



GLOBAL JOURNAL OF RESEARCHES IN ENGINEERING: C  
CHEMICAL ENGINEERING

Volume 15 Issue 1 Version 1.0 Year 2015

Type: Double Blind Peer Reviewed International Research Journal

Publisher: Global Journals Inc. (USA)

Online ISSN: 2249-4596 & Print ISSN: 0975-5861

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**Keywords:** *viscosity, density, ultrasonic velocity, acetophenone, ethylchloroacetate, volumetric properties.*

**GJRE-C Classification :** FOR Code: 090499



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# Prediction of Volumetric and Viscometric Properties of Acetophenone – Ethylchloroacetate Binary Mixture at 303K & 323K with different Model Analysis

M. Sathiyamoorthy <sup>α</sup> & Dr. Mazda Biglari <sup>σ</sup>

**Abstract-** In this present investigation the volumetric properties and viscosity of the acetophenone ethylchloroacetate liquid binary mixture were determined. The properties were found as a function of mole fraction and at a temperature of 303 K and 323 K. The excess molar volumes and ultrasonic velocity are also determined. It is used to predict the intermolecular interactions in the process calculation, pipe design and automobile fuel section. The kinematic viscosities of this mixture were analyzed with four different models namely McAllister, Krishnan-Laddha, Jouyban-Acree and Redlich-kister. The different properties were plotted against mole fraction of the liquid mixtures at various compositions and temperatures.

**Keywords:** viscosity, density, ultrasonic velocity, acetophenone, ethylchloroacetate, volumetric properties.

## I. INTRODUCTION

Liquid mixtures have attracted considerable attention due to their unusual behavior. In chemical process industries, material are normally handled in fluid form and as the consequence, the physical, chemical, and transport properties of fluids assume importance. Fluid mixtures in process industries are often separated into their components by mass transfer operations. Design of such operations requires quantitative estimation of the properties of fluid mixtures. Recently there has been considerable progress in the studies on intermolecular interactions and the internal structure of liquid mixtures. Thus data on some of the properties associated with the liquids and liquid mixture like density, viscosity and ultrasonic velocity find extensive application in solution theory and molecular dynamics. These results are necessary in chemical, electrochemical, biochemical and kinetic studies.

### a) Thermo Physical Properties

Thermo physical properties of liquid mixtures have extensive practical applications in day to day life. Any problem connected with heat, momentum and mass transfer entails knowledge of thermo physical properties and their variation with temperature.

The data on some of the thermo physical properties associated with the liquids and liquid mixtures find applications in solution theory and molecular dynamics (Mchaweh et al 2004). These results are necessary for interpretation of data obtained from thermo chemical, electrochemical, biochemical and kinetic studies (Kenart et al 2000). These are needed in many engineering problems such as process calculations, simulations and pipe design and automobile fuel selection. The automobile fuel has to be checked for the consistency of its properties before it is supplied to the engine. The thermo physical properties of liquid mixtures like density, viscosity, refractive index, surface tension and ultrasonic velocities are often applied for calculations of other parameters characterizing binary and ternary liquid mixtures.

#### i. Density

Density belongs to the group of most useful intensive physiochemical properties widely applied studies of pure liquids and liquid mixtures. It behaves as an additive volumetric property for ideal solutions. Results of many experimental works show that the analysis of deviation from density as a function of the composition of the mixture is more useful for studies of intermolecular interactions in liquid mixtures that the analogous examination of changes of density. The knowledge of density of liquid mixtures is necessary for calculations of other properties like viscosity and thermo acoustical parameters.

#### ii. Viscosity

Viscosity is not a simple additive property. It is an important transport property for process design in petroleum, petrochemical and other chemical industries involving fluid transportation, mixing, agitation, filtration, heat exchange and concentration. The investigation of viscosity can be a powerful tool for characterization of interactions present in the mixtures.

#### iii. Ultrasonic Velocity

The ultrasonic studies are extensively used to estimate the thermodynamic properties and predict the intermolecular interaction of liquid mixtures. Ultrasonic velocity of binary liquid mixtures could be related either to size and shape of the molecules or to the entropy

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effect because of volume and space filling effects with mixing processes. The principle used in the measurement of velocity is based on the accurate determination of the wavelength in the medium. The high frequency generator generates variable frequency, which excites the quartz crystals. The excited quartz crystal generates ultrasonic waves in the experimental liquid. The liquid will serve as an acoustical grating element when ultrasonic waves passes through the ruling of the grating, successive maxima and minima occurs, satisfying the condition for diffraction. Ultrasonic waves are high frequency mechanical waves. Ultrasonic velocity in a medium depends inversely on density and the compressibility of the medium. The variation in the ultrasonic velocity of the liquid mixtures increases or decreases of intermolecular free length of mixing and vice versa.

iv. *Intermolecular Forces*

Intermolecular forces are electrostatic forces of attraction that exist between an area of negative charge on one molecule and an area of positive charge on a second molecule. Intermolecular forces are a secondary method of holding a solid state structure together. As the name implies, these are forces that exist between molecules. Bonds exist within molecules. For reasons that will not be discussed here, intermolecular forces are only associated with systems that use covalent bonding within the molecules. Intermolecular forces are not

$$\ln v = x_1^3 \ln v_1 + 3 x_1^2 x_2 \ln v_{12} + 3 x_1 x_2^2 \ln v_{21} + x_2^3 \ln v_2 -$$

$$\ln(x_1+x_2m_2/m_1) + 3x_1^2x_2 \ln((2 + m_2/m_1)/3) + 3x_1x_2^2 \ln(1+2m_2/m_1)/3 + x_2^3 \ln(m_2/m_1)$$

The above equation is McAllister equation based on three body model. It contains 2 constants namely  $v_{12}$  and  $v_{21}$ . The constants can be evaluated using least square method.

ii. *Kirshnan-Laddha model*

Krishnan and Laddha (1963) have proposed an equation to predict the viscosities of binary liquid mixtures based on Eyring's theory of absolute reaction rates.

$$\ln v_{mix} = x_1 \ln v_1 + x_2 \ln v_2 - 2.303x_1x_2 (A + B(x_1 - x_2)) - \ln(x_{1M1} + x_2M_2) + x_1 \ln M_1 + x_2 \ln M_2$$

The constants can be evaluated if the viscosity data is available for binary system at a particular temperature using least squares method.

iii. *Jouyban-Acree model*

Jouyban proposed a model for correlating the viscosity of liquid mixture at various temperatures.

$$\ln v_m = x_1 \ln v_1 + x_2 \ln v_2 + (x_1 x_2 / T) \sum a_i (x_1 - x_2)^i$$

Where  $v_m$ ,  $v_1$ , and  $v_2$  are the viscosities of the mixture and solvents 1 and 2 at temperature T, respectively.  $A_i$  are the model constants.

