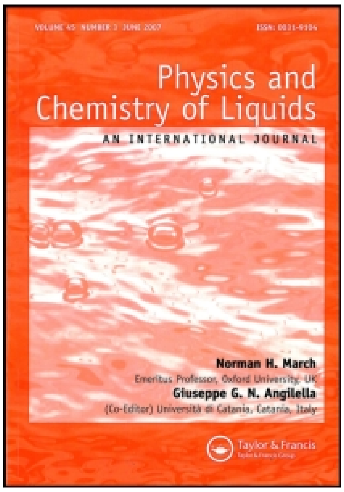

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V. Crupi[a]; M. P. Jannelli[a]; S. Magazu[a]; G. Maisano[a]; D. Majolino[a]; P. Migliardo[a]
[a] Dipartimento di Fisica, dell'Universita' and INFM, Universita' di Messina, S. Agata (Messina), Italy

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GROWTH PROCESSES AND ASSOCIATIVE PROPERTIES IN ALCOHOLS BY DIELECTRIC AND FTIR SPECTROSCOPY*

V. CRUPI, M. P. JANNELLI, S. MAGAZU', G. MAISANO,
D. MAJOLINO and P. MIGLIARDO

Dipartimento di Fisica dell'Universita' and INFM, Universita' di Messina, Contrada Papardo, P.O. BOX 55, 98166 S. Agata (Messina), Italy

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Dielectric permittivity and FTIR data of two isomeric alcohols, normal Pentanol (n-PeOH) and 2-Methyl-2-Butanol (2M-2BuOH) dissolved in an inert and apolar solvent, carbon tetrachloride, are presented. The extracted values of the Kirkwood correlation factor g_k, from the two techniques, allow to explain the growth mechanism in these associated liquids starting from the monomeric state up to oligomers for increasing values of concentration. In particular, the Kirkwood factor plotted versus concentration exhibits, in the case of n-PeOH, a minimum lower than unity followed by a rise up to values larger than unity in the neat alcohol indicating that H-bond favours cyclic multimers at low concentrations and open multimers at high concentrations. In the case of 2M-2BuOH, instead, the g_k behaviour suggests the persistence of both of cyclic and open dimers in all the concentration region.

KEY WORDS: Isomeric pentanols, IR and permittivity data.

1 GENERAL CONSIDERATIONS

It is well known that the existence, in liquid alcohols, of intermolecular H-bond can originate, because of its high anisotropy and directionality, the presence of the inter-molecular aggregates that, owing to the continuous H-bond breaking and reforming process, are dynamically stable. As a consequence, the fundamental O—H stretching band, relative to the hydrogen-bonded group, is frequency shifted of several tens of cm^{-1} from that of the free O—H group ($\omega_{OH} \simeq 3620\,\mathrm{cm}^{-1}$) with an intensity variation[1]. The different kinds of inter-molecular arrangements give rise to the appearance of peculiar bands according to the number of the possible associative species. This occurrence can be explained by Badger–Bauer's rule[2] affirming that the frequency shift between the vibration of the free O—H groups and that of the O—H bonded ones is proportional to the H—bond potential well.

The present work constitutes a part of an extensive study our research group have performed on two isometric alcohols, namely normal pentanol and 2-Methyl-2-Butanol. The choise of these isomers is mainly due to the different position of the hydroxil group within the alkyl chain. Specifically, normal pentanol and 2-Methyl-2-Butanol

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* A preliminary report of this work has been presented at the X^{th} International Workshop "Horizons in Hydrogen Bond Research", Autrans (France) 12–17, September 1993

have the same chemical formula $C_5H_{11}OH$, but the former is a primary alcohol whereas the latter is a tertiary one. These differences induce different structural and dynamical properties. In particular, n-PeOH tends to form linear n-mers ($n = 1, 2, 3, 4$) with a zig-zag structure[5]. The relative population of these species is strongly temperature dependent, as evidenciated by Raman scattering results[3,4]. Furthermore, the ultrasonic relaxation time τ_u is lower than τ_D (the dielectric relaxation time); the bulk to shear viscosity ratio η_v/η_S is close to one over a wide temperature range; the temperature dependence of τ_D, τ_u, η_S is Arrhenius-like; the shear relaxation time τ_S and the shear modulus G_∞ (as measured by Brillouin scattering[6]) show a temperature dependence characteristic of "glass-forming liquids". All these results support the conjecture that n-PeOH behaves like a strongly associated liquid.

