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MOLECULAR INTERACTIONS WITH REFERENCE TO MANIFESTATION OF SOLVATION EFFECTS IN BINARY MIXTURES OF ETHYL ACETOACETATE WITH SOME METHANE DERIVATIVES BY PHYSICOCHEMICAL TECHNIQUES

Mahendra Nath Roy*, Lovely Sarkar and Rajani Dewan

Department of Chemistry, North Bengal University, Darjeeling 734013, India

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ABSTRACT. Density, ρ, viscosity, η, speed of sound, u, and refractive index, n_D, were measured for the binary systems of ethyl acetoacetate with dichloromethane, chloroform, carbon tetrachloride, nitromethane, methyl acetate, acetonitrile and acetic acid at 298.15 K over the entire composition range. From the experimental results, the excess molar volume, V^E and the deviation in viscosity, $\Delta\eta$, were calculated. Isentropic compressibility, k_S^E, and deviation in molar refractive index, ΔR, were also calculated. These results were fitted to Redlich-Kister polynomial equation. The density and viscosity data were analyzed by some semi-empirical viscosity models, and the results have been discussed in terms of molecular interactions and structural effects. The excess properties were found to be either negative or positive depending on the molecular interactions and the nature of liquid mixtures. To explore the nature of the interactions, various thermodynamic parameters (e.g., intermolecular free length, specific acoustic impedance, etc.) have also been derived from the density and ultrasonic speed data.

KEY WORDS: Density, Viscosity, Speed of sound, Isentropic compressibility, Molar refractive index, Ethyl acetoacetate

INTRODUCTION

The mixing of different solvents gives rise to solutions that generally do not behave ideally. This deviation from ideality is expressed by many thermodynamic variables, particularly by excess properties. Excess thermodynamic properties of solvent mixtures correspond to the difference between the actual property and the property if the system behaves ideally and are useful in the study of molecular interactions and arrangements. In particular, they reflect the interactions that take place between solute-solute, solute-solvent, and solvent-solvent species [1]. This work is a part of our program to provide data for the characterization of the molecular interactions between solvents in binary systems [2, 3]. Having wide usage in flavouring, perfumery, artificial essences, and cosmetics, esters become one of the industrially important classes of liquids. Esters are also used as solvents in pharmaceutical and paint industries and as plasticizers in plastic industries. Among different type of esters, ethyl acetoacetate is commonly used. A fundamental understanding of the mixing behavior of ethyl acetoacetate with common solvents such as dichloromethane, chloroform, carbon tetrachloride, nitromethane, methyl acetate, acetonitrile and acetic acid is therefore important from a technical and engineering viewpoint. The experimental data are used to calculate excess molar volumes, V^E, deviations in viscosity, $\Delta\eta$, and deviations in isentropic compressibility, k_S^E, of the mixtures. Also, from refractive index data, Lorenz-Lorentz molar refractivity, ΔR, has been computed using mole fraction, x_1, of ethyl acetoacetate. Various thermodynamic parameters (e.g., intermolecular free length, specific acoustic impedance, etc.) and their deviations have also been derived from the density and ultrasonic speed data. These results are useful for the interpretation of the nature of interactions that occur between solvents. The work also provides a test of various empirical equations to correlate viscosity and acoustic data of binary mixtures in terms of pure component properties.

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*Corresponding author. E-mail: mahendraroy2002@yahoo.co.in

EXPERIMENTAL

Materials

High-purity spectroscopic and analytical grade samples of ethyl acetoacetate, dichloromethane, chloroform, carbon tetrachloride, nitromethane, methyl acetate, acetonitrile and acetic acid were procured from s.d Fine Chemicals Ltd., Mumbai, India. All the samples were used without further purification because their purities exceeded 99% as tested by gas chromatography (HP 6890 series, Canada) using a flame ionization detector with a packed column. Experimental values of ρ, η, u and n_D of the pure liquids are compared in Table 1 at 298.15 K, and these values agree well with the published results. Mixtures were prepared by mass in specially designed glass stopper bottles, and the properties were measured on the same day. An electronic Mettler balance, with a precision of 0.01 mg was used for mass measurements. The error in mole fraction was around 0.0002.

Apparatus and procedure

The densities were measured with an Ostwald-Sprengel type pycnometer (Borosil Glass Works Limited, Mumbai) having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm, calibrated at 298.15 K with doubly distilled water and benzene. The pycnometer with the test solution was equilibrated in a thermostatic water bath maintained at ± 0.01 K of the desired temperature, removed from the bath, properly dried, and weighed in an electronic balance. The evaporation losses remained insignificant during the time of actual measurements. Averages of triplicate measurements were taken into account. The mixtures were prepared by mixing known volume of pure liquids in air-tight stoppered bottles. The reproducibility in mole fraction was within ± 0.0002. The mass measurements, accurate to ± 0.01 mg, were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The total uncertainty of density was $\pm 3 \times 10^{-4}$ $g.cm^{-3}$, and that of temperature was ± 0.01 K.

