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Research Article

FT-IR, Volumetric and Viscometric Studies of Interaction between Alkyl Formates and iso-butanol at Temperature 298.15, 303.15, 308.15 and 313.15 K.

Mehdi Hasan[1], Satishkumar D. Thakare[*2], Vijaykumar M. Joshi[2]

[1]P.G. Department of Physical Chemistry, M. S. G. College Malegaon Camp - 423105, Maharashtra, India.

[2]K. R. A. Arts, Science and Commerce College, Deola-423102, Maharashtra, India.

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***Corresponding author E-mail address:** *thakaresatish67@gmail.com*

ABSTRACT

Densities and viscosities of binary mixtures of iso-butanol with ethyl formate, butyl formate and hexyl formate have been measured over the entire range of composition, at T= (298.15, 303.15, 308.15 and 313.15) K and at atmospheric pressure. The V^E values are positive for all the binary mixtures studied over the entire composition range, while $\Delta\eta$ are negative for all the binary mixtures. These parameters have been fitted to Redlich-Kister polynomial equation. McAllister's multibody model has been used to co-relate the kinematic viscosities of the binary mixtures. Neat FT-IR spectra are also taken.

KEYWORDS

Excess molar volumes, deviation in viscosity, FT-IR, iso-butanol, ethyl formate, butyl formate, hexyl formate.

1. INTRODUCTION

Studies on excess molar properties of binary liquid mixtures are of considerable importance in understanding the nature of molecular interaction. Measurements of densities and viscosities of binary liquid mixtures enable one to gather some information about the nature of interaction taking place in the binaries. The literature provides extensive data on the densities and viscosities of liquid mixtures, but a combined study of density, viscosity and FT-IR is quite scarce. FT-IR is very useful in elucidating the structure of molecule/ complex [1-2] and provides supporting evidence to the conclusions drawn from the volumetric and viscometric measurements. The effects of molecular size, shape, chain length and degree of molecular association of iso-butanol on the volumetric, viscometric and acoustic properties of binary mixtures containing alkyl formates have been reported earlier. [3-4] The present work reports the densities, viscosities and FT-IR studies for the binary mixtures of iso-Butanol with ethyl formate, butyl formate and hexyl formate at T= (298.15, 303.15, 308.15 and 313.15) K.

2. MATERIALS AND METHODS

iso-Butanol (s. d. Fine Chem, purity 99%) was used. Ethyl Formate, Butyl Formate and Hexyl formate were double distilled and the middle fraction was used. The purity of the solvents were further ascertained by comparing their experimental density and viscosity with those reported in the literature values at T/K = 298.15 Table 1. Binary mixtures were prepared by mass in air tight stoppered glass bottles. The masses were recorded on an Adairdutt balance to an accuracy of ± 1×10^{-4} g. The estimated uncertainty in mole fraction was $< 1\times10^{-4}$. Densities were determined by using a 15 cm^3 bicapillary pycnometer as described earlier.[4-5] The estimated uncertainty of density measurements of solvent and binary mixtures was ± $0.1 \times 10^{-3} kg.m^{-3}$. The dynamic viscosities were measured using an Ubbelohde suspended level[7] viscometer calibrated with conductivity water. An electronic digital stop watch with readability of ± 0.01s was used for the flow time measurements. At least three repetitions of each data reproducible to ± 0.05s were obtained, and the results were averaged. The dynamic viscosity η of the liquids was calculated by

$\eta = \rho\ (at - b/t)$ ---Equation 1

Where η is the viscosity, ρ is density of the liquid, t is the flow time, a and b are the constants for a given viscometer. The uncertainties in dynamic viscosities are estimated to be of the order of ± 0.003 mPa.s.

FTIR spectra were recorded on a FTIR spectrometer (Model: SHIMADZU 8400s pc) by using KBr pellet in the region 400 -4000 cm^{-1} with 4.0 cm^{-1} resolution. The transmission values were read in steps of 5%. The spectrophotometer possesses out to aligned energy optimization and dynamically aligned interferometer. It is fitted with KBr beam splitter, a DLATGS detector. A base line correction was made for the spectra recorded.

