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Thermodynamic Study on Density and Viscosity of Binary Mixtures of Ethyl acetoacetate with (C_4-C_9) Aliphatic Ketones at (303.15 and 308.15) K

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Abstract:- Investigation on Density (ρ) and viscosity (η) of various binary mixtures of ethylacetoacetate and straight chain aliphatic ketones (butan-2-one, pentan-2-one, hexan-2-one, heptan-2-one, octan-2-one and nonan-2-one) have been carried out over the entire solvents composition range at temperatures of 303.15K and 308.15K. From the data obtained, the excess molar volumes (V^E), the excess viscosity (η^E) and excess Gibbs free energy of activation for viscous flow (ΔG^{*E}) have been calculated from the experimental density and viscosity measurements at the working temperatures. Excess molar volumes, V^E results are negative and positive over the entire range of mole fractions and become more positive as the chain length increases. The excess viscosities, η^E were both positive and negative over the entire mole fraction range. While the observed excess Gibbs free energies of activation of viscous flow, ΔG^{*E} data are positive throughout the entire mole fraction range of solvents composition at all investigated temperatures. These observed results of the excess functions have been interpreted in terms of possible molecular interactions in the binary mixtures.

Keywords:- *Density, Viscosity, Binary mixtures, Molecular Interactions, Ketoester, Ketones, Excess molar volumes, Excess viscosities, Excess Gibbs free energies.*

I. INTRODUCTION

The studies of thermodynamic properties of liquids and liquid mixtures are useful tools in the study and understanding of the nature of molecular and intermolecular interactions between the various components of the mixtures in binary liquid systems [1]. The estimation of the interrelation of thermodynamic properties and the nature of molecular interaction between liquids is of paramount importance. These properties find widespread use in chemical industries. The knowledge of the properties of binary liquid mixtures is essential in designs, involving chemical separation, heat and mass transfer, and fluid flow processes. The measurement of density and viscosity is adequately employed in the understanding of the nature of molecular interactions in pure liquids and their binary mixtures. These measurements are highly sensitive to molecular interaction and can be used to provide qualitative information about the physical nature and the strength of molecular interaction in the liquid mixture [2-5].

In this paper, we report an experimental determinations of density, (ρ) and viscosity, (η) of ethylacetoacetate (EAA) with straight chain (C_4-C^9) aliphatic ketones and their binary mixtures with ethylacetoacetate as common solvent at temperatures of (303.15 and 308.15)K covering the entire composition range of the solvents systems.

This is part of our research [6-9] on the accumulation of data of binary organic liquid mixtures of these solvents systems. The work is aimed at improving the understanding of the molecular interactions of these solvents systems at the molecular level and to characterize their physico-chemical behavior in their mixtures.

Esters have a variety of applications in medicinal, industrial, chemical and biological processes. They are an important constituent of marine engine oils, drugs, printing inks, hydraulic fluids, cosmetics, compressor and automotive oils. Esters are widely known and used in food industry for their diverse aroma and flavours [10]. Ethylacetoacetate is a ketoester, which has vast applications at industrial level because it works as an alkylating agent in organic synthesis and as a chemical intermediate in the production of a variety of compounds, and as a flavour [11]. Ketones on the other hand are class of chemical compounds containing the carbonyl group in which the carbon atom is covalently bonded to an oxygen atom. Ketones are chosen because of their variety of applications such as solvent, lacquers, oils, and resins, etc. The excess molar volume and excess viscosity are properties sensitive to different kinds of association in the pure components and in the mixtures. These properties have been used to investigate the molecular structures, the strengths of the various types of intermolecular interactions. They are influenced by the size, shape, and chemical nature of the component molecules [12-13]. In view of this fact, it was thought worthwhile to study the binary mixtures of ethylacetoacetate (EAA) with butan-2-one, pentan-2-one, hexan-2-one, heptan-2-one, octan-2-one and nonan-2-one in order to understand the interactions between these component molecules above ambient temperature and provide data for the characterization of the molecular interaction of these mixtures in order to examine the effects of increasing carbon chain-length. In continuation of our work on thermodynamic properties of binary liquid mixtures of ethylacetoacetate with ketones [6–9], in this present study we report densities and viscosities of butan-2-one, pentan-2-one, hexan-2-one, heptan-2-one, octan-2-one

and nonan-2-one with ethyl acetoacetate (EAA) over the entire solvent composition range at (303.15 and 308.15)K. The lack of information of these solvent systems at this temperature range has motivated us to undertake the present study. To give more clear understanding of the interactions between these binary systems, some viscosity models, namely, Frenkel, Hind, Grunberg–Nissan, and Kendall and Monroe have been employed to study their viscosity interaction.

II. MATERIALS AND METHOD

Materials: All reagents were supplied by Acros Organics Belgium and used without any further purification. The purity of these materials is (99%) for ethyl acetoacetate, (99.9%) butan-2one, pentan-2-one, hexan-2-one for, and (99.95%) for heptan-2-one, octan-2-one and nonan-2-one. The chemicals were degassed by ultrasound, kept out of light over Fluka 0.3 nm molecular sieves for several days before the experiments were performed. The mass percent water content was determined using a Metrohm 702 SM Titrino Metter before the experiments, and was found to be < 0.05 % in all chemicals. The densities and viscosities of the pure solvents are shown in Table1. The purity of the pure liquids was ascertained by comparing their measured densities (ρ), with those reported in the literature[14–17]. The experimental values are in proximity with the literature values as shown in Table 1.

Pure Solvents	Acronym	Density, ρ(gm/cm^3)		Viscosity, η(mPa.s)	
		Experimental	Literature	Experimental	Literature
Butan-2-one	But-2-	0.8034	0.8050	0.3531	
Pentan-2-one	Pen-2-	0.8059	0.809[a], 0.8086[b]	0.4546	
Hexan-2one	Hex-2-	0.8103	0.8113[a], 0.8105[b]	0.5812	
Heptan-2-one	Hep-2-	0.8148	0.8166	0.8062	
Octan-2-one	Oct-2-	0.8174	0.8171	1.0201	
Nonan-2-one	Non-2-	0.8204	0.822	1.2891	
Ethylacetoacetate	EAA	1.0263	1.0282, 1.029	1.8035	

(a).CRC Handbook 87th ed.; (b) Yuvraj Sudake et al (2011); (c) Bunger and Riddick (1970); (d). Robert, R. Dreisbach (1961).
(a) = 8, (b) = 9, (c) = 10, (d) = 11

Table 1**:-** Comparison of Experimental density, ρ (gm/cm^3) and viscosity, η (mPa.s) of pure solvents at 303.15 K with Literature values.

Mixture Preparation: Binary mixtures were prepared by mass in airtight stoppered glass bottles. The mass was recorded on a digital electronic balance. An AE Adam balance (Adam Equipment Inc. USA) model PW124 with a maximum capacity of 120 g, a readability ranges 0.0001 g and repeatability (S.D.) of 0.00015 g, linearity 0.0002 g, was used. To prevent the samples from preferential evaporation, the mixtures were prepared by transferring aliquots via syringe into stoppered bottles. The uncertainty in mole fraction was thus estimated to be less than ±0.0001. A set of nine binary mixtures was prepared for each system, and their physical properties were measured at the respective composition of the mole fraction varying from 0.0000 to 1.0000 in interval of 0.1.

Density Measurement: The densities of the pure liquids and their binary mixtures were measured with an Anton Paar DMA-4500 M digital densitometer at the investigated temperatures. Two integrated Pt 100 platinum thermometers were provided for good precision in temperature control internally (T = ±0.01 K). The densitometer protocol includes an automatic correction for the viscosity of the sample. The apparatus is precise to within 1.0 x 10^{-5} g/cm^3, and the uncertainty of the measurements was estimated to be better than ± 0.0031 g/cm^3. Calibration of the densitometer was performed at atmospheric pressure using doubly distilled and degassed water and ethanol before the start of the actual experiments. The instrument has a temperature sensor which measures the sample temperature right at the measuring cell. The density of all the binary mixtures was measured after achieving thermal equilibrium at the working temperatures. The reproducibility of the densities of the pure solvents was ± 0.0030 gcm^{-3}.

Viscosity Measurement: Kinematic viscosity, υ and dynamic viscosity, η determinations were carried out using Anton Paar SVM 3000 Stabinger Viscometer. The viscometer has a dynamic viscosity range of 0.2 to 20 000 mPa.s, a kinematic viscosity ranges of 0.2 to 20 000 mm^2/s and a density range of 0.65 to 3 g/cm^3. The instrument is equipped with a maximum temperature range of +105^{o}C and a minimum of 20^{o}C below ambient. Instrument viscosity reproducibility is 0.35% of measured value and density reproducibility of 0.0005 g/cm^3.

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III. RESULTS AND DISCUSSION

The experimentally determined results of densities, ρ and viscosities, η of binary mixtures and their excess thermodynamic properties viz. excess molar volumes (V^E), excess viscosities (η^E) and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) at (303.15 and 308.15)K as a function of composition of the binary mixtures have been presented in Table 2.

