

Hydrogen Bonding Interaction between 1-Propanol and Acrylic Esters in Non-polar Solvents: An FTIR Study

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ABSTRACT

The association between 1-propanol and acrylic esters (methyl methacrylate, ethyl methacrylate and butyl methacrylate) in non-polar solvents, viz. n-heptane, CCl₄ and benzene has been investigated by means of FTIR spectroscopy. 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 OH...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. The results also show a significant dependence of the association constant upon the solvent used. The solvent effect on the hydrogen bond equilibria is discussed in terms of specific interactions between the solute and the solvent.

KEYWORDS

FTIR spectroscopy, acrylic esters, hydrogen bonding, solvent effects.

1. Introduction

Acrylic esters are industrially important chemicals and precursors in the synthesis of polymers.¹ 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. Solvent effects play an important role in organic reactivity phenomena, such as chemical equilibria, the rates of chemical reactions, polymerization, and so on. Recently solvent effects on the infrared spectra of binary systems of MMA with organic solvents to investigate solute-solvent interactions were extensively reported by Zheng *et al.*² and Liu *et al.*³ Recently our research group has investigated the complex formation of acrylic esters with proton donors (alcohols) in non-polar solvents using FTIR spectroscopic⁴⁻¹¹ and dielectric¹² methods. The complex formation has been interpreted in terms of formation constants. Thus, the study and knowledge of the spectroscopic properties of 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 the 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 the hydroxyl group of 1-propanol and the carbonyl groups of acrylic esters in non-polar solvents and 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 the hydroxyl group of 1-propanol and the carbonyl groups of acrylic esters using FTIR spectroscopy.

2. Experimental

A Nicolet Avatar 360 FTIR spectrometer with a resolution of

ca. 1 cm⁻¹ was used. Spectra were recorded at room temperature (25°C) in the region of 4000 to 400 cm⁻¹ and a NaCl cell of path length 0.1 mm was used. The spectrometer possesses autoalign energy optimization and a dynamically aligned interferometer. It is fitted with a KBr beam splitter, a DTGS detector and an Everlgo™ mid-IR source. A baseline correction was made for the spectra recorded. The peak intensities (absorbances) were calculated by the formula

$$\text{Absorbance} = \log_{10}(I_0/I),$$

where (I₀/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% were purchased from Aldrich and were used without further purification. AR grade n-heptane, CCl₄, benzene and 1-propanol were purified by standard methods.^{13,14}

3. Results and Discussion

The observed spectroscopic data of 1-propanol in non-polar solvents (n-heptane, CCl₄ and benzene) are provided in Table 1. 1-Propanol in non-polar solvents exhibits two hydroxyl bands in the region of 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 bonded) absorption.¹⁵ The position of the monomeric OH absorption band and the wavenumber difference between the monomeric OH (ν_f) and the bonded OH (ν_b) bands (i.e. $\Delta\nu = \nu_f - \nu_b$) are observed in the solvent order

Table 1 Spectroscopic data of 1-propanol in non-polar solvents.

Solvent	ν_f/cm^{-1}	ν_b/cm^{-1}	$\Delta\nu/\text{cm}^{-1}$
n-heptane	3639	3354	285
CCl ₄	3632	3354	278
benzene	3607	3447	160

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n-heptane > carbon tetrachloride > benzene. An immediate observation is that the wavenumber of the free OH band decreases with the polarizability of the solvent, indicating that intermolecular interaction between 1-propanol and solvent molecules increases with increase of the polarizability of the solvent. This demonstrates that the wavenumber of the free OH band is very sensitive to the solvent environment. A hydrogen bonded OH absorption band around 3354 cm^{-1} is observed for the 1-propanol with n-heptane and 1-propanol with carbon tetrachloride systems. In the case of the 1-propanol with benzene system an absorption band is observed at 3447 cm^{-1} .^{11,16}

Benzene produces lower free OH stretching wavenumbers than the other solvents due no doubt to the tendency for association with the π electrons of the aromatic ring. It is generally found that the positions, intensities and shapes of absorption bands are influenced by solvents of different polarity. As the polarity of the solvent increases the OH stretching wavenumber decreases; this is due to a stronger polarization of the OH bond, which leads to a decrease of the OH bond stretching force constant. It is apparent that the solvent environment has a strong determining effect on the wavenumber of the donor OH group, a similar effect having been observed by Bellamy *et al.*^{17,18} These results fully confirm that the solvent shifts of OH stretching vibrations are primarily due to local association effects with solvent molecules. The above observation suggests that a solute–solvent interaction exists for the 1-propanol + benzene and 1-propanol + carbon tetrachloride systems, i.e. an interaction between the π -electrons in the benzene ring with $\text{H}^{\delta+}$ in 1-propanol and with $\text{Cl}^{\delta-}$ in carbon tetrachloride with $\text{H}^{\delta+}$ in 1-propanol. No such interaction is possible in the 1-propanol + n-heptane system.¹⁹

