

Viscometric Studies of the Thermodynamic Properties of Binary Mixtures of a Ketoester and some Straight and Branched Chain Aliphatic Ketones at 298.15 K

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Abstract

The kinematic viscosities of the binary mixtures of ethyl acetoacetate with butan-2-one, pentan-3-one, 3-methylbutan-2-one and 4-methylpentan-2-one have been determined using single capillary Ostwald viscometer at various range of solvent composition at 298.15 K. The corresponding dynamic viscosities, η , at the different compositions were calculated from the experimental kinematic viscosity data. The excess viscosities, η^E of the binary mixtures and excess Gibbs free energies of activation for viscous flow, G^{*E} , were derived from the dynamic viscosities and molar volumes of the mixtures. The values of η^E and G^{*E} obtained were fitted to a Redlich-Kister type polynomial to derive their coefficients and standard deviations. These parameters have been discussed in terms of the nature of the molecular interactions and structural effects due to the components of binary mixtures. The excess viscosities, η^E were negative throughout the entire range of solvents composition. The negative excess viscosities were attributed to dispersion forces in the solvent systems. The values of the excess Gibbs free energies of activation for viscous flow, G^{*E} , were all positive in the ethyl acetoacetate + 4-methylpentan-2-one solvent system while in the binary mixtures of ethyl acetoacetate + pentan-3-one and the excess Gibbs free energies of activation for viscous flow were positive at lower EAA concentrations and negative at higher EAA concentrations. The values of G^{*E} in the binary mixtures of EAA and 3-methylbutan-2-one were entirely negative over the range of solvents composition, and negative at lower EAA concentrations for EAA + butan-2-one and positive at higher EAA concentrations. The viscosity data were correlated using some semi-empirical one-parameter polynomial proposed by Frenkel, Hind, Grunberg-Nissan and Kendall and Monroe. The viscosity data were interpreted on the basis of intermolecular interactions between unlike and like molecules of the mixtures.

Keywords: Intermolecular interactions, Ketoesters, Ketones, Kinematic viscosities, Excess viscosities, Excess Gibbs free energies of activation for viscous flow.

Introduction

We have developed kin interest in the study of intermolecular interactions taking place in ketoesters and selected carbonyl compounds. Arising from our studies, we have published our results on the volumetric behavior of binary mixtures of ethylacetoacetate, a ketoester, and some named aliphatic ketones¹. The results show that the volumetric behaviors of binary mixtures of these solvent systems were both physical and chemical in nature. The interstitial fitting of smaller ketone molecules into the larger molecular volumes of ethylacetoacetate accounted for the physical contribution. However, in some regions in solvent composition, dipole-dipole interactions accounted for the chemical behavior for the binary mixtures. Viscosity data also provide some potent thermodynamic information on the structure of liquids and are required in the design of many chemical and industrial processes which involve mass transfer, fluid flow, etc., and for the interpretation of intermolecular interactions in binary mixed solvents². Therefore, in continuation of our studies in these binary solvent systems, we provide in this paper the thermodynamic viscosity data in these solvent systems. We report here the viscosity data obtained in various binary mixtures of ethylacetoacetate (EAA) and the named aliphatic ketones with a view to providing excess viscosities, η^E and excess Gibbs free energies of activation for viscous flow, G^{*E} data for the binary mixtures at 298.15 K. Amalendu and Gaba³ have reported viscosities of binary liquid mixtures of some n-alkoxypropanols with methanol, ethanol and 1-propanol at 298.15K, Rathnam et al⁴ have studied the viscosities and Kemeakegha et al⁵ have undertaken a viscometric study of binary mixtures of ethylacetoacetate (EAA) with (C₄-C₉) aliphatic ketones at 298.15K. These excess functions have been used to interpret the mixing behavior of these solvents. The excess viscosity data obtained have also been correlated with some empirical equations such as that of Redlich Kister in order to obtain the standard deviations of mixing.

Experimental

Materials. The reagents, ethyl acetoacetate and 4-methylpentan-2-one were products of Riedel-De Haenag Seelze Hannover, Germany. Pentan-3-one and 3-methylbutan-2-one, products of BDH, England, were of analytical grade. Butan-2-one of purified grade was a product of Merck, Germany. All the solvents were dried using molecular sieves and the pure solvents recovered via distillation.

The densities of the pure solvents were determined according to our previous procedure¹. The mole fractions of the mixtures ranged from 0.0003 to 0.9994 composition of ethyl acetoacetate and were calculated as previously described¹. The purities of the pure solvents were checked by comparing the experimental values of their densities and viscosities with those reported in the literature as shown in Table 1.

The kinematic viscosities, ν , of the pure solvents and the binary mixtures were determined at 298.15 K using an Ostwald viscometer which was calibrated with deionized water at the working temperature. The viscometer containing a known volume of the liquid was allowed to attain thermal equilibrium in a thermostated water bath maintained at 298.15 K. The flow times of the mixture was recorded with an electronic stop watch with a precision of ± 0.01 s. Three sets of flow times were taken for each solvent mixture and an average flow time obtained which was used to calculate the kinematic viscosity at each mixture composition. Values of the kinematic viscosities so obtained were converted to dynamic viscosities, η .

Results and discussion

The experimentally determined kinematic viscosities of mixtures of EAA and the aliphatic ketones were calculated from the flow – time data using equation 1. The viscometer constant k was obtained at the working temperature from the calibration data.

$$\nu = kt \quad (1)$$

In equation 1, ν is kinematic viscosity, k is viscometer constant and t , the flow time of the mixture through viscometer capillary.

