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Excess volumes, Viscosities and Speeds of Sound for Binary Mixtures of Ethyl methanoate +Alkanes: Application of Viscosity Models

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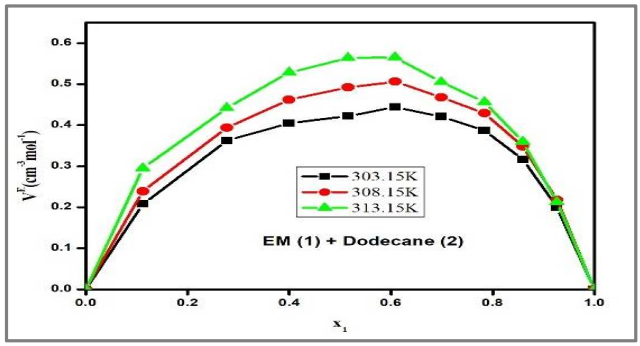
ABSTRACT

Densities (ρ), viscosities (η) and speeds of sound (u) of binary mixtures of ethyl methanoate with alkanes (heptane, decane, dodecane and tridecane) at 303.15, 308.15 and 313.15K temperature were measured over the entire composition range. In this experimental data excess volume V^E, deviation in viscosity Δη, isentropic compressibility Ks and excess isentropic compressibility K^E_s were calculated. These quantities have been fitted to the Redlich-Kisterpolynomial equation and results analyzed in terms of molecular interactions and structural effects. It is shown that the values of V^E are positive and Δη are negative over the entire composition range for each binary system investigated. The viscosity data have been correlated using Katti-Chaudhri, McAllister's three body and Auslander models at the studied temperature.

Graphical Abstract



Excess volume (V^E) Vs mole fraction(x_1) for Ethyl methanoate with dodecane

Keywords: Ethyl methanoate, Alkanes, Excess volumes, Isentropic compressibility, Binary liquid mixture.

INTRODUCTION

Thermodynamics plays an important role in numerous industries in the design of separation equipment and process as well as for product design and optimizing formulations. Complex polar and

associating molecules are present in many applications for which different type of thermodynamic and transport properties need to be known over wide ranges of temperature and pressure. For several years our research team has been investigating the physico-chemical properties for binary mixtures of esters containing different types of organic liquids and analyzing their molecular interactions. In continuation of our ongoing research[**1-4**],in this paper we report density (ρ), viscosity (η), and speeds of sound (u) data for binary mixtures of ethyl mathanoate with heptane ,decane, dodecane or tridecane at (303.15,308.15 and 313.15)K over the entire composition range. Ethyl methanoate is a polar simple aliphatic ester that is full of benefits and concerns and finds many industrial applications. The ester occurs in many food substances including fruits, coffee, rum, tea, and grains. It is used industrially as a solvent and as a fungicide and larvicide [**5-6**], in processed food such as dried fruits and cereals. It is additive to soap, detergent, and perfumes. These characteristics of this ester made it useful as a fumigant for grains, however it is presently restricted to dried fruits [**7**]. Likewise alkanes are used for many purposes and find good applications in chemical engineering areas. Some of the most common uses are heating, electricity generation, cooking, production of polymers, making of drug, pesticides and other chemicals. Moreover the uses can be differentiated according to the number of carbon atoms in the alkanes. The manner where by solute and solvent molecules are associated with one another in a mixed solvent brings about the marked effect on resulting liquid. This has mainly prompted us to undertake the present study with an aim to investigate the effect caused by the structure of these compounds on the thermodynamic and transport properties of solutions.

Survey of literature reveals that there are several reports on VLE, V_m^E, and H_m^E for alkyl methanoate + alkanes [**8-11**], alkyl butanoate + alkane [**12**], methyl ester + heptane [**13**], propyl ester + alkanes [**14**]. Density (ρ), viscosity (η), refractive index (n_D), and speed of sound (u) for ethyl chloroacetate + alkanes were reported [**15**]. However a systematic and combined study on thermodynamic and transport properties for ethyl methanoate +alkanes binary mixtures is still lacking. Therefore these binary systems are selected in our present work. Another important aspect of our present research is to assess the predictive power of some viscosity models proposed by Katti-Chaudhri [**16**], McAllister's three body [**17**] interaction model and Auslander [**18**] to verify their applicability for correlating experimental mixture viscosities.

MATERIALS AND METHODS

All chemicals utilized in this study were of analytical grade supplied by Sigma-Aldrich. The mass fraction purity of these chemicals was approximately higher than 0.99. These chemicals were stored over 0.4 nm molecular sieves to reduce water content and distilled just before the use. The purity of all these chemicals was further checked by gas chromatography (GC-8610) and the analysis of the purity was found to be >0.995. The specifications of deployed chemicals are listed in table 1.