The viscosity was measured by means of a suspended Ubbelohde type viscometer (Borosil Glass Works Limited, Mumbai), which was calibrated at 298.15 K with triple-distilled water and purified methanol using density and viscosity values from the literature. The flow times were accurate to 0.1 s, and the uncertainty in the viscosity measurements, based on our work on several pure liquids, was within 0.03 % of the reported value. Details of the methods and techniques of density and viscosity measurements have been described earlier [4-6].

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 details of the methods and techniques have been described earlier [4, 5]. The uncertainty of ultrasonic speed measurements is ± 0.2 $m.s^{-1}$.

The refractive indices of pure liquids and their binary mixture were measured by using a thermostated Abbe refractometer (Atago 3T, Japan). The values of refractive index were obtained using sodium D light. The uncertainty of refractive index measurements was within 0.0001. The thermostat temperature was constant to ± 0.01 K. Water was circulated into the prism of the refractometer by a circulation pump connected to an external thermostated water bath. Calibration was performed by measuring the refractive indices of double-distilled water, toluene, cyclohexane, and carbon tetrachloride at defined temperature. The sample mixtures were directly injected into the prism assembly of the instrument using an airtight hypodermic syringe, and an average of four measurements was taken for each mixture. The reliability of experimental measurements of n_D was ascertained by comparing the experimental data of pure liquids with the corresponding values available in the literature at 298.15 K.

The solutions were pre-thermostated at 298.15 K before the experiments to achieve quick thermal equilibrium. A minimum of three independent readings was taken for each composition, and their average value was considered in all of the calculations.

RESULTS AND DISCUSSION

The physical properties of the pure liquids along with their literature values are recorded in Table 1 [7-16]. Table 2 lists the excess molar volumes, V^E and viscosity deviations, $\Delta\eta$ along with the corresponding mole fractions of ethyl acetoacetate, x_1. The plots of V^E and $\Delta\eta$ against x_1 at 298.15 K are represented in Figures 1 and 2, respectively. The excess molar volumes, V^E, were calculated using the equation [17]:

$$V^E = \sum_{i=1}^{j} x_i M_i (1/\rho - 1/\rho_i) \quad (1)$$

where ρ is the mass density of the mixture and M_i, x_i, and ρ_i, are the molar mass, mole fraction, and density of the i^{th} component in the mixture, respectively.

Table 1. Comparison of density ρ, viscosity η, sound speeds u and refractive index n_D with literature data at 298.15 K.

Pure solvent	$\rho \cdot 10^{-3}/(kg \cdot m^{-3})$		$\eta/(mPa \cdot s)$		$u/(m \cdot s^{-1})$		n_D	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
Ethylacetoacetate	1.021	1020.8 [7]	1.4828	-	1331.6	-	1.419	1.4189 [7]
Dichloromethane	1.3216	1.3161 [8]	0.3803	-	1035.3	-	1.4222	1.4212 [9]
Chloroform	1.4798	1.4760 [10]	0.498	-	985.1	-	1.4360	1.4432 [11]
Carbon tetrachloride	1.5874	1.5844 [12]	0.8258	-	917.7	-	1.4578	1.4574 [12]
Nitromethane	1.1298	1.13042 [13]	0.6172	-	1317	1317.4 [13]	1.3929	-
Methylacetate	0.9273	0.92698 [14]	0.368	0.367 [14]	1162.3	1151 [14]	1.3611	1.3586 [15]
Acetonitrile	0.7772	0.7771 [16]	0.3435	0.390 [16]	1282.6	1288 [16]	1.3419	1.3407 [16]
Acetic acid	1.0431	1.04365 [14]	1.1296	1.115 [14]	1132.5	1132 [14]	1.3700	-

A persual of Table 2 shows that the values of V^E vary for the binary systems with ethyl acetoacetate in the following order:

> methyl acetate > carbon tetrachloride > dichloromethane > nitromethane > chloroform > acetic acid > acetonitrile

The largest deviations in V^E are in the range $x_1 = 0.45$-0.6 (Figure 1). The positive values of excess molar volume, V^E for the system ethyl acetoacetate + methyl acetate may be attributed to the dispersion type interactions due to repulsion among the electrons on oxygens. Carbon tetrachloride, dichloromethane and nitromethane interact very weakly with ethyl acetoacetate resulting in positive values of excess molar volume, V^E. A similar result for the system ethyl acetoacetate + ethyl acetate was reported earlier [18]. On the contrary the ethyl acetoacetate + chloroform, acetic acid and acetonitrile systems behave rather in a opposite manner. This implies dominance of specific interaction [19] most probably through intermolecular hydrogen bonding between the component liquids, dipole-dipole or dipole-induced dipole interaction [20, 21] and also the interstitial accommodation of the mixing components because of the difference in molar volumes [22].

