



The correlation between carbon tetrachloride Raman spectra and methanol configuration in CH₃OH/CCl₄ mixtures

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Abstract: In this study, we investigate the possibility of using the numerical data from the mathematical processing of Raman spectra of carbon tetrachloride to obtain a graphical curve that summarizes the structural changes of methanol resulting from changes in concentration for CH₃OH/CCl₄ mixtures. To find this empirical model, we supposed that there are two factors affecting intensity. The first factor is the decrease of carbon tetrachloride concentration due to dilution with methanol, and the other is the degree of order of the C-Cl polarized bonds distributed around the methanol clusters. The obtained results indicate that the changes of intensity resulting from the second factor are in accordance with the changes of the methanol structure in the solution. The results show also, that the relationship between the shape factor and the intensity changes related to the degree of order of C-Cl polarized bonds depend on both the pattern of vibration of the bond and the structure of methanol clusters in the solution.

Keywords: Raman; carbon tetrachloride; methanol; Shape factor.

1. Introduction

The effect of the sample interaction with the solvent appears clearly in the Raman spectra where the interactions lead to concentration-dependent alteration of the intensity, so that the linearity of the relationship between concentration and intensity no longer exists [1]. Stronger interactions between the sample and the solvent may also cause shifting of the bond maxima of the dissolved sample by a few wavenumbers [2].

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In Raman spectroscopy, the obtained shape of the spectral line results from the accumulation of individual scattered molecules, and is heavily influenced by the environment. All molecules vibrate together in a consistent manner, but movement and the slight differences in the vibrational frequency makes it random with time [1]. The identification of the main features of the measured spectrum, and so the accuracy of characterization process depends largely on the convenience of the used peak fitting process. In liquids, the line shape has features of both Gaussian and Lorentzian character [1]. The simplest model for this involves the combination Gaussian-Lorentzian (G-L) profile, represented as $a \cdot G + (1-a) \cdot L$ with a (shape factor) being the fraction of Gaussian character ($0 \leq a \leq 1$). The increased in the a factor value demonstrates the increased

Gaussian form of the spectral line, where the value of the coherence life time is getting close to the value of amplitude correlation time, which in turn increases the coherent of the molecules vibrations [1].

CCl_4 is considered to be a non-polar solvent as it doesn't express any permanent molecular dipole moment. This feature is very important in the spectral studies in the cases of using carbon tetrachloride as a dilute for some polar substances such as methanol and acetone [3-5]; this is because it is possible to study the interactions between the molecules of the dissolved substances without having a strong influence of the carbon tetrachloride molecules.

Methanol/carbon tetrachloride mixture gained the attention of many research groups [3,5-8], where the attention was focused on developing an ideation for the microscopic structure of the mixture, and the changes that happen as a result of concentration alteration. Some of these studies relied on the use of Raman spectroscopy, which is the appropriate way to study the structure as a function of concentration, because in liquid mixtures, the band shape of a reference vibrational mode of the molecule is influenced by the concentration fluctuations of the environment [9–11]. In addition, the dependence of the bandwidth and frequency of Raman bands on the environment provides useful information regarding the solute–solvent interactions and intermolecular forces [9].

In methanol/carbon tetrachloride mixture, the methanol molecules are linked together in hydrogen bonds forming winding chains in the range of the high concentrations level, and cyclic structures in the range of the low concentrations level [8]. The mutual influence between methanol molecules and CCl_4 molecules increases up to the solvent cage effect at the high concentration levels of methanol, where the molecules of carbon tetrachloride are confined in a potential well created by methanol molecules [9]. Some researches [8,12] suggest that solvent cage effect may be accompanied with forming $\text{HO}\cdots\text{Cl}$ bonds, although there is no structural evidence to support this prediction.

This study aims to clarify the possibility of using the spectral analysis data of carbon tetrachloride Raman spectra to investigate the changes in the methanol structure associated with the change in the concentration of the methanol in $\text{CH}_3\text{OH} / \text{CCl}_4$ mixtures.

