A Mean Field Analysis of the O−H Stretching Raman Spectra in Methanol/Carbon Tetrachloride Mixtures

B. Fazio, M. Pieruccini,* and C. Vasi

CNR, Istituto per i Processi Chimico-Fisici Sez. Messina, Via La Farina 237, I-98123 Messina, Italy

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The O−H stretching region of the Raman spectra obtained from methanol/carbon tetrachloride mixtures of different compositions is analyzed. The various components of the spectra associated with methanol molecules with different H-binding states (i.e., non-H-bonded, chain-end, and doubly bonded) are quantitatively related with the alcohol cluster distribution derived by means of a simple lattice model. This comparison allows for the estimate of the mean overall hydrogen bonding energy by means of a best fitting procedure on the Raman data obtained at low-to-moderate alcohol contents; the solvation energy contribution of carbon tetrachloride is then also included. The result (∼3 kcal/mol) is found to be in agreement with the estimates from calorimetric and dielectric measurements.

1. Introduction

The configurational statistics of molecular aggregates, forming as an effect of the hydrogen bonding interaction, has been shown to affect rather dramatically the dielectric behavior of methanol/carbon tetrachloride liquid mixtures.[1] More generally, the same was found in a number of similar systems, where methanol is substituted by larger (linear, monohydric) alcohol species.[2] The reason is that association is responsible of the presence of cyclic aggregates which, together with CCl_4, in fact constitute a further nonpolar component of the mixtures. This determines a negative deviation of the relative dielectric constant ϵ, with respect to the value expected in the absence of association at the same volume fraction ϕ of the alcohol. The amount of alcohol eventually involved in cyclic clusters results from a competition between the configurational entropy loss ΔS_{conf} and the corresponding stability gain, accompanying the mutual H-binding of the end molecules of open aggregates. Thus, it is possible to estimate the H-binding energy, E_h, by an appropriate analysis of the observed ϵ vs ϕ dependence, provided a statistical model for the cluster equilibrium distribution is available.

This has been done in ref 2, where a simple lattice model for the equilibrium cluster statistics has been presented. Although a number of drastic simplifying assumptions have been adopted in order to obtain analytical expressions in a closed form (among the others, the description of the clusters as freely jointed chains is central in this respect; in a subsequent paper,[3] it has been shown how chain stiffness can be introduced as a refinement, to extract information on the molecular dipole magnitude from the dependence of ϵ on the temperature T), an estimate of $E_h \approx$ 4 kcal/mol was first furnished by this analysis,[2] which was then lowered a little bit down to 3−3.5 kcal/mol by improving the computation technique.[4] This result is to be considered in good agreement with former estimates from calorimetry, yielding $E_h \approx$ 4−6 kcal/mol for alcohols up to 1-octanol diluted in CCl_4.[5]

The significance of this result is 2-fold: on one hand, the formulation of the model allows for the estimate of the binding energy also from dielectric measurements; on the other, it establishes a link of consistency between calorimetric and dielectric observations.

Of course the model can be used to calculate other quantities of relevance for the characterization of the cluster distribution as a function of both ϕ and the temperature. In particular, it is possible to derive the fractions of chain-end and of nonassociated alcohol molecules in the solution.

Raman spectroscopy has proved already to be able to reveal the presence of methanol aggregates, even at relatively high dilutions, through the noncoincidence effect.[6] It is the aim of this paper to show that the Raman investigation technique, supported by the above-mentioned model, is also sensitive to the cluster distribution features if an appropriate analysis of the O−H stretching mode region of the spectrum is performed. In particular, it will be shown that an estimate of the H-binding energy E_h is possible by fitting the model to the Raman data and that its value is very close to that derived from the dielectric response.

Section 2 is devoted to the experimental details concerning the sample preparation and the analysis of the Raman spectra obtained from the methanol/CCl_4 solutions with different alcohol contents. For completeness, we devote section 3 to a brief outline of the lattice model (and to a comparison with some independent simulation results as well) which will be used to analyze the data as explained in section 4. The concluding remarks are in section 5.