The infrared data of methyl methacrylate (MMA), ethyl methacrylate (EMA) and butyl methacrylate (BMA) in non-polar solvents are given in Table 2. The position of the carbonyl absorption band of acrylic esters in non-polar solvents is observed in the ester order methyl methacrylate > ethyl methacrylate > butyl methacrylate and in the solvent order n-heptane > CCl_4 > benzene.²⁰ The higher wavenumber values of acrylic esters + n-heptane than acrylic esters + carbon tetrachloride and acrylic esters + benzene indicate the absence of specific solute–solvent interactions. This observation suggests that specific interactions occur between the π^* orbitals in acrylic esters and the lone pair electrons of Cl, or between the lone pair electrons of the $>\text{C}=\text{O}$ group in esters and the empty d-orbitals in the chlorine atoms of carbon tetrachloride, or the lone pair of electrons in the carbonyl oxygen atom of acrylic esters and the π^* orbitals of benzene. Similar results are reported by Oswal *et al.*²¹

For ternary mixtures, the proton acceptor (acrylic ester) concentration was fixed at 0.05 mol dm^{-3} and the proton donor (alcohol) concentration varied from 0.05 to 0.15 mol dm^{-3} in steps

Table 2 Spectroscopic data of acrylic esters in non-polar solvents.

Acrylic ester	Solvent	$\nu_{\text{C=O}}/\text{cm}^{-1}$
MMA	n-heptane	1731
	CCl_4	1726
	benzene	1724
EMA	n-heptane	1724
	CCl_4	1720
	benzene	1717
BMA	n-heptane	1723
	CCl_4	1719
	benzene	1716

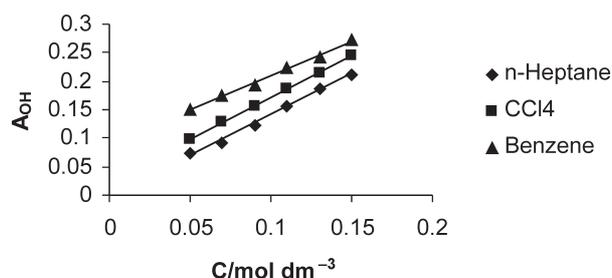


Figure 1 Absorbance versus concentration for methyl methacrylate with 1-propanol.

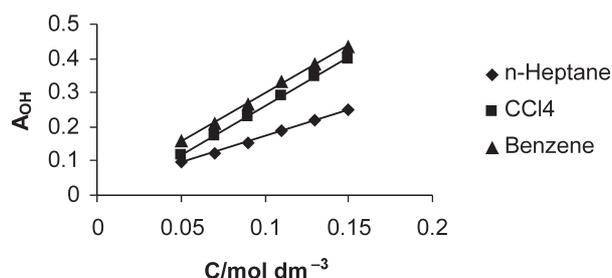


Figure 2 Absorbance versus concentration for ethyl methacrylate with 1-propanol.

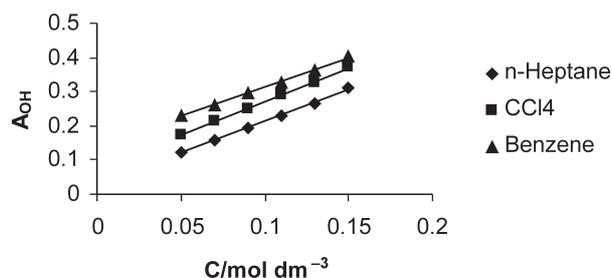


Figure 3 Absorbance versus concentration for butyl methacrylate with 1-propanol.

of 0.02 mol dm^{-3} . The OH band intensity and half-band width increase with increasing alcohol concentration but the reverse trend is observed for the carbonyl absorption band (Tables 3–11 and Figs 1–3). This observation indicates that there is 1:1 complex formation between the hydroxyl and carbonyl groups, i.e. $(\text{OH}\cdots\text{O}=\text{C})$.^{4–12,22} Utilizing Nash's²³ method, the formation constants K associated with the hydrogen bonding process were determined.