The more close-packed 2M-2BuOH, in the liquid state, is characterized by more molecular, and hence less associative, properties. In such a system, in fact, τ_u is near equal to τ_D, the ratio η_v/η_S is higher than 1, and the temperature dependence of η_S and τ_S fulfils the Vogel–Fulcher–Tammann law. In this tertiary alcohol the growth processes of monomers into linear n-mers, with $n > 2$, are excluded and the system tends to form dimeric inter-molecular aggregates in linear and/or cyclic configurations[6]. The different structural configurations originate chemical-physical differences that reflect themselves on the growth processes taking place when these systems are dispersed in non polar and inert solvents. In fact, it is well known that, by dissolving liquid alcohols in inert solvents (like octane, cyclohexane, carbon tetrachloride), at low concentration, the IR O—H stretching band analysis reveals the appearance of a band at concentration values where the dipole moment (by static permittivity measurements) shows a well defined minimum. This occurrence has allowed some author to assign this band to small aggregates (dimers or trimers) with a cyclic structure.

The paper describes FTIR and static dielectric experiments performed on n-PeOH and on 2M-2BuOH in CCl_4, as a function of concentration. We will show that simultaneous FTIR and static dielectric measurements allow to clarify the origin of the O—H stretching sub-bands and to evaluate the contribution of linear and/or cyclic clusters.

2 EXPERIMENTAL PROCEDURE AND RESULTS

High purity CCl_4, normal-pentanol and 2-Methyl-2-Butanol (certified grade quality products), were used. The two isomers were further purified and dried as previously described[3]. The physical impurities were removed by filtering the samples in a dry box. The water content, as determined by vapor phase chromatography, using the Hogan technique was less than 0.010% ± 0.001%.

Densities were measured with a Sodev vibrating tube flow densimeter with an accuracy better than 5×10^{-6} gr/cm^3 at the temperature of $T = 20 \pm 0.002$°C. Static dielectric constant measurements were performed at the fixed frequency of 1 MHz using a Boonton Electronic Corporation Bridge (mod. 750) and a two terminal cell. Refractive indices n were measured at sodium light (wavelength 589.59 nm) by means of a Pulfrich refractometer (Hilger and Watt) equipped with a V block thermostated at $T = 20$°C within ± 0.02°C.

Infrared absorption spectra for all the samples were taken with a BOMEM DA8 FTIR spectrometer working with a Globar lamp source, a KBr beamsplitter and a DTGS/KBr detector. A Specac variable sample holder with CaF_2 windows was used and the entire apparatus was purged with dry nitrogen at $T = 20°C$. The FTIR spectrometer worked at a resolution of $4\,cm^{-1}$ in the spectral region $2800 \div 3800 cm^{-1}$. A Microvax II was used as an interfaced computer for the acquisition and the analysis of data. The IR spectra were properly normalized in order to take into account the effective number of absorbers.

The molar concentration values M for n-PeOH + CCl_4 liquid mixtures were: 0.0082, 0.0730, 0.0840, 0.0960, 0.1910, 1.0940 and pure n-PeOH, for the IR data; 0.1230, 0.8910, 1.5380, 2.1070, 2.5720, 3.1070 and the pure, for the permittivity data. For 2M-2BuOH + CCl_4 liquid mixtures the molarity was: 0.0170, 0.0450, 0.0550, 0.0870, 0.2090, 0.5360 and the pure 2M-2BuOH, for the IR data; 0.0880, 0.8540, 1.5250, 2.0420, 2.5570, 3.0720 and the pure, for the permittivity data.