Table 2. Values of excess molar volume, V^E and viscosity deviation, $\Delta\eta$.

x_1	$V^E \cdot 10^6$/m^{3}mol^{-1}	$\Delta\eta$/(mPa·s)	x_1	$V^E \cdot 10^6$/m^{3}mol^{-1}	$\Delta\eta$/(mPa·s)
Ethylacetoacetate + dichloromethane			Ethylacetoacetate + chloroform		
0.0000	0.0000	0.000	0.0000	0.0000	0.000
0.0676	0.0380	0.010	0.0925	-0.1040	0.049
0.1403	0.0760	0.018	0.1865	-0.1900	0.092
0.2186	0.1240	0.025	0.2822	-0.2720	0.122
0.3032	0.1450	0.034	0.3795	-0.3030	0.150
0.3949	0.1720	0.041	0.4784	-0.3030	0.168
0.4947	0.1770	0.047	0.5791	-0.2620	0.171
0.6036	0.1560	0.046	0.6816	-0.1900	0.156
0.7230	0.1090	0.034	0.7858	-0.1180	0.117
0.8545	0.0530	0.016	0.8920	-0.0520	0.068
1.0000	0.0000	0.000	1.0000	0.0000	0.000
Ethylacetoacetate + carbontetrachloride			Ethylacetoacetate + nitromethane		
0.0000	0.0000	0.000	0.0000	0.0000	0.000
0.1161	0.1780	0.007	0.0495	0.0200	0.010
0.2281	0.3180	0.015	0.1050	0.0570	0.024
0.3362	0.4450	0.021	0.1674	0.0790	0.039
0.4407	0.5150	0.025	0.2382	0.0930	0.052
0.5417	0.5140	0.027	0.3193	0.1050	0.065
0.6394	0.4090	0.023	0.4130	0.0960	0.075
0.7339	0.3020	0.016	0.5225	0.0950	0.081
0.8254	0.1850	0.009	0.6523	0.0640	0.073
0.9141	0.0790	0.005	0.8085	0.0470	0.046
1.0000	0.0000	0.000	1.0000	0.0000	0.000
Ethylacetoacetate + methylacetate			Ethylacetoacetate + acetonitrile		
0.0000	0.0000	0.000	0.0000	0.0000	0.000
0.0595	0.2210	-0.005	0.0339	-0.0670	0.001
0.1246	0.4330	-0.027	0.0731	-0.1580	-0.006
0.1961	0.6270	-0.044	0.1191	-0.2730	-0.012
0.2751	0.7830	-0.069	0.1737	-0.3760	-0.020
0.3627	0.9380	-0.089	0.2398	-0.5030	-0.027
0.4606	1.0310	-0.104	0.3212	-0.6320	-0.038
0.5705	0.9770	-0.113	0.4240	-0.7900	-0.047
0.6948	0.7700	-0.109	0.5579	-0.8640	-0.055
0.8367	0.4020	-0.080	0.7395	-0.7000	-0.045
1.0000	0.0000	0.000	1.0000	0.0000	0.000
Ethylacetoacetate + acetic acid					
0.0000	0.0000	0.000			
0.0488	-0.0790	0.045			
0.1034	-0.1550	0.079			
0.1651	-0.2410	0.119			
0.2353	-0.3180	0.155			
0.3157	-0.3810	0.191			
0.4090	-0.4550	0.220			
0.5185	-0.5060	0.241			
0.6486	-0.4650	0.235			
0.8059	-0.2920	0.167			
1.0000	0.0000	0.000			

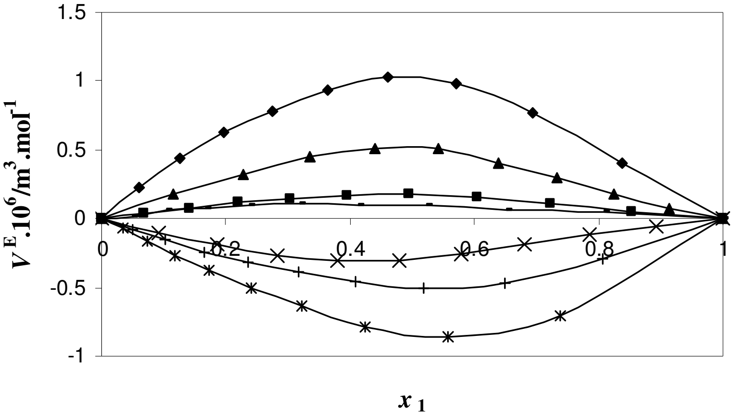

Figure 1. Excess molar volumes (V^E) for binary mixtures of ethyl acetoacetate (1) with dichloromethane (■), chloroform (×), carbon tetrachloride (▲), nitromethane (-), methyl acetate (♦), acetonitrile (✱) and acetic acid (+).

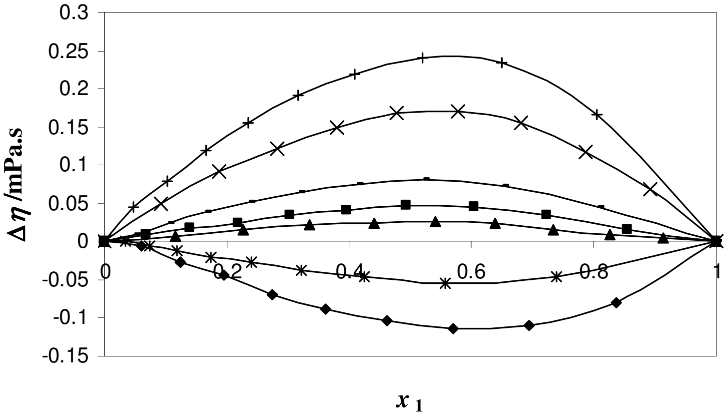

Figure 2. Viscosity deviations ($\Delta\eta$) for binary mixtures of ethyl acetoacetate (1) with dichloromethane (■), chloroform (×), carbon tetrachloride (▲), nitromethane (-), methyl acetate (♦), acetonitrile (✱) and acetic acid (+).

