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Full Length Research Paper

Volumetric, viscometric and ultrasonic studies on binary mixtures of oleic acid with alkyl esters at 303.15, 308.15 and 313.15 K

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Density (ρ), viscosity (η) and speed of sound (u) for binary mixtures of oleic acid with methyl acetate, ethyl acetate, n-propyl acetate and n-butyl acetate were measured at 303.15, 308.15 and 313.15 K over the whole composition range at atmospheric pressure. These results were used to calculate excess molar volumes (V^E), deviations in viscosity ($\Delta\eta$), deviations in speed of sound (Δu), the excess Gibbs free energies of activation of viscous flow (G^{*E}), deviation in adiabatic compressibility (Δk_S), acoustic impedance (Z) and deviation in acoustic impedance(ΔZ). These results were fitted to Redlich-Kister type polynomial equation of the third degree to derive the binary coefficients. The standard error values were estimated between the calculated and experimental data.

Key words: Density, viscosity, ultrasonic speed, oleic acid, alkyl esters.

INTRODUCTION

Physical properties of liquid mixtures are required in most of the engineering calculations where fluid flow or mixing is an important factor in many practical problems concerning mass transport applications. Oleic acid is a monounsaturated omega-9 fatty acid found in various animal and vegetable sources (Young, 2002). The saturated form of this acid is stearic acid. It is used in Lorenzo's oil (Arudi et al., 1983). Oleic acid is emitted by decaying bee corpses and triggers the instincts of living bees to remove the dead bodies from the hive (Ayasse et and Paxton, 2002). Oleic acid is the most abundant fatty acid in human adipose tissue (Kokantur et al., 1979). It is also used as excipient in pharmaceuticals and as an emulsifying agent in aerosol products (Smolinske, 1992). Oleic acid may hinder the progression of ADL or anfrenoleukodystarpy, a fatal disease that affect the brain and adrenal glands (Rizzo et al., 1986). Oleic acid and monosaturated fatty acid levels in the membranes of red blood cells have been associated with the increased risk of breast cancer and it is also responsive for the hypotensive (blood pressure reducing) effect of olive oil (Pala et al., 2001; Teres et al., 2008). Esters on the other hand find applications as plasticizers in polymer-processing industries in order to impart favorable thermoplastic behavior (Nallani et al., 2007; Riemenschneider and Bolt, 2005). An understanding of the mixing behavior of oleic acid with esters is therefore important and may have applications in many engineering areas. We now report the results of density, viscosity and speed of sound for the binary mixtures of oleic acid with methyl acetate, ethyl acetate, n-propyl acetate and *n*-butyl acetate over the entire range of composition at 303.15, 308.15 and 313.15 K. With this data, the excess molar volume, deviations in viscosity, deviations in speed of sound, deviation in adiabatic compressibility, acoustic impedance, deviation in acoustic impedance and excess Gibbs free energy of activation of viscous flow have been computed. These results have been fitted to the Redlich-Kister polynomial equation using a multi parametric nonlinear regression analysis technique to derive the binary coefficients and to estimate the standard deviation (σ) between experimental and calculated data (Redlich and Kister, 1948).

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Table 1. Comparison of experimental densities (*ρ*), viscosities (*η*) and speeds of sound (*u*) of pure components with available literature at 303.15 K and at atmospheric pressure.

Component	ρ (g·cm^{-3})		η (mPa·s)		u (m·s^{-1})	
	Experimental	Literature	Experimental	Literature	Experimental	Literature
oleic acid	0.8841	0.8839 [e]	24.173	27.343[f]	1412	-
methyl acetate	0.9219	0.9204[a]	0.368	0.3440[c]	1136	1136[d]
ethyl acetate	0.8884	0.8896[a]	0.410	0.4000[c]	1122	1119[b]
n-propyl acetate	0.8762	0.8774[b]	0.527	0.5120[c]	1149	1149[b]
n-butyl acetate	0.8712	0.8713[a]	0.624	0.6444[b]	1176	1176[b]

[a], Data from reference (Sastry and Patel, 2003); [b], data from reference (Patwari et al., 2009); [c], data from reference (Aralaguppi et al., 1999); [d], data from reference (Oswal and Patel, 1995); [e], data from reference (Bernardo-Gil et al., 1990); [f], data from reference (Cedeno et al., 2000).

METHODOLOGY

Materials

High-purity spectroscopic and analytical grade samples of oleic acid, methyl acetate and ethyl acetate were procured from S.D. Fine Chemicals Ltd., Mumbai, India. n-Propyl acetate and n-butyl acetate were purchased from E. Merck (Germany). Solution of oleic acid in acetonitrile is filtered into the recrystallization vessel at room temperature and purged with ultra high purity nitrogen for 15 min. While N_2 is passing through the solution via the vessel is slowly lowered into the acetone dry ice cooling mixture. The temperature of this cooling mixture is controlled by periodic addition of pulverized dry ice. Oleic acid crystals begin to appear within a few minutes and the crystallization goes to completion within 15 to 20 min. The mother liquor is removed from the crystals by changing the direction of nitrogen flow. Methyl acetate, ethyl acetate, n-propyl acetate and n-butyl acetate were dried over anhydrous K_2CO_3 for more than 72 h and were fractionally distilled twice before use (Riddick et al., 1986). The mass fraction purities in percentage as determined by gas chromatography are: oleic acid > 0.997, methyl acetate > 0.995, ethyl acetate > 0.994, n-propyl acetate > 0.995, n-butyl acetate > 0.993. Densities and viscosities of pure substances and their comparison with literature values are shown in Table 1. The experimental values found in Table 1 are very close to literature values.