3. RESULTS AND DISCUSSION

The density values have been used to calculate V^E using the following equation

$V^E\ (m^3mol^{-1}) = (x_1M_1+x_2M_2)/\rho_{12} - (x_1M_1/\rho_1) - (x_2M_2/\rho_2)$ ---Equation 2 where ρ_{12} is the density of the mixture and x_1, M_1, ρ_1 and x_2, M_2, ρ_2 are the mole fraction, the molecular weight and density of pure components 1 and 2 respectively. The uncertainty in V^E is of ±0.008 m^3mol^{-1}. Δη were calculated using,

$\Delta\eta$ (mPa.s.) = $\eta_{12} - x_1\eta_1 - x_2\eta_2$ ---Equation 3

where η_{12} is the viscosity of the mixture and x_1, x_2 and η_1, η_2 are the mole fraction and the viscosity of pure components 1 and 2 respectively. The excess molar volumes and deviation in viscosity were fitted to Redlich-Kister [8] equation of the type,

$Y = x_1x_2 \Sigma a_i(x_1-x_2)I$ ---Equation 4

where Y is either V^E, or Δη and n is the degree of polynomial. Coefficient a_i were obtained by fitting equation 4 to experimental results using a least-squares regression method. In each case, the optimum number of coefficients is ascertained from an examination of the variation in standerd deviation σ.σ was calculated using the relation,

$\sigma (Y) = [\Sigma(Y_{expt} - Y_{calc})/N\text{-}n]^{1/2}$ ---Equation 5

where N is the number of data points and n is the number of coefficients. The determined values of the coefficients a_i along the standard deviation σ are given in Table 2.

The variation of V^E with mole fraction of alkyl formate (ethyl, butyl and hexyl) with iso- butanol at T/K = 298.15 K is represented in Fig. 1. The excess molar volume for the mixture of iso-butanol with ethyl formate (0.429 at 298.15 K) is in good agreement with excess molar volumes (0.427 at 298.15 K) at $x_1 = 0.5$ reported by Ortega et al.[3] where as the excess molar volumes for the binary mixture of butyl formate with iso-butanol (0.266 at 298.15 K) is in good agreement with excess molar volumes reported by Ortega et al. as (0.261 at 298.15 K) at x1 = 0.5.

The V^E for these mixtures are positive over entire composition range at all temperatures indicating that the dispersive forces dominate over the chemical or specific interactions. The positive V^E values may also arise due to the predominance of declustering of butanol in presence of formates. It is seen that as the alkyl part in the formates increases from ethyl to hexyl, the V^E values decrease. This may be due to the fact that the iso-butanol molecules may be fitting in to the interstitial spaces of higher alkyl formates. The molar volumes of iso-butanol and ethyl formate are not much different; hence iso-butanol finds it much difficult to enter the interstitial voids in the ethyl formate net work. But for butyl and hexyl formates the molar volumes are much different from that of iso-butanols and there are chances that the iso-butanol molecules may find it much easier to accommodate themselves in the ester networks of butyl and hexyl formates leading to a decrease in the V^E. It is a well established fact that alcohols are self-associated [9-14] through hydrogen bonding, with the strength and extent decreasing with branching in alcohols, while formates having dipolar nature are also associated through intermolecular hydrogen bonding. Thus, mixing of formates with an alcohol (butanol) can be expected to induce changes in hydrogen-bonding equilibria and electrostatic interactions, with different resultant contributions to the volumes of the mixtures. Weakening of the interactions between the molecules of formates tends to results in an increase in volume. Similarly, the disruption of butanol multimers through breaking of hydrogen-bonds makes a positive contribution to V^E. [15-16] V^E increases with increase of temperature from 298.15 to 313.15 K for all these three binary mixtures, which may be attributed partly to thermal agitation and partly due to the fact that more hydrogen bonds are broken at higher temperatures. Homo and hetero associations are also weakened at higher temperatures leading to an increase in V^E values. The values of $\Delta\eta$ for the binary mixtures of ethyl formate, butyl formate and hexyl formate with iso-butanol are negative over entire composition range at all temperatures indicating that the dispersive forces dominate over the chemical or specific interactions. Fig. 2 exhibits the variation of $\Delta\eta$ with x_1 [alkyl formates] for binary mixtures of ethyl formate, butyl formate and hexyl formate with iso-butanol at 298.15 K. It is seen that the $\Delta\eta$ values are almost the same for all the three binary mixtures of alkyl formate with iso-butanol signifying that the nature of interactions which govern the $\Delta\eta$ values remain almost the same irrespective of the alkyl moiety in the ester. The $\Delta\eta$ values in all the three binary systems studied here show a marked dependence on temperature. These values decrease systematically as the temperature is increased. It can be concluded that the mixture viscosities decrease to a greater extent as compared with the decrease in the viscosities of pure binary components with increase in temperature. Further it is seen that the effect of temperature is more pronounced for $\Delta\eta$ than for V^E.

Kinematic viscosities (ν) of the binary liquid mixtures were obtained from their dynamic viscosities and densities. McAllister's three body and four body interaction models [17] have been used to correlate the kinematic viscosities of binary liquid mixtures.

$$\mathrm{Ln}\nu = x_1^3 \ln \nu_1 + x_2^3 \ln \nu_2 + 3 x_1^2 x_2 \ln \nu_{12} + 3 x_1 x_2^2 \ln \nu_{21} - \ln [x_1+(x_2M_2/M_1)] + 3 x_1^2 x_2 \ln [(2/3) + (M_2/3M_1)] + 3x_1x_2^2 \ln [(1/3) + (2M_2/3M_1)] + x_2^3 \ln (M_2/M_1) \quad \text{---Equation 6}$$

Where ν_{12} and ν_{21} are interaction parameters.