Table 1. Chemical specifications and purity estimation

Chemical	CAS No	Source	Mass fraction purity (Supplier)	Purification method	Analysis method	Final mass fraction purity
Ethyl methanoate	109-94-4	Sigma-Aldrich	0.995	Distillation	GC*-8610	>0.996
Heptane	142-82-5	Sigma-Aldrich	0.992	Distillation	GC-8610	>0.995
Decane	124-18-5	Sigma-Aldrich	0.998	None	GC-8610	>0.998
Dodecane	112-40-3	Sigma-Aldrich	0.998	None	GC-8610	>0.998
Tridecane	629-50-5	Sigma-Aldrich	0.992	Distillation	GC-8610	>0.995

GC* Gas Liquid Chromatography

The binary liquid mixtures were prepared by mixing known masses of pure liquids in airtight stoppered bottles. All mass measurements were made using a Mettler one-pan balance (AE, 240, Switzerland). The resulting mole fraction uncertainty was estimated to be less than ± 0.0001.

Densities of pure and their binary mixtures were determined using a density meter (DDM -2910 Rudolph Research Analytical). The instrument has high precision platinum thermometer in the density sensor for the accurate measuring temperature. The instrument was calibrated frequently before the start of the actual experiments, using deionized doubly distilled water and dry air. The estimated uncertainties associated with density measurements are ± 0.0004 g cm^{-3}. Viscosities of the pure liquids and their mixtures were determined by using Ubbelohde viscometer. The viscometer bulb has a capacity of about 15 ml and the capillary tube with a length of about 90 mm and 0.5 mm internal diameter. The viscometer thoroughly cleaned and perfectly dried is filled with the sample liquid and its limbs were closed with Teflon caps to avoid evaporation. The viscometer is kept in a transparent walled water bath with a thermal stability of ± 0.01K for about 20 min to obtain thermal equilibrium. An electronic digital stopwatch with an uncertainty of ± 0.01s was used for flow time measurements. At least 3-4 repetitions of each mixture were obtained and the results were averaged. The viscosity was calculated from reflux time't' using the following relation.

$$\eta = \rho\,(At - B/t) \qquad (1)$$

Where ρ is the density and 't' is flow time, A and B are the characteristic constants of the viscometer, which were determined by taking water and benzene as the calibrating liquids. The uncertainty in the viscosity thus estimated was found to be ±0.007mPa.s .The speeds of sound of pure liquids and liquid mixtures were determined by using a single-crystal variable path interferometer (model F-81) supplied by Mittal Enterprises, New Delhi, India operating at frequency of 2 MHz. The instrument was calibrated by measuring the velocity in standard liquids viz AR grade benzene and carbon tetrachloride. The estimated uncertainty in speeds of sound thus was found to be ± 1%. In all property measurements the temperature was controlled within ± 0.01K using a constant low temperature bath (INSREF model IRI 016 C, India) by circulating water from thermostat. The experimental values of density and viscosity for pure components were compared with literature values at temperature 303.15 K as shown in table 2.

Table 2. Comparison of experimental values of density (ρ) and viscosity (η) of pure liquids with corresponding literature values at 303.15 K

Liquid	Densities(ρ)		Viscosities(η)	
	Experiment	Literature	Experiment	Literature
Ethyl methanoate	0.9081	0.9078[19]	0.371	0.373[19]
		0.9081[20]		0.366[20]
Heptane	0.6753	0.6745[21]	0.376	0.375[21]
		0.6757[22]		0.3774[22]
Decane	0.7227	0.7230[23]	0.790	0.786[24]
		0.7224[25]		0.785[25]
Dodecane	0.7416	0.7425[26]	1.240	1.243[26]
		0.7417[25]		1.238[25]
Tridecane	0.7491	0.749324[27]	1.540	1.577[27]
		0.7494[28]		

RESULTS AND DISCUSSION

The experimental values of density ρ, viscosity η, speeds of sound *u* and isentropic compressibility Ks for the studied binary mixtures over the entire composition range expressed as a function x_1 of ethyl methanolate at (303.15, 308.15 and 313.15 K) temperature are reported in table 3.

The excess volumes V^E, deviation in viscosity Δη, isentropic compressibility Ks and excess isentropic compressibility K^E_S are calculated using the following relations.

$$V^E\ (cm^3.mol^{-1}) = (x_1M_1 + x_2M_2)/\rho_{12} - (x_1M_1/\rho_1 + x_2M_2/\rho_2) \qquad (2)$$

$$\Delta\eta = \eta_{12} - (x_1\eta_1 + x_2\eta_2) \qquad (3)$$

Table 3. Densities (ρ),excess volumes (V^E), viscosities (η) and speeds of sound (u) and isentropic compressibility's (Ks) for the binary mixtures at different temperature

