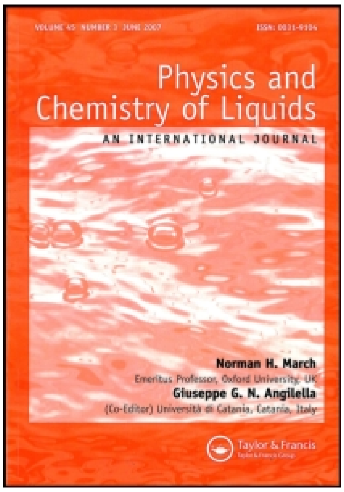

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Infrared studies on hydrogen bonding interaction between acrylic esters with 1-dodeconal and phenol in carbon tetrachloride

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Infrared studies on hydrogen bonding interaction between acrylic esters with 1-dodeconal and phenol in carbon tetrachloride

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The influence of the hydroxyl group in 1-dodeconal and phenol on the carbonyl vibration of representative compounds belonging to methyl methacrylate, ethyl methacrylate and butyl methacrylate in carbon tetrachloride has been studied by Fourier transform infrared spectroscopic method. The integrated intensities and change in dipole moments for O–H and C=O bonds were calculated. The formation constants of the 1 : 1 complexes have been calculated using Nash's method. The values of the formation constant and Gibbs energy vary with the ester chain length, which suggests that the strengths of the intermolecular hydrogen bonds (O–H ··· O=C) are dependent on the alkyl group of the acrylic ester and the results show that the proton accepting ability of acrylic esters is in the order methyl methacrylate < ethyl methacrylate < butyl methacrylate. The strength of the intermolecular C=O: HO bonds is also shown to be dependent on the basicity of the C=O group of acrylic esters and the acidity of the proton donor.

Keywords: FTIR; alkyl methacrylate; phenol; 1-Dodeconal; hydrogen bonding

1. Introduction

Hydrogen bonds constitute a very interesting class of intermolecular interactions, which are extremely important in many fields of chemistry and molecular biology. The compounds containing the carbonyl group are among the most important organic compounds, because they are of central importance to organic chemistry and biochemistry. The study of binary and ternary mixtures of acrylic esters such as methyl methacrylate (MMA), ethyl methacrylate (EMA) and butyl methacrylate (BMA) with polar and nonpolar solvents is expected to provide useful parameters for efficient design of transesterification process [1]. The results from such studies are also useful in solving many problems associated with heat flow and fluid flow [2]. Recently our research group has investigated the complex formation of acrylic esters with proton donors (alcohols) in nonpolar solvents using Fourier transform infrared (FTIR) spectroscopy and dielectric methods [3–10]. Kempter and Mecke [11] have determined the formation constant of phenol in carbon tetrachloride for higher associated complexes, and a number of investigators, including Wulf [12], Gordy and Niclsen [13], Luttke and Mecke [14], have made spectrophotometric studies of phenol and a number of substituted phenols in a

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variety of solvents. In the present study, an attempt has been made to study the hydrogen bonding between the free hydroxyl and carbonyl groups of 1-dodeconal and phenol and acrylic esters (MMA, EMA and BMA) in carbon tetrachloride using FTIR spectroscopy.

2. Experimental details

A Perkin–Elmer Spectrum RX-1 spectrometer with resolution of $\pm 1\,\text{cm}^{-1}$ was used. Spectra were recorded at room temperature (298 K) in the region of 4000–400 cm^{-1} and NaCl cell of path length 0.1 mm was used. Transmission values were read in steps of 5%. The spectrometer possesses autoalign energy optimisation and dynamically aligned Interferometer. It is fitted with a KBr beam splitter, a DTGS-Detector and Everlgo$^{\text{TM}}$ mid-IR source.

A base line correction was made for the spectra recorded. Methyl methacrylate, EMA and BMA with purity >99% (Spectroscopic grade) used in this investigation were purchased from Aldrich and used without further purification. Analar grade 1-dodecanol, phenol and carbon tetrachloride were purified by standard methods [15,16] and redistilled before use.