The four body interaction model is given by,

$$\ln\nu = x_1^4 \ln \nu_1 + 4 x_1^3 x_2 \ln \nu_{1112} + 6 x_1^2 x_2^2 \ln \nu_{1122} + 4 x_1 x_2^3 \ln \nu_{2221} + x_2^4 \ln \nu_2 - \ln [x_1+(x_2M_2/M_1)] + 4 x_1^3 x_2 \ln [\{3 + (M_2/M_1)\}/4] + 6 x_1^2 x_2^2 \ln [\{1+ (M_2/M_1)\}/2] + 4 x_1 x_2^3 \ln[\{(1+3 M_2/M_1)\}/4] + x_2^4 \ln (M_2/M_1) \quad \text{---Equation 7}$$

Where ν_{12}, ν_{21}, ν_{1112}, ν_{1122}, ν_{2221}, are interaction parameters and M_1 and M_2 are molecular weights of components 1 and 2.

The correlating ability of equations 6 and 7 was tested by calculating the percentage standard deviation (σ %) between the experimental and calculated viscosity as

$$\sigma \,\% = [1/(n-m)\sum \{(100(\nu_{exptl} - \nu_{calcd})/ \nu_{exptl})^2)\}^{1/2}] \quad \text{---Equation 8}$$

Where n represents the number of experimental points and m represents the number of coefficients. Table 4 includes the different parameters for McAllister's three- body and four body models. From Table 4, it is clear that McAllister's four-body interaction model gives a better result than the three- body model for correlating the kinematic viscosities of the binary mixtures studied.

The neat FTIR data of the three binary mixtures are represented in table 5.The IR –OH frequencies at x_1=0.5 for all the three binary mixtures are (3360, 3360, 3381cm-[1]) for mixtures of alkyl (ethyl, butyl and hexyl) formates with iso-butanol. As the IR frequency increase, the intermolecular hydrogen bonding in butanols decreases and hence there are more monomer butanol molecules in the mixtures. As the alkyl chain in formates increases, the molar volume also increases and there are more voids or empty space available in the alkyl formate network and the butanol molecules find it much easier to accommodate and geometrically fit into the alkyl formate network. Therefore the trend observed for excess molar volume for alkyl formates with all the iso- butanol is very well supported by the FTIR spectroscopic studies of these mixtures. Fig. 3 (a) to 3 (c) show the cut sections for –OH stretching frequency of all the three binary mixtures.

4. CONCLUSION

From the density, viscosity and FTIR studies of the binary mixture, it can be concluded that the dispersive interaction are operative between the components of the mixture.

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Table 1. Comparison of Experimental Density and Viscosity of pure liquids with Literature Values.

Liquid	**Temp /K**	**ρ x10^{-3}/ kg.m^{-3}**		**η / mPa.s**	
		Expt	Lit	Expt	**Lit**
Ethyl Formate	298.15	0.9158	0.91582[a]	0.385	**0.381[b]**
	303.15	0.9091	0.9086[c]	0.363	**0.362[b]**
	308.15	0.9025	0.9026[d]	0.353	**0.345[b]**
	313.15	0.8951	0.8949[e]	0.325	**0.329[b]**
Butyl Formate	298.15	0.8873	0.8869[c]	0.648	-
	303.15	0.8824	0.8818[f]	0.591	-
	308.15	0.8771	0.87824[g]	0.550	-
	313.15	0.8725	0.8744[h]	0.529	-
Hexyl Formate	293.15	0.8821	0.8816[i]	-	-
	298.15	0.8771	-	0.879	-
	303.15	0.8721	-	0.829	-
	308.15	0.8672	-	0.784	-
	313.15	0.8643	-	0.747	-
iso-Butanol	298.15	0.7985	0.7987[j]	3.435	**3.435[k]**
	303.15	0.7945	0.7946[j]	2.917	**2.881[j]**

308.15	0.7904	0.79029[l]	2.517	**2.508[m]**
313.15	**0.7864**	**0.7864[c]**	**2.163**	**2.1520[n]**

[a]Ref.18, [b]Ref.19, [c]Ref.20, [d]Ref.21, [e]Ref.22, [f]Ref.23, [g]Ref.24, [h]Ref.25, [i]Ref.26, [j]Ref.27, [k]Ref.28, [l]Ref.29, [m]Ref.30, [n]Ref.31.