	T=303.15K					T=308.15K				
	ρ/	η/	V^E/	η^E/	ΔG^{*E}/	ρ/	η/	V^E/	η^E/	ΔG^{*E}/
X_1	($g.cm^{-3}$)	(mPa.s)	(cm^3mol^{-1})	(mPa.s)	($Jmol^{-1}$)	($g.cm^{-3}$)	(mPa.s)	(cm^3mol^{-1})	(mPa.s)	($Jmol^{-1}$)
	EAA (1) + Butan-2-one (2)									
0.0000	0.7931	0.3530	0.0000	0.0000	0.0000	0.7878	0.3184	0.0000	0.0000	0.0000
0.1152	0.8239	0.4696	-0.5648	0.0007	0.5643	0.8187	0.4220	-0.0382	0.0042	0.6374
0.2047	0.8523	0.5153	-0.7460	0.0008	0.8847	0.8470	0.4807	-0.0544	0.0054	0.9943
0.3106	0.8799	0.5848	-0.7630	-0.0018	1.1379	0.8746	0.5612	-0.0612	0.0050	1.2709
0.4115	0.9053	0.6600	-0.6561	-0.0039	1.2590	0.9000	0.6534	-0.0580	0.0034	1.3976
0.5038	0.9275	0.7219	-0.5069	-0.0058	1.2733	0.9222	0.7429	-0.0493	0.0014	1.4051
0.6047	0.9462	0.7733	-0.3328	-0.0074	1.1901	0.9410	0.8200	-0.0361	-0.0009	1.3043
0.7006	0.9687	0.8668	-0.1874	-0.0081	1.0214	0.9634	0.9473	-0.0225	-0.0026	1.1118
0.8027	0.9825	0.9216	-0.0754	-0.0074	0.7527	0.9775	1.0287	-0.0096	-0.0035	0.8131
0.9015	1.0007	1.0229	-0.0163	-0.0048	0.4120	0.9958	1.1623	-0.0013	-0.0027	0.4416
1.0000	1.0164	1.1473	0.0000	0.0000	0.0000	1.0113	1.3417	0.0000	0.0000	0.0000
	EAA (1) + Pentan-2-one (2)									
0.0000	0.7960	0.4997	0.0000	0.0000	0.0000	0.5277	0.4173	0.0000	0.0000	0.0000
0.1152	0.8229	0.5525	-0.0368	0.0024	0.4431	0.6005	0.4912	0.0523	0.0016	0.4649
0.2047	0.8479	0.5986	-0.0517	0.0026	0.7026	0.6550	0.5522	0.0761	0.0016	0.7354
0.3106	0.8718	0.6496	-0.0572	0.0016	0.9162	0.7131	0.6182	0.0886	0.0006	0.9561
0.4115	0.8957	0.7062	-0.0529	-0.0002	1.0276	0.7828	0.6972	0.0879	-0.0010	1.0693
0.5038	0.9187	0.7681	-0.0435	-0.0021	1.0526	0.8597	0.7854	0.0790	-0.0026	1.0925
0.6047	0.9404	0.8110	-0.0301	-0.0040	0.9980	0.9188	0.8593	0.0634	-0.0041	1.0328
0.7006	0.9624	0.9120	-0.0167	-0.0051	0.8687	1.0342	0.9900	0.0454	-0.0050	0.8964
0.8027	0.9805	0.9820	-0.0049	-0.0052	0.6502	1.1206	1.0929	0.0261	-0.0048	0.6688
0.9015	0.9998	1.0642	0.0015	-0.0036	0.3615	1.2224	1.2157	0.0102	-0.0033	0.3707
1.0000	1.0164	1.1473	0.0000	0.0000	0.0000	1.3267	1.3417	0.0000	0.0000	0.0000
	EAA (1) + Hexan-2-one (2)									
0.0000	0.8013	0.5921	0.0000	0.0000	0.0000	0.7968	0.5104	0.0000	0.0000	0.0000
0.1152	0.8256	0.6479	-0.0226	-0.0053	0.4142	0.8210	0.5848	0.0755	-0.0036	0.4642
0.2047	0.8472	0.6867	-0.0357	-0.0085	0.6615	0.8425	0.6372	0.1086	-0.0060	0.7313
0.3106	0.8659	0.7203	-0.0465	-0.0113	0.8701	0.8611	0.6878	0.1242	-0.0083	0.9461
0.4115	0.8892	0.7703	-0.0521	-0.0128	0.9840	0.8843	0.7595	0.1203	-0.0098	1.0530
0.5038	0.9110	0.8189	-0.0532	-0.0133	1.0157	0.9061	0.8330	0.1052	-0.0105	1.0710
0.6047	0.9328	0.8770	-0.0504	-0.0127	0.9712	0.9279	0.9173	0.0807	-0.0105	1.0074
0.7006	0.9550	0.9370	-0.0438	-0.0112	0.8522	0.9500	1.0112	0.0543	-0.0096	0.8700
0.8027	0.9759	1.0012	-0.0327	-0.0085	0.6434	0.9708	1.1109	0.0276	-0.0075	0.6457
0.9015	0.9865	1.0356	-0.0181	-0.0048	0.3607	0.9813	1.1652	0.0083	-0.0044	0.3559
1.0000	1.0164	1.1473	0.0000	0.0000	0.0000	1.0113	1.3417	0.0000	0.0000	0.0000
	EAA (1) + Heptan-2-one (2)									
0.0000	0.8061	0.7657	0.0000	0.0000	0.0000	0.8018	0.6821	0.0000	0.0000	0.0000
0.1152	0.8239	0.7683	0.0172	-0.0078	0.3805	0.8195	0.6991	0.0754	-0.0046	0.3850
0.2047	0.8449	0.7921	0.0262	-0.0123	0.6043	0.8403	0.7423	0.1092	-0.0075	0.6111
0.3106	0.8641	0.8195	0.0325	-0.0160	0.7894	0.8595	0.7880	0.1262	-0.0099	0.7979
0.4115	0.8873	0.8572	0.0347	-0.0178	0.8870	0.8826	0.8504	0.1240	-0.0113	0.8960
0.5038	0.9065	0.8904	0.0339	-0.0182	0.9102	0.9017	0.9059	0.1103	-0.0118	0.9189
0.6047	0.9282	0.9305	0.0304	-0.0172	0.8647	0.9234	0.9740	0.0869	-0.0113	0.8724
0.7006	0.9487	0.9749	0.0250	-0.0150	0.7540	0.9438	1.0481	0.0608	-0.0100	0.7603
0.8027	0.9710	1.0217	0.0175	-0.0112	0.5655	0.9660	1.1300	0.0335	-0.0076	0.5699
0.9015	0.9946	1.0842	0.0091	-0.0062	0.3150	0.9895	1.2346	0.0120	-0.0043	0.3172
1.0000	1.0164	1.1473	0.0000	0.0000	0.0000	1.0113	1.3417	0.0000	0.0000	0.0000

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	EAA (1) + Octan-2-one (2)									
0.0000	0.8091	0.9071	0.0000	0.0000	0.0000	0.8049	0.8274	0.0000	0.0000	0.0000
0.1152	0.8245	0.9255	0.0744	-0.0084	0.3757	0.8203	0.8535	0.0960	-0.0045	0.3755
0.2047	0.8444	0.9281	0.1068	-0.0134	0.5974	0.8401	0.8791	0.1435	-0.0074	0.5972
0.3106	0.8641	0.9461	0.1219	-0.0175	0.7815	0.8597	0.9199	0.1735	-0.0100	0.7816
0.4115	0.8806	0.9557	0.1177	-0.0197	0.8794	0.8761	0.9486	0.1796	-0.0116	0.8796
0.5038	0.9017	0.9770	0.1025	-0.0202	0.9035	0.8970	0.9957	0.1698	-0.0123	0.9040
0.6047	0.9226	0.9996	0.0781	-0.0193	0.8595	0.9179	1.0453	0.1461	-0.0120	0.8602
0.7006	0.9434	1.0269	0.0520	-0.0168	0.7505	0.9386	1.1023	0.1146	-0.0108	0.7514
0.8027	0.9677	1.0611	0.0259	-0.0126	0.5637	0.9628	1.1727	0.0756	-0.0083	0.5645
0.9015	0.9926	1.1008	0.0073	-0.0071	0.3144	0.9875	1.2533	0.0365	-0.0048	0.3150
1.0000	1.0164	1.1473	0.0000	0.0000	0.0000	1.0113	1.3417	0.0000	0.0000	0.0000
	EAA (1) + Nonan-2-one (2)									
0.0000	0.8124	1.1046	0.0000	0.0000	0.0000	0.8084	1.0170	0.0000	0.0000	0.0000
0.1152	0.8271	1.0976	0.0990	-0.2977	0.3334	0.8230	1.0291	0.1108	-0.0079	0.3392
0.2047	0.8462	1.0478	0.1479	-0.4755	0.5342	0.8419	1.0126	0.1648	-0.0125	0.5430
0.3106	0.8636	1.0756	0.1786	-0.6255	0.7053	0.8593	1.0543	0.1978	-0.0163	0.7162
0.4115	0.8838	1.0725	0.1848	-0.7074	0.8005	0.8793	1.0778	0.2032	-0.0183	0.8121
0.5038	0.9028	1.0759	0.1746	-0.7302	0.8291	0.8982	1.1072	0.1904	-0.0187	0.8403
0.6047	0.9229	1.0805	0.1500	-0.6982	0.7956	0.9182	1.1371	0.1619	-0.0178	0.8056
0.7006	0.9437	1.0895	0.1175	-0.6127	0.7005	0.9389	1.1762	0.1252	-0.0155	0.7086
0.8027	0.9670	1.1025	0.0774	-0.4626	0.5308	0.9621	1.2198	0.0810	-0.0116	0.5364
0.9015	0.9928	1.1215	0.0372	-0.2594	0.2987	0.9877	1.2783	0.0381	-0.0064	0.3015
1.0000	1.0164	1.1473	0.0000	0.0000	0.0000	1.0113	1.3417	0.0000	0.0000	0.0000

Table 2:- Densities, ρ, Viscosities, η, Excess Molar Volumes, V^E, Excess Viscosities, η^E, and Excess Gibbs Free energies of activation for viscous flow, ΔG^{*E} for Ethylacetoacetate (EAA) (1) + Aliphatic ketones (2) at T = (303.15 and 308.15) K.

The excess thermodynamic parameters were calculated from the determined data using the following equations 1 to 4.

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

$$\eta^E = \eta - (x_1\eta_1 - x_2\eta_2) \quad (2)$$

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

$$V_m = \frac{x_1 M_1 + x_2 M_2}{\rho} \quad (4)$$

where ρ, η and V are density, viscosity and molar volume of the mixture, M_1 and M_2 are molar masses, η_1 and η_2 are viscosities, V_1 and V_2 are molar volumes of the Ethylacetoacetate (EAA) and the named ketones respectively. R is the universal gas constant and T, absolute temperature in Kelvin. X is the mole fraction of EAA.