2. Experimental Section

Liquid mixtures were prepared mixing CH_3OH and CCl_4, both purchased from Sigma-Aldrich (99.8 and 99.9 as purity grade respectively) and used as received without further purification. The set of samples were prepared with the following methanol volume fractions $\phi = 0.05$, 0.1, 0.15, 0.2, 0.4, and 0.7. Since the relative excess mixing volume is known not to be larger than 10^{-3},[5] ϕ is considered to coincide with the nominal volume fraction

$$\phi \equiv \frac{V_a}{V_a + V_s} \tag{1}$$

where V_a and V_s are the actual volumes of alcohol and solvent, respectively, used to prepare the solution.

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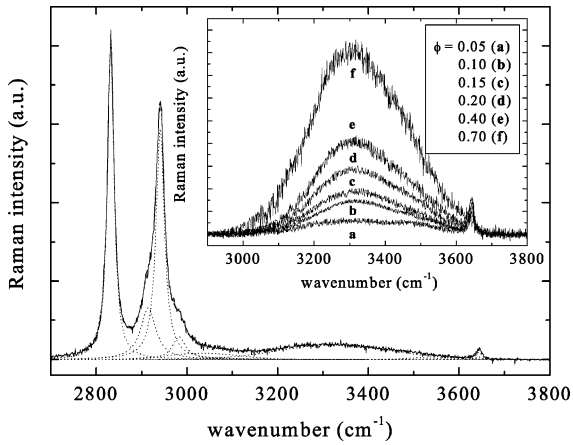

Figure 1. Methyl and hydroxyl stretching Raman bands fit for the $\phi = 0.15$ mixture. The inset shows the O−H stretching bands for different values of ϕ, obtained after subtraction of the methyl contribution tail.

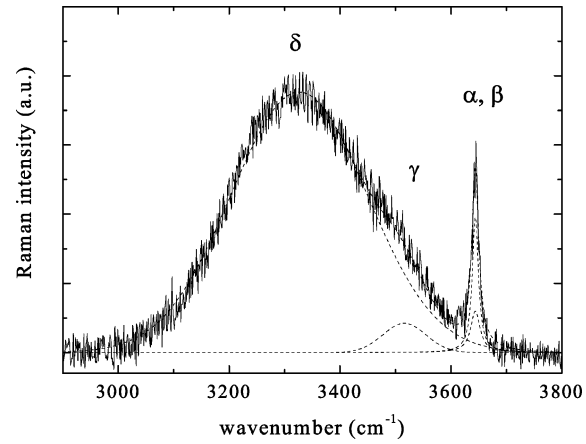

Figure 2. Raman spectrum of the $\phi = 0.15$ mixture in the hydroxyl stretching region. The detailed fit of the O−H stretching bands is shown explicitly (dashed lines): α and β form together the "free O−H peak", referring to O−H vibrations of monomers and nondonating hydrogen bonded terminal molecules respectively; γ is ascribed to O−H oscillators of terminal molecules donating, but not accepting, a H-bond; finally the δ band is referred to molecules which both donate and accept H-bonds.

Raman spectra were performed at room temperature (23 °C) using a 90° scattering geometry on a Jobin-Yvon U-1000 spectrometer; the signals were detected by a Hamamatsu photomultiplier (series R943-02). The excitation source used was the 514.5 nm line of an Ar laser (Spectra Physics 2020) vertically polarized and operating at a mean power of 300 mW. The spectral range investigated was between 2500 and 4000 cm^{-1} (i.e., comprising the C−H and O−H stretching regions) with a sampling point distance of 1 cm^{-1}, an integration time of 3 *s* and the slit width set to 200 μm (in this condition, the resolution was 2.5 cm^{-1}).

The Raman signals coming from the samples were collected in both polarization configurations, parallel VV and crossed VH. The isotropic and anisotropic spectra can be obtained by the relations $I_{ISO} = I_{VV} - I_{VH}4/3$ and $I_{ANIS} = I_{VH}$ respectively. Anyway, in the present work we are interested in just the total Raman spectra, i.e., the sum of I_{VV} and I_{VH}.