x_1	ρ	V^E	η	U	Ks	x_1	ρ	V^E	η	U	Ks
	$cm^3\ mol^{-1}$	$cm^3 mol^{-1}$	m Pa.s	$m.s^{-1}$	Tpa^{-1}		$cm^3\ mol^{-1}$	$cm^3 mol^{-1}$	m Pa.s	$m.s^{-1}$	Tpa^{-1}
Ethyl Methanoate + Heptane						Ethyl Methanoate + Decane					
T = 303.15K						T = 303.15K					
0.0000	0.6753		0.376	1116		0.0000	0.7227		0.790	1212	
0.1022	0.6883	0.146	0.361	1112	1174.9	0.0972	0.7299	0.182	0.731	1208	939.6
0.2016	0.7023	0.264	0.353	1109	1157.7	0.2528	0.7442	0.292	0.649	1197	937.2
0.3087	0.7192	0.353	0.348	1105	1138.7	0.3657	0.7567	0.358	0.597	1188	936.8
0.3769	0.7312	0.370	0.345	1102	1126.2	0.4654	0.7698	0.381	0.555	1178	936.1
0.4268	0.7406	0.375	0.344	1100	1115.9	0.5681	0.7858	0.384	0.514	1166	935.2
0.5986	0.7775	0.373	0.343	1095	1072.7	0.6665	0.8042	0.370	0.480	1154	933.9
0.6933	0.8014	0.369	0.345	1093	1044.5	0.7528	0.8236	0.338	0.450	1141	932.4
0.7996	0.8326	0.297	0.349	1091	1009.1	0.8417	0.8477	0.297	0.420	1126	930.5
0.8907	0.8644	0.125	0.356	1090	973.7	0.9226	0.8750	0.195	0.393	1111	926.7
1.0000	0.9081		0.371	1092		1.0000	0.9081		0.371	1092	
T = 308.15K						T= 308.15K					
0.0000	0.6710		0.342	1106		0.0000	0.7189		0.717	1188	
0.1022	0.6838	0.166	0.332	1102	1204.2	0.0972	0.7260	0.185	0.666	1186	979.6
0.2016	0.6976	0.299	0.326	1098	1189.0	0.2528	0.7400	0.321	0.590	1177	975.8
0.3087	0.7144	0.377	0.321	1093	1171.7	0.3657	0.7523	0.393	0.544	1167	975.4
0.3769	0.7262	0.410	0.319	1091	1156.9	0.4654	0.7652	0.418	0.507	1158	974.7
0.4268	0.7355	0.416	0.318	1089	1146.5	0.5681	0.7809	0.433	0.473	1147	973.8
0.5986	0.7720	0.419	0.319	1082	1106.4	0.6665	0.7990	0.421	0.441	1135	972.6
0.6933	0.7957	0.410	0.320	1079	1079.5	0.7528	0.8181	0.387	0.417	1122	971.1
0.7996	0.8266	0.335	0.326	1076	1044.9	0.8417	0.8420	0.322	0.391	1107	969.0
0.8907	0.8580	0.169	0.333	1074	1010.4	0.9226	0.8693	0.175	0.368	1092	964.7
1.0000	0.9017		0.345	1074		1.0000	0.9017		0.345	1074	
T = 313.15K						T= 313.15 K					
0.0000	0.6667		0.334	1073		0.0000	0.7151		0.691	1164	
0.1022	0.6793	0.183	0.326	1070	1285.8	0.0972	0.7220	0.211	0.644	1163	1024.0
0.2016	0.6929	0.329	0.321	1066	1270.0	0.2528	0.7358	0.345	0.572	1156	1017.1
0.3087	0.7094	0.431	0.315	1063	1247.5	0.3657	0.7479	0.418	0.528	1147	1017.0
0.3769	0.7211	0.458	0.313	1061	1231.9	0.4654	0.7605	0.463	0.493	1137	1016.8
0.4268	0.7302	0.481	0.312	1059	1221.1	0.5681	0.7760	0.466	0.459	1126	1016.2
0.5986	0.7664	0.465	0.312	1054	1174.5	0.6665	0.7938	0.454	0.429	1114	1015.3
0.6933	0.7900	0.432	0.313	1052	1143.8	0.7528	0.8127	0.403	0.404	1102	1014.1
0.7996	0.8207	0.340	0.318	1051	1103.1	0.8417	0.8362	0.337	0.379	1087	1012.4
0.8907	0.8517	0.180	0.323	1051	1062.9	0.9226	0.8630	0.192	0.356	1072	1008.9
1.0000	0.8950		0.332	1054		1.0000	0.8950		0.332	1054	
Ethyl Methanoate + Dodecane						Ethyl Methanoate +Tridecane					
T = 303.15K						T = 303.15K					
0.0000	0.7416		1.240	1260		0.0000	0.7491		1.539	1300	
0.1119	0.7480	0.208	1.110	1252	853.4	0.0956	0.7538	0.208	1.388	1292	795.1
0.2772	0.7601	0.362	0.936	1237	859.8	0.2907	0.7666	0.392	1.115	1271	807.5
0.3996	0.7716	0.405	0.823	1224	865.1	0.4151	0.7775	0.430	0.962	1255	817.3
0.5155	0.7851	0.422	0.722	1208	872.6	0.5299	0.7901	0.452	0.827	1236	828.6
0.6080	0.7982	0.444	0.651	1194	878.8	0.6248	0.8031	0.455	0.728	1218	840.1
0.6988	0.8141	0.421	0.583	1177	886.1	0.7119	0.8179	0.440	0.642	1197	852.9
0.7839	0.8325	0.387	0.520	1159	894.5	0.7913	0.8348	0.395	0.565	1175	867.2
0.8592	0.8529	0.316	0.465	1139	903.4	0.8677	0.8556	0.290	0.489	1150	883.9
0.9262	0.8757	0.200	0.420	1118	914.3	0.9335	0.8781	0.197	0.425	1124	901.6
1.0000	0.9081		0.371	1092		1.0000	0.9081		0.371	1092	
T= 308.15K						T= 308.15K					
0.0000	0.7379		1.115	1242		0.0000	0.7455		1.318	1283	
0.1119	0.7441	0.239	1.002	1233	884.3	0.0956	0.7500	0.247	1.214	1275	820.7
0.2772	0.7560	0.394	0.853	1219	890.5	0.2907	0.7625	0.449	0.999	1254	834.3
0.3996	0.7672	0.462	0.750	1206	896.2	0.4151	0.7731	0.509	0.870	1237	845.3
0.5155	0.7804	0.492	0.658	1191	903.4	0.5299	0.7854	0.540	0.753	1218	857.7
0.6080	0.7933	0.506	0.593	1177	910.9	0.6248	0.7982	0.530	0.664	1201	870.3
0.6988	0.8090	0.468	0.531	1160	918.6	0.7119	0.8128	0.497	0.590	1180	884.3

