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Solid-liquid equilibrium and kinematic viscosity of binary mixture of fatty acid alkyl esters

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Abstract−The separation and recovery of fatty acid alkyl esters (FAAE) is of great significance for various industries. Crystallization is a well-suited separation process for fatty acid mixtures which may be evolved by the understanding of solid-liquid equilibrium (SLE). The SLE and kinematic viscosity (ν) at (T=298.15-318.15 K) and (P=0.1 mPa) for binary mixture of FAAE: methyl decanoate (1)+ethyl decanoate or methyl dodecanoate or methyl tetradecanoate (2) has been studied. The deviation in kinematic viscosity ($\Delta\nu$) data was derived using experimental ν data. The measured SLE exhibit general single eutectic point like other organic mixtures. The SLE data fit well with universal quasi-chemical (UNIQUAC) equation. The ν values were interrelated using different equations recommended by Heric-Brewer, Krishnan-Ladda, and Lulian et al. Theoretically estimated values using these empirical equations are in accordance with the experimental values with percentage standard deviation less than 0.35. The ν were also analyzed by means of the McAllister equation. The $\Delta\nu$ data were also fitted with the Redlich-Kister polynomial equation. All three binary mixtures showed negative $\Delta\nu$ values.

Keywords: Esters, Solid-liquid Equilibria, Kinematic Viscosity, Deviation In Kinematic Viscosity

INTRODUCTION

Fatty acid alkyl esters (FAAE, biodiesel) can be transesterified from sustainable natural resources like vegetable oils, animal fats, and others [1]. The separation and recovery of fatty acids is of great significance for various industries such as cosmetics, pharmaceutical, food, and oil industry [2]. The cleanliness of fatty acid products and separation of short chain ($<C_{12}$) FAAE from long chain ($>C_{12}$) FAAE is needed in the production process of the fatty acids and biodiesel [3]. Common distillate separation and purification of certain fatty acids from fatty acid mixtures is difficult because they have a relatively high boiling point and may thermally decompose easily; therefore, crystallization could be a well-suited separation process for fatty acid mixtures. Because alkyl esters of fatty acids having a carbon chain length of 12 do not have a deep freezing point; therefore, crystallization may be evolved by the understanding of solid-liquid equilibrium (SLE). Thermodynamic properties like density and viscosity are very important for separation/purification process designing and for optimization of operation. In addition, for using fatty acid esters as biodiesel, we should have knowledge of their thermodynamic behavior at different temperature. These properties also help to know about the molecular interactional behavior of fluid mixtures. In this paper, the SLE and kinematic viscosities (ν) at (T=298.15, 308.15, 318.15 K) of the binary mixture methyl decanoate ($C_{11}H_{22}O_2$) (1)+ethyl decanoate ($C_{12}H_{24}O_2$) or methyl dodecanoate ($C_{13}H_{26}O_2$) or methyl tetradecanoate ($C_{15}H_{30}O_2$) (2) were determined. There is no data available for SLE and kinematic viscosity (ν) of these binary systems in the literature. The ν data were interrelated via different empirical relations. The ν data were further used to derive deviations in kinematic viscosity ($\Delta\nu$). The experimental SLE was correlated with universal quasi-chemical (UNIQUAC) equations [4]. The kinematic viscosity (ν) values were also analyzed using the Mc Allister equation [5,6].

EXPERIMENT

1. Material

All used chemicals methyl decanoate (CAS No 110-42-9, TCI UK), ethyl decanoate (CAS No. 110-38-3, TCI UK), methyl dodecanoate (CAS No. 111-82-0, TCI UK) and methyl tetradecanoate (CAS No. 124-10-7, TCI UK) were kept over 3 Å pellet type molecular sieves in amber colored bottles for more than 72 hours and degassed before use. The mass fraction purity of the chemical used, experimental melting point and kinematic viscosity values along with literature values of all used chemicals are given in Table 1 [7-12].

2. Method

The SLE for a binary system was determined using jacketed glass vessel as an equilibrium cell and with a cryostat. The temperature when homogeneous liquid formed by heating from a heterogeneous mixture of solid/liquid phase was carefully reported using a platinum resistance thermometer. A triple jacketed glass equilibrium cell was used and a vacuum was created in the outermost exterior

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Table 1. The physical properties for pure chemicals

Compound	Purity	Melting point, (K)		T/K	ν ($mm^2 \cdot s^{-1}$)	
		This work	Literature		Exptl.	Lit.
Methyl decanoate	≥0.98	261.05	260.10 [7]	298.15 K	2.2257	2.1989 [9], 2.2270 [10]
			260.05 [7]	308.15 K	1.8751	1.8467 [9], 1.8710 [10]
			255.15 [8]	318.15 K	1.5992	1.5744 [9], 1.5980 [10]
Ethyl decanoate	≥0.98	254.35	255.18 [11]	298.15 K	2.4452	2.4447 [10]
			253.35 [12]	308.15 K	2.0472	2.0482 [10]
				318.15 K	1.7454	1.7453 [10]
Methyl dodecanoate	≥0.98	278.75	278.2 [7]	298.15 K	3.2221	3.2263 [9], 3.2614 [10]
			278.45 [7]	308.15 K	2.6513	2.6390 [9], 2.6685 [10]
			278.35 [8]	318.15 K	2.2163	2.2067 [9], 2.2287 [10]
Methyl tetradecanoate	≥0.98	292.55	291.8 [7]	298.15 K	4.6103	4.6088 [9], 4.6105 [10]
			291.55 [7]	308.15 K	3.6953	3.6144 [9], 3.6975 [10]
			292.15 [8]	318.15 K	3.0301	2.9995 [9], 3.0303 [10]