The C−H and O−H stretching bands partially overlap, so it was necessary to fit the whole spectrum in order to separate the O−H stretching region. Gaussian−Lorentzian bands have been used as fitting functions, and the strong and dominating contributions due to symmetric and antisymmetric methyl stretches needed be subtracted from the total fits (see Figure 1). Then, more detailed fits were performed afterward just in the O−H stretching region (3000−4000 cm^{-1}).

It is known that the alcohol molecules can mutually hydrogen bond through O−H groups, giving rise to supramolecular structures such as open chains or closed rings. This leads to significant changes in the vibrational frequencies associated with the O−H group and this occurrence can be detected by Raman spectroscopy[6] in a similar manner as in IR investigations of CH_3OD/CCl_4 mixtures.[7,8] In general, the different components contributing to the O−H stretching region of the spectra are ascribed to methanol molecules with different association states, i.e., nonbonded, H-bonded nondonating or nonaccepting, and doubly bonded (molecules accepting two H-bonds at the same time are very few[9]). These components will be labeled according to ref 8. At very high dilution of methanol in carbon tetrachloride the Raman spectra are dominated by a sharp peak centered at 3646 cm^{-1}, reflecting the O−H stretching of free methanol molecules; we refer to this component as to the α contribution (see Figure 2). Upon increasing the concentration of methanol, the aggregates start to form and in the Raman spectra two more bands appear. The first one, γ, is relatively broad and centered at a lower frequency (3500 cm^{-1}); it is associated with H-bonded methanol molecules donating, but not accepting, a H-bond. The emergence of this band is accompanied by an enhancement of the formerly mentioned sharp band because of the contribution of the nondonor chain-end molecules (β component in Figure 2). The second band, δ, is very broad and centered at 3300 cm^{-1}; it is attributed to the O−H stretching of methanol molecules arranged within oligomers, i.e., which both donate and accept H-bonds. This latter band is subjected to a large increase in intensity and bandwidth, and to a shift toward lower frequencies when the methanol concentration is increased.

The areas of the different components (α, β, γ, and δ) carry information about the fractional populations from which they arise. This information will be analyzed in terms of the statistical model outlined in next section.

3. Theory

A. Cluster Distribution in a Lattice. Here we give a short account of the lattice model through which the cluster distribution in an alcohol/CCl_4 solution can be derived; more details can be found in previous work.[2,4]

The frequent breaking and re-forming of hydrogen bonds between the molecules of the alcohol component establishes a population of clusters of varying shapes and dimensions. The number $\{n_{k,i}\}$ of clusters made of *k* molecules (*k*-clusters) in either closed ($i = 1$) or open ($i = 2$) configuration will be derived by the methods of statistical thermodynamics under some simplifying conditions.

The system is assumed to be incompressible; its volume *V* is ideally partitioned by a cubic lattice (coordination $z = 6$) whose elementary cell has the same volume of an alcohol molecule. Then, if N_t is the resulting number of cells of which *V* consists, the total number *N* of alcohol molecules within *V* can be expressed in terms of the alcohol volume fraction ϕ as $N = \phi N_t$.

The total energy associated with a *k*-cluster is

$$E_{k,i} = \begin{cases} -kE_h & i = 1 \text{ (cyclic)} \\ -(k-1)E_h & i = 2 \text{ (open)} \end{cases} \quad k > 2 \qquad (2)$$

$$E_k = -E_h\delta_{k,2} \qquad k \leq 2$$

i.e. $-E_h$ times the number of bonds. The possibility that dimers

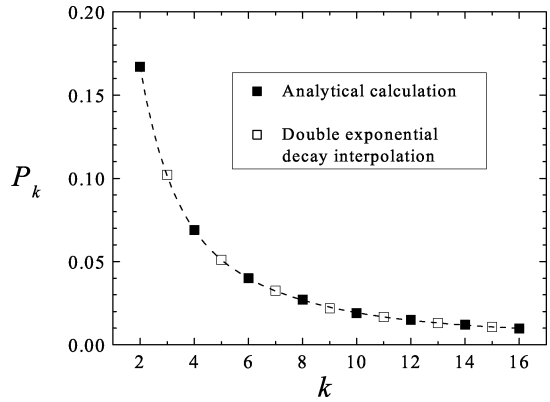

Figure 3. Fraction P_k of cyclic configurations out of all possible ones W_k. The full symbols are obtained from eq 6, the open ones are an interpolation from a sum of two exponential decays.

can form with two hydrogen bonds is excluded at the outset: these configurations are possible, but very unstable.

