FTIR study of hydrogen bonding interactions between alkyl esters and hexanol, *p*-cresol in carbon tetrachloride

F Liakath Ali Khan*, P Sivagurunathan[a] & J Asghar

Department of Physics, Islamiah College, Vaniyambadi, Tamilnadu 635 752

[a]Department of Physics, Annamalai University, Annamalai Nagar, Tamilnadu 608 002

*Email: shamisardar@yahoo.com

The effect of hydroxyl group in hexanol and *p*-cresol on the carbonyl vibration of representative compounds belonging to methyl methacrylate, ethyl methacrylate and butyl methacrylate in carbon tetrachloride has been studied by FTIR spectroscopic method. The integrated intensities and change in dipole moments for O-H and C=O bonds were calculated. Utilizing Nash method, the formation constant and free energy of the 1:1 complexes have been calculated. The formation constant and free energy change values vary with chain length of acrylic esters, which suggests that the strengths of the intermolecular hydrogen bonds (O–H…O=C) are dependent on chain length of acrylic esters. The strength of the intermolecular C=O: HO bonds is shown to be dependent on the basicity of the C=O group of alkyl esters and the acidity of the proton donor.

Keywords: Methyl methacrylate, Ethyl methacrylate, Butyl methacrylate, *p*-cresol, 1-hexanol, Hydrogen bonding

1 Introduction

The study of hydrogen bonding by means of infrared spectroscopy has found wide applications and an exhaustive account of the procedures adopted has been reported by Pimental and McClellan[1]. The study of binary and ternary mixtures of acrylic esters such as methyl methacrylate, ethyl methacrylate and butyl methacrylate with polar and non-polar solvents is expected to provide useful parameters for efficient design of transesterification process[2].

The results from such studies are also useful in solving many problems associated with heat flow and fluid flow[3]. Kempter and Mecke [4] have determined the formation constant of phenol in carbon tetrachloride for higher associated complexes and numbers of researchers, including Wulf[5], Gordy and Niclsen[6], Luttke and Mecke[7], have made spectrophotometric studies of phenol and a number of substituted phenols in a variety of solvents. Recently our research group has investigated the complex formation of acrylic esters with proton donors (alcohols) in non-polar solvents using FTIR spectroscopy and dielectric methods[8-15]. Whetsel and Kagarise[16] and Krishna Pillai *et al*[17].have made an extensive study of the effect of different types of solvents-strongly interacting and weakly interacting on the carbonyl absorption bands representative compounds of esters, ketones and aldehydes, and

confirmed the existence of the formation of 1:1 and 1:2 complexes in the different systems studied. Acrylic esters [methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA), methyl methacrylate (MMA), ethyl methacrylate (EMA) and butyl methacrylate (BMA)] are important industrial chemicals used as precursors in the production of technically important high polymeric species. It has a wider area of utility in the fields like dentistry, medicine, pharmaceuticals, industry as a monomer for synthetic rubber, optical plastics, in the manufacture of leather finish resins, textile resins, solvent coatings, adhesives and oil additives, in emulsions for textiles, in paper finishing and in the manufacture of contact lenses[18]. Keeping both the industrial and scientific interests in mind, an attempt has been made in the present work to study the hydrogen bonding between the hydroxyl group of 1-hexanol, *p*-cresol and the carbonyl groups of acrylic esters (methyl methacrylate, ethyl methacrylate and butyl methacrylate) in carbon tetrachloride using FTIR spectroscopy.

2 Experimental Details

A Perkin-Elmer Spectrum RX-1 spectrometer with resolution of $\pm$ 1 cm^{-1} was used. Spectra were recorded at room temperature (298 K) in the region 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 auto align energy optimization and dynamically aligned interferometer. It is fitted with a KBr beam splitter, a DTGS-Detector and Everlgo[TM] mid-IR source. A base line correction was made for the spectra recorded. The peak intensities (absorbances) were calculated by the formula:

Absorbance = $\log_{10}(I_o/I)$

where (I_o/I) is the ratio of the intensity of the incident light to the transmitted light.