The calculated excess molar volumes, 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 Table 2 and represented in Figures. (1a, b - 3a, b) The dependence of V^E, η^E and ΔG^{*E} on the mole fraction of EAA for all binary systems obtained were correlated by four parameter Redlich – Kister [18] polynomial (equation 5 and 6) by the least-squares method and the values are given in Table 3 along with the standard deviations (σY^E) of the binary solvents systems defined by equation 7.

$$Y^E = x_1x_2[A_0 + A_1(x_1\text{-}x_2) + A_2 (x_1\text{-}x_2)^2 + A_3 (x_1\text{-}x_2)^3] \quad (5)$$

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

where Y^E represents V^E, η^E or ΔG^{*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 Table 3 along with the standard deviations (σY^E) of the binary solvent systems defined by equation 7.

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

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

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	T/K	A_0	A_1	A_2	A_3	σ
EAA (1) + Butan-2-one (2)						
V^E (Cm^3mol^{-1})	303.15	0.11168738	0.390628895	2.762E-16	5.707E-16	0.1254681
	308.15	0.108353429	0.420549406	-4.5369E-16	-8.5602E-16	0.460607477
η^E (mPa.s)	303.15	-0.1034	0.0648	0.0000	0.0000	0.3289
	308.15	-0.066679033	0.076463528	-4.1029E-17	0	0.271470902
ΔG^{*E} (J/mol)	303.15	7.5481	0.9475	0.0000	0.0000	14.4174
	308.15	8.02315467	1.353072002	-1.6569E-14	-1.2711E-14	14.75691731
EAA (1) + Pentan-2-one (2)						
V^E (Cm^3mol^{-1})	303.15	0.156695728	0.069814526	1.006E-15	1.14136E-15	0.577881318
	308.15	0.10001855	0.638304237	8.8765E-16	1.14136E-15	0.835858146
η^E (mPa.s)	303.15	-0.115021332	-0.006649002	-1.2052E-09	-7.1854E-10	0.251289553
	308.15	-0.091683671	0.009973504	-2.5643E-11	-1.7899E-09	0.212895985
ΔG^{*E} (J/mol)	303.15	6.72791445	0.292556109	-8.3242E-10	-6.6147E-10	13.75883262
	308.15	6.877942275	0.408913652	1.51887E-09	1.27107E-09	13.87677062
EAA (1) + Hexan-2-one (2)						
V^E (Cm^3mol^{-1})	303.15	-0.039894015	-1.047217889	-2.76157731	-2.7497E-16	23.8921999
	308.15	0.050009275	-0.380655391	-7.1012E-16	-8.5602E-15	0.732274461
η^E (mPa.s)	303.15	-0.081681816	0.068152275	-8.2847E-16	-7.0038E-16	0.286066365
	308.15	-0.073346937	0.056516521	1.10463E-15	1.08948E-15	0.248209112
ΔG^{*E} (J/mol)	303.15	6.771255821	0.001662251	1.43997E-14	1.1673E-14	14.32771923
	308.15	6.56788477	0.576800964	-9.6655E-15	-8.3008E-15	12.95188785
EAA (1) + Heptan-2-one (2)						
V^E (Cm^3mol^{-1})	303.15	-0.336729118	-0.018284757	-4.5369E-16	-3.6316E-15	0.682515442
	308.15	0.576773637	0.696483009	7.89022E-16	1.14136E-15	0.076656243
η^E (mPa.s)	303.15	-0.131691091	-0.003324501	-3.9451E-16	-3.3722E-16	0.275533987
	308.15	-0.12002226	-0.004986752	2.36707E-16	2.33461E-15	0.244233457
ΔG^{*E} (J/mol)	303.15	5.626043426	-0.098072786	-2.9588E-15	-3.1128E-15	12.06787245
	308.15	5.674385725	-0.071476777	-4.3396E-15	-3.6316E-15	12.12714926
EAA (1) + Octan-2-one (2)						
V^E (Cm^3mol^{-1})	303.15	0.583441541	0.583449967	4.33962E-16	5.70682E-16	0.278986347
	308.15	0.573439686	0.561840709	-3.1561E-16	2.85341E-16	0.293043266
η^E (mPa.s)	303.15	-0.098351574	-4.770884825	1.298E-11	-3.6988E-09	1.573090557
	308.15	-0.085015767	0.014960256	1.18353E-16	9.07904E-17	0.207477735
ΔG^{*E} (J/mol)	303.15	5.874422825	0.196145573	-2.3671E-15	-8.5602E-16	12.11102172
	308.15	5.912763269	0.21609258	1.006E-14	9.33844E-15	12.15998042
EAA (1) + Nonan-2-one (2)						
V^E (Cm^3mol^{-1})	303.15	0.001666976	0.684847254	-1.1441E-16	-0.057068E-16	1.119948129
	308.15	0.02000371	0.684847254	2.16981E-15	0.00228273E-15	1.080196371
η^E (mPa.s)	303.15	-0.090016695	0.001662251	1.97256E-17	0.00181581E-17	0.195205632
	308.15	-0.081681816	0.003324501	-1.7753E-16	-0.0015564E-16	0.174374925
ΔG^{*E} (J/mol)	303.15	5.872755849	0.152927057	-1.1046E-15	-0.0010117E-15	12.17589384
	308.15	5.88442468	0.144615804	1.22298E-14	0.001.8948E-14	12.21481376

Table 3:- Redlich-Kister adjustable parameters and standard deviation values for the excess functions for the binary mixtures of EAA and (C_4 – C_9) aliphatic ketones at T = (303.15 and 308.15) K.

IV. DISCUSSION

➢ *Excess molar volumes:*

Figures 1a and 1b show the variation of excess molar volume (V^E) with mole fraction of the binary mixtures of EAA with the aliphatic ketones at (303.15 and 308.15) K.

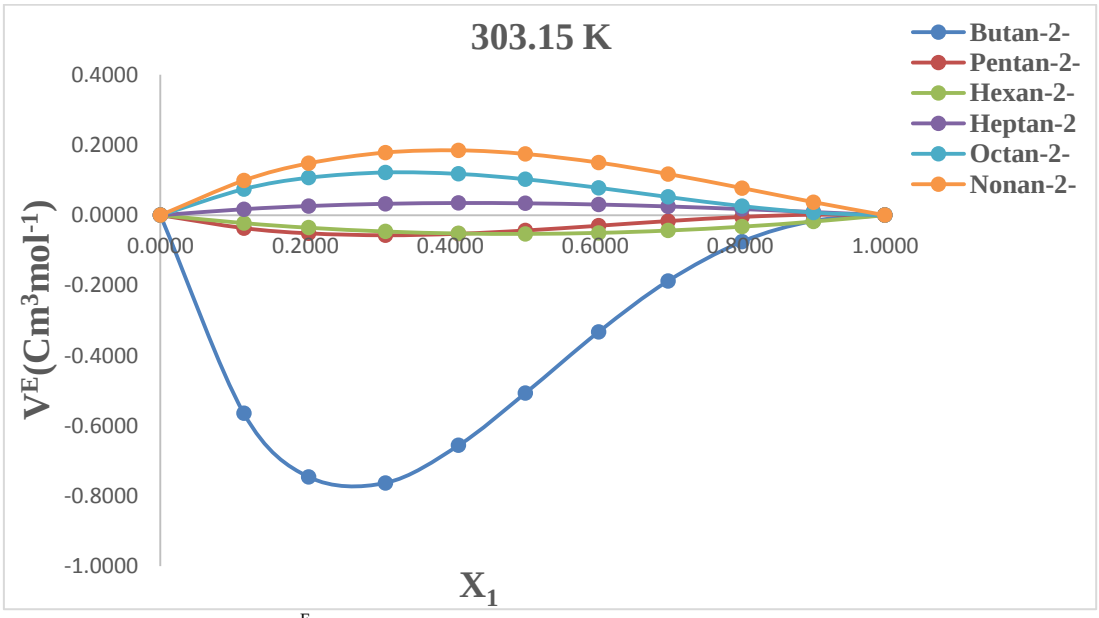

Fig. 1a:- Plots of excess molar volume (V^E) vs. mole fraction of Ethylacetoacetate (EAA) for binary mixtures of Ethylacetoacetate (EAA) + butan-2-one (1), + pentan-2one (2), + hexan-2-one (3), + heptan-2-one (4), + octan-2-one (5), + nonan-2-one (6) at 303.15 K

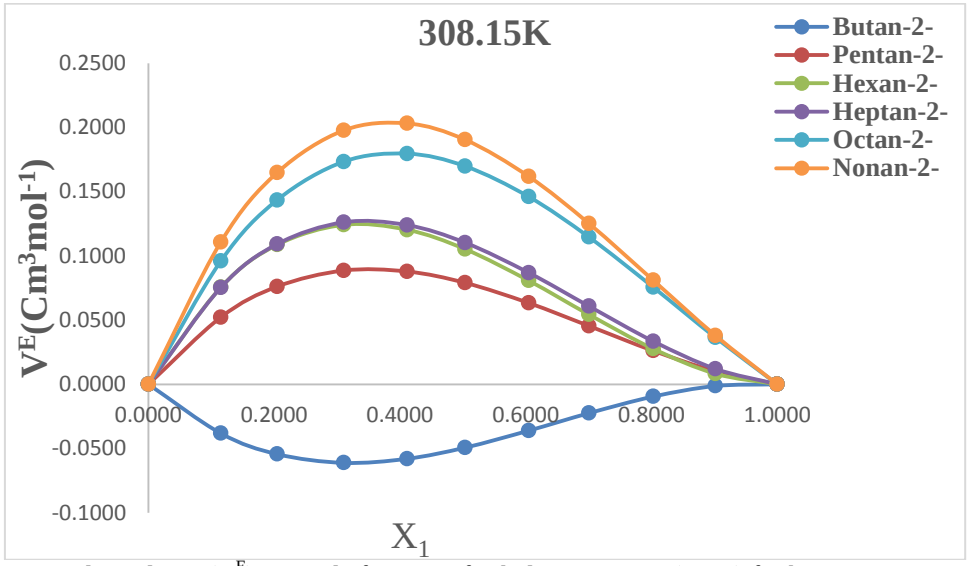

Fig. 1b:- Plots of excess molar volume (V^E) vs. mole fraction of Ethylacetoacetate (EAA) for binary mixtures of Ethylacetoacetate (EAA) + butan-2-one (1), + pentan-2one (2), + hexan-2-one (3), + heptan-2-one (4), + octan-2-one (5), + nonan-2-one (6) at 303.15 K