The energy E_h consists of both a pure hydrogen bonding and a solvation contribution; however, we cannot be more specific at present. On the other hand, considering the results of simulations about the effect of cooperativity,[10,11] we allow E_h to be a function of k as

$$E_h(k,i) \equiv E_{h0} + \frac{a(k-\delta_{i,2})}{b+k-\delta_{i,2}}. \tag{3}$$

This empirical functional dependence describes a cooperativity effect which is approximated by a linear dependence for relatively small aggregation numbers (i.e., a Taylor expansion truncated to lowest significant order), followed by a saturation for chain lengths increasing beyond some value defined by the parameter b.

To associate a configurational entropy to the clusters, each alcohol molecule (e.g., its permanent electric dipole) is allowed to be oriented only along the z directions defined by the lattice. Then, the number of ways a chain made of k elements can be accommodated in the lattice is in general given by

$$W_k = N_t z^k. \tag{4}$$

However, to find the number of *physically distinguishable* conformations $W_{k,i}$ of a k-cluster, we have to normalize W_k in order to account for the intrinsic indeterminacy relating to which molecule in the cluster can be considered to be the first, that is: between the two end molecules in an open configuration, or else among all the molecules in a cyclic configuration (in the latter case, one also has to get rid of one of the two possible ordering sequences still remaining after a "first" molecule has been chosen). Explicitly:

$$W_{k,i} \equiv \frac{W_k}{2} \times \begin{cases} P_k(k-\delta_{k,2})^{-1} & i = 1 \text{ (cyclic)} \\ 1 - P_k & i = 2 \text{ (open)} \end{cases} \tag{5}$$

where P_k, the fraction of cyclic configurations out of W_k, is a rapidly decreasing function of k (see below). For k even, P_k has the following analytical expression:[2,4]

$$P_k = \frac{k!}{z^k}\sum_{j,l=0}^{k/2}\left[l!\,j!\left(\frac{k}{2}-j-l\right)!\right]^{-2}; \begin{cases} j+l \le \dfrac{k}{2} \\ k \text{ even} \end{cases} \tag{6}$$

For k odd, no cyclic configurations are possible in a cubic lattice; nevertheless, the use of a lattice is just a method to simplify the calculation of the configurational entropy (cyclic trimers or pentamers do in fact exist), so in these cases we take for P_k an interpolation between the closest values given by eq 6. Figure 3 reports P_k as a function of the aggregation number k.

The overall configurational entropy associated with the cluster distribution is then $S = k_B \ln W_t$, with

$$W_t = \prod_{k,i}\frac{(W_{k,i})^{n_{k,i}}}{n_{k,i}!}; \tag{7}$$

the equilibrium distribution $\{n_{k,i}\}$ can thus be obtained by extremizing S under the following constraints.

1. The total number N of alcohol molecules is fixed:

$$n_1 = N - \sum_{k=2,N;i=1,2} k\, n_{k,i} \tag{8}$$

(n_1 is the number of nonbonded molecules, or 1-clusters; moreover, by definition, $n_{2,1} \equiv 0$ in the summation).

2. Both the total volume V and the alcohol volume fraction ϕ are fixed, so that all terms in the relationship

$$N = \phi N_t \tag{9}$$

are also fixed.

3. The *average* energy

$$U = -\sum_{k=2,N;i=1,2} E_h(k,i)\, n_{k,i}\{\delta_{k,2} + (k-\delta_{i,2})(1-\delta_{k,2})\} \tag{10}$$

must be held constant.