The alkyl methacrylate monomers of molecular weight 100.12 (methyl methacrylate), 114.15 (ethyl methacrylate) and 142.20 (butyl methacrylate) with purity > 99% (spectroscopic grade) used in this investigation were purchased from Aldrich and used without further purification. AR grade 1-hexanol, *p*-cresol and carbon tetrachloride were purified by standard methods[19,20] and redistilled before use.

2.1 Calculation of spectral parameters

The integrated intensities of the C=O band were calculated using the relation[21].

$$As = \frac{2.303}{Cl} \int_{v_2}^{v_2} \log_{10}\left[\frac{Io}{I}\right] dv \frac{C^1 M}{\rho T N_A} \, cm^2 s^{-1} mol^{-1}$$

where v_1 and v_2 are the upper and lower frequencies in cm^{-1} of the absorption band, C the concentration (mol^{-1}) of the carbonyl molecules, l the cell thickness in cm. C^1 the velocity of light, M the molecular weight, ρ the density, T 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[22]:

$$\frac{d\mu}{dr} = \left(\frac{1}{m_c} + \frac{1}{m_o}\right)^{-\frac{1}{2}} \frac{d\mu}{dQ} \text{ and } \frac{d\mu}{dQ} = \pm\left(\frac{3C^1}{\pi} As\right)^{\frac{1}{2}}$$

where m_c and m_o are the masses of carbon and oxygen atoms. The ratio As/A_{CCl_4}, where A_{CCl_4} represents the value of integrated intensity of pure carbonyl vibration in carbon tetrachloride. In units of $10^{-7} \, cm^2$ $mole^{-1}$, and As 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.

3 Results and Discussion

Figures 1 and 2 show the hydroxyl (O-H) and carbonyl (C=O) absorption of solution of methyl methacrylate (MMA), ethyl methacrylate (EMA) and butyl methacrylate (BMA) containing varying amounts of hexanol and *p*-cresol. The hexanol and *p*-cresol in carbon tetrachloride exhibit two hydroxyl bands in the region 3700-3300 cm^{-1}, i.e. one is due to monomeric (O-H) and other is due to polymeric absorption (O-H bonded). Similar results were reported by Bellamy and Pace[23] for alcohols and phenols in carbon tetrachloride system. For ternary mixtures, the proton acceptor (MMA, EMA and BMA) is fixed at 0.05 moles/l and proton donor (*p*-cresol and 1-hexanol) concentration varies from 0.03 to 1.5 moles/l. In the pure solvent, a single band is formed for MMA at 1726 cm^{-1}, EMA at 1720 cm^{-1} and BMA at 1718 cm^{-1}. The shift in $v_{C=O}$ frequency for MMA occurs at a higher frequency than $v_{C=O}$ 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 $\oplus$ C–O– causing the $v_{C=O}$ mode to vibrate at a lower frequency[24].