Table 2. Density ρ, Viscosity η , Excess Volume V^E and Deviation in Viscosity Δη for Alkyl Formate(1)+ iso-Butanol(2) at T=(298.15 to 313.15)K.

x_1	ρ/g.cm^{-3}	η/ mPa.s	V^E/ cm^3.mole^{-1}	Δη/ mPa.s
Ethyl Formate (1) + iso-Butanol (2)				
T/K =298.15				
0.0000	0.7985	3.435	0.000	0.000
0.0994	0.8073	2.330	0.169	-0.802
0.1998	0.8169	1.659	0.284	-1.167
0.2994	0.8269	1.267	0.370	-1.255
0.3984	0.8375	1.029	0.412	-1.191
0.4989	0.8488	0.878	0.429	-1.035
0.5951	0.8602	0.760	0.416	-0.860
0.7003	0.8734	0.642	0.364	-0.657
0.7994	0.8865	0.552	0.289	-0.445
0.9004	0.9008	0.459	0.163	-0.230
1.0000	0.9158	0.385	0.000	0.000
		T/K =303.15		
0.0000	0.7945	2.917	0.000	0.000
0.0994	0.8030	2.104	0.181	-0.559
0.1998	0.8123	1.598	0.304	-0.809
0.2994	0.8222	1.270	0.377	-0.882
0.3984	0.8326	1.062	0.415	-0.837
0.4989	0.8435	0.906	0.446	-0.737
0.5951	0.8547	0.791	0.426	-0.606
0.7003	0.8676	0.666	0.374	-0.462
0.7994	0.8803	0.554	0.307	-0.321
0.9004	0.8943	0.448	0.177	-0.169
1.0000	0.9091	0.363	0.000	0.000

Ethyl Formate (1) + iso-Butanol (2)				
T/K =308.15				
0.0000	0.7904	2.517	0.000	0.000
0.0994	0.7986	1.873	0.194	-0.429
0.1998	0.8077	1.454	0.318	-0.631
0.2994	0.8173	1.185	0.399	-0.684
0.3984	0.8274	1.001	0.445	-0.654
0.4989	0.8382	0.865	0.462	-0.572
0.5951	0.8491	0.749	0.447	-0.480
0.7003	0.8618	0.632	0.386	-0.370
0.7994	0.8742	0.536	0.321	-0.251

0.9004	0.8879	0.437	0.190	-0.132
1.0000	0.9025	0.353	0.000	0.000
		T/K =313.15		
0.0000	0.7864	2.163	0.000	0.000
0.0994	0.7942	1.636	0.211	-0.344
0.1998	0.8030	1.288	0.337	-0.508
0.2994	0.8124	1.062	0.409	-0.551
0.3984	0.8222	0.906	0.454	-0.525
0.4989	0.8327	0.784	0.468	-0.462
0.5951	0.8432	0.682	0.461	-0.387
0.7003	0.8554	0.577	0.411	-0.299
0.7994	0.8674	0.492	0.347	-0.202
0.9004	0.8807	0.401	0.213	-0.107
1.0000	0.8951	0.325	0.000	0.000

Butyl Formate (1) + iso-Butanol (2) T/K =298.15				
0.0000	0.7985	3.435	0.000	0.000
0.0993	0.8085	2.376	0.080	-0.782
0.1997	0.8182	1.767	0.153	-1.111
0.3004	0.8276	1.371	0.211	-1.227
0.3994	0.8366	1.153	0.247	-1.169
0.5001	0.8455	1.033	0.266	-1.008
0.6000	0.8543	0.930	0.243	-0.833
0.7000	0.8628	0.839	0.213	-0.645
0.8000	0.8712	0.759	0.153	-0.446
0.8997	0.8794	0.695	0.074	-0.233
1.0000	0.8873	0.648	0.000	0.000
		T/K =303.15		
0.0000	0.7945	2.917	0.000	0.000
0.0993	0.8042	2.090	0.102	-0.596
0.1997	0.8138	1.623	0.176	-0.829
0.3004	0.8231	1.337	0.235	-0.881
0.3994	0.8321	1.167	0.261	-0.821
0.5001	0.8409	1.050	0.282	-0.704
0.6000	0.8496	0.949	0.260	-0.572
0.7000	0.8580	0.847	0.232	-0.442
0.8000	0.8663	0.750	0.174	-0.306
0.8997	0.8744	0.653	0.097	-0.171
1.0000	0.8824	0.591	0.000	0.000

Butyl Formate (1) + iso-Butanol (2) T/K =308.15				
0.0000	0.7904	2.517	0.000	0.000
0.0993	0.7999	1.887	0.113	-0.435
0.1997	0.8094	1.483	0.183	-0.641

