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Infrared studies on hydrogen bonding interaction between alkyl esters and *p*-cresol in carbon tetrachloride

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Abstract : The influence of the hydroxyl group in *p*-cresol on the carbonyl vibration of representative compounds belonging to methyl methacrylate, ethyl methacrylate and butyl methacrylate in carbon tetrachloride has been investigated by means of FTIR spectroscopy 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 the Gibbs energy vary with ester chain length, which suggests that the strengths of the intermolecular O–H O=C bonds 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

Keywords : Methyl methacrylate, ethyl methacrylate, butyl methacrylate, *p*-cresol, hydrogen bonding

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1. Introduction

Hydrogen bonds constitute a very interesting class of intermolecular interaction, which are of extremely importance 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. Alcohols play an important role in many chemical reactions due to their ability to undergo self-association with manifold internal structures. Experimental investigation of the spectroscopic properties of organic compounds is of great value in understanding the nature of complex formation between the molecules.

Infrared study of alkyl acrylates and alkyl methacrylates in $CHCl_3$ and/or CCl_4 solutions have been reported by Nyquist and Streck [1]. Sastry and Dave [2,3] have measured the excess volumes, isentropic compressibilities and dielectric behaviour of fifteen binary mixtures of alkyl (methyl, ethyl and butyl) methacrylates with several

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alkanols at 308.15 K. Mecke and Kempter [4] have determined the formation constant of phenol in carbon tetrachloride for higher associated complexes and number of investigators 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]. The complex formation has been interpreted in terms of formation constants. Thus, the study and knowledge of spectroscopic properties of the binary and ternary mixtures of acrylic esters with polar associating liquids (alcohols) in non-polar solvents is expected to provide useful and vital process parameters for efficient design of transesterification processes of industrial interest. Keeping both the industrial and scientific interests in mind, an attempt has been made in the present work to study the hydrogen bonding between phenolic group of *p*-cresol and the carbonyl groups of acrylic esters in carbon tetrachloride using FTIR spectroscopy.

2. Experimental details

A Perkin-Elmer Spectrum RX-1 spectrometer with resolution of ±1 cm^{-1} was used. Spectra were recorded at room temperature (298 K) in the region of 4000 to 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 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

$$\text{Absorbance} = \log_{10} (Io/I),$$

where (Io/I) is the ratio of the intensity of the incident light to the transmitted light. Methyl methacrylate (MMA), ethyl methacrylate (EMA) and butyl methacrylate (BMA) with purity > 99% (Spectroscopic grade) used in this investigation were purchased from Aldrich and used without further purification. AR grade carbon tetrachloride and *p*-cresol were purified by standard methods [16,17].

3. Results and discussion

Figure 1 shows the carbonyl absorption bands of approximately 0.03 m/l solutions of methyl methacrylate (MMA), ethyl methacrylate (EMA) and butyl methacrylate (BMA) in carbon tetrachloride. The carbonyl absorption band of acrylic esters in carbon tetrachloride is observed in the order of methyl methacrylate > ethyl methacrylate > butyl methacrylate. From this observation, it may suggest that the specific interactions exist between π-bonds in acrylic esters and the lone pair electrons of *cl* or between lone pair electrons of >C=O group in ester and empty *d*-orbital in chlorine atom of carbon tetrachloride [18]. The *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

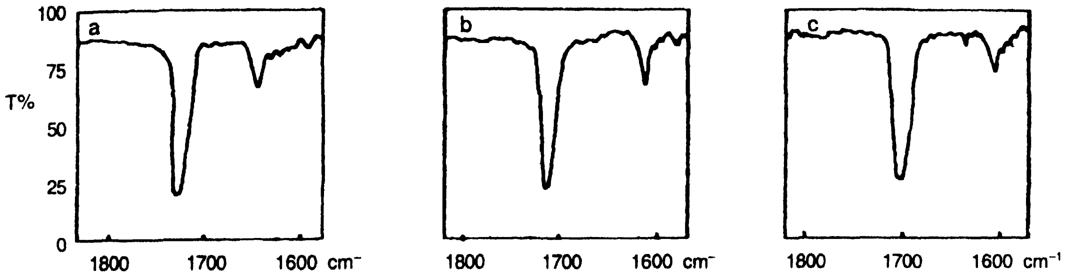

Figure 1. FTIR spectrum of 0.03 concentration of (a) methyl methacrylate (MMA), (b) ethyl methacrylate (EMA) and (c) butyl methacrylate (BMA) in carbon tetrachloride at 298 K

Ramaswamy *et al.* [19] for *p*-cresol with aldehydes, ketones and esters in carbon tetrachloride system. For ternary mixtures, the proton acceptor (MMA, EMA and BMA) is fixed at 0.03 moles/l and proton donor (*p*-cresol) concentration varies from 0.03 to1.5 moles/l.