The free O-H band intensity increases with increasing hexanol concentration but at the same time the reverse trend is observed for carbonyl absorption band which is shown in Figs 1 and 2. This observation indicates that there is 1:1 complex formation between free hydroxyl and carbonyl group (i.e.) O–H···O=C (Ref.14). With the addition of *p*-cresol, the intensity of free O-H band increases and decreasing trend is observed in free carbonyl band. When concentration of *p*-cresol increases above 0.05-moles/l, a new band appears at 1702 cm^{-1} for MMA, 1704 cm^{-1} for EMA and 1707 cm^{-1} for BMA. The intensity of original band decreases, as more and more of *p*-cresol 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 24 cm^{-1} for MMA, 16 cm^{-1} for EMA and 11 cm^{-1} for BMA, do not change their positions on further addition of *p*-cresol, Evidently this behaviour also indicate that existence of a 1:1 complex. The appearance of new band at lower frequency side of free carbonyl band is more prominent in BMA than EMA and MMA (Figs 1 and 2), this shows strength of hydrogen bond is formed between BMA with *p*-cresol in CCl₄ is greater than EMA and MMA. But this trend (appearance of new band) is not observed in hexanol with MMA, EMA
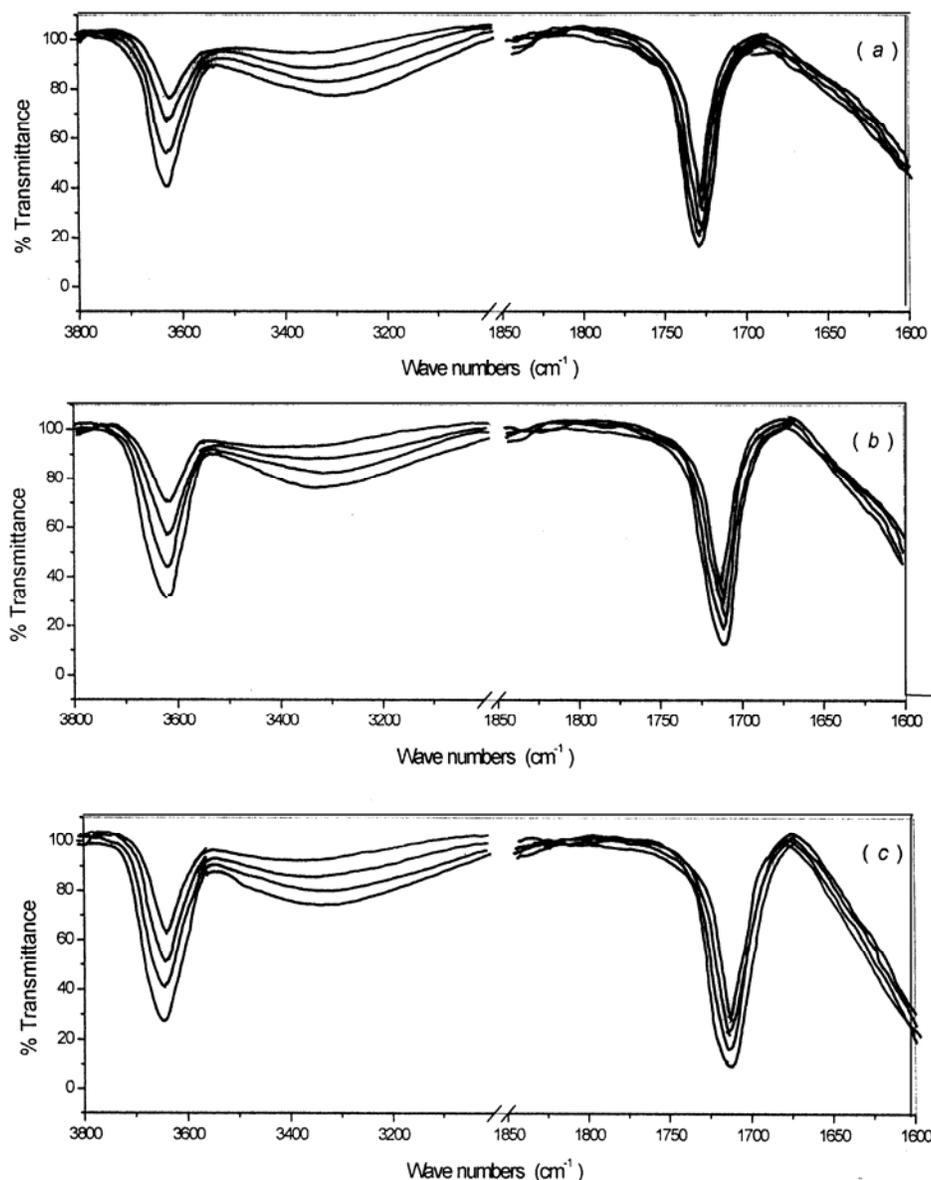
Fig. 1 — FTIR spectra of O-H and C=O regions of various concentrations (0.05, 0.50, 1.00, 1.50M) of 1-hexanol with (a) methyl methacrylate, (b) ethyl methacrylate, (c) butyl methacrylate in carbon tetrachloride

and BMA in carbon tetrachloride, which reveals that the strength of intermolecular hydrogen bond is greater in *p*-cresol than in hexanol. Further, the intensity of new band at lower frequency side of free carbonyl band in butyl methacrylate is greater than EMA and MMA, which shows that the basicity of BMA is higher than MMA and EMA.