Figures 1 and 2 represent IR spectra at four concentrations for n-PeOH and 2M-2BuOH dissolved in CCl_4. As expected, for increasing values of the molarity, besides the primitive O—H stretching mode (easily identified as the main band at low concentration) connected with monomeric unities a spread spectral contribution, indicative of the cooperative character of these vibrations at high concentration, appears. The dashed symmetric sub-bands in the same spectra are Voigt profiles and represent the spectral components of the present molecular aggregates.

The comparison of FTIR and permittivity data allows to follow the growth processes in the two alcohols.

3 DISCUSSION

The Kirkwood–Fröhlich correlation factor g_k[7], which depends only on the number of neighboring molecules and on their relative configurations, is an explicit measure of the extent and nature of molecular association. In particular $g_k > 1$ and $g_k < 1$ indicate parallel (as in open n-mers) and antiparallel (cyclic species) alignment between neighboring dipoles, respectively. $g_k = 1$ denotes the absence of a potential barrier restricting the rotation of neighboring dipoles, as in the case of free monomers. Under these circumstances for mixtures of associated polar liquids in non polar solvents, the study of g_k as a function of mixture composition gives useful information on the modification of the structure of the polar component.

i) *Permittivity data*

In a static dielectric measurement g_k is calculated using the relation[7]:

$$g_k \equiv \frac{\langle \mu^2 \rangle_{app}}{\mu_0^2} \tag{1}$$

where μ_0 is the gas-phase dipole moment of the alcohol which has been estimated[8] 1.65 D for n-PeOH and 1.70 D for 2M-2BuOH ($D = 10^{18}$ u.e.s.). Values of the square of

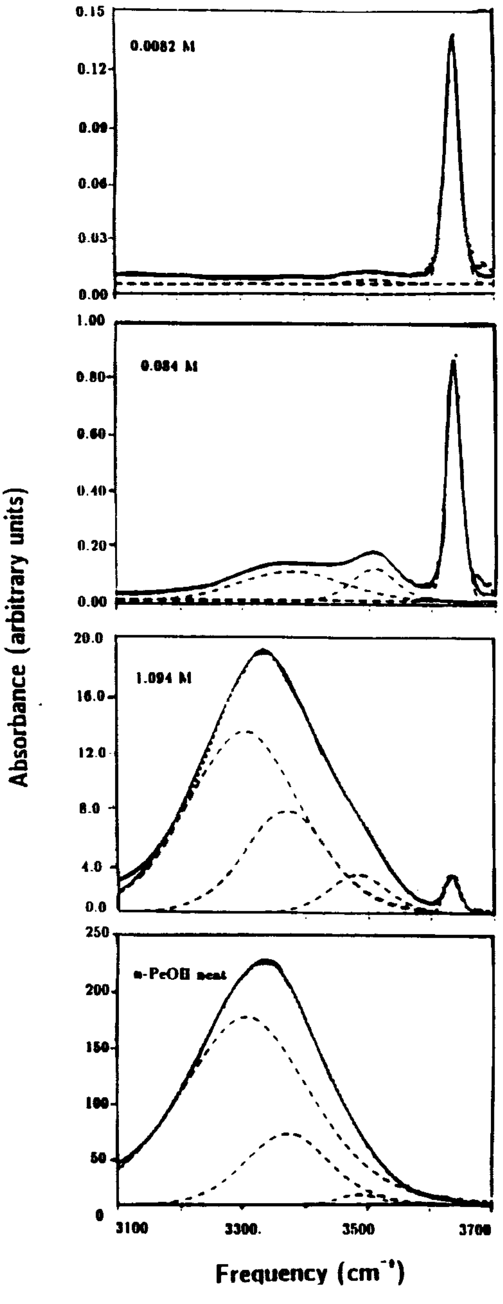

Figure 1 Concentration evolution of FTIR spectra in n-PeOH + CCl_4 solutions. The points are the experimental data; the dashed lines are the deconvolution Voigt profiles; the continuous lines represent the fit results.