c) *Models based on excess properties*

i. *Redlich-Kister model*

Redlich and Kister have proposed an equation to predict deviation in excess values of binary liquid mixtures. The equation is as follows

encountered in systems that employ ionic bonding. Some elements, such as the noble gases, exist with intermolecular forces and no bonding at all. Intermolecular forces exist in three different levels of strength. The differing strengths are a function of the magnitude of the areas of charge that hold them together. These three different forces are Hydrogen bonding (the strongest), Dipole-dipole forces, London dispersion forces (the weakest). Two of the intermolecular forces are associated with polar structures Hydrogen bonding and Dipole-dipole forces. One of the intermolecular forces is associated with non polar structures is London dispersion forces.

b) *Models based on viscosities of pure component*

i. *McAllister model*

The Eyring's theory of absolute reaction rates was used to develop a model to predict the viscosity of liquid mixtures. Mcallister (1960) proposed a model which assumes the free energy of activation for viscosity are additive on mole fraction basis.

$$\text{From Eyring's Theory } v = h \lambda_1 / \lambda_2 \lambda_3 \lambda^2 e^{\delta G/RT}$$

$$Y = (h n / m) e^{\delta G/RT}$$

McAllister used the above equation for binary liquid mixtures considering various interactions between the molecules in one plane. The size ratio of the 2 molecules should be less than 1.5.

$$Y = x_1 x_2 \sum a_{i-1} (x_1 - x_2)^{i-1}$$

Where, Y refers to  $V^E$  or  $\delta \eta$

d) *Models based on ultrasonic velocity*

Sound speed by Jacobson's free length theory "Jacobson (1952) is calculated using the following formula.

$$U^{fl} = k / l_{(mix)} \rho^{1/2}_{exp}$$

Where k is the Jacobson's constant ( $k = (93.875 + 0.375t) \cdot 10^{-8}$ ) and depends only on temperature and  $l_{(mix)}$  is intermolecular free length of mixture.

Vandael vangeal (1969) ideal mixing relation is compared from the following formula.

$$U^{van} = [(x_1/m_1 u_1^2 + x_2/m_2 u_2^2) (x_1 m_1 + x_2 m_2)]^{-1/2}$$

Where  $x_1$  and  $x_2$  are mole fractions and  $u_1$  and  $u_2$  is speed of sound of acetophenone and benzene respectively. The sound speed in the mixture is given by impedance dependence relation "shipra and parsania (1995) as

$$U^{idr} = [(x_1 z_1 + x_2 z_2) / (x_1 \rho_1 + x_2 \rho_2)]$$

Where  $x_i$ ,  $z_i$  and  $\rho_i$  are the mole fractions, impedance and density of the  $i^{th}$  component respectively.

## II. EXPERIMENTAL SETUP & PROCEDURE

The aim of this research is to measure the density and Viscosity of the Acetophenone Ethylchloroacetate binary mixtures at two different temperatures (303, and 323) K and over the entire composition. These values have been used to calculate the excess molar volume ( $V^E$ ), deviation in viscosity ( $\Delta\eta$ ). The Viscosity values were fitted to the models of McAllister, Krishnan-Laddha and Jouyban-Acree. The excess values were (like excess molar volumes, deviation in viscosity) fitted to Redlich-Kister type equation to obtain their coefficients and standard deviations. The experimental setup has been shown in the figure 1.

### a) Viscometers

Capillary viscometers are the most commonly used instruments for Newtonian liquids. Most glass capillary viscometers are operated by force of gravity. Because of small driving force this class of devices is useful for low viscosity liquids ranging from 0.4 to 16000 centistokes. Glass capillary instruments are low stress instruments the shear stress ranges from 10 to 500 dynes/cm<sup>2</sup>. The principle of these instruments is derived from viscometer originally used by Ostwald.

The Kinematic viscosities were measured at the desired temperature using Ostwald viscometer as shown in Figure 2. The time was measured with a precision of 0.01s and the uncertainty in the viscosity was estimated to be less than 0.0003mpa.s. Ostwald viscometer was previously calibrated using water. In the viscometer a sample of liquid was charged from tube 1 to bulb C, so that level in the arm stands at the mark. The viscometer with the sample is immersed in a water bath so that it attains the desired temperature. Suction is applied so that liquid is drawn up to mark 'A' through bulb D. The efflux time of the liquid between marks A and B is noted after releasing the vacuum. The liquid mixture was charged into the viscometer. After the mixture had attained bath temperature, flow time has been determined. The above steps were continued and reported. The kinematic viscosity was obtained from the working equation

$$v = at - b/t$$

Where the two constants a and b were obtained by measuring the flow time t of benzene.

### b) Pycnometer

Pycnometer is a vessels with capillary necks in which volume of liquid is weighed. The volume is determined by weighing the vessel filled with water at definite temperature. Densities were determined by using 25cm<sup>3</sup> bicapillary Pycnomete. The quantity of liquid is adjusted so that the liquid meniscus is at the mark on the horizontal capillary while the other arm is completely filled. Tilting the completely filled unit slightly makes this adjustment and drawing liquid slowly from other capillary by touching a piece of filter paper to it. The Pycnometer filled with air bubble free experimental liquids was kept in a transparent walled water bath (maintained constant to  $\pm 0.01K$ ) for 15 minutes to attain thermal equilibrium. The precision density measurements were within  $\pm 0.0003g.cm^{-3}$ .

### c) Thermostatic bath

Water bath was used for maintaining a constant temperature during the testing. It was capable of controlling temperature with an accuracy of  $\pm 0.01^\circ C$ .