In this method at low concentration of alcohol the influence of the higher order complexes on the absorption spectrum of the base is neglected. The concentrations of the proton donor $[A]$, proton acceptor $[B]$ and complexed species $[AB]$ involved in the interaction are assumed to obey Beer's law at a given characteristic wavenumber of the 1:1 complex. The total absorbance of B per unit path length is given by

$$A = \epsilon_b [B] + \epsilon_{ab} [AB] \quad (1)$$

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

In the absence of a complexing agent, A , the total absorbance per unit path length is given by

$$a_0 = \epsilon_b [B^0] \quad (2)$$

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

Dividing Eq. (1) by Eq. (2)

$$\frac{a}{a_0} = \frac{[B]}{[B^0]} + \frac{[AB]}{B^0} \cdot \frac{\epsilon_{ab}}{\epsilon_b} \quad (3)$$

Table 3 Absorbance values of OH and C=O absorptions of 1-propanol and methyl methacrylate in n-heptane for different concentrations of 1-propanol and in the absence and presence of 1-propanol.

Concentration /mol dm ⁻³	Absorbance		Absorbance	
	OH band of 1-propanol in the absence of MMA	C=O band of MMA in the absence of 1-propanol	OH band of 1-propanol in the presence of MMA	C=O band of MMA in the presence of 1-propanol
0.05	0.0925	0.9651	0.0743	0.9237
0.07	0.1117		0.0926	0.9141
0.09	0.1449		0.1231	0.9033
0.11	0.1812		0.1558	0.8928
0.13	0.2036		0.1872	0.8827
0.15	0.2402		0.2125	0.8750

Table 4 Absorbance values of OH and C=O absorptions of 1-propanol with methyl methacrylate in CCl₄ for different concentrations of 1-propanol and in the absence and presence of 1-propanol.

Concentration /mol dm ⁻³	Absorbance		Absorbance	
	OH band of 1-propanol in the absence of MMA	C=O band of MMA in the absence of 1-propanol	OH band of 1-propanol in the presence of MMA	C=O band of MMA in the presence of 1-propanol
0.05	0.1210	1.0688	0.0966	1.0473
0.07	0.1398		0.1285	1.0414
0.09	0.1875		0.1567	1.0350
0.11	0.2091		0.1859	1.0277
0.13	0.2463		0.2140	1.0203
0.15	0.2820		0.2447	1.0125

Table 5 Absorbance values of OH and C=O absorptions of 1-propanol with methyl methacrylate in benzene for different concentrations of 1-propanol and in the absence and presence of 1-propanol.

Concentration /mol dm ⁻³	Absorbance		Absorbance	
	OH band of 1-propanol in the absence of MMA	C=O band of MMA in the absence of 1-propanol	OH band of 1-propanol in the presence of MMA	C=O band of MMA in the presence of 1-propanol
0.05	0.1772	1.2664	0.1513	1.2061
0.07	0.2075		0.1732	1.2040
0.09	0.2382		0.1933	1.2019
0.11	0.2791		0.2225	1.1998
0.13	0.2905		0.2423	1.1980
0.15	0.3238		0.2728	1.1962

The formation constant K may be defined as

$$K = \frac{[AB]}{[A][B]} \quad (4)$$

Combining Eqns. (3) and (4)

$$\frac{\alpha}{\alpha_0} = \frac{[B]}{[B^0]} \left[1 + \frac{\epsilon_{ab}}{\epsilon_b} K[A] \right] \quad (5)$$

Introducing the conservation of species B

$$[B^0] = [B] + [AB] \quad (6)$$

Invoking Eq. (4),

$$\frac{[B]}{[B^0]} = (1 + K[A])^{-1} \quad (7)$$

When Eq. (7) is substituted into Eq. (5)

$$\frac{\alpha}{\alpha_0} = \frac{1 + \frac{\epsilon_{ab}}{\epsilon_b} K[A]}{1 + K[A]} \quad (8)$$

Taking

$$\frac{a}{a_0} = z \quad (9)$$

$$K \frac{\epsilon_{ab}}{\epsilon_b} = \alpha \quad (10)$$

and

$$[A] = \frac{1}{y}$$

Eq. (8) becomes

$$z = \frac{1 + \frac{\alpha}{y}}{1 + \frac{K}{y}} \quad (11)$$

$$y = \frac{zK - \alpha}{1 - z} \quad (12)$$

Expressing

$$x = \frac{1}{1 - z}$$

Table 6 Absorbance values of OH and C=O absorptions of 1-propanol with ethyl methacrylate in n-heptane for different concentrations of 1-propanol and in the absence and presence of 1-propanol.