The integrated intensity and change in dipole moment at various concentrations of donors (1-hexanol and *p*-cresol) with methyl methacrylate, ethyl methacrylate and butyl methacrylate in CCl$_4$ systems are presented in Tables1 and 2. In the case of the system MMA with *p*-cresol 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 concentrations of donor molecule, results in a slight decrease in value of the change in dipole moment. Similar trend is also observed for other two systems (EMA and BMA). This result is closely in agreement with Ramaswamy *et al.*[25] and Malathi *et al.*[26] for the system of phenol derivatives with different C=O groups in carbon tetrachloride. But this behaviour is not observed in hexanol with acrylic esters (MMA, EMA and BMA), which reveals that the acidity of *p*-cresol is in higher order than in hexanol. This may
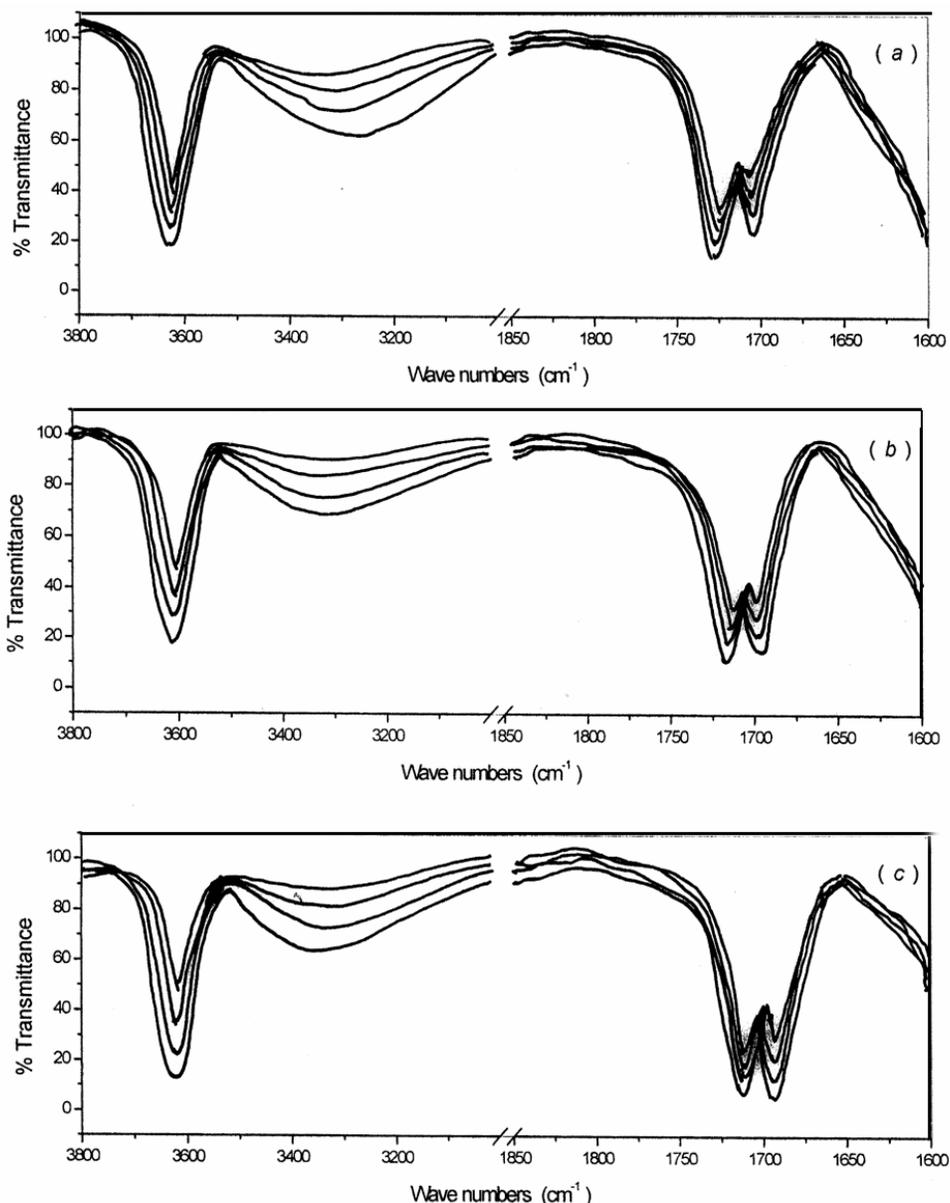
Fig. 2 — FTIR spectra of O-H and C=O regions of various concentrations (0.05, 0.50, 1.00, 1.50M) of *p*-cresol with
(a) methyl methacrylate, (b) ethyl methacrylate, (c) butyl methacrylate in carbon tetrachloride