The deviation in viscosities, $\Delta\eta$ can be computed using the equation [23, 24]:

$$\Delta\eta = \eta - \sum_{i=1}^{j} (x_i\eta_i) \tag{2}$$

where η is the dynamic viscosity of the mixture and x_i and η_i are the mole fraction and viscosity of the i^{th} component in the mixture, respectively.

As far as $\Delta\eta$ values are concerned, the experimental binary mixtures exhibit positive as well as negative values over the entire composition range at the experimental temperature. The maxima and minima of the curves lie within mole fraction x_1 = 0.45-0.65. According to Fort and

Moore [17] excess viscosities are negative in mixtures of components having unequal size and in which dispersion forces are present. The positive values of $\Delta\eta$ increase for the seven systems with ethyl acetoacetate are in the following sequence:

methyl acetate < acetonitrile < carbon tetrachloride < dichloromethane < nitromethane < chloroform <acetic acid

The positive $\Delta\eta$ values indicate specific interaction and its negative values indicate dominance of disruption forces. Thus the order of $\Delta\eta$ values (Figure 2) supports our earlier results obtained from V^E values.

Isentropic compressibilities, k_S, the deviations in isentropic compressibilities, k_S^E, deviations in intermolecular, free length, ΔL_f and deviations in specific acoustic impedance, ΔZ, are calculated from the experimental densities, ρ, speeds of sound, u, intermolecular free length, L_f, and specific acoustic impedance, Z of the mixture using the required equations [25-27].

Experimental values of u, k_S, k_S^E, ΔL_f, and ΔZ are listed in Table 3, and the plots of k_S^E, ΔL_f, and ΔZ against x_1 are shown in Figures 3 to 5. For the investigated binary mixtures, the deviations in isentropic compressibility are just parallel to that of V^E. The composition dependence of k_S^E for the investigated binary mixtures is shown in Figure 3; it shows that k_S^E values for the binary systems with ethyl acetoacetate decrease in the following order:

methyl acetate > carbontetrachloride > dichloromethane > nitromethane > chloroform > acetic acid > acetonitrile.

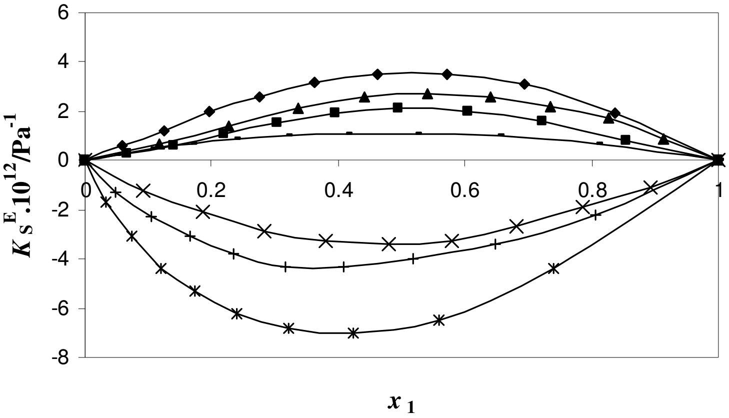

Figure 3. Deviations in isentropic compressibility (k_S^E) for binary mixtures of ethyl acetoacetate (1) with dichloromethane (■), chloroform (×), carbon tetrachloride (▲), nitromethane (-), methyl acetate (♦), acetonitrile (✳) and acetic acid (+).

These results can be explained in terms of molecular interactions and structural effects. Figures 4 and 5 illustrate that ΔL_f values are opposite to ΔZ. Positive and negative deviations in these functions from linear dependence on composition of the mixtures indicate the extent of association or dissociation between the mixing components [28]. The observed values of k_S^E and ΔL_f can be qualitatively explained by considering the following factors: (i) the mutual disruption of associates present in pure liquids, (ii) dipole-induced interaction between the mixing liquids, and (iii) interstitial accommodation [29] of one component into another. Thus the graded behaviors of these functions support the results obtained earlier.