0.7839	0.8271	0.429	0.475	1141	929.0	0.7913	0.8294	0.446	0.518	1157	900.0
0.8592	0.8472	0.348	0.431	1122	937.6	0.8677	0.8499	0.326	0.454	1132	918.2
0.9262	0.8697	0.218	0.391	1102	947.5	0.9335	0.8721	0.216	0.398	1106	937.7
1.0000	0.9017		0.345	1074		1.0000	0.9017		0.345	1074	
		T= 313.15 K						T= 313.15 K			
0.0000	0.7343		1.054	1224		0.0000	0.7419		1.178	1265	
0.1119	0.7402	0.295	0.952	1215	914.6	0.0956	0.7462	0.283	1.091	1256	848.9
0.2772	0.7519	0.442	0.814	1201	922.4	0.2907	0.7584	0.499	0.914	1235	864.1
0.3996	0.7628	0.528	0.719	1187	930.4	0.4151	0.7687	0.578	0.803	1218	876.4
0.5155	0.7757	0.564	0.634	1172	939.2	0.5299	0.7807	0.615	0.700	1199	890.3
0.6080	0.7884	0.565	0.570	1157	947.5	0.6248	0.7933	0.588	0.627	1181	904.3
0.6988	0.8039	0.505	0.513	1140	956.5	0.7119	0.8077	0.536	0.556	1160	919.9
0.7839	0.8217	0.456	0.459	1122	966.7	0.7913	0.8240	0.476	0.494	1138	937.3
0.8592	0.8415	0.360	0.416	1102	978.5	0.8677	0.8442	0.338	0.432	1112	957.5
0.9262	0.8637	0.213	0.377	1081	990.8	0.9335	0.8661	0.208	0.386	1086	979.1
1.0000	0.8950		0.332	1054		1.0000	0.8950		0.332	1054	

Table 4. Parameters of Eq. (6) for various functions and corresponding standard deviations (σ) of the binary mixtures at 303.15,308.15,313.15K

Binary mixture	T/K	Excess property	A_0	A_1	A_2	σ
Ethyl Methanoate+ Heptane	303.15	V^E	1.5985	0.0564	0.1206	0.025
		$\Delta\eta$	-0.1227	-0.0076	-0.0521	0.001
		K^E_S	16.8335	4.9081	1.0749	0.064
	308.15	V^E	1.7546	0.1293	0.3402	0.019
		$\Delta\eta$	-0.1031	-0.0084	-0.0202	0.001
		K^E_S	16.3216	4.8896	1.9410	0.060
	313.15	V^E	1.9702	0.0058	0.1322	0.013
		$\Delta\eta$	-0.0871	-0.0071	0.0001	0.001
		K^E_S	19.2444	6.3144	1.9357	0.066
Ethyl Methanoate+ Decane	303.15	V^E	1.4967	0.2546	1.0929	0.014
		$\Delta\eta$	-0.1578	0.0498	-0.0130	0.001
		K^E_S	1.2370	2.3154	-0.1348	0.028
	308.15	V^E	1.6970	0.3275	0.8927	0.009
		$\Delta\eta$	-0.1450	0.0595	0.0184	0.001
		K^E_S	0.4141	3.9173	-1.7029	0.041
	313.15	V^E	1.8316	0.2970	0.9372	0.013
		$\Delta\eta$	-0.1236	0.0535	0.0274	0.001
		K^E_S	-0.9957	5.1699	-2.2277	0.044
Ethyl Methanoate+ Dodecane	303.15	V^E	1.7011	0.3558	1.2078	0.006
		$\Delta\eta$	-0.2762	0.0798	-0.0032	0.002
		K^E_S	-6.1663	-2.2616	0.4865	0.077
	308.15	V^E	1.9451	0.3890	1.1823	0.008
		$\Delta\eta$	-0.2367	0.0411	0.0278	0.002
		K^E_S	-7.0024	-3.6318	-0.0594	0.067
	313.15	V^E	2.2066	0.2165	1.1282	0.018
		$\Delta\eta$	-0.1922	0.0331	0.0309	0.001
		K^E_S	-7.8430	-3.7048	-1.3717	0.044
Ethyl Methanoate+ Tridecane	303.15	V^E	1.7924	0.2685	1.2473	0.009
		$\Delta\eta$	-0.3697	0.0960	-0.0261	0.003
		K^E_S	-12.4663	-6.5272	-2.9535	0.031
	308.15	V^E	2.1115	0.2458	1.2531	0.011
		$\Delta\eta$	-0.1932	-0.0136	0.0577	0.002
		K^E_S	-13.5594	-7.0803	-3.1689	0.030
	313.15	V^E	2.3910	0.1308	1.0845	0.017
		$\Delta\eta$	-0.1055	-0.0107	0.0567	0.002
		K^E_S	-15.0231	-7.9216	-3.7364	0.039

