

Scientific paper

# Densities and Viscosities of Alkylethanoates +Cyclohexane, +Benzene, +1,4-dimethylbenzene, and +1,3,5-trimethylbenzene at 308.15 K

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## Abstract

Densities ( $\rho_{12}$ ) and viscosities ( $\eta_{12}$ ) of binary mixtures of alkylethanoates, + cyclohexane, benzene, 1,4-dimethylbenzene and 1,3,5-trimethylbenzene have been measured over the whole mole fractions range at atmospheric pressure and temperature 308.15 K. Deviations of experimental viscosities from the linear mixing rule ( $\Delta\eta$ ) for binary mixtures of the esters and cyclohexane are large and negative.  $\Delta\eta$  values are less and negative for binary mixtures of esters and aromatic hydrocarbons except binary mixtures of n-propylethanoate and benzene which show less positive  $\Delta\eta$  values.  $\Delta\eta$  values for binary mixtures of ethylethanoate + 1,4-dimethylbenzene, +1,3,5-trimethylbenzene and n-propylethanoate +1,4-dimethylbenzene are both less negative and less positive.  $\Delta\eta$  values are fitted into Redlich-Kister polynomial equation and standard deviations,  $\sigma$  of  $\Delta\eta$  for all the binary mixtures are reported. Several viscosity equations are critically analysed. The strengths of molecular interactions are discussed on the basis of Grunberg-Nissan interaction parameters.

**Keywords:** Density, viscosity, binary mixture, esters, hydrocarbons, molecular interactions.

## 1. Introduction

Recently much attentions have been given on the studies of viscosities<sup>1-5</sup> for binary mixtures containing one component as either aliphatic or aromatic esters. Viscosities of binary mixtures of some alkanooates and bromoalkanoates with n-hexane at 303.15 K have been measured and the data have been analyzed<sup>6</sup> in terms of dipole-dipole interaction in alkanooates and intramolecular Br...O interaction in bromoalkanoate. Binary mixtures of several alkylalkanoate with several glycols<sup>7</sup> have been studied at several temperatures employing measurements of viscosities together with other physical properties and qualitative analysis of deviation and excess functions have been made to ascertain the nature and type of bulk state interactions. In wine distillation processes the main components are water and ethanol and several other minor components called as congeners are higher alcohols, aldehydes and esters<sup>8</sup>. Esters are important class of compound used in pharmaceutical aid, artificial fruit essences, manufacturing of artificial

leather and perfumes. Ethylethanoate is also used in protein sequencing. A very few investigations for the binary mixtures of alkanooate with aromatic hydrocarbons<sup>9-11</sup> have been reported either by viscosity or by some other methods. In our laboratory binary mixtures of several polar aliphatic molecules with non-polar aromatic molecules have been studied by viscosities<sup>12-15</sup> measurements.

In view of the several industrial importances of the esters and limited studies on binary mixtures of esters with aromatic hydrocarbon solvents it is intended to perform viscosity measurements on binary mixtures containing aliphatic esters viz. methylethanoate, ethylethanoate and n-propylethanoate and aromatic hydrocarbon solvents viz. benzene, 1,4-dimethylbenzene and 1,3,5-trimethylbenzene at 308.15 K. Binary mixtures of these esters with inert solvent cyclohexane are also studied to have a reference point for assessing the interactions. Moreover, successive alkylated ethanoates and aromatic hydrocarbon solvents are deliberately chosen to have an idea of the effect of substituents on either of the interacting components over molecular interactions. The chosen esters suc-

cessively differ in their dipole moments and the aromatic hydrocarbons also successively differ in their polarisabilities. Thus the present investigation is also intended to throw light on the effects of dipole moments and polarisabilities over such interactions.

## 2. Experimental

All Chemicals in this study methylethanoate (mass fraction purity 0.99), ethylethanoate (mass fraction purity 0.995), n-propylethanoate (mass fraction purity 0.98), benzene (mass fraction purity 99.7), 1,4-dimethylbenzene (mass fraction purity 0.99) and 1,3,5-trimethylbenzene (mass fraction purity 0.98) were obtained from Merck and purified by fractional distillation over one meter long column and collecting only the middle fractions for the study. Cyclohexane (mass fraction purity 0.997) was used without further purification. The purities of the liquids were further verified by density measurements.

Tabela 1:

Compound	Density $\times 10^{-3}$ at 308.15 K	
	experimental ( $\text{kg m}^{-3}$ )	literature ( $\text{kg m}^{-3}$ )
Cyclohexane	0.76477	0.7645 <sup>a</sup>
Benzene	0.86302	0.86300 <sup>b</sup> 0.86290 <sup>c</sup>
1,4-dimethylbenzene	0.84878	0.84791 <sup>d</sup> 0.84787 <sup>e</sup>
1,3,5-trimethylbenzene	0.85447	0.85315 <sup>f</sup>
Methylethanoate	0.91561	0.91522 <sup>g</sup>
Ethylethanoate	0.88252	0.88250 <sup>h</sup>
n-propylethanoate	0.87105	0.8718 <sup>i</sup>

a: Ref.16; b: Ref.17; c: Ref.18; d: Ref.19; e: Ref.20; f: Ref.15; g: Ref.21; h: Ref.7; i: Ref.22.

Binary liquid mixtures of esters and hydrocarbon solvents were prepared by weight covering whole mole fractions range employing a single pan analytical balance (Model K-15 Deluxe, K. Roy Instruments Pvt. Ltd., Varanasi) with an uncertainty of  $\pm 0.00001 \times 10^{-3}$  kg. Liquids were injected into sealed glass vials by means of syringe in order to minimize evaporation losses during sample preparation. Densities of samples were measured by single stem pycnometer within  $\pm 0.00001 \times 10^3$   $\text{kg m}^{-3}$  uncertainty. Times of flow ( $t$ ) with  $\pm 0.01$  Sec uncertainty and dynamic viscosities ( $\eta_{12}$ ) with an uncertainty of  $\pm 0.0001$  mPa.s for liquids and their binary mixtures were measured employing Tuan and Fuoss viscometer as described elsewhere<sup>15</sup>. All measurements were carried out at constant temperature at  $308.15 \pm 0.03$  K employing water thermostat with toluene regulator.

