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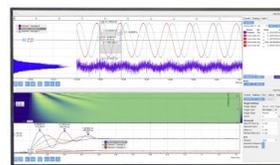
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Infrared spectroscopy of methanol-hexane liquid mixtures. I. Free OH present in minute quantities

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Methanol and hexane mixtures covering the whole solubility range are studied by Fourier transform infrared attenuated total reflectance spectroscopy in order to evaluate OH groups that are H-bond-free. The mixtures from 0 to 0.25 and from 0.75 to 1.00 mole fractions form homogeneous solutions, whereas those from 0.25 to 0.75 mole fractions are inhomogeneous, forming two phases. Factor analysis (FA) was used to find out if free OH groups were present. These were found in minute quantities at the lowest mole fraction by evaluating the OH stretch absorption. The bulk of the absorption is due to the greater than 99.9% of hydrogen-bonded methanol molecules, with a band maximum situated at 3340 cm^{-1} . The stretch band of the free OH groups absorbs at 3654 cm^{-1} , with a full width at half maximum of 35 cm^{-1} . The concentration is very weak but constant at less than 5 mM in the mole fraction between 0.252 and 0.067. Below this range, OH concentrations are even smaller. This represents less than 1% of the amount of methanol at the mole fraction of 0.067 (0.543M). Above 0.25 mole fraction, free methanol OH groups are not observed. Since the free OH band is very weak, almost at the noise level, we verified its presence with mixtures of hexanol in hexane. There, we found a similar free OH band with almost the same band characteristics, but with almost three times the concentrations found with methanol, which we attribute to the difference in the hydrocarbon chain length. The present study indicates clearly that solutions of methanol in hexane contain free OH groups but in minute quantities and only in the low methanol concentrations. This situation is much different from that observed in solutions of methanol in CCl_4 , where free OH groups are clearly observed at all concentrations except at the concentration limits. Whereas in CCl_4 , methanol is believed to form H-bonded chains, the situation is different in *n*-hexane: methanol in the low concentration region would form reverse micelles with the OH groups in the core and the CH_3 groups mixed with *n*-hexane molecules. © 2008 American Institute of Physics. [DOI: [10.1063/1.2929839](https://doi.org/10.1063/1.2929839)]

I. INTRODUCTION

This study of methanol–*n*-hexane mixtures is one of series of papers aimed at understanding the role that hydrogen bonds play in the intermolecular network that water and alcohol make. The OH groups of these form two kinds of hydrogen bonds: the oxygen lone electron pair can accept a hydrogen atom from a neighbor molecule and the hydrogen can make a bond with the oxygen of a second neighbor molecule. These hydrogen bonds (H-bonds) will weaken the covalent OH bonds, whose infrared (IR) spectra undergo a bathochromic shift. This is used to evaluate the strength of the hydrogen bond.¹ Being highly sensitive to these vibration modifications, IR spectroscopy is a good analytical technique to obtain information from the ensuing spectra. Because of the high absorptivity of these systems, transmission measurements requiring micrometer path lengths are not easy to realize, which renders quantitative values difficult to obtain. However, attenuated total reflection infrared (ATR-IR) can

surmount these difficulties because the intensity is governed by the evanescent waves that penetrate the sample with a fixed path length. The penetration depth, which depends on the sample refractive index, is inversely proportional to the frequency. Because of this, there is some differences between the ATR spectra and those obtained by transmission measurements. These differences do not influence the quantitative outcome of the two types of measurements; we showed in a previous publication that IR spectra obtained by ATR could be directly used without the necessity to transform them into optical or dielectric constants (complex values: n and k) to obtain quantitative measurements of the system.² We verified this relation on many systems.^{3,4}

In a study done by ATR-IR spectroscopy of acetone-water mixtures and acetone-methanol mixtures covering the whole solubility range, we reported a detailed analysis of the H-bonding network and the molecular interactions of these systems.^{3,4} In aqueous solutions, acetone accepts up to two H-bonds.³ Acetone makes similar bonds in methanolic solutions. There, all methanol OH groups are H-bonded, which implicates that no free OH groups are present. However, isolated acetone molecules with no H-bonding and almost no dipole-dipole interaction are present.⁴ In these systems, the

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OH band of water and methanol (MeOH) are very similar: the redshift of the OH stretch frequency strongly depends on the number of H-bonds accepted by the oxygen atom. When an hydroxyl oxygen accepts two H-bonds and gives one (for MeOH) or two (for water), the redshift from the gas phase position is around 400 cm^{-1} .³⁻⁵ However, when labile hydrogen of an OH group is strongly bonded (as to acetone) while the oxygen of this group does not accept any H-bond, the redshift is decreased to around 160 cm^{-1} .³⁻⁵ Moreover, when the oxygen of water is coordinated to the magnesium of MgTHTMP (tetrahexyl tetramethyl porphyrin) while the H atoms are not bonded, the redshift is almost 80 cm^{-1} .⁶ These results indicate that the oxygen atom is the governing atom in the weakening of the OH valence bond and therefore in the hydrogen bonding network.

Since the previous methanol H-bonding study was done in a hydrophilic environment, where, as expected, free OH was not observed, we wanted to obtain information on bonding in a hydrophobic environment. CCl_4 , which is such an environment, shows by IR that large amounts of MeOH free OH are present in this system.^{7,8} However, we wanted a more benign environment than CCl_4 for our study, and we choose hexane, a hydrocarbon liquid with a net dipole moment of almost zero.⁹ Hexane with its hydrocarbon chain is a model molecule of lipid chains in living tissue. The van der Waals interactions between the hexane aliphatic groups and that of methanol are responsible for its solubility.

This study of methanol in hexane in 0%–100% MeOH range has the following objectives: (1) to evaluate the free OH content, (2) to provide a detailed description of the methanol-hexane system, (3) to determine the number of species in the system, (4) to evaluate the existence of distinct methanol OH and CO stretch regimes that depend on the number and strength of the H-bonding interactions, and (5) to evaluate the competitive forces that are at play in such systems. As in our previous studies,^{3,10-14} factor analysis (FA) will be used to separate the principal factors. This method should give (1) the number of species, (2) the principal factors, and (3) the real exclusive spectra and real abundances. These, in turn, will allow a detailed description of the mixtures. Molecular dynamics (MD) simulations have reported that 1%–2.5% of free monomers are present in liquid methanol.^{15,16} However, none was detected by IR spectroscopy.⁴ Since methanol free OH groups should exist in hexane solutions, we first address this problem because a significant amount will influence the overall molecular organization. This is done here which is Part I of this two-paper series, and the rest of the above objectives will be addressed in Part II.

In our literature search, we found only one study of an alcohol-hydrocarbon system that uses FA as a discriminating tool. This consisted in determining the concentration of methanol and methyl *tert*-butyl ether in gasoline.¹⁷ Recall that gasoline is made of hydrocarbons similar to that of hexane. Like in the present work, the authors of that study used ATR to obtain their IR spectra. Their analysis was performed with a partial least-squares regression on the CO stretch bands of the oxygenated molecules. Although this study is useful for analytical purposes, it does not address, as we do

here, the molecular organization of alcohols in hydrophobic environments and, especially in this case, of that in hydrocarbons (i.e., lipidic).

