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SURFACE TENSION OF LIQUID BINARY MIXTURES AT DIFFERENT TEMPERATURES (FROM 298.15K TO 318.15K)

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CERTIFICATION

The undersigned certify that they have read and hereby recommend for the acceptance by the Department of Chemistry, University of Botswana, a Thesis entitled **“SURFACE TENSION OF LIQUID BINARY MIXTURES AT DIFFERENT TEMPERATURES (FROM 298.15K TO 318.15K)”** as part of the work recommended in fulfillment of the requirements for a Master degree in chemistry at the University of Botswana.

Supervisor …………………………………………. Date………………

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I hereby declare that the dissertation/thesis submitted for the degree of M.Sc. Physical Chemistry to the University of Botswana, is my own original work and has not previously been submitted to any other institution and any work quoted is indicated and acknowledged by means of a comprehensive list of references.

……………………………………………

Lesedi Ratsatsi

……………………

Date

DEDICATION

I dedicate this to my mom Agnes Ratsatsi and my family for being my strength when I was weak.

ACKNOWLEDGEMENTS

I would like to extend my gratitude to the Almighty God for remaining my strength and light, my supervisor Professor Jamil Ahmad for the patience and guidance throughout the course of this project, Dr W. Ddamba for further help to tighten my explanations and Thesis. The Department of Chemistry for making this possible with the guidance and the financial support, the warmth they gave me to enjoy working here.

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ABSTRACT

Thermodynamic properties of binary liquid mixtures of ketones with alkyl esters, (methyl acetate + cyclohexanone, ethyl acetate + cyclohexanone, methyl acetate + cycloheptanone, methyl acetate + acetophenone, ethyl acetate + acetophenone, methyl acetate + acetone) and esters with esters (ethyl acetate + methyl acetate) have been investigated experimentally at various temperatures in the range 298K to 318K by measurements of surface tensions and density as a function of mole fraction. The properties were also investigated theoretically using Sudgen's equation, containing parachor and density, to predict surface tension values. Most of the experimental and predicted trends of surface tension values as a function of mole fraction showed good agreement. Surface entropies were obtained from surface tension - temperature data, whilst excess molar volumes of the systems were calculated from experimental density values. The density values were fitted onto a polynomial expression before being used for prediction. The information obtained was used to better understand intermolecular interactions between components of the solutions at infinite dilution.

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LIST OF ABBREVIATIONS

- MRSD – mean relative standard deviation

CHAPTER 1

1.0 INTRODUCTION

1.1 Definition of Surface Tension

Surface tension, also known as interfacial tension, is defined as the free energy per unit area of the surface. It is the work required to increase the area of a surface isothermally and reversibly by unit amount. In the bulk of a liquid, a molecule experiences forces from all sides around it. However, a molecule on the surface experiences forces only towards the sides and the bulk as depicted in Figure 1.1. This imbalance of forces causes the molecules in the surface of a liquid to experience a net attraction toward the bulk of the liquid. Surface tension is the measure of this inward pull [1], [2], [3]. Work must be done to increase the area of the surface by bringing the molecules from the interior to the surface against the cohesive forces in the liquid [4].

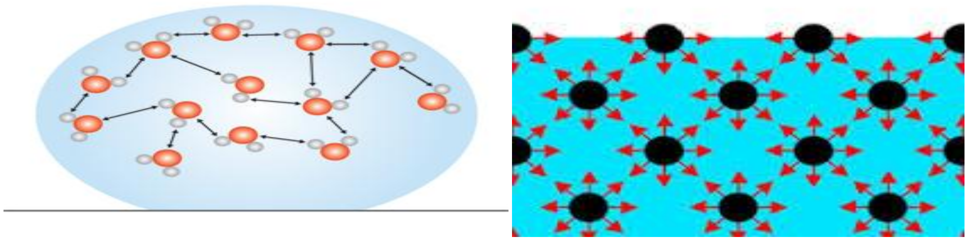

Figure 1.1 Forces around the molecules in the bulk of water and at the air-water interface.

Liquids tend to attain the shape with the least surface free energy, usually that of a sphere. Numerically, surface free energy is equal to surface tension when SI units are employed, surface tension being in $N.m^{-1}$ and surface free energy in $J.m^{-2}$. The value of surface tension is determined by several factors pertaining to the surface and the bulk region of the liquid [3].

There are several factors that influence the surface tension of a liquid. It depends on molecular forces and density of packing and molecular size [5]. Molecular forces keep the liquid together and if attractive forces between molecules of a liquid are strong, the work needed to get them to the surface will be high; hence a high surface tension. Molecules that form hydrogen bonds have a lower tendency to adsorb at the liquid-vapour interface and therefore a high surface tension. [6].

1.2 Determination of Surface Tension

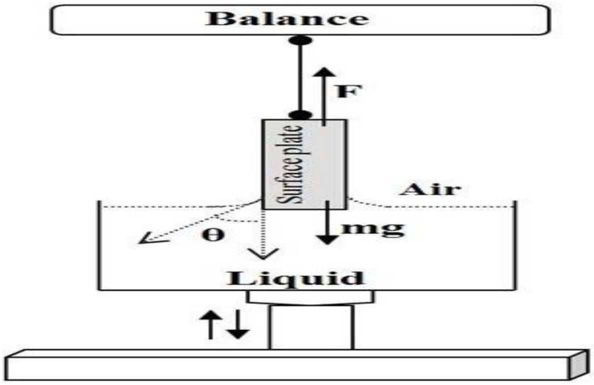

Figure 1.2 Wilhelmy plate method set up

The surface tension of liquid-air interfaces can be measured by several methods. Among them are detachment methods which include pin, the ring, Wilhelmy slide/plate which mostly need minor to no corrections, the drop methods which include the sessile drop method, drop weight and drop volume methods, maximum bubble pressure which can be used to measure surface tensions of not easily accessible liquids such as molten metals and drop profiles which include thermal ripplons and capillary waves [7], [8], [9]. In the Wilhelmy plate method, a plate made of platinum or another suitable material is lowered into the liquid and partially pulled out. The force exerted on the plate is measured using a sensitive balance. This method does not involve any corrections and is very simple to use. A modification of the method is the determination of the curvature of the meniscus using a laser beam. The Du Nouy ring method involves the determination of the force to detach a ring or loop of wire from the surface of a liquid and is quite precise. A zero or near zero contact angle is necessary to avoid error [9]. Wetting properties of the surface or interface have little influence on this measuring technique. Maximum pull exerted on the ring by the surface is measured [10]. The Du Nouy ring which is used in this study will be explained in detail in the experimental section.

1.3 Effects of Temperature and Pressure on Surface Tension

The surface tension of a liquid depends on temperature and pressure. Generally the surface tension decreases as temperature increases, since the cohesive forces are lower at higher temperatures [5]. Also as temperature rises towards the critical temperature, the restraining force on the surface diminishes and the vapour pressure increases. When the critical temperature is reached, the surface tension vanishes altogether. Therefore, a negative surface tension is impossible for a liquid because it can only occur above the critical temperature where the liquid cannot exist [1]. This excludes ionic liquids because they have negligible vapour pressure, therefore their surface tension can be measured beyond the critical temperature [11].

