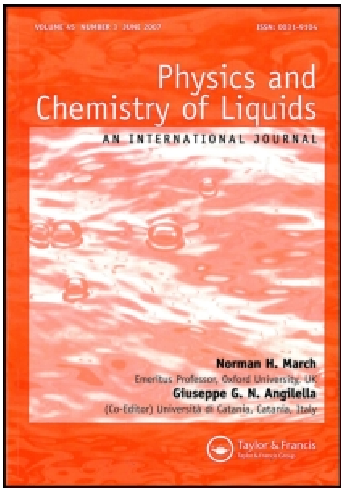

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Viscous synergic behaviour and solvent-solvent interactions occurring in liquid mixtures of aqueous alkanols with some alkanoic acids

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Viscous synergic behaviour and solvent–solvent interactions occurring in liquid mixtures of aqueous alkanols with some alkanoic acids

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The densities and viscosities of six ternary mixtures of the water, monoalkanols; 1-propanol, 2-propanol and monoalkanoic acids; formic acid, acetic acid and propionic acid are determined over the entire range of composition at 298.15, 308.15 and 318.15 K. From the experimental observations, the viscous synergy and synergy interaction index are derived from the equations developed by Kalentunc-Gencer, Peleg and Howell, respectively. The speeds of the sound of these ternary mixtures have been measured over the whole composition range at the same temperatures, and also the excess molar volumes, the isentropic compressibilities and excess isentropic compressibilities have been evaluated from the experimental data.

Keywords: synergy; water–monoalkanol–acid system; density; viscosity; ultrasonic speed

1. Introduction

Water is the most widely used solvent in the chemical and pharmaceutical industry, since it is the most physiological and best tolerated excipient. However, in some cases water cannot be used as a solvent because the active substance or solute is insoluble or slightly soluble in water. For this and other reasons, solvents possessing the common characteristics of being soluble or mixable in water, may be used; as a result, such solvents can be used for the preparation of binary and tertiary mixtures, etc., with different purposes such as increasing water solubility, or modifying the viscosity or absorption of the dissolved substances [1]. For example, alcohol and acid solutions are widely used with water in pharmaceutical industry as solvents for their hydrophilic (polar) and protic nature. The increasing use of monoalkanols and their aqueous mixtures in many industrial processes such as pharmaceutical and cosmetics has greatly stimulated the need for extensive information on their properties. Rheology, the branch of science studies the material deformation and flow, is increasingly applied to analyse the viscous behaviour of many pharmaceutical products [2–6]. In addition, the rheological and molecular behaviours of a formulation can influence aspects such as patient acceptability,

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since it has been well demonstrated that both viscosity and density influence the absorption rate of such products in the body [7,8].

The present study investigates and quantifies the viscous synergy in the ternary mixtures of water, alcohols and acids. The sets of ternary mixtures are formed from water (A) and propanol (B) taken in combination with acids (C); formic acid (set I-a), acetic acid (set I-b), propanoic acid (set I-c) and again from water (A) and isopropanol (B) taken in combination with the same acids (C), i.e. formic acid (set II-a), acetic acid (set II-b), propanoic acid (set II-c), respectively. Water (A), monoalkanols (B) and acids (C) have proton donor and proton acceptor groups leading to self-association in pure state and mutual association in combined state through the significant degree of H-bonding [9,10].

2. Experimental

2.1. *Sources and purity of samples*

All the chemicals used were from Merck (India). Formic acid was treated with boric anhydride to obtain 98% pure acid. Acetic acid was purified by adding some acetic anhydride to react with the water present and then heating for 1 h to just below the boiling point in presence of 2 g of CrO_3, whereas propionic acid was dried by fractional distillation. The source and purification of pure alcohols, 1-propanol and 2- propanol, have been described earlier [11,12]. Triply distilled water was used for the experiments. The purity of the chemicals was ascertained by GLC and also by comparing the experimental values of densities and viscosities with those reported in the literature [13–24] as listed in Table 1.

2.2. *Method*

Densities were measured with an Ostwald–Sprengel-type pycnometer having a bulb volume of about 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15 K with doubly distilled water. The pycnometer with experimental liquid was equilibrated in a glass-walled thermostated water bath maintained at ±0.01 K of the desired temperature. The pycnometer was then removed from the thermostat, properly dried and weighed in an electronic balance with a precision of ±0.01 mg. Adequate precautions were taken to avoid evaporation losses during the time of measurements. An average of triplicate measurement was taken into account. The uncertainty of density values is $\pm 3 \times 10^{-4}\,g\,cm^{-3}$. The details of the methods and measurement techniques have been described earlier [25].

Solvent viscosities were measured by means of a suspended Ubbelohde-type viscometer, calibrated at 298.15 K with doubly distilled water and purified methanol using density and viscosity values from the literature [26–28]. A thoroughly cleaned and perfectly dried viscometer filled with experimental liquid was placed vertically in the glass-walled thermostat maintained to ±0.01 K. After the attainment of thermal equilibrium, efflux times of flow were recorded with a stopwatch correct to ±0.1 s. At least three repetitions of each data reproducible to ±0.1 s were taken to average the flow times. The uncertainty of viscosity values is ±0.003 mPa s. The details of the methods and measurement techniques have been described elsewhere [29,30].

Table 1. Comparison of physical properties at different temperatures of the pure solvents with literature data.