The dynamic viscosities (η) of the binary mixtures were calculated from the measured kinematic viscosities and densities (ρ) using equation 2 and are shown in Table 2. In equation 2, ρ is the density of the solvent at the working temperature.

$$\eta = \nu\rho \quad (2)$$

The excess viscosities, η^E , and excess Gibbs free energies of activation for viscous flow, G^{*E} of the various binary mixtures of the solvent systems were calculated using equations 3 and 4 respectively.

$$\eta^E = \eta - (x_1\eta_1 - x_2\eta_2) \quad (3)$$

$$G^{*E} = RT\ln\eta - [l\eta V - (x_1\ln\eta_1V_1 + x_2\ln\eta_2V_2)] \quad (4)$$

In equations 3 and 4, X_1 is the mole fraction of EAA while X_2 is the mole fraction of the named aliphatic ketone. η_1 , η_2 and η are the dynamic viscosities (mPa.s) of EAA, the aliphatic ketones and mixtures respectively while V_1 , V_2 and V are the corresponding molar volumes. R is the universal gas constant and T , absolute temperature in Kelvin. V is obtained from the molar masses and mole fractions of the pure solvents as indicated in equation 5.

$$V = \frac{x_1 M_1 + x_2 M_2}{\rho} \tag{5}$$

where M_1 is the molar mass of EAA; M_2 , the molar mass of the named ketone; and ρ is the density of the binary mixtures. The calculated excess viscosities and excess Gibbs free energies of activation for viscous flow of the solvent systems over the entire solvents composition range are shown in Tables 3. The values of η^E and G^{*E} obtained were fitted into the Redlich – Kister⁶ polynomial (equation 6).

$$Y^E = x(1 - x) \sum_{i=0}^n A_i (2x - 1)^i \tag{6}$$

where Y^E represents η^E or G^{*E} , n is the number of coefficients and A_i , the fitting coefficients. The method of least-squares was employed to determine the values of the coefficients which are given in Tables 4 along with the standard deviations (σY^E) of the mixed solvent systems defined by equation 7.

$$\sigma Y^E = \sqrt{\frac{\sum(Y^E \text{ expt.} - Y^E \text{ calc.})^2}{m - n}} \tag{7}$$

In Eq. 7, m is the number of experimental data points and n , the number of coefficients, which was considered to be 4 in this present calculations.

Table 1: Densities, ρ and dynamic viscosities, η , of pure solvents at 298.15 K.

Solvents	Acronym	ρ (g/cm ³)		η (mPa.s)	
		Exp.	Lit	Exp.	Lit.
Butan-2-one	2-BUT	0.7980	0.7997 ^a , 0.7996 ^c	0.3836	0.385 ^c , 0.386 ^d , 0.381 ^e
Pentan-3-one	3-PEN	0.8182	0.8095 ^a , 0.8015 ^b , 0.80932 ^d ,	0.4416	0.446 ^c , 0.442 ^d , 0.443 ^e
3-methyl butan-2-one	3-MBUT-2	0.8081	0.8081 ^a , 0.8076 ^b ,	0.4436	0.435 ^c , 0.438 ^d , 0.450 ^e
4-methyl pentan-2-one	4-MPENT-2	0.7980	0.7961 ^a , 0.8010 ^b , 0.7961 ^d	0.5505	0.543 ^c , 0.541 ^d , 0.542 ^e
Ethylaceto	EAA	1.0202	1.0213 ^a , 1.0213 ^b	1.6768	

acetate

^a[26], ^b[27], ^c[28], ^d[29] and ^e[30]. Numbers refer to references.

Table 2: Dynamic viscosities, η (mPa.s) of binary mixtures of ethyl acetoacetate (EAA) and (C₄ – C₆) aliphatic ketones at 298.15 K.

X_1	Butan -2-one	Pentan -3-one	3-methyl butan-2- one	4-methyl pentan-2- one
0.0003	0.3836	0.4416	0.4436	0.5505
0.0998	0.5852	0.5862	0.6201	0.7012
0.2020	0.7695	0.6910	0.7036	0.7753
0.3010	0.9023	0.8213	0.7984	0.8482
0.3999	1.0417	0.9408	0.9003	0.9462
0.5052	1.1587	1.0549	1.0199	1.0479
0.6011	1.2596	1.1902	1.1758	1.1606
0.7029	1.3599	1.3008	1.3245	1.2929
0.7990	1.4591	1.4369	1.4615	1.4167
0.8971	1.6475	1.5912	1.6064	1.589
0.9994	1.6758	1.6537	1.7285	1.7013

Table 3: Excess viscosities, (η^E) and excess Gibbs free energy of activation of viscous flow (G^{*E}) of binary mixtures of ethyl acetoacetate and (C₄ – C₆) aliphatic ketones at 298.15 K.