The V^E curves for the binary mixtures of EAA + butan-2-one, + pentan-2-one, + hexan-2-one are negative over the entire solvent compositions range at 303.15K and EAA + butan-2-one binary mixture negative at 308.15K over the entire composition range. The negativity decreases as temperature increase, this suggests that the binary mixtures at this lower carbon chain have a more compact structure in solution. Reddy *et al* [19]. It is suggestive that the component molecules are more close together in the liquid mixture, indicating that strong attractive interaction between component molecules are taking place, such interactions like hydrogen bonding, dipole – dipole interactions and other specific interaction between unlike molecules are operative in the systems. For the systems EAA + hept-2-one, + octan-2-one, +nonan-2-one at 303.15K and EAA + pentan-2-one, + hexan-2-one, +heptan-2-one, + octan-2-one + nonan-2-one at 308.15K over the entire solvents compositions range increases as the

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carbon chain length increases. The positive V^E indicates that dispersion force is prevailing between the binary mixtures. The positive values may be as a result of repulsive forces caused by electronic charges on the component liquids.

The sign of excess molar volume, V^E depends upon the contraction and expansion of volume of the solvents as a result of mixing. The excess molar volume is the resultant contribution from several opposing effects, namely, chemical, physical, and structural Reddy *et al* [19], Sankar *et al* [20] and Gowrisanker *et al* [21]. The chemical or specific interactions result in volume contractions, leading to negative excess molar volume, and these include charge transfer complexes, dipole-dipole, dipole-induced dipole interactions and formation of H-bonding between component molecules. The physical interactions or nonspecific interactions are weak and these include breaking of the structure of one or both of the component molecules in a solution, that is, the loss of dipolar association between the molecules (dispersion forces), steric hindrance of the molecules and rupture of H-bond. The structural contributions are mostly negative and arise from several effects such as interstitial accommodation and geometrical fitting of one component into another due to the differences in the molar volume and free volume between component molecules. In the present study, the sign of the excess molar volumes, V^E is found to be both negative at lower carbon chain length and positive at higher carbon chain length over the entire composition range. The observed negative values of V^E in the mixtures indicate strong interaction between the two component molecules. The positive V^E values are suggestive of dispersion type of forces which is as a result of weak interactions between unlike molecules. Similar trend of V^E values was observed by Zahid *et al* [22] on their study of 1-propanol, 2-methyl-2-propanol and 1-hexanol with hexane at different temperatures, Mahajan and Mirgane [23] on binary mixtures of *n*-octane, *n*-decane, *n*-dodecane and *n*-tetradecane with octan-2-ol and Sharma *et al* [24] on 1-iodobutane with benzene, toluene, o-xylene, m-xylene, p-xylene and mesitylene binary mixture. The excess negative *VE* values also suggest that dipole – dipole interactions and other specific interactions between unlike molecules are operative in the solvent systems, [Reddy *et al* [25], Shelar *et al* [4]. Further, the negative V^E values for the systems are attributed to the small structured molecules being easily accommodated interstitially in the void space of the larger molecules. The molecular volumes of ethyl acetoacetate, (EAA), butan-2-one, pentan-2- one, hexan-2-one, heptan-2-one, octan-2-one and nonan-2-one are 2.1154×10^{-22} cm^3, 1.1497×10^{-22} cm^3, 1.7842×10^{-22} cm^3, 2.0602×10^{-22} cm^3, 2.3396×10^{-22} cm^3, 2.6103×10^{-22} cm^3 and 2.8893×10^{-22} cm^3, respectively.

The positive contribution of V^E is due to the disruptive effects of the individual molecules leading to the mutual loosening of dipole – dipole interactions between like molecules in the binary mixtures [Izonfuo and Kemeakegha [6], Kemeakegha and Benson [9], Gowrisankar *et al* [26] This shows that the interaction between component molecules of the two mixed solvents is weaker than the individual pure components Rajashri B. Sawant [27]. This trend was also observed by Ahmed *et al* [28] in the binary and ternary mixtures of cyclohexanol with 2-hexanone and heptanone.

- *Excess Viscosity*

A perusal of Table 2 shows that the values of η^E are positive and negative for the present systems.

The positive η^E values decrease with increasing chain length. The positive η^E values indicate specific interactions while the negative η^E values indicate dispersion forces Nayeem *et al* [29]. In the present investigation, the positive values of all binary systems may be attributed to the dipole-dipole interactions.

According to Fort and Moore [30], deviation in viscosity tends to become more positive as the strength of the interaction increases. The deviation in viscosity variation gives a qualitative estimation of the strength of the intermolecular interactions. The deviation in viscosities may be generally explained by considering the following factors. (i) The difference in size and shape of the component molecules and the loss of dipolar association in pure component which may contribute to a decrease in viscosity and (ii) specific interactions between unlike component molecules such as hydrogen bond formation or dipole-dipole interactions or charge-transfer complexes may cause increase in viscosity in mixtures compared to the pure components Pikkarainan [31]. The former effect produces negative deviation in viscosity and the latter effect give rise to positive deviation in viscosity.

Figures 2a and 2b show the variations of η^E with x_1, for the binary mixtures of EAA + butan-2-one and EAA + pentan-2-one which is positive at 303.15K and shows sigmoid nature at 308.15K.

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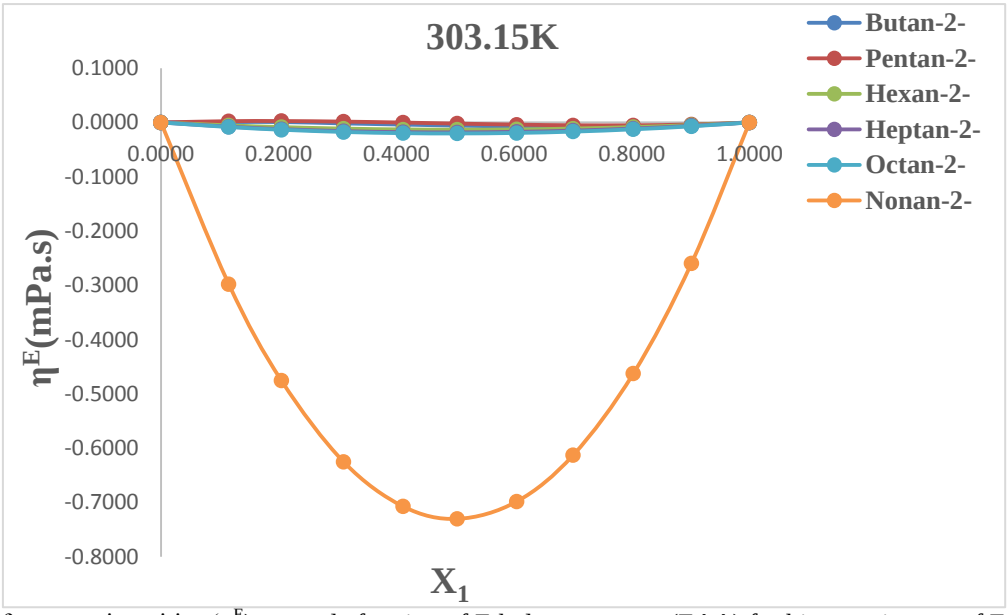

Fig. 2a:- Plots of excess viscosities (η^E) vs. mole fraction of Ethylacetoacetate (EAA) for binary mixtures of Ethylacetoacetate (EAA) + butan-2-one (1), + pentan-2one (2), + hexan-2-one (3), + heptan-2-one (4), + octan-2-one (5), + nonan-2-one (6) at 303.15 K

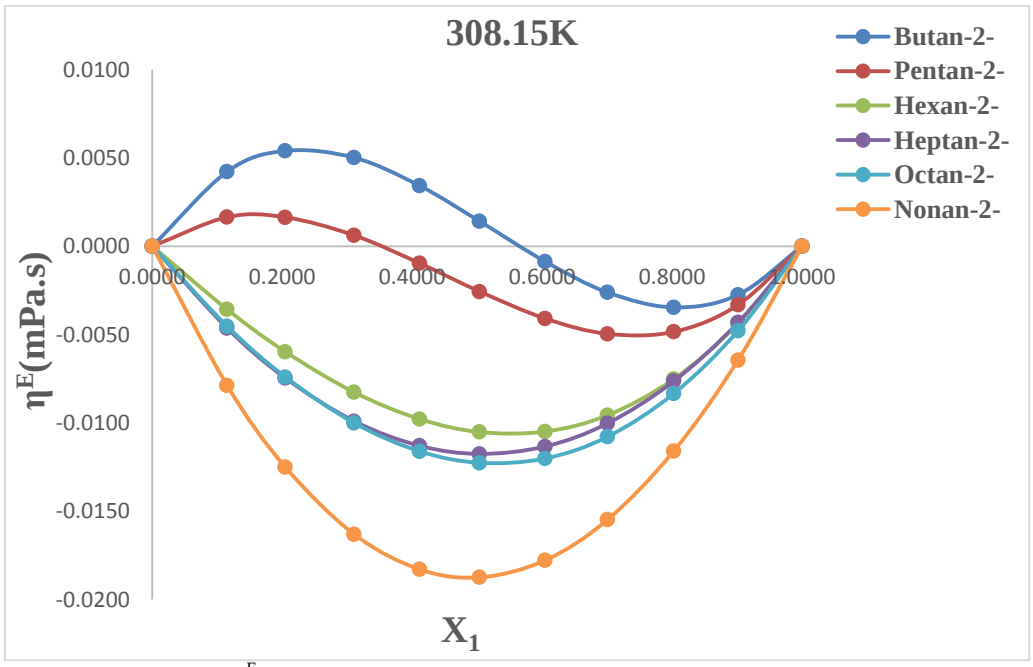

Fig. 2b:- Plots of excess viscosities (η^E) vs. mole fraction of Ethylacetoacetate (EAA) for binary mixtures of Ethylacetoacetate (EAA) + butan-2-one (1), + pentan-2one (2), + hexan-2-one (3), + heptan-2-one (4), + octan-2-one (5), + nonan-2-one (6) at 308.15 K