[a] Standard uncertainties u are u(ν)=0.001 $mm^2 \cdot s^{-1}$, u(T)=0.01 K. The range of Ubbelehode viscometer utilized in this experiment was approximately 1.2 to 10 $mm^2 \cdot s^{-1}$

glass column to inhibit moisture freezing on the walls of the cell. The cooling or heating fluids were channeled through the center jacket not only for cooling/heating the sample mixture but also insulation from the environment. The sample in the inmost equilibrium cell was continuously mixed rigorously using a magnetic stirrer. The nitrogen gas was purged in the equilibrium cell for dehumidification [13-15]. The heating and cooling involved circulating media from a cryostat. The sample mixtures were gravimetrically prepared using an analytical microbalance (OHAUS Co. DV215CD). The standard uncertainty in sample preparation was ±0.0002 in terms of mole fraction. The innermost equilibrium cell with sample mixture was dipped into and out very shortly in liquid nitrogen in order to make a solid crystal. Then the sample in the equilibrium cell was heated at a heating rate of 3 K h^{-1} very carefully by circulating cooling/heating media from the cryostat until the last crystal of the sample was melted completely and this (pseudo) melting temperature was noted. The temperature of cryostat was fixed with above noted melting temperature, the same procedure (crystallization and melting of the same sample) was carried out. Then we took temperature visually at the instant when the last crystal of the sample wiped out again as the true SLE temperature for this sample. The temperature in the cell was measured with platinum resistance thermometer from Automatic System Laboratories (F250, UK); the estimated temperature uncertainty due to the thermometer and the temperature fluctuation of the bath during temperature measurement was ±0.02 K for the SLE temperature determination.

The v values were measured using apt Ubbelohde viscometers (SI Analytics GmbH, model 530 10, Germany, measurement ranges of 1.2 to 10 $mm^2 \cdot s^{-1}$) placed in water thermostat (Lauda MD 20). The viscometer was immersed in the thermostat for 35 min to attain system temperature through adequate heat transfer [16]. After this the v data was calculated using the measured time taken for the flow of liquid from one mark to other mark in measuring cell. The accuracy in the measurement of flow time was 0.01 s. The average of four coincident readings of flow time was taken for the estimation of v values using the Eq. (1).

$$\nu_i = At_i - \frac{B}{t_i} \tag{1}$$

where t_i is the flow time. A and B are constants whose values were calculated in the manner described in our previous papers [5,6,17, 18]. A and B are the viscometer constant whose values vary with different temperature as: follows: at 298.15 K; A=9.954×10^{-3} $mm^2 \cdot s^{-2}$ and B=20.203 mm^2, at 308.15 K; A=10.713×10^{-3} $mm^2 \cdot s^{-2}$ and B= 40.848 mm^2 and at 318.15 K; A=10.733×10^{-3} $mm^2 \cdot s^{-2}$ and B=30.631 mm^2. The experimental data for kinematic viscosity of pure components were compared with literature data in Table 1. After considering the experimental systematic errors, the standard uncertainty in our experimental measured data was estimated as u(ν)=0.001 $mm^2 \cdot s^{-1}$, u(T)=0.01 K. The range of Ubbelehode viscometer utilized in this experiment was approximately 1.2 to 10 $mm^2 \cdot s^{-1}$. The ν values for binary mixtures are tabulated in Table 4. These v values were used to evaluate $\Delta\nu$ values.

RESULTS AND DISCUSSION

At the solid liquid equilibrium, the fugacity of component in the liquid phase must be equal to the fugacity of the same component in the solid phase: $f_i^s = f_i^l$. After some simplification, the following Eq. (2) was obtained for determining SLE for eutectic system at constant pressure conditions, and it involved the properties of pure solute, such as enthalpy of fusion, melting temperature, and so forth [19].

$$x_i = \frac{1}{\gamma_i}\exp\left\{\frac{\Delta H^{fus}}{R}\left(\frac{1}{T_{m,i}} - \frac{1}{T}\right) + \frac{\Delta H^{trs}}{R}\left(\frac{1}{T_{trs}} - \frac{1}{T}\right)\right\} \tag{2}$$

In the present two-component miscible system, the last term in Eq. (2) may be ignored and simplified to Eq. (3).

