUSSION AND CONCLUSIONS

As it is well known, the Raman scattering double differential cross section, i.e. the spatial-temporal Fourier transform of the polarizability tensor correlation function, reflects the rotational and vibrational molecular motions. As a consequence, the Raman spectrum is composed by a series of lines, each of them results the convolution of a vibrational and a rotational part centered at the vibration frequencies.

Since the polarized spectrum (VV configuration) results the sum of a purely vibrational term plus a term identical to that obtained in the depolarized case (VH configuration), a comparison of both spectra allows to obtain information about the nature, the time scale and the degree of coupling between the various motions.

It is well established that the O—H stretching vibration study allows to look through the environments of this molecular group[15]. In fact the spectroscopic features

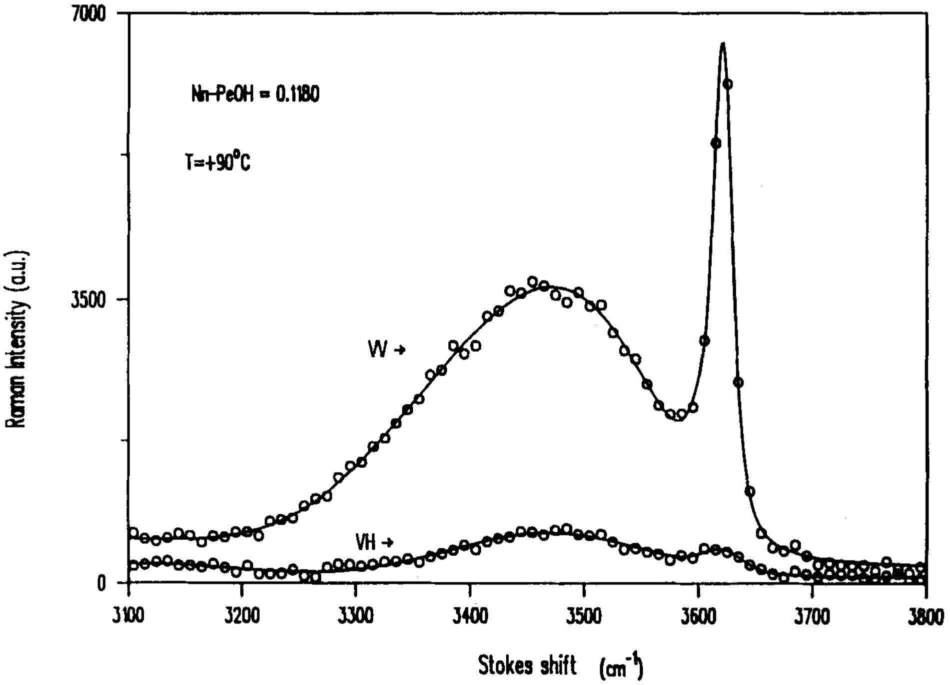

Figure 3 Polarized (VV) and depolarized (VH) Raman spectra in the 3100 ÷ 3800 cm^{-1} Stokes range for the molar fraction value of 0.1180. Circles: experimental data; continuous lines: theoretical fits.

of this band can be explained in terms of different positions of the hydroxyl group inside the molecular arrangements. In fact, for example, the O—H end group center frequency differs from that of the hydroxyl group sited in an internal position. Because in our case the experimentally obtained data result highly polarized, as evidenced for instance in Figure 3, to interpret our data we have analyzed only the VV spectra.

Table 1 Raman deconvolution band fit parameters in the *n*-PeOH + 2M-2BuOH mixtures at various molar fractions.

a) $N_{n\text{-PeOH}} = 0.1180$

T °C	ω_1 cm^{-1}	ω_2 cm^{-1}	ω_3 cm^{-1}	ω_4 cm^{-1}	Γ_1 cm^{-1}	Γ_2 cm^{-1}	Γ_3 cm^{-1}	Γ_4 cm^{-1}	I_1 %	I_2 %	I_3 %	I_4 %
−10	3272	3351	3423	3614	66	74	70	6.6	33.7	47.9	17.6	0.8
10	3285	3365	3441	3616	68	70	69	7.3	34.5	40.3	23.4	1.8
30	3300	3385	3464	3618	79	71	68	8.6	35.8	38.4	22.6	3.2
60	3340	3424	3499	3619	93	66	58	10.0	41.2	32.3	19.2	7.3
90	3376	3455	3527	3621	107	58	48	10.5	41.2	26.4	18.7	13.7