### d) Experimental Procedure

The charge for viscometer was prepared by taking 20 cc of the solution obtained by mixing the two liquids in different proportions. The thermostat was set to the desired temperature. After it had been cleaned and dried the viscometer was immersed in the bath so that the mark A is at least 2 cm below the surface of the bath liquid. The liquid

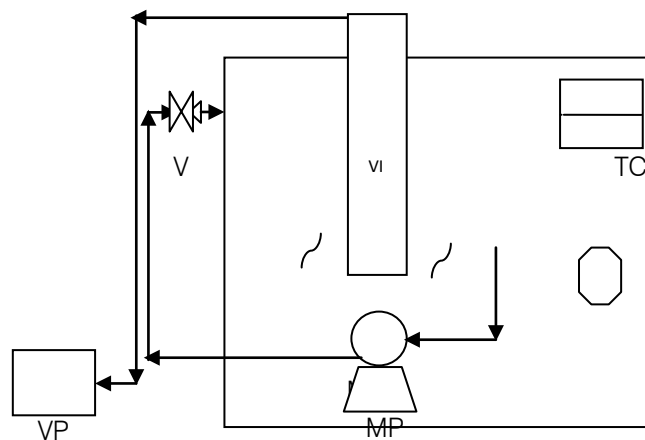


Figure 1 : Experimental setup

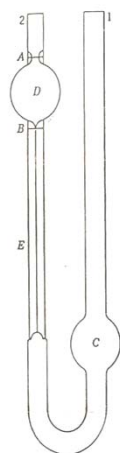


Figure 2 : Oswald viscometer



Figure 3 : Oswald Sprengel pycnometer

VI-Viscometer TC-Temperature controller, V-Control valve MP-Monobloc pump VP - Vacuum pump mixture was charged into tube 1 of the viscometer so that the air bubbles were absent and the level in this arm stood at the mark at the bulb when the temperature was attained. After the sample had attained the bath temperature it was blown up to a point 2cms above the mark A and the liquid was allowed to flow freely and time required for the liquid to flow from top to bottom mark was taken as the flow time. The above steps were continued and an average of 5 sets of flow time was reported. The stop watch used had an accuracy of 0.01 sec.

The chemicals used in this investigation are:

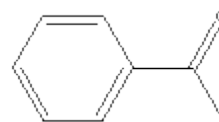
- Acetophenone.
- Ethylchloroacetate.

The purities of the compounds were checked by comparing the measured densities and viscosities with those reported in the literature.

i. *Properties of Chemicals - Acetophenone*

- Acetylbenzene
- 1-Phenylethanone
- Phenyl methyl ketone
- Methyl phenyl ketone

a. *Structure*



b. *Description*

Colorless liquid, sweet, almond odor

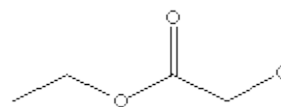
c. *Uses*

In perfumery to impart an orange-blossom-like odor, catalyst for polymerization of olefins, in organic synthesis, especially as photo sensitizer.

ii. *Properties of Chemicals - Ethylchloroacetate*

- Chloroacetic acid, ethyl ester
- Ethyl Chloro ethanoate

a. *Structure*



b. *Description*

Colorless liquid, mobile liquid, extremely irritating, pungent, fruity odor, lachrymator.

c. *Uses*

Solvent, organic syntheses, military poison, vat dyestuffs.

Table 1 : Properties of pure components

S. No.	Properties	Unit	Acetophenone	Ethylchloroacetate
1	Formula	--	C <sub>8</sub> H <sub>8</sub> O	C <sub>4</sub> H <sub>7</sub> ClO <sub>2</sub>
2	Molar mass	Kg/kmol	120.15	122.55
3	Melting Point	°C	20	-26
4	Boiling Point	°C	201.7	144
5	V.Pressure Saturation	mmHg	0.3	5
6	Concentration	ppm	1300ppm	13160ppm
7	Critical Temp	°C	428	345
8	Critical Press	mmHg	3.8	37.4
9	Density	Kg/m <sup>3</sup>	1.027	1.15
10	Solubility in Water	g/L	5.5	Insoluble
11	Viscosity	cp	2.28	2.93 x10 <sup>-3</sup>
12	Surface Tension	g/s <sup>2</sup>	39.8	31.7
13	Refractive index	--	1.5339	1.4235
14	Heat of Vaporization	kJ/mol	49.0	49.4

### III. RESULTS & DISCUSSIONS

Assuming the shapes of the molecules are spherical, the size ratio of the molecules is given by the formula

$$r_1/r_2 = [(M_1/M_2)(\rho_2/\rho_1)]^{1/3}$$

For McAllister model the size ratio should be less than 1.5.

Where,

$r_1, r_2$  are the radius of the component 1 and 2

$\rho_1, \rho_2$  are the density of the pure component 1 and 2

$M_1, M_2$  are the molecular mass of component 1 and 2

Ethylchloroacetate/Acetophenone = 0.9897

Since the size ratio for binary system is less than 1.5, so the system was considered for McAllister three-body model. McAllister model, Krishnan and Laddha model were tested with experimentally obtained viscosity data for the binary and ternary mixtures at 30°C, 50°C for the following mixtures.

Ethylchloroacetate (1) + Acetophenone (2)

The respective binary and ternary constants  $v_{12}, v_{21}$ , were determined by the method of least squares for each system. With these constants viscosity was then calculated for binary and ternary systems at each composition. The deviation of experimental value from the predicted was calculated as follows.

$$\text{Percentage Deviation, } d = ((v_{\text{exp}} - v_{\text{calc}})/v_{\text{calc}}) * 100$$

Standard Deviation was calculated using the relationship,

$$SD = (\sum (v_{\text{exp}} - v_{\text{calc}})^2 / (N-m))^{1/2}$$

Where,

N-Number of data points, m – Number of coefficients

The binary viscosity and density values are used to calculate viscosity deviation using the relationship

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

The density values have been used to calculate excess molar volume using the formula

$$V^E = (x_1m_1 + x_2m_2) / \rho_{12} - x_1m_1 / \rho_1 - x_2m_2 / \rho_2$$

Results of Present Investigation show that McAllister model, Joubyan-Acree can be used to predict viscosity of binary mixtures. Redlich- Kister equation can be used to predict Excess molar volume of binary liquid mixtures.

#### a) Discussion

Deviation of physical property of liquid mixtures from the ideal behavior is the measure of the interaction between the molecules which is attributed to either adhesive or cohesive forces.

McAllister equation, Krishnan-Laddha equation and Joubyan-Acree equation were tested with the experimentally obtained data at 30°C and 50°C. The constants were obtained by the method of least squares. With these constants the viscosity values were calculated at each composition. The calculated values agreed with the experimental values with a high degree of precision for McAllister model compared to Krishnan-Laddha model. The viscosity of a mixture strongly depends on entropy of the mixture, which is related to liquid structure and enthalpy; and consequently to molecular interactions between the components of the mixtures.

The variation of  $\Delta\eta$  and  $V^E$  with mole fraction of Ethylchloroacetate for the system Ethylchloroacetate (1) + Acetophenone (2) was studied at 30°C and 50°C respectively. The excess molar volume and deviation in viscosity were fitted with Redlich - Kister type equation.

For the mixtures without strong interactions the viscosity deviations are negative. According to this,  $V^E$  is the result of contributions from several opposing effects. This may be divided arbitrarily into three types namely, physical, chemical and structural. Physical effects contribute to positive term of  $V^E$ . The chemical or specific intermolecular interactions result in a volume decrease and contribute negative values to  $V^E$ . The structural contributions are mostly negative and arise from interstitial accommodation and changes in free volume. The actual volume change therefore depends on the relative strength of these effects.