Table 3. Values of ultrasonic speeds u, deviations in isentropic compressibility k_S^E, deviations in intermolecular free length (ΔL_f), and deviations in specific acoustic impedance (ΔZ) for binary mixtures at 298.15 K.

x_1	u/(m.s^{-1})	$k_S^E\cdot10^{12}$/Pa^{-1}	ΔL_f/Å	ΔZ/kg.m^2·s^{-1}	x_1	u/(m.s^{-1})	$k_S^E\cdot10^{12}$/Pa^{-1}	ΔL_f/Å	ΔZ/kg·m^2·s^{-1}
Ethylacetoacetate + dichloromethane					Ethylacetoacetate + chloroform				
0.0000	1035.3	0.0	0.0000	0.0000	0.0000	985.1	0.0	0.0000	0.0000
0.0676	1056.0	0.3	0.0015	-12.7111	0.0925	1025.5	-1.2	0.0046	5.3877
0.1403	1078.0	0.6	0.0027	-22.9827	0.1865	1064.5	-2.1	0.0079	9.0260
0.2186	1099.0	1.1	0.0048	-33.9252	0.2822	1104.5	-2.9	0.0111	14.4225
0.3032	1121.0	1.5	0.0067	-42.5015	0.3795	1142.5	-3.3	0.0127	17.0045
0.3949	1144.0	1.9	0.0086	-49.4499	0.4784	1179.5	-3.4	0.0135	18.6577
0.4947	1171.0	2.1	0.0093	-51.1459	0.5791	1214.7	-3.3	0.0130	18.3646
0.6036	1201.0	2.0	0.0093	-48.9938	0.6816	1246.2	-2.7	0.0108	14.3884
0.7230	1238.0	1.6	0.0074	-39.0438	0.7858	1275.9	-1.9	0.0078	9.6250
0.8545	1282.0	0.8	0.0039	-22.0355	0.8920	1304.8	-1.1	0.0043	5.2215
1.0000	1331.6	0.0	0.0000	0.0000	1.0000	1331.6	0.0	0.0000	0.0000
Ethylacetoacetate + carbon tetrachloride					Ethylacetoacetate + nitromethane				
0.0000	917.7	0.0	0.0000	0.0000	0.0000	1317.0	0.0	0.0000	0.0000
0.1161	953.4	0.7	0.0034	-14.1335	0.0495	1318.5	0.2	0.0011	-8.1683
0.2281	989.5	1.4	0.0063	-25.0445	0.1050	1319.8	0.5	0.0022	-15.8238
0.3362	1024.4	2.1	0.0095	-35.7114	0.1674	1320.4	0.7	0.0033	-22.5983
0.4407	1060.0	2.6	0.0119	-43.2380	0.2382	1321.8	0.9	0.0039	-26.9142
0.5417	1099.5	2.7	0.0122	-43.9161	0.3193	1322.0	1.0	0.0047	-30.8279
0.6394	1139.4	2.6	0.0121	-42.3719	0.4130	1322.9	1.1	0.0050	-31.7248
0.7339	1183.1	2.2	0.0103	-36.1015	0.5225	1323.4	1.1	0.0051	-30.8999
0.8254	1228.5	1.7	0.0081	-27.8866	0.6523	1324.5	1.0	0.0046	-26.1930
0.9141	1279.0	0.9	0.0042	-14.6030	0.8085	1326.8	0.7	0.0031	-16.8819
1.0000	1331.6	0.0	0.0000	0.0000	1.0000	1331.6	0.0	0.0000	0.0000
Ethylacetoacetate + methyl acetate					Ethylacetoacetate + acetonitrile				
0.0000	1162.3	0.0	0.0000	0.0000	0.0000	1282.6	0.0	0.0000	0.0000
0.0595	1165.1	0.6	0.0025	-7.0616	0.0339	1287.2	-1.7	-0.0062	17.0227
0.1246	1168.0	1.2	0.0055	-15.1055	0.0731	1290.2	-3.1	-0.0113	32.5476
0.1961	1171.4	2.0	0.0086	-23.8561	0.1191	1293.7	-4.4	-0.0160	47.8348
0.2751	1177.0	2.6	0.0114	-31.7498	0.1737	1296.1	-5.3	-0.0195	60.2472
0.3627	1184.0	3.2	0.0142	-40.2780	0.2398	1300.4	-6.2	-0.0227	72.1069
0.4606	1196.0	3.5	0.0156	-45.6670	0.3212	1306.8	-6.8	-0.0253	81.9853
0.5705	1212.0	3.5	0.0162	-48.3628	0.4240	1314.5	-7.0	-0.0265	87.6259
0.6948	1236.0	3.1	0.0146	-44.9859	0.5579	1323.2	-6.5	-0.0248	83.7725
0.8367	1274.0	1.9	0.0093	-30.1245	0.7395	1329.4	-4.4	-0.0172	59.5406
1.0000	1331.6	0.0	0.0000	0.0000	1.0000	1331.6	0.0	0.0000	0.0000
Ethylacetoacetate + acetic acid									
0.0000	1132.5	0.0	0.0000	0.0000					
0.0488	1150.1	-1.3	-0.0045	8.6245					
0.1034	1168.0	-2.3	-0.0084	16.2624					
0.1651	1185.4	-3.1	-0.0113	22.0754					
0.2353	1204.5	-3.8	-0.0139	27.7398					
0.3157	1224.4	-4.3	-0.0157	31.9949					
0.4090	1243.5	-4.3	-0.0160	33.0547					
0.5185	1263.8	-4.0	-0.0151	31.8966					
0.6486	1286.5	-3.4	-0.0130	28.1691					
0.8059	1309.8	-2.2	-0.0084	18.6277					
1.0000	1331.6	0.0	0.0000	0.0000					