Dynamic viscosities ( $\eta_{12}$ ) of either component liquids or their binary mixtures were determined by equation

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

where  $v$  and  $\rho$  are the kinematic viscosity and density respectively.  $a$  and  $b$  are characteristic constants of viscometer determined by method of least squares using known viscosities of several liquids viz. cyclohexane, benzene, methylbenzene and propanone at experimental temperature. The constants 'a' and 'b' were 0.004320 and 0.331602 respectively.

## 3. Results and Discussion

Experimental values of densities ( $\rho_{12}$ ) and viscosities ( $\eta_{12}$ ) at temperature 308.15 K with mole fractions of non-polar hydrocarbon solvents ( $x_1$ ) for all the binary mixtures studied are recorded in table 3. Deviations of experimental viscosities from the binary mixing rule,  $\Delta\eta$  for the binary mixtures are evaluated from equation

$$\Delta\eta = \eta_{12} - x_1\eta_1 - x_2\eta_2 \quad (2)$$

and also recorded in table 3.  $\eta_1$ ,  $\eta_2$  and  $x_1$ ,  $x_2$  are the viscosities and mole fractions in the mixtures respectively of the components 1 and 2.

Variations of  $\Delta\eta$  values with mole fractions of the hydrocarbon solvents for the binary mixtures of methylethanoate, ethylethanoate and n-propylethanoate with all the four non-polar hydrocarbon solvents are shown in figs. 1, 2 and 3 respectively.

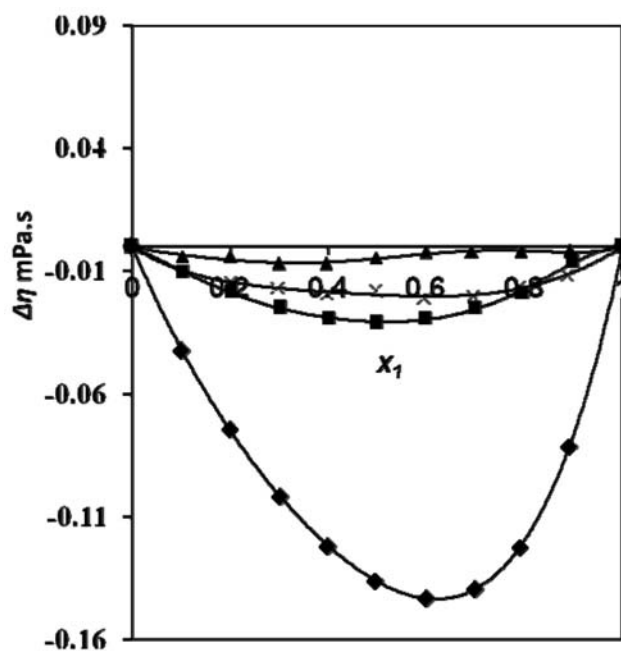
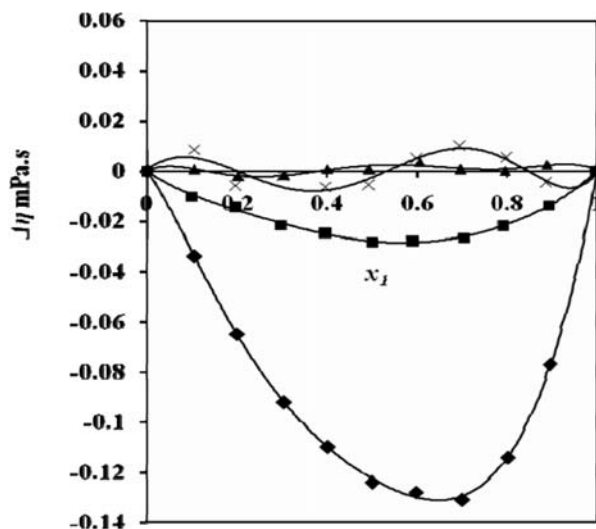
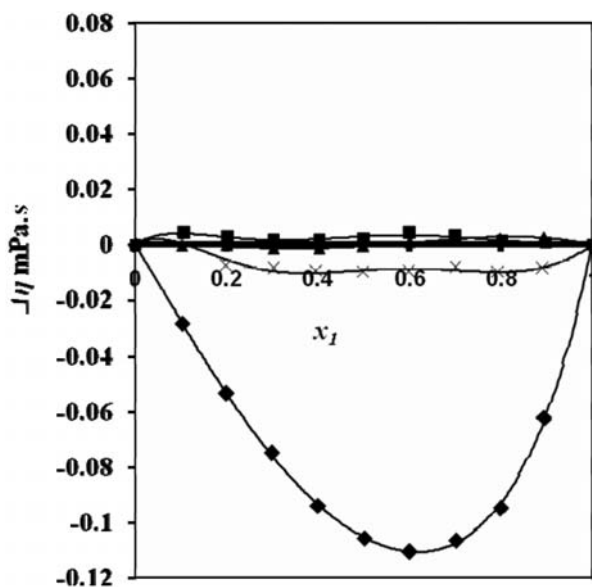


Figure 1: Deviations in viscosities ( $\Delta\eta$ ) of binary mixtures of methylethanoate + hydrocarbons ( $\blacklozenge$ -cyclohexane,  $\blacksquare$ -benzene,  $\blacktriangle$ -1,4-dimethylbenzene,  $\times$ -1,3,5-trimethylbenzene) versus mole fractions of hydrocarbon ( $x_1$ ) at 308.15 K.