2. Experimental

Different CCl_4 and CH_3OH solutions were prepared with different concentrations of methanol ranged from 0 to 1 (v/v). The compounds (Aldrich), which are commercial products, have been used without further purification. The Raman spectra has been measured as a function of the concentration at room temperature using a Nicolet-6700/NXR-Raman, supplied with laser source He/Ne at 632.8 nm, for resolution of 4cm^{-1} .

The Raman spectra has been fitted by a Gaussian-Lorentzian function using the peak fitting tool of Peak-Fit software to determine the peak position, intensity, area, and shape factor (proportion of Gaussian and Lorentzian functions).

It's known that assigning the characteristics of the measured spectrum, as well as the accuracy of the characterization process depend largely on performing the suitable peak fit process of the spectral line. There is a large variety of forms for spectral lines, but the form that we preferred for performing the peak fit process is characterized by having the ability to give a quantitative description of the changes of some amounts relating to the homogeneity of the environment surrounding the chemical bond.

3. Results and discussion

Figure 1 shows an example of the Raman spectrum which belong to the sample prepared at $c=0\text{v/v}$. We can notice that there are five Raman peaks, which are located at 220.9, 316.8, 462.1, 762.6 and 790.7 cm^{-1} . The Raman peaks of 220.9, 316.8 and 462.1 cm^{-1} are assigned to C- Cl symmetric stretching mode $\nu_4(\text{F}_2)$, C- Cl asymmetric bending mode $\nu_2(\text{E})$ and C-Cl symmetric stretching mode $\nu_1(\text{A}_1)$, respectively. The pair of peaks in the vicinity of 762.6 and 790.7 cm^{-1} is the b Fermi resonance doublet, which is due to an harmonic mixing of the ν_3 fundamental and the $\nu_1 + \nu_4$ combination [14].

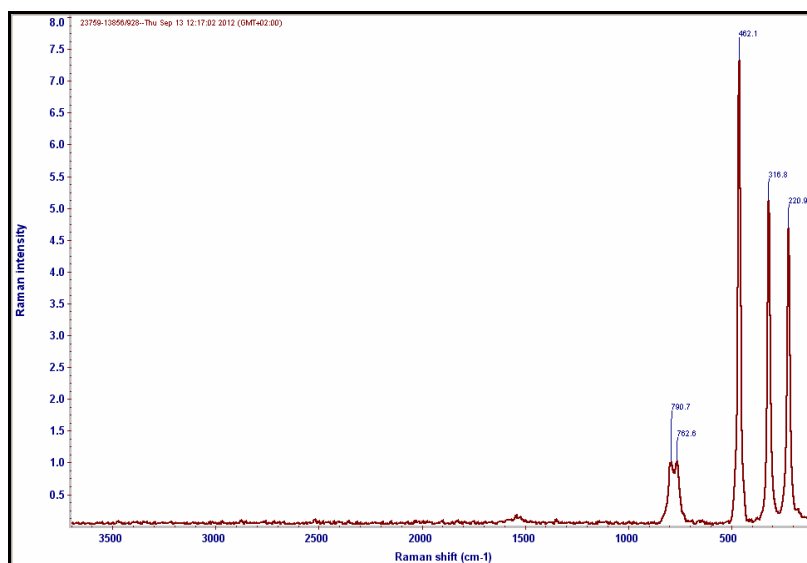


Figure 1: Raman spectrum of the sample prepared at $c=0v/v$.

Figure 2 shows the intensity as a function of concentration for ν_1 , ν_2 , ν_3 , and ν_4 CCl_4 Raman spectral lines. From this Figure, it can be seen that the intensity changes in the same manner in all curves and that it decreases dramatically to a minimum value at a concentration of $0.3v/v$. This decrease is followed by an increase for higher concentrations. In order to illustrate the departure from linearity in the previous curves, it is useful to compare these curves to a virtual straight line representing the ideal case of the relation between the intensity and concentration. This is the case in which the intensity is only related to concentration. This straight line is drawn for all cases in Figure 2, it is the line connecting the two points: $(0,10)$ & $(1,0)$ in each curve.