II. THEORETICAL CONSIDERATIONS: FACTOR ANALYSIS

The FA procedure that we used here is described in Ref. 14 and references therein. Briefly, a set of n experimental IR spectra of solutions S^e giving absorbance intensity at ℓ wavenumbers $(S^e)_{\ell,n}$ are obtained. A subset of f experimental spectra $(S^e)_{\ell,f}$ is used in the determination of the minimum number of principal factors present in the mixture. The multiplying factors (MFs) are the abundances of each of the S^e_p at the sample concentration $(\mathbf{MF})_{f,n}$. The Beer-Lambert law is satisfied when the product of the two terms $[(S^e)_{\ell,f}$ and $(\mathbf{MF})_{f,n}]$ reproduces the entire set of the experimental spectra which is a linear combination of the principal factor spectra. This is verified by obtaining the residue spectra which are the difference between the recombined spectra and the original ones. These should be null, if not, the procedure is repeated with appropriate modifications until they are obtained. In Part I of this two part series, we principally deal with free OH groups that do not necessitate the orthogonalization procedure because these form a well separated band from the other OH bands. However, for the analysis of these, this procedure is necessary and will be presented in Part II.

III. EXPERIMENTAL AND DATA TREATMENT

A. Chemicals and solutions

Methanol (Fisher Scientific, high performance liquid chromatography grade purity >99.9% *w/w*, water content <0.1%) and hexane (Fisher Scientific, spectranalyzed, purity >99.9% *w/w*, water content <0.02%) were used without further purification.

A first series of samples was obtained with 24 ml methanol to which was added by steps up to 121 ml of *n*-hexane. The second series of samples was obtained with 115 ml hexane to which methanol was added by steps up to 22.1 ml. The sample compositions are given in Table I. Homogeneous¹⁸ solutions were obtained in the 1–0.75 and 0.25–0 methanol mole fraction ranges and inhomogeneous ones in between. For these, stirring was made during measurements. For some of these mixtures, agitation was stopped and the spectra of the upper- and subphases were obtained. Eight methanol-hexane mixtures were carefully weighed to determine the relationship between solution density and methanol and hexane concentrations. These will give the component concentrations.

B. IR measurements

The IR measurements were obtained using a model 510P Nicolet Fourier transform infrared (FTIR) spectrometer with a deuterium triglycine sulfate detector. Two KBr windows isolated the measurement chamber from the outside. The samples were contained in a Circle cell (SpectraTech, Inc.), equipped with a ZnSe crystal rod (8 cm long) in an ATR configuration (the beam is incident at an angle of 45° with

TABLE I. Composition of the methanol-hexane mixtures.

Spectrum No.	MeOH (ml)	Hexane (ml)	MeOH mole fraction x_{MeOH}	Concentration ^a	
				MeOH (mol/L)	Hex (mol/L)
High methanol content—homogeneous solutions					
1	24.00	0.00	1.000	24.423	0.000
2	24.00	0.50	0.994	23.927	0.156
3	24.00	1.00	0.987	23.451	0.306
4	24.00	2.00	0.975	22.553	0.588
5	24.00	3.00	0.962	21.721	0.849
6	24.00	4.50	0.945	20.582	1.207
7	24.00	7.00	0.916	18.929	1.727
8	24.00	9.00	0.895	17.786	2.086
9	24.00	12.00	0.865	16.308	2.550
10	24.00	16.00	0.827	14.682	3.061
11	24.00	23.00	0.769	12.501	3.747
Inhomogeneous solutions—two phases					
12	24.00	30.00	0.719	10.884	4.255
13	24.00	40.00	0.657	9.186	4.788
14	24.00	50.00	0.605	7.947	5.178
15	24.00	50.00	0.605	7.947	5.178
16	24.00	60.00	0.561	7.002	5.475
17	24.00	60.00	0.561	7.002	5.475
18	24.00	80.00	0.490	5.657	5.897
19	24.00	100.0	0.434	4.745	6.184
20	24.00	100.0	0.434	4.745	6.184
21	24.00	121.0	0.388	4.059	6.400
22	24.00	121.0	0.388	4.059	6.400
23	22.10	115.0	0.381	3.953	6.433
24	22.10	115.0	0.381	3.953	6.433
25	22.10	115.0	0.381	3.953	6.433
26	22.10	115.0	0.381	3.953	6.433
27	22.10	115.0	0.381	3.953	6.433
28	22.10	115.0	0.381	3.953	6.433
29	22.10	115.0	0.381	3.953	6.433
30	19.10	115.0	0.347	3.493	6.577
31	19.10	115.0	0.347	3.493	6.577
32	19.10	115.0	0.347	3.493	6.577
Low methanol content—homogeneous solutions					
33	12.10	115.0	0.252	2.335	6.941
34	10.10	115.0	0.219	1.981	7.053
35	8.10	115.0	0.184	1.614	7.168
36	6.60	115.0	0.155	1.332	7.257
37	5.10	115.0	0.124	1.042	7.348
38	4.10	115.0	0.102	0.845	7.410
39	3.10	115.0	0.079	0.644	7.473
40	2.60	115.0	0.067	0.543	7.505
41	2.10	115.0	0.055	0.440	7.537
42	1.10	115.0	0.030	0.233	7.602
43	0.60	115.0	0.016	0.129	7.635
44	0.45	115.0	0.012	0.087	7.645
45	0.27	115.0	0.007	0.058	7.657
46	0.15	115.0	0.004	0.036	7.665
47	0.00	115.0	0.000	0.000	7.675

^aCalculated, see text.

the rod's axis and makes 11 internal reflections of which nearly 3.3 were in contact with the liquid sample).¹⁹

The spectral range of this system is 4800–650 cm^{-1} . The spectra were taken under nitrogen flow to ensure low CO_2

and water vapor in the spectrometer. Each spectrum represents an accumulation of 500 scans at 2 cm^{-1} resolution (0.965 cm^{-1} sampling interval). The measurements were made at 27.1 ± 0.3 °C. The cell was carefully dried before

each series of measurements. Model 510P being a single-beam spectrometer, a background reference was taken with the empty cell before measuring the sample spectra. These were obtained by circulating the liquid mixtures into the cell (approximately 1 ml volume) at a rate of 1.1 ml min⁻¹.

The IR measurements consisted in obtaining the ATR background and sample interferograms. These are transformed into spectral intensities R_0 and R , respectively. The ratio of R/R_0 is the intensity I for the spectral range being studied. Thereafter, the 4302 data points $\{I(\tilde{\nu})\}$ versus $\tilde{\nu}$ (in cm⁻¹) of each spectrum were transferred to a spreadsheet program for numerical analysis. The intensities I were transformed into absorbance units, $\log(1/I)$ (abbreviated in some cases as AU). A small baseline shift (less than +0.004 AU) was necessary to obtain a null mean absorbance in the 4800–4600 cm⁻¹ region where the species do not absorb.

IV. RESULTS AND DISCUSSION

Methanol in hexane forms two types of solutions: limpid solutions in methanol mole fractions (x_{MeOH}) between 0.00–0.25 and 0.75–1.00 and in $x_{\text{MeOH}}=0.25$ –0.75 unlimpid solutions that separate into two phases. We first deal with the limpid solutions.