From the temperature dependence of the surface tension values of thermodynamic functions such as surface enthalpy (H^S) and surface entropy (S^S) can be derived. Surface entropy provides very useful information on the molecular interactions in the interface of a liquid [12]. The influence of temperature on surface tension and surface properties of binary mixtures has often been used to obtain information on the effect of added solutes on the structure of the solvent [13]. These can be derived from a straight line plot of surface tension against temperature, according to an empirical equation of the form [14]:

$$\gamma\left({}^{\mathrm{mN}}/_{\mathrm{m}}\right) = c - mT(K) \qquad (1)$$

Where; γ is surface tension of solution, T is the temperature, m is the slope which represents surface entropy and c is the intercept which represents surface enthalpy. The surface entropy, (S^S) and surface enthalpy, (H^S) can also be calculated from the following equations [6], [11], [15], [16].

$$\mathrm{S}^{\mathrm{S}} = -\frac{d\gamma}{dT} \qquad (2)$$

$$\mathrm{H}^{\mathrm{S}} = \gamma \pm T\left(\frac{d\gamma}{dT}\right) \qquad (3)$$

As for the effect of pressure, surface tension increases as pressure is increased [12]. This effect is related to the change in molar volume when a molecule goes from the bulk to the surface region. In turn the change would be positive and the effect of pressure should therefore be to increase the surface tension. But this cannot happen without introduction of external substance such as gases to increase the pressure on the surface [8].

1.4 Effect of dissolved Solutes on the Surface Tension of Water

When a solute is dissolved in a solvent, the effect on surface tension can be of four types. In the first case, the solute might not have any effect, for instance in case of addition of sucrose to water. Secondly, it can increase the surface tension of the solvent, for example sodium chloride in water. This is caused by depletion of solute at the interface or negative adsorption that takes place at the interface [10]. It may originate from electrostatic forces or solute-solvent attraction. When the repulsion is large enough, the surface tension increment is entropy-driven and approaches an asymptotic limit [17]. Thirdly, the surface tension can progressively decrease due to adsorption of the solute onto the surface; this happens, for example, when an alcohol is added. Lastly, a decrease in surface tension can be observed to a certain point, a minimum, after which no more effect will be observed. This is the case for surfactants[10].

1.5 Surface Tension of Mixed Solutions

Surface tension of mixtures is an important thermodynamic property of binary liquids affecting mass and heat transfer at the interface [5], [18]. The mass transfer processes include liquid-liquid extraction, gas absorption, distillation and condensation. These have applications in scientific and technological areas, together with environmental sciences, material sciences, process simulation and molecular industries [5], [18], [19], [20], [21], [22]. This thermophysical property contains information about the structure and energy of the surface region, and helps in understanding and interpreting the nature of interactions between the molecules of the mixtures. The surface tension of an immiscible interface is so high that no molecules can cross the interface, while that of a miscible interface is considerably lower so some molecules are able to cross [23].

Surface tension of mixtures also plays a role in processes used in several industries such as the paints, detergents, agrochemicals and petroleum industries. It is the most accessible experimental parameter that describes the thermodynamic state and contains at least some information about the internal structure of a liquid state. For successful modeling and calculations of surface properties, experimental surface tension data of high quality is necessary [21].

Many properties can be used to study the molecular interactions and/or structure in liquid mixtures. These are calorimetric parameters, heat capacities, enthalpies and densities. Surface tension, being convenient to measure and showing a strong dependence on the nature of constituents and their concentration, offers unique advantages.

1.5.1 Binary Mixtures Studied

Binary mixtures that have been studied widely are listed below.

i. Methanol with n-butyl acetate or n-amyl acetate and/or n-hexyl acetate and n-amyl acetate with methanol or ethanol or 1-propanol and/or 2-proponal [5]
ii. Heavy water with methanol, ethanol, 1-propanol [6]
iii. 1-butyl-3-methylimidazolium thiocyanate [BMIM][SCN] with 1-butanol or 1-pentanol and/or 1-hexanol[11]

iv. Dimethyl sulfoxide (DMSO) with propanol or butanol and/or hexanol [13]

v. 1-butyl-3-methylimidazolium L-lactate [bmim][L-lactate] with methanol or ethanol or 1-butanol and/or water [14]

vi. Ethylene glycol with cyclohexanol or cycloheptanol [15]

vii. N-octylisoquinolinium bis{(trifluoromethyl)sulfonyl}imide [C_8iQuin][NTf_2]with 1-hexanol [16]

viii. Water with methanol[24] or ethanol or 1-propanol and/or 2-propanol [18]

ix. Acetonitrile with formamide or N-methylacetamide or N,N-di-methylformamide and/or N,N-di-methylacetamide [19]

x. Formamide with acetonitrile [20]

xi. Benzene with benzonitrile and/or benzyl alcohol [21]

xii. 1-butyl-3-methylimidazolium [C_4mim][NTf_2] with 3-methyl-1-propylpyridinium [C_3mpy][NTf_2] or 1-methyl-1-propylpyrrolidinium [C_3mpyr] [NTf_2] or 1-methyl-1-propypiperidinium [C_3mpip] [NTf_2] and/or 1-butyl-2,3-dimethylimidazolium [C_4C_1mim] [NTf_2] [25]

xiii. Dimethyl sulfoxide with tert-butyl alcohol (TBA) and/or iso-amyl alcohol (IAA) [26]

xiv. 1, 2, 4-trimethlebenzene with propyl acetate or butyl acetate, also 1, 3, 5-trimethlbenzene with propyl acetate or butyl acetate [27]

xv. 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide [C_4mim][NTf_2] with methanol or ethanol or 1-propanol or 1-propanol or 1-butanol and/or 1-pentanol, also 1-octyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide [C_8mim][NTf_2] with the same alcohols [28]

xvi. 1,2-ethanediamine (EDA) with diethylene glycol (DEG) [29]

xvii. 1-propylpyridinum tetrafluoroborate, 1-butylpyridinum tetrafluoroborate, 1-butyl-3-methylpyridinum tetrafluoroborate and 1-butyl-4-methylpyridinum tetrafluoroborate with methanol or ethanol [30]

xviii. Dimethyl sulfoxide (DMSO) with water or methanol or ethanol or 1-propanol or 1-propanol or acetone and/or cyclohexanone [31]

xix. Hexamethylenetetramine (HMT) with water [32]

xx. 1-methyl-3-methylimidazolium methylsulfate [MMIM][CH_3SO_4], 1-butyl-3-methylimidazolium methylsulfate [BMIM][CH_3SO_4], 1-butyl-3-methylimidazolium octylsulfate [BMIM][$OcSO_4$], 1-hexyloxymethyl-3-methylimidazolium tetrafluoroborate [C_6H_{13})CH_2MIM][BF_4] and 1,3-dihexyloxymethylimidazolium tetrafluoroborate with methanol or ethanol and/or 1-butanol. Hexyl(2-hydroxyethyl)dimethylammonium bromide (C_6Br), ethyl(2-hydroxyethyl)dimethylammonium bromide (C_2Br), ethyl(2-hydroxyethyl)dimethyl ammonium tetrafluoroborate (C_2BF_4), ethyl(2-hydroxyethyl)dimethyl ammonium haxafluorophosphate (C_2PF_6), ethyl(2-hydroxyethyl)dimethyl ammonium ammonium dicyanamide ($C_2N(CN)_2$), propyl(2-hydroxyethyl)dimethylammonium bromide (C3Br) and butyl(2-hydroxyethyl)dimethylammonium bromide (C4Br) with 1-octanol [33]