Apparatus and procedure

Binary mixtures were prepared by mass in airtight bottles. The mass measurements of pure liquid and liquid mixtures were performed on a Reptech RA-2012. It can measure weight in range of 210 g to 0.1 mg. It works with accuracy of ±0.0001 g. The required properties of the mixture were measured on the same day. The uncertainty in mole fraction was estimated to be less than 0.0001.

Densities accurate to ±0.0001 g·cm^{-3} were measured by using pycnometer having bulb volume of 10 cm^3 and capillary orifice with internal diameter 1 cm^3 for each measurement. The pycnometer filled with required liquid was kept in water bath with thermal stability ±0.01°C as checked by calibrated thermometer to attain the equilibrium. An average of triplicate measurements was taken into account and their reproducibility was within the range of ±0.3%. The suspended level Ubbelohde viscometer was used to determine the viscosity of pure liquids and their mixtures. An electronic digital stopwatch with readability of ±0.01 s was used for the flow time measurements. To check the calibration at 303.15, 308.15 and 313.15 K, the viscometer used was recalibrated against water, and in each case the measured viscosity of water agreed to within experimental uncertainty with literature values. The estimated error in the viscosity measurements was within ±0.001 mPa·s. All glasswares were thoroughly cleaned with warm chromic acid cleaning solution.

The speed of sound values were measured using a variable path single-crystal interferometer model M-81S supplied by Mittal Enterprises, New Delhi, with an accuracy ±2 m·s^{-1}. In the present study, frequency of 2 MHz was employed and instrument was calibrated using water and benzene.

RESULTS AND DISCUSSION

The experimentally measured density (*ρ*), viscosity (*η*) and speed of sound (*u*) have been used to evaluate derived properties like adiabatic compressibility (k_S) and acoustic impedance (*Z*) using well established equations:

$$k_S = \frac{1}{(u^2\rho)} \quad (1)$$

$$Z = u\rho \quad (2)$$

where, *u* stands for speed of sound and *ρ* for density.

Excess molar volume, deviation in viscosity, deviation in speed of sound, deviation in adiabatic compressibility and deviation in acoustic impedances were calculated, respectively from the following equations:

$$V^E = \sum_{i=1}^{2} x_i M_i(\rho^{-1} - \rho_i^{-1}) \quad (3)$$

$$\Delta\eta = \eta - \sum_{i=1}^{2} x_i \eta_i \quad (4)$$

$$\Delta u = u - \sum_{i=1}^{2} x_i u_i \quad (5)$$

$$\Delta k_S = k_S - \sum_{i=1}^{2} x_i k_{S_i} \quad (6)$$

$$\Delta Z = Z - \sum_{i=1}^{2} x_i Z_i \qquad (7)$$

where, ρ, η, u, k_S and Z are the density, viscosity, speed of sound, adiabatic compressibility and acoustic impedance of pure components, and ρ_i, η_i, u_i, k_{Si} and Z_i denotes corresponding mixture properties. x_i is the mole fraction.

The excess Gibb's free energy of activation (G^{*E}) for viscous flow has been calculated as:

$$G^{*E} = RT[\ln(\eta V) - \sum_{i=1}^{2} x_i \ln(\eta_i V_i)] \qquad (8)$$

where, η and η_i are the viscosities of the mixture and pure component, and V and V_i are the molar volumes of pure component and mixture respectively.

The resultant values for the binary mixtures at 303.15, 308.15 and 313.15 K are shown in Table 2. These values are plotted against the mole fraction of oleic acid as shown in Figure 1. Each set of results were fitted using Redlich-Kister Equation 9 for binary mixtures.

$$Y^E = x_1 x_2 \sum_{i=o}^{i=n} A_i (2x_1 - 1)^i \qquad (9)$$

where Y^E = (V^E, $\Delta\eta$, G^{*E}, Δu, Δk_S and ΔZ) and x_1 is the mole fraction of the first component. The co-efficient A_i was calculated by unweighted least square method. In each case, the optimum numbers of coefficient are ascertained from the examination of the variation in standard deviation in Y^E of Equation 9. The standard deviation (σ) was calculated using the following equation:

$$\sigma^E = [\sum (Y^E_{obs} - Y^E_{cal})^2 / (N-n)]^{1/2} \qquad (10)$$

where N is the number of experimental points and n is the number of parameters (n=3 in the present case). The estimated values of A_i and σ for Y^E versus x_1 are shown in Table 3. In all the cases, the best fit was obtained by using only three fitting coefficients.

In Figure 1, the points represent the data calculated from Equations 3 to 8, while smooth curve are drawn from the best fitted data calculation using Equation 9.