A. Methanol molar ATR-IR spectra in homogeneous regions of $x_{\text{MeOH}}=0$ –0.25 and 0.75–1

To follow the methanol spectral features in the hexane mixtures, the hexane spectrum was subtracted from that of the solutions in the same proportion as its amount calculated from the measured volumes (Table I).²⁰ The resulting spectra were normalized to 1M methanol. These are shown in Figs. 1 and 2 for the high and low methanol concentrations, respectively. In Fig. 1, we have added the spectrum of pure hexane to indicate that the subtraction procedure was adequate because we do not see any bands of this species except a very small absorption near 730 cm⁻¹, where the hexane band has left a tiny residual. This does not influence the rest of the analysis.

Figure 1 shows the spectra of pure liquid hexane and that of methanol solutions in the mole fraction of 1.000–0.769 (values in Table I). Figure 1(a) shows that the addition of hexane shifts, but very little, the methanol OH stretch and COH deformation bands at 3350 and 1400 cm⁻¹, respectively. However, they are accompanied by a small intensity increase (up to 20% in amplitude). Figure 1(b) illustrates the low frequency region where the spectra show that the methanol CO stretch band near 1025 cm⁻¹ is blueshifted and increased with the addition of hexane.

Methanol molar spectra for the mole fraction of 0.252–0.004 (values in Table I) are illustrated in Fig. 2 together with the spectrum of pure methanol as reference. The noise intensity has increased by a factor of around 700 (24/0.036) that also contains the perturbations from hexane subtraction, which become important at these concentrations. The spectra in Fig. 2(a) indicate that even at high hexane concentrations, the methanol OH stretch and COH deformation bands are only slightly shifted, but the $x=0.252$ spectrum has its intensity increased by around 25% compared to that of pure

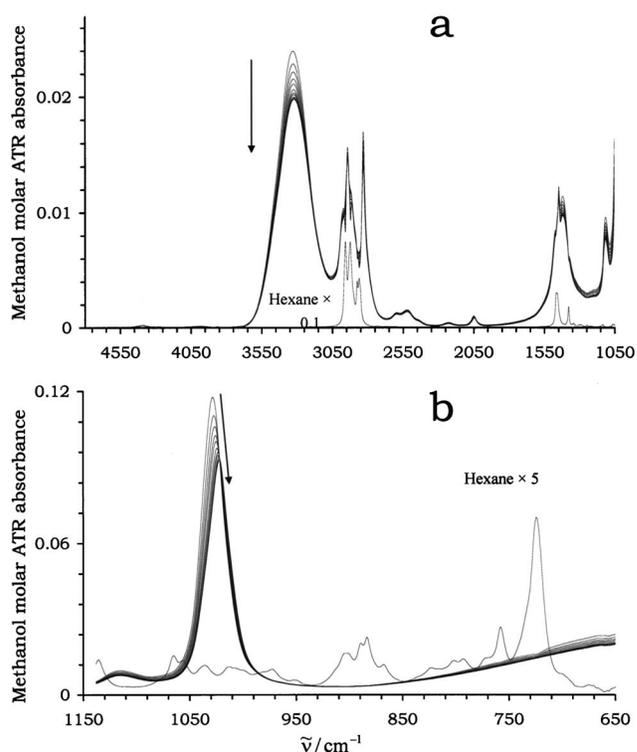


FIG. 1. IR spectra of molar methanol in hexane at the high concentration range ($1.00 > x_{\text{MeOH}} > 0.75$; the values are in Table I) with the hexane spectrum subtracted. In (a) are the ν_{OH} , ν_{CH} , δ_{COH} and δ_{HCH} regions; (b) ν_{CO} and libration regions. The pure *n*-hexane spectrum is presented as a reference. The arrows indicate increasing methanol concentrations.

methanol. Its intensity has increased a little compared to the spectrum of $x=0.769$. However, the intensity remains constant from $x=0.252$ to $x=0.012$ (0.087M). The spectra of the two weakest methanol samples are not shown in frame (a) because of the high noise level due to the normalization procedure.

The spectra in Fig. 2(b) show the low frequency region where the strong CO stretch absorption is observed near 1025 cm⁻¹. Perturbations associated with the hexane spectrum are almost not present. With hexane addition, the CO stretch band is blueshifted with an intensity increase compared to $x=0.769$. However, this band is redshifted toward the liquid methanol position at very low methanol mole fractions. For these, the noise level increases very much because of the normalization procedure. The ensuing division corresponds to a factor of approximately 28 ($=1/0.036$) of the subtracted spectrum at $x=0.004$ (0.036M, Table I).

The spectra displayed in Figs. 1(a) and 2(a) can be compared to the methanol molar ATR absorption spectra obtained in acetone-methanol solutions (Fig. 2 in Ref. 4). There, the methanol spectra showed a strong blueshift (from ~ 3300 to 3509 cm⁻¹) when acetone was added to methanol. The strong blueshift was attributed to the removal of the hydrogen bonds accepted by methanol molecules, while keeping one hydrogen bond given to either methanol or acetone. Since the methanol-hexane system does not show such a strong blueshift, we conclude that methanol molecules in hexane keep both their given and accepted H-bonds down to a very low methanol mole fraction ($x < 0.004$). Conse-

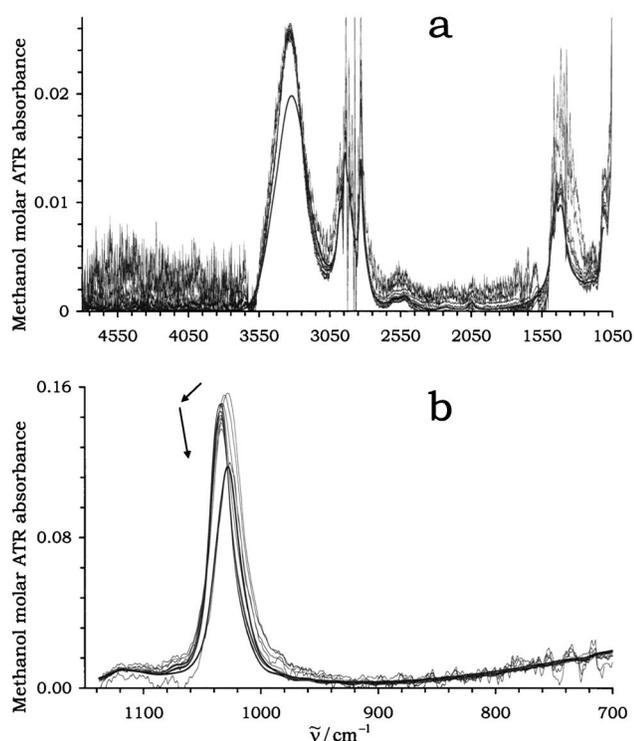


FIG. 2. IR spectra of molar methanol in hexane in the low concentration range ($0.25 > x_{\text{MeOH}} > 0.00$; the values are in Table I) with the hexane spectrum subtracted. In (a) ν_{OH} , ν_{CH} , δ_{COH} , and δ_{HCH} regions; (b) ν_{CO} and libration regions. The bottom spectrum is that of pure liquid methanol. The arrows indicate increasing methanol concentrations.

quently, the methanol hydrogen-bond network survives to high dilution in hexane. However, minute amounts of “free” OH could exist, masked by the bonded methanol. If present in this system, it should be apparent at $x=0.004$ level or below.