Concentration /mol dm ⁻³	Absorbance		Absorbance	
	OH band of 1-propanol in the absence of EMA	C=O band of EMA in the absence of 1-propanol	OH band of 1-propanol in the presence of EMA	C=O band of EMA in the presence of 1-propanol
0.05	0.1154	0.9810	0.0993	0.9404
0.07	0.1411		0.1238	0.9294
0.09	0.1925		0.1545	0.9160
0.11	0.2368		0.1982	0.9045
0.13	0.2789		0.2209	0.8908
0.15	0.3046		0.2510	0.8786

Table 7 Absorbance values of OH and C=O absorptions of 1-propanol with ethyl methacrylate in CCl₄ for different concentrations of 1-propanol and in the absence and presence of 1-propanol.

Concentration /mol dm ⁻³	Absorbance		Absorbance	
	OH band of 1-propanol in the absence of EMA	C=O band of EMA in the absence of 1-propanol	OH band of 1-propanol in the presence of EMA	C=O band of EMA in the presence of 1-propanol
0.05	0.1501	1.1590	0.1181	1.1127
0.07	0.1823		0.1633	1.1037
0.09	0.2595		0.2374	1.0960
0.11	0.3257		0.2925	1.0871
0.13	0.3634		0.3392	1.08
0.15	0.4056		0.3774	1.0721

Table 8 Absorbance values of OH and C=O absorptions of 1-propanol with ethyl methacrylate in benzene for different concentrations of 1-propanol and in the absence and presence of 1-propanol.

Concentration /mol dm ⁻³	Absorbance		Absorbance	
	OH band of 1-propanol in the absence of EMA	C=O band of EMA in the absence of 1-propanol	OH band of 1-propanol in the presence of EMA	C=O band of EMA in the presence of 1-propanol
0.05	0.1803	1.2212	0.1592	1.1801
0.07	0.2090		0.2075	1.1743
0.09	0.2975		0.2663	1.1681
0.11	0.3581		0.3292	1.1602
0.13	0.3996		0.3841	1.1529
0.15	0.4339		0.4342	1.1459

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

$$\text{since } z = \frac{a}{a_0}$$

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

Eq. (12) may be rewritten in the form of a linear equation as

$$y = x(K - \alpha) - K \quad (13)$$

The physical significance of Eq. (13) is that when the reciprocal of the donor concentration is plotted against the reciprocal of one minus the absorbance ratio the appearance of a straight line indicates 1:1 complex formation, and the intercept of the plot gives the negative value of the formation constant. The graphs are shown in Figs 4–6.

The Gibbs energies, ΔG , of the systems were calculated using the following relation²⁴

$$\Delta G = -RT \ln K \quad (14)$$

where R , T and K represent the universal gas constant, the absolute temperature and the formation constant of the hydrogen bonded complex, respectively.

The formation constants and the Gibbs energy values for all the systems studied are provided in Table 12. It is evident from Table 12 that the strength of the intermolecular hydrogen bond formed between a C=O group and an OH group, i.e. OH...O=C, is dependent on the basicity of the C=O group. In this study the basicity of the C=O group increases in the order methyl < ethyl < butyl methacrylate. 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 of the methyl group. Therefore, one would expect that the strongest intermolecular hydrogen bonds would be formed between the C=O group of butyl methacrylate and the OH group of propyl alcohol and the weakest between the C=O group of methyl methacrylate and the OH group of propyl alcohol.²¹

It has been found that two opposing effects, namely specific

Table 9 Absorbance values of OH and C=O absorptions of 1-propanol with butyl methacrylate in n-heptane for different concentrations of 1-propanol and in the absence and presence of 1-propanol.

Concentration /mol dm ⁻³	Absorbance		Absorbance	
	OH band of 1-propanol in the absence of BMA	C=O band of BMA in the absence of 1-propanol	OH band of 1-propanol in the presence of BMA	C=O band of BMA in the presence of 1-propanol
0.05	0.1522	0.9915	0.1247	0.9445
0.07	0.1832		0.1594	0.9434
0.09	0.2334		0.1925	0.9424
0.11	0.2637		0.2313	0.9415
0.13	0.3023		0.2642	0.9406
0.15	0.3452		0.3096	0.9399

Table 10 Absorbance values of OH and C=O absorptions of 1-propanol with butyl methacrylate in CCl₄ for different concentrations of 1-propanol and in the absence and presence of 1-propanol.