xxi. Gasoline with ethanol [34]

xxii. Water with methyl acetate or ethyl acetate or propyl acetate and/or butyl acetate [35]

xxiii. 1-ethyl-3-methylimidazolium tricyanomethanide [EMIM][TCM] with thiophene [36]

xxiv. [C_4mim][NTf_2] with [$C_n$mim][NTf_2] where (n=1, 2, 5, 6, 8 and 10) [37]

xxv. 1-chlorobutane, 2-chorobutane, 2-methyl-2-chloropropane and 2-methyl-1-chloropropane with butyl ethyl ether and/or diisopropyl ether [38]

xxvi. N,N-dimethylformamide (DMF) with 1-octanol or 1-nonanol and/or 1-decanol [39]

xxvii. 4-methyl-2-pentanone with ethyl benzoate [40]

xxviii. 1-ethyl-3-methylimidazolium alkyl sulfate (alkyl: ethyl, butyl, hexyl and octyl) with water or ethanol [41].

1.5.2 Interpretations and findings

A linear dependence of surface tension on mole fraction of the solute is associated with strong interaction between the solute and the solvent molecules. For example, in the study of imidazolium and ammonium-based ionic liquids (ILs) with alcohols, the change in surface tension with mole fraction of ionic liquids in methanol solutions was found to be nearly linear. It was concluded that the methanol molecules have strong intermolecular interactions with ionic liquid anions [33]. A regular decrease or increase in the value of the solution surface tension indicates that both the compounds are present at gas/liquid interface. For example, the surface tension of solution of alcohols in heavy water decreases with increasing concentration but the trend is non-linear [6].

However, there are cases where the surface tension is not linear, but changes in parabola-like manner. This behaviour is typical of surface active substances. For instance, addition of small amounts of diethylene glycol (DEG) to 1, 2-ethanediamine (EDA) results in an increase in the values of the surface tension at the beginning and then a decrease over the whole composition range for mixtures. It is assumed that on addition of solute (DEG) many competing processes occur at the surface, for example repulsion or attraction of DEG molecules by EDA, formation of new interaction between them and polymerization of DEG + EDA or DEG + DEG , in addition to possible structural changes [30]. Ideally, a compound with lower surface tension is expelled to the surface of the liquid-vapour interface from the bulk region, due to attractive forces between the molecules of the solvent. Hydrophobic and hydrophilic characters of the alcohols also play a part in that when the alcohol is expelled to the liquid-vapour interface, the hydrophilic part remains in the solution and the hydrophobic part pokes outwards to the air [13].

Excess surface tension is a useful parameter. It can be defined as:

$$\Delta\gamma = \gamma(exp) - \sum_{i=1}^{i=2} x_i \gamma_i \tag{4}$$

Where $\Delta\gamma$ is the surface tension deviation, γ(exp) is the experimentally measured surface tension of mixture, x_i and γ_i are the mole fraction and the surface tension of the pure component *i*, respectively [16], [22], [26], [28], [34].

The surface tension deviations may be fitted to a Redlich-Kirster polynomial

$$\Delta\gamma = x_i \, x_j \sum_{k=0}^{n} A_k \, \left(x_i - x_j\right)^k \tag{5}$$

Where A_k are the coefficients determined using the method of least squares, x_i and x_j are the mole fractions of the components *i* and *j* in the mixture, *k* is the number of coefficients and *n* is the least order of the polynomial.

The excess surface tension gives an insight into the interactions between the components at the interface and in the bulk of the solution [25]. Surface tension deviations can either be negative or positive or both for a system. Examples of negative surface tension deviation are found in the systems of heavy water and methanol or ethanol or 1-propanol [9] and of 1-butyl-3-

methylimidazolium [C_4mim][NTf_2] with 3-methyl-1-propylpyridinium [C_3mpy][NTf_2] or 1-methyl-1-propypiperidinium [C_3mpip] [NTf_2].[27]. Negative values of the surface tension deviations imply that there is a different distribution of components between the surface and bulk region and the compositions of the components at the surface and in bulk are not identical. The surface of the mixture is instead richer in the component with the lower surface tension [11], [16], [19], [25], [37]. For example, ionic liquids have lower surface tension values and therefore it is observed that in almost all the binary mixtures involving ionic liquids the deviations are negative indicating that the proportion of the ionic liquid at the surface phase is larger than in the bulk phase. It is to be noted that the extent of surface tension deviations becomes larger as the difference in the surface tension values of the pure components increases [26].

A positive surface tension deviation indicates stronger interactions between the like molecules (self-association) in the mixture as compared to the unlike molecules (dipolar-dipolar interactions or dispersive forces), and it is more prevalent at higher temperatures [40], [42], [43]. The system 1-butyl-3-methylimidazolium [C_4mim][NTf_2]+ 1-methyl-1-propylpyrrolidinium [C_3mpyr] [NTf_2] is an example [25]. In some cases, the deviations are both positive and negative, where an S-shaped plot is formed between the surface tension deviation and the composition of the mixture. Examples are the systems 1-butyl-3-methylimidazolium L-lactate [bmim][L-lactate] and methanol as well as 1-butyl-3-methylimidazolium L-lactate [bmim][L-lactate] and ethanol [13]. This could imply that at certain dilutions the surface is enriched with the substance of lower surface tension where negative deviations are observed and where positive, the surface is richer in the substance of higher surface tension.

In studies involving mixtures where one of the components is an ionic liquid, surface tension increases with an increase in the proportion of the ionic liquid content in the binary mixture. There is however a “break point”, also known as aggregation onset (AO), where there is a small minimum at a certain mole fraction of ionic liquid said to be the concentration at which the solvent molecules are strongly bonded with the ionic liquid [16], [26], [28], [34].

1.5.3 Surface entropy

Surface entropies provide information on the degree of association of molecules in the surface. For a highly ordered molecular arrangement in the surface lower entropy would be observed. Very high surface entropy is indicative of low surface ordering in the surface of a solution [11].

1.6 Excess molar volumes

Volumetric properties such as excess molar volume and partial molar volume are useful in characterizing the structure and properties of the mixture. A study on these properties of a mixture helps to test the molecular theories of solutions and provides information on the nature of constituents of the system. Excess molar volume (V_m^E) is a fundamental and useful from both theoretical and practical stances. It is defined as the difference in molar volume of the mixture and the sum of molar volume of each component at given conditions [44]. Excess molar volumes of binary mixtures are calculated by [44], [45]:

$$V_m^E = x_1\, M_1 \left(\frac{1}{\rho} - \frac{1}{\rho_1}\right) + x_2\, M_2 \left(\frac{1}{\rho} - \frac{1}{\rho_2}\right) \qquad (6)$$

Where; ρ_1, ρ_2 and ρ are densities of component 1, 2 and their mixture, respectively. M_1 and M_2 are molar masses and x_1 and x_2 are mole fractions of components 1 and 2.

Excess molar volumes result from three contributions due to the (i) interaction between unlike molecules, (ii) the free volume change and (iii) change in internal pressure and reduced volume [46]. Positive values of V_m^E indicate a weakening of self-association of the solvent or solute or van der Waals association between the components [45]. That is there is reduction of intermolecular interactions (hydrogen bonds or dipole-dipole interactions), the presence of repulsive forces is significant [47].

