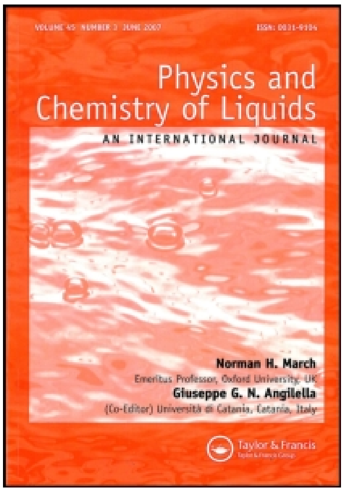

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Solvent effects on hydrogen bonding between 1-pentanol and butyl methacrylate

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Solvent effects on hydrogen bonding between 1-pentanol and butyl methacrylate

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The hydrogen bonding between 1-pentanol and butyl methacrylate (BMA) was investigated in *n*-heptane, CCl_4, and benzene as solvents by using FTIR spectroscopic method. Utilizing Nash method the formation constant and free energy change of 1 : 1 complexes has been determined. The results show a significant dependence of the association constant upon the solvents used. The solvent effect on the formation of hydrogen bond equilibria is discussed in terms of specific interaction between the solute and the solvent. The variation of formation constant values with the solvents confirm the solvent environment which may affect the strength of intermolecular hydrogen bond formation between free O–H group of 1-pentanol and the carbonyl group of BMA (O–H···O=C).

Keywords: 1-Pentanol; Butyl methacrylate; Hydrogen bonding; Solvent effect

1. Introduction

Hydrogen bonds constitute a very interesting class of intermolecular interactions, which are of extreme importance in many fields of chemistry and molecular biology. The study of the effect of solute–solvent interaction and solute–solute interaction is of interest to solution chemists. This motivates investigators to apply the infrared spectroscopy of various research fields. The solvent effects play an important role in organic reactivity phenomena such as the chemical equilibrium, the rate of chemical reactions, the conversion of the polymerization, and so on. Butyl methacrylate (BMA) is a monomer of poly(BMA), a common thermoplastic that is widely used in industry [1]. Alcohols play an important role in many chemical reactions due to the ability to undergo self-association with manifold internal structures. The interaction study between associated liquid and non-associated liquid in inert media gives valuable information about solute–solute and solute–solvent interactions. Recently, the solvent effects on infrared spectra of binary system of methyl methacrylate (MMA) with

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Table 1. Spectral data of 1-pentanol and butyl methacrylate alone in inert solvents.

	1-Pentanol			Butyl methacrylate
Solvent	ν_{OH} 'free' (cm^{-1})	ν_{OH} bonded (cm^{-1})	$\Delta\nu_{OH}$ (cm^{-1})	$\nu_{C=O}$ (cm^{-1})
n-Heptane	3650	3354	296	1723
Carbon tetrachloride	3635	3354	281	1719
Benzene	3609	3447	162	1716

organic solvents to investigate solute–solvent interactions was extensively reported by Zheng *et al.* [2]. The results from such studies also provide information on the nature of molecular interactions in binary and ternary mixtures. The objective of the present study is to elucidate the effect of the medium, and particularly the role of specific solute–solvent interactions on the stability of 1 : 1 complexes as well as on the hydrogen bond formation between free hydroxyl group of 1-pentanol and carbonyl group of BMA.

2. Experimental details

A Nicolet Avatar 360 FTIR spectrometer with a resolution of $\pm 1\,cm^{-1}$ was used for this study. Spectra were obtained at room temperature (25°C) in the region of $4000–400\,cm^{-1}$. The BMA was an Aldrich product used without further purification. 1-Pentanol, carbon tetrachloride, benzene, and *n*-heptane are of Analar grade, purified by standard methods [3,4].

3. Results and discussion

The observed spectral data for the binary systems of 1-pentanol and butyl methacrylate alone with inert solvents (*n*-heptane, carbon tetrachloride (CCl_4) and benzene) are shown in table 1. 1-Pentanol in inert solvents exhibits two hydroxyl bands in the region of $3700–3300\,cm^{-1}$. One is due to monomeric (OH-free) and the other is due to polymeric absorption (OH-bonded) [8] and is shown in table 1. The monomeric absorption band is observed in the order of *n*-heptane > CCl_4 > benzene. Hydrogen-bonded absorption band around $3354\,cm^{-1}$ is observed for 1-pentanol with *n*-heptane and 1-pentanol with Carbon tetrachloride systems. In the case of 1-pentanol with benzene system an absorption band is observed at $3447\,cm^{-1}$. The lowest frequencies recorded for 1-pentanol with benzene, an effect no doubt attributable to the influence of the π-electron cloud of the benzene ring.

It is generally found that, as the polarity of the solvent increases the O–H stretching frequency decreases, this is due to a stronger polarization of O–H bond which leads to a decrease of the O–H bond force constant. It is apparent that the solvent environment has a strong determining effect on the frequency of the free donor, a similar effect having been observed by Bellamy and Hallam [5]. These results fully confirm Bellamy and Hallam [6] suggestion that the solvent shifts of free O–H stretching vibrations are primarily due to the local association effects with solvent molecules.