The positive η^E values are in the lower region and negative η^E values in higher region of mole fraction of EAA for the present systems at the investigated temperature. The investigated excess viscosities, η^E of the binary mixtures tend to change to negative values at mole fractions ($x1 \geq 0.40$ *and* 0.60) of EAA. The positive ηE values decrease with increasing chain length. The positive η^E values indicate the presence of strong specific interactions among unlike molecules, while the negative η^E values indicate dispersion forces or weak dipole-dipole interactions primarily responsible for the interaction between the component molecules.[32 –33]. The sigmoid behaviour was also observed by Shelar *et al* [4] and Rani *et al* [34] for viscosity deviation of binary mixtures of o-chlorophenol with esters, and for binary mixtures of formamide with alkanols.

The excess viscosities, η^E values of Figs. 2a and 2b show negative for (C_6 – C_9) over the entire composition range for all the mixtures at all temperatures and increases with increase in carbon chain length. The negative η^E values at equimolar concentration on EAA and the named aliphatic ketones vary as follows:
Nonan-2->Octan-2->Heptan-2->Hexan-2-

A correlation between the sign of excess viscosity, η^E and excess molar volume, V^E has been observed for a number of binary solvent systems, when η^E is negative, the excess molar volume, V^E will become positive or vice versa as shown in this study.

➢ *Excess Gibbs' free energy of activation*

The variation of excess Gibbs free energy of activation for viscous flow, ΔG^{*E} with mole fraction of EAA has been presented in Figures 3a and 3b at the investigated temperatures.

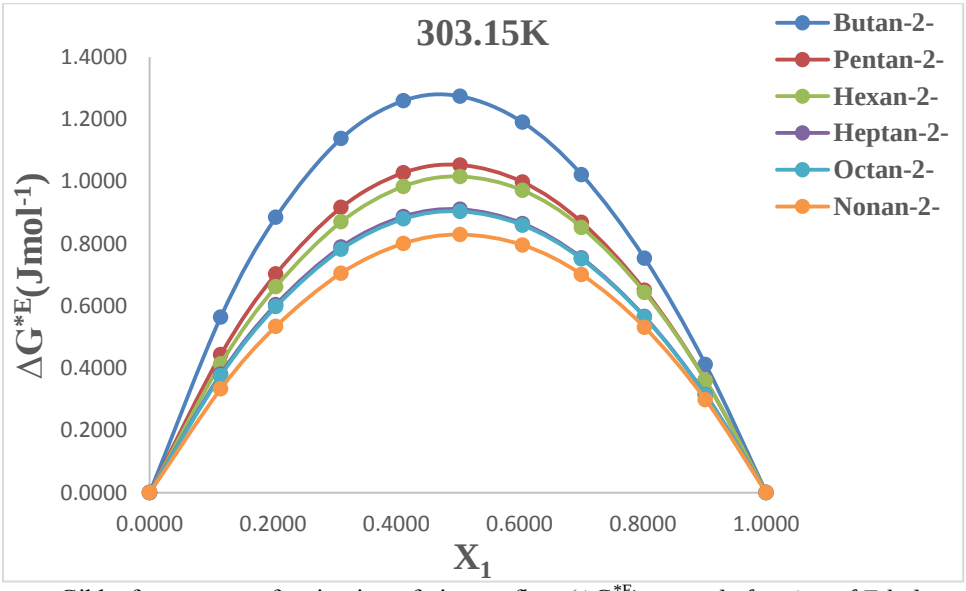

Fig. 3a:- Plots of excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) vs. mole fraction of Ethylacetoacetate (EAA) for binary mixtures of Ethylacetoacetate (EAA) + butan-2-one (1), + pentan-2one (2), + hexan-2-one (3), + heptan-2-one (4), + octan-2-one (5), + nonan-2-one (6) at 303.15 K

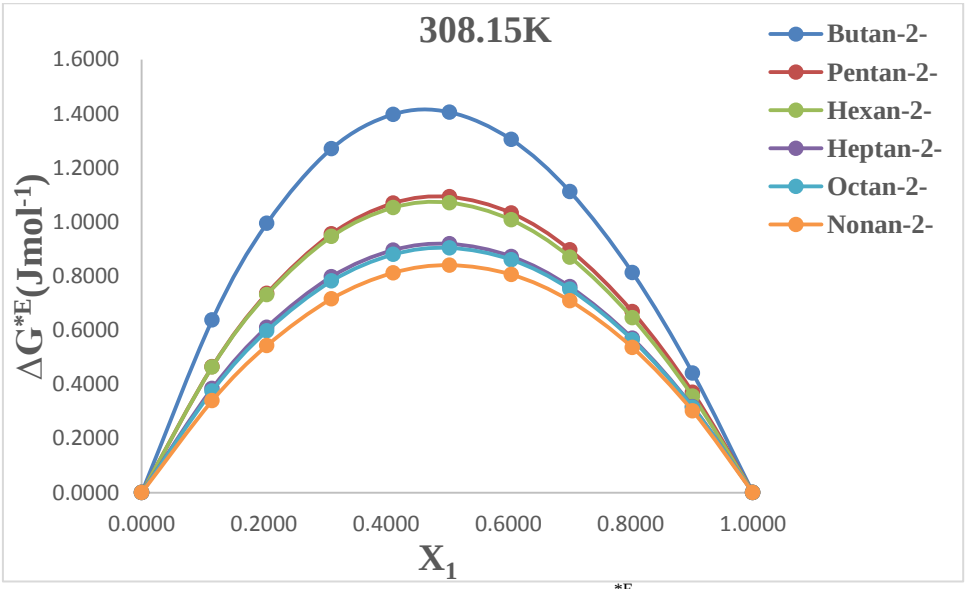

Fig. 3b:- Plots of excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) vs. mole fraction of Ethylacetoacetate (EAA) for binary mixtures of Ethylacetoacetate (EAA) + butan-2-one (1), + pentan-2one (2), + hexan-2-one (3), + heptan-2-one (4), + octan-2-one (5), + nonan-2-one (6) at 308.15 K

The excess Gibbs free energy of activation for viscous flow, ΔG^{*E} is positive all over the entire solvents composition range for all the studied binary mixtures. The positive values of ΔG^{*E} indicate the presence of specific interaction among unlike molecules. On the other hand the negative values of ΔG^{*E} suggest the presence of weak interaction among unlike molecules and strong interaction among like molecules. The excess Gibbs free energy of activation for viscous flow, ΔG^{*E} follows the order: Butan-2-one>pentan-2-one>hexan-2-one>heptan-2-one>octan-2-one>nonan-2-one.

The observed positive values of ΔG^{*E} in the binary mixtures of ethyl acetoacetate + aliphatic ketones are indicative of strong dipole – dipole interactions between EAA molecules and the named aliphatic ketones. Patil, and Mirgane [35], Ciocirlan and Iulian [36] made similar observations in their various studies of binary mixtures and

Sharma *et al* [4] and Rani *et al* [34] observed the same trend in their works. Positive values of ΔG^{*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 positive values of excess Gibbs free energies of activation of viscous flow, ΔG^{*E} decrease with increase in carbon chain length of the aliphatic ketones. Satyanarayana *et al* [37] have also reported large positive values of ΔG^{*E} for their work which was attributed to dipole-dipole interactions between unlike molecules.

➢ *Viscosity Interaction Parameters*

Several empirical equations have been employed to correlate viscosity of the binary liquid mixtures in terms of their pure component data. The predictive ability of some of the selected one parameter viscosity models such as Frenkel [38], Hind [39], Grunberg-Nissan [40] and modified Kendall-Monroe [41] were tested. The equations of these models were applied to the studied binary mixtures as follows.

According to Frenkel [38] and Hind [39], the viscosities of mixtures and those of the pure components can be related by the following equations:

$$ln\eta = x_1^2 ln\eta_1 + x_2^2 ln\eta_2 + 2x_1x_2 ln\eta_{12} \quad (8)$$

where η is expressed as follows:

$$\eta = x_1^2\eta_1 + x_2^2\eta_2 + 2x_1x_2\eta_{12} \quad (9)$$

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 Figures (4a,b and 5a,b)

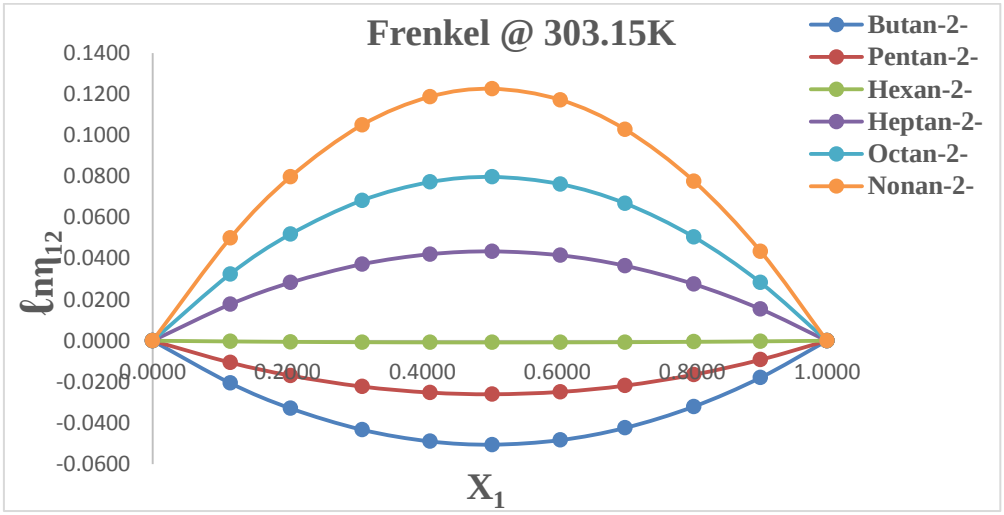

Fig. 4a:- Plots of Frenkel correlation (ln η_{12}) vs. mole fraction of Ethylacetoacetate (EAA) for binary mixtures of Ethylacetoacetate (EAA) + butan-2-one (1), + pentan-2one (2), + hexan-2-one (3), + heptan-2-one (4), + octan-2-one (5), + nonan-2-one (6) at 303.15 K