Negative values usually arise from predominance of specific and attractive interactions factor to possible difference in size and shape of components in mixture. Interstitial accommodation that comes from change in free volumes and formation of new polymers or components will lead to negative excess molar volumes, thus contraction in volume of mixture. The effect intensifies as temperature rises [48]. It could be due to associations between the solute and solvent through polar group attractions, bringing the different species closer together; smaller molecules fitting in voids between the larger ones[45].

Excess thermodynamic functions such as the excess molar volume, V_m^E measure the extent of deviation from ideal solution behavior. In addition, the temperature dependent measurements of V_m^E in general are of interest for a better understanding of the structural effects between unlike molecules in the bulk of a binary mixture.

1.7 Predictions

The need for validating the use of surface tension of binary mixtures has led to equations being formulated and models being developed to predict or estimate surface tension of binary mixtures. In many cases, the results show good agreement with experimental values. Examples are 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide $[C_4mim][NTf_2]$ with methanol or ethanol or 1-propanol or 1-butanol or 1-pentanol, and 1-octyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide $[C_8mim][NTf_2]$ with the same alcohols systems, where experimental values are compared to predicted values. These were found to be in very good agreement with experimental values [28]. Some examples of the predictions are mentioned in the work by Nino-Amezquita and Enders [49].

Predictions using density values are amongst the common approaches. The theory is referred to as density profiles. In this method, the parameter parachor, [P] is used. Parachor is additive and so can be used to get the surface tension of the mixture, if the surface tension and the density of each component is known and hence parachor of each is known. Parachor is defined using Sudgen's equation [11], [16], [36], [50];

$$[P] = \gamma^{1/4} \frac{M}{\rho} \qquad (7)$$

Where; [P] is the parachor, which is temperature independent, M is the molar mass of pure component and ρ is the density. Since parachor is additive, we get for a binary mixture;

$$\gamma = \left\{[P_1]\frac{x_1}{M_1} + [P_2]\frac{1-x_1}{M_2}\right\}^4 \rho^4 \qquad (8)$$

Where; ρ is density of the mixture. The density is fitted to a polynomial expression;

$$\rho = \sum_{k=0}^{k=n} B_k {x_1}^k \qquad (9)$$

The coefficients, A_k and B_k in equation (5) and (9) are calculated using the method of least squares and an F-test is used to define the polynomial degree. This is done at confidence level of 95%. Experimental values of density were least-square fitted to get these coefficients; thus we have an analytical expression which gives the density of a mixture as a function of mole fraction. The polynomial line obtained from equation (9) is used as a check of the validity of the methodology.

1.8 Objective

A search of the literature for surface tension of binary liquid mixtures did not reveal any studies on surface tension of the binary systems of alkyl acetates with ketones or with alkyl acetates. I was therefore motivated to study some of these systems since some of the acetates and ketones find use in cosmetics and other everyday products. For example, ethyl acetate can be used in glues, nail polish removers, for decaffeinating tea and coffee and in cigarettes. Ketones are used as solvents and in pharmaceuticals; hence the large scale production of acetone and cycohexanone. The objective of this study was to investigate surface tension, excess molar volume and surface entropy of binary mixtures of methyl acetate and ethyl acetate with each other, methyl acetate with cyclohexanone, cycloheptanone, acetone and acetophenone and ethyl acetate with cyclohexanone and acetophenone, and hence to draw conclusions about interactions between molecules of these substances at the surface and in the bulk. I will use Sudgen's equation to predict surface tension and compare the predicted values to those determined experimentally.

CHAPTER 2

2.0 EXPERIMENTAL

2.1 Materials and chemicals

The brands and purity levels of chemicals used are presented in Table 2.1. The chemicals with purity less than 99% were re-distilled and the rest (with purity >99%) were used without further purification. For density measurements the pure samples were filtered gravitationally through a Whatman 1 filter paper before making mixtures.

Table 2.1 The specification of the chemicals

Name	**Purity and Brand**	**Literature Surface Tension (mN/m) at 298.15K**	**Literature Density (g/cm^3) at 298.15K**
Methyl acetate	>99% Merck	24.79[35], 24.7[51], 24.54[52]	0.9273[53], 0.9244[54], 0.932[55]
Ethyl acetate	99.9% Merck	23.93[35], 23.2[51], 23.24[52]	0.89468[53], 0.902[56]
Acetophenone	99% Sigma-Aldrich	39.0[51], 38.95[52]	1.02081[53], 1.03[57], 1.033[58]
Acetone	99.5% Merck	23.0[51], 23.04[52], 23.1[59]	0.79032[31], 0.791[60], 0.78458[61]
Cyclohexanone	98.5% Merck	34.4[51], 34.37[52]	0.94644[31], 0.9421[62]
Cycloheptanone	97% Fluka	34.05[52]	0.951[63][64]

2.2 Procedure

2.2.1 Sample preparation

To prepare the mixtures for the measurements, appropriate masses of the each component was weighed using an analytical balance. These, contained in stoppered bottles, were brought to the desired temperatures by placing in thermostat bath of accuracy ±0.1K. The use of stoppered bottles was to maintain a homogenous temperature which is the same throughout the sample. For density measurements, the solvents were filtered first with fluted filter paper to remove impurities which and then placed in 10 mL volumetric flasks.

2.2.2 Surface tension measurements

Surface tension was measured with a Kruss K9 tensiometer by the platinum ring detachment method. This is a method that is capable of good precision, convenient to use and does not require any corrections unlike the capillary rise which has been proven to be very accurate. The ring used in this work is model R21 with a diameter of (19.0 ± 0.5) mm. A thermostat water bath was used to bring the samples to the desired temperatures. The platinum ring was first rinsed with distilled water and then heated to red-hot in a Bunsen burner flame to remove impurities. It was then attached to the Kruss K9 tensiometer and the instrument was tared. The calibration was done by measuring surface tension of distilled water at room temperature (25.0 °C) and the value obtained was very close to the literature value for pure water, which is 72.8 mN/m [2]. The measurements of the samples followed. The sample was placed into a 50 mL sample vessel, which was three-quarters full. All measurements were repeated two to three times with the ring rinsed and heated red-hot in between measurements and the sample container rinsed with the next sample before taking the reading. To ascertain the limit within which the temperature of the sample varied during the course of the measurement, the temperature of the sample was taken before and after the surface tension measurement. The limit within which the temperature varied was ± 0.2 K.

The Figure 2.1 depicts the ring being detached from the surface of the liquid/solution. The maximum force on the ring during this process is a measure of the surface or interfacial tension.

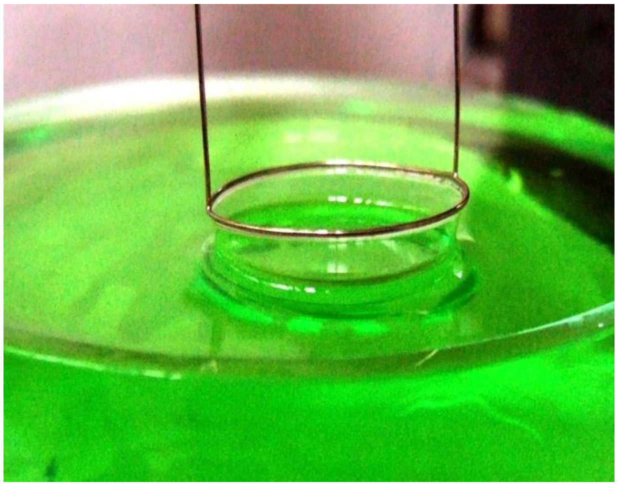

Figure 2.1 The ring as it is lifted from the liquid or solution.