Concentration /mol dm ⁻³	Absorbance		Absorbance	
	OH band of 1-propanol in the absence of BMA	C=O band of BMA in the absence of 1-propanol	OH band of 1-propanol in the presence of BMA	C=O band of BMA in the presence of 1-propanol
0.05	0.2092	1.0024	0.1740	0.9875
0.07	0.2531		0.2135	0.9835
0.09	0.2917		0.2485	0.9795
0.11	0.3280		0.2888	0.9754
0.13	0.3663		0.3268	0.9717
0.15	0.4138		0.3711	0.9682

Table 11 Absorbance values of OH and C=O absorptions of 1-propanol with butyl methacrylate in benzene for different concentrations of 1-propanol and in the absence and presence of 1-propanol.

Concentration /mol dm ⁻³	Absorbance		Absorbance	
	OH band of 1-propanol in the absence of BMA	C=O band of BMA in the absence of 1-propanol	OH band of 1-propanol in the presence of BMA	C=O band of BMA in the presence of 1-propanol
0.05	0.2734	1.0431	0.2318	1.0284
0.07	0.3195		0.2627	1.0191
0.09	0.3482		0.2944	1.0086
0.11	0.3961		0.3263	0.9999
0.13	0.4353		0.3621	0.9911
0.15	0.4774		0.4010	0.9838

interactions between the ester and the OH group of the alcohol, and non-specific dispersion interactions, i.e. breaking of intermolecular hydrogen bonds in the alcohol are possibly operative in these mixtures.

It is evident from Table 12 that the formation constants and Gibbs energies for hydrogen bond formation of acrylic esters with 1-propanol in non-polar solvents are quite high for benzene. Next in order comes CCl₄, while for n-heptane the

equilibrium constant and Gibbs energy 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 1-propanol in the order benzene > CCl₄ > n-heptane. The higher values of K in benzene solutions suggest that, besides structure disruptions, weak but specific interactions of the OH... π type occur between the hydroxyl group of 1-propanol and the π electrons of the aromatic ring, which is in agreement

Table 12 Formation constants, K, and Gibbs energies, ΔG , for acrylic esters with 1-propanol in non-polar solvents.

Proton acceptor	K /dm ³ mol ⁻¹			- ΔG /kJ mol ⁻¹		
	n-Heptane	CCl ₄	Benzene	n-Heptane	CCl ₄	Benzene
MMA	0.7	4.5	9.5	-0.88	3.73	5.58
EMA	1.1	5.0	10.0	0.24	3.99	5.7
BMA	1.8	6.0	10.4	1.46	4.44	5.8

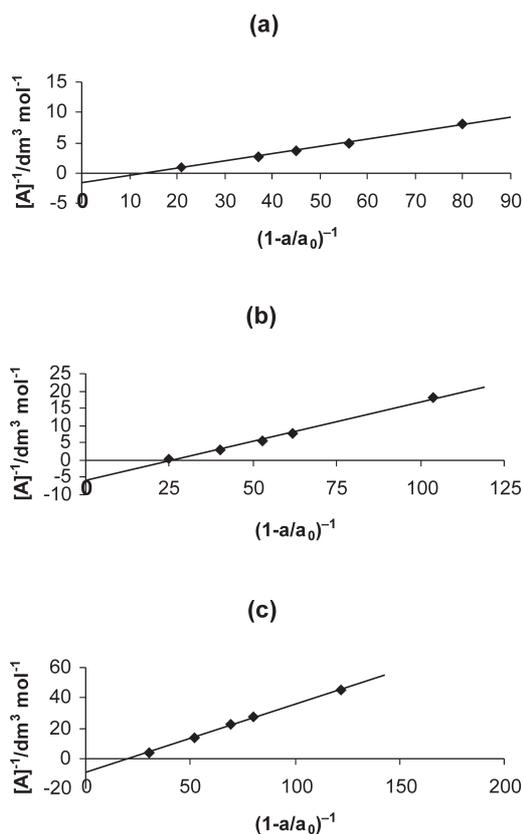


Figure 4 Formation constants of 1:1 complexes of methyl methacrylate with 1-propanol in (a) n-heptane, (b) CCl_4 and (c) benzene determined by Nash's method at 298 K.

with the observation of low OH stretching wavenumbers with specific interaction with the solvent molecules present. The opposite effect is shown by n-heptane. This molecule would tend to solvate the associated complex due to its large size compared with that of benzene and would tend to oppose the formation of the associated groups with the acceptors, giving rise to the low formation constants observed. Intermediate between these two groups are association in the so-called inert solvent, CCl_4 , which allows solvent association by interaction with specific groups of the solvent molecules, such as the CCl bonds. This observation is in close agreement with that of Sivagurunathan *et al.*¹¹ for the 1-butanol – ethyl methacrylate system in different solvents.