Figures 2–4 shows the carbonyl (C=O) absorption bands of methyl methacrylate (MMA), ethyl methacrylate (EMA) and butyl methacrylate (BMA) containing varying amounts of *p*-cresol in carbon tetrachloride.

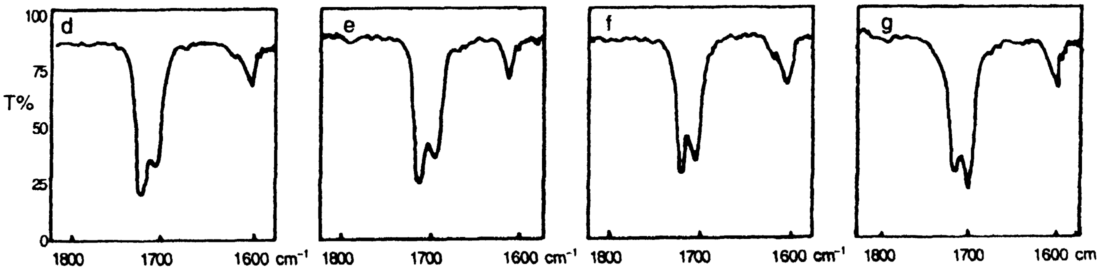

Figure 2. FTIR spectrum of various concentrations of (MMA and *p*-cresol in CCl_4 [d–0 05M, e–0 2M, f–1 00M and g–1.50M].

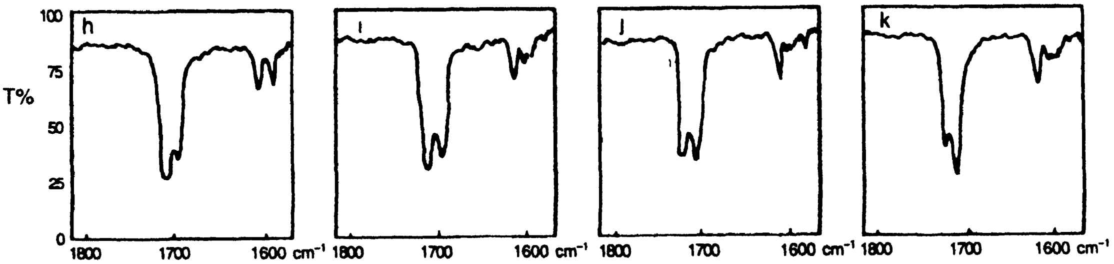

Figure 3. FTIR spectrum of various concentrations of (EMA and *p*-cresol in CCl_4 [h–0.05M, i–0 2M, j–1 00M and k–1.50M].

In pure carbon tetrachloride, a single band representing the free C=O band is found at 1726 cm^{-1} for MMA, at 1720 cm^{-1} for EMA and at 1718 cm^{-1} for BMA. The shift in $\nu_{C=O}$ frequency for MMA occurs at a higher frequency than $\nu_{C=O}$ frequency for EMA and BMA. This is due to the inductive electron contribution of methyl group to

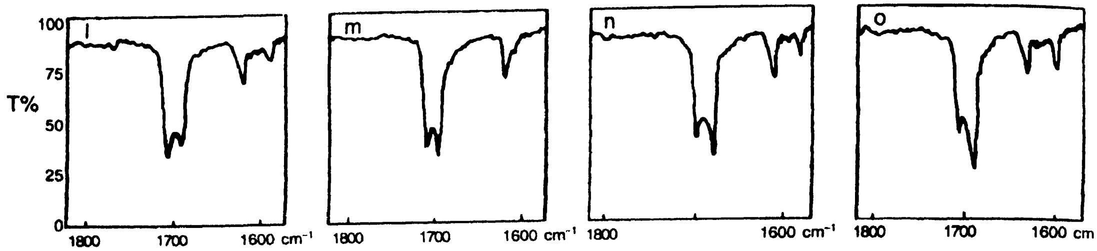

Figure 4. FTIR spectrum of various concentrations of (BMA and *p*-cresol in CCl_4 [l–0.05M, m–0.2M, n–1.00M and o–1.50M].