b) $N_{n\text{-PeOH}} = 0.2056$

T °C	ω_1 cm^{-1}	ω_2 cm^{-1}	ω_3 cm^{-1}	ω_4 cm^{-1}	Γ_1 cm^{-1}	Γ_2 cm^{-1}	Γ_3 cm^{-1}	Γ_4 cm^{-1}	I_1 %	I_2 %	I_3 %	I_4 %
−20	3256	3327	3399	3613	57	63	70	2.8	32.3	40.5	26.6	0.6
10	3288	3371	3444	3615	84	71	67	7.8	48.5	33.9	16.2	1.4
30	3313	3402	3475	3618	103	69	62	8.6	60.2	25.3	12.1	2.4
60	3345	3436	3512	3619	125	69	48	9.9	62.9	24.4	7.7	5.0
90	3370	3467	3539	3621	96	65	47	11.0	42.5	32.3	12.4	12.8
96	3377	3476	3545	3622	99	60	44	11.0	44.0	31.4	10.9	13.7

c) $N_{n\text{-PeOH}} = 0.4616$

T °C	ω_1 cm^{-1}	ω_2 cm^{-1}	ω_3 cm^{-1}	ω_4 cm^{-1}	Γ_1 cm^{-1}	Γ_2 cm^{-1}	Γ_3 cm^{-1}	Γ_4 cm^{-1}	I_1 %	I_2 %	I_3 %	I_4 %
−20	3241	3324	3406	3612	80	88	77	2.5	35.4	46.6	17.8	0.2
10	3271	3367	3447	3617	107	85	74	7.7	57.9	29.7	11.7	0.7
30	3288	3391	3473	3618	128	89	72	10.0	63.7	26.6	8.6	1.1
60	3324	3423	3503	3620	96	84	75	13.0	48.1	32.4	15.2	4.3
90	3332	3445	3528	3622	126	81	64	14.1	52.3	27.1	13.2	7.4
100	3348	3458	3536	3623	133	81	58	14.0	50.8	28.5	11.7	9.0

d) $N_{n\text{-PeOH}} = 0.7081$

T °C	ω_1 cm^{-1}	ω_2 cm^{-1}	ω_3 cm^{-1}	ω_4 cm^{-1}	Γ_1 cm^{-1}	Γ_2 cm^{-1}	Γ_3 cm^{-1}	Γ_4 cm^{-1}	I_1 %	I_2 %	I_3 %	I_4 %
−20	3221	3305	3396	3618	92	129	127	2.5	31.6	49.3	18.9	0.2
10	3232	3341	3450	3620	95	127	130	9.6	36.4	46.2	16.9	0.5
30	3275	3367	3457	3622	108	81	73	10.0	58.2	26.8	13.9	1.1
60	3311	3410	3493	3623	126	77	64	14.0	64.4	21.2	10.7	3.7
90	3349	3444	3520	3625	119	68	51	16.0	53.8	24.6	12.3	9.3
110	3338	3451	3529	3628	102	76	59	18.0	38.0	29.8	19.1	13.1

Table 1 summarizes the values of the center frequencies ω, half-widths at half maximum Γ and of the percentage intensities I_n (%) for all the investigated molar fractions and in all the spanned temperature ranges.

As far as the temperature evolution of the center frequencies is concerned, as for the pure components[5], a large shift towards higher frequencies is evident for all the examined concentrations. More precisely such a behaviour is more pronounced for the ω_1, ω_2 and ω_3 frequencies whereas the ω_4 exhibits a very low shift. In particular the values assumed by the latter parameter are very close to the ones obtained for monomers in the pure components[8], indicating the presence of these unities in the entire mixture range.

An important parameter that can be examined is the frequency shift respect to the original free O—H center frequency, $\Delta\omega = \omega_4 - \omega_i$ $(i = 1, 2, 3)$. In fact, as pointed out by several authors[15,16], $\Delta\omega$ is strictly connected with the variation of the potential surface minimum that reflects the $O \cdots O$ distance change. In Figure 4, as an example, the $\Delta\omega$ shift as a function of temperature for the connection of 0.2056 is shown. As it can be seen, with the rising temperature, a decreasing trend of the frequency shifts for all the different present species exists. The general behaviour of the lowering of $\Delta\omega$ is consistent with the fact that at higher temperatures the binding energy decreases and suggests the intermolecular $R_{O \cdots O}$ distance becomes longer.