0.3004	0.8185	1.245	0.252	-0.681
0.3994	0.8274	1.103	0.275	-0.628
0.5001	0.8361	0.990	0.293	-0.543
0.6000	0.8446	0.899	0.281	-0.438
0.7000	0.8529	0.804	0.251	-0.336
0.8000	0.8611	0.708	0.191	-0.235
0.8997	0.8691	0.615	0.113	-0.132
1.0000	0.8771	0.550	0.000	0.000
		T/K =313.15		
0.0000	0.7864	2.163	0.000	0.000
0.0993	0.7957	1.619	0.130	-0.382
0.1997	0.8051	1.314	0.205	-0.523
0.3004	0.8142	1.116	0.266	-0.556
0.3994	0.8230	1.001	0.294	-0.509
0.5001	0.8316	0.909	0.318	-0.437
0.6000	0.8401	0.831	0.299	-0.352
0.7000	0.8483	0.749	0.274	-0.270
0.8000	0.8564	0.667	0.220	-0.189
0.8997	0.8645	0.588	0.121	-0.105
1.0000	0.8725	0.529	0.000	0.000

Hexyl Formate (1) + iso-Butanol (2)				
T/K =298.15				
0.0000	0.7985	3.435	0.000	0.000
0.1000	0.8096	2.411	0.088	-0.768
0.1999	0.8199	1.843	0.128	-1.081
0.3000	0.8293	1.506	0.150	-1.162
0.3998	0.8378	1.325	0.167	-1.088
0.4997	0.8456	1.232	0.174	-0.926
0.5998	0.8529	1.144	0.155	-0.758
0.6988	0.8595	1.060	0.138	-0.589
0.8000	0.8657	0.984	0.122	-0.406
0.8982	0.8714	0.903	0.081	-0.236
1.0000	0.8771	0.879	0.000	0.000
		T/K =303.15		
0.0000	0.7945	2.917	0.000	0.000
0.1000	0.8054	2.214	0.098	-0.494
0.1999	0.8155	1.792	0.147	-0.708
0.3000	0.8247	1.512	0.181	-0.779
0.3998	0.8331	1.342	0.198	-0.740
0.4997	0.8408	1.220	0.206	-0.654
0.5998	0.8480	1.128	0.188	-0.537
0.6988	0.8546	1.056	0.159	-0.402
0.8000	0.8607	0.958	0.146	-0.289
0.8982	0.8663	0.884	0.110	-0.158
1.0000	0.8721	0.829	0.000	0.000

Hexyl Formate (1) + iso-Butanol (2)				
T/K =308.15				
0.0000	0.7904	2.517	0.000	0.000
0.1000	0.8010	1.942	0.123	-0.402
0.1999	0.8110	1.595	0.173	-0.576
0.3000	0.8200	1.385	0.222	-0.612
0.3998	0.8284	1.250	0.229	-0.574
0.4997	0.8360	1.143	0.240	-0.508
0.5998	0.8431	1.067	0.228	-0.411
0.6988	0.8496	0.991	0.205	-0.315
0.8000	0.8558	0.909	0.166	-0.222
0.8982	0.8614	0.838	0.121	-0.122
1.0000	0.8672	0.784	0.000	0.000
		T/K =313.15		
0.0000	0.7864	2.163	0.000	0.000
0.1000	0.7968	1.709	0.135	-0.312
0.1999	0.8067	1.442	0.183	-0.438
0.3000	0.8156	1.253	0.232	-0.485
0.3998	0.8239	1.146	0.239	-0.451
0.4997	0.8314	1.047	0.252	-0.408
0.5998	0.8385	0.986	0.227	-0.328
0.6988	0.8449	0.916	0.207	-0.257
0.8000	0.8510	0.849	0.173	-0.181
0.8982	0.8565	0.791	0.133	-0.100
1.0000	0.8623	0.747	0.000	0.000

Table 3. Parameters and Standard Deviations σ of Eqs. 4 and 5 for a Alkyl (ethyl, butyl and hexyl) Formates (1) with iso-Butanol (2).

	T/K	**a_0**	**a_1**	**a_2**	**a_3**	**σ**
	Ethyl Formate (1) + iso-Butanol(2)					
	298.15	1.7145	-0.0211	0.2136	-	0.0026
$V^E.10^6$/	303.15	1.7463	-0.0119	0.3987	-	0.0053
(m^3mol^{-1})	308.15	1.8239	-0.0231	0.4840	-	0.0051
	313.15	1.8574	0.0238	0.7810	-	0.0042
	298.15	-4.1433	3.4516	-2.5132	0.8437	0.0031
Δη /	303.15	-2.9192	2.6307	-1.7626	-	0.0090
(mPa.s)	308.15	-2.2941	2.0113	-1.3018	-	0.0077
	313.15	-1.8494	1.6101	-0.0161	-	0.0061
	Butyl Formate (1) + iso-Butanol(2)					
$V^E.10^6$/	298.15	1.05	-0.0251	-0.2904	-	0.0034
(m^3mol^{-1})	303.15	1.1023	-0.0279	0.0024	-	0.0034
	308.15	1.1583	0.01	0.1305	-	0.0043
	313.15	1.2436	-0.006	0.2388	-	0.0062