		$\rho \times 10^{-3}$ (kg m^{-3})		$\eta \times 10^{2}$ (mPa s)		u (m s^{-1})	
Solvent	T (K)	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
Water	298.15	0.9971	0.9971 [13]	0.894	0.8903 [13]	1497.0	1497.4 [41]
	308.15	0.9941	0.9940 [13]	0.723	0.7190 [13]	–	–
	318.15	0.9903	0.9902 [13]	0.599	0.5972 [13]	–	–
1-Propanol	298.15	0.7996	0.7995 [14,15]	1.940	1.9324 [14,15]	1207.2	1207.2 [42]
	308.15	0.7916	0.7916 [14,15]	1.560	1.5600 [14,15]	–	–
	318.15	0.7832	0.7846 [16]	1.178	1.1500 [16]	–	–
2-Propanol	298.15	0.7825	0.7808 [17]	2.031	2.0890 [17]	1138.9	1138.9 [43]
	308.15	0.7723	0.7723 [17]	1.564	1.5640 [17]	–	–
	318.15	0.7636	0.7633 [17]	1.190	1.1920 [17]	–	–
Formic acid	298.15	1.2114	1.2114 [18]	1.470	1.5100 [19]	1097.0	–
	308.15	1.1997	1.2012 [19]	1.225	1.2500 [19]	–	–
	318.15	1.1883	–	1.175	–	–	–
Acetic acid	298.15	1.0439	1.0438 [21]	1.070	1.0600 [19]	1132.0	–
	308.15	1.0328	1.0325 [19]	0.978	–	–	–
	318.15	1.0218	–	0.859	–	–	–
Propionic acid	298.15	0.9888	0.9880 [21]	1.013	1.0300 [19]	1172.0	–
	308.15	0.9770	0.9776 [22]	0.914	0.8900 [19]	–	–
	318.15	0.9669	–	0.658	–	–	–

Ultrasonic speeds of sound were determined by multifrequency ultrasonic interferometer (Mittal Enterprise, New Delhi) working at 1 MHz, calibrated with water, methanol and benzene at 298.15 K. The precision of ultrasonic speed measurements was ±0.2 m s^{-1}. The temperature stability was maintained within ±0.01 K by circulating thermostated water around the cell with a circulating pump. The details of the methods and techniques have been described earlier [31].

3. Results and discussion

3.1. *Viscous synergy*

The measurements yielded the viscosity values, η_{exp}, for the different mixtures at different concentrations (w/w), listed in Table 2 along with the viscosity values, η_{calc}, in the absence of interactions. The method most widely used to analyse the antagonic and synergic behaviour of various solvent mixtures is that developed by Roy and Hazra [32] allowing for the quantification of the synergic and antagonic interactions taking place in mixtures involving variable proportions of the constituent components. Viscous synergy is the term applied to the interaction between the components of a system which causes the total viscosity to be greater than the sum of the viscosities of each component in the system. In contraposition to viscous synergism, viscous antagonism is defined as the interaction between the components of a system causing the net viscosity to be less than the sum of the viscosities of each component in the system. If the total viscosity of the system is equal to the sum of the viscosities of each component, the system is said to lack interaction [33]. The viscosity in the absence of interaction, η_{calc}, is defined by the 'simple mixing rule'

$$\eta_{\text{calc}} = \sum_{i=1}^{3} x_i \eta_i, \tag{1}$$

where x_i is the mole fraction and η_i is the viscosity, measured experimentally, of the i-th component. Viscous synergy exists when, $\eta_{\text{exp}} > \eta_{\text{calc}}$. The procedure is valid for Newtonian fluids, since in non-Newtonian systems shear rate must be taken into account and consequently, other synergy indices have been defined [34]. The values in Table 2 show that $\eta_{\text{exp}} > \eta_{\text{calc}}$ for all the systems, indicating viscous synergy; the values in Table 2 are graphically represented in Figure 1, where the viscosity is seen to increase non-linearly for all the mixtures, reaching maximum values (saturation point) and thereafter to decrease.

The explanation of this type of behaviour is based on the known phenomenon of solvation, as a consequence of the hydrogen bonds formed between the molecules of the components of the mixture – producing an increase in the size of the resulting molecular package, which logically implies a rise in viscosity [35]. After reaching the maximum viscosity, the subsequent addition of more water induces a decrease in mixture viscosity, as the latter tends to approach the viscosity of water.

Such characteristics in the viscosity versus composition curve is a manifestation of specific interaction [36] between the unlike molecules, predominated by hydrogen bonding interaction. Maximum viscosity is found in the mixtures when the mole fractions are in the following ratios:

(set I-a, II-a) water (A) + propanol (B)/isopropanol (B) + formic acid (C) = 1:1.35:1.76
(set I-b, II-b) water (A) + propanol (B)/isopropanol (B) + acetic acid (C) = 1:1.35:1.35
(set I-c, II-c) water (A) + propanol (B)/isopropanol (B) + propionic acid (C) = 1:1.35:1.09.

It can be concluded that the affinity of monoalkanoic acid molecules towards monoalkanols in the presence of water is enhanced by the following order:

$$\mathrm{A + B + HCOOH > A + B + CH_3COOH > A + B + CH_3CH_2COOH}.$$

The monoalkanols with hydroxyl group positioned at the second carbon atom accept more acid and water than those with the terminal hydroxyl group. Similar results were also reported earlier by Herraez and Belda [17].

3.2. *Synergy interaction index*

The corresponding viscosity increment given by $\Delta\eta = \eta_{\text{exp}} - \eta_{\text{calc}}$ and the synergy interaction indices, I_{S}, introduced by Howell [34] is calculated by the following equation:

$$I_{\text{S}} = (\eta_{\text{exp}} - \eta_{\text{calc}})/\eta_{\text{calc}} = \Delta\eta/\eta_{\text{calc}}. \tag{2}$$

The values recorded in Tables 2 and 3 allow us to plot the graphical representations shown in Figures 2–5. Figures 2 and 4 show the variations of

Table 2. Comparison of experimental and calculated viscosities (η) for the indicated water (A)-soluble mixtures of monoalkanols (B) and acids (C) as a function of mass % of water at 298.15, 308.15 and 318.15 K.