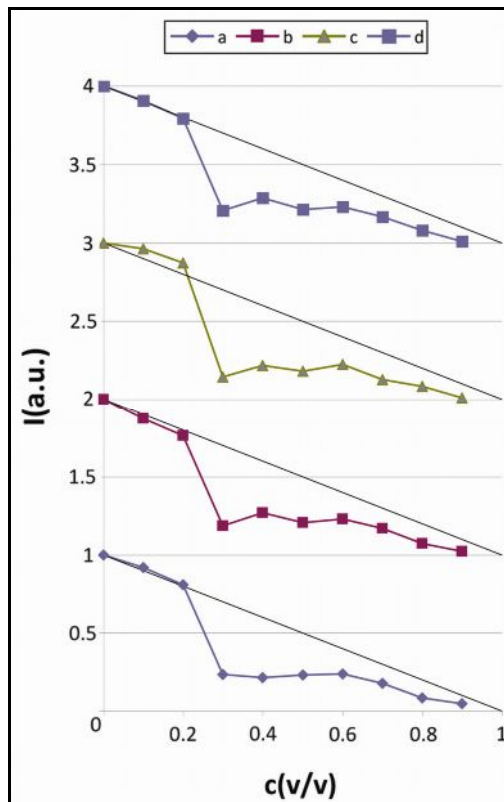


Figure 2: The variation of Raman intensity as a function of concentration
 (a) line ν_1 (b) line ν_2 (c) line ν_3 (d) line ν_4 .

For each spectral line, it is clear that as the methanol concentration increases, the intensity curve departs from the virtual straight line. This departure from linearity continues until the concentration reaches the value of 0.3v/v. For more increase in the methanol concentration, the intensity curve gradually comes back closer to the straight line. This behavior can be interpreted by assuming that with increasing in the methanol concentration, the intensity of the fundamental features in Raman's spectra changes as a result of two main factors:

The First factor is the decrease in the carbon tetrachloride concentration. This decrease corresponding to the first factor has a fixed average value.

The Second factor is the mutual interaction between the molecules of carbon tetrachloride and those of methanol. This interaction causes a lack of linearity in the relationship between the concentration and intensity of the peak as it leads to an irregular distribution of the C-Cl bonds around the rings of methanol, and a decrease in the intensity of the spectral line. However, when moving to the chains structure the intensity increases due to the regularity in distributing the bonds around the methanol chains. Consequently, the degree of order of the C-Cl polarized bonds decreases with the increase in the number and size of methanol rings at low concentrations, and increases when moving to chains structure at higher concentrations. Based on this interpretation we can represent the amount of the deviations from the ideal case using a new parameter Δ . This parameter corresponds to the change of intensity as a result of the mutual interaction between the carbon tetrachloride and methanol molecules. The parameter can be calculated using the following formula:

$$\Delta = \hat{s}_v - s_v$$

Where \hat{s}_v and s_v are the true and ideal values of the intensity for a certain value of concentration, respectively.

Figure 3 shows the value of Δ as a function of methanol concentration for the spectral lines ν_1 , ν_2 , ν_3 and ν_4 . We can see that all curves have the same shape, and they all have a maximum value of intensity at concentration equal to 0.3v/v. Also we can notice that as the concentration increases, the parameter increases and moves away from ideal case for concentration ranges from 0 to 0.3 v/v, while, at higher concentration (0.3 – 0.9 v/v) it decreases and approaches the ideal case with the increase in the concentration.