The experimentally measured densities and excess molar volumes (V^E) calculated from the measured densities of pure and mixture components of oleic acid + methyl acetate, ethyl acetate, n-propyl acetate and n-butyl acetate mixtures at 303.15, 308.15 and 313.15 K are shown as a function of oleic acid mole fraction in Table 2. The parameters A_i and standard deviation σ are shown in Table 3 at 303.15, 308.15 and 313.15 K. The graphical variation of V^E values as a function of oleic acid mole fraction V^E versus x_1 at 303.15 K are shown in Figure 1. It can be seen from the figures that the V^E values for oleic acid + methyl acetate, ethyl acetate, n-propyl acetate and n-butyl acetate mixtures are negative over the whole composition range at three temperatures. The excess molar volume (V^E) has decreased with increase of alkyl chain length from methyl to n-butyl acetate. The graphs are not systematic for all the binaries. The graphs of oleic acid + n-butyl acetate are different from methyl acetate, ethyl acetate and n-propyl acetate. The H-bonding in lower esters is more as compared to higher one that is, buty acetate, so V^E values are large for butyl acetate. The minima occur between 0.27 and 0.39 mole fraction of oleic acid + methyl acetate, ethyl acetate, n-propyl acetate and n-butyl acetate mixtures at three temperatures and have the following sequence at minima.

Methyl acetate < ethyl acetate < n-propyl acetate < n-butyl acetate.

The interaction in these mixtures may be classified as dipole-dipole type forces resulting from the polarizability of ester molecules by the dipoles of oleic acid molecules. There may be chemical or specific interaction involved in decreasing the V^E. Palaiologou, (1996) presented similar behavior for alkyl ester + 4-chlorotoluene systems.

The experimentally measured, theoretically calculated viscosities and deviation in viscosities ($\Delta\eta$) calculated from the measured viscosities of pure and mixture components of oleic acid + methyl acetate, ethyl acetate, n-propyl acetate and n-butyl acetate mixtures at temperatures 303.15, 308.15 and 313.15 K are given as function of oleic acid mole fraction in Table 2 and corresponding statistical parameters are shown in Table 3. A perusal of Figure 1 of $\Delta\eta$ versus x_1 reveals that, the $\Delta\eta$ values are negative over the whole composition range for oleic acid + methyl acetate, ethyl acetate, n-propyl acetate and n-butyl acetate mixtures. The negative $\Delta\eta$ values show a positive effect with an increase in chain length of ester at all three temperatures. The curves are systematic and explain for identical nature in the binaries. The minima appear between 0.26 and 0.39 mole fraction of oleic acid in all selected binaries at three temperatures.

The negative $\Delta\eta$ values in general indicate that oleic acid and ester complexes are closer to each other and hetero interactions are more predominant than homo contacts. Since higher esters are more associated, mixture of oleic acid with higher esters give less negative values (positive effect). $\Delta\eta$ values at equimolar concentrations of oleic acid and ester are in the following order:

Methyl acetate < ethyl acetate < n-propyl acetate <n-butyl acetate.

From the curves of the G^{*E} versus x_1, it can be seen that the excess free energy of activation of flow, G^{*E} values are positive for oleic acid + methyl acetate, ethyl acetate, n-propyl acetate and n-butyl acetate binary mixtures at all three temperatures. The G^{*E} values have decreased with

Table 2. Density (ρ), viscosity (η), speed of sound (u), adiabatic compressibility (k_S) acoustic impedance (Z), excess molar volume (V^E), deviation in viscosity ($\Delta\eta$), excess Gibb's free energy of activation (G^{*E}), deviation in speed of sound (Δu), deviation in adiabatic compressibility (Δk_S) and deviation in acoustic impedance (ΔZ) of oleic acid (1) + alkyl esters (2) at 303.15, 308.15 and 313.15 K.