3. Results and discussion

Figure 1(a–f) shows the carbonyl (C=O) absorption of solution of MMA, EMA and BMA containing varying amounts of 1-dodeconal and phenol with carbon tetrachloride. 1-Dodecanol and phenol in carbon tetrachloride exhibit two hydroxyl bands in the region 3700–3300 cm^{-1}; a sharp peak above 3600 cm^{-1} is ascribed to the OH stretching vibrations of the free OH bond of alcohol molecules and the second band, near 3350 cm^{-1}, is due to polymeric (hydrogen bond) absorption. Similar results were reported by Bellamy and Pace [17] for 1-alcohols and phenols in a carbon tetrachloride system. For ternary mixtures, the proton acceptor (MMA, EMA and BMA) is fixed at 0.03 mol L^{-1} and proton donor (1-dodeconal and phenol) concentration varies from 0.03 to 1.5 mol L^{-1}. In the pure solvent, a single free carbonyl band is formed for MMA at 1726 cm^{-1}, EMA at 1720 cm^{-1} and 1718 cm^{-1} for BMA.

The shift in $\nu_{\text{C=O}}$ frequency for MMA occurs at a higher frequency than the $\nu_{\text{C=O}}$ frequency for EMA and BMA. This is due to the inductive electron contribution of methyl group to the carbonyl group which weakens the C=O bond via ⊕C–O–, causing the $\nu_{\text{C=O}}$ mode to vibrate at a lower frequency [18].

The free O–H band intensity increases with increasing 1-dodeconal concentration, but at the same time the reverse trend is observed for carbonyl absorption band are shown in Figure 1(a–c). This observation indicates that there is 1 : 1 complex formation between the free hydroxyl and carbonyl group (i.e.) $\text{O–H}\cdots\text{O=C}$ [19]. With addition of phenol the intensity of free O–H band increases and a decreasing trend is observed in the free carbonyl band. When the concentration of phenol increases above 0.05 mol L^{-1}, a new band appears at 1714 cm^{-1}, for MMA, 1706 cm^{-1} for EMA and 1701 cm^{-1} for BMA. The intensity of the original band decreases, as more and more phenol is added, the intensity of the low frequency band continues to increase, and gradual asymmetry on the low frequency side develops. The two bands, which are separated by 12 cm^{-1} for MMA, 14 cm^{-1} for EMA and 17 cm^{-1} for BMA, do not change their positions on further addition of phenol.

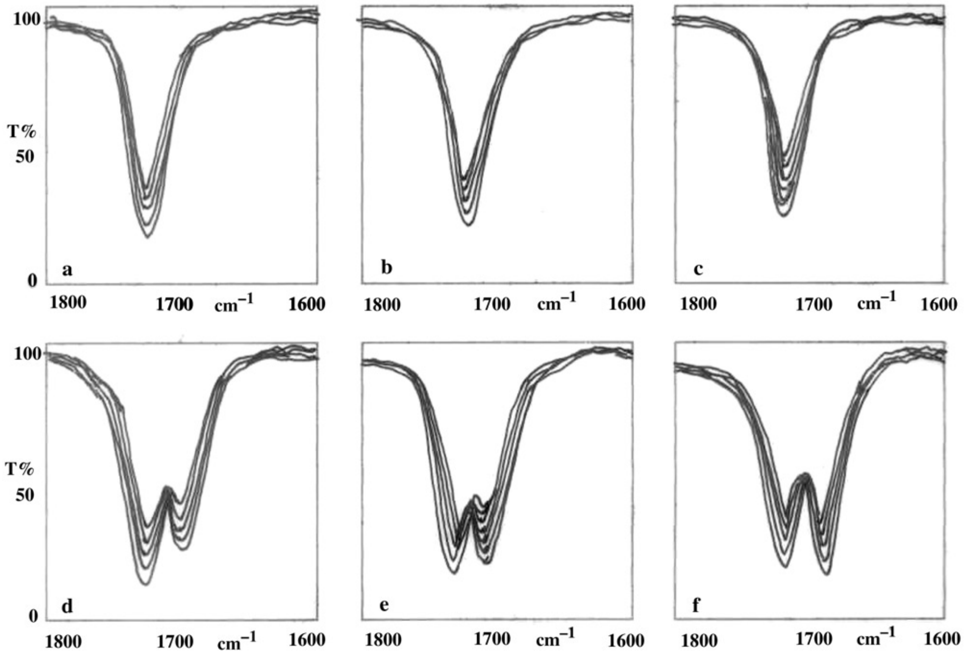

Figure 1. (a–c) MMA, EMA and BMA with various concentration of 1-dodeconal in CCl_4; (d–f) MMA, EMA and BMA with various concentration of phenol in CCl_4.