B. Looking for free OH groups in $x_{\text{MeOH}}=0-0.25$

Since *n*-hexane does not form hydrogen bonds with methanol, it is expected that a free OH band could be observed in highly diluted methanol in hexane where methanol monomers should be present as observed in CCl_4 , which is another hydrophobic solvent.^{7,8,21,22} Free OH oscillators have been reported to absorb in the 3600 cm^{-1} region when alcohol is dissolved into an organic hydrophobic solvent.^{7,8,22} This position should be close to the 3681 cm^{-1} gas phase position.²³ In the high methanol concentration region [Fig. 1(a)], we do not see any such band and, consequently, no free OH as that in CCl_4 .^{7,8} The situation is almost the same in the low methanol concentration region [Fig. 2(a)]. However, notwithstanding the high noise, one can detect the presence of a very small absorption band in the 3654 cm^{-1} region. Although this position is 27 cm^{-1} redshifted from the gas phase absorption but is much higher than that of ν_{OH} of the bulk (3340 cm^{-1}), the 3654 cm^{-1} band could still be assigned to free OH groups.

1. The difference spectra

To find out if free OH groups are present in the methanol low concentration region (below 0.252 MeOH mole fractions

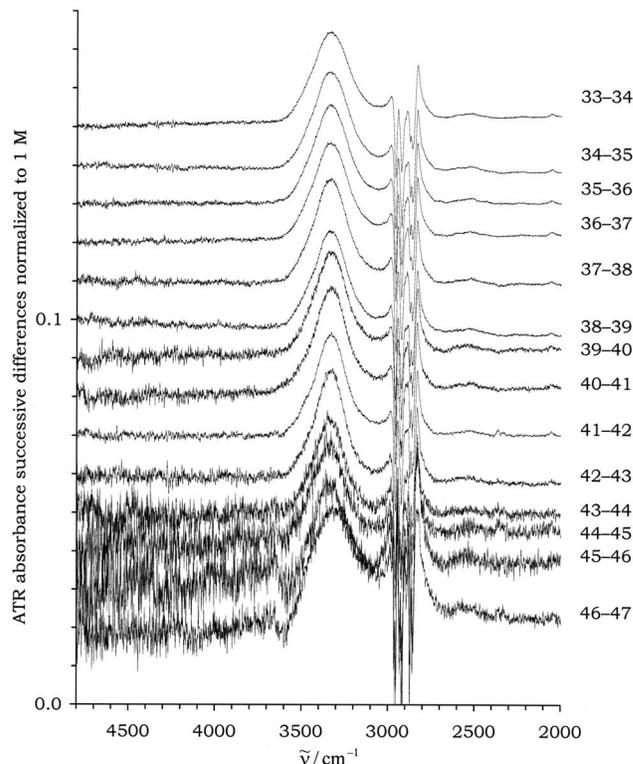


FIG. 3. Difference IR spectra between two successive solutions of methanol in hexane in the low concentration range ($0.25 > x_{\text{MeOH}} > 0.00$). The spectra are normalized to methanol $1M$ and separated by 0.01 ATR AU. The numbers at right are that of Table I.

in hexane), we took the difference between two successive concentration spectra (Table I) and normalized the results to $1M$ methanol. For this, we subtracted the $1.981M$ solution spectrum from that of the $2.335M$ MeOH and the $1.614M$ spectrum from that of $1.981M$; the procedure is repeated until pure hexane is reached. The subtracted spectra are normalized to $1M$ methanol and displayed in Fig. 3. Because the amount of hexane in the first solutions is lower than that of the subtracted ones (inversely to methanol concentration), subtraction generated small negative hexane bands (near 2900 cm^{-1}). These narrow negative hexane bands in a limited spectral range do not impede the analysis of the difference spectra relative to the OH stretch bands. From top to bottom in Fig. 3, the noise level increases because the methanol abundance difference decreases (Table I), thus the normalization factor increases. Figure 3 indicates that the main OH stretch band remains almost constant near 3350 cm^{-1} with the same pattern except for the three bottom spectra. For these, the pattern is changed a little because of the very low intensity of the signal. However, from the bottom spectra, we observe near 3654 cm^{-1} a low intensity band whose intensity rapidly decreases with the increase in alcohol concentration. This band is assigned to the free OH groups. In the eight top spectra, this band is not perceptible. This indicates that adding methanol to hexane solution does not create any new free OH absorption.

2. FA using one single factor

Because of the importance of the free OH band (3654 cm^{-1}) and its very weak intensity, we decided to

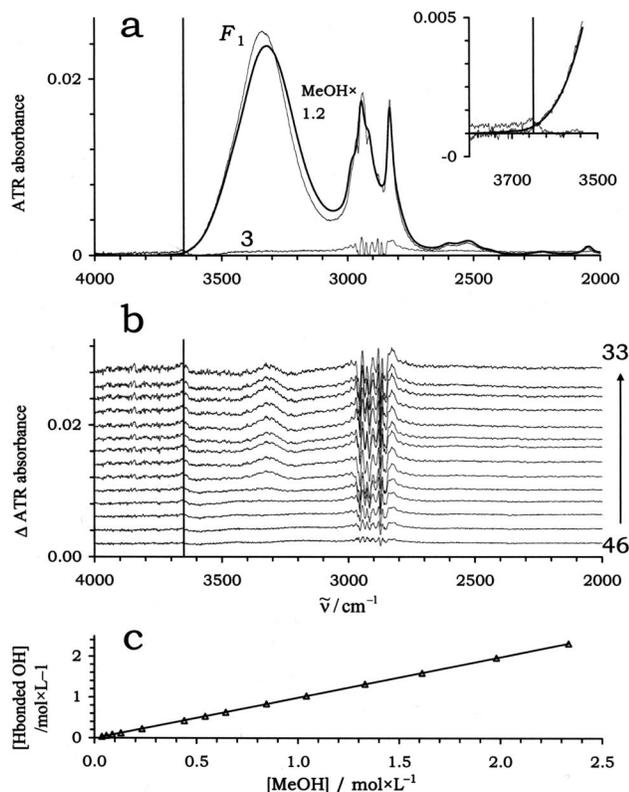


FIG. 4. FA results using one methanol principal factor in the OH stretch region. (a) Pure liquid methanol and principal methanol factor F_1 spectra (see text); (b) residue spectra (the arrow at right indicates increasing MeOH concentrations and the numbers are from Table I); and (c) methanol principal factor concentration retrieved as a function of prepared MeOH solutions.

