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Solvent effects on hydrogen bonding between primary alcohols and esters

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Abstract: The interaction by hydrogen bond formation of some primary alcohols (1-heptanol, 1-octanol and 1-decanol) with esters (methyl methacrylate, ethyl methacrylate and butyl methacrylate) was investigated in non-polar solvents viz., *n*-heptane, CCl_4 and benzene by means of FTIR spectroscopy. Formation constants and free energy changes of complex formation were determined. The dependence of the equilibrium constants and free energy changes of complex formation on the alkyl chain length of both the alcohols and esters are discussed. The solvent effect on the hydrogen bond formation is discussed in terms of specific interaction between the solute and solvent.

Key words: FTIR spectroscopy, Primary alcohols, Esters, Hydrogen bonding, Solvent effect
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INTRODUCTION

Hydrogen bonds constitute a very interesting class of intermolecular interactions, which are of extreme importance in many fields of chemistry and molecular biology. Acrylic esters are industrially important chemicals and precursors in the synthesis of polymers (Schildknecht, 1977). Alcohols play an important role in many chemical reactions due to the ability to undergo self-association with manifold internal structures and are in wide use in industry and science as reagents, solvents and fuels and attract great attention as useful solvents in the green technology (Savage, 1999). The study of the H-bonds of the type O−H···O=C occupies a position of considerable importance as it relates to the study of biopolymers. 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. Recently our research group investigated complex formation in liquid mixtures of acrylic esters with some alcohols using FTIR spectroscopic (Sivagurunathan, *et al*., 2005a; 2005b; 2005c; 2005d; 2006a; Dharmalingam *et al*., 2006a; 2006b; 2005; Dharmalingam and Ramachandran, 2006) and dielectric (Sivagurunathan *et al*., 2005e; 2006b; 2006c) methods. Organic solvent mixtures are important chemicals for different industrial purposes. Therefore, the study of spectral properties of the liquid mixtures has considerable current interest in chemical engineering research fields. Thus the study and knowledge of spectral properties of the mixtures of acrylic esters with polar associating liquids (alcohols) with non-polar solvents is expected to provide useful and vital process parameters for efficient design of transesterification processes of industrial interest. In the present work, the dependence of strength of the hydrogen bonding between the alcohol and the ester on the nature of the interacting components (alcohols and esters) and solvents used is discussed in terms of formation constant. The results from such studies also provide better understanding of the nature of molecular interactions in ternary mixtures.

EXPERIMENTAL DETAILS

The alkyl methacrylate monomers used in the present study were Aldrich product with >99% purity, used without further purification. The analytical reagent product *n*-heptane, CCl_4, benzene and alcohols were purified by standard methods (Vogal, 1957). The purities are better than 99.5 wt%.

Spectra were recorded with a Nicolet Avatar 360 FTIR spectrometer and a NaCl cell, using 0.1 mm spacer at 298 K in the region of 4000 to 400 cm^{-1}. The spectrometer has 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 intensity (absorbance) is calculated by the formula Absorbance=$\log_{10}(I_0/I)$, where I_0/I is the ratio of the intensity of the incident light and transmitted light and the example spectrum is shown in Fig.1.

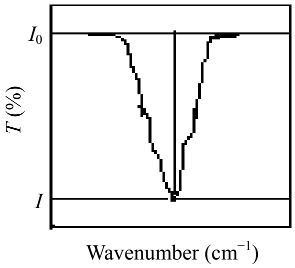

Fig.1 Example spectrum

The formation constants K associated with the hydrogen bonding process were determined using the method described by Nash (1960). In this method, 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 ester in the presence and absence of alcohol, respectively. It gives a straight line which confirms the 1:1 complex formation. The intercept of the graph in the ordinate yields the negative value of K. A graph with Nash algorithm for 1-heptanol with MMA in *n*-heptane is shown in Fig.2. The proton acceptor (ester) concentration is fixed at 0.05 mol/L and proton donor (alcohol) concentration varies from 0.03 to 0.15 mol/L. The free energy change (ΔG^0) in the ternary mixture may be calculated using the formation constant (Vinogradov, 1971) such that

$$\Delta G^0=-2.303RT\log K, \qquad (1)$$

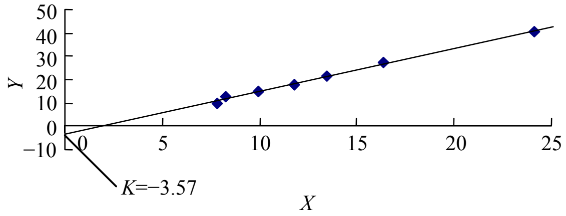

Fig.2 Formation constant for the 1:1 complexes of 1-heptanol with MMA in *n*-heptane determined by Nash method

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

RESULTS AND DISCUSSION

The ternary systems selected were some primary alcohols (1-heptanol, 1-octanol and 1-decanol) with esters (methyl methacrylate, ethyl methacrylate and butyl methacrylate) using *n*-heptane, CCl_4 and benzene as solvents.