Mole fraction of Ethylacetoacetate (EAA) X_1	Excess viscosity (η^E) mPa s	Excess Gibbs free energy (G^{*E}) J mol ⁻¹
EAA + Butan – 2 – one		
0.0003	0.0000	0.0000
0.0998	-0.0809	-0.3974
0.2020	-0.1804	-0.8925
0.3010	-0.2723	-1.4432
0.3999	-0.3033	-1.5494
0.5052	-0.2633	-0.9507
0.6011	-0.1979	-0.0738
0.7029	-0.1202	0.7441
0.7990	-0.0608	1.0415
0.8971	-0.0219	0.7238
0.9994	0.0000	0.0000
EAA + Pentan – 3 – one		
0.0003	0.0000	0.0000
0.0998	-0.0986	7.0087
0.2020	-0.1886	10.828
0.3010	-0.2685	9.0131
0.3999	-0.3054	5.7685

0.5052	-0.3197	2.6486
0.6011	-0.2890	-0.2533
0.7029	-0.2153	-2.8364
0.7990	-0.1334	-4.4569
0.8971	-0.0618	-3.5979
0.9994	0.0000	0.0000
EAA + 3 - Methylbutan – 2 – one		
0.0003	0.0000	0.0000
0.0998	-0.1466	-1.3172
0.2020	-0.2416	-2.5365
0.3010	-0.2935	-3.6011
0.3999	-0.3238	-4.1301
0.5052	-0.3152	-4.2659
0.6011	-0.2720	-4.0744
0.7029	-0.1854	-3.4006
0.7990	-0.1118	-2.4829
0.8971	-0.0515	-1.4649
0.9994	0.0000	0.0000
EAA + 4 - Methylpentan – 2 – one		
0.0003	0.0000	0.0000
0.0998	-0.1702	4.7311
0.2020	-0.2768	8.4177
0.3010	-0.3399	10.548
0.3999	-0.3648	10.465
0.5052	-0.3463	8.3342
0.6011	-0.2768	5.9345
0.7029	-0.1969	3.7494
0.7990	-0.1313	1.8642
0.8971	-0.0616	0.6371
0.9994	0.0000	0.0000

Table 4: Coefficients of Redlich-Kister equation and standard deviation values for ($\eta^E/\text{mPa}\cdot\text{s}$) and G^{*E} (Jmol^{-1}) of the binary mixtures of EAA and ($C_4 - C_6$) aliphatic ketones at 298.15 K

Parameters	A_0	A_1	A_2	A_3	σ
EAA + Butan – 2 – one					
η^E (mPa s)	-1.7623	0.0076	0.4897	-0.0013	0.003
G^{*E} (J mol^{-1})	-6.5686	0.0917	4.5324	-0.0285	15.76
EAA + Pentan – 3 – one					
η^E (mPa s)	0.0101	-1.5179	1.9490	-0.4358	0.005
G^{*E} (J mol^{-1})	-2.6411	-0.1952	4.8726	-0.1673	3.036
EAA + 3 - Methylbutan – 2 – one					
η^E (mPa s)	0.0029	-2.1061	3.5448	-1.4484	0.005
G^{*E} (J mol^{-1})	0.0625	-17.927	19.445	-1.5425	0.046
EAA + 4 - Methylpentan – 2 – one					
η^E (mPa s)	0.0092	-1.5913	2.1934	-0.6022	0.007
G^{*E} (J mol^{-1})	-2.0921	-0.1766	4.2142	-0.1428	0.138

Table 5: Viscosity data correlation parameters [Frenkel ($\ln\eta_{12}$), Hind (η_{12}), Grunberg-Nissan (d') and Kendall-Monroe ($E\eta_m$) of binary mixtures of ethylacetoacetate and named ketone solvent systems at 298.15 K

X_1	$\ln\eta_{12}$	η_{12}	d'	$E\eta_m$ (mPa.s)
Ethyl acetoacetate (1) + Butan-2-one (2)				
0.0003	0.0000	0.0000	0.0000	0.0000
0.0998	0.0425	0.2276	-9.1538	0.1454
0.2020	0.0762	0.4083	-4.0692	0.2427
0.3010	0.0994	0.5329	-1.9963	0.2949
0.3999	0.1134	0.6078	-0.8323	0.3125
0.5052	0.1181	0.6332	-0.0468	0.3005
0.6011	0.1133	0.6074	0.6094	0.2674
0.7029	0.0987	0.5289	1.4443	0.2146
0.7990	0.0759	0.4068	2.7801	0.1525
0.8971	0.0436	0.2338	6.9755	0.0807
0.9994	0.0000	0.0000	0.0000	0.0000
Ethyl acetoacetate (1) + Pentan-3-one (2)				
0.0003	0.0000	0.0000	0.0000	0.0000
0.0998	0.0316	0.2142	-10.982	0.1431
0.2020	0.0566	0.3843	-4.4784	0.2348
0.3010	0.0739	0.5016	-2.1485	0.2804
0.3999	0.0843	0.5722	-0.9134	0.2918
0.5052	0.0878	0.5959	-0.0057	0.2748
0.6011	0.0843	0.5716	0.8896	0.2397
0.7029	0.0734	0.4978	1.9251	0.1882
0.7990	0.0564	0.3829	3.7098	0.1307
0.8971	0.0324	0.2200	8.6016	0.0675
0.9994	0.0000	0.0000	0.0000	0.0000
Ethyl acetoacetate (1) + 3-methylbutan-2-one (2)				
0.0003	0.0000	0.0000	0.0000	0.0000
0.0998	0.0333	0.2163	-0.0012	0.1435
0.2020	0.0598	0.3880	-0.0009	0.2362
0.3010	0.0781	0.5065	-0.0006	0.2828
0.3999	0.089	0.5778	-0.0004	0.2952
0.5052	0.0927	0.6018	-0.0005	0.2790
0.6011	0.0889	0.5773	0.0002	0.2442
0.7029	0.0775	0.5028	0.0005	0.1924
0.7990	0.0596	0.3866	0.0007	0.1342
0.8971	0.0342	0.2222	0.0009	0.0695
0.9994	0.0000	0.0000	0.0000	0.0000
Ethyl acetoacetate (1) + 4-methylpentan-2-one (2)				
0.0003	0.0000	0.0000	0.0000	0.0000