Δη / (mPa.s)	298.15	-4.0459	3.2523	-2.4665	0.8811	0.0124
	303.15	-2.7923	2.4796	-2.2633	0.7606	0.0078
	308.15	-2.1678	2.0427	-1.5591	0.1338	0.0034
	313.15	-1.7253	1.5785	-0.016	0.5480	0.0059
			Hexyl Formate(1) + iso-Butanol(2)			
	298.15	0.6479	-0.0532	0.4190	-	0.0060
$V^E.10^6$/ (m^3mol^{-1})	303.15	0.7622	0.0164	0.5490	-	0.0110
	308.15	0.9171	-0.0384	0.6061	-	0.0080
	313.15	0.9302	-0.0537	0.7714	-	0.0116
Δη / (mPa.s)	298.15	-3.7021	3.3203	-2.8374	0.6138	0.0096
	303.15	-2.581	2.2791	-1.5715	-	0.0084
	308.15	-1.9969	1.8902	-1.4004	-	0.0083
	313.15	-1.5907	1.4167	-0.0161	-	0.0076

Table 4. McAllister 3 Body and 4 body Interaction Parameters for mixtures of Alkyl Formates with Butanol.

Temp T/K	**McAllister 3 Body**			**McAllister 4 Body**			
	υ_{12}	υ_{21}	σ %	υ_{1122}	υ_{1122}	υ_{2221}	**σ %**
Ethyl Formate(1) + iso-Butanol (2)							
298.15	0.8815	0.9742	1.51	0.623	1.358	1.125	**1.19**
303.15	0.9613	1.0721	1.50	0.635	1.585	1.129	**1.29**
308.15	0.9313	1.0434	0.53	0.731	1.043	1.342	**0.29**
313.15	0.8556	0.9602	0.52	0.672	0.963	1.215	**0.27**
Butyl Formate(1) + iso-Butanol (2)							
298.15	1.0251	1.0713	1.96	0.748	2.015	1.14	**1.41**
303.15	1.12	1.0827	2.95	0.79	2.166	1.104	**1.04**
308.15	1.0724	1.0833	1.62	0.858	1.527	1.296	**0.60**
313.15	1.0215	0.9591	1.68	0.803	1.469	1.118	**0.33**
Hexyl Formate(1) + iso-Butanol(2)							
298.15	1.3007	1.1742	3.25	0.939	2.934	1.144	**1.41**
303.15	1.3142	1.3343	1.72	0.882	3.293	1.181	**1.84**
308.15	1.2706	1.2387	1.24	1.084	1.892	1.447	**0.26**
313.15	**1.1601**	**1.1777**	**1.1**	**1.007**	**1.735**	**1.354**	**0.27**

Table 5: Neat FT-IR frequencies (cm^{-1}) of –OH groups of alkyl (ethyl, butyl and hexyl) Formates (1) with iso-Butanol (2).

Ethyl Formate (1) with iso-Butanol (2)		**Butyl Formate (1) with iso-Butanol (2)**		**Hexyl Formate (1) with iso-Butanol (2)**	
x_1	-OH	x_1	-OH	x_1	-OH
Ethyl Formate	- -	Butyl Formate	--	Hexyl Formate	- -
0.2993	3350.46	0.3004	3351.43	0.3001	3358.18
0.3981	3354.32	0.3993	3353.36	0.3998	3362.04
0.4989	3360.11	0.5001	3360.11	0.4998	3381.33
0.2952	3365.90	0.6000	3394.83	0.5999	3439.19
0.7002	3390.90	0.7000	3434.37	0.6988	3443.05
0.7994	3433.41	0.8000	3436.30	0.8001	3439.19
iso-butanol	3346.61	iso-butanol	3346.61	iso-butanol	3346.61