$$K_S = 1 / u^2 \rho \quad (4)$$

$$K^E_S = (K_S)_{12} - [\, x_1 (K_S)_1 + x_2 (K_S)_2 \,] \quad (5)$$

Where *x*, *M*, ρ, *u*, and K_S are mole fraction, molar mass, density, speed of sound and isentropic compressibility respectively while 1, 2 and 12 indicate pure component and their mixture respectively. The results of V^E, Δη and K^E_S are graphically represented in figures 1-3. Further the results of all excess or deviation properties were fitted to the following Redlich-Kister [29] polynomial equation by the method of least squares to derive the binary coefficients Ai.

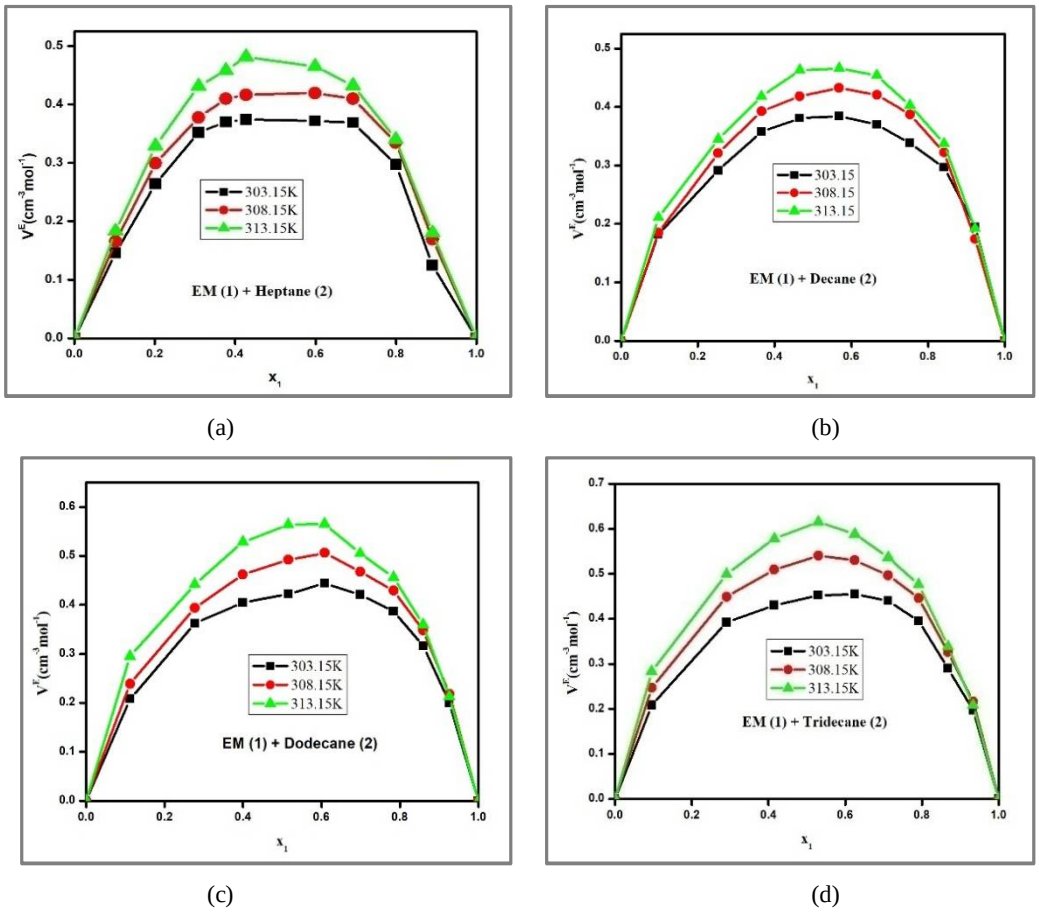
$$Y = x_1x_2 \sum A_i (x_1 - x_2)^i \qquad (6)$$

Where, Y represents the concerned excess or deviation property. The standard deviation for V^E, Δη and K^E_S were calculated using the relation

$$\sigma (Y) = [\ \sum (Yexpt - Ycal)^2/(N - n)\ ]^{1/2} \qquad (7)$$

Where, N is number of data points and n is number of coefficients. The calculated values of the polynomial coefficients A_i along with their standard deviation σ, are given in table 4.