0.0998	0.0423	0.2273	-9.2135	0.1454
0.2020	0.0758	0.4078	-4.0185	0.2426
0.3010	0.0990	0.5324	-2.2855	0.2946
0.3999	0.1129	0.6072	-1.2275	0.3122
0.5052	0.1176	0.6325	-0.4423	0.3000
0.6011	0.1128	0.6067	0.2761	0.2669
0.7029	0.0982	0.5284	1.2133	0.2142
0.7990	0.0756	0.4064	2.6126	0.1521
0.8971	0.0434	0.2335	6.6156	0.0804
0.9994	0.0000	0.0000	0.0000	0.0000

Table 8: Fitting parameters with Average Percentage Deviation (APD) values of the binary mixtures of ethyl acetoacetate and C₄ – C₆ aliphatic ketones at 298.15 K.

Solvents	Frenkel		Hind	
	η_{12}	APD	η_{12}	APD
EAA + Butan-2-one	2.0295	7.3003	13.924	-3.1947
EAA + Pentan-3-one	1.0350	1.7504	13.105	-11.838
EAA + 3-methylbutan-2-one	1.2036	7.9524	13.234	-3.4273
EAA + 4-methylpentan-2-one	2.0135	7.2189	13.724	-3.6686

Excess Viscosities and excess Gibbs free energies of activation for viscous flow of the mixed solvent systems.

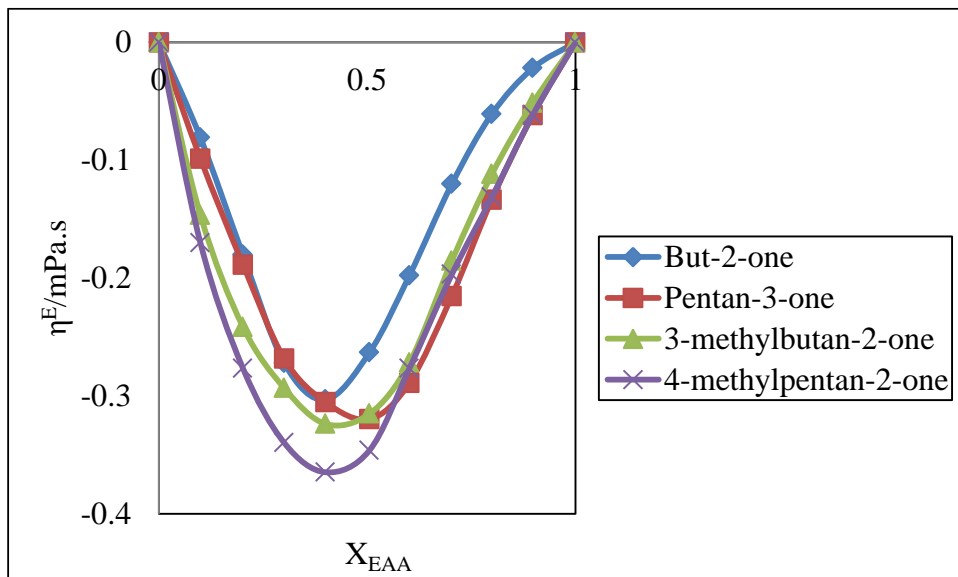


Figure 1: Variation of η^E as a function of EAA concentration in binary mixtures of EAA and aliphatic ketones at 298.15 K

Figure 1 show plots of the excess viscosities, η^E , versus composition of EAA for EAA + but-2-one + pent-3-one + 3-methylbut-2-one and + 4-methylpent-2-one at 298.15 K. The excess viscosities, η^E ,

of the binary mixtures were all negative throughout the entire range of solvents composition. All the plots show minima in the mole fraction region of about 0.40 – 0.50 EAA. The observed order of magnitude of the minima is But-2-one < Pent-3-one < 3-methylbut-2-one < 4-methylpent-2-one. This suggests that 4-methylpentan-2-one, the most branched and with the longest chain length, interacted with EAA most strongly thus resulting in very large η^E values. The relative magnitudes of the negative excess viscosities, (η^E), show that as the chain length and branching of the ketones increase, the value of the (η^E) becomes more negative. This suggests that the strength of interactions between unlike molecules becomes stronger as chain length and branching increase. This observed trend of excess viscosities is similar to that observed by Ali et al⁷ for binary mixtures of dimethyl sulfoxide (DMSO) + benzene, + toluene, + *o*-xylene, + *m*-xylene, + *p*-xylene and + mesitylene, Patil and Mirgane⁸ for binary mixtures of acrylic esters with hexane-2-ol, Garcia et al⁹ for the binary mixtures of 2-pyrrolidone with 1-alkanol and Lea et al¹⁰ for mixtures of pyrrolidone with (C₆-C₁₀) n-alkan-1-ols in which co – solvents of longer chain length and more branching showed greater negative excess viscosities. Katz *et al*¹¹, Latifi and Revue¹², Urieta *et al*¹³, Naidu and Reddy¹⁴, and Ali and Nain^{15, 16} have suggested that increases in chain length and branching decrease self-association between like molecules. According to Pikkarainen¹⁷, viscosity deviations arise from a number of factors, which include: (i), differences in size and shape of component molecules and the loss or decrease in dipole – dipole interactions in the pure solvents; (ii) specific interactions between unlike molecules such as hydrogen bonding and charge transfer complex formations. Negative deviations usually arise from the first factor. The obtained viscosity deviation data reveals that both differences in size and shape of component molecules as well as loss in dipole-dipole interactions of like molecules are responsible for the negative viscosity deviations. The minima observed on the plots of negative excess viscosities as a function of mole fraction of EAA shifts to lower concentrations of EAA in the order 4-methylpentan-2-one > 3-methylbutan-2-one > pentan-3-one butan-2-one. Negative excess viscosities are also associated with the predominance of dispersive forces in the mixed solvent systems. In solvent systems where dispersive forces are predominant, excess molar volumes are generally positive as reported by Rathnam *et al*⁴. Therefore, the observed negative excess viscosities in these mixed solvent systems are consistent with the positive excess molar volumes we reported¹ previously for the same solvent systems. In the solvent systems studied, dipole-dipole interactions between unlike molecules, loss of or decrease in dipole – dipole interactions between like molecules in addition to differences in molecular sizes of the mixture component molecules account for the dispersion forces.