	298.15 K		308.15 K		318.15 K	
Mass % of H_2O	$\eta_{exp} \times 10^2$ (mPas)	$\eta_{calc} \times 10^2$ (mPas)	$\eta_{exp} \times 10^2$ (mPas)	$\eta_{calc} \times 10^2$ (mPas)	$\eta_{exp} \times 10^2$ (mPas)	$\eta_{calc} \times 10^2$ (mPas)
HCOOH + 1-PrOH (w/w = 1 : 1)						
0	1.795	1.617	1.508	1.370	1.270	1.164
10	1.845	1.441	1.540	1.213	1.295	1.027
20	1.736	1.313	1.443	1.098	1.213	0.927
30	1.570	1.217	1.292	1.012	1.082	0.851
40	1.407	1.141	1.152	0.944	0.963	0.792
50	1.272	1.079	1.042	0.889	0.867	0.744
60	1.165	1.029	0.951	0.844	0.792	0.705
70	1.072	0.987	0.871	0.806	0.719	0.672
80	1.005	0.951	0.813	0.774	0.671	0.644
90	0.947	0.920	0.767	0.747	0.634	0.620
100	0.894	0.894	0.723	0.723	0.599	0.599
HCOOH + 2-PrOH (w/w = 1 : 1)						
0	1.888	1.656	1.546	1.372	1.328	1.182
10	1.927	1.471	1.575	1.214	1.342	1.040
20	1.847	1.336	1.509	1.099	1.276	0.937
30	1.699	1.234	1.381	1.013	1.164	0.859
40	1.545	1.154	1.254	0.944	1.048	0.798
50	1.374	1.090	1.110	0.889	0.933	0.749
60	1.227	1.037	0.987	0.844	0.823	0.708
70	1.117	0.992	0.899	0.806	0.749	0.674
80	1.031	0.954	0.829	0.774	0.688	0.645
90	0.962	0.922	0.769	0.747	0.639	0.620
100	0.894	0.894	0.723	0.723	0.599	0.599
CH_3COOH + 1-PrOH (w/w = 1 : 1)						
0	1.755	1.655	1.333	1.269	1.049	1.004
10	1.765	1.449	1.352	1.121	1.072	0.895
20	1.644	1.309	1.273	1.020	1.021	0.820
30	1.453	1.207	1.130	0.947	0.910	0.766
40	1.297	1.130	1.016	0.892	0.826	0.725
50	1.175	1.069	0.924	0.849	0.750	0.692
60	1.088	1.021	0.856	0.814	0.699	0.666
70	1.013	0.980	0.806	0.785	0.661	0.645
80	0.960	0.947	0.768	0.761	0.633	0.627
90	0.922	0.918	0.743	0.740	0.614	0.612
100	0.894	0.894	0.723	0.723	0.599	0.599
CH_3COOH + 2-PrOH (w/w = 1 : 1)						
0	1.835	1.700	1.358	1.271	1.087	1.024
10	1.846	1.482	1.382	1.123	1.109	0.909
20	1.709	1.334	1.299	1.022	1.054	0.831
30	1.510	1.226	1.160	0.949	0.942	0.774
40	1.346	1.144	1.042	0.893	0.848	0.731
50	1.218	1.080	0.949	0.849	0.773	0.697
60	1.116	1.028	0.876	0.814	0.718	0.670
70	1.038	0.986	0.818	0.785	0.673	0.647

(*continued*)

Table 2. Continued.

	298.15 K		308.15 K		318.15 K	
Mass % of H_2O	$\eta_{exp} \times 10^2$ (mPas)	$\eta_{calc} \times 10^2$ (mPas)	$\eta_{exp} \times 10^2$ (mPas)	$\eta_{calc} \times 10^2$ (mPas)	$\eta_{exp} \times 10^2$ (mPas)	$\eta_{calc} \times 10^2$ (mPas)
80	0.978	0.950	0.777	0.761	0.640	0.629
90	0.932	0.920	0.746	0.740	0.617	0.613
100	0.894	0.894	0.723	0.723	0.599	0.599
			CH_3CH_2COOH + 1-PrOH (w/w = 1 : 1)			
0	1.712	1.691	1.327	1.320	0.933	0.930
10	1.616	1.460	1.262	1.146	0.913	0.834
20	1.476	1.309	1.160	1.034	0.863	0.771
30	1.308	1.203	1.032	0.954	0.783	0.727
40	1.182	1.125	0.934	0.895	0.722	0.695
50	1.092	1.064	0.866	0.850	0.679	0.669
60	1.031	1.016	0.822	0.814	0.654	0.650
70	0.983	0.977	0.789	0.785	0.636	0.633
80	0.948	0.944	0.763	0.761	0.622	0.620
90	0.918	0.917	0.741	0.740	0.609	0.609
100	0.894	0.894	0.723	0.723	0.599	0.599
			CH_3CH_2COOH + 2-PrOH (w/w = 1 : 1)			
0	1.810	1.742	1.361	1.322	0.977	0.952
10	1.714	1.495	1.309	1.148	0.949	0.834
20	1.570	1.335	1.212	1.035	0.902	0.771
30	1.378	1.223	1.070	0.955	0.812	0.727
40	1.228	1.139	0.960	0.896	0.741	0.695
50	1.127	1.075	0.884	0.851	0.692	0.669
60	1.050	1.024	0.831	0.814	0.660	0.650
70	0.994	0.982	0.793	0.785	0.639	0.633
80	0.953	0.948	0.765	0.761	0.624	0.620
90	0.921	0.919	0.742	0.740	0.610	0.609
100	0.894	0.894	0.723	0.723	0.599	0.599

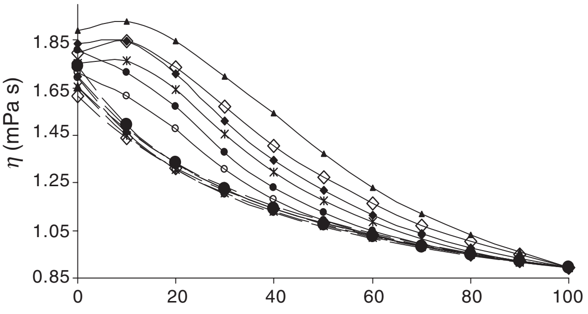


Figure 1. Experimental and calculated viscosity (η) of: (◇), water (A) + propanol (B) + formic acid (C); (▲), water (A) + 2-propanol (B) + formic acid (C); (∗), water (A) + propanol (B) + acetic acid (C); (◆), water (A) + 2-propanol (B) + acetic acid (C); (○), water (A) + propanol (B) + propionic acid (C); (●), water (A) + 2-propanol (B) + propionic acid (C) mixtures with mass % of water (A) at 298.15 K, exp (—), calc (- - -).