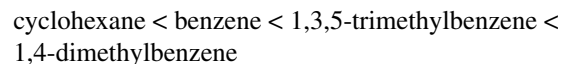
**Figure 2:** Deviations in viscosities ( $\Delta\eta$ ) of binary mixtures of ethylethanoate + hydrocarbons (◆-cyclohexane, ■-benzene, ▲-1,4-dimethylbenzene, x-1,3,5-trimethylbenzene) versus mole fractions of hydrocarbon ( $x_1$ ) at 308.15 K.



**Figure 3:** Deviations in viscosities ( $\Delta\eta$ ) of binary mixtures of n-propylethanoate + hydrocarbons (◆-cyclohexane, ■-benzene, ▲-1,4-dimethylbenzene, x-1,3,5-trimethylbenzene) versus mole fractions of hydrocarbon ( $x_1$ ) at 308.15 K.

$\Delta\eta$  values for binary mixtures of all the esters with cyclohexane are large and negative. It decreases at lower side of the mole fractions of cyclohexane come to a minimum at around 0.6 mole fraction of cyclohexane in the binary mixture and then increases. Similar observations i.e. large and negative  $\Delta\eta$  values are reported for binary mixtures of bromoalkane + cyclohexane<sup>15</sup> at 308.15 K and 2-butanone + cyclohexane<sup>23</sup> at 303.15 K.  $\Delta\eta$  values for binary mixtures of methylethanoate with three aromatic hydrocarbon solvents viz. benzene, 1,4-dimethylbenzene

and 1,3,5-trimethylbenzene are also negative at all composition and follow the order :



In binary mixtures of ethylethanoate with aromatic hydrocarbon solvent, benzene,  $\Delta\eta$  values are negative at all composition. However, for binary mixtures of ethylethanoate with either 1,4-dimethylbenzene or 1,3,5-trimethylbenzene,  $\Delta\eta$  values are both positive and negative, and both types of values are lesser in magnitude for ethylethanoate + 1,4-dimethylbenzene than that for the mixtures of ester + 1,3,5-trimethylbenzene. When n-propylethanoate is taken as a component for binary mixtures of ester + aromatic hydrocarbon solvents,  $\Delta\eta$  values are positive and small at all composition for n-propylethanoate + benzene and negative at all composition except one positive value at lower mole fraction of the hydrocarbon solvents for binary mixtures of n-propylethanoate + 1,3,5-trimethylbenzene,  $\Delta\eta$  values for n-propylethanoate + 1,4-dimethylbenzene binary mixture are vanishingly small in magnitude and negative at lower and positive at higher mole fractions of the hydrocarbon.

The smallest values of  $\Delta\eta$  for the binary mixtures of all the esters + cyclohexane suggest the presence of weakest unlike interactions between the components. The enhanced values of  $\Delta\eta$  in case of the binary mixtures of ester + aromatic hydrocarbon solvents show the presence of strong specific interactions between the components of such mixtures. On the basis of measurements of excess volume and excess Gibb's energy of activation of flow, presence of specific molecular interactions between unlike molecules in binary mixtures of ester + benzene<sup>9</sup> is suggested. It is pointed out that specific interaction in mixtures of esters with benzene may be due to the formation of *n*- $\pi$  complex between the free electrons of the carboxylic group and  $\pi$ -electrons of the aromatic ring. Earp and Glasstone<sup>24</sup> have observed greater values of molar polarization for binary mixtures of ester + benzene than that for mixtures of ester + cyclohexane and suggested the formation of coordinate link where oxygen atom of the ester acts as a donor and benzene as acceptor. Rastogi et al.<sup>25</sup> have suggested that observed excess property is a combination of an interaction and a non-interaction part. Thus,

$$Y^E (\text{observed}) = Y^E (\text{interaction}) + Y^E (\text{size effect})$$

where  $Y^E$  refers to the excess or deviation in the property. The non-interaction part in the form of the size effect can be comparable to the interaction part and may be sufficient to reverse the trend set by the latter. In the present investigation, importance of size effect is evident in binary mixtures of all the esters with 1, 3, 5-trimethylbenzene where  $\Delta\eta$  values are lesser than the binary mixtures of esters with 1,4-dimethylbenzene, although polarisability<sup>26</sup> of

the former hydrocarbon is higher than the latter which requires higher interactions in the former case and subsequently  $\Delta\eta$  values would have been larger for the former case than for the latter.

The values of  $\Delta\eta$  are fitted into second degree Redlich-Kister polynomial of the type

$$\Delta\eta/x_1x_2 = A + B(x_1-x_2) + C(x_1-x_2)^2 \quad (3)$$

where  $x_1, x_2$  are the mole fractions of the hydrocarbons and ester respectively in the binary mixtures and  $A, B$  and  $C$  are the constants of the polynomial. The values of these constants and the standard deviations,  $\sigma$  for all the mixtures studied in present investigation are recorded in table 2.

**Table 2:** Values of constants  $A, B$  and  $C$  of Redlich-Kister equation and standard deviations of deviation in viscosity,  $\sigma$  for different systems at 308.15 K.