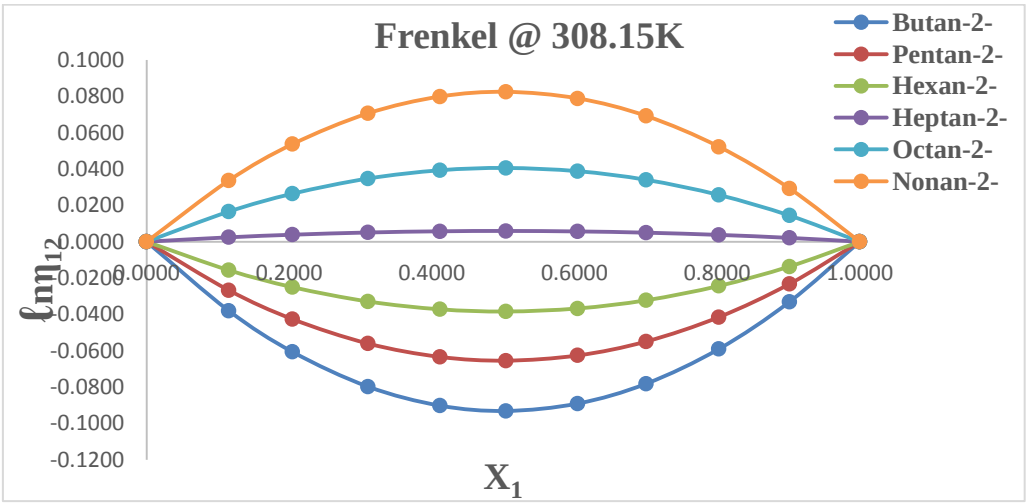

Fig. 4b:- Plots of Frenkel correlation (ln η_{12}) vs. mole fraction of Ethylacetoacetate (EAA) for binary mixtures of Ethylacetoacetate (EAA) + butan-2-one (1), + pentan-2one (2), + hexan-2-one (3), + heptan-2-one (4), + octan-2-one (5), + nonan-2-one (6) at 308.15 K

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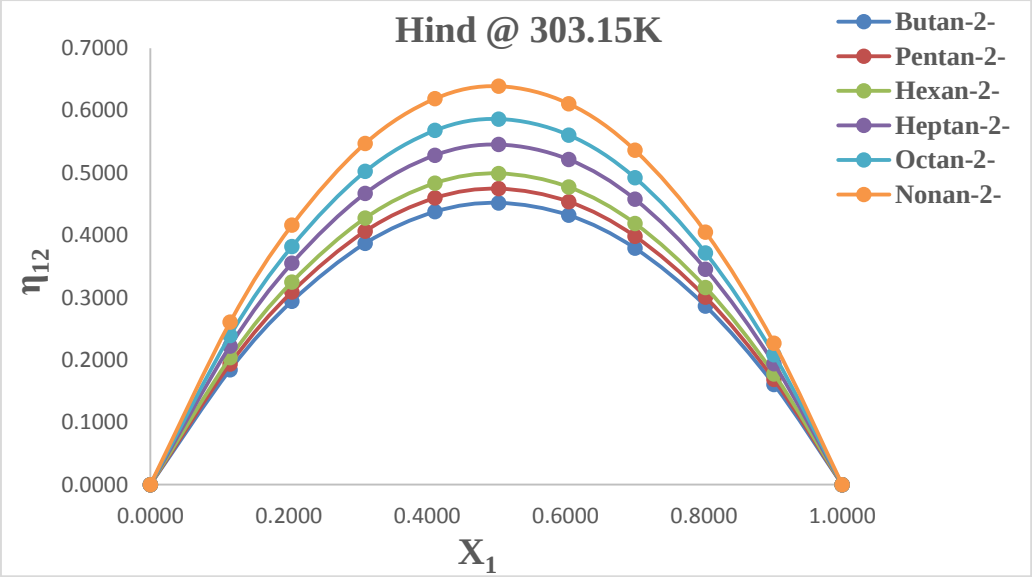

Fig. 5a:- Plots of Hind correlation (η_{12}) vs. mole fraction of Ethylacetoacetate (EAA) for binary mixtures of Ethylacetoacetate (EAA) + butan-2-one (1), + pentan-2one (2), + hexan-2-one (3), + heptan-2-one (4), + octan-2-one (5), + nonan-2-one (6) at 303.15 K

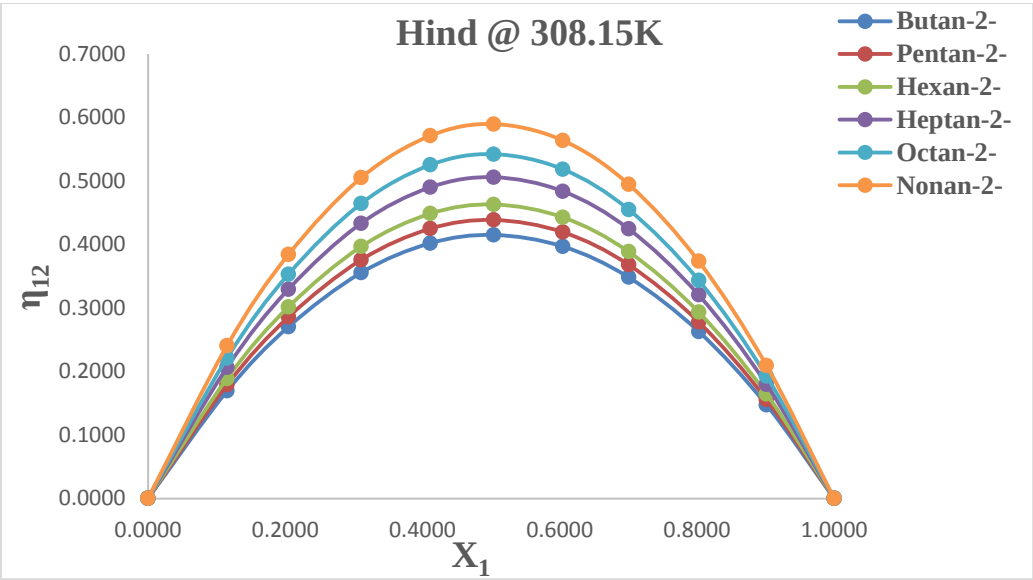

Fig. 5b:- Plots of Hind correlation (η_{12}) vs. mole fraction of Ethylacetoacetate (EAA) for binary mixtures of Ethylacetoacetate (EAA) + butan-2-one (1), + pentan-2one (2), + hexan-2-one (3), + heptan-2-one (4), + octan-2-one (5), + nonan-2-one (6) at 308.15 K

where η_{12} is defined as

$$\eta_{12} = 0.5\eta_1 + 0.5\eta_2 \quad (10)$$

Grunberg and Nissan [40] proposed a relationship between the dynamic viscosities of binary liquid mixtures and those of the pure liquid components to assess the molecular interactions due to viscosity changes 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. The equation is probably the most extensively examined relationship for the theoretical prediction of the viscosities of liquid mixtures.

The d' values calculated for the various binary mixtures are shown in Table 4 and plotted in Figures 6a and 6b.

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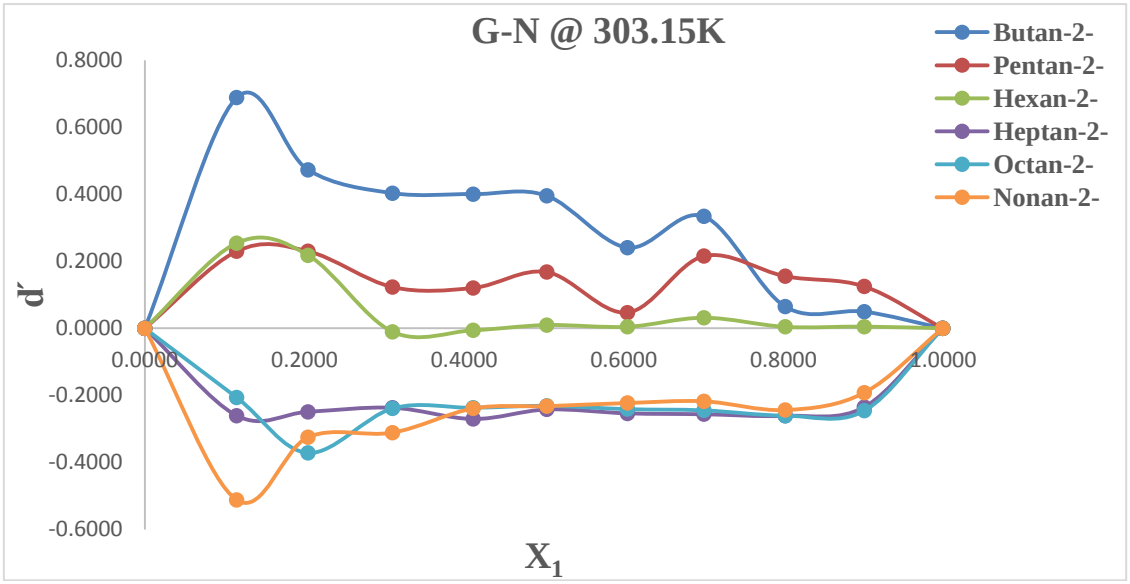