$$x_i = \frac{1}{\gamma_i}\exp\left\{\frac{\Delta H^{fus}}{R}\left(\frac{1}{T_{m,i}} - \frac{1}{T}\right)\right\} \tag{3}$$

where x_i is the mole fraction in the liquid phase, γ_i is the activ-

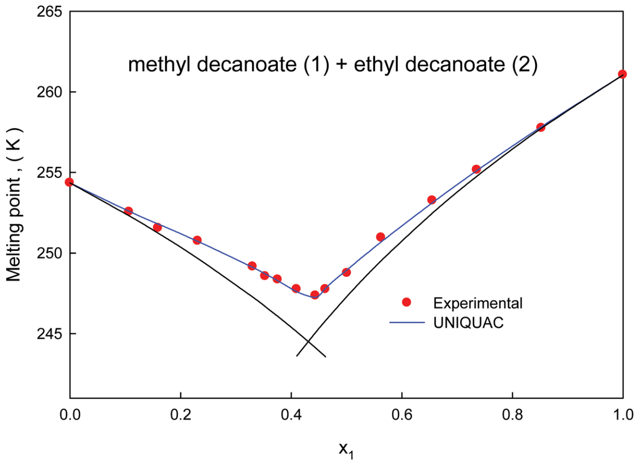

Fig. 1. SLE for the system methyl decanoate (1)+ethyl decanoate (2). Solid (black) line represents ideal behavior.

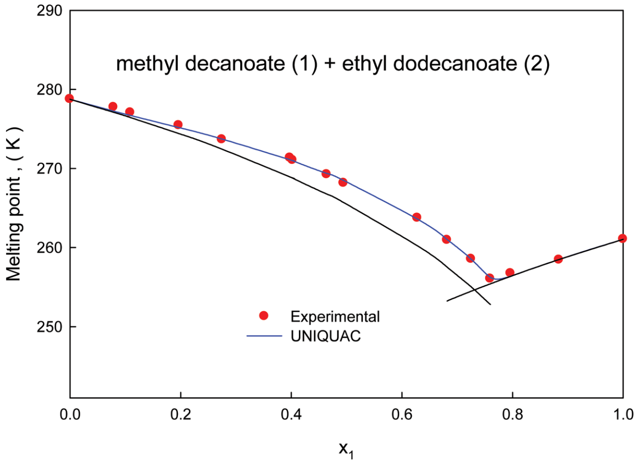

Fig. 2. SLE for the system methyl decanoate (1)+methyl dodecanoate (2). Solid (black) line represents ideal behavior.

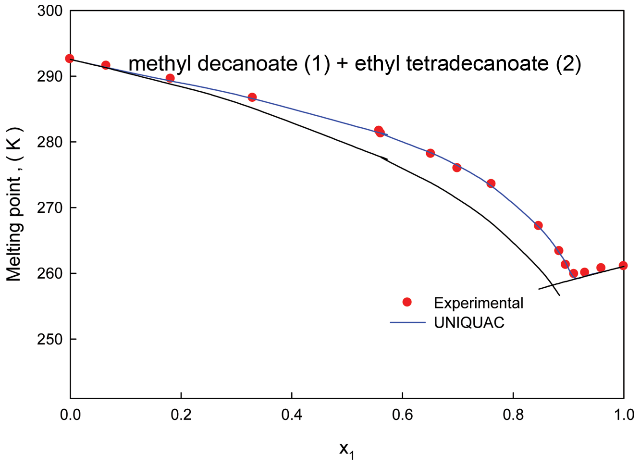

Fig. 3. SLE for the system methyl decanoate (1)+methyl tetradecanoate (2). Solid (black) line represents ideal behavior.

Table 2. The SLE data for three binary systems

x_1	T/K	x_1	T/K	x_1	T/K
Methyl decanoate (1)+ethyl decanoate (2)					
0.0000	254.35	0.3759	248.35	0.6555	253.25
0.1071	252.55	0.4101	247.75	0.7358	255.15
0.1594	251.55	0.4440	247.35	0.8525	257.75
0.2313	250.75	0.4620	247.75	1.0000	261.05
0.3305	249.15	0.5010	248.75		
0.3530	248.55	0.5629	250.95		
Methyl decanoate (1)+methyl dodecanoate (2)					
0.0000	278.75	0.4025	271.05	0.7598	256.05
0.0789	277.75	0.4643	269.25	0.7964	256.75
0.1093	277.05	0.4947	268.15	0.8840	258.45
0.1966	275.45	0.6281	263.75	1.0000	261.05
0.2748	273.65	0.6819	260.95		
0.3976	271.35	0.7252	258.55		
Methyl decanoate (1)+methyl tetradecanoate (2)					
0.0000	292.55	0.6519	278.15	0.9104	259.85
0.0654	291.55	0.6996	275.95	0.9302	260.05
0.1817	289.55	0.7613	273.55	0.9596	260.75
0.3299	286.65	0.8467	267.15	1.0000	261.05
0.5582	281.65	0.8836	263.35		
0.5613	281.25	0.8955	261.25		