x_1	ρ ($g \cdot cm^{-3}$)	η (mPa·s)	u ($m \cdot s^{-1}$)	k_S (TPa^{-1})	Z ($g \cdot m^{-2} \cdot s^{-1}$)	V^E ($cm^3 \cdot mol^{-1}$)	$\Delta\eta$ (mPa·s)	G^{*E} ($J \cdot mol^{-1}$)	Δu ($m \cdot s^{-1}$)	Δk_S (TPa^{-1})	ΔZ ($g \cdot m^{-2} \cdot s^{-1}$)
Oleic acid(1) + methyl acetate(2) at 303.15 K											
0.0000	0.9220	0.368	1136	840	1047						
0.0273	0.9182	0.755	1158	812	1063	-0.003	-0.263	1625	14	-20	11
0.0594	0.9144	1.263	1181	784	1080	-0.006	-0.519	2685	29	-40	21
0.0977	0.9107	1.954	1205	756	1097	-0.009	-0.739	3481	42	-57	31
0.1441	0.9069	2.870	1229	730	1115	-0.011	-0.929	4055	53	-71	39
0.2016	0.9031	4.113	1254	704	1132	-0.013	-1.055	4440	62	-81	45
0.2748	0.8993	5.814	1282	677	1153	-0.013	-1.095	4608	70	-88	51
0.3708	0.8955	8.190	1305	656	1169	-0.012	-1.005	4493	67	-83	47
0.5026	0.8917	11.538	1335	629	1190	-0.009	-0.793	3939	60	-74	42
0.6945	0.8879	16.385	1374	597	1220	-0.005	-0.515	2651	46	-54	33
1.0000	0.8841	24.173	1412	567	1248						
At 308.15 K											
0.0000	0.9152	0.350	1112	884	1018						
0.0273	0.9119	0.671	1129	860	1030	-0.003	-0.223	1486	10	-16	7
0.0594	0.9086	1.107	1150	832	1045	-0.005	-0.426	2538	23	-36	16
0.0977	0.9053	1.679	1173	803	1062	-0.007	-0.617	3307	37	-55	26
0.1441	0.9019	2.433	1195	776	1078	-0.009	-0.788	3870	48	-69	34
0.2016	0.8986	3.473	1218	750	1095	-0.011	-0.895	4270	56	-80	40
0.2748	0.8953	4.882	1241	725	1111	-0.012	-0.942	4450	61	-85	44
0.3708	0.8919	6.854	1262	704	1126	-0.011	-0.884	4355	59	-80	41
0.5026	0.8886	9.662	1288	678	1145	-0.008	-0.701	3837	52	-70	36
0.6945	0.8852	13.762	1321	647	1169	-0.004	-0.425	2597	38	-50	26
1.0000	0.8819	20.274	1358	615	1198						
At 313.15 K											
0.0000	0.9090	0.330	1094	919	994						
0.0273	0.9059	0.613	1107	901	1003	-0.002	-0.185	1434	7	-11	5
0.0594	0.9028	0.991	1127	872	1017	-0.004	-0.357	2457	21	-32	15
0.0977	0.8997	1.495	1146	846	1031	-0.006	-0.510	3234	31	-48	22
0.1441	0.8966	2.151	1169	816	1048	-0.008	-0.650	3798	45	-67	32
0.2016	0.8935	3.021	1188	793	1062	-0.009	-0.767	4175	52	-76	37
0.2748	0.8904	4.227	1204	775	1072	-0.011	-0.815	4362	52	-76	37
0.3708	0.8873	5.911	1221	756	1083	-0.010	-0.778	4278	49	-71	33
0.5026	0.8842	8.319	1243	732	1099	-0.007	-0.629	3778	43	-62	29
0.6945	0.8810	11.824	1270	704	1119	-0.003	-0.415	2558	30	-42	20
1.0000	0.8779	17.478	1304	670	1145						
Oleic acid(1) + ethyl acetate(2) at 303.15 K											
0.0000	0.8884	0.410	1122	894	997						
0.0335	0.8881	1.050	1143	862	1015	-0.010	-0.156	2108	11	-21	10
0.0723	0.8877	1.831	1164	831	1033	-0.019	-0.297	3191	21	-39	18
0.1179	0.8873	2.788	1187	800	1053	-0.026	-0.423	3859	31	-56	27
0.1721	0.8869	3.953	1211	769	1074	-0.031	-0.546	4252	39	-69	34
0.2377	0.8864	5.408	1235	740	1095	-0.034	-0.650	4427	44	-77	38
0.3186	0.8860	7.277	1260	711	1116	-0.036	-0.705	4385	46	-79	39
0.4211	0.8855	9.716	1288	681	1141	-0.032	-0.701	4074	44	-76	38

Table 2. Contd.

0.5550	0.8851	13.000	1320	648	1168	-0.024	-0.598	3398	37	-64	32
0.7372	0.8846	17.557	1360	611	1203	-0.016	-0.372	2165	24	-42	21
1.0000	0.8841	24.173	1412	567	1248						
At 308.15 K											
0.0000	0.8826	0.383	1101	935	972						
0.0335	0.8826	0.912	1119	905	988	-0.009	-0.137	1965	9	-19	8
0.0723	0.8826	1.567	1139	873	1005	-0.016	-0.254	3038	19	-38	17
0.1179	0.8825	2.369	1161	841	1025	-0.023	-0.358	3711	30	-57	26
0.1721	0.8825	3.312	1183	810	1044	-0.028	-0.494	4089	38	-70	33
0.2377	0.8824	4.528	1205	780	1063	-0.032	-0.582	4283	43	-78	38
0.3186	0.8823	6.089	1227	753	1083	-0.031	-0.632	4261	44	-80	39
0.4211	0.8822	8.132	1251	724	1104	-0.028	-0.627	3973	42	-76	36
0.5550	0.8821	10.888	1278	694	1127	-0.022	-0.534	3325	34	-63	30
0.7372	0.8820	14.730	1310	661	1155	-0.013	-0.318	2127	20	-38	17
1.0000	0.8819	20.274	1358	615	1198						
At 313.15 K											
0.0000	0.8760	0.362	1082	975	948						
0.0335	0.8762	0.818	1098	947	962	-0.008	-0.117	1868	9	-18	8
0.0723	0.8765	1.375	1116	916	978	-0.016	-0.225	2910	18	-37	16
0.1179	0.8767	2.052	1136	884	996	-0.021	-0.327	3571	28	-55	25
0.1721	0.8769	2.882	1157	852	1015	-0.026	-0.425	3979	37	-71	33
0.2377	0.8771	3.925	1177	823	1032	-0.030	-0.505	4182	42	-80	38
0.3186	0.8773	5.260	1196	797	1049	-0.027	-0.556	4170	43	-81	38
0.4211	0.8774	7.019	1216	771	1067	-0.025	-0.551	3900	41	-76	36
0.5550	0.8776	9.392	1238	743	1086	-0.020	-0.469	3272	33	-62	29
0.7372	0.8777	12.702	1263	714	1109	-0.011	-0.279	2098	17	-36	15
1.0000	0.8779	17.478	1304	670	1145						
Oleic acid(1) + propyl acetate(2) at 303.15 K											
0.0000	0.8763	0.527	1149	864	1007						
0.0391	0.8771	1.346	1166	840	1022	-0.012	-0.106	2053	7	-12	5
0.0839	0.8780	2.317	1184	814	1039	-0.022	-0.194	3054	13	-25	11
0.1357	0.8788	3.472	1204	786	1057	-0.030	-0.264	3633	19	-37	18
0.1963	0.8796	4.850	1225	759	1077	-0.037	-0.319	3944	24	-47	22
0.2681	0.8804	6.520	1247	732	1097	-0.040	-0.347	4039	27	-53	25
0.3547	0.8812	8.588	1270	704	1119	-0.043	-0.325	3925	28	-55	27
0.4609	0.8819	11.129	1294	678	1140	-0.038	-0.296	3557	24	-49	22
0.5944	0.8827	14.359	1323	648	1167	-0.030	-0.223	2879	18	-39	17
0.7673	0.8834	18.537	1360	613	1201	-0.018	-0.134	1763	9	-23	9
1.0000	0.8841	24.173	1412	567	1248						
At 308.15 K											
0.0000	0.8713	0.487	1139	885	992						
0.0391	0.8725	1.168	1153	864	1005	-0.010	-0.093	1935	5	-11	5
0.0839	0.8736	1.976	1169	839	1020	-0.019	-0.171	2919	12	-23	11
0.1357	0.8747	2.942	1186	813	1037	-0.027	-0.230	3503	17	-36	17
0.1963	0.8757	4.096	1204	789	1054	-0.033	-0.275	3825	22	-43	21
0.2681	0.8768	5.499	1222	764	1071	-0.036	-0.294	3936	24	-49	24
0.3547	0.8779	7.218	1242	738	1090	-0.038	-0.287	3833	25	-51	25
0.4609	0.8789	9.355	1262	714	1109	-0.034	-0.251	3486	22	-46	22