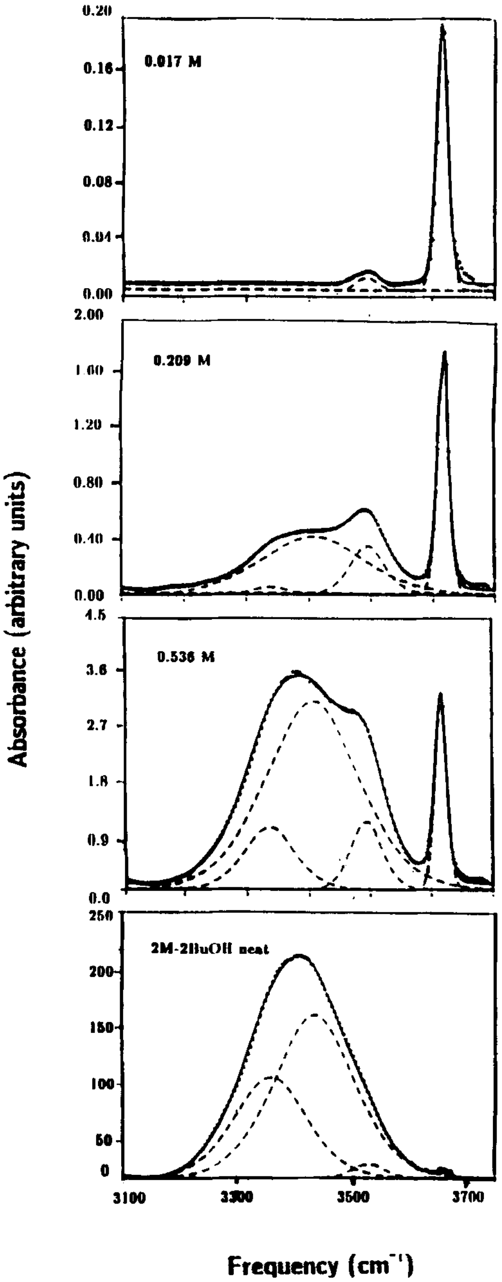

Figure 2 Concentration evolution of FTIR spectra in 2M-2BuOH + CCl_4 solutions. The points are the experimental data; the dashed lines are the deconvolution Voigt profiles; the continuous lines represent the fit results.

the apparent molecular dipole moment $\langle\mu^2\rangle_{\text{app}}$ were calculated using the relation[9]:

$$\langle\mu^2\rangle_{\text{app}} = \left(\frac{9K_B T(2\varepsilon+\varepsilon_\infty)^2}{4\pi N\chi(\varepsilon_\infty+2)^2(2\varepsilon+1)}\right)\cdot\left\{\left(\frac{\phi(\varepsilon-1)}{\varepsilon}\right) - \left(\frac{3\phi_1(1-\chi)(\varepsilon_0-1)}{2\varepsilon+\varepsilon_0}\right) - \left(\frac{3\chi\phi_2(\varepsilon_\infty-1)}{2\varepsilon+\varepsilon_\infty}\right)\right\} \tag{2}$$

In Eq. (2) ε is the dielectric constant of the mixture; ε_∞ is the dielectric constant of the induced polarization for the pure solutes (alcohols), estimated according to Dannhauser[10] to be $\varepsilon_\infty = 1.1\, n_D^2$ (the 10% added accounts the atomic polarization); ε_0 is the dielectric constant of the pure solvent; χ is the molar fraction of the solute and ϕ, ϕ_1 and ϕ_2 are the molar volumes of the solution, pure solvent and pure solute calculated using the density measurements. Table 1 shows the measured g_k values for n-PeOH and 2M-BuOH in CCl_4 as a function of concentration. As it can be seen for pure normal pentanol g_k is greater than one, goes through a minimum, as its concentration decreases, and thereafter increases since the dipoles become completely unhindered in their rotation as infinite dilution. In the case of the more hindered tertiary alcohol, instead, the g_k values, in all the investigated concentration region, remain less than one.