The  $V^E$  values were found to be negative. Negative values of  $V^E$  suggest specific interaction between mixing components. Ethylchloroacetate is a weak dipolar molecule, with a dipolar moment of 2.69. Whereas Acetophenone is strong dipolar molecule, with a dipole moment of 3.028. Oxygen group in Acetophenone is attracted towards the Chlorine group in Ethylchloroacetate, which forms dipole-dipole bond. The negative deviations in viscosity over the whole composition range suggest that in these mixtures, the forces between unlike molecules are lesser than the force between like molecules.

Table 2 : Determination of Excess Molar Volume At 303K

S.No	Molefraction of Ethyl Chloroacetate ( $x_1$ )	Density $\rho$ (g/cc)	Excess Volume $V^E$ (cc/gmole)	Kinematic Viscosity $\gamma$ (cS)	Absolute Viscosity $\eta$ (cP)	Viscosity Deviation $\Delta\eta$ (cP)
1	0	0.947	0	1.4969	1.41831	0
2	0.1089	1.000	-4.4368	1.1523	1.15287	-0.2596
3	0.2151	1.002	-2.4388	1.1222	1.12489	-0.2068
4	0.3199	1.006	-0.7810	1.058	1.06580	-0.1887
5	0.4223	1.047	-0.3277	1.015	1.06300	-0.1522
6	0.5231	1.064	-3.0582	0.9312	0.99135	-0.1574
7	0.6224	1.072	-1.8051	0.8809	0.94454	-0.1302
8	0.7191	1.058	1.65118	0.8474	0.89722	-0.0882
9	0.8144	1.085	0.82216	0.8273	0.89786	-0.0339
10	0.9086	1.094	1.8223	0.787	0.86145	-0.000
11	1	1.132	0	0.7164	0.81114	0

In this work density ( $\rho$ ), viscosity ( $\mu$ ) and ultrasonic velocity ( $u$ ) of pure acetophenone and ethylchloroacetate as well as binary mixture constituted by these two chemicals at temperatures of 303k and

323k respectively. The literature survey showed that no measurements have been previously reported for the mixture studied in this project.

Table 3 : Determination of isentropic compressibility, molar volume, intermolecular free length at 303 K

Molefraction of ethylchloroacetate ( $x_1$ )	Density $\rho$ g/cc	Ultra-sonic velocity $U$ ms <sup>-1</sup>	Isentropic compress-ibility ( $K_s$ ) $\times 10^{-10}$ m <sup>2</sup> N <sup>-1</sup>	Molar Volume cm <sup>3</sup> /mol	Inter-molecular free length $L_f \times 10^{-11}$ m	Acoustical Impedance ( $Z$ ) $\times 10^6$ kg/m <sup>2</sup> s
0	0.9475	1478	4.8287	126.860	4.559	1400.78
0.10	1.0005	1430	4.8850	120.390	4.586	1431.11
0.21	1.0024	1472	4.6040	120.405	4.452	1475.53
0.31	1.0069	1396	5.0903	120.107	4.681	1406.43
0.42	1.0473	1364	5.1261	115.698	4.698	1429.35
0.52	1.0646	1340	5.2249	114.036	4.743	1427.41
0.62	1.0722	1403	4.7365	113.435	4.515	1504.58
0.71	1.0588	1324	5.3812	115.086	4.813	1402.69
0.81	1.0853	1222	6.1662	112.478	5.153	1326.67
0.90	1.0946	1390	4.7256	111.725	4.510	1521.93
1	1.1322	1188	6.2494	108.191	5.187	1346.01

Table 4 : Predicted kinematic viscosities of ethylchloroacetate + acetophenone mixture at 303 K

Molefraction of Ethyl Chloroacetat	$U_{Exp}$	$U^{IDR}$	$U^{VAN}$	$U^{FLT}$	% Deviation		
	$m s^{-1}$	$m s^{-1}$	$m s^{-1}$	$m s^{-1}$	$U^{FLT} m s^{-1}$	$U^{VAN} m s^{-1}$	$U^{IDR} m s^{-1}$
0	1478	1478.4	1478	1478	-1.538x10 <sup>-14</sup>	0	0
0.1089	1430	1441.49	1448	1430	0	-1.227	-0.7698
0.2151	1472	1406.95	1444	1472	0	1.924	4.6229
0.3199	1396	1374.19	1464	1396	1.628x10 <sup>-14</sup>	-4.624	1.6451
0.4223	1364	1343.37	1510	1364	0	-9.656	1.5949
0.5231	1340	1314.12	1589	1340	1.696x10 <sup>-14</sup>	-15.64	2.0296
0.6224	1403	1286.31	1714	1403	1.62x10 <sup>-14</sup>	-18.70	9.0865
0.7191	1324	1260.14	1915	1324	0	-30.81	5.1307
0.8144	1222	1235.18	1435	1222	0	-14.86	-1.0349
0.9086	1390	1211.29	1304	1390	0	6.615	14.786
1	1188	1188.8	1188	1188	0	0	-1.9x10 <sup>-14</sup>

Table 5 : Predicted absolute viscosities of ethylchloroacetate + acetophenone mixture at 303 K

Molefraction of Ethyl Chloroacetate (X <sub>1</sub> )	$\gamma_{expt}$ (cS)	$\gamma_{pred}$ (cS) (McAllister Model)	$\gamma_{pred}$ (cS) (Jouyban- Acree Model)	$\gamma_{pred}$ (cS) (K-L model)
0	1.4969	1.5268	1.4969	1.4969
0.1089	1.1523	1.9793	1.1862	1.1864
0.2151	1.1222	1.8463	1.0538	1.0540
0.3199	1.0585	1.3875	1.0666	1.0668
0.4223	1.015	0.9373	1.0478	1.0481
0.5231	0.9312	0.6241	0.9555	0.9558
0.6224	0.8809	0.4437	0.8637	0.8640
0.7191	0.8474	0.3607	0.8286	0.8289
0.8144	0.8273	0.3529	0.8294	0.8296
0.9086	0.787	0.4347	0.7931	0.7933
1	0.7164	0.7164	0.7164	0.7164

Table 6 : Predicted excess molar volume, isentropic compressibility (ks) , intermolecular free length(l<sub>i</sub>) by (R-K model) for the mixture at 303 K