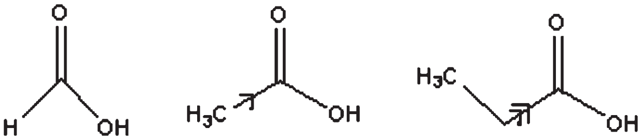
$\Delta\eta$ and I_S with increasing mass % of water. These graphs also show the same trend as shown by the viscosity curves.

Figure 3 represents the viscosities η_{max}, as a function of the number of carbon atoms for the alkanoic acids and shows that the values of η_{max} decrease almost linearly with the number of carbon atoms. For the monoalkanol with the hydroxyl group at the second carbon atom, expected to be greater than primary monoalkanol, also decreases in the same way. Similar results were reported in an earlier paper [35].

Figures 4 and 5 show the viscous synergy interaction index, I_S, as a function of mass % of H_2O and the number of carbon atoms corresponding to the monoalkanols with the hydroxyl group at the end of the molecular chain and the second carbon atom, respectively. These figures show that the synergic indices of the monoalkanoic acids in aqueous monoalkanols follow the order:

$$A + B + HCOOH > A + B + CH_3COOH > A + B + CH_3CH_2COOH$$

showing the same trend as $\Delta\eta$ values and monoalkanols with the hydroxyl group at the second carbon atom of the molecular chain due to more symmetric nature are greater than those of the monoalkanols with terminal hydroxyl group. Similar results reported earlier [17,35] are in excellent agreement with the results obtained from the viscosity values recorded in this article.



The gradual decrement of synergy interaction values from HCOOH to CH_3CH_2COOH can be explained in view of +I-effect. $-C_2H_5$ has more +I-effect than $-CH_3$ which has in turn than –H. This facilitates more interactions of HCOOH with unlike molecules than CH_3COOH and CH_3CH_2COOH rendering to higher values of synergy interaction parameters.

3.3. *Excess molar volume*

The experimentally determined density values along with the derived parameter, V^E, the excess molar volume, are listed in Table 4.

The excess molar volumes, V^E, are calculated from density data according to the following equation [37]:

$$V^E = \sum_{i=1}^{3} x_i M_i (1/\rho - 1/\rho_i), \tag{3}$$

where M_i, ρ_i and ρ are the molar mass, density of the i-th component and density of the mixture, respectively.

Figure 6 represents the V^E values for the six ternary mixtures under experiment. In general, V^E is found to be negative throughout all the temperatures for all the ternary mixtures. However, the value at first decreases to a minima and then it

Table 3. Deviation in viscosity ($\Delta\eta$) and viscous synergy interaction index (I_S) values for the ternary liquid mixtures of water (A) + monoalkanols (B) + acids (C) at 298.15, 308.15 and 318.15 K.

	298.15 K		308.15 K		318.15 K	
Mass % of H_2O	$\Delta\eta \times 10^2$ (mPas)	I_S	$\Delta\eta \times 10^2$ (mPas)	I_S	$\Delta\eta \times 10^2$ (mPas)	I_S
		$HCOOH$ + 1-PrOH (w/w = 1 : 1)				
0	0.178	0.110	0.138	0.101	0.106	0.091
10	0.404	0.280	0.327	0.270	0.268	0.261
20	0.422	0.322	0.345	0.314	0.286	0.309
30	0.354	0.291	0.280	0.277	0.231	0.271
40	0.267	0.234	0.208	0.220	0.171	0.216
50	0.192	0.178	0.153	0.172	0.123	0.166
60	0.136	0.132	0.107	0.127	0.087	0.124
70	0.085	0.086	0.065	0.081	0.047	0.070
80	0.054	0.056	0.039	0.050	0.028	0.043
90	0.027	0.029	0.020	0.027	0.014	0.023
100	0.000	0.000	0.000	0.000	0.000	0.000
		$HCOOH$ + 2-PrOH (w/w = 1 : 1)				
0	0.232	0.140	0.174	0.127	0.146	0.124
10	0.456	0.310	0.361	0.297	0.302	0.291
20	0.510	0.382	0.409	0.372	0.339	0.362
30	0.465	0.377	0.368	0.364	0.305	0.355
40	0.391	0.338	0.309	0.328	0.250	0.313
50	0.284	0.261	0.221	0.249	0.185	0.247
60	0.190	0.183	0.143	0.170	0.116	0.163
70	0.125	0.126	0.093	0.115	0.075	0.111
80	0.077	0.081	0.055	0.071	0.043	0.066
90	0.040	0.043	0.023	0.031	0.019	0.030
100	0.000	0.000	0.000	0.000	0.000	0.000
		CH_3COOH + 1-PrOH (w/w = 1 : 1)				
0	0.100	0.060	0.064	0.050	0.045	0.044
10	0.316	0.218	0.231	0.206	0.177	0.198
20	0.335	0.256	0.252	0.247	0.201	0.245
30	0.246	0.204	0.183	0.193	0.144	0.188
40	0.167	0.148	0.124	0.139	0.101	0.139
50	0.106	0.099	0.075	0.089	0.058	0.083
60	0.067	0.066	0.043	0.053	0.033	0.049
70	0.032	0.033	0.022	0.028	0.016	0.025
80	0.013	0.014	0.008	0.010	0.006	0.010
90	0.004	0.004	0.003	0.004	0.003	0.004
100	0.000	0.000	0.000	0.000	0.000	0.000
		CH_3COOH + 2-PrOH (w/w = 1 : 1)				
0	0.135	0.079	0.087	0.068	0.063	0.061
10	0.364	0.245	0.259	0.231	0.199	0.219
20	0.375	0.281	0.277	0.271	0.224	0.269
30	0.284	0.232	0.211	0.223	0.168	0.217
40	0.202	0.176	0.150	0.168	0.117	0.160
50	0.138	0.128	0.100	0.117	0.076	0.109
60	0.088	0.086	0.062	0.076	0.048	0.072

(*continued*)

Table 3. Continued.

