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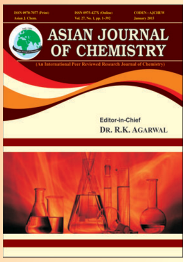

Ultrasonic Studies in Binary Mixtures of N-Propyl Formate with 1-Alcohols At 303 K

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Density (ρ), viscosity (η) and ultrasonic velocity (U) have been measured for binary mixtures composed of *n*-propyl formate with 1-butanol, 1-pentanol and 1-hexanol at 303 K. From the experimental data, various parameters such as adiabatic compressibility (β), free length (L_f), free volume (V_f), Internal pressure (π_i), viscous relaxation time (τ) and Gibbs free energy (ΔG) have been deduced. Excess values of the above parameters (β^E, L_f^E, V_f^E, π_i^E, τ^E and ΔG^E) from their ideal values have also been calculated and fitted in Redlich-Kister polynomial equation. The results have been interpreted in terms of molecular interactions. The deviations in sign and excess values from the ideal mixing reveal that strength of intermolecular interactions between *n*-propyl formate with selected 1-butanol, 1-pentanol and 1-hexanol have been observed in the order of 1-butanol < 1-pentanol < 1-hexanol.

Keywords: *n*-Propyl formate, 1-Butanol, 1-Pentanol, 1-Hexanol, Ultrasonic velocity and hydrogen bonding.

INTRODUCTION

In recent years, the study of density, viscosity and acoustic properties of liquid mixtures is of considerable interest in the elucidation of intermolecular interactions. Since ultrasonic velocity is fundamentally related with intermolecular forces acting between atoms or molecules present in liquid system. It is one of the reliable techniques to elucidate molecular interactions in liquid mixtures. Such studies have shown that the structure and bonding of associated molecular complex in binary and ternary mixtures and found wide applications in research, pharmaceutical and bio-chemical industries[1-7]. The interaction studies of binary liquid mixtures of methyl formate with *o*-, *m*- and *p*-xylenes using viscosity data reported by Rathnam *et al.*[8]. Excess molar volumes and viscosities for binary mixtures of butyrolactone with methyl formate, ethyl formate, methyl acetate, ethyl acetate and acetonitrile at 298.15 K studied by Lu *et al.*[9]. A survey of literature has shown that no attempts have been made to investigate the molecular interaction of the selected liquid mixtures at 303 K. In this present work, we have been made an attempt to elucidate molecular interaction between binary mixtures of *n*-propyl formate with 1-butanol; 1-pentanol and 1-hexanol at 303 K by using ultrasonic technique.

EXPERIMENTAL

Binary mixtures were prepared by mixing appropriate volume of the liquid components in the standard flasks with air tight caps. The masses were recorded on digital electronic balance (ACM-78094L, ACMAS Ltd., India) to an uncertainty of ± 1 mg. The density and viscosity were measured by using specific gravity bottle and Ostwald's viscometer with accuracy $\pm 0.1\ kg\ m^{-3}$ and $\pm 0.001\ Ns\ m^{-2}$, respectively. The ultrasonic velocities in the liquid mixtures were measured by using a single crystal ultrasonic interferometer (Mittal Enterprizes, New Delhi Model: f81) operated at 2 MHz, which was calibrated with water. The accuracy in the ultrasonic velocity measurement was in the order of $\pm 1\ m\ s^{-1}$. All measurements were made using a constant temperature bath [INSREF model IRI-016C, India] by circulating water from the thermostat with accuracy ± 0.01 K.

n-Propyl formate and 1-butanol, 1-pentanol and 1-hexanol were in AnalaR grade, procured from Fluka and SD Fine Chemicals; India, with mass fraction purities greater than 99 % used without further purification. Table-1 shows the purity of these chemicals which were ascertained by a comparison of densities and viscosities with the available literature data[10].