With respect to the intensities of the spectral bands, as it is well known, in a first approximation, they are proportional to the scatterers population. In Figure 5 the

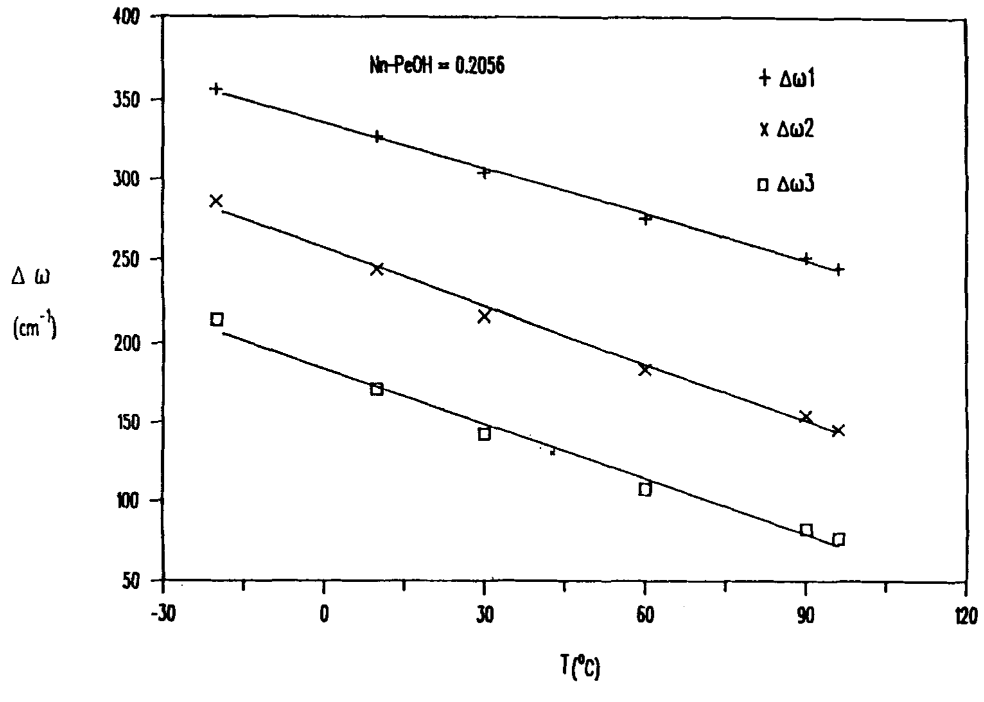

Figure 4 Temperature dependence of the frequency shift $\Delta\omega$ ($\Delta\omega = \omega_4 - \omega_i$), $i = 1, 2, 3$ for the components of the polarized Raman spectra at the concentration of 0.2056. Crosses, stars and squares: experimental data; continuous lines: guides for eye.

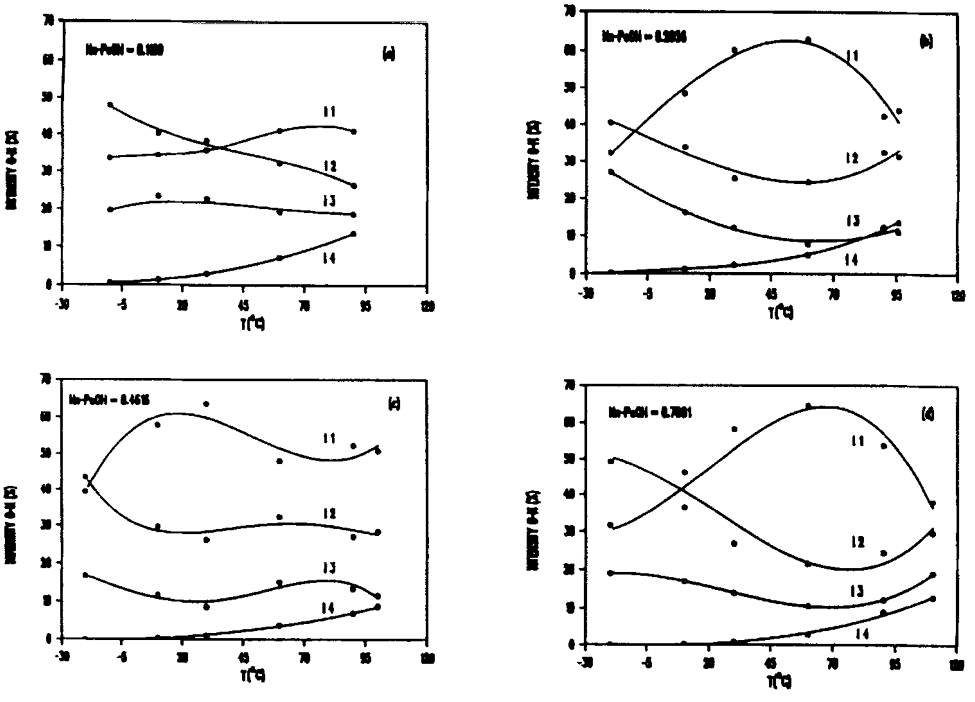

Figure 5 Temperature dependence of the percentage intensities I_n ($n = 1, 2, 3, 4$) *of the O*—H polarized sub-bands. Circles: experimental data; continuous lines: guides for eye.

relative intensities, as a function of T for the concentrations of 0.1180 and 0.2056, are reported.