Table 2. Contd.

0.5944	0.8799	12.063	1285	688	1131	-0.027	-0.185	2828	16	-36	16
0.7673	0.8809	15.557	1315	657	1157	-0.015	-0.113	1735	8	-20	7
1.0000	0.8819	20.274	1358	615	1198						
At 313.15 K											
0.0000	0.8667	0.452	1126	910	976						
0.0391	0.8679	1.037	1138	891	987	-0.009	-0.081	1858	5	-9	4
0.0839	0.8691	1.741	1151	869	1000	-0.017	-0.140	2846	10	-21	10
0.1357	0.8702	2.570	1167	844	1016	-0.024	-0.193	3428	17	-34	17
0.1963	0.8713	3.557	1181	823	1029	-0.029	-0.237	3751	20	-40	20
0.2681	0.8725	4.764	1196	801	1043	-0.033	-0.253	3872	22	-44	22
0.3547	0.8736	6.233	1212	779	1059	-0.035	-0.257	3775	23	-46	23
0.4609	0.8747	8.074	1228	758	1074	-0.032	-0.225	3441	20	-41	20
0.5944	0.8758	10.403	1245	737	1090	-0.025	-0.169	2796	13	-31	14
0.7673	0.8768	13.418	1269	709	1112	-0.014	-0.098	1720	6	-17	6
1.0000	0.8779	17.478	1304	670	1145						
Oleic acid(1) + butyl acetate(2) at 303.15 K											
0.0000	0.8695	0.624	1176	832	1023						
0.0445	0.8715	1.608	1190	810	1037	-0.015	-0.064	2033	3	-9	2
0.0948	0.8731	2.754	1206	787	1053	-0.027	-0.103	2975	8	-18	7
0.1523	0.8741	4.065	1223	765	1069	-0.036	-0.145	3474	11	-25	10
0.2184	0.8753	5.591	1242	741	1087	-0.043	-0.176	3708	14	-32	13
0.2953	0.8765	7.381	1264	714	1108	-0.047	-0.198	3729	18	-38	17
0.3860	0.8780	9.517	1288	687	1131	-0.048	-0.197	3550	21	-42	20
0.4944	0.8795	12.076	1311	662	1153	-0.043	-0.191	3148	18	-38	18
0.6264	0.8810	15.219	1336	636	1177	-0.036	-0.155	2484	12	-29	12
0.7904	0.8825	19.140	1369	605	1208	-0.021	-0.098	1478	6	-18	7
1.0000	0.8841	24.173	1412	567	1248						
At 308.15 K											
0.0000	0.8654	0.587	1155	866	1000						
0.0445	0.8673	1.411	1167	847	1012	-0.013	-0.052	1897	3	-8	3
0.0948	0.8691	2.366	1181	825	1026	-0.023	-0.088	2815	7	-17	8
0.1523	0.8703	3.460	1196	803	1041	-0.032	-0.125	3316	10	-24	11
0.2184	0.8715	4.739	1213	780	1057	-0.039	-0.147	3562	14	-31	14
0.2953	0.8731	6.232	1231	756	1075	-0.041	-0.169	3596	16	-36	16
0.3860	0.8746	8.019	1251	731	1094	-0.043	-0.167	3436	18	-39	18
0.4944	0.8763	10.163	1272	705	1115	-0.039	-0.158	3057	17	-37	17
0.6264	0.8781	12.786	1293	681	1135	-0.032	-0.132	2417	11	-28	11
0.7904	0.8800	16.070	1321	651	1162	-0.020	-0.078	1442	6	-16	6
1.0000	0.8819	20.274	1358	615	1198						
At 313.15 K											
0.0000	0.8604	0.547	1135	902	977						
0.0445	0.8622	1.259	1145	885	987	-0.011	-0.041	1824	2	-7	4
0.0948	0.8641	2.084	1157	865	1000	-0.020	-0.069	2733	6	-15	8
0.1523	0.8653	3.028	1170	844	1012	-0.028	-0.097	3236	9	-22	11
0.2184	0.8667	4.123	1184	823	1026	-0.035	-0.121	3485	12	-28	13
0.2953	0.8683	5.402	1199	801	1041	-0.038	-0.145	3526	14	-32	15
0.3860	0.8699	6.931	1216	777	1058	-0.039	-0.151	3374	16	-35	17
0.4944	0.8718	8.776	1233	755	1075	-0.035	-0.142	3008	14	-33	15
0.6264	0.8738	11.046	1250	732	1092	-0.028	-0.106	2386	9	-24	10
0.7904	0.8758	13.872	1273	705	1115	-0.016	-0.058	1426	4	-14	5
1.0000	0.8779	17.478	1304	670	1145						