perhaps be due to the fact that at higher concentrations the donor molecules probably interact with 1:1 complex also. Further, 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 bond like O−H···O=C to indicate that the H bond joins together with two bonds and not with 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 thus, accounting for the observed increased intensity, hence dμ/dr of the O-H bond. In the case of C=O frequencies, the C=O induces a moment in O-H bond and this will lead to the increase in the observed intensity of the carbonyl stretch. Since the polarizability of C=O is small, the induced moment change will be small compared to the change in the O-H bond dipole. This is clearly seen from the changes in intensity observed in O−H bond and C=O

Table1 — C=O Stretching vibration of alkyl methacrylates (MMA, EMA and BMA) and 1-hexanol concentration in carbon tetrachloride

Concentration of 1-hexanol (moles/liter)	$As \times 10^7$ $cm^2\ mole^{-1}\ sec^{-1}$	$\left(\dfrac{d\mu}{dr}\right) \times 10^{10}$ $esu\ cm^{-1}$	$\dfrac{\left(\dfrac{d\mu}{dr}\right)}{\left(\dfrac{d\mu}{dr}\right)_{CCl_4}}$	$\dfrac{As}{A_{CCl_4}}$
Methyl methacrylate 1:1 complexes				
0.00	0.722	1.439	1.000	1.000
0.05	0.987	1.682	1.169	1.367
0.09	1.259	1.900	1.320	1.744
0.15	1.464	2.048	1.424	2.028
0.20	1.758	2.245	1.560	2.435
0.50	1.912	2.341	1.627	2.648
1.00	2.132	2.472	1.718	2.953
1.50	2.327	2.583	1.795	3.223
Ethyl methacrylate 1:1 complexes				
0.00	0.924	1.627	1.000	1.000
0.05	1.183	1.841	1.132	1.280
0.09	1.322	1.947	1.196	1.431
0.15	1.571	2.122	1.304	1.700
0.20	1.889	2.327	1.430	2.044
0.50	2.153	2.484	1.527	2.330
1.00	2.269	2.550	1.567	2.456
1.50	2.522	2.689	1.652	2.729
Butyl methacrylate 1:1 complexes				
0.00	1.107	1.781	1.095	1.000
0.05	1.256	1.897	1.166	1.135
0.09	1.397	2.001	1.230	1.262
0.15	1.649	2.174	1.336	1.490
0.20	1.981	2.383	1.465	1.791
0.50	2.268	2.550	1.567	2.049
1.00	2.339	2.589	1.591	2.113
1.50	2.686.	2.775	1.705	2.426

A_{CCl_4} represents the value of integrated intensity of pure carbonyl vibration in carbon tetrachloride

Table 2 — C=O Stretching vibration of alkyl methacrylates (MMA, EMA and BMA) and *p*-cresol concentration in carbon tetrachloride

Concentration of *p*-cresol (moles/liter)	$As \times 10^7$ $cm^2\ mole^{-1}\ sec^{-1}$	$\left(\dfrac{d\mu}{dr}\right) \times 10^{10}$ $esu\ cm^{-1}$	$\dfrac{\left(\dfrac{d\mu}{dr}\right)}{\left(\dfrac{d\mu}{dr}\right)_{CCl_4}}$	$\dfrac{As}{A_{CCl_4}}$
Methyl methacrylate 1:1 complexes				
0.00	3.117	2.989	1.000	1.000
0.05	3.986	3.380	1.131	1.279
0.09	4.593	3.628	1.214	1.474
0.15	5.213	3.865	1.293	1.672
0.20	6.857	4.433	1.483	2.200
0.50	6.762	4.025	1.473	2.169
1.00	6.487	4.312	1.443	2.081
1.50	5.939	4.126	1.380	1.905
Ethyl methacrylate 1:1 complexes				
0.00	3.359	3.103	1.000	1.000
0.05	4.396	3.550	1.144	1.309
0.09	5.126	3.833	1.235	1.526
0.15	6.359	4.269	1.376	1.893
0.20	7.123	4.518	1.456	2.121
0.50	6.959	4.466	1.439	2.072
1.00	6.523	4.324	1.393	1.942
1.50	6.196	4.214	1.358	1.845