The formal expression of $n_{k,i}$ resulting from the above conditions is as follows:

$$n_{k,i} = n_1^k \frac{W_{k,i}}{W_1^k}\exp\left\{\frac{E_h(k,i)}{k_B T}[\delta_{k,2} + (k-\delta_{i,2})(1-\delta_{k,2})]\right\}; \tag{11}$$

and the actual solution, once ϕ and the parameters E_{h0}, a, and b are assigned some values, can be found as a (numerical) solution of the N-degree polynomial in n_1 obtained by inserting eq 11 back into eq 8.

It is worth noticing that the lattice discretization of the molecular orientation does not affect the ratio $W_{k,i}/W_1^k$, and that the only dependence of $n_{k,i}$ on z is through P_k. An even more important point to be stressed is that although multiple site occupation is implicitly allowed by eq 4, the extremization procedure rules out all anomalous states by constraining N, V, and ϕ (and not their averages) to be constant.

Once the actual cluster distribution is obtained, a number of properties of the mixture can be calculated. For instance, the fraction of alcohol molecules involved in the formation of cyclic clusters, η, can be readily obtained by the (approximate) expression

$$\eta \equiv \frac{\sum_{k=3,\bar{N}} k\, n_{k,1}}{n_1 + \sum_{k=2,N;i=1,2} k\, n_{k,i}}, \tag{12}$$

where $\bar{N}$ is suitably larger than the average aggregation number of open clusters

$$\langle n_o \rangle \equiv \frac{n_1 + \sum_{k=2,\bar{N}} k\, n_{k,2}}{n_1 + \sum_{k=2,\bar{N}} n_{k,2}}. \tag{13}$$

Figure 4a reports η as a function of ϕ for different values of the ratio $r \equiv E_{h0}/k_BT$ (i.e., $a \equiv 0$ is assumed in eq 3 for the sake of simplicity). Note the impressive increase of η at low ϕ values for $r \sim 5-7$, corresponding to hydrogen bonding energies of 3−4 kcal/mol at room temperature. This gives an idea about how large the fraction of alcohol behaving as a third nonpolar component in the mixture can be. This mechanism has been thought to be responsible for the negative deviation of the relative dielectric constant with respect to the case where the alcohol molecules were assumed not to be able to associate.[1,2]

Figure 4b shows the total fraction ψ of nondonating molecules (i.e., both nonbonded *and* chain-end ones) out of all alcohol molecules present in the mixture:

$$\psi \equiv \frac{n_1 + \sum_{k=2,\bar{N}} n_{k,2}}{n_1 + \sum_{k=2,\bar{N};i=1,2} k n_{k,i}} \simeq \frac{1-\eta}{\langle n_o \rangle}. \tag{14}$$

The fraction κ of nonbonded molecules out of all nondonating ones

$$\kappa \equiv \frac{n_1}{n_1 + \sum_{k=2,\bar{N}} n_{k,2}} \tag{15}$$

is shown in Figure 4c.

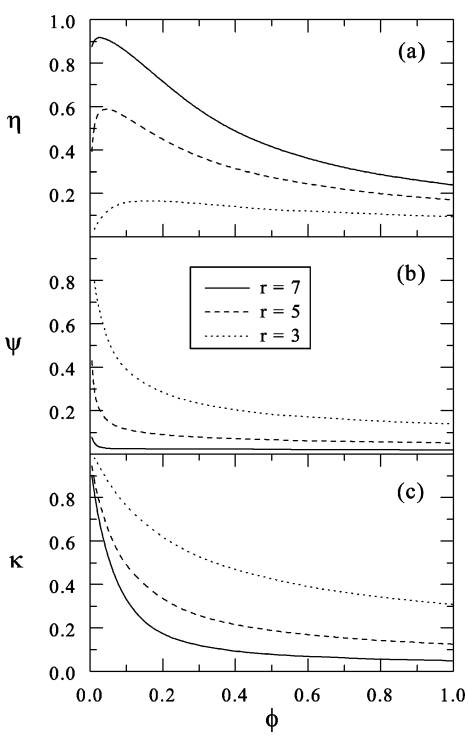

Figure 4. Fraction of methanol in cyclic clusters η (a), fraction of nondonating molecules ψ (b), and fraction of nonbonded molecules out of all nondonating ones κ (c), as functions of ϕ (see eqs 12, 14, and 15 respectively) for three values of the ratio $r \equiv E_{h0}/k_BT$ ($a \equiv 0$ has been set for simplicity).