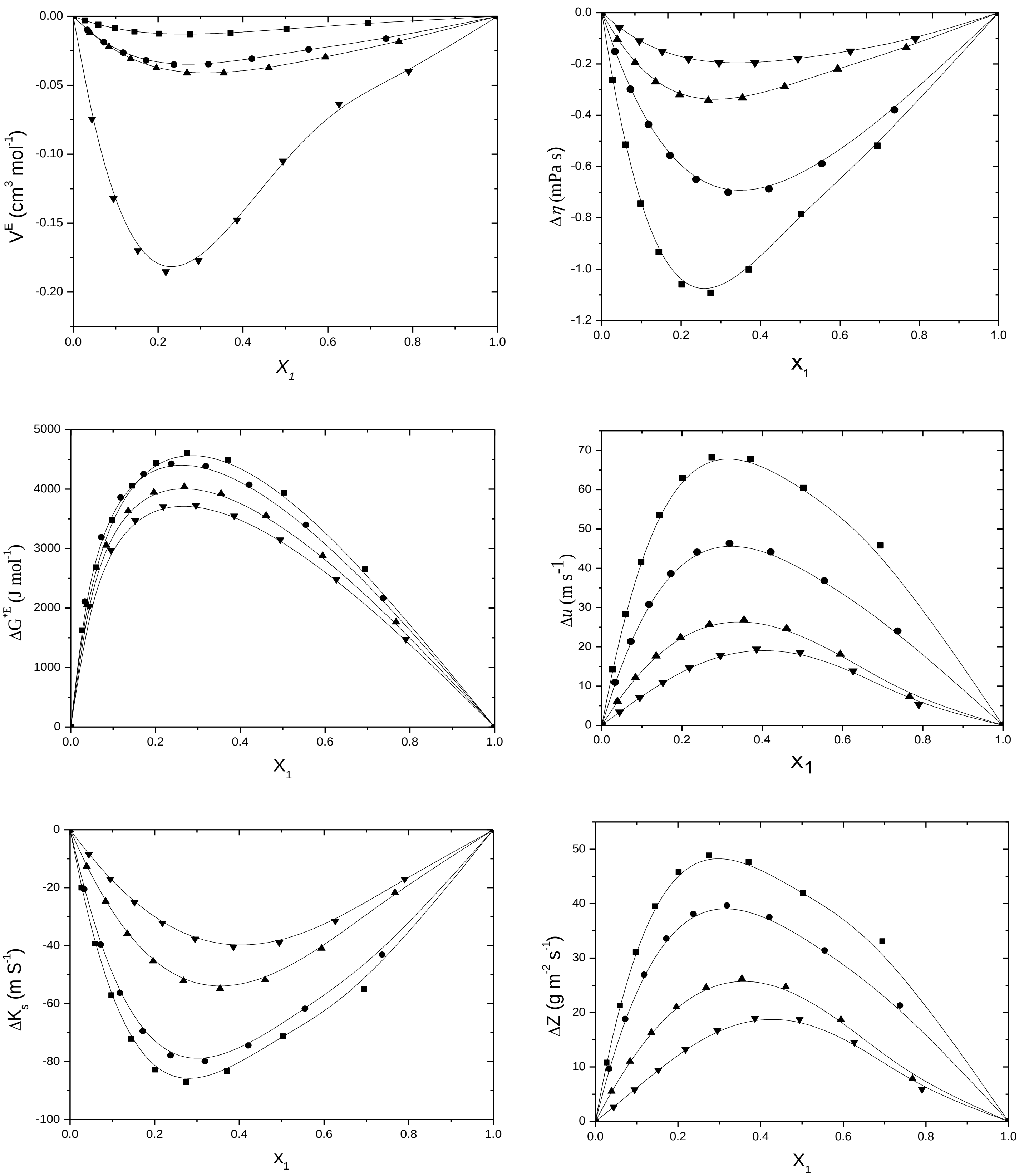

Figure 1. Excess molar volume (V^E), deviation in speed of sound (Δu), deviation in adiabatic compressibility (Δk_S), deviation in acoustic impedance (ΔZ), deviation in viscosity ($\Delta\eta$) and excess Gibb's free energy of activation of flow (G^{*E}), with mole fraction (x_1) for oleic acid (1) + methyl acetate(2) (■), oleic acid(1) + ethyl acetate(2) (●), oleic acid(1) + n-propyl acetate(2) (▲) and oleic acid (1) + n-butyl acetate (2) (▼) at 303.15 K.