Such evidence indicates the presence of both the alcohols, at low molarity, of cyclic aggregates that persist, as expected, at higher concentration for 2M-2BuOH, whereas a partial substitution with linear oligomers appears in n-PeOH.

ii) *FTIR data*

Following Brot's model[11,12] that successfully evaluates the various terms entering in the g_k factor for linear hexanol on the basis of a chain statistics approach, we have derived the correlation factor using the formula:

$$g_k = g' \sum_{n=2}^{\infty} \alpha'_n + \sum_{n=1}^{\infty} g_n \alpha_n \tag{3}$$

Table 1 g_k values, evaluated by means of permittivity measurements, as a function of molarity M for n-PeOH and 2M-2BuOH in CCl_4.

n-PeOH in CCl_4		*2M-2BuOH in CCl_4*	
Molarity	g_k	*Molarity*	g_k
0.1230	0.78	0.0880	0.97
0.8910	0.63	0.8540	0.69
1.5380	0.72	1.5250	0.58
2.1070	0.92	2.0420	0.55
2.5720	1.05	2.5570	0.54
3.1070	1.24	3.0720	0.51
neat	2.80	neat	0.91

where g' is the common contribution to g_k of any molecule belonging to a cyclic multimer, g_n is the contribution to g_k of a molecule belonging to an open n-mer. α'_n and α_n are the fraction of molecules belonging to cyclic and acyclic n-mers respectively, evaluated by the percentage areas obtained by the deconvolution of the IR O—H stretching band. As above stressed the procedure of connecting vibrational bands to different species has been well employed in the past by the chemical-physics community[2]. Roughly speaking this approximation holds if: i) only internal optical modes are considered, ii) the intensity, i.e. the integrated area (%) firstly depends on the oscillators number that suffers the specific vibration. The results of such a procedure are reported in Table 2 for both the alcohols.

As it can be seen in Figure 1, the IR spectra evolution vs. concentration clearly shows a growth mechanism in the primary alcohol. In the very dilute region the sharp band centered at $\omega \simeq 3635\,\mathrm{cm}^{-1}$, characteristic of monomeric unities is the main contribution. As concentration increases new contributions at lower wavenumber values appear. On the basis of the Badger–Bauer's rule, the new sub-bands centered at $\omega \simeq 3500\,\mathrm{cm}^{-1}$, $\omega \simeq 3370\,\mathrm{cm}^{-1}$ and $\omega \simeq 3305\,\mathrm{cm}^{-1}$ have been interpreted in terms of cyclic n-mers ($n = 2, 3, 4$ respective). The consistence of such a phenomenological method is supported by the comparison between the spectroscopic and the permittivity data.

Finally the calculated g_k, for the pure linear alcohol, obtained hypothesizing the existence of open and cyclic dimers and open trimers results equal to 2.7, which is very close to the g_k value resulting from permittivity data. A different assignment of the spectral deconvolution gives rise to a disagreement between the two g_k values.

As far as the tertiary alcohol is concerned, instead, the IR spectra, see Figure 2, reveal the "monomeric" band at $\omega \simeq 3615\,\mathrm{cm}^{-1}$ plus three contributions centered at $\omega \simeq 3495\,\mathrm{cm}^{-1}$, $\omega \simeq 3405\,\mathrm{cm}^{-1}$ and $\omega \simeq 3335\,\mathrm{cm}^{-1}$. To interpret these latter it should be noticed that the more sterically hindered 2M-2BuOH is not able to form cyclic n-mers with $n > 2$. Therefore, in order to obtain an agreement between IR and dielectric data, we assumed that two different species of cyclic dimers and open dimers are the responsible of the three sub-bands. Finally, for the pure alcohol, the g_k value, resulting from both the techniques, indicates that the structures, created at the low concentration, persist.