Standard uncertainties u are u(x)=0.0002, u(T)=0.02 K

ity coefficient in the liquid phase, $\Delta H_{fus,i}$ is the molar enthalpy of fusion, $T_{fus,i}$ is the melting temperature, $\Delta H_{trs,i}$ is the molar enthalpy of transition, $T_{trs,i}$ is the transition temperature of component I, T is the absolute temperature, and R is the universal gas constant. The x_i, γ_i is the liquid phase mole fraction and the activity coefficient, respectively. The ΔH_{fus} values for methyl decanoate, ethyl decanoate, methyl dodecanoate and methyl tetradecanoate are 27,030 J/mol, 29,620 J/mol, 32,210.002 J/mol, 37,390.00 J/mol, respectively. The binary SLE diagram is made by plotting the cooling curves of the mixtures for different compositions (Fig. 1 to 3). The eutectic temperature is the lowest possible melting temperature over all of the mixing ratios for the involved component species. The SLE data for the studied binary mixtures are shown in Figs. 1-3 and tabulated in Table 2. More than 70% of all the organic binary mixtures showed single eutectic point like Figs. 1-3 (compare to metallic alloys). Therefore, the experimented systems showed general single eutectic point like other organic mixtures as usual. This may be due to enthalpic interactions (Gibbs free energy) between species like azeotrope formation. The experimental SLE values were also regressed with the UNIQUAC equation [4], which is shown in Figs. 1-3 with solid lines. Model interaction parameters (A_{ij}/cal·mol^{-1}) along with the root-mean-square deviation (RMSD) between experimental and regression data are listed in Table 3.

$$\mathrm{RMSD}=\sqrt{\frac{1}{n}\sum_{n}(T_{exp}-T_{calc.})^2} \tag{4}$$

The eutectic points calculated using UNIQUAC parameters are x_1=0.4440/T=247.35 K for the methyl decanoate (1)+ethyl decanoate (2), x_1=0.7598/T=256.05 K for methyl decanoate (1)+methyl

Table 3. The adjustable model parameters of UNIQUAC model and the RMSD for each binary system

Systems	A_{ij}/cal·mol^{-1}	A_{ji}/cal·mol^{-1}	RMSD
Methyl decanoate (1)+ethyl decanoate (2)	−212.169	325.496	0.13
Methyl decanoate (1)+methyl dodecanoate (2)	−249.786	371.896	0.23
Methyl decanoate (1)+methyl tetradecanoate (2)	−179.254	270.057	0.30

Table 4. Experimental kinematic viscosity (ν) and deviation in kinematic viscosity ($\Delta\nu$) of binary mixtures at 298.15 K, 308.15 K and 318.15 K

x_1	298.15 K		308.15 K		318.15 K	
	ν/mm^2·s^{-1}	$\Delta\nu$/mm^2·s^{-1}	ν/mm^2·s^{-1}	$\Delta\nu$/mm^2·s^{-1}	ν/mm^2·s^{-1}	$\Delta\nu$/mm^2·s^{-1}
Methyl decanoate (1)+ethyl decanoate (2)						
0.0000	2.4452	0.0000	2.0472	0.0000	1.7454	0.0000
0.1071	2.4091	−0.0126	2.0212	−0.0076	1.7244	−0.0054
0.2313	2.3773	−0.0171	1.9965	−0.0109	1.7042	−0.0074
0.3613	2.3475	−0.0184	1.9732	−0.0119	1.6846	−0.0080
0.4613	2.3256	−0.0183	1.9561	−0.0117	1.6700	−0.0080
0.5504	2.3073	−0.0171	1.9416	−0.0109	1.6574	−0.0076
0.6551	2.2859	−0.0155	1.9249	−0.0096	1.6427	−0.0069
0.8036	2.2574	−0.0114	1.9015	−0.0073	1.6236	−0.0043
0.9072	2.2401	−0.0060	1.8870	−0.0041	1.6107	−0.0021
0.9422	2.2351	−0.0032	1.8825	−0.0025	1.6064	−0.0012
1.0000	2.2257	0.0000	1.8751	0.0000	1.5992	0.0000
Methyl decanoate (1)+methyl dodecanoate (2)						
0.0000	3.2221	0.0000	2.6513	0.0000	2.2163	0.0000
0.1093	3.0869	−0.0263	2.5472	−0.0192	2.1366	−0.0121
0.1876	2.9919	−0.0433	2.4725	−0.0332	2.0789	−0.0216
0.2748	2.8877	−0.0606	2.3898	−0.0482	2.0138	−0.0329
0.3678	2.7813	−0.0743	2.3079	−0.0578	1.9465	−0.0428
0.4947	2.6453	−0.0839	2.2031	−0.0642	1.8652	−0.0458
0.6593	2.4866	−0.0786	2.0832	−0.0564	1.7697	−0.0398
0.7897	2.3773	−0.0579	2.0001	−0.0383	1.7007	−0.0283
0.8586	2.3256	−0.0409	1.9601	−0.0247	1.6690	−0.0175
0.9237	2.2789	−0.0228	1.9211	−0.0132	1.6387	−0.0076
1.0000	2.2257	0.0000	1.8751	0.0000	1.5992	0.0000
Methyl decanoate (1)+methyl tetradecanoate (2)						
0.0000	4.6103	0.0000	3.6953	0.0000	3.0301	0.0000
0.0654	4.4231	−0.0312	3.5547	−0.0214	2.9244	−0.0121
0.1817	4.1077	−0.0693	3.3081	−0.0564	2.7379	−0.0322
0.3299	3.7230	−0.1005	3.0199	−0.0748	2.5102	−0.0478
0.5313	3.2292	−0.1141	2.6418	−0.0864	2.2162	−0.0537
0.6519	2.9494	−0.1065	2.4306	−0.0781	2.0468	−0.0505
0.7613	2.7068	−0.0882	2.2431	−0.0666	1.9003	−0.0404
0.8467	2.5233	−0.0681	2.1032	−0.0510	1.7868	−0.0319
0.9104	2.3922	−0.0471	2.0032	−0.0350	1.7062	−0.0211
0.9596	2.2903	−0.0316	1.9271	−0.0215	1.6438	−0.0132
1.0000	2.2257	0.0000	1.8751	0.0000	1.5992	0.0000