Table 3. Binary coefficients (A_i) and standard errors (σ) of oleic acid (1) + alkyl esters (2).

Component		Temperature	A_0	A_1	A_2	σ
Oleic acid(1) + methyl acetate(2)	V^E (cm^3·mol^{-1})	303.15	-0.0369	0.0493	-0.0352	0.0000
		308.15	-0.0313	0.0416	-0.0341	0.0001
		313.15	-0.0307	0.0455	-0.0016	0.0001
	$\Delta\eta$ (mPa·s)	303.15	-3.1568	3.3729	-3.9716	0.0015
		308.15	-2.7679	3.0170	-2.9287	0.0024
		313.15	-2.5234	2.3251	-2.3521	0.0024
	Δu (m·s^{-1})	303.15	242.48	-139.63	182.29	0.2639
		308.15	224.93	-165.21	45.51	0.8084
		313.15	196.83	-182.08	-22.96	1.2676
	G^{*E} (J·mol^{-1})	303.15	12000.00	-7546.56	3500.70	428.43
		308.15	11957.30	-7541.13	3491.90	383.95
		313.15	11905.50	-7537.41	3321.40	365.49
	Δk_S (TPa^{-1})	303.15	-285.82	192.22	-319.96	0.4220
		308.15	-292.20	234.58	-162.32	0.7427
		313.15	-278.94	273.24	-1.44	2.0107
	ΔZ(g·m^{-2}·s^{-1})	303.15	168.31	-96.11	165.14	0.2608
		308.15	158.23	-124.63	21.63	0.7213
		313.15	134.28	-134.24	-12.94	1.1011
Oleic acid(1) + ethyl acetate(2)	V^E (cm^3·mol^{-1})	303.15	-0.1073	0.1035	-0.1153	0.0003
		308.15	-0.0958	0.0994	0.0905	0.0002
		313.15	-0.0853	0.0961	-0.0854	0.0003
	$\Delta\eta$ (mPa·s)	303.15	-2.5496	1.5952	-0.7299	0.0027
		308.15	-2.2932	1.4987	-0.3923	0.0030
		313.15	-2.0174	1.3220	-0.3753	0.0020
	Δu (m·s^{-1})	303.15	160.81	-115.52	79.85	0.1122
		308.15	158.51	-135.38	14.09	0.4022
		313.15	152.11	-143.08	0.20	0.3762
	G^{*E} (J·mol^{-1})	303.15	10082.80	-10610.50	4147.50	444.56
		308.15	10219.60	-10310.00	2909.20	417.82
		313.15	10300.30	-10050.80	2752.40	389.28
	Δk_S (TPa^{-1})	303.15	-269.12	197.12	-208.21	0.3849
		308.15	-276.83	232.20	-125.17	0.3581
		313.15	-282.55	250.98	-71.28	0.5565
	ΔZ(g·m^{-2}·s^{-1})	303.15	136.65	-96.21	83.96	0.1271
		308.15	137.55	-120.59	14.60	0.3274
		313.15	134.69	-128.72	0.12	0.3318
Oleic acid(1) + propyl acetate(2)	V^E (cm^3·mol^{-1})	303.15	-0.1411	0.1121	-0.0772	0.0003
		308.15	-0.1286	0.1058	-0.0452	0.0001
		313.15	-0.1193	0.0931	-0.0357	0.0002
	$\Delta\eta$ (mPa·s)	303.15	-1.0749	1.0433	0.8671	0.0015
		308.15	-0.9078	0.9206	-0.7988	0.0010
		313.15	-0.8133	0.7835	-0.6081	0.0016
	Δu (m·s^{-1})	303.15	92.42	-89.06	-12.68	0.4472
		308.15	108.25	-53.48	35.34	1.5356
		313.15	80.51	-89.10	-41.15	0.4870
	G^{*E} (J·mol^{-1})	303.15	9957.86	-11943.90	10403.80	249.75
		308.15	10023.40	-11507.30	7148.20	257.99
		313.15	10068.60	-11245.60	4436.70	272.56

Table 3. Contd.