TABLE 1: Comparison with Simulations for Neat Methanol

	ref 9 (323 K)	lattice (323 K)	ref 12 (298 K)	lattice (298 K)
$\langle n \rangle$	9.3	17.6	11	18.2
η	0.07	0.26	$\lesssim$0.1	0.28

B. Comparison with Simulations. Independent studies of the cluster distribution in neat methanol, as well as in its mixtures with CCl_4, have been carried out by means of different simulation techniques. We consider here some of those studies, the results of which can be easily compared with ours.

Concerning neat methanol, both molecular dynamics[9] and Monte Carlo[12] simulations (on samples of 256 and 500 molecules and at the temperatures of 323 and 298 K respectively) yield a value $E_h \approx 5$ kcal/mol for the mean H-bonding energy. This is in good agreement with the result of ab initio molecular orbital calculations carried out on a methanol dimer.[13] If we use this energy in our calculations (we also set $a \equiv 0$), we obtain estimates of η and of the average aggregation number

$$\langle n \rangle \equiv \frac{n_1 + \sum_{k=2,\bar{N};i=1,2} k\, n_{k,i}}{n_1 + \sum_{k=2,\bar{N};i=1,2} n_{k,i}} \tag{16}$$

which are compared in Table 1 with the results of refs 9 and 12. The values of η calculated with our model are clearly much larger than those predicted by simulation (by the way, this is not the rule; for instance, a reverse Monte Carlo simulation[14] yields $\eta \simeq 0.27$, although with the rather low value $\langle n \rangle \simeq 2.7$); we note however that the number of H-bonds in these papers is counted on the basis of a geometrical criterion which is rather more restrictive than ours. With regards to $\langle n \rangle$, an independent calculation by means of a quasi-chemical model[15] yields a value larger than 60; these authors also point out that the rather lower value obtained in their previous work (ref 12 in Table 1) could be attributed to a probably insufficient size of the simulation box.

Concerning the H-bond statistics, we compare our results with those obtained in ref 9 at low alcohol molar fractions x (this quantity is readily found to be related to the alcohol volume fraction by $\phi = x/[x + (1-x)v_s/v_a]$, with v_s and v_a the molar volumes of the solvent and the alcohol respectively) because this dilution range is relevant to the forthcoming data analysis, although the temperature is different. We perform our calculations with an energy $E_h = 3.2$ kcal/mol (again $a \equiv 0$), i.e., about the value we find by fitting the Raman data below. The difference between the latter and the H-binding energy used for the calculations of neat methanol is consistent with the results presented in ref 13, because in the presence of large enough amounts of CCl_4 the overall H-binding energy consists of the methanol/methanol contribution diminished by the solvation energy (the latter is not at all negligible: in a methanol/CCl_4 dimer, in the configuration where CCl_4 is close to the oxygen, the interaction energy is about 2 kcal/mol[13]).

In Table 2, the approximate percentages of nonbonded (f_0), singly bonded (f_1), doubly bonded (f_2), and triply bonded (f_3) molecules as obtained from the simulation of an ensemble of 256 molecules[9] are compared with our results. Remember that molecules involved in three H-bonds at one time are ruled out in the lattice model; however, their occurrence is relatively low, as found by simulation. We find an acceptable agreement at $\phi \simeq 0.15$ (i.e., $x = 0.3$); this is not so for the case of $\phi \simeq 0.05$ (i.e., $x = 0.1$), where the fractions f_1 are rather different. We do not know the reason, but the trend found by simulation with

TABLE 2: Comparison with Simulations for Methanol Diluted in CCl_4 ($T = 323$ K)

	f_0	f_1	f_2	f_3	η	$\langle n \rangle$
$\phi \simeq 0.05$						
ref 9	8	19	69	3	0.41	4
lattice	9	35	56	−	0.6	2.9
$\phi \simeq 0.15$						
ref 9	6	24	65	5	0.173	5.3
lattice	4	22	74	−	0.49	4.3