2.2.3 Density measurements

The DMA 4500 density meter was used to measure density. The measurement is based on the proven oscillating U-tube principle ensuring highly accurate density values. This method is based on the law of harmonic oscillation, and uses a U-tube which is completely filled with the target sample (about 0.7 mL). It is then subjected to an electromagnet field. The values of the frequency and the duration of the vibration of the tube filled with the sample allow the density of the sample to be determined. The tube is double-walled and the space in between is filled with a gas with high coefficient of thermal conductivity. Also a platinum resistant thermometer placed in that space allows the temperature of the fluid to be measured during the density measurement [65].

The densitometer was rinsed with acetone and pumped to complete dryness. The sample was then injected in, taking care to remove bubbles in the syringe. The temperature was set at 298.15±0.01 K. When the injected volume reached thermal equilibrium, the density was read off. At least two readings were recorded and their average taken. The measurements were repeated at other temperatures of 308.15 K and 318.15 K. After the measurement the sample was purged out and the instrument dried.

CHAPTER 3

3.0 RESULTS AND DISCUSSION

3.1 Surface Tension

3.1.1 Surface tension table and graphs

A sample of the values of the surface tension of the binary mixtures of ketones and acetates at the indicated temperatures are presented in Table 3.1. The rest of the tables are in the Appendix section. The surface tension of the pure ketone was greater than that of the acetate in every case, except for methyl acetate/acetone pair. For all the mixtures, the surface tension decreased as the concentration of the acetate increased.

The surface tension graphs of the (acetate and ketone) binary mixtures show a linear trend with change in mole fraction of the acetate, as in the case of Figure 3.1 or change in mole fraction of the ketone, as in the case of Figure 3.3 and Figure 3.4. indicating that the molecules of ketones and those of acetates have a strong molecular interactions between them [33]. This is also the case with the (methyl acetate + ethyl acetate) in Figure 3.7. For Figure 3.2, Figure 3.5 and Figure 3.6 the surface tension change is non-linear with change in mole fraction of the solute. A non-linear trend indicates weaker molecular interactions between components and this would be explained by a difference in distribution of molecules between the surface and the bulk of the mixture. In an ideal case, the compound with a lower surface tension is expelled from the bulk to the liquid-vapour interface due to the stronger attractive forces between the solvent molecules [5], [6].

Table 3.1 Surface tension for methyl acetate (1) and cyclohexanone (2) at three different temperatures

Mole fraction of 1, X_1	**Surface tension, γ (mN/m)**		
	T = 298.15K	**T = 308.15K**	**T = 318.15K**
0	35.0	34.1	33.4
0.1163	33.8	32.9	32.0
0.2292	32.8	31.5	31.0
0.3376	31.8	30.2	29.8
0.4422	30.8	29.4	29.2
0.5432	29.8	28.4	27.8
0.6334	28.9	27.6	27.0
0.7351	27.9	26.9	26.5
0.8259	27.1	25.5	25.6
0.9147	26.4	25.0	24.6
1	25.7	24.5	23.4

Surface tension of the mixture varies linearly with composition at all the temperatures studied, indicating that the two components have strong intermolecular interactions [33] (see Figure 3.1), most probably dipole-dipole ones.

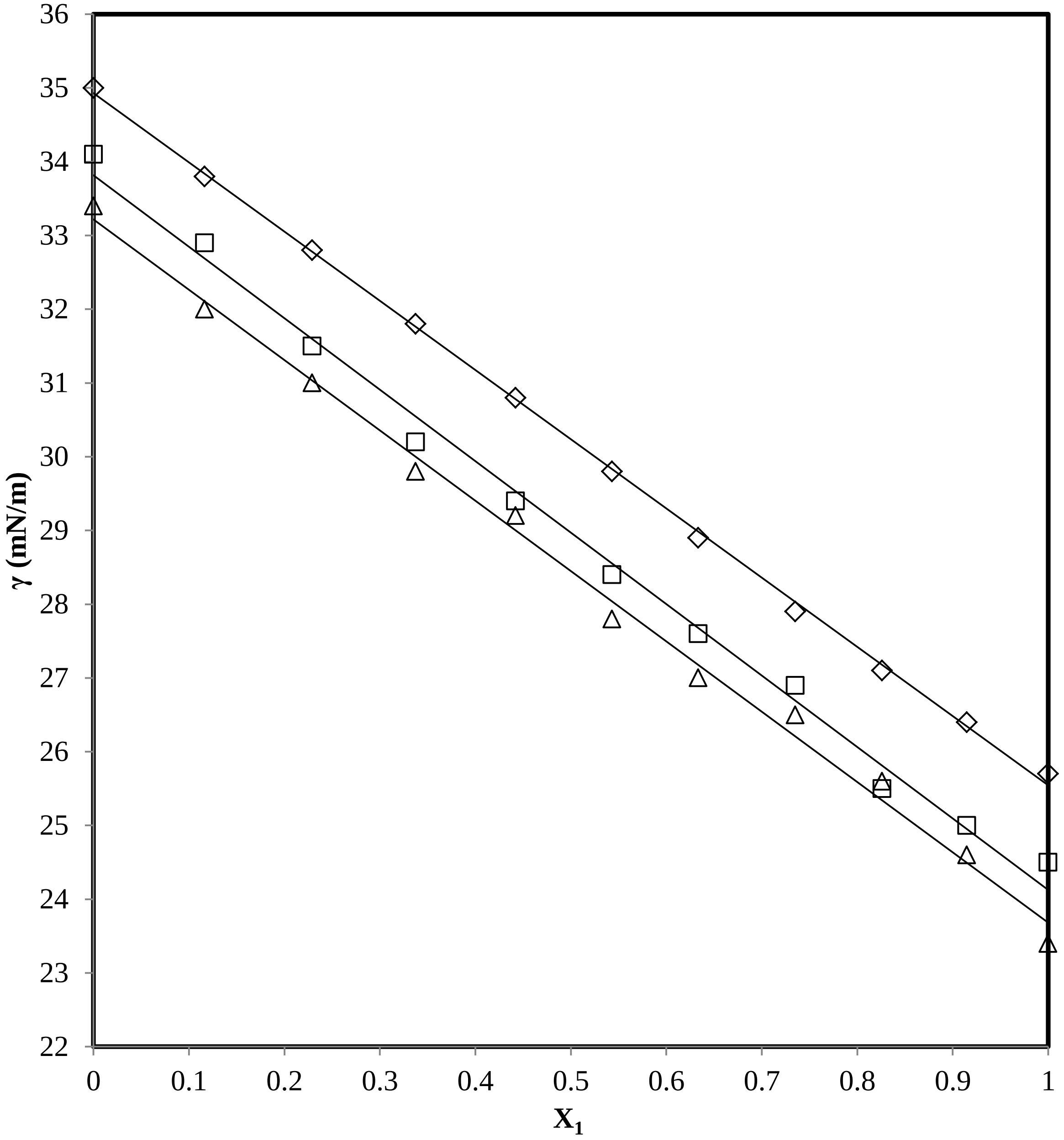

Figure 3.1 Surface tension against mole fraction for the methyl acetate (1) and cyclohexanone (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K

For ethyl acetate-cyclohexanone binary system the surface tension varies non-linearly with varying mole fraction, indicating that there are weaker solute-solvent interactions between the molecules at the surface (Figure 3.2). It also indicates that the substance with the lower surface tension has been preferentially expelled to the surface. In this case, the surface is richer in the ethyl acetate molecules which have stronger solute-solute interactions.