System	A	B	C	$\sigma$ m Pa.s
Cyclohexane + Methylmethanoate	-0.4421	-0.3454	-0.3537	$\pm 0.0220$
Benzene + Methylmethanoate	-0.1258	+0.0145	+0.0541	$\pm 0.0015$
1,4-dimethylbenzene+Methylmethanoate	-0.0174	+0.0171	-0.0194	$\pm 0.0013$
1,3,5-trimethylbenzene+Methylmethanoate	-0.0785	-0.0101	-0.0513	$\pm 0.0009$
Cyclohexane + Ethylethanoate	-0.4973	-0.2690	-0.1587	$\pm 0.0032$
Benzene + Ethylethanoate	-0.1106	-0.0260	-0.0077	$\pm 0.0011$
1,4-dimethylbenzene+Ethylethanoate	+0.0002	+0.0130	+0.0146	$\pm 0.0018$
1,3,5-trimethylbenzene+Ethylethanoate	-0.0065	-0.0141	+0.0445	$\pm 0.0082$
Cyclohexane + n-propylethanoate	-0.4211	-0.2113	+0.0985	$\pm 0.0104$
Benzene + n-propylethanoate	+0.0088	-0.0127	+0.0222	$\pm 0.0016$
1,4-dimethylbenzene+n-propylethanoate	-0.0017	+0.0184	+0.0239	$\pm 0.0004$
1,3,5-trimethylbenzene+n-propylethanoate	-0.0426	-0.0395	+0.0011	$\pm 0.0032$

Several viscosity equations are critically analyzed with a view to select a suitable equation for the mixtures undertaken in the present investigation. Grunberg and Nissan<sup>27</sup> equation for viscosities of liquid mixtures is

$$\ln \eta_{12} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d \quad (4)$$

where  $\eta_{12}, \eta_1$  &  $\eta_2$  and  $x_1$  &  $x_2$  are the viscosity of the mixture, viscosities and mole fractions of the components 1 & 2 respectively.  $d$  is the interaction parameter which is proportional to  $W/RT$ ,  $W$  being the interchange energy.  $d$  may be regarded as an approximate measure of the strength of interaction between the components. It has been suggested<sup>28</sup> that variations of  $d$  and  $\Delta\eta$  are similar with strength of interaction at any given composition. Both are negative for systems in which dispersion forces are dominant. They become less negative and then increasingly positive as the strengths of interactions increase.

Values of  $d$  evaluated for all the systems in the present investigation at 308.15 K are recorded in table 3. Perusal of table 3 shows that the  $d$  values are large negative for mixtures of methylmethanoate + cyclohexane, lesser negative for methylmethanoate + benzene, least negative for methylmethanoate + 1,3,5-trimethylbenzene and positive

for methylmethanoate + 1,4-dimethylbenzene. The order of  $d$  values for methylmethanoate + hydrocarbons is similar to that observed for  $\Delta\eta$  values. This is quite in line with the suggestion made by Fort et al.<sup>28</sup> that  $d$  and  $\Delta\eta$  values have similar variation with the strength of interactions. Large negative  $d$  values for methylmethanoate + cyclohexane show the existence of dispersion forces. Higher (lesser negative)  $d$  values for methylmethanoate + benzene suggest the stronger interactions and still higher (least negative) values for methylmethanoate + 1,3,5-trimethylbenzene are due to further stronger interactions between the components of the mixture. The  $d$  values are positive for mixtures of methylmethanoate + 1,4-dimethylbenzene at experimental temperature. This shows that interactions between

components are strongest in this system amongst the studied binary mixtures with methylmethanoate. The lesser  $d$  values for mixture of methylmethanoate + 1,3,5-trimethylbenzene than that for methylmethanoate + 1,4-dimethylbenzene once again show the dominance of size effect over interaction in the former mixture. In binary mixtures of ethylethanoate with cyclohexane,  $d$  values are large negative, lesser negative for ethylethanoate + benzene system and positive for mixtures of ethylethanoate with 1,4-dimethylbenzene or 1,3,5-trimethylbenzene systems. For binary mixtures of n-propylethanoate with several hydrocarbon solvents,  $d$  values are again large negative for mixtures with cyclohexane, positive for mixtures with benzene, and both, positive and negative values for mixtures with 1,4-dimethylbenzene and negative for those with 1,3,5-trimethylbenzene. These variations also follow the trend similar to those of  $\Delta\eta$  values for the systems.

Hind-McLaughlin-Ubbelohde<sup>29</sup> equation for mixture viscosity is

$$\eta_{12} = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1 x_2 H_{12} \quad (5)$$

where  $H_{12}$  is the interaction parameter.  $x_1, x_2$  and  $\eta_1, \eta_2$  are the mole fractions of the components in the mixture and

**Table 3:** Mole fraction ( $x_1$ ), of hydrocarbons, densities ( $\rho_{12}$ ), Viscosities ( $\eta_{12}$ ), deviations in viscosities ( $\Delta\eta$ ), interaction parameters ( $d$ ), ( $H_{12}$ ) and ( $K_{12}$ ), interaction energy ( $w_{vis}$ ) are excess free energies of activation for viscous flow ( $G^{*E}$ ) for binary mixtures of different esters + hydrocarbon solvents at 308.15K.