The dependence of excess volumes V^E, on the mole fraction of ethyl methanoate xi, is shown in figure 1(a-d). A perusal of these isotherms reveals that all the studied systems are characterized by positive deviation over the whole composition range at the studied temperatures.



(a) (b)

(c) (d)

Figure 1(a-d). Excess volumes Vs mole fraction (x_1).

These positive deviations may be ascribed due to size effects of alkanes resulting by the fewer holes available in the alkane's framework. Further it is observed that the variation of V^E for the mixtures of heptane, decane and dodecane is almost similar with the maxima at x_1=0.5; However for ethyl methanoate + tridecane the maxima slightly shifted towards x_1 = 0.4 moreover the effect of

temperature for all the mixtures is found to be systematic as the V^E values increase with increase in temperature. The V^E values at about (x_1=0.5) follow the following order

Tridecane > Dodecane > Decane > Heptane

This order may be attributed to the effect of increasing chain length of alkanes resulting in to poor interstitial accommodation, which is consistent with trapping of lower alkanes in ethyl methanoate network. The longer the chain length, greater will be the polarizability and shorter the range of orientation order in pure alkanes [**30**]. The size effect also appears with increasing chain length.

The variation of Δη with x_1 is shown in figure 2(a-d). It is observed that the Δη values follow negative deviation over the entire composition range for all the studied systems at the respective temperatures.

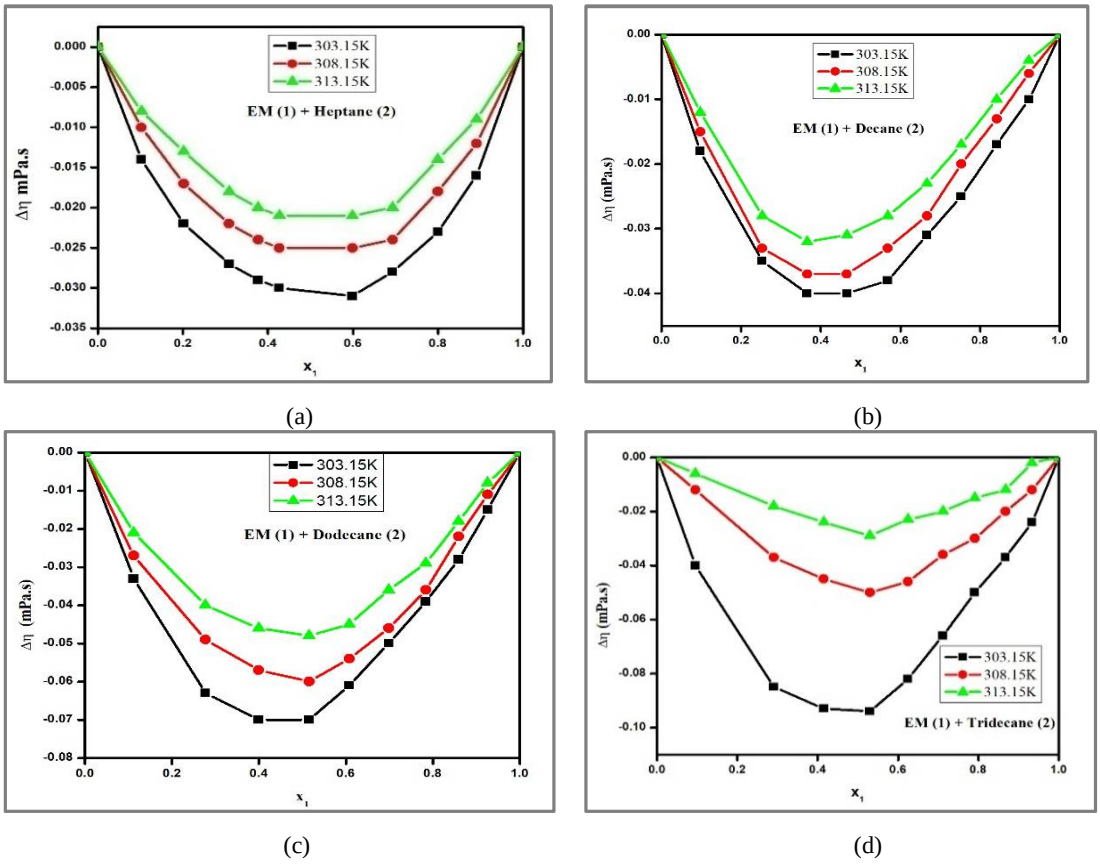
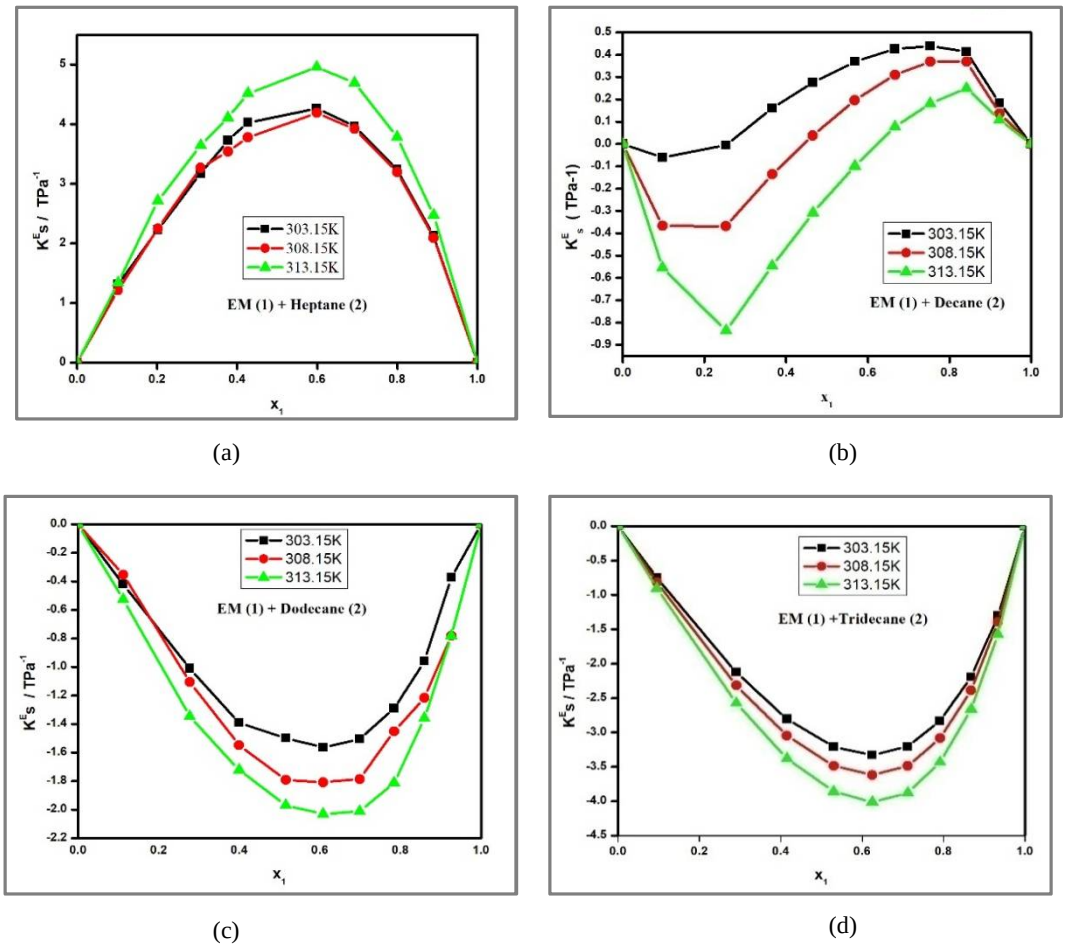