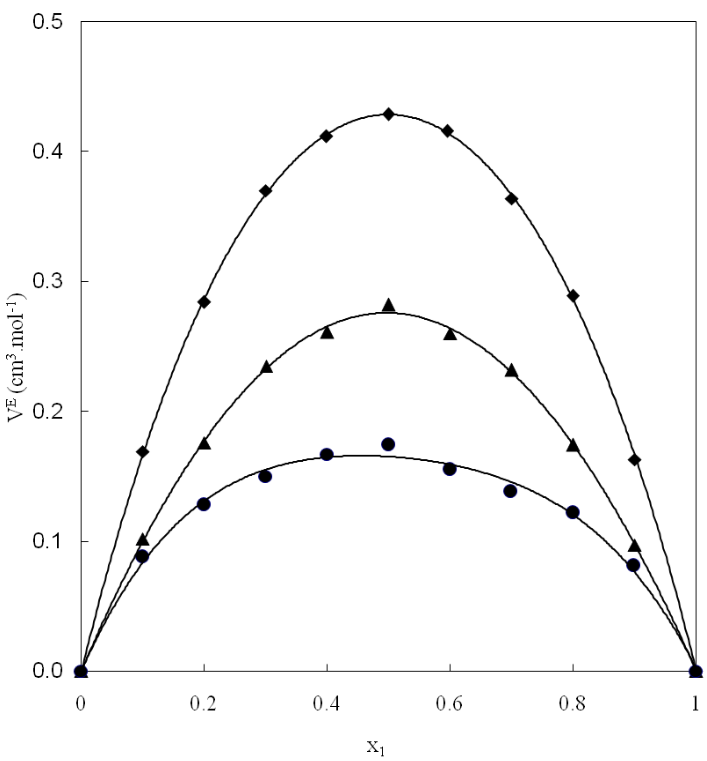


Fig 1. V^E values at 298.15 K for Alkyl formates(x_1): (♦) Ethyl formate; (▲) Butyl formate; (●) Hexyl formate + iso-Butanol ($1-x_1$).

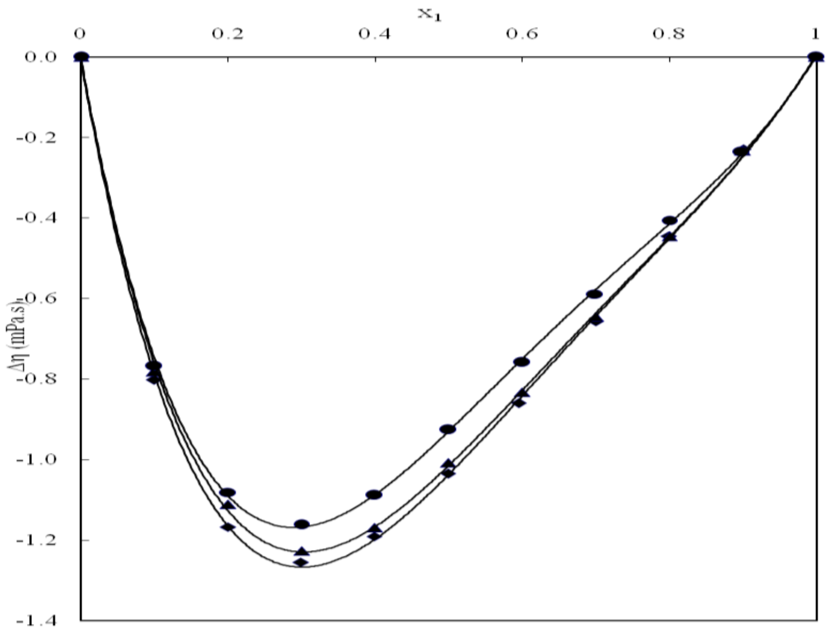


Fig 2. Δη values at 298.15 K for Alkyl formates (x_1): (♦) Ethyl formate; (▲) Butyl formate; (●) Hexyl formate + iso-Butanol (1-x_1).