Fig. 6a:- Plots of Grunberg-Nissan correlation (d′) vs. mole fraction of Ethylacetoacetate (EAA) for binary mixtures of Ethylacetoacetate (EAA) + butan-2-one (1), + pentan-2one (2), + hexan-2-one (3), + heptan-2-one (4), + octan-2-one (5), + nonan-2-one (6) at 303.15 K

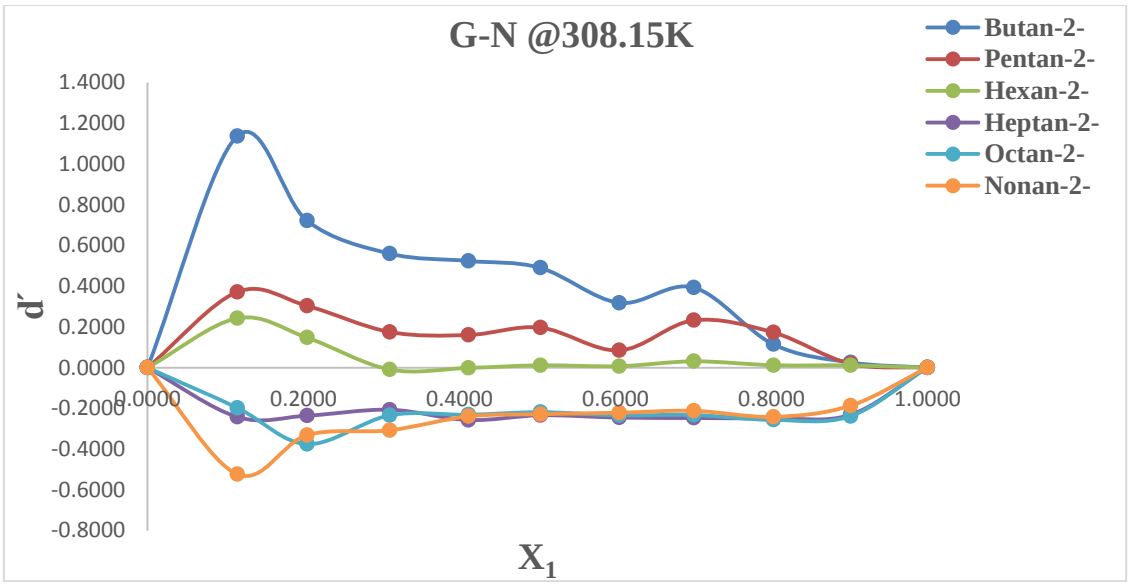

Fig. 6b:- Plots of Grunberg-Nissan correlation (d′) vs. mole fraction of Ethylacetoacetate (EAA) for binary mixtures of Ethylacetoacetate (EAA) + butan-2-one (1), + pentan-2one (2), + hexan-2-one (3), + heptan-2-one (4), + octan-2-one (5), + nonan-2-one (6) at 308.15 K

The *d′* values are entirely positive for lower ketones (C_4 – C_6) over the whole mole fraction range and are negative for (C_7 – C_9) ketones over the entire solvents range composition at the investigated temperatures.

The Grunberg and Nissan (*d′*) parameter is a measure of the strength of interactions between unlike molecules 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 mixtures Rambabu *et al* [42]. Positive and negative *d′* values are indicative of the presence of both strong and weak interactions between unlike molecules Fort and Moore [30]. Grunberg-Nissan interaction parameters are positive at low carbon chain but negative at higher carbon chain for the solvent systems over the entire solvent composition range. The values of Frenkel are negative for lower ketones (C_4 – C_6) over the whole mole fraction range and are positive for higher ketones (C_7 – C_9) over the entire solvents range composition at the investigated temperatures. Hind and Kendall-Monroe correlations show that (C_4 – C_9) values are positive throughout the solvent compositions range at all temperatures and are shown in Table 4, and are presented in Figures (5a, 5b, 7a and 7b).

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	303.15K				308.15K			
	lnη12	**η12**	**d′**	**Eηm**	**lnη12**	**η12**	**d′**	**Eηm**
X_1	EAA (1) + Butan-2-one				EAA (1) + Butan-2-one			
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1152	-0.0206	0.1842	0.6882	0.0435	-0.0380	0.1692	1.1380	0.0399
0.2047	-0.0329	0.2943	0.4726	0.0807	-0.0606	0.2703	0.7217	0.0740
0.3106	-0.0433	0.3871	0.4033	0.1256	-0.0798	0.3555	0.5604	0.1152
0.4115	-0.0490	0.4377	0.4004	0.1654	-0.0902	0.4020	0.5244	0.1517
0.5038	-0.0506	0.4519	0.3955	0.1949	-0.0931	0.4150	0.4904	0.1789
0.6047	-0.0484	0.4321	0.2408	0.2141	-0.0891	0.3968	0.3188	0.1966
0.7006	-0.0424	0.3792	0.3338	0.2131	-0.0781	0.3482	0.3937	0.1957
0.8027	-0.0320	0.2863	0.0647	0.1830	-0.0590	0.2629	0.1146	0.1681
0.9015	-0.0180	0.1605	0.0498	0.1156	-0.0331	0.1474	0.0259	0.1062
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
X_1	EAA (1) + Pentan-2-one				EAA (1) + Pentan-2-one			
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1152	-0.0106	0.1935	0.2296	0.0528	-0.0267	0.1788	0.3717	0.0495
0.2047	-0.0170	0.3091	0.2298	0.0953	-0.0426	0.2856	0.3039	0.0891
0.3106	-0.0223	0.4065	0.1229	0.1440	-0.0561	0.3757	0.1754	0.1343
0.4115	-0.0252	0.4598	0.1204	0.1849	-0.0634	0.4249	0.1607	0.1719
0.5038	-0.0260	0.4746	0.1678	0.2133	-0.0654	0.4386	0.1971	0.1980
0.6047	-0.0249	0.4538	0.0469	0.2294	-0.0626	0.4194	0.0848	0.2124
0.7006	-0.0218	0.3982	0.2155	0.2241	-0.0549	0.3680	0.2329	0.2070
0.8027	-0.0165	0.3007	0.1552	0.1889	-0.0415	0.2779	0.1731	0.1742
0.9015	-0.0092	0.1686	0.1250	0.1174	-0.0232	0.1558	0.0194	0.1081
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
X_1	EAA (1) + Hexan-2-one				EAA (1) + Hexan-2-one			
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1152	-0.0003	0.2035	0.2544	0.0626	-0.0157	0.1888	0.2427	0.0592
0.2047	-0.0005	0.3251	0.2179	0.1104	-0.0250	0.3015	0.1477	0.1040
0.3106	-0.0007	0.4275	-0.0105	0.1628	-0.0329	0.3966	-0.0088	0.1528
0.4115	-0.0008	0.4835	-0.0058	0.2044	-0.0372	0.4485	-0.0010	0.1912
0.5038	-0.0008	0.4991	0.0098	0.2316	-0.0384	0.4630	0.0117	0.2158
0.6047	-0.0008	0.4773	0.0046	0.2443	-0.0367	0.4427	0.0075	0.2270
0.7006	-0.0007	0.4188	0.0316	0.2347	-0.0322	0.3885	0.0313	0.2174
0.8027	-0.0005	0.3162	0.0044	0.1945	-0.0243	0.2933	0.0121	0.1797
0.9015	-0.0003	0.1773	0.0051	0.1191	-0.0136	0.1645	0.0113	0.1097
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
X_1	EAA (1) + Heptan-2-one				EAA (1) + Heptan-2-one			
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1152	0.0177	0.2224	-0.2603	0.0805	0.0024	0.2063	-0.2416	0.0758
0.2047	0.0283	0.3552	-0.2490	0.1377	0.0039	0.3295	-0.2355	0.1292
0.3106	0.0373	0.4672	-0.2370	0.1959	0.0051	0.4334	-0.2063	0.1833
0.4115	0.0421	0.5284	-0.2704	0.2384	0.0057	0.4901	-0.2569	0.2223
0.5038	0.0435	0.5454	-0.2421	0.2627	0.0059	0.5059	-0.2335	0.2444
0.6047	0.0416	0.5215	-0.2537	0.2693	0.0057	0.4838	-0.2449	0.2499
0.7006	0.0365	0.4577	-0.2563	0.2522	0.0050	0.4245	-0.2470	0.2334
0.8027	0.0276	0.3455	-0.2611	0.2037	0.0037	0.3205	-0.2479	0.1881