From the spectrum of MMA, EMA and BMA with phenol in CCl_4 (Figure 1, d–f), the appearance of new band on lower frequency side of free carbonyl band is more prominent in BMA than EMA and MMA, this shows that BMA is more basic than EMA and MMA. Therefore, one would expect that the strongest intermolecular hydrogen bonds formed between the C=O group of BMA and the OH proton of phenol. The new band on lower frequency side of free carbonyl band is not observed in 1-dodeconal with MMA, EMA and BMA in carbon tetrachloride. This may be due to the fact that 1-dodeconal is less associative because of its steric properties.

The integrated intensities of the C=O band were calculated using the relation [20].

$$\mathrm{As} = \frac{2.303}{Cl}\int_{\nu_2}^{\nu_2} \log_{10}\left[\frac{Io}{I}\right] \mathrm{d}\nu \frac{C^1 M}{\rho T N_{\mathrm{A}}} \mathrm{cm}^2\ \mathrm{s}^{-1}\ \mathrm{mol}^{-1},$$

where ν_1 and ν_2 are the upper and lower frequencies in cm^{-1} of the absorption band, C is the concentration (mol^{-1}) of the carbonyl molecules, l is the cell thickness in cm. C^1 is the velocity of light, M the molecular weight, ρ is the density, T is the absolute temperature and N_{A} is Avogadro's number. Using the integrated intensity values and assuming that the vibration is a pure stretching mode, the change in bond moment on stretching was calculated from the relation [21]:

$$\frac{\mathrm{d}\mu}{\mathrm{d}r} = \left(\frac{1}{m_{\mathrm{C}}} + \frac{1}{m_{\mathrm{O}}}\right)^{-1/2} \frac{\mathrm{d}\mu}{\mathrm{d}Q} \quad \text{and} \quad \frac{\mathrm{d}\mu}{\mathrm{d}Q} = \pm\left(\frac{3C^1}{\pi}\mathrm{As}\right)^{1/2}.$$

As represents the integrated intensity of the C=O at the concentration of alcohols and phenols at which most of the carbonyl bond is H-bonded as the 1 : 1 complex.

Table 1. C=O stretching vibration of alkyl methacrylates (MMA, EMA and BMA) and 1-dodeconal concentration in carbon tetrachloride.

Concentration of 1-dodeconal (mol L^{-1})	As × 10^7 ($cm^2\,mol^{-1}\,s^{-1}$)			($d\mu/dr$) × 10^{10} (esu cm^{-1})		
	MMA	EMA	BMA	MMA	EMA	BMA
0.00	1.213	1.278	1.325	1.865	1.914	1.949
0.05	1.347	1.402	1.459	1.965	2.005	2.045
0.09	1.522	1.578	1.627	2.089	2.127	1.159
0.15	1.651	1.715	1.748	2.175	2.217	2.238
0.20	1.745	1.962	1.988	2.236	2.371	2.387
0.50	1.924	2.212	2.269	2.348	2.518	2.550
1.00	2.206	2.348	2.422	2.515	2.594	2.635
1.50	2.258	2.469	2.597	2.544	2.660	2.728

Table 2. C=O stretching vibration of alkyl methacrylates (MMA, EMA and BMA) and phenol concentration in carbon tetrachloride.

Concentration of phenol (mol L^{-1})	As × 10^7 ($cm^2\,mol^{-1}\,s^{-1}$)			($d\mu/dr$) × 10^{10} (esu cm^{-1})		
	MMA	EMA	BMA	MMA	EMA	BMA
0.00	1.486	1.679	1.821	2.064	2.194	2.285
0.05	1.779	2.106	2.356	2.258	2.457	2.599
0.09	2.358	2.689	2.721	2.601	2.776	2.793
0.15	2.841	3.123	3.486	2.854	2.992	3.161
0.20	3.127	3.875	3.822	2.994	3.331	3.310
0.50	2.916	3.456	3.543	2.891	3.147	3.187
1.00	2.723	3.289	3.369	2.794	3.070	3.107
1.50	2.458	2.867	2.914	2.654	2.867	2.890

The integrated intensity and change in dipole moment at various concentrations of proton donor (1-dodeconal and phenol) with methyl methacrylate, ethyl methacrylate and butyl methacrylate in the CCl_4 system are given in Tables 1 and 2. In the case of the system MMA with phenol in carbon tetrachloride, the change in dipole moment for 1 : 1 complex increases and reaches a maximum value as the donor concentration is increased. Further increase in the concentration of donor molecule results in a slight decrease in the value of the change in dipole moment.