Figure 2(a-d). Deviation in viscosity Vs mole fraction (x_1).

The deviation in viscosity Δη gives a quantitative estimation of intermolecular interactions. Negative deviation in viscosity occurs where dispersion or weak dipole-dipole forces are dominant between the component molecules [**31-32**]. Negative Δη values may also be observed due to the difference in the molecular size of the component molecules [**33-37**]. Further it is observed that the values of deviation in viscosity become large negative with increase in temperature. Figure 3(a-d) represents the variation of K^E_S Vs mole fraction (x_1) of ethyl methanoate. Here we observe that the K^E_S values are positive for ethyl methanoate + heptane and negative for ethyl methanoate + dodecane and ethyl methanoate + tridecane, over the entire range of composition at all the studied temperatures. While for ethyl methanoate + decane the K^E_s values are negative (up to x_1=0.4) but at higher concentration of ethyl methanoate (x_1 >0.4) at 313.15K the K^E_S values shifted to positive deviation. The positive K^E_S values suggest that the interaction between ethyl methanoate + heptane are weaker as compared to

interaction between like molecules, while the negative K^E_S values indicate the presence of specific interactions.



(a) (b)

(c) (d)

Figure 3(a-d). Excess isentropic compressibility Vs mole fraction (x_1).

APPLICATION

Viscosity models: In order to estimate the mixture viscosity in this study we selected the following one- parameter Katti-Chaudhri [16], two-parameter McAllister three body [17] and three-parameter Auslander [18] model equations with an aim to analyzed their respective abilities for the present reported binary mixtures. Katti-Chaudhri [16] proposed the following expression

$$\ln \eta_{12}V_{12}=x_1 \ln\eta_1V_1+x_2\ln \eta_2V_2 + x_1x_2(W_{visc}/RT) \qquad (8)$$

Where, W_{visc} is an adjustable interaction parameter and $V_{1\ and}\ V_2$ are molar volumes of first and second components respectively.