Theory: Ultrasonic wavelength $\lambda = \frac{2d}{n}$ (1)

where d is the distance moved by the reflector and n is the number of oscillation produced by the ultrasonic interferometer.

$$\text{Ultrasonic velocity } U = f\lambda \quad (2)$$

where f is the frequency of ultrasonic wave

TABLE-1
PHYSICAL PROPERTIES OF THE PURE LIQUIDS AT 303 K

S. No	Liquid	(ρ) kg m^{-3}		(η) × 10^{-3} Nm^{-2}s		U (m s^{-1})		Reference
		Expt	Lit	Expt	Lit	Expt	Lit	
1	1-Butanol	805	804	2.149	1.150	1228	1229	10
2	1-Pentanol	808	807	2.761	2.766	1252	1253	10
3	1-Hexanol	809	810	3.512	3.513	1289	1289	10
4	*n*-Propyl formate	1002.5	–	1.096	–	1142	–	–

Adiabatic compressibility $$\beta = \frac{1}{U^2\rho} \quad (3)$$

where U is the ultrasonic velocity and ρ is the density of the liquid mixture.

Free length $$L_f = K_T\sqrt{\beta} \quad (4)$$

Here K_T = [(93.875) + (0.375 T)] × 10^{-8} kelvin

Free volume $$V_f = \left[\frac{M_{eff}U}{\eta K}\right]^{3/2} \quad (5)$$

where M_{eff} is the effective molecular weight. η is the viscosity of the solution is a temperature independent constant which is equal to 4.28 × 10^9 for all liquid system.

Internal pressure $$\pi_i = bRT\left[\frac{K\eta}{U}\right]^{1/2}\left[\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right] \quad (6)$$

where b is a cubical packing fraction and is equal to 2 for all liquids. R is the universal gas constant, T is the experimental temperature and K is the temperature independent constant.

Relaxation time $$\tau = \frac{4}{3}\beta\eta \quad (7)$$

Gibb's free energy $$\Delta G = kT\ln\left(\frac{kT\tau}{h}\right) \quad (8)$$

Here k is Boltzmann's constant; T is absolute temperature, τ is viscous relaxation time and h is Planck's constant.

Excess parameters have been calculated using the following relation

$$Y^E = Y_{exp} - Y_{id} \quad (9)$$

Here $$Y_{id} = \Sigma Y_i x_i \quad (10)$$

A_i represents any acoustical parameter and x_i is the corresponding mole fraction.

The excess parameters have been fitted to Redlich-Kister[11] polynomial equation,

$$Y^E = x_1 x_2 \sum_{i=1}^{m} A_i (x_1 - x_2)^i \quad (11)$$

where Y^E represents the excess value of any parameters,x_1 and x_2 are the mole fraction of the binary mixtures. The coefficients A_i were obtained by fitting equation to experimental values using least square regression method.

The standard deviation σ has been calculated from the following relation,

$$\sigma = \left[\frac{\sum(Y^E_{exp} - Y^E_{cal}}{n - m}\right] \quad (12)$$

where n and m represent the number of experimental points and number of coefficients (A_i) considered, respectively.

RESULTS AND DISCUSSION

Table-2 listed the experimentally measured values of density (ρ), viscosity (η), ultrasonic velocity (U) and computed values of adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π_i), viscous relaxation time (τ) and Gibbs free energy (ΔG) for selected three systems.

It is observed that values of ρ in the binary mixtures increased with increasing concentration of *n*-propyl formate in alcohol medium. Moreover, the values are increased with increasing carbon chain length of alcohols. This trend may be due to the concentration of the *n*-propyl formate increased then the number of particles in a given region is also increased[12]. A reverse trend has been observed in η values. It elucidates that intermolecular interactions between the *n*-propyl formate and 1- alcohols are weakened. The values of ρ and η increased with increase in chain length of 1-alcohols indicating loosening of intermolecular forces due to increasing proton donating ability of 1-alcohol molecules in the mixture[13].

Fig. 1 signifies that the values of U decreased with increase in *n*-propyl formate concentrations. Increasing trend of U is obtained from 1-butanol to 1-hexanol. It may be due to the structural changes occurring in the mixtures resulting in weakening of intermolecular forces.