[a]Standard uncertainties u are u(ν)=0.001 mm^2·s^{-1}, u(T)=0.01 K. The range of Ubbelehode viscometer utilized in this experiment was approximately 1.2 to 10 mm^2·s^{-1}

dodecanoate (2) systems and x_1=0.9104/T=259.85 K for methyl decanoate (1)+methyl tetradecanoate (2) systems, respectively. As the chain length of alkyl alkanoate increases, eutectic temperature increases due to increase in the magnitude of van der Waal interactions. Also, eutectic temperature occurs at higher mole fraction of methyl decanoate with increase in chain length of second component.

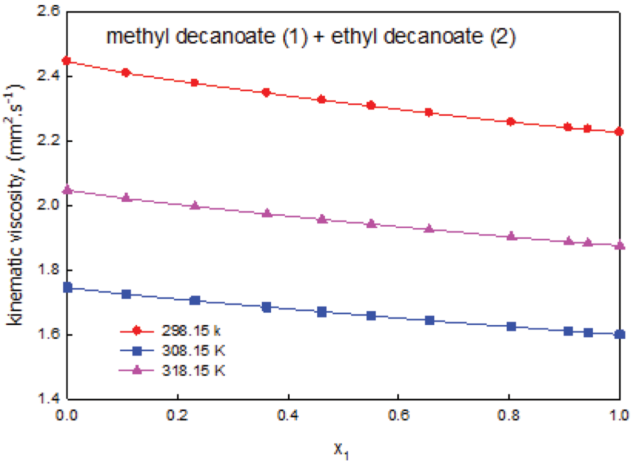

Fig. 4. Kinematic viscosity, ν (mm^{2}s^{-1}) of binary mixtures methyl decanoate (1)+ethyl decanoate (2) at 298.15 K, 308.15 K and 318.15 K.

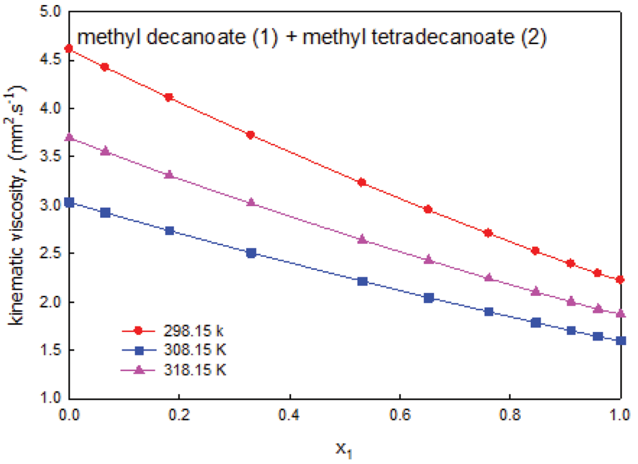

Fig. 6. Kinematic viscosity, ν (mm^{2}s^{-1}) of binary mixture of methyl decanoate (1)+methyl tetradecanoate (2) at 298.15 K, 308.15 K and 318.15 K.

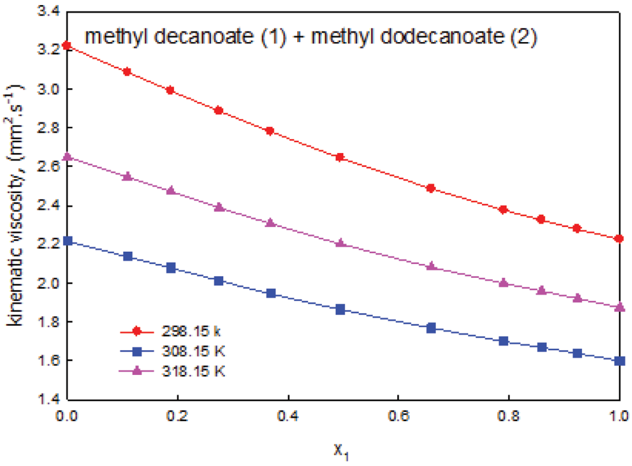

Fig. 5. Kinematic viscosity, ν (mm^{2}s^{-1}) of binary mixture of methyl decanoate (1)+methyl dodecanoate (2) at 298.15 K, 308.15 K and 318.15 K.