	Δk_S (TPa^{-1})	303.15	-197.06	144.72	-6.41	0.4702
		308.15	-182.96	142.45	3.85	0.4106
		313.15	-166.58	139.46	24.51	0.6660
	ΔZ(g·m^{-2}·s^{-1})	303.15	93.41	-79.82	-23.50	0.4151
		308.15	87.30	-84.05	-24.35	0.2730
		313.15	82.05	-83.31	-36.47	0.4116
Oleic acid(1) + butyl acetate(2)	V^E (cm^3·mol^{-1})	303.15	-0.4110	0.7516	-0.7899	0.0100
		308.15	-0.3627	0.7001	-0.5386	0.0130
		313.15	-0.2791	0.5689	-0.3171	0.0155
	$\Delta\eta$ (mPa·s)	303.15	-0.7176	0.3924	-0.3801	0.0018
		308.15	-0.6099	0.3566	-0.2667	0.0013
		313.15	-0.5364	0.3348	-0.0585	0.0016
	Δu (m·s^{-1})	303.15	73.75	-46.46	-44.00	0.2821
		308.15	66.70	-39.80	-32.98	0.2096
		313.15	58.63	-41.07	-45.41	0.2435
	ΔG^{*E} (J mol^{-1})	303.15	9693.91	-12246.70	2567.10	275.03
		308.15	9618.98	-11582.20	2340.50	251.03
		313.15	9585.50	-11218.40	2222.2	238.52
	Δk_S (TPa^{-1})	303.15	-154.96	74.45	27.27	0.3562
		308.15	-146.51	76.00	25.96	0.2403
		313.15	-130.77	71.12	27.96	0.2642
	ΔZ(g·m^{-2}·s^{-1})	303.15	74.62	-35.59	-54.07	0.4230
		308.15	66.51	-42.29	-28.12	0.1732
		313.15	57.07	-44.45	-4.32	0.1733

increase of $–CH_2$ group in esters (methyl to butyl). The curves of G^{*E} versus x_1 are systematic for all these binaries at three temperatures. The maxima occur between 0.26 and 0.32 mole fraction of oleic acid with methyl acetate, ethyl acetate, n-propyl acetate and n-butyl acetate at three temperatures. The pattern of graphs is identical in all the binaries.

Positive G^{*E} values suggest for strong interactions for unlike molecules of oleic acid and esters. It has been reported that G^{*E} parameter can be considered as a reliable criterion to detect or exclude the presence of interactions between unlike molecules (Eswaribai et al., 2005). According to these authors, the magnitude of the positive values is an excellent indicator of the strength of specific interactions. G^{*E} values for these binaries have the following order at maxima.

Methyl acetate < ethyl acetate < n-propyl acetate < n-butyl acetate.

The plots of Δu versus x_1 are shown in Figure 1 where Δu is positive for all selected binaries. The variation of Δk_S with mole fraction x_1 of oleic acid at 303.15, 308.15 and 313.15 K is shown in Table 2. Negative values are obtained with minima between 0.27 and 0.42 mole fractions of oleic acid, Δu and k_S values show the following trend at minima value.

Methyl acetate < ethyl acetate < n-propyl acetate < n-butyl acetate.

The observed value of V^E, Δk_S and G^{*E} can be quantitatively explained by considering the following factors influencing the function namely: (1) Mutual disruption of associates present in pure liquids, (2) Formation of weak bonds by dipole-dipole or dipole induced dipole interaction between unlike molecule and (3) Geometrical fitting of component molecules into each other structure.

The first factor contributes to positive V^E, Δk_S and negative G^{*E} values while remaining two factors contributes to negative V^E, Δk_S and positive G^{*E}. The negative values of V^E, Δk_S and positive G^{*E} for all the binaries over whole composition range suggest that dipole-dipole type of interactions may be possible between these unlike molecules. Interstitial accommodation of one component into other is ruled out because of large differences in molar volumes of pure components, oleic acid (313.8 cm^3·mol^{-1}), ethyl acetate (98.5 cm^3·mol^{-1}), n-propyl acetate (114.5 cm^3·mol^{-1}) and n-butyl acetate (131.0 $cm^3 \cdot mol^{-1}$). $\Delta\eta$ values are negative that explain for weaker interactions in general. Moreover, there is a large difference in the viscosities of pure components as shown in Table 1.

It is well known that when two liquid components having largely different properties are mixed, significant variation in the properties is bound to either decrease or increase depending upon the properties of individual components. Here, oleic acid having compressibility (567 TPa^{-1}) is added to a component having higher adiabatic compressibility methyl acetate (840 TPa^{-1}) or ethyl acetate (894 TPa^{-1}) or n-propyl acetate (864 TPa^{-1}) or n-butyl acetate (830 TPa^{-1}). The values of k_S of mixture should decrease. The positive values of G^{*E} are attributed to large size differences and cohesive energy difference between the two unlike components.

With increase in temperature from 303.15 to 313.15K, V^E, $\Delta\eta$ and Δk_S have increased and Δu, ΔZ and G^{*E} have decreased for all the selected binaries. The interactions become weaker with rise of temperature, the kinetic energy of molecules increases both in pure and mixed solutions when temperature increases. Thus, it leads to decrease in interaction between unlike molecules, so contraction and adiabatic compressibility decreases with the result of increase in V^E and Δk_S.

Conclusions

In binary mixture of oleic acid and alkyl esters V^E, $\Delta\eta$ and Δk_S values are negative and Δu, G^{*E} and ΔZ values are positive. In these binaries, dipole-dipole type of interactions is expected because oleic acid is polar and protic in nature while esters are weakly polar and aprotic solvents. With increases in alkyl chain in esters, structure making effect has preceded the structure breaking effect in these binary mixtures. V^E, $\Delta\eta$ and Δk_S have negative values and the values have increased with increase of temperature from 303.15 to 313.15 K because of volume expansion and increase in kinetic energy of molecules of mixtures.

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