$x_1$	$\rho_{12} \times 10^3$ kg m <sup>3</sup>	$\eta_{12}$ mPa s	$\Delta\eta$ mPa s	$d$	$H_{12}$ mPa s	$K_{12}$	$w_{vis}$ J mol <sup>-1</sup>	$G^{*E}$ J mol <sup>-1</sup>
Cyclohexane (1) + Methyleneoate (2)								
0.00000	0.91561	0.3470	–	–	–	–	–	–
0.10176	0.88989	0.3470	–0.0423	–0.8758	0.3236	–0.7566	–1938.42	–1.77
0.19971	0.86793	0.3554	–0.0745	–0.8328	0.3217	–0.7153	–1832.54	–2.93
0.30251	0.84792	0.3711	–0.1016	–0.8107	0.3140	–0.6970	–1785.68	–3.77
0.40017	0.83067	0.3913	–0.1219	–0.8114	0.3008	–0.6982	–1788.90	–4.29
0.49683	0.81571	0.4176	–0.1359	–0.8237	0.2831	–0.7117	–1823.41	–4.56
0.60098	0.80211	0.4536	–0.1431	–0.8556	0.2564	–0.7473	–1914.52	–4.59
0.70000	0.79075	0.4986	–0.1393	–0.8987	0.2230	–0.7932	–2032.11	–4.27
0.79112	0.78142	0.5537	–0.1221	–0.9415	0.1854	–0.8370	–2144.31	–3.54
0.89061	0.77293	0.6359	–0.0812	–0.9808	0.1379	–0.8803	–2255.41	–2.20
1.00000	0.76477	0.7626	–	–	–	–	–	–
			$\% \Delta d = \pm 0.0003$	$\% \Delta H = \pm 0.0013$	$\% \Delta K = \pm 0.0001$			
Benzene (1) + Methyleneoate (2)								
0.00000	0.91561	0.3470	–	–	–	–	–	–
0.10333	0.90885	0.3553	–0.0101	–0.2064	0.3818	–0.1911	–489.67	–0.45
0.20217	0.90220	0.3647	–0.0184	–0.2122	0.3793	–0.1936	–495.89	–0.80
0.30174	0.89597	0.3760	–0.0249	–0.2137	0.3773	–0.1942	–497.63	–1.05
0.40155	0.89124	0.3899	–0.0289	–0.2088	0.3764	–0.1941	–497.32	–1.20
0.49845	0.88577	0.4050	–0.0311	–0.2098	0.3742	–0.1939	–496.87	–1.24
0.59729	0.88135	0.4247	–0.0291	–0.1919	0.3759	–0.1789	–458.42	–1.10
0.69852	0.87656	0.4472	–0.0248	–0.1744	0.3776	–0.1624	–415.10	–0.88
0.79661	0.87279	0.4709	–0.0186	–0.1591	0.3791	–0.1531	–392.20	–0.64
0.89755	0.87093	0.5014	–0.0061	–0.0532	0.4034	–0.0852	–218.36	–0.20
1.00000	0.86302	0.5258	–	–	–	–	–	–
			$\% \Delta d = \pm 0.0001$	$\% \Delta H = \pm 0.1975$	$\% \Delta K = \pm 0.0000$			
1,4dimethylbenzene (1) + Methyleneoate (2)								
0.00000	0.91561	0.3470	–	–	–	–	–	–
0.10315	0.90577	0.3628	–0.0041	–0.0118	0.4213	0.0918	235.09	0.22
0.20182	0.89724	0.3818	–0.0041	0.0400	0.4308	0.1403	359.55	0.58
0.30094	0.88904	0.3980	–0.0071	0.0197	0.4268	0.1189	304.62	0.64
0.39561	0.88195	0.4163	–0.0071	0.0298	0.4287	0.1271	325.69	0.78
0.49725	0.87508	0.4385	–0.0045	0.0564	0.4345	0.1512	387.46	0.97
0.60002	0.86957	0.4605	–0.0023	0.0736	0.4387	0.1621	415.29	0.99
0.69291	0.86425	0.4787	–0.0021	0.0712	0.4385	0.1574	403.15	0.86
0.79307	0.85988	0.4981	–0.0020	0.0648	0.4373	0.1415	362.46	0.59
0.89376	0.85537	0.5177	–0.0019	0.0487	0.4335	0.1110	284.44	0.27
1.00000	0.84878	0.5401	–	–	–	–	–	–
			$\% \Delta d = \pm 0.0003\%$	$\Delta H = \pm 0.0001$	$\% \Delta K = \pm 0.0003$			
1, 3,5trimethylbenzene (1) + Methyleneoate (2)								
0.00000	0.91561	0.3470	–	–	–	–	–	–
0.10375	0.90463	0.3631	–0.0097	–0.1146	0.4196	0.0711	182.25	0.17
0.20201	0.89499	0.3829	–0.0145	–0.0675	0.4269	0.1156	296.14	0.48
0.30079	0.88732	0.4053	–0.0168	–0.0368	0.4319	0.1377	352.68	0.74
0.39898	0.88039	0.4274	–0.0192	–0.0325	0.4318	0.1361	348.60	0.84
0.49755	0.87450	0.4529	–0.0184	–0.0138	0.4351	0.1487	380.90	0.95
0.59872	0.86997	0.4756	–0.0209	–0.0385	0.4284	0.1147	293.81	0.71
0.69588	0.86539	0.5008	–0.0200	–0.0493	0.4246	0.0993	254.46	0.54
0.79113	0.86241	0.5284	–0.0162	–0.0511	0.4228	0.0866	221.93	0.37
0.88838	0.85960	0.5573	–0.0116	–0.0798	0.4134	0.0411	105.22	0.10
1.00000	0.85447	0.5968	–	–	–	–	–	–
			$\% \Delta d = \pm 0.0000$	$\% \Delta H = \pm 0.0001$	$\% \Delta K = \pm 0.0004$			