1. Viscosity

The measured ν values at different temperatures (T=298.15 K-318.15 K) are in Table 4 and shown in Figs. 4-6. The higher value of ν for ester with longer chain is because of the strong interaction of longer carbon chain as compared to shorter chain length molecule. The ν values decrease with increase in temperature due to weakening of intermolecular physical interactions at the higher temperature. These ν values were used to derive $\Delta\nu$ values (Table 4) using Eq. (5).

$$\Delta\nu = \nu_{mix} - \sum_i x_i \nu_i \qquad (5)$$

The $\Delta\nu$ values were fitted with Redlich-Kister equation [20].

$$\Delta\nu = x_1 x_2 \left[\sum_{j=1}^{n} A_j (x_2 - x_1)^{j-1}\right] \qquad (6)$$

The adjustable parameters (A_j) of Eq. (6) and the standard deviations ($\sigma(\Delta\nu)$) obtained by means of Eq. (7) are tabulated in Table 5.

$$\sigma(\Delta\nu) = \{[\sum(\Delta\nu_{exp.} - \Delta\nu_{calc.(Eq.\ (6))})^2]/(m-n)\}^{1/2} \qquad (7)$$

where m is number of experimental data points and n is number of adjustable parameters used in Eq. (6).

From Figs. 7-9 we can see that the $\Delta\nu$ values decrease due to weakening of intermolecular physical interactions at higher temperature. All three binary mixture shows negative $\Delta\nu$ values as shown in Fig. 10-12. The negative deviation in kinematic viscosity for all studied binary mixtures indicates that the dispersion forces are predomi-

Table 5. Redlich-Kister equation parameters for deviation in kinematic viscosity and standard deviation $\sigma(\Delta\nu)$

System	T/K	A_1	A_2	A_3	A_4	$\sigma(\Delta\nu)$
Methyl decanoate (1)+ ethyl decanoate (2)	298.15 K	−0.0709	0.0141	−0.0458	0.0397	0.0003
	308.15 K	−0.0451	0.0138	−0.0289	0.0092	0.0002
	318.15 K	−0.0314	0.0060	−0.0144	0.0221	0.0001
Methyl decanoate (1)+ methyl dodecanoate (2)	298.15 K	−0.338	−0.0589	0.0591	0.0306	0.0003
	308.15 K	−0.2584	−0.0059	0.0972	0.0112	0.0005
	318.15 K	−0.1872	−0.0073	0.0942	−0.0011	0.0011
Methyl decanoate (1)+ methyl tetradecanoate (2)	298.15 K	−0.4505	0.0020	−0.1175	−0.1055	0.0033
	308.15 K	−0.3386	0.0119	−0.0942	−0.0771	0.0021
	318.15 K	−0.2041	0.0154	0.0048	−0.0967	0.0014

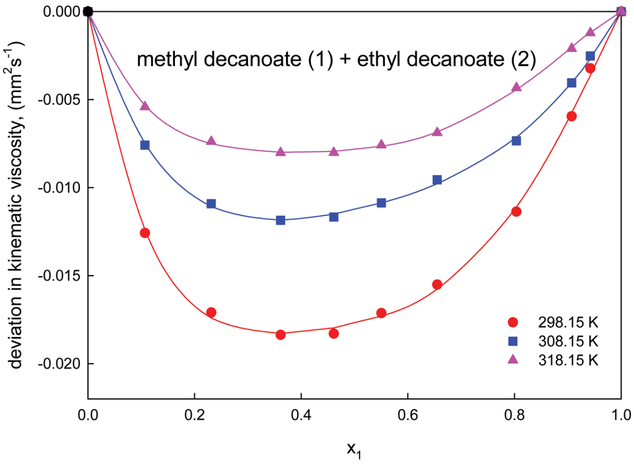

Fig. 7. Deviation in kinematic viscosity, $\Delta\nu$ (mm^{2}s^{-1}) of binary mixtures methyl decanoate (1)+ethyl decanoate (2) at 298.15 K, 308.15 K and 318.15 K.

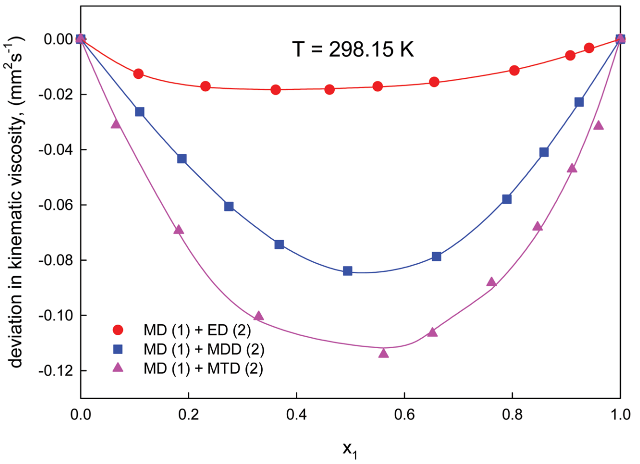

Fig. 10. Deviation in kinematic viscosity, $\Delta\nu$ (mm^{2}s^{-1}) of binary mixtures at 298.15 K.

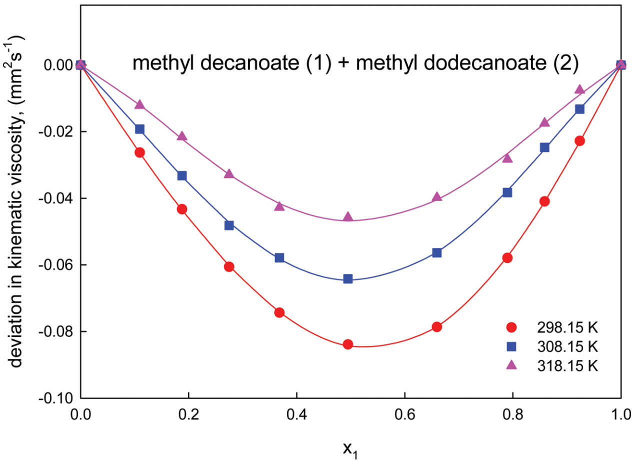

Fig. 8. Deviation in kinematic viscosity, $\Delta\nu$ (mm^{2}s^{-1}) of binary mixture of methyl decanoate (1)+methyl dodecanoate (2) at 298.15 K, 308.15 K and 318.15 K.