Figure 3 and 4 show the behaviour of g_k, determined by dielectric measurements and calculated from IR data, as a function of molar concentration, for n-PeOH and for

Table 2 g_k values, evaluated by FTIR data, as a function of molarity M for n-PeOH and 2M-2BuOH in CCl_4.

n-PeOH in CCl_4		*2M-2BuOH in CCl_4*	
Molarity	g_k	*Molarity*	g_k
0.0082	0.96	0.0170	0.95
0.0730	0.72	0.0450	0.94
0.0840	0.67	0.0550	0.87
0.0960	0.66	0.0870	0.84
0.1910	0.59	0.2090	0.80
1.0940	0.62	0.5360	0.77
neat	2.70	neat	1.15

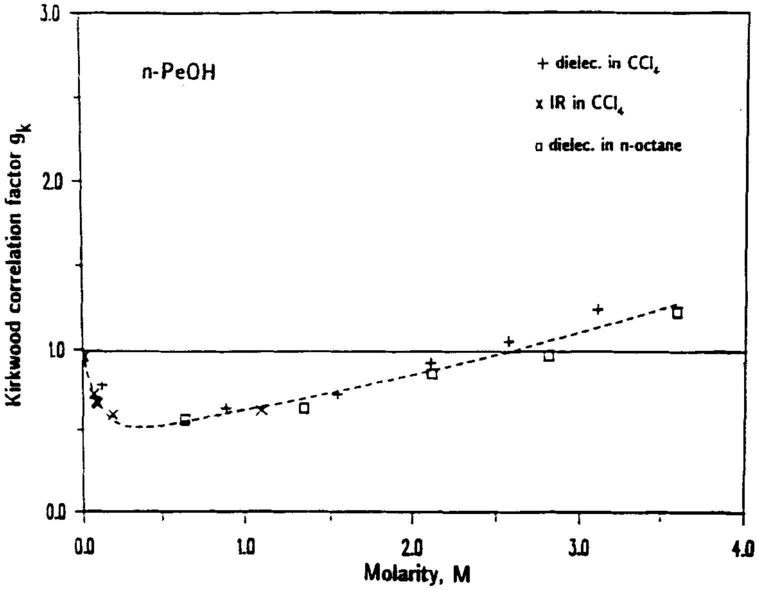

Figure 3 Concentration dependence of the Kirkwood correlation factor g_k in n-PeOH. (+) Permittivity data with carbon tetrachloride as solvent; (□) permittivity data with n-octane as solvent; (×) IR data.