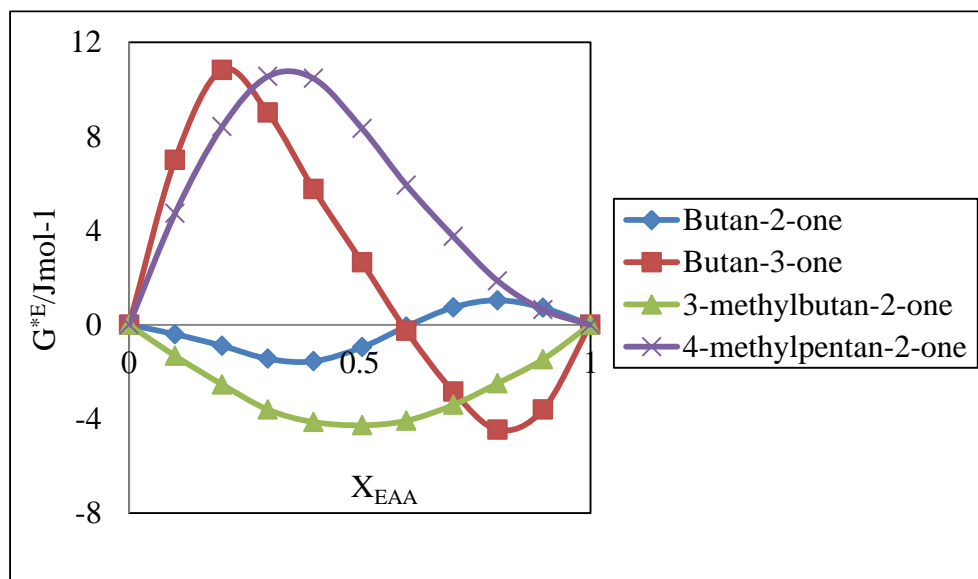


Figure 2: Variation of G^{*E} as a function of EAA concentration in binary mixtures of EAA and aliphatic ketones at 298.15 K

The excess Gibbs free energies of activation for viscous flow, G^{*E} for the binary mixtures of EAA + the named aliphatic ketones over the entire range of solvents composition are shown in Table 3. Figure 2 present the G^{*E} as a function of mole fraction of EAA in the mixed solvent systems. The values of the excess Gibbs free energies of activation for viscous flow, G^{*E} are all positive over the entire range of solvent compositions in binary mixtures of EAA + 4-methylpentan-2-one while for the binary mixtures of EAA + 3-methylbutan-2-one, G^{*E} values are all negative over the entire range of solvent compositions. For the binary mixtures of EAA + butan-2-one, the excess Gibbs free energies of activation for viscous flow, G^{*E} are negative in the lower composition of EAA and become positive at higher composition of EAA, $x_1 > 0.6$. In binary mixtures of EAA + pentan-3-one, the excess Gibbs free energies of activation for viscous flow are largely positive in the mole fraction range of 0.00 – 0.60 EAA. Beyond this mole fraction range $x_1 = 0.60$ the excess Gibbs free energies of activation for viscous flow are negative. From a thermodynamics point of view, negative values of excess Gibbs free energies of activation for viscous flow suggest that the binary mixtures flow more freely than the pure component solvents and that the interactions between unlike molecules are weaker than those between like molecules. Positive values of the excess Gibbs free energies of activation for viscous flow indicate stronger interactions between unlike molecules than those between like molecules in the binary mixed solvent systems. Singh and Diwedi¹⁸, Patil and Mirgane¹⁹ have explained the behavior of liquids based upon the sign and magnitude of the values of excess Gibbs free energies of activation for viscous flow and excess viscosities. According to the authors, the positive values of G^{*E} are indicative of strong interactions while negative values indicate weak interactions between unlike molecules. Thus, it is suggested that the positive values of

G^{*E} indicate that the flow of binary mixtures is more difficult as compared to that of the pure solvents. The negative values of G^{*E} on the other hand indicate easier flow of the mixtures compared to the flow of the pure components.