$x_1$	$\rho_{12} \times 10^3$ kg m <sup>3</sup>	$\eta_{12}$ mPa s	$\Delta\eta$ mPa s	$d$	$H_{12}$ mPa s	$K_{12}$	$w_{vis}$ J mol <sup>-1</sup>	$G^{*E}$ J mol <sup>-1</sup>
Cyclohexane (1) + Ethylethanoate (2)								
0.00000	0.88252	0.3950	–	–	–	–	–	–
0.10463	0.86615	0.3993	–0.0341	–0.6164	0.3970	–0.5759	–1475.41	–1.38
0.20008	0.85151	0.4036	–0.0649	–0.6873	0.3759	–0.6422	–1645.40	–2.63
0.30369	0.83660	0.4144	–0.0922	–0.7170	0.3609	–0.6694	–1715.11	–3.63
0.40048	0.82399	0.4321	–0.1100	–0.7223	0.3497	–0.6748	–1728.87	–4.15
0.49957	0.81191	0.4544	–0.1242	–0.7541	0.3303	–0.7061	–1809.09	–4.52
0.59675	0.80098	0.4862	–0.1281	–0.7675	0.3126	–0.7192	–1842.49	–4.43
0.69868	0.78942	0.5208	–0.1310	–0.8700	0.2675	–0.8152	–2088.50	–4.40
0.79949	0.78061	0.5746	–0.1143	–0.9428	0.2223	–0.8911	–2283.05	–3.66
0.89495	0.77284	0.6468	–0.0772	–1.0166	0.1683	–0.9678	–2479.52	–2.33
1.00000	0.76477	0.7626	–	–	–	–	–	–
			$\% \Delta d = \pm 0.0003$	$\% \Delta H = \pm 0.0001$	$\% \Delta K = \pm 0.0000$			
Benzene (1) + Ethylethanoate (2)								
0.00000	0.88252	0.3950	–	–	–	–	–	–
0.10020	0.88116	0.3979	–0.0102	–0.2370	0.4037	–0.2379	–609.45	–0.55
0.19794	0.87827	0.4061	–0.0148	–0.1808	0.4140	–0.1713	–438.80	–0.70
0.29588	0.87606	0.4118	–0.0219	–0.2055	0.4080	–0.1949	–499.38	–1.04
0.39660	0.87417	0.4218	–0.0251	–0.1991	0.4081	–0.1893	–485.07	–1.16
0.50010	0.87183	0.4319	–0.0285	–0.2145	0.4034	–0.2033	–520.82	–1.30
0.59110	0.87029	0.4440	–0.0283	–0.2153	0.4019	–0.2050	–525.27	–1.27
0.70227	0.86811	0.4603	–0.0266	–0.2286	0.3969	–0.2177	–557.83	–1.17
0.79038	0.86624	0.4762	–0.0222	–0.2358	0.3935	–0.2228	–570.72	–0.95
0.89202	0.86459	0.4978	–0.0139	–0.2472	0.3884	–0.2337	–598.70	–0.58
1.00000	0.86302	0.5258	–	–	–	–	–	–
			$\% \Delta d = \pm 0.0001$	$\% \Delta H = \pm 0.0001$	$\% \Delta K = \pm 0.0001$			
1, 4dimethylbenzene (1) + Ethylethanoate (2)								
0.00000	0.88252	0.3950	–	–	–	–	–	–
0.10408	0.87904	0.4106	0.0006	0.0686	0.4707	0.0858	219.74	0.21
0.20239	0.87493	0.4223	–0.0020	0.0230	0.4614	0.0457	116.98	0.19
0.30413	0.87128	0.4373	–0.0018	0.0319	0.4633	0.0543	139.09	0.29
0.40065	0.86821	0.4538	0.0007	0.0565	0.4690	0.0772	197.71	0.47
0.49394	0.86393	0.4672	0.0006	0.0539	0.4687	0.0794	203.44	0.51
0.60558	0.86080	0.4864	0.0036	0.0786	0.4750	0.1013	259.54	0.62
0.69676	0.85818	0.4967	0.0006	0.0529	0.4690	0.0737	188.89	0.40
0.79593	0.85477	0.5105	0.0001	0.0464	0.4676	0.0689	176.39	0.29
0.88762	0.85228	0.5264	0.0026	0.0952	0.4806	0.1145	293.32	0.29
1.00000	0.84878	0.5401	–	–	–	–	–	–
			$\% \Delta d = \pm 0.0004$	$\% \Delta H = \pm 0.0001$	$\% \Delta K = \pm 0.0001$			
1, 3, 5trimethylbenzene (1) + Ethylethanoate (2)								
0.00000	0.88252	0.3950	–	–	–	–	–	–
0.10355	0.87881	0.4245	0.0086	0.3182	0.5427	0.3802	973.96	0.90
0.19815	0.87434	0.4287	–0.0062	0.0021	0.4763	0.0717	183.73	0.29
0.30053	0.87069	0.4534	–0.0022	0.0670	0.4907	0.1352	346.49	0.73
0.39593	0.86842	0.4685	–0.0064	0.0312	0.4826	0.0943	241.50	0.58
0.49361	0.86525	0.4888	–0.0058	0.0383	0.4844	0.1017	260.62	0.66
0.60022	0.86256	0.5210	0.0049	0.1224	0.5062	0.1841	471.62	1.13
0.69472	0.86064	0.5451	0.0099	0.1677	0.5194	0.2266	580.63	1.23
0.79823	0.85872	0.5613	0.0053	0.1374	0.5123	0.1925	493.08	0.79
0.88565	0.85681	0.5689	–0.0048	0.0050	0.4725	0.0490	125.58	0.13
1.00000	0.85447	0.5968	–	–	–	–	–	–
			$\% \Delta d = \pm 0.0003$	$\% \Delta H = \pm 0.0001$	$\% \Delta K = \pm 0.0002$			
Cyclohexane (1) + n-Propylethanoate (2)								
0.00000	0.87105	0.4958	–	–	–	–	–	–
0.10248	0.86001	0.4950	–0.0281	–0.4973	0.4762	–0.4861	–1245.35	–1.15
0.19888	0.84916	0.4956	–0.0533	–0.5400	0.4621	–0.5250	–1345.03	–2.14
0.29761	0.83625	0.5003	–0.0750	–0.5697	0.4501	–0.5421	–1388.86	–2.90
0.39914	0.82460	0.5086	–0.0937	–0.6103	0.4339	–0.5803	–1486.62	–3.57