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0.9015	0.0155	0.1937	-0.2351	0.1218	0.0021	0.1797	-0.2313	0.1122
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
X_1	EAA (1) + Octan-2-one				EAA (1) + Octan-2-one			
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1152	0.0325	0.2391	-0.2065	0.0961	0.0165	0.2211	-0.1971	0.0895
0.2047	0.0519	0.3819	-0.3716	0.1609	0.0264	0.3531	-0.3750	0.1497
0.3106	0.0683	0.5023	-0.2389	0.2236	0.0348	0.4645	-0.2337	0.2076
0.4115	0.0772	0.5681	-0.2371	0.2662	0.0393	0.5253	-0.2311	0.2468
0.5038	0.0797	0.5864	-0.2314	0.2878	0.0406	0.5422	-0.2185	0.2665
0.6047	0.0762	0.5607	-0.2412	0.2893	0.0388	0.5185	-0.2340	0.2674
0.7006	0.0669	0.4921	-0.2447	0.2659	0.0341	0.4550	-0.2321	0.2455
0.8027	0.0505	0.3715	-0.2604	0.2108	0.0257	0.3435	-0.2562	0.1943
0.9015	0.0283	0.2083	-0.2460	0.1238	0.0144	0.1926	-0.2378	0.1140
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
X_1	EAA (1) + Nonan-2-one				EAA (1) + Nonan-2-one			
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1152	0.0500	0.2605	-0.5120	0.1156	0.0336	0.2404	-0.5231	0.1072
0.2047	0.0799	0.4161	-0.3248	0.1897	0.0537	0.3840	-0.3311	0.1756
0.3106	0.1050	0.5473	-0.3111	0.2573	0.0706	0.5051	-0.3073	0.2380
0.4115	0.1188	0.6190	-0.2391	0.2997	0.0799	0.5712	-0.2389	0.2769
0.5038	0.1226	0.6390	-0.2322	0.3177	0.0825	0.5896	-0.2283	0.2933
0.6047	0.1173	0.6110	-0.2229	0.3126	0.0789	0.5638	-0.2211	0.2883
0.7006	0.1029	0.5361	-0.2177	0.2818	0.0692	0.4948	-0.2117	0.2597
0.8027	0.0777	0.4048	-0.2438	0.2190	0.0523	0.3736	-0.2415	0.2016
0.9015	0.0436	0.2270	-0.1923	0.1262	0.0293	0.2094	-0.1864	0.1161
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4:- Viscosity Data Correlation Parameters (Frenkel, $\boldsymbol{ln\eta_{12}}$, Hind, η_{12}, Grunberg–Nissan, d' and Kendall–Monroe, $E\eta_m$) of Binary Mixtures of Ethylacetoacetate (EAA) and (C_4–C_9) Aliphatic ketones Solvent Systems at (303.15 and 308.15) K.

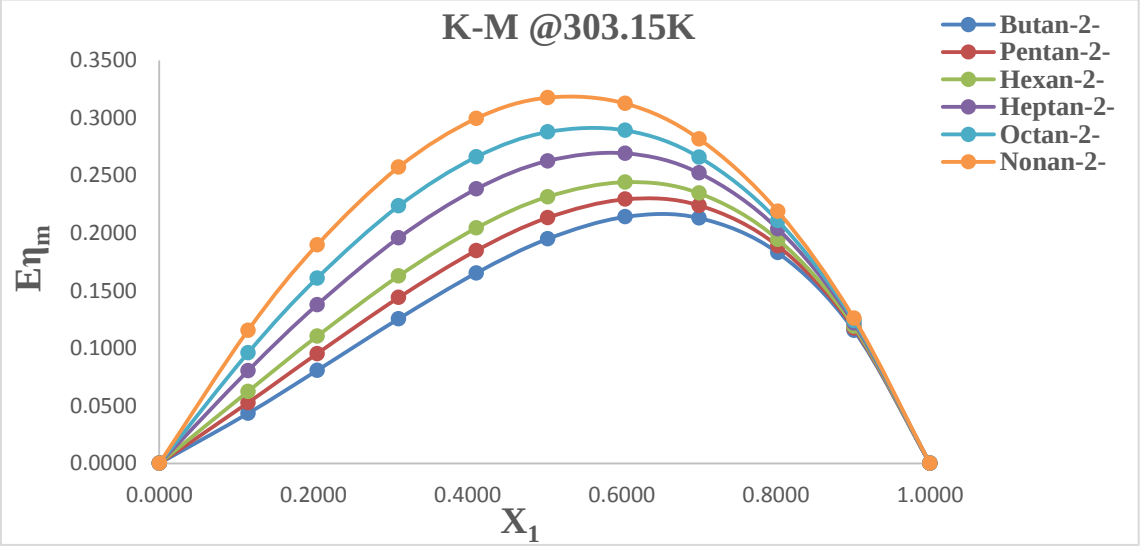

Fig. 7a:- Plots of Kendell-Monroe modified correlation (Eηm) vs. mole fraction of Ethylacetoacetate (EAA) for binary mixtures of Ethylacetoacetate (EAA) + butan-2-one (1), + pentan-2one (2), + hexan-2-one (3), + heptan-2-one (4), + octan-2-one (5), + nonan-2-one (6) at 303.15 K

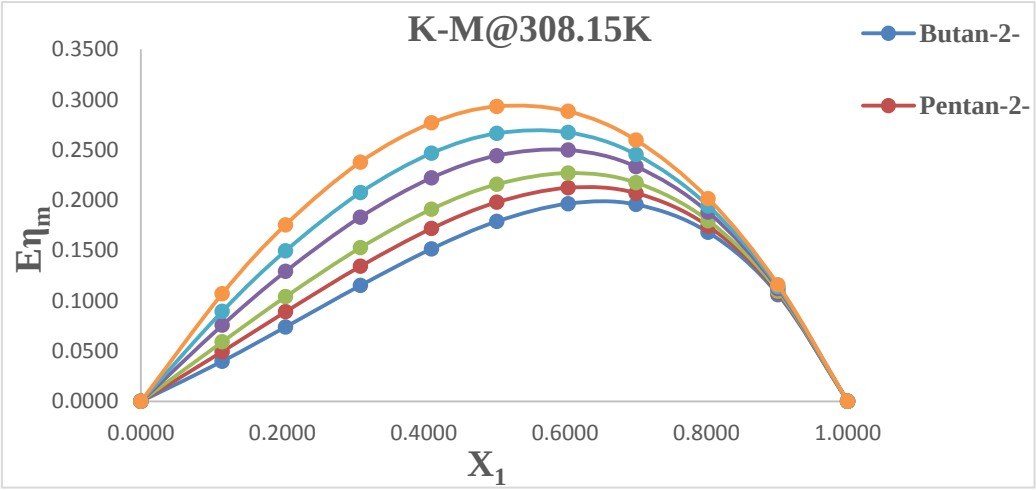

Fig. 7b:- Plots of Kendell-Monroe modified correlation (Eηm) vs. mole fraction of Ethylacetoacetate (EAA) for binary mixtures of Ethylacetoacetate (EAA) + butan-2-one (1), + pentan-2one (2), + hexan-2-one (3), + heptan-2-one (4), + octan-2-one (5), + nonan-2-one (6) at 308.15 K

According to Reddy and co-workers [19] 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 values observed in this present study reveal that both specific and dispersive forces of interactions are taking place. This trend is in line with the results obtained for η^E and ΔG^{*E} for the solvent systems.

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

$$E\eta_m = x_1x_2\left(x_1\eta_1^{1/3} + x_2\eta_2^{1/3}\right)^3 \quad (13)$$

which is the modified Kendall – Monroe equation [40].

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.

T/K	Frenkel		Hind		Grunberg-Nissan		Kendall-Monroe	
	$ln\eta_{12}$	APD	η_{12}	APD	d'	APD	$E\eta_m$	APD
EAA (1) + Butan-2-one (2)								
303.15	-0.3472	9.4263	11.5884	-2.1010	0.1402	8.9555	1.5468	7.5971
308.15	-2.8568	11.9466	10.0033	-0.9083	2.9495	6.1426	1.3360	7.7555
EAA (1) + Pentan-2-one (2)								
303.15	-1.8159	10.7908	10.4982	-0.7364	1.4732	7.7119	1.4500	7.7336
308.15	-2.6351	11.7347	9.7017	-0.6427	1.8963	7.1884	1.3444	7.7421
EAA (1) + Hexan-2-one (2)								
303.15	-0.8845	9.8745	11.0329	-0.6824	-0.0272	9.1150	1.5642	7.7052
308.15	-1.6540	10.6639	10.2325	-0.6405	-0.0731	9.1604	1.4567	7.7056
EAA (1) + Heptan-2-one (2)								
303.15	0.5302	8.6596	12.0407	-0.7028	-2.4959	11.1210	1.7622	7.6576
308.15	-0.2629	9.3208	11.1674	-0.6744	-2.4895	11.2678	1.6385	7.6581
EAA (1) + Octan-2-one (2)								
303.15	1.5452	7.9420	12.9336	-0.5259	-2.2649	10.7750	1.9244	7.6601
308.15	0.6978	8.5315	11.9585	-0.4962	-2.1450	10.8106	1.7812	7.6629
EAA (1) + Nonan-2-one (2)								
303.15	2.6357	7.3125	14.0781	-0.4081	-2.2777	10.6277	2.1195	7.6608
308.15	1.7566	7.8084	12.9908	-0.3941	-2.2155	10.7085	1.9566	7.6624

Table 5:- Fitting parameters with Average Percentage Deviation (*APD*) values of the binary mixtures of ethyl acetoacetate and (C_4 – C_9) aliphatic ketones at T = (303.15 and 308.15) 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 and the number of numerical coefficients in the equation. The values of the Average Percentage Deviations (*APD*) for the various binary mixtures are presented in Table 5. The *APD* values obtained for Hind are very small compared to Frenkel. The values of Hind are negative while that of Frenkel, Grunberg – Nissan and Kendall – Monroe are positive at the investigated temperatures.

V. CONCLUSION

The excess molar volumes, V^E, excess viscosity, η^E, and excess Gibbs' free energy of activation of viscous flow, ΔG^{*E}, of the binary mixtures of ethylacetoacetate (EAA) + aliphatic ketones (butan-2-one, pentan-2-one, hexan-2-one, heptan-2-one, octan-2-one and nonan-2-one) have been determined at (303.15 308.15) K over the entire range of solvent compositions. The values of excess molar volume, V^E of the binary mixtures has been found to be both positive and negative over the entire solvent composition range at all temperatures studied. The observed values of V^E for the binary mixtures can be explained in terms of the following factors (i) the dissociation of the associated polar molecules (ii) dipole – dipole interactions between the component molecules and (iii) geometric effect due to differences in molar volumes. The excess viscosity, η^E of all the binary mixtures were also positive and negative at all temperatures. The excess Gibbs free energy of activation of viscous flow, ΔG^{*E} of the binaries were found to be positive all over the mole fraction (x_1) range and at all temperatures. The experimental viscosity results were also correlated by using some empirical relations proposed by Frenkel, Hind, Grunberg–Nissan and modified Kendall–Monroe.

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