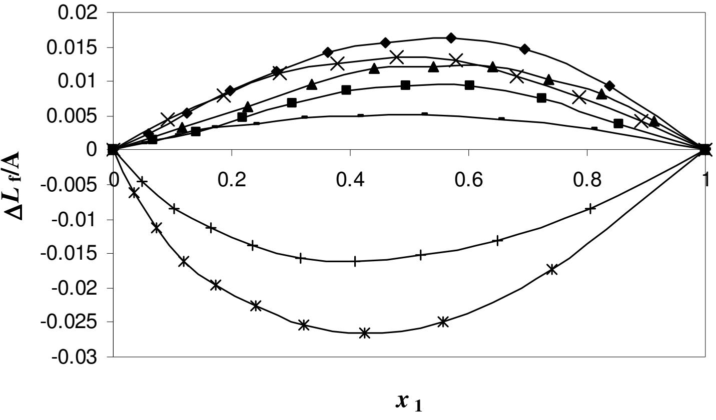

Figure 4. Deviations in intermolecular free length (ΔL_f) for binary mixtures of ethyl acetoacetate (1) with dichloromethane (■), chloroform (×), carbon tetrachloride (▲), nitromethane (-), methyl acetate (♦), acetonitrile (✳) and acetic acid (+).

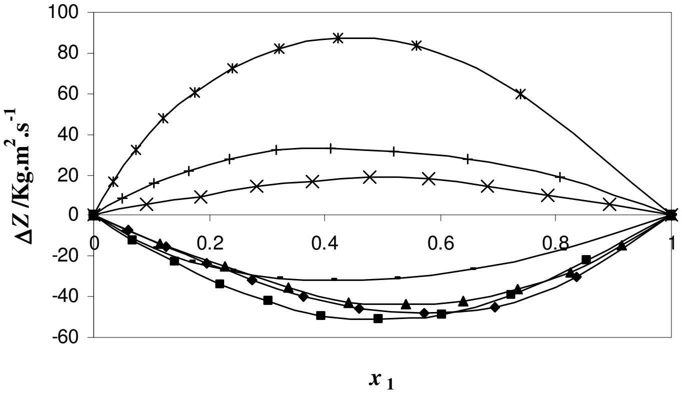

Figure 5. Deviations in specific acoustic impedance (ΔZ) for binary mixtures of ethyl acetoacetate (1) with dichloromethane (■), chloroform (×), carbon tetrachloride (▲), nitromethane (-), methyl acetate (♦), acetonitrile (✳) and acetic acid (+).

Table 4 represents the experimental refractive index, molar refractivity by Lorentz-Lorenz Equation and deviation in molar refractivity at 298.15 K. The molar refractions, R, which were calculated using the Lorentz-Lorenz equation [30]

$$R = (n_D^2 - 1/n_D^2 + 2)V \tag{3}$$

where n_D and V being the refractive index and the molar volume, respectively; and ΔR the molar refraction changes of mixing, which were obtained from the following equation.

$$\Delta R = R - \sum_{i=1}^{j} (x_i R_i) \tag{4}$$

where R is the molar refraction of the mixture and x_i and R_i are the mole fraction and molar refraction of the i^{th} component in the mixture, respectively. The dependence of molar refraction, ΔR on mole fraction, x_1, of ethyl acetoacetate at 298.15 K is displayed in Figure 6. It is observed that, for all the mixtures ΔR contains both positive and negative values. It may be attributed to the electronic perturbation of the individual molecules during mixing and, therefore, depends on the nature of the mixing molecules and only on the wavelength of the light used for measurement [31]. The positive ΔR values vary in the order:

> methyl acetate < carbon tetrachloride < dichloromethane < nitromethane < chloroform < acetic acid < acetonitrile.

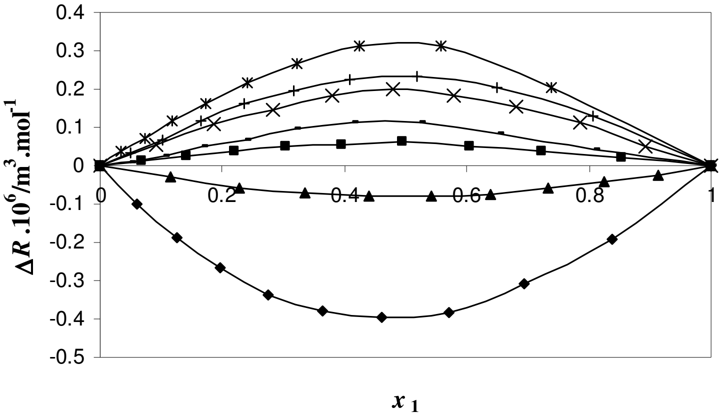

Figure 6. Deviations in molar refractive index (ΔR) for binary mixtures of ethyl acetoacetate (1) with dichloromethane (■), chloroform (×), carbon tetrachloride (▲), nitromethane (-), methyl acetate (♦), acetonitrile (✳) and acetic acid (+).