Table 2 — C=O Stretching vibration of alkyl methacrylates (MMA, EMA and BMA) and *p*-cresol concentration in carbon tetrachloride—*Contd*

Concentration of *p*-cresol (moles/liter)	$As \times 10^7$ cm^2 mole^{-1} sec^{-1}	$\left(\dfrac{d\mu}{dr}\right) \times 10^{10}$ esu cm^{-1}	$\dfrac{\left(\dfrac{d\mu}{dr}\right)}{\left(\dfrac{d\mu}{dr}\right)_{CCl_4}}$	$\dfrac{As}{A_{CCl_4}}$
		Butyl methacrylate 1:1 complexes		
0.00	3.986	3.380	1.000	1.000
0.05	5.219	3.868	1.144	1.309
0.09	6.598	4.349	1.287	1.655
0.15	7.436	4.617	1.366	1.866
0.20	7.565	4.657	1.378	1.898
0.50	7.329	4.583	1.356	1.839
1.00	6.887	4.443	1.314	1.728
1.50	5.638	4.020	1.189	1.414

A_{CCl_4} represents the value of integrated intensity of pure carbonyl vibration in carbon tetrachloride

region. The values of $(d\mu/dr)/(d\mu/dr)_{CCl_4}$ for the 1:1 complex of carbonyl + *p*-cresol systems, indicate that the moment induced by the O-H bond in the lone pair of electrons present in the carbonyl group is largely affected by the bulkiness of the carbonyl compound.

Figures 3 and 4 show that a molecular association is arising from hydrogen bonding between the hydrogen atom of alcohol or phenol molecule and the oxygen atom of the ester molecule (O-H···O=C).

The equilibrium constant (K) for the 1:1 complex is calculated using the following relation[27]:

$$K = [AB]/[A][B]$$

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= $(1-(a/a_o)^{-1}$, where a and a_o are the absorbances of the carbonyl band of acrylic ester in the presence and absences of alcohol, respectively (Fig. 5). The intercept of the graph in the ordinate yields *K*. The free energy change (ΔG) of the system is calculated using the following equation[28]:

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

where *R*, *T* and *K* represent the universal gas constant, absolute temperature and formation constant of the relative system, respectively. Table 3 presents the formation constant (*K*) and the free energy change (ΔG) value of the hydrogen-bonded complexes in carbon tetrachloride. Figure 5(a-f) shows the formation constant of 1:1 complexes for MMA, EMA,

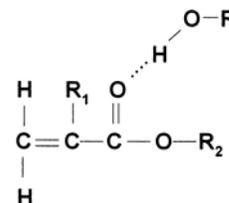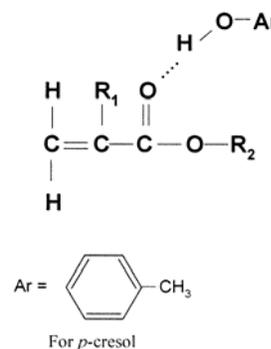Fig. 3 — Hydrogen bonding between alcohols and acrylic esters

where, R= C_6H_{13} (1-hexanol), R_1=CH$_3$, R_2=CH$_3$ for MMA; R_1=CH$_3$, R_2=C$_2$H$_5$ for EMA and R_1=CH$_3$, R_2=C$_4$H$_9$ for BMA

Fig. 4 — Hydrogen bonding between *p*-cresol and acrylic esters

R_1=H, R_2=CH$_3$ (MA), R_1=H, R_2=C$_2$H$_5$ (EA); R_1=H, R_2=C$_4$H$_9$ (BA) R1=CH$_3$, R_2=CH$_3$ (MMA); R_1=CH$_3$, R_2=C$_2$H$_5$ (EMA) and R1=CH$_3$, R_2=C$_4$H$_9$ (BMA)

BMA, with hexanol and *p*-cresol in carbon tetrachloride. From Table 3, it can be seen that the formation constant and free-energy change for hydrogen-bond formation of hexanol and *p*-cresol with alkyl methacrylate are observed in the order