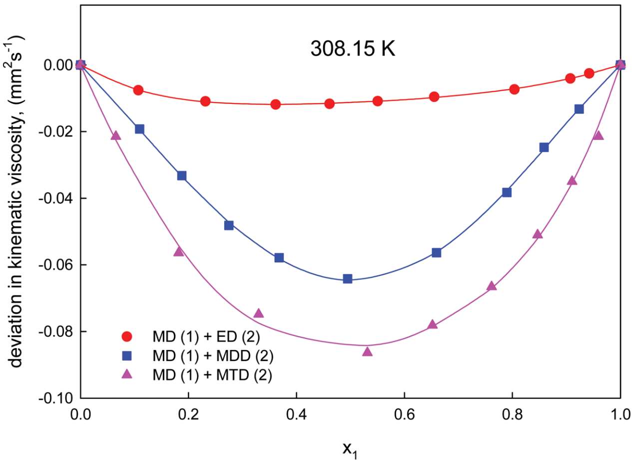

Fig. 11. Deviation in kinematic viscosity, $\Delta\nu$ (mm^{2}s^{-1}) of binary mixtures at 308.15 K.

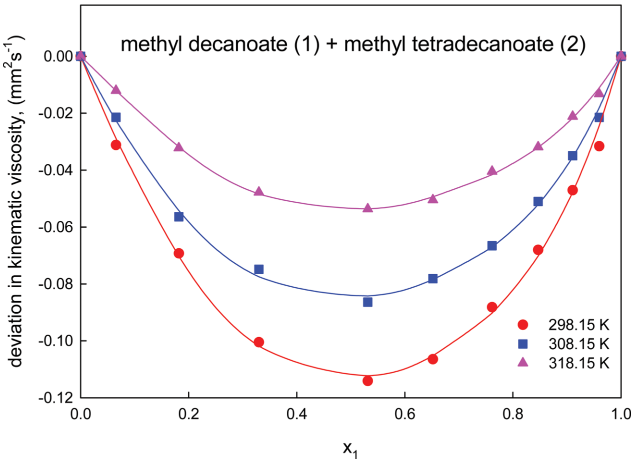

Fig. 9. Deviation in kinematic viscosity, $\Delta\nu$ (mm^{2}s^{-1}) of binary mixture of methyl decanoate (1)+methyl tetradecanoate (2) at 298.15 K, 308.15 K and 318.15 K.

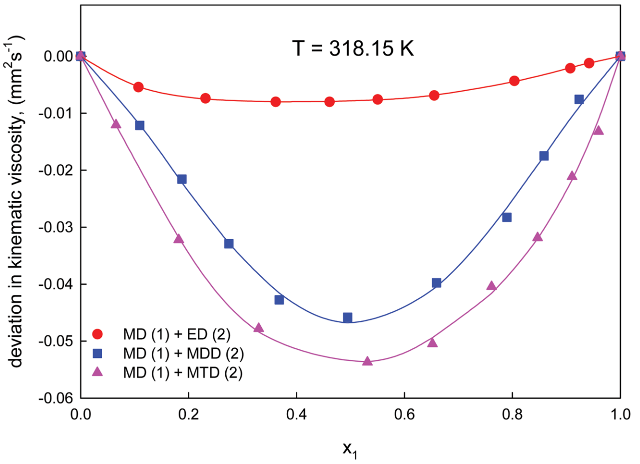

Fig. 12. Deviation in kinematic viscosity, $\Delta\nu$ (mm^{2}s^{-1}) of binary mixtures at 318.15 K.

Table 6. McIlister equation parameters and standard deviation $\sigma(\Delta\nu)$

System	T/K	ν_{12}	ν_{21}	$\sigma(\Delta\nu)$
Methyl decanoate (1)+ ethyl decanoate (2)	298.15 K	2.3182	2.3039	0.1278
	308.15 K	1.9484	1.9433	0.1007
	318.15 K	1.6648	1.6606	0.1162
Methyl decanoate (1)+ methyl dodecanoate (2)	298.15 K	2.4890	2.7966	0.3902
	308.15 K	2.0928	2.3180	0.4910
	318.15 K	1.7793	1.9589	0.5274
Methyl decanoate (1)+ methyl tetradecanoate (2)	298.15 K	3.0744	3.5999	0.1497
	308.15 K	2.5214	2.9239	0.2155
	318.15 K	2.1340	2.4383	0.3219

nant in the mixture. Order of magnitude of $\Delta\nu$ is as follows: methyl decanoate (1)+methyl tetradecanoate (2)>methyl decanoate (1)+ methyl dodecanoate (2)>methyl decanoate (1)+ethyl decanoate (2). Large negative deviation in methyl decanoate (1)+methyl tetradecanoate (2) is due to the longer carbon chain of methyl tetradecanoate, which breaks the methyl decanoate molecules to a larger extent.