evaluate more specifically its abundance through FA. Since the spectra in Fig. 3 are very similar, it looks as if one single species is added when adding methanol. For this reason, we started FA with one single principal factor. We took, from the low concentration series of methanol in hexane, the difference between the 1.981M spectrum ($S^{1.981}$) and that at 0.543M ($S^{0.543}$), the latter multiplied by a factor that was adjusted so that the resulting OH absorbance on its high frequency wing almost coincides with that of pure liquid methanol. This difference is illustrated in Fig. 4(a) by spectrum (3). The insert expand the “free” OH region to show more clearly the situation. This operation was performed in order to eliminate the bandlike absorbance near 3654 cm^{-1} . The balance of hexane was obtained according to the respective hexane contents: $c_{\text{hex}}^{1.981}$, $c_{\text{hex}}^{0.543}$, and c_{hex}^0 , where as with the notation used for the spectra, the upper index indicates the methanol concentration of the solution. The last step is the normalization of the result to 1M methanol to get the spectrum of principal factor (F_1), which is obtained with

$$F_1 = \left[S^{1.981} - 1.4S^{0.543} - \frac{(c_{\text{hex}}^{1.981} - 1.4c_{\text{hex}}^{0.543})}{c_{\text{hex}}^0} S^0 \right] \times \frac{1}{1.981 - 1.4 \times 0.543}.$$

The F_1 spectrum [Fig. 4(a), thin line] is compared to that of pure liquid methanol [thick line in Fig. 4(a)] to confirm that (i) F_1 is devoid of any free OH-like absorption near

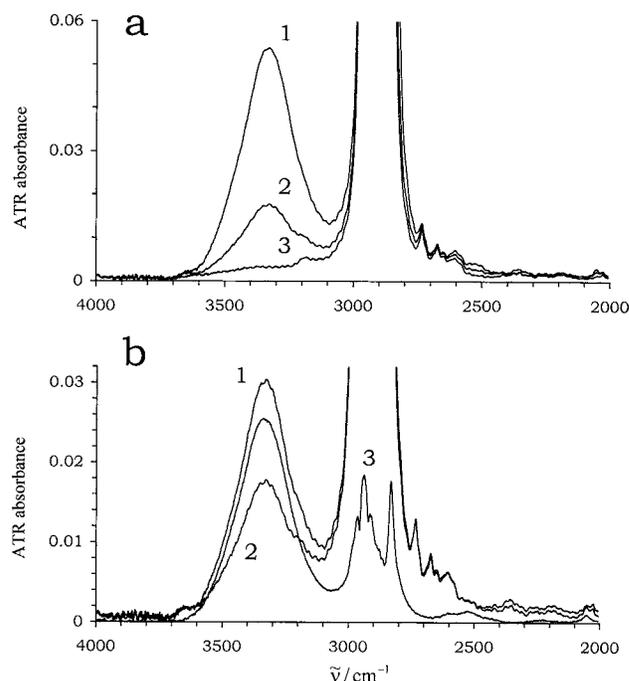


FIG. 5. (a) Experimental ATR spectra of MeOH in *n*-hexane: (1) 1.981M, (2) 0.543M, and (3) 0.000M; (b) (1) 1.042M, (2) 0.543M, and (3) MeOH factor F_1 (which is 1M). Note the absorbance scale expansion from (a) to (b).

3654 cm^{-1} [see inset in Fig. 4(a)]; (ii) is similar to pure liquid methanol in the 4000–2000 cm^{-1} region.²⁴ This confirms the proper elimination of the free OH like absorption in F_1 . Therefore, factor F_1 represents the OH bonded part in the MeOH-hexane solutions.

We used principal factor F_1 to perform the FA on the series of spectra from 2.325M to 0.036M. Figure 4(b) shows the residue spectra from the difference between experimental and calculated spectra. The relation between the concentration calculated from the bonded OH stretch absorption (without the weak absorption at 3654 cm^{-1} , see below) and the measured concentration (Table I) is presented in Fig. 4(c).

The 0.999 98 correlation factor between IR measurements and calculated values (with one single OH bonded factor F_1) indicates that the absorption in the methanol-hexane system at low methanol concentration comes from H-bonded methanol. The 0.991 slope observed for this correlation roughly indicates that the free OH content in the solution should be lower than 0.9% ($1 - 0.991$), which gives less than 0.021M free OH in the 2.335M MeOH solution. The residue spectra [Fig. 4(b)] display a low intensity band near 3654 cm^{-1} . This band indicates that a second methanol factor is present with an intensity lower than 0.001 ATR AU, which is very close to the noise level. The band position at 3654 cm^{-1} indicates that this absorption comes from the free OH groups.

We observe a small recurrent band in the residue spectra [Fig. 4(b)] near 3321 cm^{-1} . This band is situated close to ν_{max} of the principal factor F_1 at 3340 cm^{-1} . This absorption indicates the presence of a third methanol factor with H-bonds. This factor with the other H-bonded factors not apparent at this stage will be evaluated in Part II using the

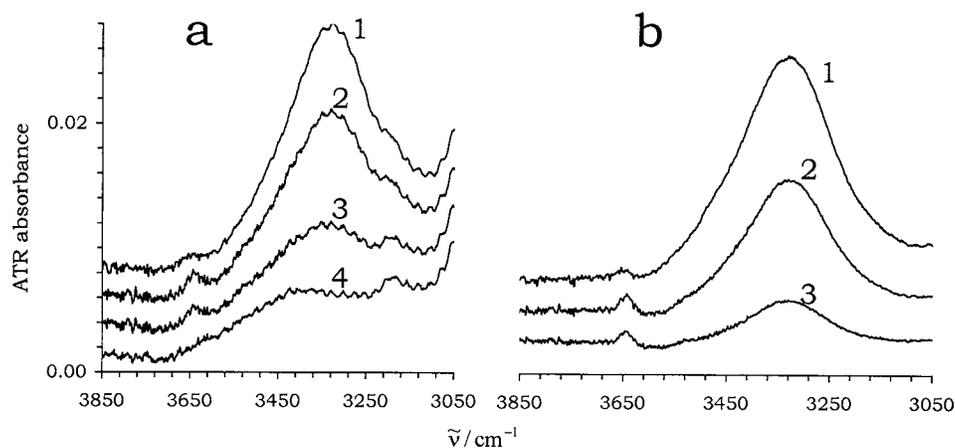


FIG. 6. (a) Experimental ATR spectra of methanol and hexanol in *n*-hexane: (1) MeOH, 0.644*M*, (2) 1-hexanol, 0.397*M*, (3) 1-hexanol, 0.137*M*, and (4) pure *n*-hexane. (b) Spectra of frame (a) after hexane subtraction. Spectra separation is 0.002 ATR AU.

CO absorption band. Since these factors are outside the absorption range of the free OH absorption, they do not influence its analysis.