The observed positive values of G^{*E} in the binary mixtures of ethyl acetoacetate + butan-2-one, + pentan-3-one and + 4-methylpentan-2-one are indicative of strong dipole – dipole interactions between EAA molecules and the named ketones. Leal *et al*^{20, 21} made similar observations in their studies of binary mixtures of pyrrolidin-2-one with (C₆ – C₁₀) alkan-1-ols. In contrast, the observed negative values of G^{*E} in the binary mixtures of EAA + 3-methylbutan-2-one suggest weaker interactions between unlike molecules. Positive values of G^{*E} suggest that the dipole – dipole interactions between unlike molecules in the binary mixtures are stronger than the interactions between like molecules in the pure components. The negative values of G^{*E} observed at low and high concentrations of ethyl acetoacetate in the mixtures of ethyl acetoacetate + butan-2-one and + pentan-3-one respectively suggest complex formations between unlike molecules. They are also characteristic of mixtures where dispersion forces are dominant, as reported by Patil and Mirgane¹⁹ for binary mixtures of *o*-chlorophenol + acetone and + ethyl methyl ketone. Oswal and Rathnam²² have also reported large positive values of G^{*E} for binary mixtures of ethyl acetate + chloroform, which was attributed to dipole-dipole interactions between unlike molecules.

Viscosity data Correlation Parameters

The viscosity data have also been analysed using some selected viscosity models which provide some predictive ability of the strength of interactions of component molecules in the binary mixtures. According to Frenkel²³ and Hind²⁴, the viscosities of mixtures and those of the pure components can be related by the following equations:

$$\ln \eta = x_1^2 \ln \eta_1 + x_2^2 \ln \eta_2 + 2x_1 x_2 \ln \eta_{12} \quad (8)$$

where η is expressed as follows:

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1 x_2 \eta_{12} \quad (9)$$

In equations 8 and 9, x_1 and x_2 are the mole fractions of the mixture components while η_1 and η_2 are the corresponding viscosities. $\ln \eta_{12}$ and η_{12} are the Frenkel and Hind correlation parameters respectively, η is the viscosity of the binary mixture. The values of $\ln \eta_{12}$ calculated from experimental dynamic viscosities of mixtures and single mixture components are shown in Figure 3

η_{12} is defined as

$$\eta_{12} = 0.5\eta_1 + 0.5\eta_2 \tag{10}$$

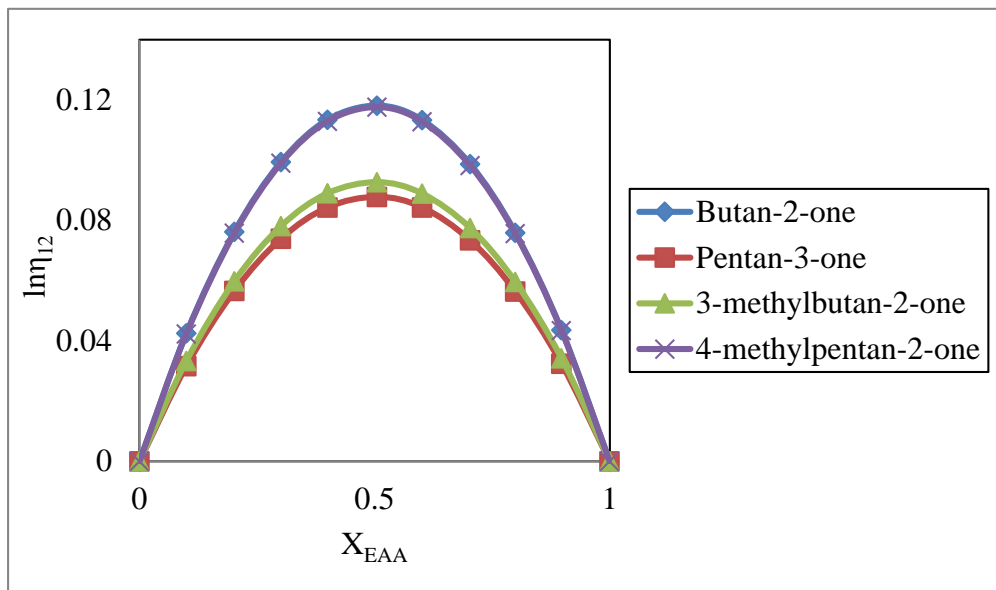


Figure 3: Variation of Frenkel correlation, $\ln\eta_{12}$ as a function of EAA concentration

Values of η can thus be obtained from equation 9 for the various mole fractions of the binary mixtures of EAA + the named aliphatic ketones. The unlike interaction parameter, η_{12} defined by equation 10 has been calculated at the various binary mixtures of the solvent systems and the values are shown in Table 5 and illustrated in Figure 4.

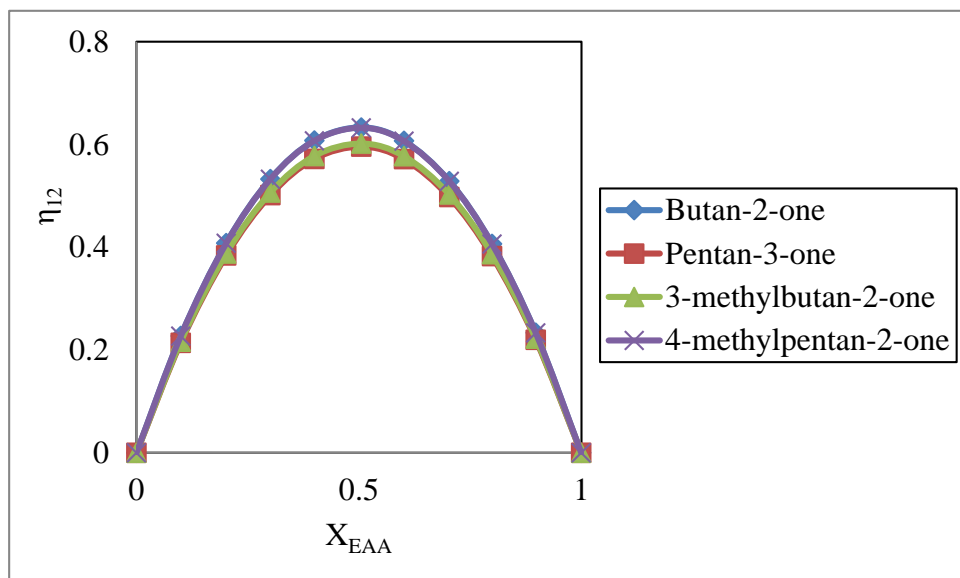


Figure 4: Variation of Hind viscosity correlation, η_{12} as a function of EAA concentration in binary mixtures of EAA and aliphatic ketones at 298.15 K.