TABLE 3: Experimental Values of ψ and Related Fitting Values

ϕ	ψ_{exp}	$\delta\psi_{exp}$	ψ	κ	$\langle n_o \rangle$	$\langle n \rangle$	$[E_{h0}]_{a\equiv 0}$
0.05	0.108	0.012	0.107	0.57	5	4	3.3
0.10	0.068	0.004	0.070	0.52	9	6	3.45
0.15	0.051	0.003	0.052	0.48	13	7.5	3.6
0.20	0.046	0.002	0.042	0.46	17	9	3.65
0.40	0.024	0.002	0.024	0.43	35	16	4.15
0.70	0.012	0.002	0.014	0.41	63	27	4.8

regards to f_1 seems to contrast the experimental evidences presented in the following section [note that within the lattice model $\psi = 10^{-2} \times (f_0 + f_1/2)$].

4. Results and Discussion

The area of each spectral component (α, β, γ, or δ) is proportional to the number of molecules belonging to the appropriate association state. The proportionality constant is not the same for all components, since the molecular dipoles are influenced by H-bonding. This is known to characterize IR spectra and, to a lesser extent, Raman spectra as well.[16] In the present case, however, we shall assume that a unique proportionality constant relates the area of each component to the number of molecules in the appropriate association class. This of course represents a source of systematic errors; as an a posteriori justification, however, the rather impressive consistency of the forthcoming results with those obtained from the dielectric analysis (where the problem of the area vs population is obviously of no concern) suggests that these errors can be overlooked at present.

The relative areas of the spectral components allow in principle for a direct determination of all fractional populations in the different association classes. As a matter of facts, however, the fitting of the intensity profile in the O−H region does not yield a sharp value for the ratio $\kappa \equiv \alpha/(\alpha + \beta)$ (see eq 15) because the function to be minimized has a very shallow minimum with respect to this variable. On the contrary, the fraction ψ of all nondonating molecules out of the whole population is a parameter with respect to which the spectrum fitting function has a sharp minimum. In other words, roughly the same value of ψ can be found by minimizing the fitting function while setting κ as fixed within a relatively wide interval about the point of actual minimum. We do not go through this point and consider ψ as the relevant quantity linking the Raman data to the theoretical model.

The mean values of ψ obtained from the data are listed in the ψ_{exp} column of Table 3, in correspondence of the different values of the volume fraction ϕ. The associated absolute errors are reported in the $\delta\psi_{exp}$ column. The origin of these errors are ascribed to two main reasons: (i) the noise and (ii) the relative difference in magnitude of the areas of the sharp (α and β) and the broad (δ) bands. At low ϕ the former dominates, while at high ϕ the error is mainly caused by the latter.

The quantity ψ can be expressed in terms of the cluster distribution $\{n_{k,i}\}$ through eq 14. Of course, ψ can only be calculated provided the H-bonding energy is known. Alternatively, we can find the parameters entering the definition of the energy, eq 3, for which ψ best fits ψ_{exp}. When this procedure is carried out on the mean values reported in the ψ_{exp} column of Table 3, we find $E_{h0} = 3.08$ kcal/mol, $a = 0.144$ kcal/mol and $b = 3.6$; the corresponding values of ψ, together with the calculated κ, eq 15, and the mean aggregation numbers $\langle n \rangle$ and $\langle n_o \rangle$, are also reported in Table. We note that ψ and ψ_{exp} are rather close.