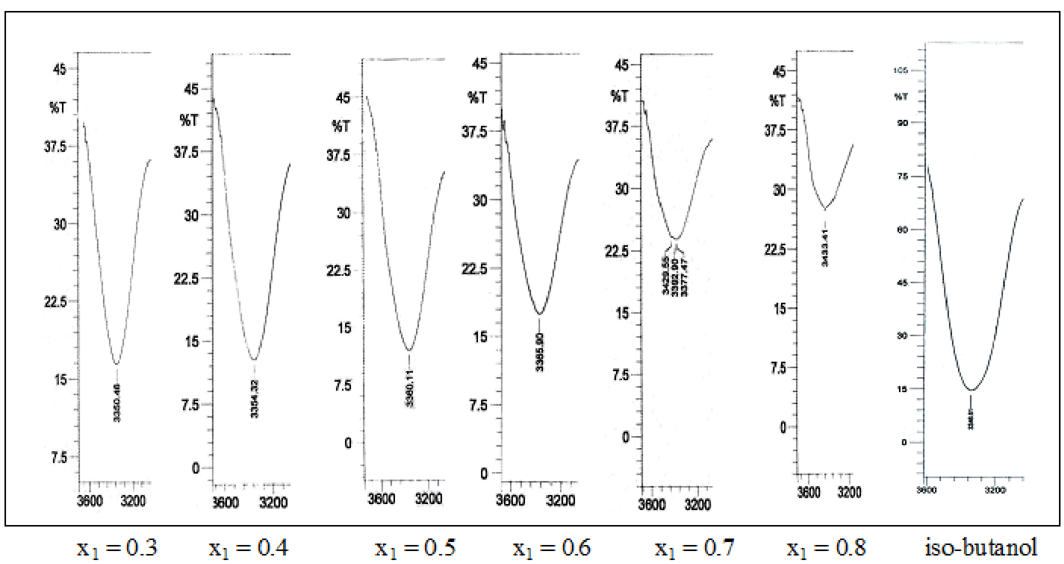
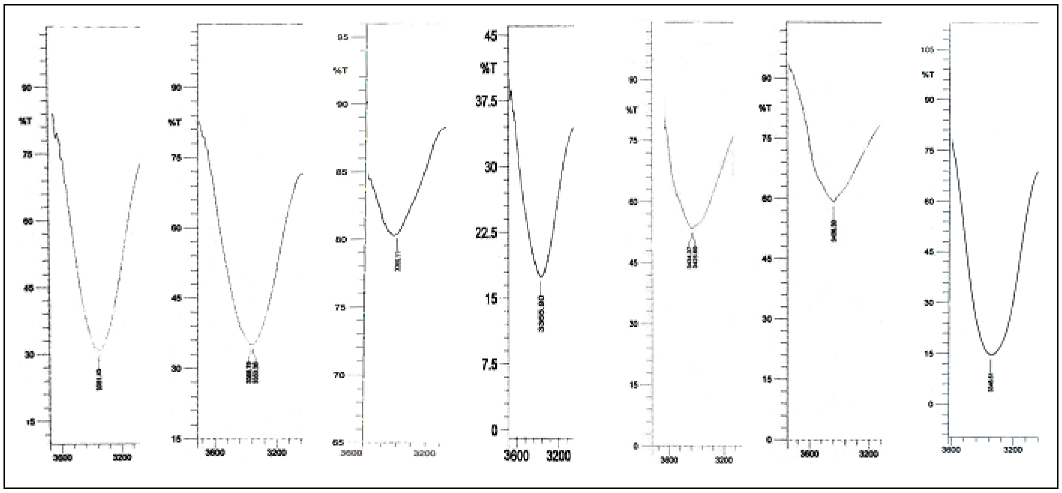
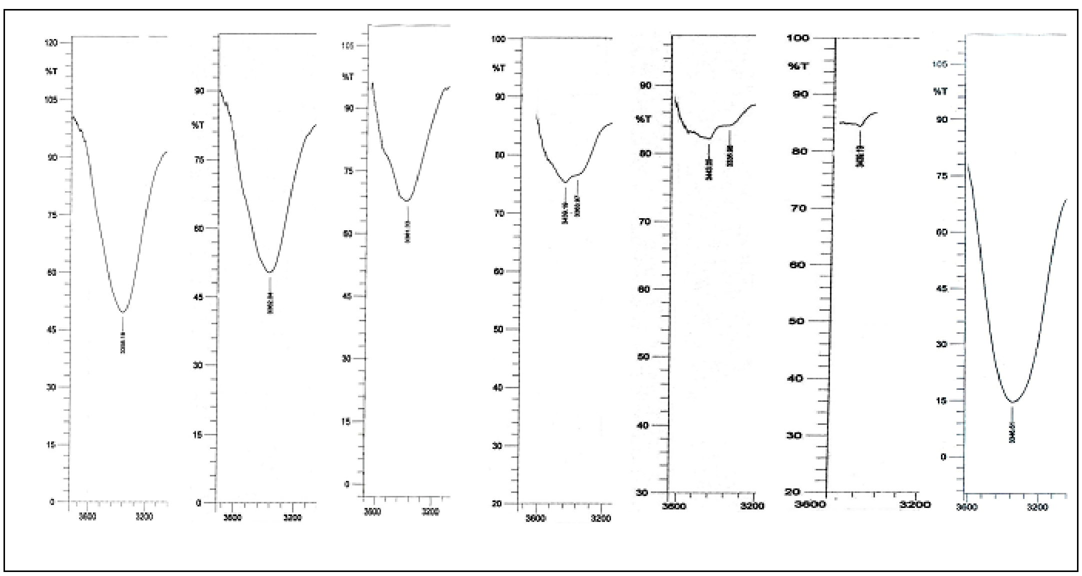


Fig. 3(a). FTIR Spectrum for –OH frequency (cm^{-1}) of Ethyl Formate (x_1) with iso- Butanol.



$x_1 = 0.3$ $x_1 = 0.4$ $x_1 = 0.5$ $x_1 = 0.6$ $x_1 = 0.7$ $x_1 = 0.8$ iso-Butanol

Fig. 3(b). FTIR Spectrum for –OH frequency (cm^{-1}) of Butyl Formate (x_1) with iso- Butanol.



$x_1 = 0.3$ $x_1 = 0.4$ $x_1 = 0.5$ $x_1 = 0.6$ $x_1 = 0.7$ $x_1 = 0.8$ iso-Butanol

Fig. 3(c). FTIR Spectrum for –OH frequency (cm^{-1}) of Hexyll Formate (x_1) with iso- Butanol.