	298.15 K		308.15 K		318.15 K	
Mass % of H_2O	$\Delta\eta \times 10^2$ (mPas)	I_S	$\Delta\eta \times 10^2$ (mPas)	I_S	$\Delta\eta \times 10^2$ (mPas)	I_S
70	0.053	0.053	0.033	0.043	0.026	0.040
80	0.028	0.029	0.016	0.021	0.012	0.019
90	0.012	0.013	0.006	0.008	0.005	0.007
100	0.000	0.000	0.000	0.000	0.000	0.000
CH_3CH_2COOH + 1-PrOH (w/w = 1 : 1)						
0	0.021	0.012	0.007	0.005	0.004	0.004
10	0.156	0.107	0.116	0.101	0.079	0.095
20	0.167	0.127	0.126	0.122	0.092	0.119
30	0.105	0.087	0.078	0.082	0.056	0.077
40	0.057	0.051	0.039	0.043	0.028	0.040
50	0.028	0.026	0.016	0.019	0.010	0.015
60	0.015	0.015	0.008	0.010	0.005	0.007
70	0.007	0.007	0.004	0.005	0.002	0.004
80	0.004	0.004	0.003	0.004	0.002	0.003
90	0.001	0.001	0.001	0.001	0.001	0.001
100	0.000	0.000	0.000	0.000	0.000	0.000
CH_3CH_2COOH + 2-PrOH (w/w = 1 : 1)						
0	0.069	0.039	0.039	0.030	0.025	0.026
10	0.219	0.146	0.161	0.140	0.116	0.139
20	0.235	0.176	0.178	0.172	0.131	0.170
30	0.155	0.127	0.114	0.120	0.085	0.116
40	0.089	0.078	0.064	0.071	0.046	0.067
50	0.052	0.048	0.033	0.039	0.023	0.034
60	0.026	0.025	0.017	0.021	0.011	0.016
70	0.012	0.012	0.008	0.010	0.006	0.009
80	0.005	0.005	0.004	0.006	0.004	0.006
90	0.002	0.002	0.002	0.002	0.001	0.002
100	0.000	0.000	0.000	0.000	0.000	0.000

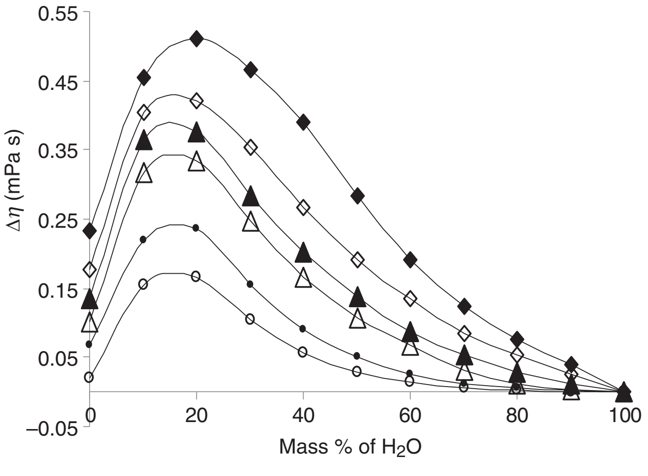


Figure 2. Viscosity deviation ($\Delta\eta$) of: (◇), water (A) + propanol (B) + formic acid (C); (◆), water (A) + 2-propanol (B) + formic acid (C); (Δ), water (A) + propanol (B) + acetic acid (C); (▲), water (A) + 2-propanol (B) + acetic acid (C); (○), water (A) + propanol (B) + propionic acid (C); (●), water (A) + 2-propanol (B) + propionic acid (C) mixtures with mass% of water (A) at 298.15 K.

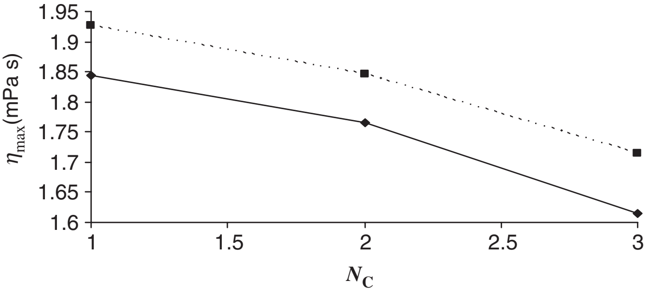


Figure 3. η_{max} of the monoalkanoic acids as a function of the number of carbon atoms, N_C, for water (A) + propanol (B), (—◆—); water (A) + 2-propanol (B), (- - -■- - -) systems at 298.15 K.