4. Conclusions

The formation constants and Gibbs energies of 1-propanol with acrylic esters (methyl methacrylate, ethyl methacrylate and butyl methacrylate) in non-polar solvents (n-heptane, CCl_4 and benzene) were determined. From this study, it may be concluded that the strength of the intermolecular OH...O=C bond formed between 1-propanol and the acrylic esters is dependent on the alkyl chain length of the acrylic esters and parallels the basicity of the acrylic esters, and the hydrogen bonding between alcohols and acrylic esters in solution is complicated, depending not only on the acidity and basicity of the interacting components, but also on the solvent properties.

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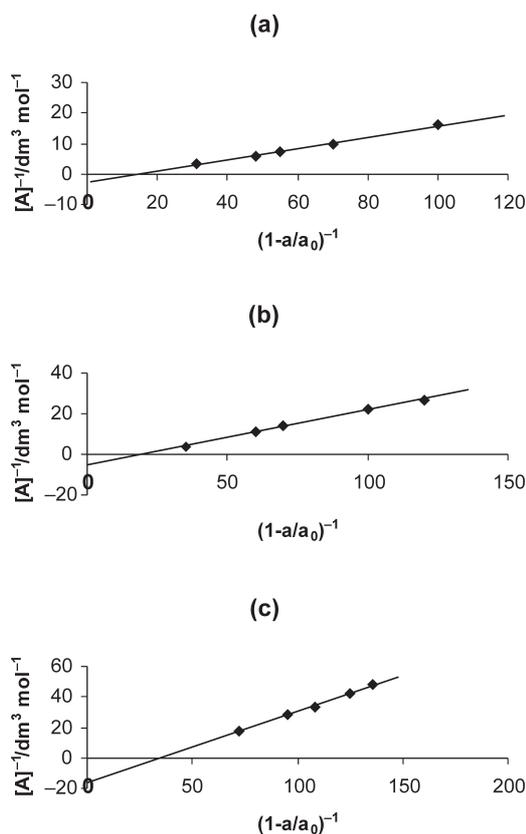


Figure 5 Formation constants of 1:1 complexes of ethyl methacrylate with 1-propanol in (a) n-heptane, (b) CCl_4 and (c) benzene determined by Nash's method at 298 K.

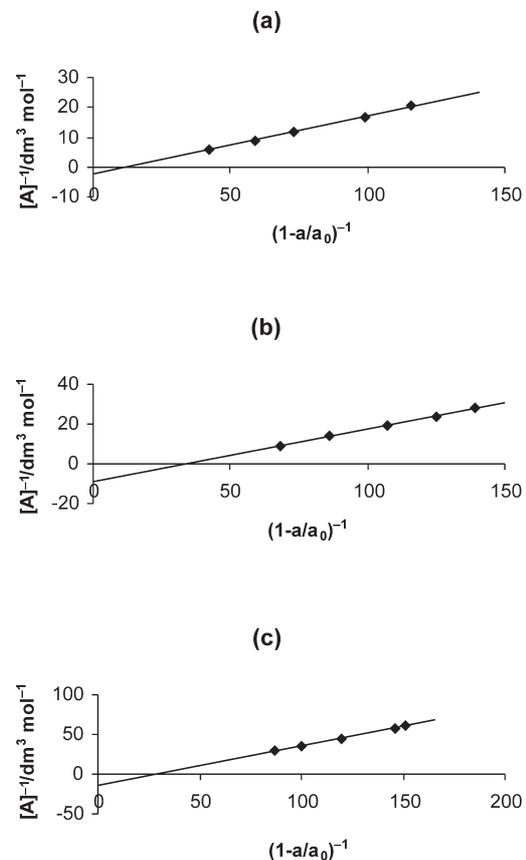


Figure 6 Formation constants of 1:1 complexes of butyl methacrylate with 1-propanol in (a) n-heptane, (b) CCl_4 and (c) benzene determined by Nash's method at 298 K.

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