the carbonyl group which weakens the C=O bond *via* ⊕ C–O- causing the $\nu_{C=O}$ mode to vibrate at a lower frequency [20]. With the addition of *p*-cresol in methyl methacrylate, a new band appears at lower frequency side of original band. The intensity of new band increases slowly with increasing *p*-cresol concentration and gradual asymmetry on the low frequency side develops but at the same time the reverse trend is observed for the intensity of original free carbonyl band. Similar observations are observed in ethyl methacrylate and butyl methacrylate.

For methyl methacrylate a new band appears at 1702 cm^{-1}, 1704 cm^{-1} for ethyl methacrylate and 1705 cm^{-1} for butyl methacrylate. The two bands (original and new band), which are separated by 24 cm^{-1} for MMA, 16 cm^{-1} for EMA and 13 cm^{-1} for BMA, do not change their positions on further addition of *p*-cresol. Evidently this behaviour indicates the existence of a 1 : 1 complex. By comparing the spectrum of MMA (Figures 2d-g), EMA (Figures 3h-k), and BMA (Figures 4l-o), the intensity of new band on lower frequency side of free carbonyl band is observed in the order of BMA > EMA > MMA. This is because 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. Therefore, one would expect that the strongest intermolecular hydrogen bonds formed would be between the C=O group of butyl methacrylate and the OH proton of *p*-cresol and weakest between the C=O group of methyl methacrylate and the OH proton of *p*-cresol [14].

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

$$As = \frac{2.303}{C\,l}\int^{\nu_2} \log_{10}\left[\frac{Io}{I}\right] d\nu \, \frac{C^1\,M}{\rho\,T\,N_A}\ \mathrm{cm^2\ sec^{-1}\ mol^{-1}} \qquad (1)$$

where ν_1 and ν_2 are lower and upper frequencies in cm^{-1} of the absorption band, *C* is the concentration (mol l^{-1}) of the carbonyl molecules, *l* is the cell thickness in cm. C^1 is the velocity of light, *M* 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 [22] :

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

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 *p*-cresol at which most of the carbonyl bond is H-bonded as the 1 : 1 complex.

The integrated intensity and change in dipole moment at various concentrations of *p*-cresol with methyl methacrylate, ethyl methacrylate and butyl methacrylate in CCl_4 systems are given in Table 1. 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 the concentration of donor molecule result in a slight decrease in the value of the change in dipole moment. Similar trend is also observed for other two systems (EMA and BMA).

This result is closely agreement with Ramaswamy *et al.* [19] and Malathi *et al.* [23] for the systems of *p*-cresol with different C=O group in carbon tetrachloride. This may perhaps be due to the fact that at higher concentrations the donor molecules probably interact with the 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 two bonds and not two atoms. This position is most favorable 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 $d\mu/dr$ of the OH 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 region. From the values of $(d\mu/dr)/(d\mu/dr)_{CCl_4}$ for the 1 : 1 complex of carbonyl + *p*-cresol systems, suggests 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.

The spectral data of the characteristic bands of the interactive systems are used for the calculation of formation constant [24]. In this method at low concentration of

Table 1. 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}	$\left(\frac{d\mu}{dr}\right) \times 10^{10}$ esu cm^{-1}	$\left(\frac{d\mu}{dr}\right)/\left(\frac{d\mu}{dr}\right)_{CCl_4}$	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
		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

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

p-cresol the influence of the higher order complexes on the absorption spectrum of base is neglected.

The concentrations of the proton donor [*A*], proton acceptor [*B*] and complexed species [*AB*] involved in the interaction are assumed to be obeying Beer's law at a given characteristic frequency of the 1 : 1 complex. The total absorbance per centimeter path of *B* is given by

$$a = \varepsilon_b\,[B] + \varepsilon_{ab}\,[AB] \tag{3}$$

where ε_b and ε_{ab} are the molar absorbtivities of the species B and complexed species AB respectively.

In the absence of a complexing agent 'A' the total absorbance per centimeter is given by

$$a_0 = \varepsilon_b\,[B^0] \tag{4}$$

where $[B^0]$ is the initial concentration of B.