A similar trend is also observed for other two-alkyl methacrylates (EMA and BMA). This result is closely in agreement with Ramaswamy *et al.* [22] and Malathi *et al.* [23] for the systems of *p*-cresol with different C=O group in carbon tetrachloride. But this trend does not exist in 1-dodeconal with alkyl methacrylates (MMA, EMA and BMA), which reveals that the acidity of phenol is in higher order than in 1-dodeconal. This may perhaps be due to the fact that at higher concentrations the donor molecules probably interact with the 1 : 1 complex also. Furthermore, the oxygen atom in the C=O bond contains two lone pairs of electrons in hybrid orbitals, which are oriented at 120° to each other. During the complex formation, the donor hydrogen aligns itself with one of the lone pairs to form a

Table 3. Carbonyl frequencies, formation constant (K) and free energy change (ΔG) of alkyl methacrylates with 1-dodeconal and phenol in carbon tetrachloride.

Proton acceptor	Frequencies (cm^{-1})		Formation constant (K) ($\mathrm{L\,mol}^{-1}$)	Free energy change (ΔG) ($\mathrm{kcal\,mol}^{-1}$)
	Free (C=O) (cm^{-1})	(C=O) (1 : 1) (cm^{-1})		
1-Dodeconal				
Methyl methacrylate	1726	–	10.23	1.37
Ethyl methacrylate	1720	–	11.08	1.42
Butyl methacrylate	1718	–	11.86	1.46
Phenol				
Methyl methacrylate	1726	1714	11.18	1.42
Ethyl methacrylate	1720	1706	11.97	1.47
Butyl methacrylate	1718	1701	12.66	1.50

bond like $\mathrm{O{-}H \cdots O{=}C}$ to indicate that the H bond joins together two bonds and not two atoms.

This position is most favourable for the maximum interaction to occur between the lone pair atomic dipole and the O–H bond thus forming the 1 : 1 complex. When the O–H bond vibrates, the lone pair electron also vibrates in consonance with the O–H bond, and thus contributes to the changes in the dipole moment, accounting for the observed increased intensity, hence $\mathrm{d}\mu/\mathrm{d}r$ of the OH bond. In the case of C=O frequencies the C=O induces a moment in OH bond and this will lead to the increase in the observed intensity of the carbonyl stretch. Since the polarisability of C=O is small, the induced moment change will be small compared to the change in the O–H bond dipole.

The equilibrium constant (K) for the 1 : 1 complex is calculated using the following relation [24]:

$$K = \frac{[AB]}{[A][B]},$$

where $[AB]$ is the concentration of the 1 : 1 complex and $[A]$ and $[B]$ are the initial concentration of the proton donor and proton acceptor, respectively. A graph was plotted between $Y = [A]^{-1}$ and $X = 1 - (a/a_\mathrm{o})^{-1}$, where a and a_o are the absorbances of the carbonyl band of alkyl methacrylate in the presence and absences of alcohol, respectively. The intercept of the graph in the ordinate yields K. The free energy change (ΔG) of the system is calculated using the following equation [25].

$$\Delta G = -RT \ln K,$$

where R, T and K represent the universal gas constant, absolute temperature and formation constant of the relative system, respectively.

Table 3 provides the carbonyl frequency of alkyl methacrylates, formation constant (K) and the free energy change (ΔG) value of the hydrogen-bonded complexes in carbon tetrachloride. From Table 3, it can be seen that the formation constant and free-energy change for hydrogen-bond formation of 1-dodeconal, and phenol with alkyl methacrylate are observed in the order methyl < ethyl < butyl. This may be attributed to the difference in basicity of the alkyl methacrylate groups, which vary in the order methyl < ethyl < butyl [26,27]. This is because of the negative inductive effect of the alkyl groups increases in the order methyl to butyl, and the electron contribution of the butyl group to the C=O group is significantly greater than that from the methyl group.

The higher values of K and ΔG are observed in BMA than EMA and MMA, which indicates that BMA is more basic than MMA and EMA. The strength of the intermolecular hydrogen bond formed between a C=O group and ROH proton (e.g. C=O: HOR) dependent on the basicity of the C=O group, the acidity of the ROH proton and the intermolecular distances between the acid and basic sites.

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