3. The free OH absorption band

Since the free OH band is observed at a very low intensity (<0.001 ATR AU), its characterization requires special caution. In the experimental spectra in Fig. 5(a), where the MeOH concentrations are (1) 1.981*M*, (2) 0.543*M*, and (3) 0.000*M* (pure *n*-hexane), there is a small band near 3660 cm^{-1} . This figure indicates that spectrum (1) contains nearly four times more methanol than spectrum (2), but both display almost identical free OH band intensities. This indicates that there is almost no increase in the free OH concentration when increasing the total methanol concentration by a factor of 4. This is the same conclusion that was obtained from Fig. 4(b). This justifies the construction of methanol factor F_1 by subtracting spectrum (2) from spectrum (1) in Fig. 5(a), multiplied by a factor of 1.4, which represents the maximum value that could be used to completely remove the free OH absorption from the resulting spectrum F_1 . Further comparison is given in Fig. 5(b). There, spectrum (2) is the same as in Fig. 5(a): 0.543*M*, while spectrum (1) is that of solution at 1.042*M* methanol. Spectrum (3) in Fig. 5(b) is that of factor F_1 at 1.00*M*, which can be related to spectrum (1) (at 1.042*M*). The latter still contains 7.348*M* *n*-hexane that has some absorption in the 3000 cm^{-1} region (Fig. 5(a)). The difference between spectrum (1) and spectrum (3) is due to this absorption. On factor F_1 [Fig. 5(b), spectrum (3)], the free OH band has been completely removed.

C. Methanol free OH groups at higher methanol mole fraction: $x_{\text{MeOH}}=0.25-1.00$

With the determination of free OH in $x_{\text{MeOH}}=0-0.25$ region, we looked carefully in the other regions. In the intermediate region of $x_{\text{MeOH}}=0.25-0.75$, the solution separates into two phases, high and low in methanol concentration, and the volume of which evolves continuously from one limit to the other. Free OH groups were not found in these phases. We found no free OH groups in the homogeneous region at high methanol concentrations ($x_{\text{MeOH}}=0.75-1.00$).

D. Free OH groups in 1-hexanol-*n*-hexane solutions

Since the free OH band of methanol in *n*-hexane is very weak, almost at the noise level, we verified its presence with two mixtures of hexanol in hexane. For this, we used the same setup as for methanol in hexane. Two solutions of 1-hexanol in *n*-hexane were measured: 0.137*M* and 0.397*M* 1-hexanol for mole fractions of 0.0178 and 0.0516, respectively. The spectra are displayed in Fig. 6(a) with the pure *n*-hexane and for comparison a methanol solution (0.644*M* for $x=0.079$, Table I). In Fig. 6(a), the small free OH band of hexanol is more evident than in methanol. Subtraction of the *n*-hexane spectrum gives the spectra in Fig. 6(b). These give the relative proportion of free OH from both 1-hexanol and methanol in *n*-hexane. The concentration of hexanol in spectrum (2) of Fig. 6(b) is three times that of spectrum (3). However, the amount of free OH has only increased, but a little. To our surprise, the amount of free OH in 1-hexanol solutions is still very low. Since the aliphatic chains are identical in both *n*-hexane and 1-hexanol, this means that H-bonding is far stronger than the van der Waals interaction between aliphatic chains made with five more CH_2 groups than in methanol. Even at a dilution ratio of 1–56, 1-hexanol molecules form principally intermolecular H-bonds. This situation is similar to that of methanol with the difference that the free OH band intensity has increased slightly in hexanol-hexane mixtures.

A rough evaluation of the free OH proportion can be achieved by measuring the integrated intensity of the free OH and bonded OH bands. Let S_B and S_f be the integrated intensity of bonded and free OH, respectively, in OH molar 1-hexanol in hexane spectra. Let samples 1 and 2 be two different mixtures of 1-hexanol in *n*-hexane. From their molar spectra, we evaluate the bonded and free OH integrated intensities: A_i , B_i , for $i=1,2$. Let a_i and b_i be the respective fractions of the bonded and free OH in sample i . We have the following relations:

$$A_1 = a_1 S_B,$$

$$A_2 = a_2 S_B,$$

$$B_1 = b_1 S_f,$$

$$B_2 = b_2 S_f, \quad (3)$$

$$a_1 + b_1 = 1,$$

$$a_2 + b_2 = 1.$$

Solving the system of Eq. (3), one gets

$$a_1 = A_1 \frac{B_2 - B_1}{A_1 B_2 - A_2 B_1},$$

$$a_2 = A_2 \frac{B_2 - B_1}{A_1 B_2 - A_2 B_1}, \quad (4)$$

$$b_1 = B_1 \frac{A_1 - A_2}{A_1 B_2 - A_2 B_1},$$

$$b_2 = B_2 \frac{A_1 - A_2}{A_1 B_2 - A_2 B_1}.$$

Integration of the free and bonded OH was performed in the ranges of 3670–3620 and 3565–3100 cm^{-1} , respectively. The bonded OH region was limited by the two absorbance minima of this band. Integrated intensity was obtained by subtracting a trapezoidal area obtained from the two limiting points selected to define the integration region. From Eq. (4), we get 4.0% and 1.5% ($\pm 1.0\%$) of free OH in the 0.137M and 0.397M 1-hexanol solutions, respectively. These amount to a concentration of about 5.5 and 6.0 mM free OH, respectively. These results are in good agreement with the observation of the free OH absorption band in Fig. 6(b).

With Eq. (3), we obtain $S_b = 5.1$ and $S_f = 5.1 \text{ AU cm}^{-1} \text{ L/mol}$. This indicates that (i) hexanol in hexane has free OH absorptivity similar to that of the H-bonded OH; (ii) free OH in hexane absorptivity is higher than that in the gas phase; (iii) the absorptivities of OH groups in pure hexanol and diluted are the same; (iv) similarly, the absorptivities of OH groups in pure methanol and diluted are the same; and (v) the diluted H-bonded absorption is almost twice that in pure liquid water.^{12(b)}

Proper extraction of the free OH spectrum in 1-hexanol-*n*-hexane solutions could be done based on the preceding results. Let us assume that the OH absorption spectra, S_1^e and S_2^e of mixtures at concentration c_1 and c_2 are made of two parts S_{free} and S_{bonded} according to the following relations:

$$\begin{cases} S_1^e = c_1 \times \alpha_1 S_{\text{free}} + c_1(1 - \alpha_1) S_{\text{bonded}}, \\ S_2^e = c_2 \times \alpha_2 S_{\text{free}} + c_2(1 - \alpha_2) S_{\text{bonded}}. \end{cases} \quad (5)$$

S_{free} is easily obtained from Eq. (5) by

$$S_{\text{free}} = \frac{1}{c_1 c_2} \frac{c_1(1 - \alpha_2) S_1^e - c_2(1 - \alpha_1) S_2^e}{\alpha_1 - \alpha_2}. \quad (6)$$

With Eq. (6), we obtained the free OH molar absorption spectrum displayed in Fig. 7(b).