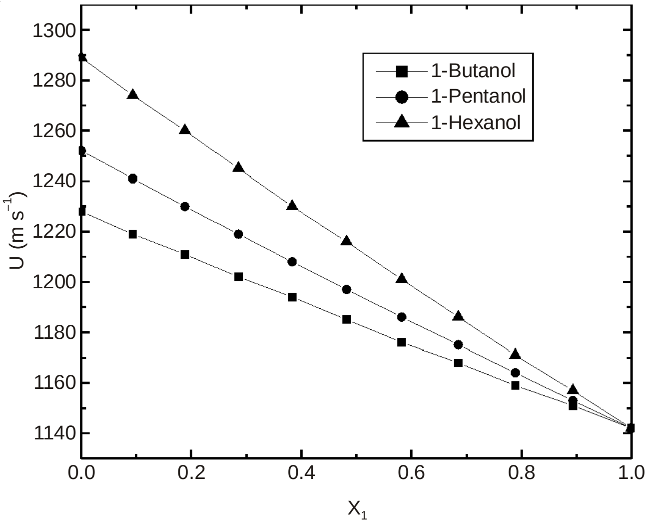

Fig. 1. Plots of ultrasonic velocity *versus* mole fraction of *n*-propyl formate with 1-alcohols at 303 K

Decreasing trend in β shows that the medium is more and more easily compressed with lower carbon chain length of the 1-alcohols (*i.e.*, 1-butanol, 1-pentanol and 1-hexanol). Obviously the proportionate variations of L_f are obtained[14]. Increasing values of V_f suggest the carbonyl group of *n*-propyl formate and hydroxyl group present in the 1-alcohols can

TABLE-2
PHYSICAL AND ACOUSTICAL PARAMETERS OF *n*-PROPYL FORMATE AND 1-ALCOHOLS AT 303 K

x_1	ρ (kg m^{-3})	η × 10^{-3} (Ns m^{-2})	U (m s^{-1})	β × 10^{-10} (m^2 N^{-1})	L_f × 10^{-10} (m)	V_f × 10^{-7} (m^{3}mol^{-1})	π × 10^{12} (N m^{-2})	τ × 10^{-12} (s)	ΔG × 10^{-20} (KJ mol^{-1})
System I: *n*-Propyl formate + 1-butanol									
0.0000	805.0	2.149	1228	8.238	0.5970	0.3113	0.7855	2.360	1.130
0.0937	824.8	2.044	1219	8.159	0.5941	0.3408	0.7656	2.223	1.105
0.1887	844.5	1.938	1211	8.074	0.5910	0.3750	0.7446	2.087	1.078
0.2851	864.3	1.833	1202	8.008	0.5886	0.4140	0.7233	1.957	1.051
0.3829	884.0	1.728	1194	7.935	0.5859	0.4596	0.7009	1.828	1.023
0.4820	903.8	1.623	1185	7.880	0.5839	0.5125	0.6781	1.705	0.993
0.5826	923.5	1.517	1176	7.830	0.5820	0.5749	0.6545	1.584	0.963
0.6847	943.3	1.412	1168	7.771	0.5798	0.6505	0.6298	1.463	0.930
0.7883	963.0	1.307	1159	7.731	0.5783	0.7411	0.6044	1.347	0.895
0.8933	982.8	1.201	1151	7.680	0.5764	0.8536	0.5779	1.230	0.857
1.0000	1002.5	1.096	1142	7.649	0.5752	0.9932	0.5504	1.118	0.817
System II: *n*-Propyl formate + 1-pentanol									
0.0000	808.0	2.761	1252	7.896	0.5845	0.2854	0.7221	2.907	1.217
0.1094	827.5	2.595	1241	7.847	0.5827	0.3092	0.7145	2.715	1.188
0.2165	846.9	2.428	1230	7.805	0.5811	0.3370	0.7051	2.527	1.158
0.3215	866.4	2.262	1219	7.767	0.5797	0.3698	0.6941	2.342	1.126
0.4243	885.8	2.095	1208	7.736	0.5785	0.4091	0.6810	2.161	1.093
0.5250	905.3	1.929	1197	7.709	0.5775	0.4568	0.6661	1.982	1.057
0.6238	924.7	1.762	1186	7.688	0.5767	0.5159	0.6488	1.806	1.018
0.7206	944.2	1.596	1175	7.671	0.5761	0.5903	0.6290	1.632	0.975
0.8156	963.6	1.429	1164	7.659	0.5756	0.6866	0.6063	1.459	0.928
0.9087	983.1	1.263	1153	7.651	0.5753	0.8150	0.5803	1.288	0.876
1.0000	1002.5	1.096	1142	7.649	0.5753	0.9932	0.5504	1.118	0.817
System III: *n*-Propyl formate + 1-hexanol									
0.0000	809.0	3.512	1289	7.440	0.5673	0.2593	0.6762	3.484	1.292
0.1244	828.4	3.270	1274	7.437	0.5672	0.2763	0.6804	3.243	1.262
0.2422	847.7	3.029	1260	7.431	0.5670	0.2974	0.6818	3.001	1.230
0.3539	867.1	2.787	1245	7.440	0.5674	0.3230	0.6805	2.765	1.196
0.4601	886.4	2.546	1230	7.457	0.5680	0.3551	0.6761	2.531	1.159
0.5610	905.8	2.304	1216	7.466	0.5683	0.3964	0.6679	2.294	1.118
0.6572	925.1	2.063	1201	7.494	0.5694	0.4495	0.6558	2.061	1.073
0.7489	944.5	1.821	1186	7.527	0.5707	0.5207	0.6391	1.828	1.023
0.8364	963.8	1.579	1171	7.567	0.5722	0.6198	0.6168	1.593	0.965
0.9200	983.2	1.338	1157	7.597	0.5733	0.7657	0.5875	1.355	0.897
1.0000	1002.5	1.096	1142	7.649	0.5752	0.9932	0.5504	1.118	0.817