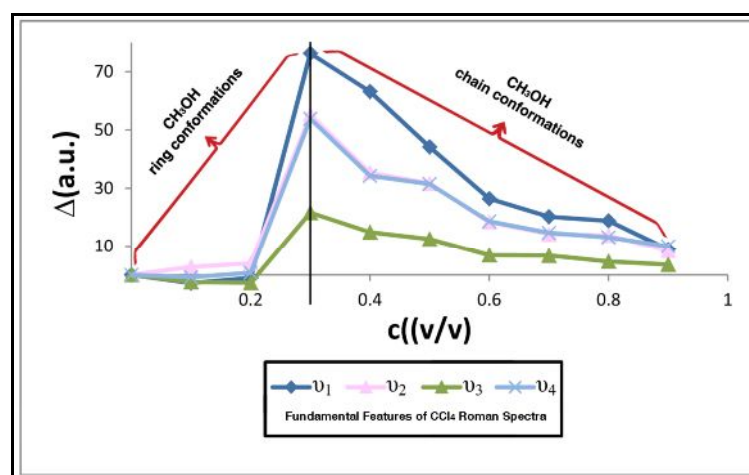


Figure 3: The variation of Δ as a function of concentration.

Interestingly, the obtained experimental results coincide with the results from earlier theoretical and experimental studies [6-13], concerning the study of the structure of methanol in methanol solutions. Our results coincide with the results from these other studies in the following:

In the case of $\text{CH}_3\text{OH}/\text{CCl}_4$ mixtures, the main interaction is expected to be between the OH bond of the solute and the C-Cl bond of the solvent molecule. The solvent CCl_4 molecule accumulates electric charge due to charge-transfer process. As a result, an electrostatic potential is developed in the vicinity of the molecule, whose value decreases with increasing the distance between the two molecules (solute and solvent)[9]. This electrostatic potential allows the emergence of a mutual effect between methanol and carbon tetrachloride molecules.

The liquid structure of pure methanol is characterized by winding chains of hydrogen-bonded monomers; upon dilution, a significant fraction of such chains moves close to each other to form cyclic structures [6,8]. CCl_4 molecules are distributed around these rings as a result of the mutual attraction forces. This means that the methanol clusters imposed a specific pattern of spatial distribution on C-Cl bonds, and this in turn leads to a larger degree of bond angle and/or bond disorder. It is known that for chemical mixture, changes in clustering and bond-angle disorder generally result in changes in the Raman spectra.

In our study, these effects are reflected through a reduction in the intensity. We notice that, the increase in the methanol concentration is associated with increase in the value of the parameter (intensity decreasing). This happens because the increase in methanol concentration causes an increase in the number and/or size of the rings in the mixture and also a larger degree of bond angle and/or bond disorder, and these changes in turn lead to a higher degree of disorder in the mixture.

Further increase in methanol concentration above a certain threshold results in forming hydrogen bonded winding chains formed by eight/ten molecules with a rather low fraction of branching points [6,8]. In this case, the carbon molecules are distributed around the methanol chains, and this leads to a removal of bond-angle disorder and may imply the formation of long ordered networks in the material. As a result, the system undergoes a disorder-order. This indicates that the addition of methanol stops the increase in the disorder in CCl_4 structure. These changes in structure are the reason for declining the parameter value with the increase of methanol concentration.

From Figure 3 we can see that the curves corresponding to the spectral lines ν_2 and ν_3 are congruent. In addition, we can observe that there is a dramatic increase in the value of with increasing in the methanol concentration to the value of $C=0.3$ v/v, where this parameter reaches its maximum value and it seems that this maximum value is a common feature of all spectral lines.

The preceding discussion leads to the following important results:

1. The Raman spectra of carbon tetrachloride depend on clustering of the methanol molecules and on bond-angle disorder.
2. We can use the details of the curves in Figure 4 to investigate the structural composition of methanol in $\text{CH}_3\text{OH}/\text{CCl}_4$ solutions.
3. The parameter can be used as a measure of the bond-angle order degree of C-Cl polarized bonds.

Some useful results can be obtained from studying the peak position shift as a function of methanol concentration, where it was noted that the frequencies corresponding to the peaks ν_2 , ν_4 , shift toward higher wave numbers. This behavior indicates that the forces acting on the corresponding bonds are repulsive forces. On the other hand, we found that the peak ν_3 shifts toward lower wave numbers. This behavior indicates that the forces acting on the corresponding bonds are attractive forces.