For each mixture, the mixing functions V^E, $\Delta\eta$, K_S^E, ΔL_f, ΔZ and ΔR were fitted to a Redlich-Kister polynomial regression [32] of the type

$$Y^E_{ij} = x_i x_j \sum_{k=1}^{m} A_k (x_i - x_j)^k \qquad (5)$$

where Y^E_{ij} refers to an excess property (V^E, $\Delta\eta$, K_S^E, ΔL_f, ΔZ, ΔR) for each $i - j$ binary pair, and x_i is the mole fraction of ith component, and A_k represents the coefficients.

The values of coefficients A_k of equation (5) and the corresponding standard deviations, σ obtained by the method of least squares with equal weights assigned to each point are calculated. The standard deviations (σ) are defined as:

$$\sigma = [(Y^E_{exp} - Y^E_{cal})^2 / (n-m)]^{1/2} \qquad (6)$$

where n represents the number of measurements and m the number of coefficients. The values of coefficients (A_k) is determined by a multiple–regression analysis based on the least square method and summarized along with the standard deviations between the experimental and fitted values of, V^E, $\Delta\eta$, K_S^E, ΔL_f, ΔZ, ΔR are presented in Table 5. Finally, it can be concluded that the expressions used for interpolating the experimental data measured in this work gave good results, as can be seen by inspecting the σ values obtained.

Table 4. Experimental and calculated values of refractive index, n_D, and deviation in molar refraction ΔR of binary mixtures at 298.15 K.

x_1	n_D	ΔR x 10^6/m^3 mol^{-1}	x_1	n_D	ΔR x 10^6/m^3 mol^{-1}
Ethylacetoacetate + dichloromethane			Ethylacetoacetate + chloroform		
0.0000	1.4222	0.0000	0.0000	1.436	0.0000
0.0676	1.4219	0.0133	0.0925	1.4355	0.0559
0.1403	1.4216	0.0263	0.1865	1.4348	0.1066
0.2186	1.4212	0.0374	0.2822	1.4339	0.1473
0.3032	1.421	0.0492	0.3795	1.4327	0.1835
0.3949	1.4206	0.0532	0.4784	1.4311	0.2019
0.4947	1.4204	0.0607	0.5791	1.4288	0.1854
0.6036	1.4200	0.0507	0.6816	1.4263	0.155
0.723	1.4197	0.0383	0.7858	1.4238	0.1131
0.8545	1.4194	0.0225	0.892	1.4212	0.0513
1.0000	1.4190	0.0000	1.0000	1.4190	0.0000
Ethylacetoacetate + carbontetrachloride			Ethylacetoacetate + nitromethane		
0.0000	1.4578	0.0000	0.0000	1.3929	0.0000
0.1161	1.4505	-0.0308	0.0495	1.3958	0.0070
0.2281	1.4442	-0.0572	0.105	1.3989	0.0264
0.3362	1.4388	-0.0701	0.1674	1.4021	0.0495
0.4407	1.4342	-0.0802	0.2382	1.4051	0.0679
0.5417	1.4305	-0.0785	0.3193	1.4082	0.0939
0.6394	1.4276	-0.0739	0.413	1.4111	0.1121
0.7339	1.4251	-0.0603	0.5225	1.4135	0.1137
0.8254	1.4229	-0.0436	0.6523	1.4154	0.0833
0.9141	1.4209	-0.0232	0.8085	1.4171	0.0419
1.0000	1.4190	0.0000	1.0000	1.4190	0.0000
Ethylacetoacetate + methylacetate			Ethylacetoacetate + acetonitrile		
0.0000	1.3611	0.0000	0.0000	1.3419	0.0000
0.0595	1.3630	-0.1014	0.0339	1.3494	0.0355
0.1246	1.3656	-0.1870	0.0731	1.3573	0.0729
0.1961	1.3687	-0.2672	0.1191	1.3657	0.1154
0.2751	1.3725	-0.336	0.1737	1.3743	0.1622
0.3627	1.3771	-0.3775	0.2398	1.3834	0.216
0.4606	1.3826	-0.3978	0.3212	1.3925	0.2646
0.5705	1.3895	-0.3834	0.424	1.4019	0.3132
0.6948	1.3981	-0.3096	0.5579	1.4100	0.3127
0.8367	1.408	-0.1919	0.7395	1.4156	0.2062
1.0000	1.419	0.0000	1.0000	1.4190	0.0000
Ethylacetoacetate + acetic acid					
0.0000	1.3700	0.0000			
0.0488	1.3765	0.0342			
0.1034	1.3828	0.0681			
0.1651	1.3894	0.1168			
0.2353	1.3956	0.1607			
0.3157	1.4013	0.1956			
0.409	1.4068	0.2264			
0.5185	1.4115	0.2318			
0.6486	1.4151	0.2041			
0.8059	1.4175	0.1305			
1.0000	1.4190	0.0000			

Table 5. Redlich-Kister coefficients A_k and standard deviations σ for the binary mixtures.