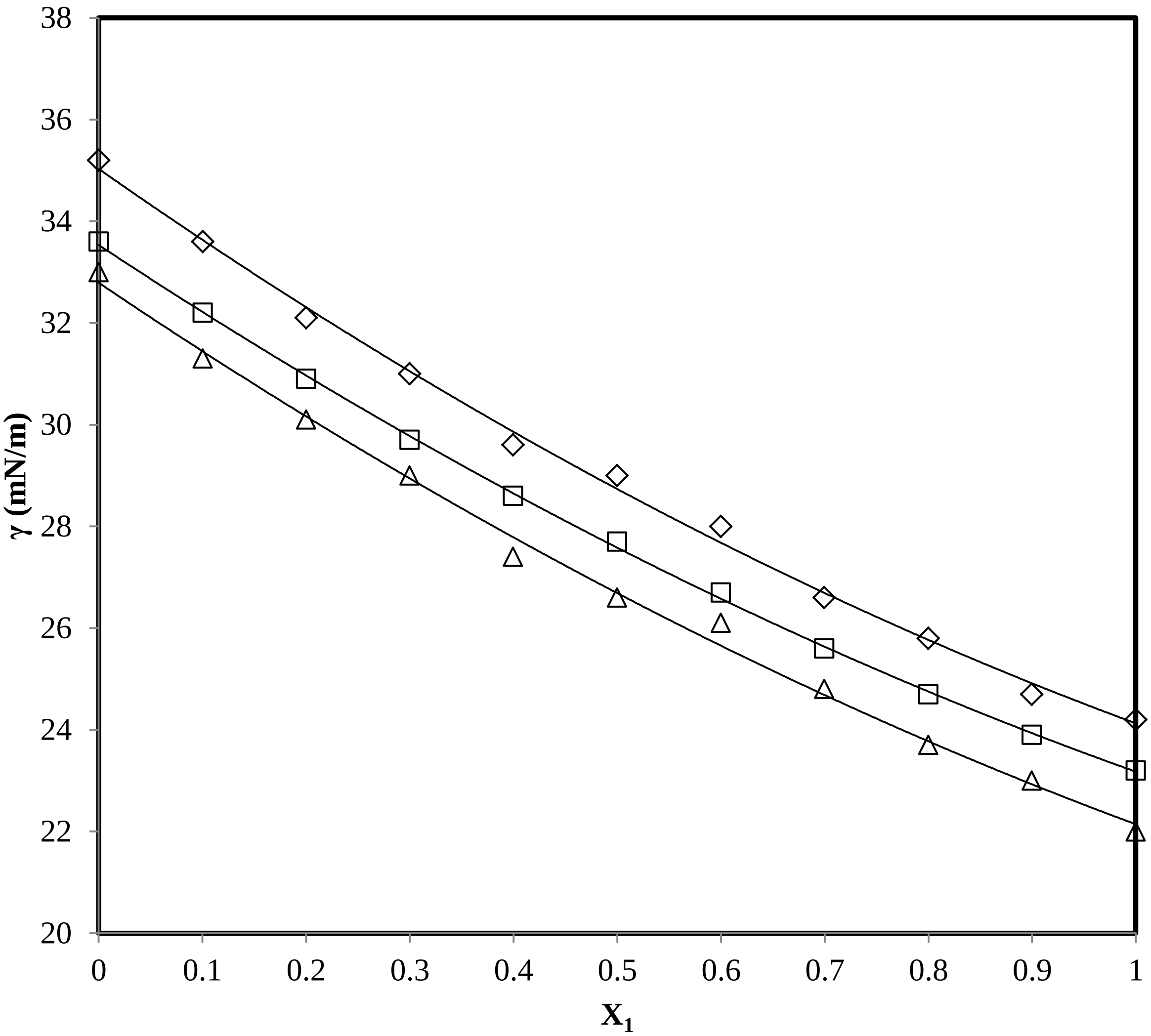

Figure 3.2 Surface tension against mole fraction for the ethyl acetate (1) and cyclohexanone (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K

Figure 3.3 shows a linear trend in surface tension as mole fractions are varied, indicating strong molecular interactions at the interface.