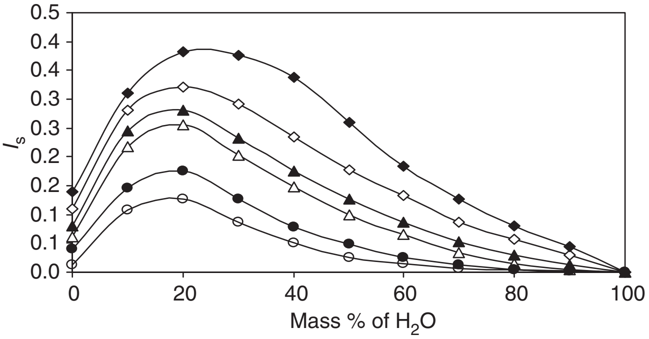


Figure 4. Viscous synergy interaction index (I_S) values of: (◇), water (A) + propanol (B) + formic acid (C); (◆), water (A) + 2-propanol (B) + formic acid (C); (Δ), water (A) + propanol (B) + acetic acid (C); (▲), water (A) + 2-propanol (B) + acetic acid (C); (○), water (A) + propanol (B) + propionic acid (C); (●), water (A) + 2-propanol (B) + propionic acid (C) mixtures with mass% of water (A) at 298.15 K.

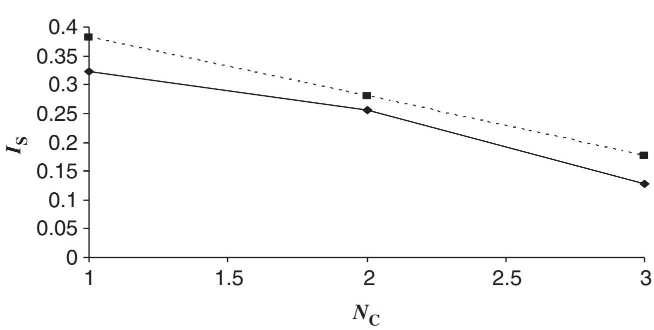


Figure 5. Viscous synergy interaction index (I_S) of the monoalkanoic acids as a function of the number of carbon atoms, N_C, for water (A) + propanol (B), (—◆—); water (A) + 2-propanol (B), (- - -■- - -) systems.

Table 4. Comparison of experimental densities (ρ) and excess molar volumes (V^E) for the indicated water (A)-soluble mixtures of monoalkanols (B) and acids(C) as a function of mass% at 298.15, 308.15 and 318.15 K.

	298.15 K		308.15 K		318.15 K	
Mass % of H_2O	$\rho_{exp} \times 10^{-3}$ (kg m^{-3})	$V^E \times 10^3$ (m^3 mol^{-1})	$\rho_{exp} \times 10^{-3}$ (kg m^{-3})	$V^E \times 10^3$ (m^3 mol^{-1})	$\rho_{exp} \times 10^{-3}$ (kg m^{-3})	$V^E \times 10^3$ (m^3 mol^{-1})
$HCOOH + 1\text{-PrOH}$ (w/w = 1 : 1)						
0	0.9770	−0.7570	0.9668	−0.7330	0.9565	−0.7140
10	0.9936	−1.2320	0.9833	−1.1910	0.9733	−1.1750
20	1.0034	−1.3010	0.9938	−1.2730	0.9842	−1.2570
30	1.0075	−1.1620	0.9982	−1.1260	0.9873	−1.0470
40	1.0085	−0.9620	0.9994	−0.9140	0.9875	−0.7940
50	1.0059	−0.7060	0.9986	−0.6900	0.9878	−0.5930
60	1.0036	−0.5020	0.9966	−0.4760	0.9881	−0.4270
70	1.0014	−0.3330	0.9960	−0.3290	0.9883	−0.2860
80	0.9996	−0.1980	0.9940	−0.1740	0.9885	−0.1670
90	0.9981	−0.0870	0.9934	−0.0680	0.9888	−0.0660
100	0.9971	0.0000	0.9941	0.0000	0.9903	0.0000
$HCOOH + 2\text{-PrOH}$ (w/w = 1 : 1)						
0	0.9656	−0.8390	0.9540	−0.8330	0.9437	−0.8290
10	0.9832	−1.3040	0.9714	−1.2680	0.9610	−1.2450
20	0.9946	−1.3810	0.9833	−1.3440	0.9734	−1.3270
30	1.0012	−1.2730	0.9903	−1.2270	0.9807	−1.2020
40	1.0034	−1.0560	0.9925	−0.9890	0.9841	−0.9820
50	1.0029	−0.8090	0.9927	−0.7420	0.9851	−0.7380
60	1.0012	−0.5770	0.9928	−0.5370	0.9860	−0.5350
70	0.9998	−0.3890	0.9930	−0.3670	0.9869	−0.3640
80	0.9986	−0.2340	0.9931	−0.2210	0.9878	−0.2200
90	0.9976	−0.1040	0.9932	−0.0950	0.9886	−0.0930
100	0.9971	0.0000	0.9941	0.0000	0.9903	0.0000
$CH_3COOH + 1\text{-PrOH}$ (w/w = 1 : 1)						
0	0.9120	−0.4700	0.9023	−0.4510	0.8920	−0.4000
10	0.9316	−1.0100	0.9219	−0.9780	0.9120	−0.9480
20	0.9454	−1.0760	0.9360	−1.0410	0.9268	−1.0310
30	0.9547	−0.9340	0.9456	−0.8930	0.9370	−0.8880
40	0.9613	−0.7300	0.9526	−0.6860	0.9446	−0.6810
50	0.9665	−0.5250	0.9595	−0.5170	0.9518	−0.5030
60	0.9725	−0.3800	0.9665	−0.3800	0.9598	−0.3780
70	0.9780	−0.2470	0.9720	−0.2300	0.9660	−0.2280
80	0.9830	−0.1230	0.9777	−0.1070	0.9724	−0.1050
90	0.9896	−0.0490	0.9847	−0.0270	0.9801	−0.0250
100	0.9971	0.0000	0.9941	0.0000	0.9903	0.0000
$CH_3COOH + 2\text{-PrOH}$ (w/w = 1 : 1)						
0	0.9020	−0.5590	0.8908	−0.5380	0.8800	−0.4660
10	0.9230	−1.1210	0.9120	−1.0950	0.9020	−1.0740
20	0.9380	−1.1810	0.9272	−1.1430	0.9175	−1.1200
30	0.9480	−1.0100	0.9379	−0.9770	0.9288	−0.9600
40	0.9560	−0.8050	0.9462	−0.7590	0.9375	−0.7370
50	0.9620	−0.5800	0.9537	−0.5600	0.9456	−0.5390
60	0.9690	−0.4240	0.9619	−0.4150	0.9538	−0.3780

(*continued*)

Table 4. Continued.