From the above observation, it may suggested that the solute–solvent interaction exists for 1-pentanol + benzene, + carbon tetrachloride systems, i.e., the interaction between the negative chlorine in carbon tetrachloride and also π-electrons in the benzene ring with H^{δ} in alcohol. No such interaction is possible in *n*-heptane system [7].

Infrared carbonyl absorption bands of BMA in inert solvents (*n*-heptane, CCl_4, and benzene) are reported in table 1. The $\nu_{C=O}$ is observed in the order of *n*-heptane > CCl_4 > benzene. These tendencies are in good agreement with the results of Nyquist [8] IR study. The general $\nu_{C=O}$ frequency decrease has been attributed to the change in the bulk dielectric effects of the solvent system. The higher frequency values of BMA + *n*-heptane than BMA + CCl_4 and BMA + benzene, indicate the absence of specific solute–solvent interaction. This observation may suggest that the specific interactions between π-bonds in BMA and the lone pair electrons of Cl or between lone pair of electrons of > C=O group in ester and empty *d*-orbital in chlorine atom of carbon tetrachloride and the lone pair of electrons in oxygen atom of BMA and the electrons of benzene. Similar results are reported by Oswal *et al.* [9].

For ternary mixtures, the proton acceptor (ester) concentration is fixed at $0.05\,\mathrm{mol\,L^{-1}}$ and proton donor (alcohol) concentration varies from 0.05 to $0.15\,\mathrm{mol\,L^{-1}}$ in steps of $0.02\,\mathrm{mol\,L^{-1}}$. The free O–H band intensity and half band width increases with increasing alcohol concentration but at the same time the reverse trend is observed for the carbonyl absorption band. This observation indicates that the 1 : 1 complex formation between free hydroxyl group of 1-pentanol and the carbonyl group i.e. (O–H···O=C) BMA [10]. Utilizing Nash [11] method, the equilibrium constant (*K*) of the 1 : 1 complex is calculated from the following equation:

$$K = \frac{[AB]}{[A][B]} \tag{1}$$

where $[AB]$ is the concentration of the 1 : 1 complex and $[A]$ and $[B]$ are the initial concentrations of the proton donor and proton acceptor, respectively. A graph was plotted between $Y = [A]^{-1}$ and $X = (1 - (a/a_0))^{-1}$, where a and a_0 are the absorbances of the carbonyl band of BMA in the presence and absence of 1-pentanol respectively. The intercept of the graph in the ordinate yields K^{-1}. The free-energy change (ΔG) of formation from the formation constant values by using the well-known relation [12]

$$\Delta G = -RT \ln K \tag{2}$$

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

Table 2 lists the formation constant and free-energy change of the hydrogen-bonded complexes in *n*-heptane, CCl_4 and benzene solvents. It is evident from table 2 that the formation constant and free-energy change for hydrogen-bond formation of 1-pentanol with BMA in inert solvents are quite high for benzene; next in order comes CCl_4; while for *n*-heptane the equilibrium constant and free-energy change values are lowest. It may, therefore, be suggested that the lowering of the formation constant in the afore-mentioned order is due to the local solvent interactions with the 1-pentanol in the order benzene > CCl_4 > *n*-heptane. The higher formation constant and free-energy change values are observed for 1-pentanol + BMA in benzene

Table 2. Formation constant (K) and free-energy change (ΔG) of 1-pentanol with butyl methacrylate in inert solvents

Proton donor	Proton acceptor	Solvent	K ($\mathrm{L\,mol^{-1}}$)	$-(\Delta G)$ ($\mathrm{k\,cal\,mol^{-1}}$)
1-Pentanol	Butyl methacrylate	*n*-Heptane	2.5	0.542
		Carbon tetrachloride	7.2	1.165
		Benzene	12.7	1.510

and in CCl_4 than in *n*-heptane which may confirm that the specific solute–solvent interactions exist in former systems, promote the proton promoting degree, and stabilize the 1 : 1 complex. An opposite effect is shown by *n*-heptane. This molecule would tend to solvate the associated complex due to its large size compared to benzene and tend to oppose the formation of the associated groups with the acceptors, and give rise to the low formation constants observed. Intermediate between these two groups are of association in the so-called inert i.e. CCl_4, which allow solvent association by interaction with specific groups on the solvent molecules, such as C–Cl. This obervation is in close agreement which Kuc *et al.* [13] for phenol–amine system in different solvents. The hydrogen bond is readily identifiable as a specific interaction of the donor–acceptor type. Other solute–solvent interactions are not so clear-cut, and the distinction between specific and non-specific interactions becomes blurred. It is generally accepted that two hydrogen bonds to such oxygen can be formed, and in the case of water solvent, it seems certain that carbonyl oxygens are solvated specifically by hydrogen bonds from two water molecules.

4. Conclusions

The formation constant and free-energy change of 1-pentanol with butyl methacrylate (BMA) in inert solvents (*n*-heptane, carbon tetrachloride, and benzene) have been carried out. From this study, it may be concluded that solvent environment may affect the strength of intermolecular hydrogen-bond formation between free O–H group of 1-pentanol and the carbonyl group of butyl methacrylate (O–H···O=C). The local specific interaction, between the solute and solvent molecules, plays an important role in the determination of the strength of the hydrogen bond formed between 1-pentanol and butyl methacrylate and is obtained in the order of benzene > carbon tetrachloride > *n*-heptane.

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