Dividing the eq. (3) by eq. (4)

$$\frac{a}{a_0} = \frac{[B]}{[B^0]} + \frac{[AB]}{[B^0]}\cdot\frac{\varepsilon_{ab}}{\varepsilon_b}\,. \tag{5}$$

The formation constant K may be defined as

$$K = [AB]/[A][B]\,. \tag{6}$$

Combining eqs. (5) and (6)

$$\frac{a}{a_0} = \frac{[B]}{[B^0]}\left[1 + \frac{\varepsilon_{ab}}{\varepsilon_b}[A]\right]. \tag{7}$$

Introducing the conservation of species of B

$$[B^0] = [B] + [AB]. \tag{8}$$

Invoking eq. (6) one can find that

$$\frac{[B]}{[B^0]} = (1 + K\,[A])^{-1}\,. \tag{9}$$

When eq. (9) is substituted in eq. (7)

$$\frac{a}{a_0} = \frac{1 + \frac{\varepsilon_{ab}}{\varepsilon_b}K[A]}{1 + K[A]}\,. \tag{10}$$

Taking

$$\frac{a}{a_0} = Z\,, \tag{11}$$

$$K\frac{\varepsilon_{ab}}{\varepsilon_b} = \alpha \tag{12}$$

and $[A] = 1/Y$.

Eq. (10) becomes

$$Z = \frac{1 + \frac{\alpha}{Y}}{1 + \frac{K}{Y}}\,, \tag{13}$$

$$Y = \frac{Zk - \alpha}{1 - Z}\,. \tag{14}$$

Expressing

$$X = \frac{1}{1-Z}$$

$$X = \frac{1}{1-\frac{a}{a_0}}$$

Since $Z =$

where a and a_0 are the absorbances of the carbonyl band of acrylic ester in the presence and absence of alcohol respectively

Eq (14) rewrite in the form of linear equation as

$$Y = X(K - \alpha) - K \qquad (15)$$

The physical significance of eq (13) is quite clear When the reciprocal of the donor concentration (i e $Y = [A]$) is plotted against the reciprocal of one minus absorbance ratio (i e $X = 1/(1 - a/a_0)$) gives a straight line, which may confirm the 1 1 complex formation The intercept of the plot of Y against X gives negative value of K

The free energy change (ΔG) is the energy difference between the products and the reactants The free energy change of the association reaction can be calculated using the following relation [25]

$$\Delta G = - RT \ln K \qquad (16)$$

where R (1 987 × 10^3 kcal/deg/mole), T and K represents the universal gas constant, absolute temperature and formation constant of the relative systems, respectively

It has been found that two opposing effects namely specific interaction between the ester and -OH group of alcohol (or packing effects due to the interaction between the p-electrons of the ester and -OH group of alcohols) and non-specific dispersion interaction, i e breaking of intermolecular hydrogen bonds in alcohols and (or weakening of dipolar forces in acrylic ester species are possibly operative in these mixtures The relative size of both acrylic ester and p-cresol molecules determines the predominance of a particular type of interactions over the other Table 2 provide the formation constant (K) and the free energy change (ΔG) value of the hydrogen-bonded complexes in

Table 2. Carbonyl frequencies, formation constant (K) and free energy of alkyl esters

System of p-cresol with	Frequencies (cm^{-1})		Formation constants (K) (l/mol)	Free energy (ΔG) (kcal/mol)
	Free (C=O) (cm^{-1})	(C=O) (1 1) (cm^{-1})		
Methyl methacrylate	1726	1702	12 83	1 51
Ethyl methacrylate	1720	1704	14 32	1.57
Butyl methacrylate	1718	1705	16 56	1 66

carbon tetrachloride. Figures 5–7 shows the formation constant of 1 : 1 complexes for MMA, EMA, BMA, with *p*-cresol in carbon tetrachloride. From Table 2, it can be seen that the formation constant and free-energy change for hydrogen-bond formation of *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 groups, which vary in the order methyl < ethyl < butyl [26,27]. 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.