$x_1$	$\rho_{12} \times 10^3$ kg m <sup>3</sup>	$\eta_{12}$ mPa s	$\Delta\eta$ mPa s	$d$	$H_{12}$ mPa s	$K_{12}$	$w_{vis}$ J mol <sup>-1</sup>	$G^{*E}$ J mol <sup>-1</sup>
0.49975	0.81585	0.5236	-0.1056	-0.6424	0.4181	-0.6224	-1594.58	-3.99
0.59907	0.80517	0.5453	-0.1104	-0.6776	0.3995	-0.6563	-1681.35	-4.04
0.70004	0.79233	0.5763	-0.1062	-0.7188	0.3762	-0.6828	-1749.32	-3.67
0.79722	0.78512	0.6138	-0.0947	-0.8030	0.3364	-0.7828	-2005.63	-3.24
0.89387	0.77614	0.6722	-0.0621	-0.8489	0.3021	-0.8390	-2149.50	-2.04
1.00000	0.76477	0.7626	-	-	-	-	-	-
% $\Delta d = \pm 0.0007$ % $\Delta H = \pm 0.0004$ % $\Delta K = \pm 0.0000$								
Benzene (1) + n-Propylethanoate (2)								
0.00000	0.87105	0.4958	-	-	-	-	-	-
0.10878	0.87809	0.5033	0.0042	0.0890	0.5327	0.0292	74.77	0.07
0.20393	0.87682	0.5044	0.0025	0.0321	0.5185	0.0139	35.60	0.06
0.30294	0.87626	0.5070	0.0021	0.0215	0.5158	0.0146	37.45	0.08
0.40286	0.87552	0.5099	0.0019	0.0182	0.5150	0.0166	42.63	0.10
0.50159	0.87475	0.5132	0.0023	0.0201	0.5155	0.0204	52.34	0.13
0.60094	0.87396	0.5180	0.0041	0.0354	0.5195	0.0348	89.27	0.21
0.70145	0.87307	0.5197	0.0029	0.0280	0.5176	0.0231	59.29	0.12
0.80146	0.86530	0.5208	0.0008	0.0133	0.5138	0.0462	118.23	0.19
0.89719	0.86448	0.5236	0.0009	0.0200	0.5156	0.0507	129.77	0.12
1.00000	0.86302	0.5258	-	-	-	-	-	-
% $\Delta d = \pm 0.0130$ % $\Delta H = \pm 0.0001$ % $\Delta K = \pm 0.0012$								
1,4dimethylbenzene (1) + n-Propylethanoate (2)								
0.00000	0.87105	0.4958	-	-	-	-	-	-
0.10242	0.87012	0.5001	-0.0003	-0.0014	0.5167	-0.0179	-45.87	-0.04
0.20099	0.86810	0.5046	-0.0002	-0.0024	0.5176	-0.0081	-20.75	-0.03
0.30236	0.86523	0.5078	-0.0014	-0.0093	0.5146	-0.0139	-35.61	-0.08
0.40210	0.86305	0.5122	0.0014	-0.0078	0.5150	-0.0120	-30.68	-0.07
0.49886	0.86100	0.5174	0.0006	-0.0002	0.5170	-0.0047	-12.08	0.00
0.60032	0.85882	0.5234	0.0010	0.0117	0.5201	0.0065	16.76	0.04
0.69962	0.85607	0.5288	0.0020	0.0217	0.5227	0.0188	48.15	0.10
0.79703	0.85394	0.5335	0.0024	0.0314	0.5253	0.0272	69.60	0.11
0.89420	0.85169	0.5381	0.0027	0.0565	0.5322	0.0501	128.25	0.12
1.00000	0.84878	0.5401	-	-	-	-	-	-
% $\Delta d = \pm 0.0038$ % $\Delta H = \pm 0.0000$ % $\Delta K = \pm 0.0021$								
1, 3,5trimethylbenzene (1) + npropylethanoate (2)								
0.00000	0.87105	0.4958	-	-	-	-	-	-
0.10218	0.86930	0.5078	0.0016	0.0542	0.5555	0.0686	175.74	0.16
0.19832	0.86660	0.5086	-0.0073	-0.0710	0.5236	-0.0490	-125.64	-0.20
0.30194	0.86437	0.5175	-0.0089	-0.0624	0.5254	-0.0399	-102.11	-0.22
0.39689	0.86259	0.5265	-0.0094	-0.0564	0.5267	-0.0341	-87.48	-0.21
0.49766	0.86090	0.5363	-0.0098	-0.0550	0.5268	-0.0331	-84.90	-0.21
0.59783	0.85951	0.5462	-0.0100	-0.0584	0.5255	-0.0376	-96.29	-0.23
0.69925	0.85810	0.5581	-0.0083	-0.0537	0.5265	-0.0334	-85.49	-0.18
0.79367	0.85631	0.5661	-0.0098	-0.0889	0.5162	-0.0650	-166.55	-0.27
0.89187	0.85505	0.5772	-0.0087	-0.1384	0.5013	-0.1112	-284.97	-0.28
1.00000	0.85447	0.5968	-	-	-	-	-	-
% $\Delta d = \pm 0.0017$ % $\Delta H = \pm 0.0000$ % $\Delta K = \pm 0.0012$								

viscosities of the pure components respectively. The experimental  $\eta_{12}$  values in the present investigation are used to evaluate values of  $H_{12}$  for all the systems and are reported in table 3.  $H_{12}$  values are positive for all the binary mixtures studied. The  $H_{12}$  values at any composition for mixtures of methylethanoate + hydrocarbon solvents follow the order:

cyclohexane < benzene < 1,3,5-trimethylbenzene < 1,4-dimethylbenzene

which is again similar to those of  $\Delta\eta$  and  $d$  values. For binary mixtures of ethylethanoate + hydrocarbons and n-propylethanoate + hydrocarbons  $H_{12}$  values also follow the trend of their  $d$  and  $\Delta\eta$  values. For a common hydrocarbon solvent,  $H_{12}$  values for binary mixtures with different esters follow the trend:

methylethanoate < ethylethanoate < n-propylethanoate

which is the order of the gas phase dipole moments<sup>30</sup> of the esters.