$U_{Exp} m s^{-1}$	$U^{IDR} m s^{-1}$	$U^{VAN} m s^{-1}$	$U^{FLT} m s^{-1}$	% Deviation			
				$U^{FLT} m s^{-1}$	$U^{VAN} m s^{-1}$	$U^{IDR} m s^{-1}$	
0	1478	1478.4	1478	1478	-1.538x10 <sup>-14</sup>	0	0
0.1089	1430	1441.49	1448	1430	0	-1.227	-0.7698
0.2151	1472	1406.95	1444	1472	0	1.924	4.6229
0.3199	1396	1374.19	1464	1396	1.628x10 <sup>-14</sup>	-4.624	1.6451
0.4223	1364	1343.37	1510	1364	0	-9.656	1.5949
0.5231	1340	1314.12	1589	1340	1.696x10 <sup>-14</sup>	-15.64	2.0296
0.6224	1403	1286.31	1714	1403	1.62x10 <sup>-14</sup>	-18.70	9.0865
0.7191	1324	1260.14	1915	1324	0	-30.81	5.1307
0.8144	1222	1235.18	1435	1222	0	-14.86	-1.0349
0.9086	1390	1211.29	1304	1390	0	6.615	14.786
1	1188	1188.8	1188	1188	0	0	-1.9x10 <sup>-14</sup>



Table 7 : Predicted ultrasonic velocity deviation for A Ethylchloroacetate+ Acetophenone mixture at 303 K

Molefraction of Ethyl Chloroacetate ( $x_1$ )	$\gamma_{\text{expt}}$ (cS)	$\gamma_{\text{pred}}$ (cS) (McAllister Model)	$\gamma_{\text{pred}}$ (cS) (Jouyban- Acree Model)	$\gamma_{\text{pred}}$ (cS) (K-L model)
0	1.4969	1.5268	1.4969	1.4969
0.1089	1.1523	1.9793	1.1862	1.1864
0.2151	1.1222	1.8463	1.0538	1.0540
0.3199	1.0585	1.3875	1.0666	1.0668
0.4223	1.015	0.9373	1.0478	1.0481
0.5231	0.9312	0.6241	0.9555	0.9558
0.6224	0.8809	0.4437	0.8637	0.8640
0.7191	0.8474	0.3607	0.8286	0.8289
0.8144	0.8273	0.3529	0.8294	0.8296
0.9086	0.787	0.4347	0.7931	0.7933
1	0.7164	0.7164	0.7164	0.7164

Table 8 : Determination of Gibbs free energy for Ethylchloroacetate + Acetophenone mixture

Molefraction of Ethyl Chloroacetate ( $x_1$ )	Gibbs free energy at 303K	Gibbs free energy at 323K
0	9.222	-6.3311
0.1089	-457.120	-688.87
0.2151	-326.553	-546.015
0.3199	-279.174	-453.261
0.4223	-194.740	-384.524
0.5231	-224.702	-374.524
0.6224	-180.233	-266.613
0.7191	-98.368	-105.783
0.8144	18.107	-139.395
0.9086	67.268	0.3919
1	-4.204x10 <sup>-5</sup>	-1.142x10 <sup>-5</sup>

Table 9 : Determination of Excess Molar Volume At 323 K

S.No	Molefraction of Ethyl Chloroacetate ( $x_1$ )	Density $\rho$ (g/cc)	Excess Volume $V_E^E$ (cc/gmole)	kinematic Viscosity $\gamma$ (cS)	Absolute Viscosity $\eta$ (cP)	Viscosity Deviation $\Delta\eta$ (cP)
1	0	0.92	0	1.3832	1.2831	0
2	0.1089	0.982	-4.7043	0.9647	0.9481	-0.3356
3	0.2151	1.000	-4.36	0.9379	0.9382	-0.2816
4	0.3199	1.005	-2.5525	0.8949	0.9000	-0.2448
5	0.4223	1.042	-4.366	0.8474	0.8832	-21443
6	0.5231	1.22	-4.2074	0.7836	0.8323	-0.2015
7	0.6224	1.069	-2.7041	0.7568	0.8096	-0.1527
8	0.7191	1.055	1.1099	0.7467	0.7881	-0.0892
9	0.8144	1.083	0.3193	0.6828	0.7399	-0.0806
10	0.9086	1.093	1.5366	0.6694	0.7317	-0.0224
11	1	1.130	0	0.6222	0.7031	0

Table 10 : Predicted kinematic viscosities of ethylchloroacetate + acetophenone mixture at 323 K

Molefraction of Ethyl Chloroacetate ( $x_1$ )	$\gamma_{\text{expt}}$ (cS)	$\gamma_{\text{pred}}$ (cS) (McAllister Model)	$\gamma_{\text{pred}}$ (cS) (Jouyban- Acree Model)	$\gamma_{\text{pred}}$ (cS) (K-L model)
0	1.3832	1.4108	1.3832	1.3832
0.1089	0.9647	1.7765	0.9768	1.6401
0.2151	0.9379	1.4981	0.8992	1.5207
0.3199	0.8949	0.9798	0.9276	1.2388
0.4223	0.8474	0.5697	0.8590	1.1215
0.5231	0.7836	0.3307	0.7721	1.0689
0.6224	0.7568	0.2111	0.7454	0.9602
0.7191	0.7467	0.1673	0.7427	0.8230
0.8144	0.6828	0.1776	0.7033	0.7314
0.9086	0.6694	0.2693	0.6572	0.6802
1	0.6222	0.6222	0.6222	0.6222

Table 11 : Predicted absolute viscosities of ethylchloroacetate + acetophenone mixture at 323 K

Molefraction of Ethyl Chloroacetate ( $x_1$ )	Molefraction of Acetophenone ( $x_2$ )	dynamic viscosity at 30 ( $\eta_{\text{mix}}$ ) (g/cm.s)( $\eta_{\text{mix}}$ )	Grunberg-Nissan deviation parameter (d)
0	1	1.2831	0
0.1089	0.8911	0.9481	-2.4435
0.2151	0.7849	0.9382	-1.0878
0.3199	0.6801	0.9000	-0.7456
0.4223	0.5777	0.8832	-0.4900
0.5231	0.4769	0.8323	-0.4735
0.6224	0.3776	0.8096	-0.3662
0.7191	0.2809	0.7881	-0.2719
0.8144	0.1856	0.7399	-0.4012
0.9086	0.09144	0.7317	-0.1819
1	0	0.7031	0

Table 12 : Predicted excess molar volume for ethylchloroacetate + acetophenone mixture at 323 K

Molefraction of Ethyl Chloroacetate( $x_1$ )	$V^E(\text{pred})$ (R-Kmodel) (cc/gmole)	$\Delta\eta$ (pred) (R-K model)
0	9.222	-6.3311
0.1089	-457.120	-688.87
0.2151	-326.553	-546.015
0.3199	-279.174	-453.261
0.4223	-194.740	-384.524
0.5231	-224.702	-374.524
0.6224	-180.233	-266.613
0.7191	-98.368	-105.783
0.8144	18.107	-139.395
0.9086	67.268	0.3919
1	-4.204x10 <sup>-5</sup>	-1.142x10 <sup>-5</sup>