The formation constant (K) and the free energy change (ΔG^0) values for all the systems studied are provided in Table 1. The K and ΔG^0 values for 1-decanol with all the proton acceptors (MMA, EMA and BMA) are found to be higher than that for 1-octanol and 1-heptanol with the same acceptors, which reveal that 1-decanol, has greater proton donating ability than that of all other alcohols studied. This is because of steric hindrance, it is likely that 1-decanol will have a greater possibility of complex formation due to head-tail linkage, whereas for 1-heptanol, the tendency is weakened due to the switching mechanism prevalent in the system (Sivagurunathan *et al.*, 2006a).

It has been found that two opposing effects namely specific interactions between −OH group of alcohol and C=O group of the ester and non-specific dispersion interactions, i.e. breaking of intermolecular hydrogen bonds in alcohols are possibly operating in these mixtures.

The K and ΔG^0 values for 1-heptanol+methyl methacrylate are found to be smaller than that of 1-octanol+ethyl methacrylate and 1-decanol+butyl methacrylate. This may be attributed to the difference in basicity of the alkyl groups, which varies in the order methyl<ethyl<butyl. This is because the negative

Table 1 Formation constant *K* and free energy change ΔG^0 for alcohols with esters in non-polar solvents at 298 K

Alcohol	Ester	*K* (L/mol)			$-(\Delta G^0)$ (kJ/mol)		
		n-heptane	CCl_4	Benzene	*n*-heptane	CCl_4	Benzene
1-heptanol	MMA	3.57	8.12	13.56	3.14	5.19	6.45
	EMA	4.29	8.93	14.34	3.60	5.40	6.57
	BMA	4.81	9.51	15.05	3.89	5.57	6.70
1-octanol	EMA	4.13	9.30	14.28	3.52	5.53	6.57
	EMA	4.97	10.05	15.06	3.98	5.69	6.70
	BMA	5.49	10.84	15.91	4.19	5.90	6.82
1-decanol	BMA	6.17	11.15	15.63	4.48	5.95	6.78
	EMA	6.84	11.87	16.42	4.73	6.11	6.91
	BMA	7.48	12.63	17.22	4.98	6.28	7.03

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 decyl alcohol and the weakest between the C=O group of methyl methacrylate and the OH proton of heptyl alcohol (Sivagurunathan *et al*., 2005a; 2006a; Dharmalingam *et al*., 2006b).

It is evident from Table 1 that the formation constant and free energy change for hydrogen bond formation of alcohols with esters in non-polar solvents are quite high for benzene; next in order come 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 above order is due to the local solvent interactions with the alcohols and esters in the order benzene>CCl_4>*n*-heptane. The high values of *K* in benzene solutions suggest that, besides structure disruptions, the weak but specific interactions of −OH-π type between the hydroxyl group of alcohol and π-electrons of benzene and of *n*-π type between the carbonyl group of ester and π-electrons of benzene. 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. Intermediates 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 (Sivagurunathan *et al*., 2005d; Dharmalingam *et al*., 2006a; Dharmalingam and Ramachandran, 2006).

CONCLUSION

The formation constant and free energy changes for the hydrogen bonded complexes of some primary alcohols (1-heptanol, 1-octanol and 1-decanol) with esters (methyl methacrylate, ethyl methacrylate and butyl methacrylate) were investigated in *n*-heptane, CCl_4 and benzene by means of FTIR spectroscopy. From this study, it may be concluded that the alkyl chain length of alcohols, esters and the properties of solvent like size, electronic structure, etc. are playing an important role in the determination of the strength of the hydrogen bond formed between the alcohols and esters. Among the solvents used benzene is regarded as a good solvent for the formation of hydrogen bond due to its specific interaction with alcohols and esters.

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