mutually form dipole and dipole interaction, reverse trend of π_i also supports the existence of more space between the components. Decreasing values of τ with increase in concentration of *n*-propyl formate and increase with carbon chain length of 1-alcohols indicate that the less time is needed for the rearrangement of the molecules in the liquid mixture which leads dissociation of the mixtures[15,16]. Reduction of ΔG in liquid mixture indicates that the energy that leads to dissociation as listed in Table-2.

Excess parameters are useful to justify the molecular interactions between components of the liquid mixtures. Non-ideal liquid mixtures show the significant deviation from linearity in their physical behaviour with respect to the concentration and temperature which interprets the presence of strong or weak interactions. The positive excess values represent the dispersion forces, while the negative values interpret that dipole-dipole, charge transfer and hydrogen bonding interactions between the unlike molecules[17].

Excess values of β^E, L_f^E, V_f^E, π_i^E, τ^E and ΔG^E are listed in Table-3. These excess values are fitted in Redlich-Kister polynomial equation[11] and corresponding coefficients and standard deviations are listed in Table-4. The values of β^E and L_f^E are negative over the entire range of composition of *n*-propyl formate in 1-alcoholic medium at 303 K. Moreover, those values are increased in the lower concentrations and decreased in the higher concentrations ($x_1 > 0.5$). The negative values may be attributed to the existence of the dispersion and dipolar interaction between the unlike molecules.

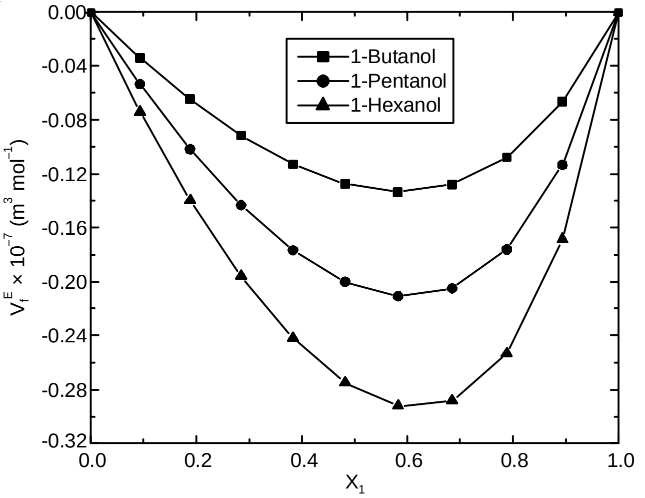

Fig. 2. Plots of excess free volume *versus* mole fraction of *n*-propyl formate with 1-butanol, 1-pentanol and 1-hexanol at 303 K