Because of weaker intensity of the free OH band in methanol-hexane mixtures, it was not possible to apply Eqs. (3)–(6) to retrieve the free OH concentration. Based on the

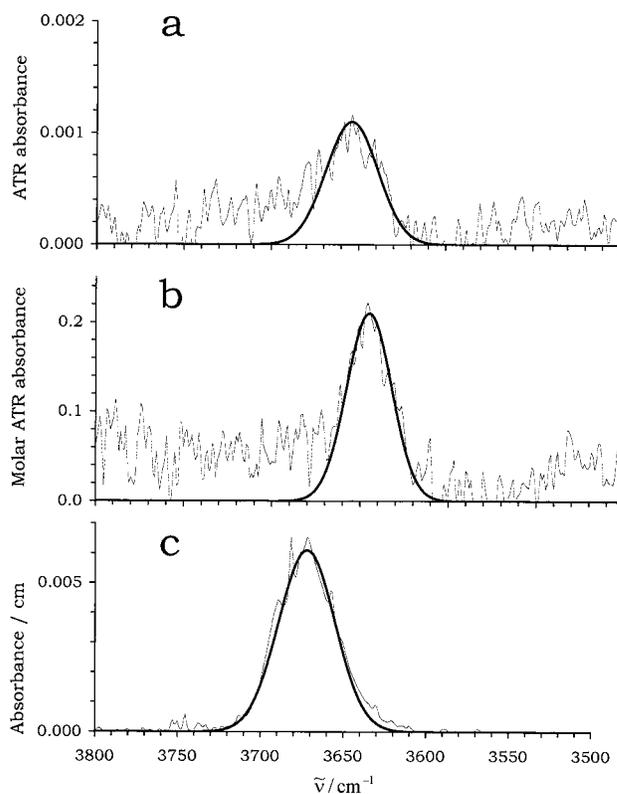


FIG. 7. (a) Average ATR free OH stretch band of methanol in hexane-methanol mixtures (from Fig. 4) after correcting for the slanted baseline. (b) Molar ATR free OH stretch band of 1-hexanol in *n*-hexane (from Fig. 6). (c) OH stretch band of gaseous *n*-propanol. Gaussian bands are fitted on each substance (parameters are in Table II).

free OH molar spectrum obtained of 1-hexanol in hexane [Fig. 7(b)], the free OH content in methanol in hexane [Fig. 6(a)] is estimated at less than 0.005M (5 mM).

E. Characteristics of methanol free OH absorption band

To further obtain adequate spectral characteristics of the free OH bands, we made an average of the five spectra at the bottom of Fig. 4(b). These residue spectra do not display any band near 3321 cm^{-1} and, therefore, could be taken to be representative of free OH absorption in methanol-*n*-hexane mixtures. The resulting spectrum is plotted in Fig. 4(a) to show the difference between a free OH band and a bonded one. The averaged spectrum is presented in Fig. 7(a), where the intensity of the free OH band is close to 0.001 ATR AU. This very weak intensity explains the high noise level and the distorted baseline. Nonetheless, the spectrum in Fig. 7(a) indicates that (i) free OH absorption is detected and (ii) free OH concentration remains at a very low level, well below 0.020M in hexane. This was unexpected because several authors consider that even pure liquid methanol contains a few percent of free OH.^{15,16} The present results deny this evaluation but confirm that obtained from the experimental IR spectra of methanol CCl_4 mixtures.⁷

Figure 7 and Table II give the free OH band characteristics of methanol and *n*-hexanol in hexane with that of gaseous methanol and propanol. The free OH absorption band in Fig. 7(a) compares well with that of gaseous *n*-propanol dis-

TABLE II. Gaussian band fit of the IR bands of free OH in methanol-hexane mixtures and model molecules.

	Methanol gas	Propanol gas ^a	MeOH in hexane	Hexanol in hexane
Intensity ^b			0.0011 AU	0.21 AU L/mol ^{-1b}
Intensity ^d	0.13 AU ^{d,e}	0.006 AU		
Position (cm ⁻¹)	3681 ^d	3672	3654	3645
FWHH (cm ⁻¹)	80 ^e	40	35	30
Conc. free OH	1.33 mM ^e		<5 mM	1M
Ratio of free OH over that of total OH	100%	100%	<1% at 0.5M	(4.0 ± 1.0) % at 0.137M (1.5 ± 1.0) % at 0.397M

^aFrom our laboratory.^bThis work, by ATR, 3.3 (reflections)^cT. Shimanouchi (Ref. 23).^dMeasured by transmission, 10 cm path length.^e25 mTorr, 298 K, J. R. Dixon *et al.* (Ref. 8).

played in Fig. 7(c) and that of gaseous methanol.⁸ For the latter, the band maxima is situated at 3681 cm⁻¹ with a full width at half-height (FWHH) of 80 cm⁻¹.^{8,23} In the hexane system, these are 3654 and 35 cm⁻¹, respectively [Fig. 7(a)]. The larger bandwidth in the gas phase compared to that in hexane solution is due to the rotational structure present in the gas phase and not in solution where the limited volume in which the methanol monomer is confined is not sufficient to permit its free rotation.²⁵ Gaseous propanol shows a FWHH of 40 cm⁻¹, which is much less than that of methanol because the rotational features are less dispersed.

The difference between the MeOH gas phase band position and that of free OH in hexane is 27 cm⁻¹ (Table II). This bathochromic shift is normal considering that van der Waals interactions between hexane and methanol molecules will weaken the covalent OH stretch of methanol, although much less than a usual H-bond. Moreover, the 3654 cm⁻¹ methanol band is close to the weak but more evident 3645 cm⁻¹ band of *n*-hexanol in hexane [Fig. 7(b)]. Also, the methanol band is close to the very weak band observed at 3660 cm⁻¹ for water at the hexane/water interface that was assigned to free OH.⁵ Therefore, our assignment of the 3654 cm⁻¹ band of methanol in hexane to free OH groups of methanol in hexane is justified. In the methanol hexane mixtures at concentration below 2.5 mol/L, the concentration of free OH is less than 0.005M.

F. Difference between hexane and CCl₄ for the formation of free OH

Dixon *et al.* reported the experimental IR spectra of both gaseous methanol and methanol diluted in CCl₄.⁸ From these, the gaseous methanol OH molar integrated intensity is estimated at around 7.5×10^3 m/mol, while that of the free OH in CCl₄ is at 2.2×10^4 m/mol.⁸ Consequently, in CCl₄, the free OH absorption is around three times that in the gas phase. At a methanol concentration of 0.198M in CCl₄, the free OH concentration is 0.115M, representing 58% of total methanol.⁸ This free OH concentration is more than 20 times higher than that in *n*-hexane. From this, we conclude that the situation is much different for methanol in *n*-hexane than in CCl₄. This is confirmed by measurements reported by Kristiansson for mixtures up to 20% methanol in CCl₄.⁷ The

reported pattern is much different than that in *n*-hexane (0%–25%, mol/mol), where the principal feature is one single broad band centered at 3350 cm⁻¹, close to the liquid methanol band, along with a very weak band at 3654 cm⁻¹. In CCl₄, (i) the 3644 cm⁻¹ band is more intense; (ii) it is transferred to two different species, one absorbing in a region close to 3550 cm⁻¹. This indicates two different bonding situations for the OH groups of methanol in CCl₄. The behavior difference of the solvents, *n*-hexane and CCl₄, is obviously reflected by the simple fact that methanol is fully soluble in CCl₄, whereas it is not in *n*-hexane. The reason for this behavior difference is not straightforward because of the high affinity of the methyl groups of *n*-hexane for the one of methanol.