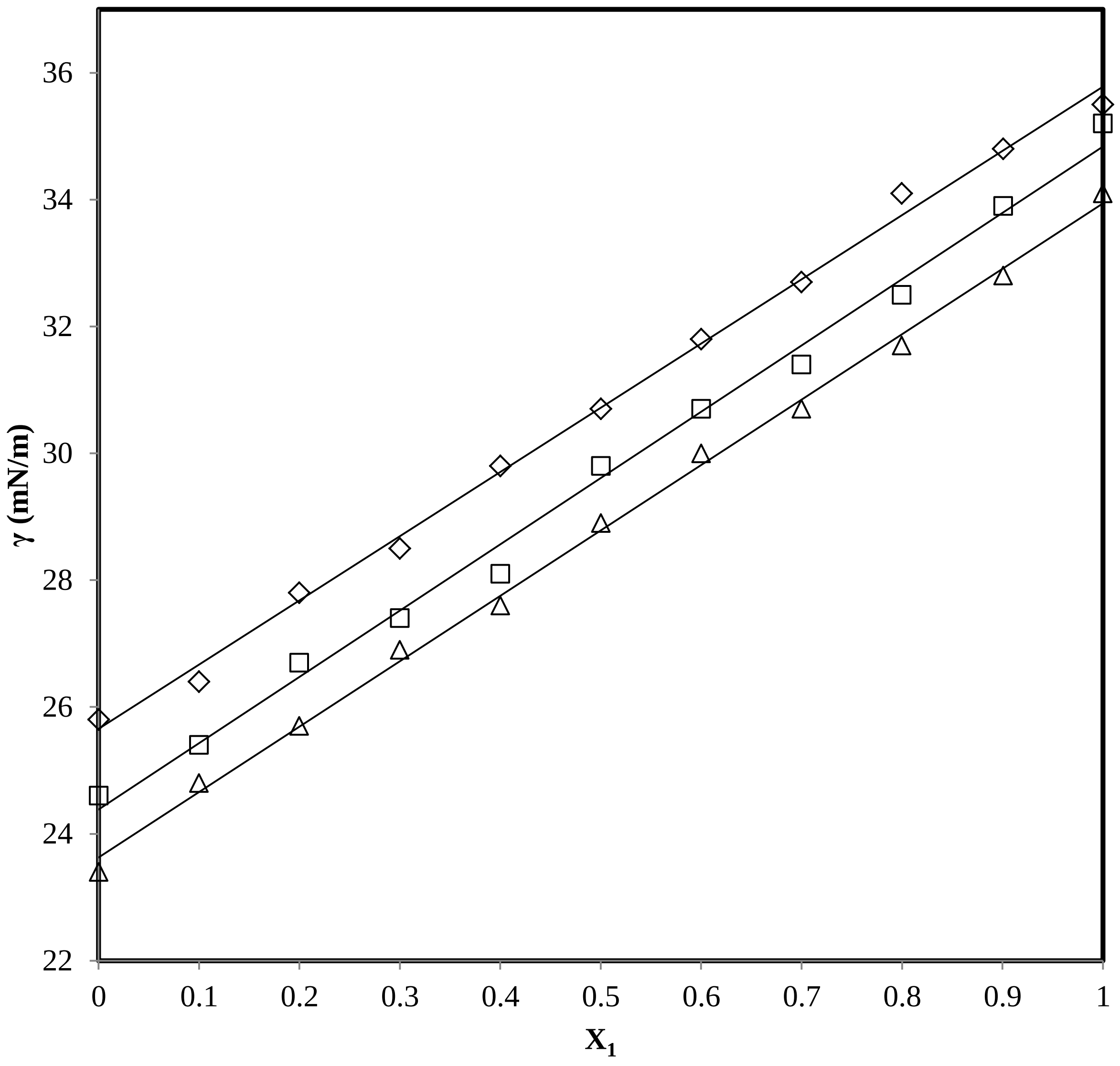

Figure 3.3 Surface tension against mole fraction for the cycloheptanone (1) and methyl acetate (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K

The surface tension values of pure acetone and methyl acetate are close to each other (24.79 mN/m [35] for methyl acetate and 23.0 mN/m [51] for acetone at temperature of 298.15 K) so their activities on the surface are nearly equal; thus the scattered but linear trend in surface tension with change in mole fraction of acetone (Figure 3.4).

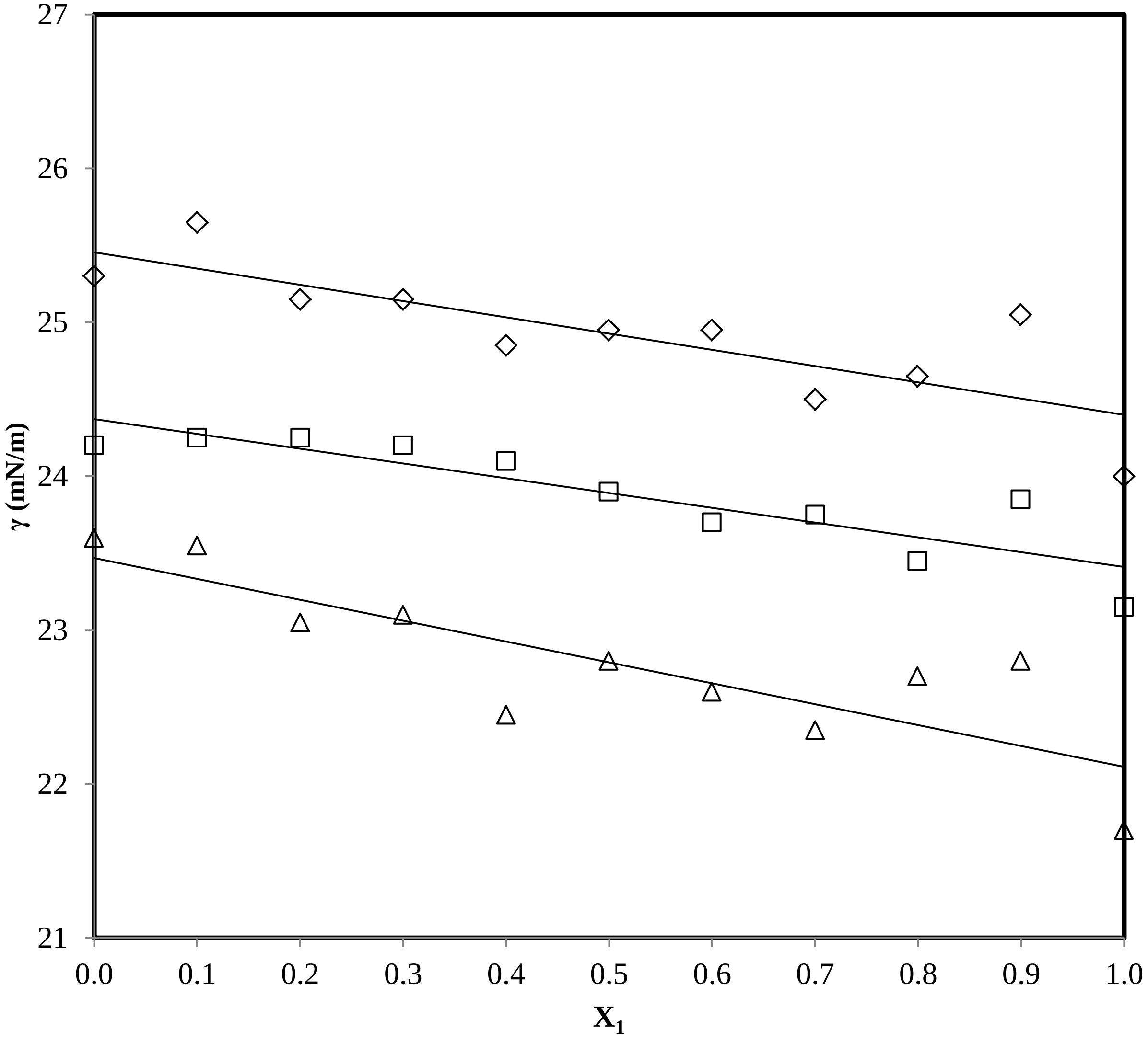

Figure 3.4 Surface tension against mole fraction for the acetone (1) and methyl acetate (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K.

The variation of surface tensions with mole fraction for the acetophenone-methyl acetate binary mixture shows a non-linear trend, which indicates that there is different distribution of molecules between the surface and bulk phases (Figure 3.5). There is dominance of self-association by the methyl acetate molecules at the surface.