Katti and Chaudhri<sup>31</sup> equation for mixture viscosities is

$$\ln \eta_{12} V_{12} = x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2 + x_1 x_2 K_{12} \quad (6)$$

where  $K_{12} = w_{\text{visc}}/RT$ ,  $w_{\text{visc}}$  is the interaction energy term.  $R$  and  $T$  are gas constant and temperature respectively.  $V_1, V_2$  are the molar volume of the components 1 and 2 and  $V_{12}$  is the molar volume of the mixture given by

$$V_{12} = (x_1 M_1 + x_2 M_2) / \rho_{12} \quad (7)$$

$M_1$  &  $M_2$  and  $\rho_{12}$  are molecular weights of the components 1 & 2 respectively and density of the mixture. The interaction parameter,  $K_{12}$  and interaction energy  $w_{\text{visc}}$  evaluated by equation (6) for all the systems are recorded in table 3. Table 3 shows that  $K_{12}$  values are negative for binary mixtures of methylethanoate and ethylethanoate with either cyclohexane or benzene and positive with 1,4-dimethylbenzene and 1,3,5-trimethylbenzene at all composition.  $K_{12}$  values for binary mixtures of n-propylethanoate + cyclohexane are negative and of n-propylethanoate + benzene are positive at all compositions. These values are positive as well as negative for the mixtures of n-propylethanoate + 1,4-dimethylbenzene and n-propylethanoate + 1,3,5-trimethylbenzene at experimental temperature. The values of  $w_{\text{visc}}$  have the similar sign as that of  $K_{12}$  for the binary systems. For a common ester  $w_{\text{visc}}$  values for binary mixtures with several hydrocarbon solvents have trend similar to  $d$  values. This is expected due to logarithmic nature of equations for both  $d$  and  $w_{\text{visc}}$ .

Excess free energies of activation for viscous flow  $G^{*E}$  are evaluated by equation

$$G^{*E} = RT [\ln \eta_{12} V_{12} - x_1 \ln \eta_1 V_1 - x_2 \ln \eta_2 V_2] \quad (8)$$

and the values are reported in table 3. The magnitude and sign of  $G^{*E}$  for each system have similar order as those of  $w_{\text{visc}}$ . The values of  $G^{*E}$  are negative for binary mixtures of all the ethanoates with cyclohexane for whole mole fraction range. The  $G^{*E}$  values increase when cyclohexane is replaced with benzene in the binary mixture. These values are less negative for mixtures of methyl and ethylethanoates with benzene and are positive for the mixtures of n-propylethanoate + benzene for the whole mole fraction range. Binary mixtures of methyl and ethylethanoates with 1,4-dimethylbenzene and 1,3,5-trimethylbenzene have positive  $G^{*E}$  values for the whole mole fraction range while mixtures of n-propylethanoate with 1,4-dimethylbenzene and 1,3,5-trimethylbenzene have positive except one negative for the former and negative except one positive  $G^{*E}$  values for the latter hydrocarbon. It has been suggested<sup>32</sup> that values of  $G^{*E}$  may be attributed to large size and cohesive energy difference between the two unlike

components. Palepu et al.<sup>33</sup> have suggested that positive values of  $G^{*E}$  may be considered as a reliable guide to the presence of interaction between the molecules. It may be noted that all the interaction parameters viz.  $d$ ,  $H_{12}$  and  $K_{12}$  vary with composition of the mixture.

In order to test the suitability of several viscosity equations, percentages of deviation of the interaction parameters evaluated on the basis of equations (4), (5) and (6) for each binary mixtures are evaluated and reported in table 3 below the column of the parameter. The viscosity equation, which gives least value of average percentage of deviation of interaction parameter, will be the most suitable equation for these binary mixtures. Table 3 reveals that none of the equations gives least values of percentage average deviation for all the systems studied. Grunberg-Nissan equation, Katti-Chaudhri equation and Hind-McLaughlin-Ubbelohde viscosity equation give least values of percentage average deviations for two, five and six systems respectively. Thus it may be concluded that the latter equation is most suitable for the viscosities of binary mixtures between alkylethanoates and hydrocarbon solvents.

## 4. Conclusions

Viscosity measurements on binary mixtures of esters + benzene, + 1,4-dimethylbenzene and 1,3,5-trimethylbenzene is suitable for molecular interactions studies.  $\Delta\eta$  values are large and negative for binary mixture of ester + cyclohexane and negative values reduce ( $\Delta\eta$  values increase) for binary mixture of esters + aromatic hydrocarbons. Hind-McLaughlin-Ubbelohde viscosity equation is most suitable for the study of binary mixtures.

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## Povzetek

Dvanajstim binarnim mešanicam z metiletanoatom, etiletanoatom in *n*-propiletanoatom z nepolarnimi topili (cikloheksan, benzen, 1,4-dimetilbenzen and 1,3,5-trimetilbenzen) smo pri 308.15 K izmerili viskoznost  $s(\eta_{12})$  in gostoto ( $\rho_{12}$ ) v celotnem koncentracijskem območju. Viskoznost mešanic narašča z naraščajočim molskim deležem nepolarnega topila, odstopanja od idealnih vrednosti,  $\Delta\eta$ , pa so negativna za vse preiskovane mešanice, kar kaže na močne medmolekulske sile, ki smo jih obravnavali s pomočjo Grunberg-Nissanovega inetrakcijskega parametra.