TABLE-3
EXCESS PHYSICAL AND ACOUSTICAL PARAMETERS OF *n*-PROPYL FORMATE AND 1-ALCOHOLS AT 303 K

x_1	$\beta^E \times 10^{-10}$ ($m^2 N^{-1}$)	$L_f^E \times 10^{-12}$ (m)	$V_f^E \times 10^{-7}$ ($m^3 mol^{-1}$)	$\pi^E \times 10^{12}$ (Nm^{-2})	$\tau^E \times 10^{-13}$ (s)	$\Delta G^E \times 10^{-20}$ (KJ mol^{-1})
System I: *n*-Propyl formate + 1-butanol						
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0937	-0.0234	-0.0857	-0.0344	0.0021	-0.2067	0.0429
0.1887	-0.0521	-0.1886	-0.0649	0.0035	-0.3902	0.0749
0.2851	-0.0617	-0.2185	-0.0917	0.0048	-0.4883	0.1082
0.3829	-0.0772	-0.2753	-0.1128	0.0054	-0.5661	0.1279
0.4820	-0.0744	-0.2592	-0.1275	0.0059	-0.5677	0.1457
0.5826	-0.0647	-0.2299	-0.1336	0.0060	-0.5246	0.1532
0.6847	-0.0635	-0.2274	-0.1277	0.0053	-0.4659	0.1404
0.7883	-0.0428	-0.1515	-0.1077	0.0042	-0.3396	0.1182
0.8933	-0.0311	-0.1126	-0.0668	0.0024	-0.2009	0.0675
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
System II: *n*-Propyl formate + 1-pentanol						
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1094	-0.0220	-0.0794	-0.0536	0.0112	0.0349	0.1511
0.2165	-0.0375	-0.1408	-0.1016	0.0202	0.0728	0.2799
0.3215	-0.0496	-0.1842	-0.1432	0.0272	0.1040	0.3814
0.4243	-0.0552	-0.2096	-0.1766	0.0318	0.1319	0.4561
0.5250	-0.0573	-0.2170	-0.2002	0.0341	0.1472	0.4974
0.6238	-0.0539	-0.2061	-0.2110	0.0338	0.1545	0.5031
0.7206	-0.0470	-0.1770	-0.2051	0.0306	0.1431	0.4658
0.8156	-0.0355	-0.1396	-0.1761	0.0242	0.1165	0.3773
0.9087	-0.0206	-0.0840	-0.1136	0.0142	0.0678	0.2273
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
System III: *n*-Propyl formate + 1-hexanol						
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1244	-0.0281	-0.1083	-0.0743	0.0198	0.5372	0.2914
0.2422	-0.0596	-0.2213	-0.1397	0.0361	0.9002	0.5264
0.3539	-0.0732	-0.2696	-0.1960	0.0488	1.1859	0.7154
0.4601	-0.0788	-0.2935	-0.2419	0.0578	1.3585	0.8513
0.5610	-0.0906	-0.3432	-0.2746	0.0623	1.3727	0.9190
0.6572	-0.0827	-0.3092	-0.2921	0.0623	1.3207	0.9293
0.7489	-0.0690	-0.2516	-0.2882	0.0571	1.1562	0.8623
0.8364	-0.0478	-0.1708	-0.2533	0.0458	0.8844	0.7042
0.9200	-0.0349	-0.1268	-0.1688	0.0270	0.4793	0.4247
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

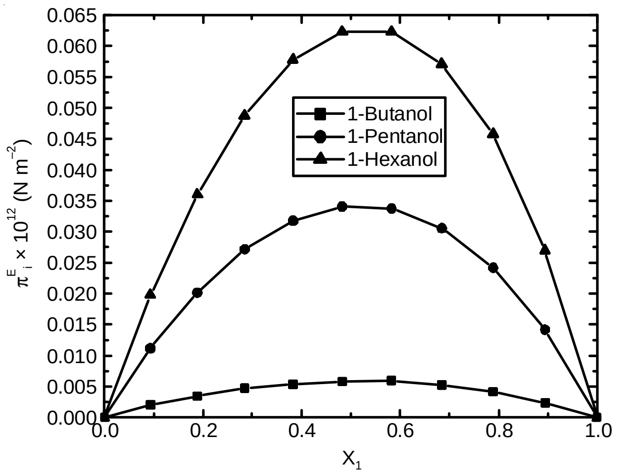

Fig. 3. Plots of excess internal pressure *versus* mole fraction of *n*-propyl formate with 1-butanol, 1-pentanol and 1-hexanol at 303 K