Grunberg and Nissan²⁵ proposed a relationship between the dynamic viscosities of binary liquid mixtures and those of the pure liquid components as follows:

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d' \quad (11)$$

In equation 11, d' is an interaction parameter proportional to the interchange energy, which is a function of the composition and temperature of the binary mixture and reflects the non – ideality of the system. According to Ali *et al*⁷ the Grunberg and Nissan relationship is the most widely used theoretical prediction for viscosities of liquid mixtures.

The d' values calculated for the various binary mixtures are shown in Table 5 and plotted in Figure 5 at different EAA mole fraction. The d' values are negative in the region of low concentrations and positive in high EAA concentrations.

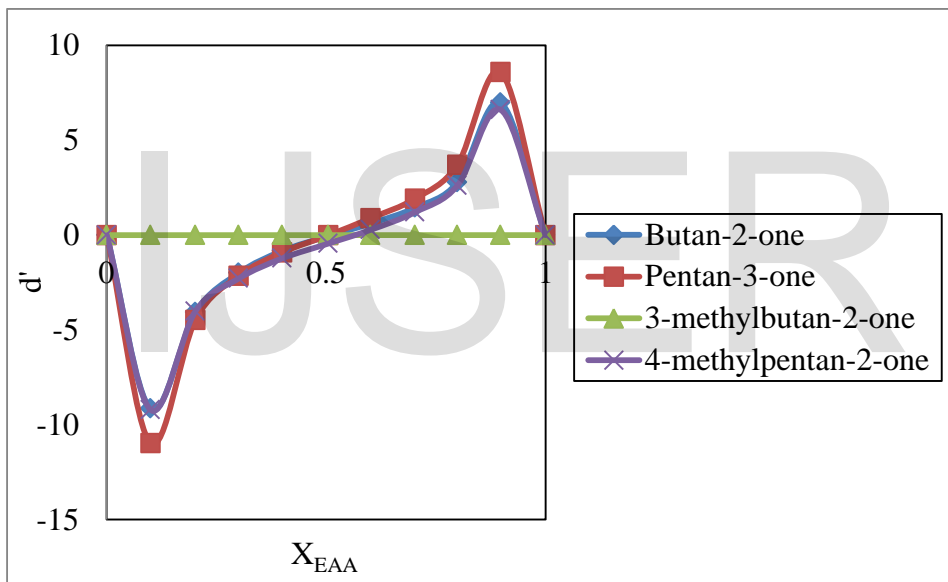


Figure 5: Plots of Grunberg-Nissan viscosity correlation, d' , against mole fraction of EAA for the binary mixtures of EAA and aliphatic ketones at 298.15 K.

The Grunberg and Nissan (d') parameter is a measure of the strength of interactions between unlike molecules^{15, 31-32} and accounts for the additional interactions that arise mainly due to the differences in free energy and free volume of molecules in liquids and liquid mixtures¹⁴. Positive and negative d' values indicate the presence of both strong and weak interactions between unlike molecules^{20, 21}. Grunberg-Nissan interaction parameters are negative at lower mole fractions but positive at higher compositions for the solvent systems over the entire solvents composition range, while values for Frenkel and Hind were all positive over the entire range of solvents composition. The viscosity data were further analysed using the Kendall and Monroe equation based on zero adjustable parameter, expressed as:

$$\eta_m = \left(x_1 \eta_1^{1/3} + x_2 \eta_2^{1/3} \right)^3 \quad (12)$$

The right hand side of equation 12 has been multiplied by the product of the mole fractions to obtain equation 13

$$E\eta_m = x_1 x_2 \left(x_1 \eta_1^{1/3} + x_2 \eta_2^{1/3} \right)^3 \quad (13)$$

which is the modified Kendall – Monroe equation³³⁻³⁴.

In equation 13, $E\eta_m$ is the Kendall-Monroe correlation parameter. The values of $E\eta_m$ for the various solvent systems have been calculated and reported in Table 5.

According to Venkateswarlu et al³⁵ positive Grunberg-Nissan values indicate the presence of specific interactions while the negative values suggests the presence of weak interactions between the unlike molecules of the mixture. The observed Grunberg – Nissan values in this present work reveals that both specific and dispersive forces of interactions are taking place. This trend is in line with the results obtained for η^E and G^{*E} for the solvent systems.