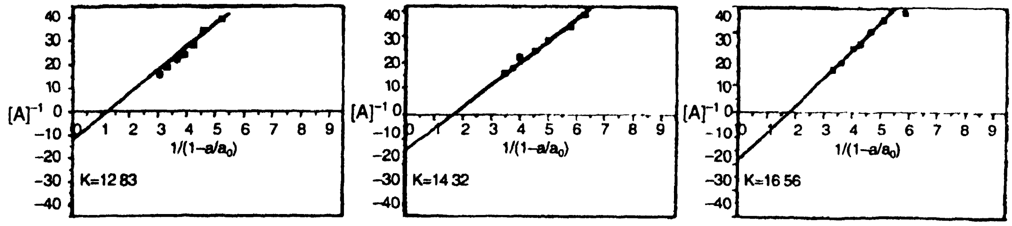

Fig-5 Fig-6 Fig-7

Figure 5. Formation constant (*K*) for MMA + *p*-cresol + CCl_4, **Figure 6.** Formation constant (*K*) for MMA + *p*-cresol + CCl_4, **Figure 7.** Formation constant (*K*) for MMA + *p*-cresol + CCl_4

4. Conclusions

The integrated intensity, dipole moment, formation constant and free energy of acrylic esters (methyl methacrylate, ethyl methacrylate and butyl methacrylate) with *p*-cresol in carbon tetrachloride are carried out. From the study, one may conclude that the intermolecular (OH···O=C) bonds formed between the *p*-cresol and acrylic esters are shown to be dependent on the alkyl chain length of the acrylic esters and lies parallel with the acidity of *p*-cresol 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 and the hydrogen bonding between acrylic esters and alcohols in solution is complicated, depending not only on the acidity and basicity of the interacting components, but also on the solvent properties.

References

[1] R A Nyquist and R Streck *Vib. Spectrosc.* **8** 71 (1994)
[2] N V Sastry and P N Dave *Int. J. Thermophys.* **17** 1289 (1996)
[3] N V Sastry and P N Dave *Indian Acad. Sci.* (*Chem. Sci.*) **109** 211 (1997)
[4] H Kempter and R Mecke *Z. Physik. Chem.* **B46** 220 (1940)
[5] O R Wulf and E J Jones *J. Chem. Phys.* **8** 745 (1940)
[6] W Gordy and Niclsen *J. Chem. Phys.* **4** 769 (1936)
[7] W Luttke and Mecke *Z. Electrochem.* **53** 753 (1949)

[8] P Sivagurunathan, K Dharmalingam and K Ramachandran *Spectrochim Acta A* **64** 127 (2006)

[9] P Sivagurunathan, K Dharmalingam and K Ramachandran *Indian J Pure Appl Phys* **43** 905 (2005)

[10] P Sivagurunathan, K Dharmalingam and K Ramachandran *Main Group Chemistry* **4** 241 (2005)

[11] P Sivagurunathan, K Dharmalingam and K Ramachandran *Phys Chem Liq* **44** 77 (2006)

[12] P Sivagurunathan, K Dharmalingam and K Ramachandran *Indian J Phys* **79** 1403 (2005)

[13] P Sivagurunathan, K Dharmalingam and K Ramachandran *Spectrochim Acta A* **66** 48 (2007)

[14] P Sivagurunathan, K Dharmalingam and K Ramachandran *Z Phys Chem* **219** 1385 (2005)

[15] P Sivagurunathan, K Dharmalingam and K Ramachandran *Main Group Chemistry* **4** 227 (2005)

[16] A Weissberger *Technique of Organic Chemistry* (NewYork Wiley Interscience) (1970)

[17] J R Riddick and W B Bunger *Organic Solvents* (New York Wiley Interscience) (1970)

[18] S L Oswal, B M Patel, A M Patel and N Y Gghael *Fluid Phase Equilib* **206** 313 (2003)

[19] K Ramaswamy, R Pichai and S G Ganandesikan *J Mol Spectroscopy* **23** 416 (1967)

[20] R A Nyquist *Spectrochim Acta* **51A** 475 (1995)

[21] D E Freeman *J Opt Soc Am* **52** 103 (1962)

[22] K Inuzuka, M Ito and S Imanishi *Bull Chem Soc Jpn* **34** 476 (1961)

[23] M Malathi, R Sabesan and S Krishnan *Current Science* **86** 838 (2004)

[24] C P Nash *J Phys Chem* **6** 950 (1960)

[25] C R H Vinogradov *Hydrogen Bonding* (New York Van Nostrand Reinhold Company) (1971)

[26] A Singh and M C Saxena *J Mol Liq* **25** 81 (1983)

[27] A Singh, R Misra, J P Shukla and M C Saxena *J Mol Liq* **26** 29 (1983)