In particular, at the first concentration value ($N_{n\text{-PeOH}} = 0.1180$), the original spectral contributions, centered at the frequencies of ω_1, ω_2, ω_3 and ω_4, that are present in the pure 2M-2BuOH in all the explored temperature range, are revealed. Together with these bands, assigned in the pure tertiary alcohol to monomers (species 4), open dimers (species 3) and cyclic dimers (species 2), a spectral contribution, whose center frequency is slightly different from that of the pure, is present. Such a contribution results probably connected with the existence, besides the more stable species of cyclic dimers[5], also with the formation of new hetero-alcoholic structures. The temperature evolution of the integrated area indicates that the number density of the open dimers keeps almost constant whereas the diminution of cyclic dimers (I_2) can be connected with the increase, triggered by temperature, of the population of the new hetero-aggregates and of the monomers. The behaviour of the intensity of these latter can be accounted for considering that the higher species, densely populated at low temperature, evolve towards these simpler unities.

Regarding the concentration of 0.2056 (see section (b) of Figure 5), a dramatic change in the temperature evolution of intensities is observed. More precisely I_1 presents a clear maximum centered at $T \simeq 50°\text{C}$ to which correspond the two minima of I_2 and I_3. Such a behaviour suggests that up to the temperature of 50°C a strong increase of the new aggregative species at the expenses of open and cyclic is occurring. The further growth of temperature determines the breaking of these hetero-structures and the restoring of the primitive aggregates of the tertiary alcohol, namely the open and cyclic dimers, with the difference that here the fourth contribution contains both kinds of monomers. Such an evidence is in strict agreement with the general frame indicating that the addition of the linear alcohol to the tertiary one favours the formation of hetero-dimers. Moreover, the Raman response furnishes the further indication that this structure mixing process quickly degrades at high temperature.

For the concentration of 0.4616 (see section (c) of Figure 5), the maximum for I_1, centered at $T \simeq 30°C$, is still present and, following the trend of the two previous concentrations, shifts towards lower temperatures indicating that the more the concentration increases the more the hetero-dimers destroy themselves at low temperature. As a matter of fact the assignment of the species at this concentration value and also for the highest one is not clear yet. In fact this concentration region represents the most "fragile" range of the entire mixture composition and a large number of possible configurations can be assumed by the system, namely the extended structures of the pure components besides the possible existing hetero-structures.

Regarding the temperature evolution of the halfwidths at half maximum (HWHM), different behaviours, as in the case of the pure alcohols[5], are evidenciated. Several mechanisms can contribute to the broadening of the bands[15] and at present no theory is able to explain these peculiar features. Therefore we'll give only a qualitative picture. By looking at Table 1 it clearly emerges that for all the investigated concentrations, Γ_4, which has been associated with free or end groups, is lower than that relative to the other species. In addition, with the exception of the values relative to the concentration of 0.7081, Γ_1, Γ_2, and Γ_3 are very close at low temperature, confirming the relative structures to have about the same extension and hence the presence of homo and hetero dimers. Concerning the concentration of 0.7081 the data reported in Table 1 could be explained by assuming the existence of more complex extended structures probably connected with the "less" molecular linear isomer. In this concentration region, new investigations and a different data analysis are required.

The existence of new aggregates not present in the pure component alcohols, is clearly also reflected in the Γ_1 temperature behaviour that, as it evidently results in Table 1, closely mimes that of $A_1\%$ so supporting the hypothesis of the hetero-dimers presence.

As regards the evolution of Γ_2 and Γ_3 the effects of the structural disorder, associated with the temperature, dominate the anharmonicity effects, so that the overall narrowing with the rising of temperature has to be expected.

In summary we have shown that the analysis of the spectral features of the O—H stretching mode show that the aggregative process present in our H-bonded liquids reflect themselves on this spectral region supporting the hypothesis of the formation of hetero-structures, that determine, in the rich region of 2M-2BuOH, a strengthened respect to the more "fragile" pure. Finally, in the n-PeOH rich region a lot of possible configurations the system can assume exist and further spectroscopic studies are required in order to get a better insight into such a complex concentration region.

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