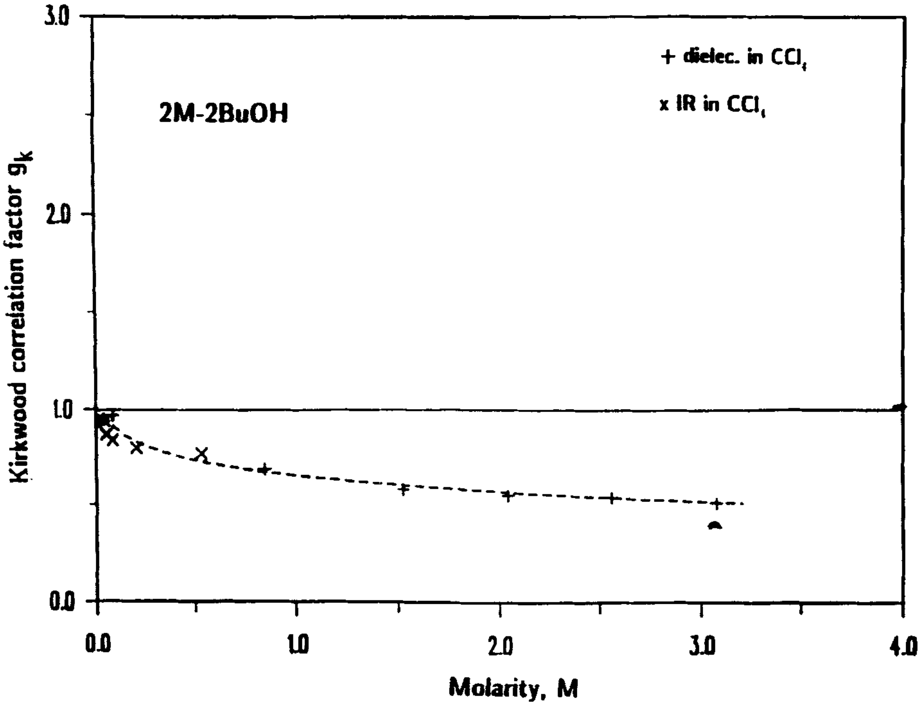

Figure 4 Concentration dependence of the Kirkwood correlation factor g_k in 2M-2BuOH. (+) Permittivity data with carbon tetrachloride as solvent; (×) IR data.

2M-2BuOH respectively. In Figure 3 the g_k values relative to normal pentanol in solution with n-octane, as reported by ref. 13, are also shown.

In order to better characterize the above described aggregative processes, by applying a similar procedure to that followed by Brot[11], we have evaluated, starting from the IR data and considering the low concentration region, three significant parameters: the fraction of molecules belonging to acyclic multimers (including monomers) S, the fraction of molecules belonging to cyclic multimers S' and the fraction of the free hydroxyles I.

Figure 5 shows the behaviors of S, S' and I in the low concentration range for the linear isomer. The absence of linear n-mers (with $n > 1$) implies that $S = I$. As it can be seen the evolution from monomers to cyclic n-mers ($n = 2, 3, 4$) is clearly evidenciated by their complementary behavior.

In Figure 6 the same parameters for the tertiary alcohol are reported. In such a case, the presence of open dimers make S different from I. In particular, as it can be seen, at the first investigated three concentrations only monomers (squares coincident with stars) together with cyclic dimers are present whereas at higher concentration also open dimers appear (S different from I).

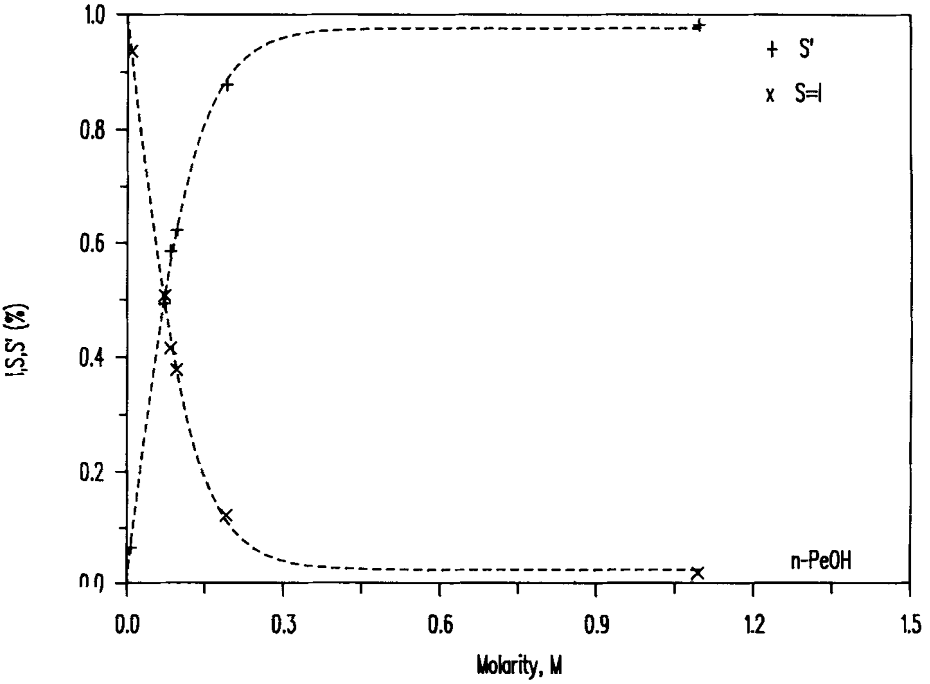

Figure 5 Fraction of alcohol molecules belonging to: open chains S (including monomers), cyclic chain S' and free hydroxyles I for n-PeOH.