**Table 13 :** Parameters of McAllister constant for ethylchloroacetate + acetophenone at 303 K & 323 K

Temperature	A	B	SD
303K	-2.25	-1.434	0.4662
323K	-30111	-2.307	0.4807

**Table 14 :** Parameters of the Krishnan and Laddha constants and standard deviations for the viscosity of ethylchloroacetate + acetophenone at 303 K & 323 K

Temp T (K)	A <sub>0</sub>	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	A <sub>5</sub>	A <sub>6</sub>	SD
303K	2.27	-0.8	-3.2	0.79	0.28	0.95	-	0.0406
323K	4.49	3.255	5.099	-3.51	-0.8	0.23	0.2	0.473

**Table 15 :** Parameters of the Jouyban Acree constants and standard deviations for the viscosity of ethylchloroacetate + acetophenone at 303 K & 323 K

Temp T (K)	A <sub>0</sub>	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	A <sub>5</sub>	A <sub>6</sub>	SD
303K	-1906	605.5	2111	-556	-200	-66	-	0.0370
323K	4605	4645	-3474	3901	47.4	-207	-19	0.0003

**Table 16 :** Parameters of the Redlich Kister constants and standard deviations for the viscosity of ethylchloroacetate + acetophenone at 303 K & 323 K

Temp T (K)	A <sub>0</sub>	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	A <sub>5</sub>	A <sub>6</sub>	SD
303K	8.89	-6.563	-9.66	6.84	1.32	-0.24	-0.54	0.596
323K	13.0	-8.493	-14.6	9.09	2.46	-0.56	-0.86	0.042

**Table 17 :** Parameters of the Redlich Kister constants and standard deviations for the excess volume of ethylchloroacetate + acetophenone at 303 K & 323 K

Temp T (K)	A <sub>0</sub>	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	A <sub>5</sub>	A <sub>6</sub>	SD
303K	207	-187	-298	208.02	103.2	-19.4	-11.9	1.214
323K	173	-179	-236	192	80.17	11.51	16.61	0.993

**Table 18 :** Parameters of the Redlich Kister constants and standard deviations for the Isentropic compressibility (K<sub>s</sub>), intermolecular free length (L<sub>f</sub>) of ethylchloroacetate + acetophenone at 303 K & 323 K

	A <sub>0</sub>	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	A <sub>5</sub>	A <sub>6</sub>	SD
K <sub>s</sub> <sup>E</sup> x 10 <sup>-10</sup> m <sup>2</sup> N <sup>-1</sup>	-358	-21	393.2	21.67	-57	-0.5	22.44	3.56
L <sub>f</sub> <sup>E</sup> X10 <sup>-11</sup> m	-353	-18	397.9	20.57	-65	-2.3	21.15	3.13

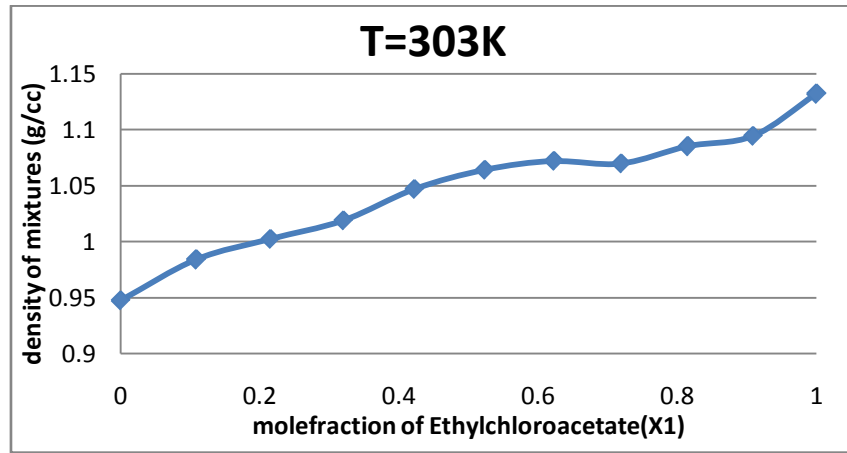


Figure 4 : Plot of mole fraction of ethylchloroacetate Vs density of mixtures at 303K

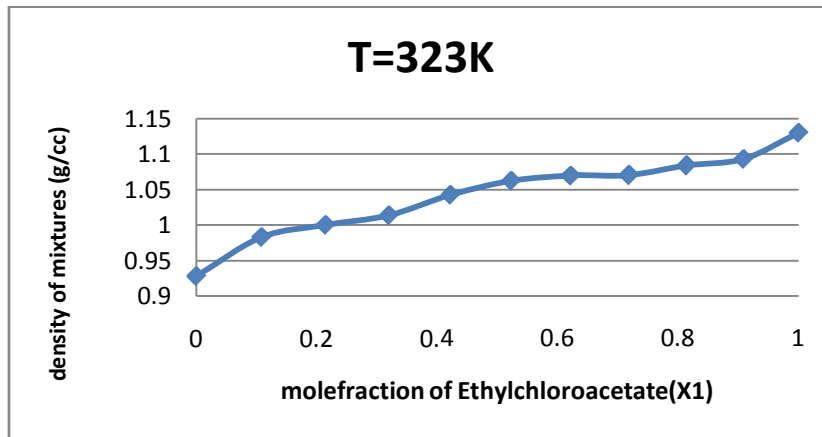


Figure 5 : Plot of mole fraction of ethylchloroacetate Vs density of mixtures at 323K

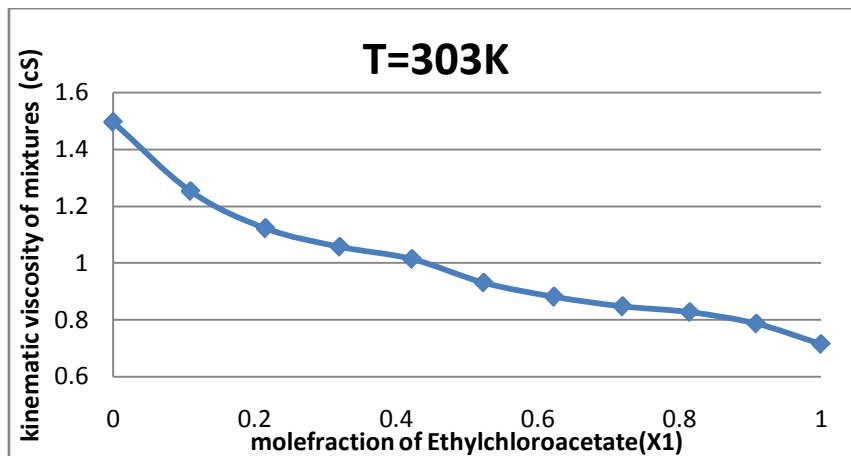


Figure 6 : Plot of mole fraction of ethylchloroacetate Vs viscosity of mixtures at 303K