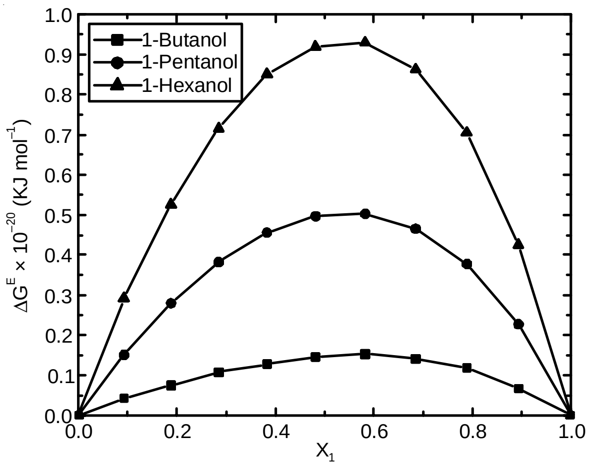

Fig. 4. Plots of excess Gibb's free energy *versus* mole fraction of *n*-propyl formate with 1-butanol, 1-pentanol and 1-hexanol at 303 K

Variation in V_f^E against the mole fraction of *n*-propyl formate is as shown in Fig. 2. It signifies that the values of V_f^E increased up to a critical mole fraction of *n*-propyl formate (x_1 = 0.5) then decreased in the higher concentration. Thus, the observed variations are due to predominance of an energetically favored hydrogen bonding (-OH....O=C) formed in the liquid system. Higher concentrations of *n*-propyl formate rupture hydrogen bonding associate with 1-alcohol medium[18,19]. It is interesting to observe from the Table-3, τ^E becomes positive in 1-pentanol and 1-hexanol. It signifies that strength of

TABLE-4
REDLICH-KISTER COEFFICIENTS AND STANDARD DEVIATIONS OF *n*-PROPYL FORMATE AND 1-ALCOHOLS AT 303 K

Parameters	System	a_0	a_1	a_2	σ
$\beta^E \times 10^{-10}$ ($m^2 N^{-1}$)	I	-0.348	0.443	-0.0986	0.004
	II	-0.218	-0.197	0.019	0.004
	III	-0.218	0.517	0.012	0.004
$L_f^E \times 10^{-12}$ (m)	I	-0.904	0.596	0.295	0.016
	II	-0.666	0.292	0.317	0.003
	III	-1.064	0.635	0.423	0.017
$V_f^E \times 10^{-7}$ ($m^3 mol^{-1}$)	I	-0.149	-0.510	0.657	0.005
	II	-0.203	-0.890	1.088	0.011
	III	-0.235	-1.348	1.512	0.019
$\pi^E \times 10^{12}$ ($N m^{-2}$)	I	0.013	0.004	-0.018	0.002
	II	0.079	0.026	-0.105	0.006
	III	0.133	0.081	-0.214	0.001
$\tau^E \times 10^{-13}$ (s)	I	-1.928	1.235	0.685	0.009
	II	0.188	0.553	-0.741	0.002
	III	0.438	-2.031	-2.309	0.016
$\Delta G^E \times 10^{-20}$ ($KJ mol^{-1}$)	I	0.206	0.480	-0.687	0.005
	II	0.948	0.973	-1.915	0.013
	II	1.817	1.633	-3.343	0.012
	III	1.816	1.632	-3.438	0.028

molecular interaction increased with increase in carbon chain length of the 1-butanol, 1-pentanol and 1-hexanol[18,19]. Figs. 3 and 4 show the variations in π_i^E and ΔG^E, respectively. They are positive in entire concentration range of the liquid mixtures. These positive curves decayed in the *n*-propyl formate rich region in the 1-alcohols medium. Moreover, the positive π_i^E are increased as 1-butanol < 1-pentanol < 1-hexanol. This trend may suggest the thermal agitation of the liquid system in the higher carbon chain length alcohol.

Conclusion

From the experimental observation, the physical and acoustical parameters were determined in the binary mixture of *n*-propyl formate with 1-butanol, 1-propanol and 1-hexanol at 303 K. Ultrasonic velocity is in the order of 1-butanol < 1-pentanol < 1-hexanol. The calculated excess values and their sign show the specific hydrogen bonding interaction obtained in the carbonyl group of the *n*-propyl formate and hydroxyl group present in the 1-alcohols. The determined parameters and their excess values confirm that molecular interactions of *n*-propyl formate with 1-alcohols are obtained in the order of 1-butanol < 1-pentanol < 1-hexanol.

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