The shape factor of each spectral line is plotted in Figure 4 as a function of the concentration of methanol in the solution. Comparing with the previous Figure, an important result can be obtained, that is, in low concentrations region each curve in Figure 4 is compatible in behavior with its counterpart in Figure 3. This compatibility continues in the area of high concentrations only for spectral lines ν_2, ν_3 . There is an exception of spectral line ν_1 , where in this case there is a discrepancy in the behavior of the two curves for all concentration values.

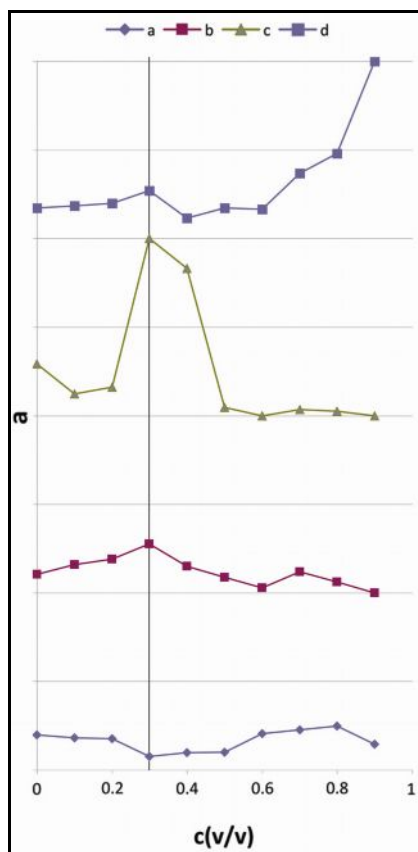


Figure 4: The variation of shape factor as a function of concentration
 (a) line ν_1 (b) line ν_2 (c) line ν_3 (d) line ν_4 .

The presence of the maximum value indicates that there is an important change in the dynamics of the interaction in the mixture, and this confirms the obtained conclusion in Figure 4. However it seems that the vibrations corresponding to the spectral line ν_4 remain independent of the mixture dynamic changes, where interdependence continues growing for the whole concentration area.

The increase in the shape factor value indicates that the spectral line has the highest proportion of Gaussian Shape. This means that the environment surrounding the chemical bond has a higher degree of symmetry. The following table summarizes the relationship between the changes in the degree of symmetry and each of the concentration, and the type of forces acting on the bond.

Table 1 The changes in the degree of symmetry and type of forces acting on the bond In the areas of low and high concentrations. (↑):Increasing similarity,(↓): Decreasing similarity.

Spectral Line	Force type	The direction of symmetry changing	
		Low concentration	High concentration
ν_1	attractive forces	↓	↑
ν_2	repulsive forces	↑	↓
ν_3	repulsive forces	↑	↓
ν_4	repulsive forces	↑	↑

By investigating the data, we can note that, in the low concentration area, symmetry increases for all the vibrations, except for those exposed to attractive forces. Adverse behavior occurs when moving to the higher pressures with the exception of the ν_4 spectral line case, which belongs to deformity vibrations, since in this case the symmetry continues to increase despite the continuous increase in concentration. The stretching vibrations are the only vibrations that are exposed to attractive forces, and this shows that the forces of the

mutual attraction effect between methanol molecules has an effect according to the axis passing through the C atom of the carbon tetrachloride molecule and the O atom in methanol molecules

4. Conclusion

In this work, several samples with different concentrations of methanol and carbon tetrachloride mixtures have been prepared. The prepared samples were characterized by Raman spectroscopy. Raman spectra for carbon tetrachloride have been analyzed.

The results from this work showed that the intensity can change as a result of two factors; the first is associated with the decreasing of carbon tetrachloride concentration due to dilution with methanol; and the second is related to the degree of order of C-Cl polarized bonds, which are distributed around the methanol clusters. The main result of this work is that with the solution diluted, the intensity changes resulting from the second factor are consistent with the changes in the structure of the methanol solution. In addition, we found that the relationship between the shape factor (Resulting from the peak fitting process) and the intensity changes resulting from the second factor is dependent on both the pattern of vibration of the bond and the structure of methanol in the solution.

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