The ν values were been correlated with McAllister semi-empirical equation [5,6] given below: (8)

$$\begin{aligned}\ln\nu=&x_1^3\ln\nu_1+3x_1^2x_2\ln\nu_{12}+3x_1x_2^2\ln\nu_{21}+x_2^3\ln\nu_2\\&-\ln[x_1+x_2M_2/M_1]+3x_1^2x_2\ln[(1+2M_2/M_1)/3]\\&+3x_1x_2^2\ln[(1+2M_2/M_1)/3]+x_2^3\ln[M_2/M_1]\end{aligned} \tag{8}$$

M_1 and M_2 are the molar mass of pure components, ν_{12} and ν_{21} are the adjustable parameters, which were determined by fitting kinematic viscosity-composition data to Eq. (8). ν_1, ν_2 and ν are the kinematic viscosities of pure components and the binary liquid mixture, respectively.

The adjustable parameters (ν_{12} and ν_{21}) of Eq. (8) and their standard deviation obtained using Eq. (16) are mentioned in Table 6. The ν data were interrelated using different equations recommended by Heric-Brewer, Krishnan-Ladda, Lulian et al.

Heric-Brewer [21] equation:

$$\ln(\nu M)=x_1\ln(\nu_1M_1)+x_2\ln(\nu_2M_2)+x_1x_2[A_1+A_2(x_1-x_2)+A_3(x_1-x_2)^2] \tag{9}$$

where A_1, A_2 and A_3 are unknown binary constants.

Krishnan-Ladda [22]

$$\begin{aligned}\ln(\nu)=&x_1\ln(\nu_1M_1)+x_2\ln(\nu_2M_2)-\ln(x_1M_1+x_2M_2)\\&-2.303x_1x_2[B_1+B_2(x_1-x_2)+B_3(x_1-x_2)^2+B_4(x_1-x_2)^3]\end{aligned} \tag{10}$$

where B_1, B_2, B_3 and B_4 are unknown binary constants.

Lulian et al. [23,24].

$$\begin{aligned}\ln(\nu)=&x_1\ln(\nu_1M_1)+x_2\ln(\nu_2M_2)-\ln(x_1M_1+x_2M_2)\\&-x_1x_2[C_1+C_2(x_1-x_2)+C_3(x_1-x_2)^2+C_4(x_1-x_2)^3]\end{aligned} \tag{11}$$

The unknown constants C_1, C_2, C_3 and C_4 mentioned in Eqs. (9), (10) and (11) were evaluated using experimental data.

The percentage standard deviation ($\sigma(\%)$) was obtained using the following equation:

$$\sigma(\%)=100\times\left[\frac{\sum\{(\nu_{exp.}-\nu_{calcd})/\nu_{exp.}\}^2}{(n-1)}\right]^{1/2} \tag{12}$$

The prediction capability of ν data using Eq. (9), (10) and (11) was estimated in terms of ($\sigma(\%)$) calculated using Eq. (12) (Table 7).

Table 7. Percentage standard deviation of calculated values of kinematic viscosity (ν) using various correlation Heric-Brewer, Krishnan-Ladda, Lulian et al. at 298.15 K, 308.15 K and 318.15 K

System	T/K	H-B	K-L	Lu
Methyl decanoate (1)+ ethyl decanoate (2)	298.15	0.025	0.011	0.047
	308.15	0.009	0.008	0.056
	318.15	0.095	0.004	0.004
Methyl decanoate (1)+ methyl dodecanoate (2)	298.15	0.024	0.011	0.349
	308.15	0.027	0.020	0.020
	318.15	0.191	0.051	0.051
Methyl decanoate (1)+ methyl tetradecanoate (2)	298.15	0.144	0.119	0.206
	308.15	0.102	0.079	0.079
	318.15	0.182	0.054	0.054

CONCLUSIONS

The SLE and kinematic viscosity (ν) at (T=298.15, 308.15, 318.15 K) of the binary mixture methyl decanoate ($C_{11}H_{22}O_2$) (1)+ethyl decanoate ($C_{12}H_{24}O_2$) or methyl dodecanoate ($C_{13}H_{26}O_2$) or methyl tetradecanoate ($C_{15}H_{30}O_2$) (2) were determined. The SLE values correlated well with UNIQUAC model. The eutectic points calculated from the UNIQUAC parameters are $x_1=0.4440/T=247.35$ K for the methyl decanoate (1)+ethyl decanoate (2), $x_1=0.7598/T=256.05$ K for methyl decanoate (1)+methyl dodecanoate (2) systems and $x_1=0.9104/T=259.85$ K for methyl decanoate (1)+methyl tetradecanoate (2) systems, respectively. The ν values of above binary system were measured at (T=298.15 K to 318.15 K) that were used to derive $\Delta\nu$. The higher value of ν for ester with longer chain is because of the strong interaction of longer carbon chain as compared to shorter chain length molecule. The ν data were interrelated using different equations. Theoretically, estimated data using these empirical equations is in accordance with the experimental data with $\sigma(\%)$ less than 0.35.

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