TABLE 4: Experimental Values of ψ Given by Ref 8 and Related Fitting Values

ϕ	ψ_{exp}	ψ	κ
0.0042	0.9	0.82	0.95
0.0111	0.6	0.57	0.91
0.0159	0.4	0.47	0.89
0.0222	0.36	0.39	0.88

The procedure we just followed is in fact a measure of the H-bonding energy E_h of methanol in the presence of CCl_4. This energy is almost a constant, as it slightly increases from $E_h \simeq 3.1$ kcal/mol for a dimer up to an asymptotic value of 3.2 kcal/mol in long chains. We must stress that, although this trend is qualitatively consistent with the cooperativity effect predicted by numerical simulations,[10,11] the present changes in E_h are much smaller. (It is not so if one assumes that the H-bonding energy is independent of k, as shown in the last column of Table 3.) This does not mean that cooperativity is not observed, but rather that the present analysis is not sensitive enough to point it out. Indeed, the model assumes that the clusters can be considered as freely jointed chains; this means that all energy variations which are much smaller than the mean H-bonding energy (e.g., from changes in local bond conformation[3] or whatever else) are in fact simply neglected. This eventually rules out the possibility to ascribe any small fluctuation of the H-bonding energy to a precise mechanism in a meaningful manner. About the formerly mentioned systematic errors, we note that accounting for the different area-vs-population proportionality constants properly would result in a change of E_h. The freely jointed chain approximation also disguises this effect.

By fitting $\psi_{exp} \pm \delta\psi_{exp}$ we found values of the energy $E_h|_{\pm\delta\psi_{exp}} \simeq E_h(1 \mp 0.03)$ irrespective of the length of the clusters. In light of the preceding discussion, we just consider this variation in energy definitely negligible.

We want to show that the same analysis can be carried out on the population distribution data of CH_3OD/CCl_4 mixtures, extracted from IR observations at very high alcohol dilutions.[8] Table 4 reports these data and the best fitting theoretical values.

In this case, the H-binding energy is found to be significantly smaller than in the case of ordinary methanol, running from $E_h \simeq 2.2$ kcal/mol for a dimer, up to 2.6 kcal/mol for long chains.

We cannot afford a serious attempt presently to see why this is so, but we must keep in mind that CCl_4 plays a role in determining the observed H-bonding energy. Thus, it is not possible at present to see whether the differences against the case of CH_3OH/CCl_4 arise from the direct CH_3OD/CH_3OD or from the CH_3OD/CCl_4 interactions or both. As another point, the dilutions considered in ref 8 are rather lower than those considered in the present and in the dielectric investigations. This means that should a possible inaccuracy in the data analysis be ascribed to the model, it does not show up upon comparison of the Raman and dielectric investigations, maybe just because the ϕ-interval where the relevant ψ and η behaviors are observed is *the same*. However, exploration of different dilution ranges may in principle point it out. As a last comment concerning the data reported in ref 8, the presence of a Fermi resonance in the IR spectral region of interest may interfere in the attribution

of the area (and eventually of the population) of the broad band associated with the doubly H-bonded molecules; this would affect the fitting energy.

5. Conclusions

We used a theoretical model to measure the H-binding energy in methanol/CCl_4 mixtures from Raman spectra. The reliability of the method seems to be satisfactory, considering the rather small changes in E_h observed upon fitting either the $\psi_{exp} + \delta\psi_{exp}$ or the $\psi_{exp} - \delta\psi_{exp}$ data. The outcomes are in very good agreement with the results from the analysis of the dielectric response of similar mixtures.[2,4] In both cases the point is to analyze the response of the mixtures in the small ϕ regions (see Figure 4). Under these conditions, the methanol clusters are short enough to let the energy associated with their configurational entropies, i.e., TS_{conf} (or to their change upon closing or opening the configuration), be comparable with the H-binding energy. Dielectric measurements focus on the η vs ϕ dependence which, as shown in section 3 is rather dramatic in the low-ϕ region. On the other hand, Raman spectroscopy is somewhat complementary, because instead of considering the molecules of closed clusters, it focuses on the nondonating ones (either H-bonded or not), i.e., on just the open clusters. Again, it is in the low-ϕ region that ψ is sufficiently sensitive to ϕ so to allow for reliable fittings.

From the practical point of view the method outlined above, as well as the dielectric analysis, furnishes a means through which the H-bonding energy can be measured. However, from the general standpoint of knowledge, the consistency of the results obtained from Raman and dielectric analyses on the same systems is a very interesting test for a model which, although very simple, provides a semiquantitative picture of methanol/CCl_4 mixtures, suited to be used for at least fast preliminary interpretations of the behavior of these complex liquids.

References and Notes

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