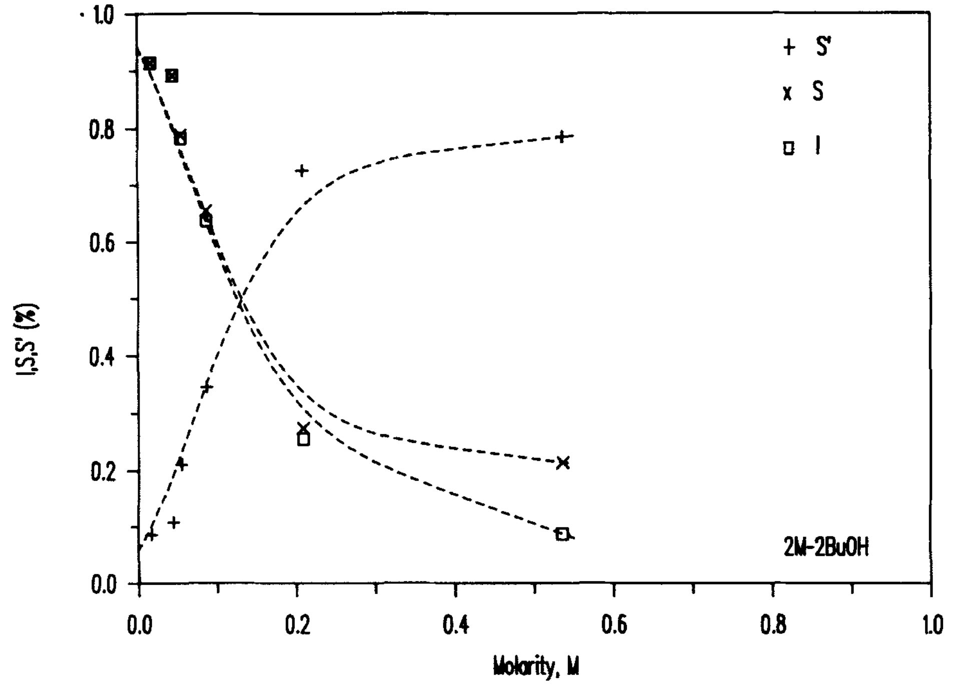

Figure 6 Fraction of alcohol molecules belonging to: open chains *S* (including monomers), cyclic chains *S'* and free hydroxyles *I* for 2M-2BuOH.

4 CONCLUDING REMARKS

The main purpose of the present work is to clarify the self-associated aggregation processes through a detailed analysis of the Kirkwood correlation factor, as obtained by means of dielectric permittivity and FTIR measurements, of two isomeric alcohols, n-PeOH and 2M-2BuOH, dissolved in an apolar and inert solvent.

In particular whereas the first technique gives clear indications about the existence of open and cyclic species, the second one allows to hypothesize the various existing species (monomers, dimers, etc...) in order to well mime the g_k dielectric behaviour. The g_k evolution allows to state that the H-bond promotes, for both the isomers, the cyclic multimer formation at low values of concentration ($g_k < 1$). When concentration increases, the associative states of n-PeOH evolve towards the linear n-mers formation ($g_k > 1$) passing through a definite minimum at $M \simeq 0.3$. On the other hand, the associative states of the more molecular 2M-2BuOH evolve towards the formation of cyclic and open dimers persisting in all the concentration range. At low concentration, the molecules of both the isomers are "forced" to assume cyclic configurations in order to optimize the hydrophilic OH heads screening effects, when they are immersed within the hydrophobic bath, constituted by CCl_4 or n-octane solvents.

Our results conclusively confirm that the Kirkwood correlation factor g_k evolution vs. concentration furnishes important information about the H-bond imposed growth mechanisms, such as the type of aggregates, their symmetries and spatial shapes.

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