	298.15 K		308.15 K		318.15 K	
Mass % of H_2O	$\rho_{exp} \times 10^{-3}$ (kg m^{-3})	$V^E \times 10^3$ (m^3 mol^{-1})	$\rho_{exp} \times 10^{-3}$ (kg m^{-3})	$V^E \times 10^3$ (m^3 mol^{-1})	$\rho_{exp} \times 10^{-3}$ (kg m^{-3})	$V^E \times 10^3$ (m^3 mol^{-1})
70	0.9750	−0.2690	0.9686	−0.2550	0.9609	−0.2140
80	0.9810	−0.1370	0.9760	−0.1350	0.9694	−0.1070
90	0.9880	−0.0440	0.9840	−0.0430	0.9787	−0.0280
100	0.9971	0.0000	0.9941	0.0000	0.9903	0.0000
			CH_3CH_2COOH + 1-PrOH (w/w = 1 : 1)			
0	0.8838	0.0160	0.8742	0.0330	0.8649	0.0450
10	0.9040	−0.6390	0.8943	−0.6000	0.8850	−0.5760
20	0.9195	−0.7780	0.9100	−0.7350	0.9011	−0.7180
30	0.9313	−0.6970	0.9224	−0.6630	0.9140	−0.6510
40	0.9413	−0.5620	0.9329	−0.5280	0.9251	−0.5210
50	0.9500	−0.4090	0.9421	−0.3740	0.9344	−0.3530
60	0.9590	−0.2920	0.9513	−0.2470	0.9441	−0.2260
70	0.9670	−0.1680	0.9605	−0.1400	0.9542	−0.1270
80	0.9760	−0.0840	0.9706	−0.0660	0.9653	−0.0630
90	0.9860	−0.0300	0.9815	−0.0160	0.9769	−0.0140
100	0.9971	0.0000	0.9941	0.0000	0.9903	0.0000
			CH_3CH_2COOH + 2-PrOH (w/w = 1 : 1)			
0	0.8742	−0.0660	0.8629	−0.0200	0.8535	−0.0170
10	0.8960	−0.7650	0.8848	−0.7150	0.8755	−0.7060
20	0.9127	−0.9000	0.9019	−0.8540	0.8929	−0.8440
30	0.9256	−0.8060	0.9152	−0.7560	0.9064	−0.7360
40	0.9360	−0.6310	0.9267	−0.6010	0.9185	−0.5870
50	0.9455	−0.4610	0.9371	−0.4380	0.9291	−0.4120
60	0.9554	−0.3310	0.9480	−0.3150	0.9412	−0.3090
70	0.9642	−0.1930	0.9581	−0.1890	0.9519	−0.1820
80	0.9743	−0.1040	0.9686	−0.0880	0.9631	−0.0820
90	0.9843	−0.0220	0.9799	−0.0150	0.9753	−0.0130
100	0.9971	0.0000	0.9941	0.0000	0.9903	0.0000

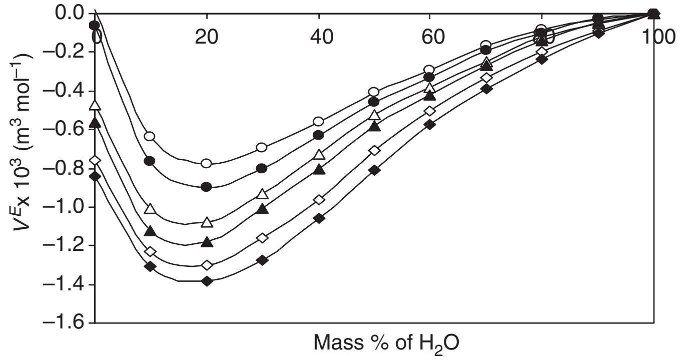


Figure 6. Excess molar volumes (V^E) of: (◇), water (A) + propanol (B) + formic acid (C); (◆), water (A) + 2-propanol (B) + formic acid (C); (Δ), water (A) + propanol (B) + acetic acid (C); (▲), water(A) + 2-propanol (B) + acetic acid (C); (○), water (A) + propanol (B) + propionic acid (C); (●), water (A) + 2-propanol (B) + propionic acid (C) mixtures with mass% of water (A) at 298.15 K.

increases with increasing mass% of water. V^{E} increases systematically from 298.15 to 318.15 K over the whole range of compositions. The six ternary mixtures show the minima in the range of $x_{A} = 0.4 - 0.5$ with an exception in set (I-c, II-c) which shows minima at $x_{A} = 0.6$. The trend is:

$$A + (B) + CH_3CH_2COOH > A + (B) + CH_3COOH > A + (B) + HCOOH.$$

The negative V^{E} indicates the presence of strong molecular interaction between the components of the mixture. Several effects contribute to the value of V^{E}, such as [38]: (1) dipolar interaction, (2) interstitial accommodation of one component into the other and (3) possible hydrogen-bonded interactions between unlike molecules. The actual volume change would, therefore, depend on the relative strength of these three effects.

3.4. *Deviation in isentropic compressibility*

Isentropic compressibility, K_{S} and deviation in isentropic compressibility, K_{S}^{E} were calculated using the following relations

$$K_{S} = 1/(u^{2}\rho_{\exp}) \tag{4}$$

$$K_{S}^{E} = K_{S} - \sum_{i=1}^{3} x_{i}K_{S,i}, \tag{5}$$

where u and K_{S} are the speed of sound, isentropic compressibility of the mixture and $K_{S,i}$, the isentropic compressibility of the i-th component in the mixture. The experimental speed of sound, isentropic compressibility and deviation in isentropic compressibility are listed in Table 5 and are graphically represented in Figure 7 as a function of mass % of water.