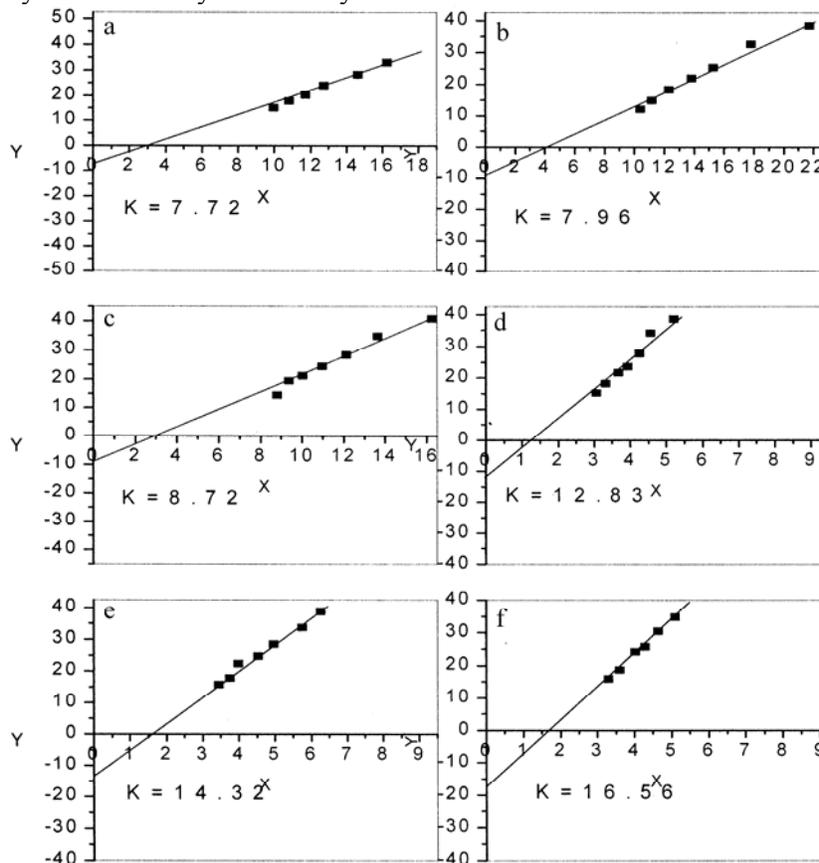methyl < ethyl < butyl. This may be attributed to the difference in basicity of the alkyl methacrylate

Fig. 5 — (a-c) Formation constant (K) for MMA, EMA and BMA with 1-hexanol in carbon tetrachloride. (d-f) Formation constant (K) for MMA, EMA and BMA with *p*-cresol in carbon tetrachloride

Table 3 — Carbonyl frequencies, formation constant (K) and free energy of alkyl esters with 1-hexanol and
p-cresol in carbon tetrachloride

Proton acceptor	Frequencies (cm^{-1})		Formation Constants (K) (l/mol)	Free energy (ΔG) (k cal/mol)
	Free (C=O) (cm^{-1})	(C=O) (1:1) (cm^{-1})		
In 1-hexanol				
Methyl methacrylate	1726	----	7.72	1.20
Ethyl methacrylate	1720	----	7.96	1.22
Butyl methacrylate	1718	----	8.72	1.28
In *p*-cresol				
Methyl methacrylate	1726	1702	12.83	1.51
Ethyl methacrylate	1720	1704	14.32	1.57
Butyl methacrylate	1718	1707	16.56	1.66

groups, which vary in the order methyl < ethyl < butyl [Refs (29-30)]. This is because of the negative inductive effect of the alkyl groups which increase 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 indicate 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.

4 Conclusions

The integrated intensity, dipole moment, formation constant and free energy of acrylic esters (methyl methacrylate, ethyl methacrylate and butyl methacrylate) with 1-hexanol and *p*-cresol in carbon tetrachloride are carried out. From the study, one may conclude that the intermolecular (O–H···O=C) bonds formed between the 1-hexanol and *p*-cresol with acrylic esters are shown to be dependent on the alkyl chain length of the acrylic esters and lies parallel with the acidity of O-H group and the basicity of the acrylic esters and the tendency of complex formation is relatively more in butyl group of acrylic ester than ethyl and methyl group.

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