Excess property	A_0	A_1	A_2	A_3	A_4	σ
Ethylacetoacetate + dichloromethane						
V^E x 10^6 / (m^3mol^{-1})	0.6977	-0.1688	-0.3257			0.0039
$\Delta\eta$ / (mPa.s)	0.1882	0.0388	-0.1411	-0.1018	0.0803	0.0009
k_S^E x 10^{12} / (Pa^{-1})	8.3903	1.3339	-4.9019	-1.1154		0.0294
ΔR x 10^6 / (m^3mol^{-1})	0.2276	-0.0331	-0.0690			0.0021
ΔL_f / Å	0.0378	0.0062	-0.0192			0.0002
ΔZ / $kg \cdot m^2 \cdot s^{-1}$	-206.1949	1.1140	40.3622	23.7161		0.4708
Ethylacetoacetate + chloroform						
V^E x 10^6 / (m^3mol^{-1})	-1.1876	0.6416	0.7055	-0.3396	-0.3519	0.0041
$\Delta\eta$ / (mPa.s)	0.6767	0.1454	-0.0686	-0.1446		0.0021
k_S^E x 10^{12}/ (Pa^{-1})	-13.6407	2.1562	2.1469			0.0593
ΔR x 10^6/ (m^3mol^{-1})	0.7853	-0.0551	-0.3069			0.0038
ΔL_f/ Å	-0.0537	0.0058	0.0096			0.0002
ΔZ / $kg \cdot m^2 \cdot s^{-1}$	74.3049	-5.1560	-34.4113			0.6037
Ethylacetoacetate + carbon tetrachloride						
V^E x 10^6 / (m^3mol^{-1})	2.0336	-0.3775	-1.2170			0.0139
$\Delta\eta$ / (mPa.s)	0.1042	-0.0046	-0.0756			0.0011
k_S^E x 10^{12}/ (Pa^{-1})	10.7064	3.0685	-2.8537			0.0423
ΔR x 10^6/ (m^3mol^{-1})	-0.3211	0.0076	0.0309			0.0012
ΔL_f/ Å	0.0488	0.0154	-0.0100			0.0003
ΔZ / $kg \cdot m^2 \cdot s^{-1}$	-175.7724	-37.5399	26.7914			0.7621
Ethylacetoacetate + nitromethane						
V^E x 10^6 / (m^3mol^{-1})	0.3658	-0.2896	0.1431	0.2418		0.0057
$\Delta\eta$ / (mPa.s)	0.3190	0.0202	-0.0850			0.0009
k_S^E x 10^{12}/ (Pa^{-1})	4.4471	-0.3546	0.7162			0.0248
ΔR x 10^6/ (m^3mol^{-1})	0.4518	-0.0849	-0.3876			0.0033
ΔL_f/ Å	0.0208	-0.0023				0.0001
ΔZ / $kg \cdot m^2 \cdot s^{-1}$	-124.7042	37.7423	-21.6414			0.2729
Ethylacetoacetate + methylacetate						
V^E x 10^6 / (m^3mol^{-1})	4.0965	-0.3689	-1.9771	-0.7811	1.0977	0.0097
$\Delta\eta$ / (mPa.s)	-0.4312	-0.1777	-0.0648	-0.1381	0.1718	0.0021
k_S^E x 10^{12} / (Pa^{-1})	14.3078	1.4510	-2.9081			0.0446
ΔR x 10^6 / (m^3mol^{-1})	-1.5823	0.2385	0.0620			0.0033
ΔL_f/ Å	0.0647	0.0121	-0.0091			0.0002
ΔZ / $kg \cdot m^2 \cdot s^{-1}$	-189.7685	-57.8767	13.8619			0.3351
Ethylacetoacetate + acetonitrile						
V^E x 10^6 / (m^3mol^{-1})	-3.3898	-1.0626	0.7564	0.8072		0.0097
$\Delta\eta$ / (mPa.s)	-0.2104	-0.0772	0.0707			0.0017
k_S^E x 10^{12} / (Pa^{-1})	-27.3834	9.1231	0.8057	6.5558	-4.0858	0.0494
ΔR x 10^6 / (m^3mol^{-1})	1.2839	-0.0260	-0.6748	-0.4276		0.0018
ΔL_f/ Å	-0.1042	0.0307	0.0094	0.0143	-0.0678	0.0001
ΔZ / $kg \cdot m^2 \cdot s^{-1}$	348.1667	-70.6471	-16.1459	-59.8619	95.3339	0.3146
Ethylacetoacetate + acetic acid						
V^E x 10^6 / (m^3mol^{-1})	-1.9880	-0.4359	0.5301	0.8299		0.0064
$\Delta\eta$ / (mPa.s)	0.9580	0.2553	0.0183	-0.2208		0.0016
k_S^E x 10^{12} / (Pa^{-1})	-16.4179	6.7081	-4.7127			0.0592
ΔR x 10^6 / (m^3mol^{-1})	0.9309	-0.0655	-0.2292	0.1317		0.0025
ΔL_f/ Å	-0.0617	0.0220	-0.0156			0.0002
ΔZ / $kg \cdot m^2 \cdot s^{-1}$	130.1334	-33.0719	25.7843			0.3620

CONCLUSIONS

It is realized that these binary data will have some relevance in industries because the esters are known to act as plasticizing agents for many industrial plastics. Furthermore, the structural changes and the appearance of dispersion forces and further hetero associations by mixing with ethyl acetoacetate make these systems particularly interesting. The interaction parameters deduced can be used to further predict these properties in multi-component mixtures.

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