In order to explain the strong behavior difference between *n*-hexane and CCl₄ as solvents for methanol, it may be important to summarize our earlier results. The OH absorption band of isolated methanol in acetone was found near 3509 cm⁻¹ similarly to water ν_1 : 3518 cm⁻¹ (ν_3 is at 3618 cm⁻¹).^{3,4} Since acetone, a dipolar molecule, is a strong hydrogen-bond acceptor, it was pointed out that (i) strong hydrogen bonds could produce a small redshift of the OH vibration (170 cm⁻¹ for MeOH and 150 cm⁻¹ for H₂O) whereas for such H-bonds a greater redshift (350–400 cm⁻¹) is expected; (ii) this was explained by the fact that the related hydroxyl group does not accept any H-bond that, in turn, strengthens the OH valence bond.^{3,4} Similarly, due to their electronegativity, the Cl atoms may be able to attract some of the hydroxyl H atoms of methanol molecules that, in turn, leaves some of the hydroxyl groups without any H-bond accepted. Such a situation is comparable to that of methanol in acetone, except that CCl₄ is a weaker H-bond maker than acetone. Furthermore, we noted that a band near 3441 cm⁻¹ was related to methanol hydroxyl groups, accepting an H-bond (from methanol, of course) and giving its own H-bond to an acetone molecule. Similarly, one could expect that in CCl₄ a band between 3440 and 3510 cm⁻¹ would be associated with hydroxyl groups, accepting one H-bond and giving their own to CCl₄. This is confirmed by the spectra reported in Refs. 7 and 8, where a band near 3517 cm⁻¹ was observed at intermediate MeOH mole fraction.

Methanol molecules in CCl₄ have been depicted to form

H-bonded chains whose length increases with increasing methanol concentration.^{7,8,15,16} The present results indicate that the situation is much different in *n*-hexane: methanol does not form chains with open ends. It rather forms reverse micelles, ball-like groupings made of OH groups in the core and the CH₃ groups outside embedded in hexane molecules. These results indicate that CCl₄ solvent does not mimic properly a lipidic environment and should not be used for that purpose.

V. CONCLUSION

In the first paper of this series dealing with solutions of methanol in hexane, we used FA on the IR spectra to determine the presence of free OH in the solutions. Contrary to what is observed in CCl₄ solutions, we found minute quantities of free OH in the region of methanol mole fractions between 0 and 0.25 in hexane mixtures. In order to ascertain this observation, difference spectra were evaluated and FA using one single factor was performed in order to underline the free OH spectral region. This was necessary to show that (i) the presence of free OH is properly detected and (ii) these are minute quantities, even at very low MeOH concentration. Between methanol mole fraction of 0 and 0.030, free OH increases gradually to around 0.005 mol/L and then remains constant until the phase separation that occurs at 0.25 mole fraction. Free OH was not found from this point up to pure methanol.

Even though MeOH is soluble in *n*-hexane, monomers are present only in minute quantities. At the methanol mole fraction of 0.067 (0.543M), more than 99% of the methanol molecules in hexane are twice H-bonded (with surrounding methanol neighbors, one H-bond given and one accepted are made). This means that the H-bonding strength is such that methanol molecules readily associate with themselves at mole fractions below 0.001, which is one methanol in 1000 hexane molecules. This new experimental result confirms that all the hydroxyl hydrogen atoms are H-bonded in pure liquid methanol.⁴ In this system as well as in liquid water,^{3,10} single free OH groups are not present. This is consistent with the fact that methanol and water are strong H-bond makers (giving and accepting). The model of an open-chained H-bonding network is not a reliable scheme for methanol in *n*-hexane. A better representation is that of micelle types: micelles in the high methanol concentrations and inverse micelles in the low methanol concentration. In the intermediate region ($0.25 < x < 0.75$), there is competition between the two types of micelles causing a phase separation.

The very low concentrations of MeOH free OH in the alcohol-hexane solutions is confirmed by that of 1-hexanol in *n*-hexane, which indicates that although both hexane and 1-hexanol molecules have similar hydrocarbon chains, van der Waals forces are not strong enough to break the H-bond networks made between the OH groups of the 1-hexanol molecules in probable micelle formations (like in methanol). In CCl₄, the amount of methanol free OH is much more abundant at all concentrations^{7,8} than in hexane. We attribute the greater abundance of free OH to the stronger interactions between methanol and CCl₄ molecules than those between

methanol and *n*-hexane. These stronger interactions disrupt more adequately the H-bond network of methanol than hexane does.²⁶ The lower amount of free OH groups in *n*-hexane than in CCl₄ indicates that it is more hydrophobic than CCl₄. This shows that the studies of alcohol in hexane or other hydrocarbon molecules are better model systems of hydrophilic groups in lipidic environments than that in CCl₄, which is a molecule far removed from biological systems.

Because the methanol free OH band is so weak in *n*-hexane and at the limit of detectability, it is difficult to have confidence in the band characteristics that we can obtain in that system. To overcome this difficulty we used hexanol in *n*-hexane which, although weak, gives a better signal than that of methanol. The band characteristics given in Table II indicate that the band appearing in the 3650 (± 5) cm⁻¹ can definitely be assigned to free OH of methanol and hexanol. Moreover, since the first one has one carbon and the second has six, we can generalize this assignment to all alcohols in hydrocarbon solvents. A Gaussian band shape with a FWHM of 32 (± 3) cm⁻¹ would be a proper model for this band. The free OH band of alcohol is therefore defined and can be used to identify such groups in spectra that may show many other bands. With some limits, this definition can be used to identify free OH groups in aqueous solutions.

Moreover, when the free OH of 1-hexanol in hexane is compared to that of methanol in hexane solutions, one is surprised that free OH is only slightly more abundant in hexanol than in methanol. This indicates that the aliphatic chain of hexanol does slightly improve its solubility. This indicates that the alcohols H-bonding aggregations are much stronger than those of the van der Waals interactions of the aliphatic chains. This new and important result can help us understand the behavior of methanol in hexane situations and of other similar systems.

Finally, more effort is needed to properly take into account hydrogen-bond behavior in molecular dynamics (MD) simulations. Here, we provide experimental results that will be useful for testing MD simulations as well as *ab initio* calculations along with the search for a better mathematical representation of the H-bonding process, energies, and dynamics. One problem encountered in such calculations is the identification of a proper hydrogen-bond. Geometric selection criteria are usually used^{15,22} that may mask the quantum and vibrating aspect of the hydrogen bonding, clearly demonstrated by the far infrared band associated with H-bonds near 650 cm⁻¹. On the matter concerning our knowledge of H-bonding, especially our lack of it, we refer to Leetmaa *et al.*, who said that "At the moment, no water model exists that can equally describe IR/Raman, x-ray absorption spectroscopy, and diffraction data."²⁷ The difficulty comes principally from our present knowledge of the H-bond organizations, which is insufficient to understand adequately the intricacies of this subtle bonding. The present study on methanol in hexane, and those of water in acetone³ and methanol in acetone,⁴ give evidence that only a limited number of stable situations is possible for the hydrogen bonding. These are clearly distinguished by their vibration characteristics and OH group situations. The experimental results and the analysis that we have presented is another piece of the

puzzle that will aid in our representation of this organization.

Having settled the problem of free OH of methanol in hexane, we will use in the second paper of this series more elaborate FA on the IR spectra of the whole mixture range to determine the number of factors, their spectra, and abundances. This will give us details of the overall molecular situation of methanol-hexane system.

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