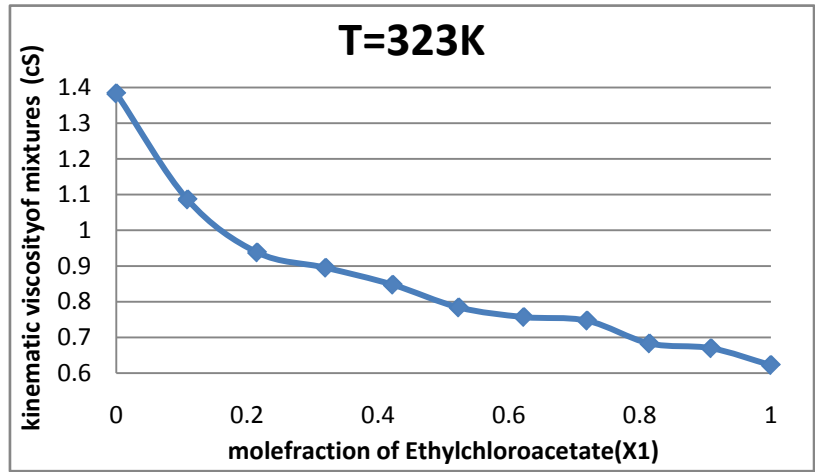


Figure 7: Plot of mole fraction of ethylchloroacetate Vs viscosity of mixtures at 323K

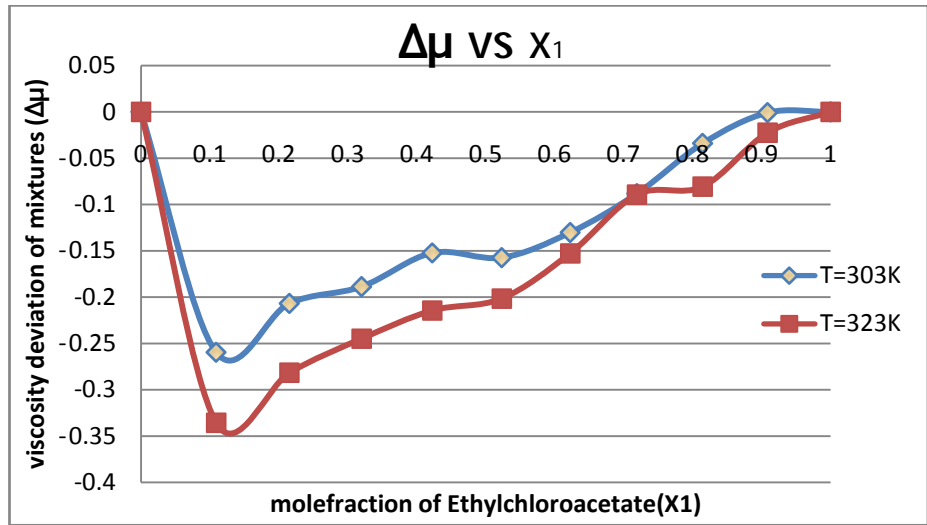


Figure 8: Plot of mole fraction of ethylchloroacetate Vs viscosity deviation at 303K & 323K

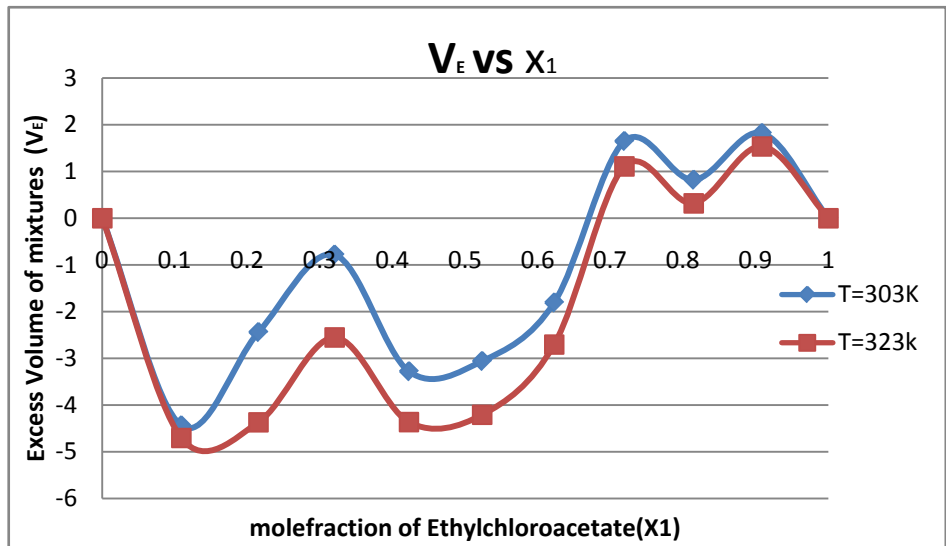


Figure 9: Plot of mole fraction of ethylchloroacetate Vs excess volume at 303K & 323K

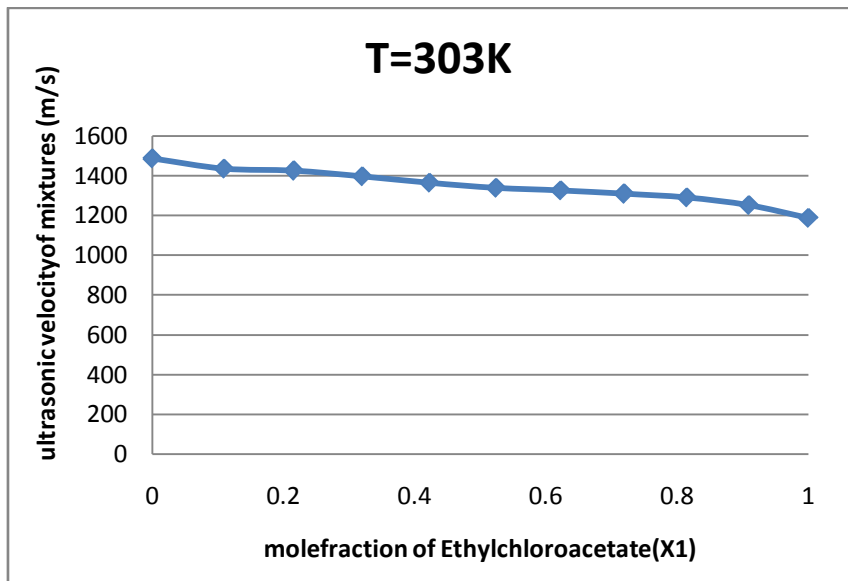


Figure 10 : Plot of mole fraction of ethylchloroacetate Vs ultrasonic velocity 303K