Figure 7 shows that K_{S}^{E} values are negative for all the mixtures under investigation, and they increase as the length of the molecular chain of the monoalkanoic acid increases. The donor–acceptor interactions between the mixing components play a pivotal role to yield negative K_{S}^{E} values, which are more negative for the lower monoalkanoic acids. However, the branched isomers have lower K_{S}^{E} values than their terminal counter parts, as they can fit well into the structure of the acids and water. Similar results were reported by some authors [35,39,40] previously.

4. Conclusion

In summary, monoalkanoic acids containing up to three carbon atoms mix with water and monoalkanol mixture in any proportion, but the synergic interactions tend to decrease with the increase of C atoms in the chain. The monoalkanols with the hydroxyl group positioned at the second carbon atom accept more water and acids than those with the terminal hydroxyl group and their I_{S}, values are, therefore, considerably higher.

Table 5. Speeds of sound (u), isentropic compressibilities (K_S) and deviation in isentropic compressibilities (K_S^E) of ternary mixtures for various compositions of (A) + (B) + (C) at 298.15 K.

Mass % of H_2O	u ($m\,s^{-1}$)	$K_S \times 10^{12}$ (Pa^{-1})	$K_S^E \times 10^{12}$ (Pa^{-1})	u ($m\,s^{-1}$)	$K_S \times 10^{12}$ (Pa^{-1})	$K_S^E \times 10^{12}$ (Pa^{-1})
	HCOOH + 1-PrOH (w/w = 1 : 1)			HCOOH + 2-PrOH (w/w = 1 : 1)		
0	1141.5	785.5	2.5	1112.0	837.5	2.2
10	1205.7	692.3	0.8	1179.1	731.6	0.5
20	1270.5	617.4	−1.2	1247.2	646.4	−1.5
30	1332.1	559.3	−2.8	1309.6	582.4	−3.0
40	1384.1	517.6	−3.7	1366.0	534.1	−3.9
50	1425.5	489.2	−3.9	1410.6	501.1	−4.1
60	1457.5	469.1	−3.7	1447.0	477.0	−3.9
70	1475.3	458.8	−3.0	1471.5	461.9	−3.3
80	1484.5	454.0	−1.9	1485.3	453.9	−2.3
90	1491.8	450.2	−0.9	1492.8	449.8	−1.1
100	1497.0	447.5	0.0	1497.0	447.5	0.0
	CH_3COOH + 1-PrOH (w/w = 1 : 1)			CH_3COOH + 2-PrOH (w/w = 1 : 1)		
0	1147.4	832.9	3.0	1114.0	893.4	2.7
10	1221.8	719.1	1.2	1191.1	763.7	1.0
20	1291.5	634.2	−0.7	1265.6	665.6	−1.0
30	1356.1	569.6	−2.4	1334.1	592.7	−2.7
40	1409.1	523.9	−3.4	1390.1	541.3	−3.6
50	1447.5	493.8	−3.6	1433.0	506.2	−3.8
60	1472.6	474.2	−3.3	1463.2	482.0	−3.5
70	1484.2	464.2	−2.4	1478.3	469.3	−2.6
80	1490.0	458.2	−1.4	1488.0	460.4	−1.6
90	1493.0	453.3	−0.6	1493.0	454.1	−0.7
100	1497.0	447.5	0.0	1497.0	447.5	0.0
	CH_3CH_2COOH + 1-PrOH (w/w = 1 : 1)			CH_3CH_2COOH + 2-PrOH (w/w = 1 : 1)		
0	1162.0	838.0	3.5	1124.0	905.4	3.2
10	1242.1	717.0	1.7	1208.8	763.8	1.4
20	1313.3	630.6	−0.2	1284.2	664.4	−0.5
30	1376.1	567.0	−1.9	1352.4	590.7	−2.2
40	1427.1	521.7	−2.9	1408.0	538.9	−3.2
50	1461.0	493.1	−3.0	1446.7	505.3	−3.3
60	1478.6	476.9	−2.5	1469.0	485.0	−2.8
70	1487.3	467.5	−1.7	1481.5	472.5	−1.9
80	1491.0	460.9	−0.9	1486.2	464.7	−1.0
90	1493.0	455.0	−0.3	1493.2	455.7	−0.4
100	1497.0	447.5	0.0	1497.0	447.5	0.0

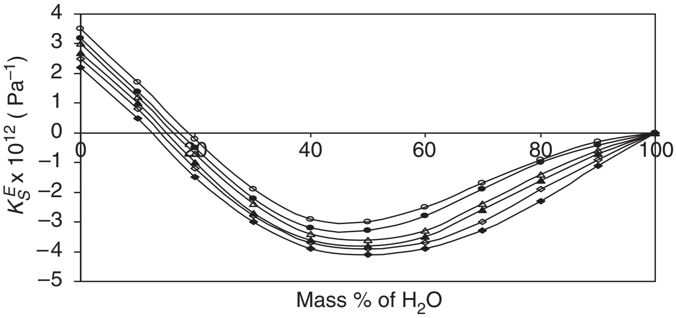


Figure 7. Deviation in isentropic compressibility (K_S^E) of: (◇), water (A) + propanol (B) + formic acid (C); (◆), water (A) + 2-propanol (B) + formic acid (C); (Δ), water (A) + propanol (B) + acetic acid (C); (▲), water (A) + 2-propanol (B) + acetic acid (C); (○), water (A) + propanol (B) + propionic acid (C); (●), water (A) + 2-propanol (B) + propionic acid (C) mixtures with mass % of water (A) at 298.15 K.

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