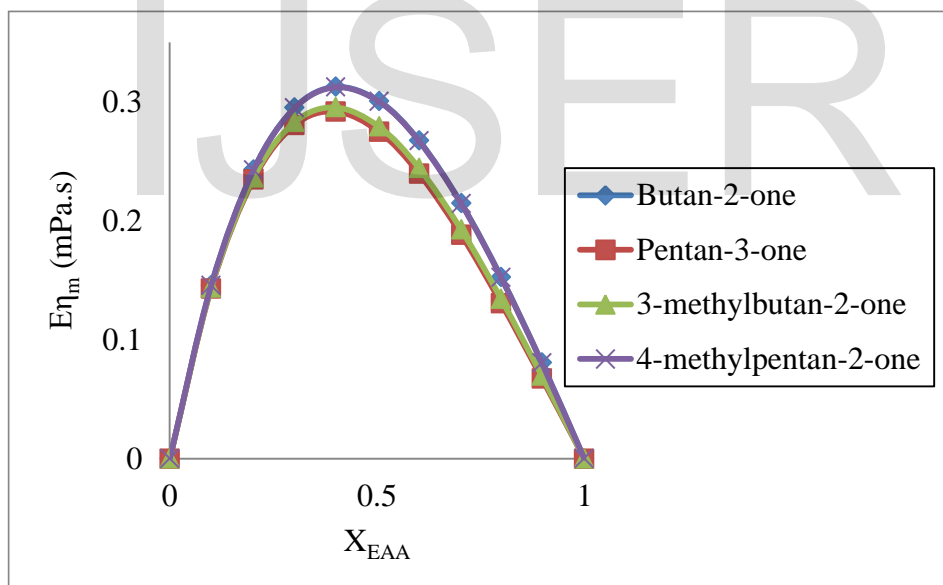


Figure 6: Plot of modified Kendall-Monroe viscosity correlation $E\eta_m$ against mole fractions of EAA in binary mixtures of EAA and aliphatic ketones at 298.15 K.

The correlating ability of equations 8, 9, 11 and 13 were tested by calculating the Average Percentage Deviations (APD) between the experimental and the calculated viscosities using equation 14.

$$APD = \frac{100}{N} \sum_{i=1}^N \left[\frac{\eta_{exptal} - \eta_{calc}}{\eta_{exptal}} \right] \quad (14)$$

In equation 14, η_{exptal} and η_{calc} represent the viscosities of the experimental and calculated data respectively, and N is the number of experimental data points. The values of the Average Percentage Deviations, APD, for the various binary mixtures are presented in Table 6. The APD values obtained for Hind are very small compared to Frenkel. The values of Hind are negative while that of Frenkel are positive.

Conclusion

The results of this study clearly show that the excess viscosities, η^E of all the solvent systems are negative over the entire range of solvents composition. This is suggestive of the dominance of dispersion forces in the systems. The excess viscosities were more negative with increase in chain length and branching of the ketones. The values of excess Gibbs free energies of activation for viscous flow, G^{*E} in the binary mixtures of ethyl acetoacetate + 3-methylbutan-2-one are also negative and thus support the presence of dispersion forces between unlike molecules as indicated from the excess viscosity data. In cases where the values of the excess Gibbs free energies for viscous flow are positive, it is an indication that the flow of the binary mixtures is more difficult than the flow of the pure solvents.

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The experimental values of density (ρ), viscosity (η), refractive index (n_D) of pure liquids and their binary mixtures were used to calculate the excess or deviation properties (V_E , $\Delta\eta$, ΔG^E , ΔR) using the following relations

$$V^E = (x_1 M_1 + x_2 M_2) / \rho - (x_1 M_1 / \rho_1 + x_2 M_2 / \rho_2) \quad (1)$$

$$\Delta\eta = \eta - (x_1 \eta_1 + x_2 \eta_2) \quad (2)$$

$$\Delta G^E = RT [\ln(\eta V) - (x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2))] \quad (3)$$

$\Delta R = R_m - (x_1 R_{1m} + x_2 R_{2m})$ (4) where M , η , V , R_m are molar mass, viscosity, molar volume, molar refraction of the binary mixtures respectively. Table 2 shows the experimental values of density (ρ), excess volume (V_E), dynamic viscosity (η), and refractive index (n_D) of the studied binary mixtures at (303.15, 308.15, 313.15) K over the entire mole fraction (x_1) range of

Interaction Study on Diethyl Maleate + Ketone Binary Mixtures: Application of PFP Theory to Excess Volumes Manapragada .V. Rathnam, Sudhir Mohite, Manapragada. S. S. Kumar Sadanand Dharap

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The magnitude of $\Delta\eta$ alter with increase in temperature indicating the effect of temperature on $\Delta\eta$. The negative $\Delta\eta$ values suggest that dispersion forces are dominant in the mixtures while the positive $\Delta\eta$ values indicate the presence of specific interaction between the component molecules (7, 8). The plots of the excess Gibb's free energy of activation of flow (ΔG^E) against mole fraction (x_1) are displayed in Fig 3. It is observed that the values of ΔG^E exhibit positive deviations for mixtures of acetophenone, cyclopentanone, and 3-pentanone, while for diethyl maleate + cyclohexanone ΔG^E values are positive in the lower composition of diethyl maleate and become negative at higher composition of ester $x_1 > 0.4$. These ΔG^E values also indicate the effect of temperature, as these values found to either increase or decrease with raise in temperature. The positive trend in ΔG^E values indicates that the strength of the interaction in component molecules is weaker, while the negative values indicate the strong interactions.

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Volumetric and viscometric study of binary systems of alcohols with alkane at (298.15, 303.15, 308.15, 313.15 and 318.15) K and atmospheric pressure

Ali A. S. M. Zahida, b, Md A. Alib and Jae Ryang Hahna

Mariano *et al*⁴ in their studies of the viscosities of binary mixtures of tetrahydrofuran with butanol and chlorobutane at different temperatures

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