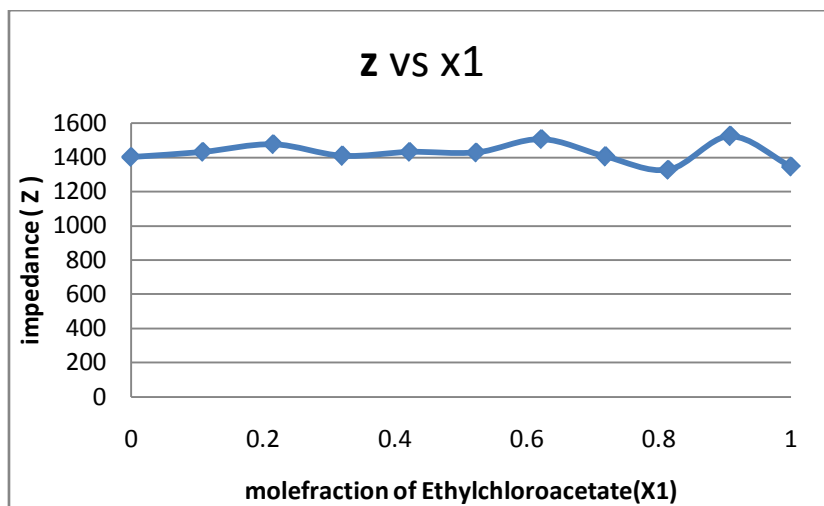


Figure 11 : Plot of mole fraction of ethylchloroacetate Vs Impedance

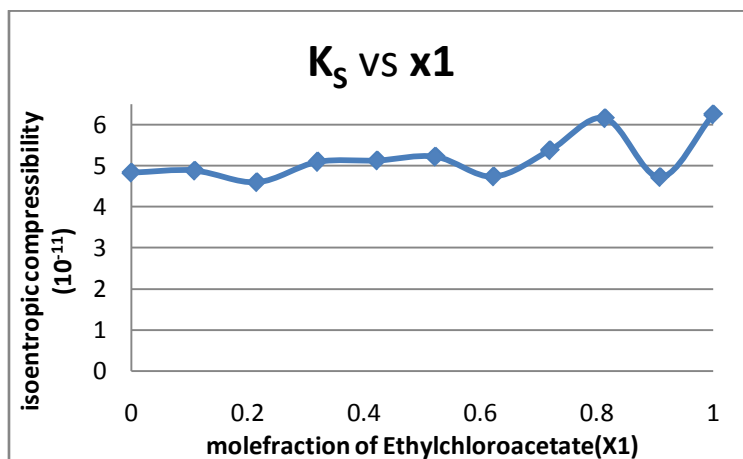


Figure 12 : Plot of mole fraction of ethylchloroacetate Vs Isentropic compressibility

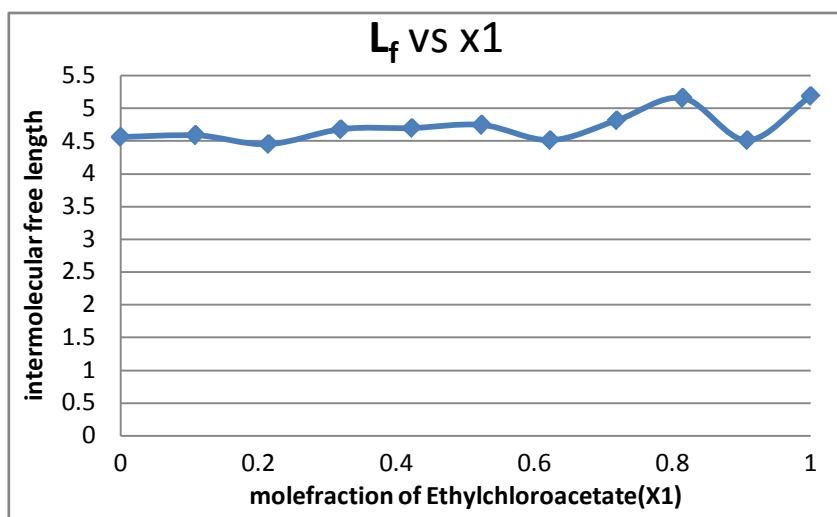


Figure 13 : Plot of mole fraction of ethylchloroacetate Vs Intermolecular free length

#### IV. CONCLUSION

Viscosities and densities for the binary liquid mixture of Ethylchloroacetate and Acetophenone system was found out as a function of mole fraction at atmospheric pressure and at temperatures of 303K and 323K. From the density and viscosity data, the values of excess molar volumes ( $V^E$ ) and the viscosity deviations ( $\Delta\eta$ ) were determined at 303K and 323K. Excess molar volumes ( $V^E$ ) and the viscosity deviations ( $\Delta\eta$ ) were used to predict the intermolecular interactions in the mixtures. McAllister's three-body-interaction model, Krishnan-Laddha model and Jouyban-Acree model were used to correlate the kinematic viscosity of the systems. The excess volume and viscosity deviation data were fitted by means of the Redlich-Kister equation. It was found that in all cases the experimental data obtained, matches with the McAllister model and Redlich-Kister equation with a high degree of precision.

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*Table 6* : Predicted excess molar volume, isentropic compressibility ( $k_s$ ), intermolecular free length( $l_i$ ) by (R-K model) for the mixture at 303 K

Molefraction of Ethylchloroacetate	$V^E$ (pred) (cc/gmole)	$\Delta\eta$ (pred)	$\Delta K_s$ (pred)	$\Delta l_i$ (pred)
0	0	0	0	0
0.1089	-4.1232	-0.2409	4.7433	4.5181
0.2151	-3.2017	-0.2639	5.1736	4.0809
0.3199	-1.0267	-0.1541	4.3877	4.0530
0.4223	-1.7988	-0.1231	5.1930	4.9025
0.5231	-3.1453	-0.1376	5.5625	5.2154
0.6224	-2.036	-0.1086	4.8229	4.3045
0.7191	0.8659	-0.0444	4.9854	4.2894
0.8144	2.4135	-0.01189	6.3702	5.6870
0.9086	1.246	-0.0147	4.7013	4.3620
1	0	0	0	0





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