McAllister three body [17] interaction model has widely used to correlate the kinematic viscosities of binary liquid mixtures with mole fraction. The three body model is defined as

$$\text{Ln } \nu=x_1^3\ln\nu_1+3x_1^2x_2\ln Z_{12}+3x_1x_2^2\ln Z_{21}+x_2^3\ln\nu_2-\ln[x_1+x_2(M_2/M_1)]+3x_1^2x_2\ln[\{2+(M_2/M_1)\}/3]+3x_1x_2^2 \ln[\{1+ 2\ (M_2/M_1)\}/3]+x_2^3\ln(M_2/M_1) \qquad (9)$$

Where, υ, υ_1, υ_2 are the kinematic viscosities of binary mixture, first and second components respectively, while Z_{12} and Z_{21} are the model parameters. *M*i and *x*i are the molecular weight and mole

fraction of the i^{th} pure component in the mixture.

Auslander [**18**] proposed the following three parameter equation

$$\eta = \eta_1 x_1 (x_1 + B_{12} x_2) + \eta_2 (A_{21} x_2 (B_{21} x_1 + x_2)) / x_1(x_1 + B_{12} x_2) + (A_{21} x_2)(B_{21} x_1 + x_2) \quad (10)$$

Where, A_{21}, B_{12} and B_{21} are parameters representing the binary specific interactions. The correlating ability of eqs.(8-10) was tested by calculating the standard percentage deviation σ(%) between the experimental and calculated viscosities as

$$\sigma(\%)=(1/n\text{-}k\sum\{100(n_{exp}-n_{cal})/n_{exp}\}^2]^{1/2} \quad (11)$$

The values of interaction parameters obtained by equations 8-10 and the values of σ% are presented in table 5. Analysis of these results shows that all the selected models predict more or less reasonable accurate estimation of the viscosity of the studied binary mixtures at (303.15,308.15 and 313.15)K.

Table 5. Adjustable parameters and percentage standard deviations (σ%) of several correlations for the viscosities of binary mixtures.

Binary Mixtures	T/K	Katti- Chaudhri		Mc Allister (3-body)			Auslander			
		Wvisc	σ%	Z_{12}	Z_{21}	σ%	A_{21}	B_{12}	B_{21}	σ%
Ethyl Methanoate + Heptane	303.15	-0.1695	0.05	-8.5562	-9.0561	0.05	-0.0108	0.2794	1.6054	0.05
	308.15	-0.1274	0.02	-8.6161	-9.1223	0.02	-0.0082	0.2604	1.6527	0.03
	313.15	-0.0766	0.02	-8.6240	-9.1285	0.01	-0.0050	0.2543	1.6961	0.01
Ethyl Methanoate + Decane	303.15	0.3998	0.13	-8.3208	-8.5947	0.06	0.0058	0.4251	1.3520	0.02
	308.15	0.3928	0.16	-8.4067	-8.6701	0.04	0.0114	0.3936	1.4121	0.04
	313.15	0.4297	0.17	-8.3951	-8.7174	0.09	0.0119	0.3852	1.4366	0.04
Ethyl Methanoate + Dodecane	303.15	0.9367	0.30	-8.0590	-8.2677	0.06	0.0071	0.5286	1.1693	0.03
	308.15	0.9190	0.27	-8.1560	-8.3473	0.08	0.0032	0.5160	1.1453	0.05
	313.15	0.9514	0.28	-8.1778	-8.3870	0.08	0.0036	0.5021	1.1810	0.05
Ethyl Methanoate + Tridecane	303.15	1.2303	0.39	-7.9077	-8.1097	0.08	0.0045	0.5830	1.0781	0.06
	308.15	1.3020	0.36	-7.9915	-8.1910	0.10	0.0007	0.5685	1.1189	0.04
	313.15	1.3150	0.38	-8.0350	-8.2789	0.11	0.0005	0.5409	1.1970	0.00

The values of σ% are in the range (0.02-0.39) for Katti-Chaudhri with one adjustable parameter and (0.01-0.11) for McAllister's three body with two adjustable parameters and (0.00-0.01) for Auslander with three adjustable parameters. The average σ% values lie in the range 0.21:0.065: 0.035 respectively for the three selected models. It is observed that analysis of the results of one parameter model reveals that σ% values are much higher than the values obtained from two parameter and three parameter models. The study of σ% values further reveals that the mixture viscosities for all the investigated systems can be satisfactorily predicted by Auslander model as evident from the lowest σ% values.

CONCLUSION

Density (ρ), viscosity (η) and speeds of sound (u) for binary mixtures of ethyl methanoate with heptane, decane, dodecane and tridecane at (303.15, 308.15 and 313.15 K) temperature have been determined experimentally over the whole composition range. Using the experimental data the excess volume (V^E), deviation in viscosity (Δη), isentropic compressibility (Ks) and excess isentropic compressibility (K^Es) have been calculated. These excess properties are analyzed in terms of molecular interactions. The excess properties show both positive and negative deviations. The observed deviation of theoretical values from the experimental values is attributed to the presence of intermolecular interactions such as dipole-dipole, and size and shape of component molecules in the

system studied. The mixture viscosities were also correlated using some selected models of Katti-haudhri, McAllister three body and Auslander. Analysis of σ% values shows that Auslander model with three adjustable interaction parameters predicts the viscosities more satisfactorily as compared to the Katti-haudhri and McAllister three body models.

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