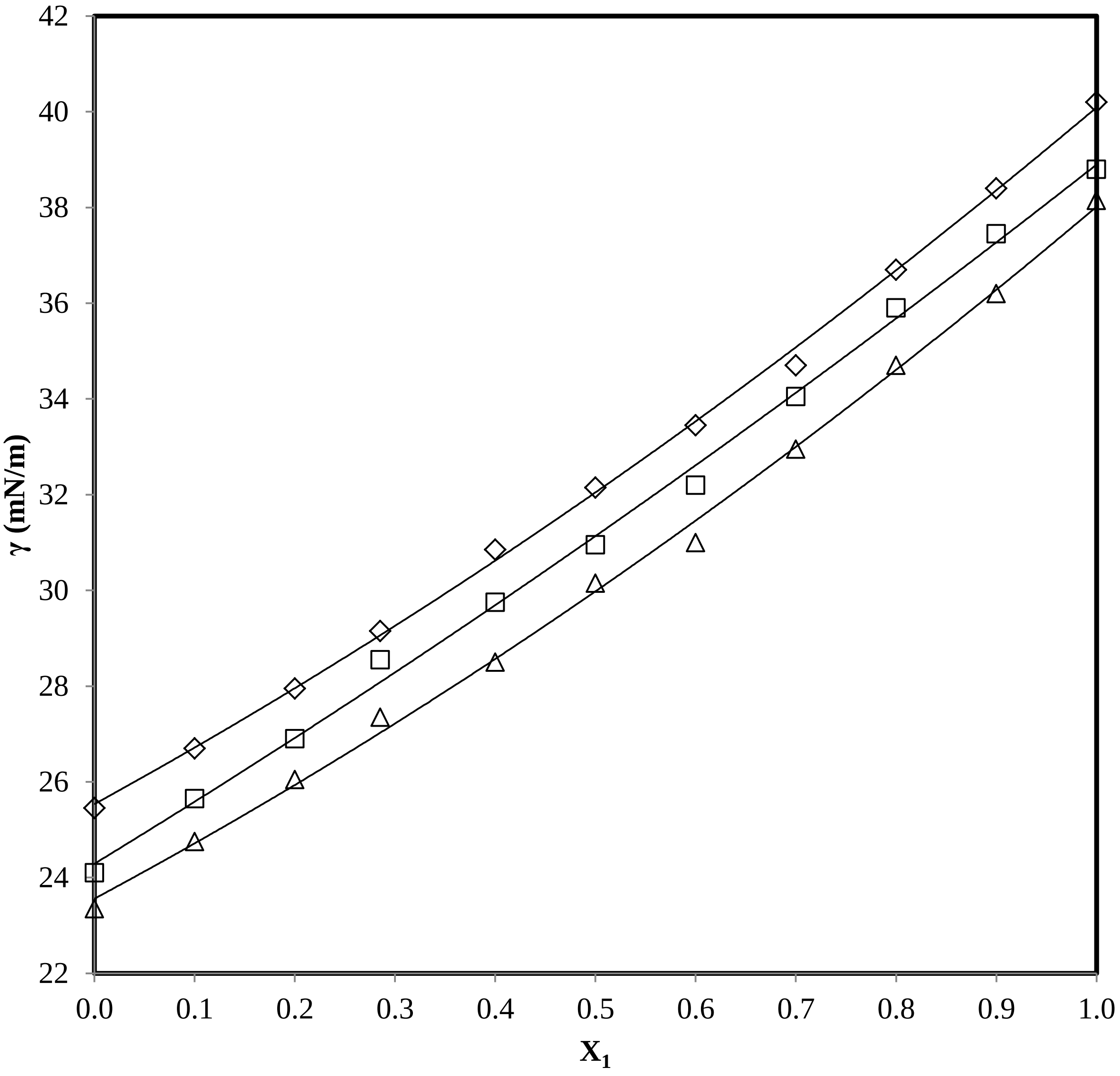

Figure 3.5 Surface tension against mole fraction for the acetophenone (1) and methyl acetate (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K.

For the system acetophenone and ethyl acetate, the surface tension varies with mole fraction of ethyl acetate in a non-linear fashion (Figure 3.6). The plot is concave downwards, which indicates that the component with the lower surface tension is preferentially present on the surface. Ethyl acetate has a lower polarizability as compared to methyl acetate leading to lower solute-solvent interactive forces with acetophenone, and consequently greater ease of expulsion to the surface. This leads to the greater deviation of surface tension of the mixture.

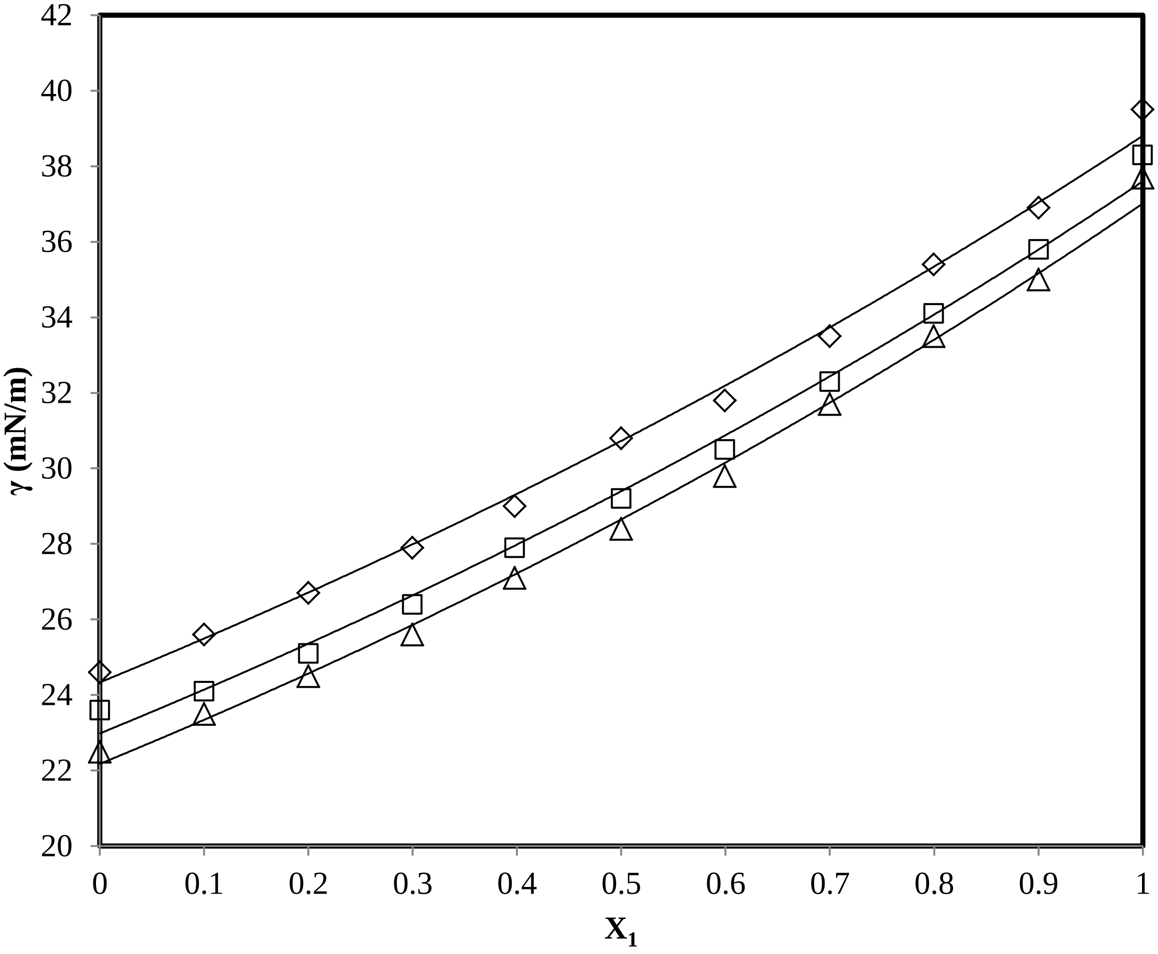

Figure 3.6 Surface tension against mole fraction for the acetophenone (1) and ethyl acetate (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K

Methyl acetate and ethyl acetate molecules have strong interactions at the interface. This is indicated by the linear trend of the variation in surface tension with mole fraction of methyl acetate, across all the three temperatures studied (Figure 3.7). This probably results from their structural similarity, which results in strong attraction between their molecules.

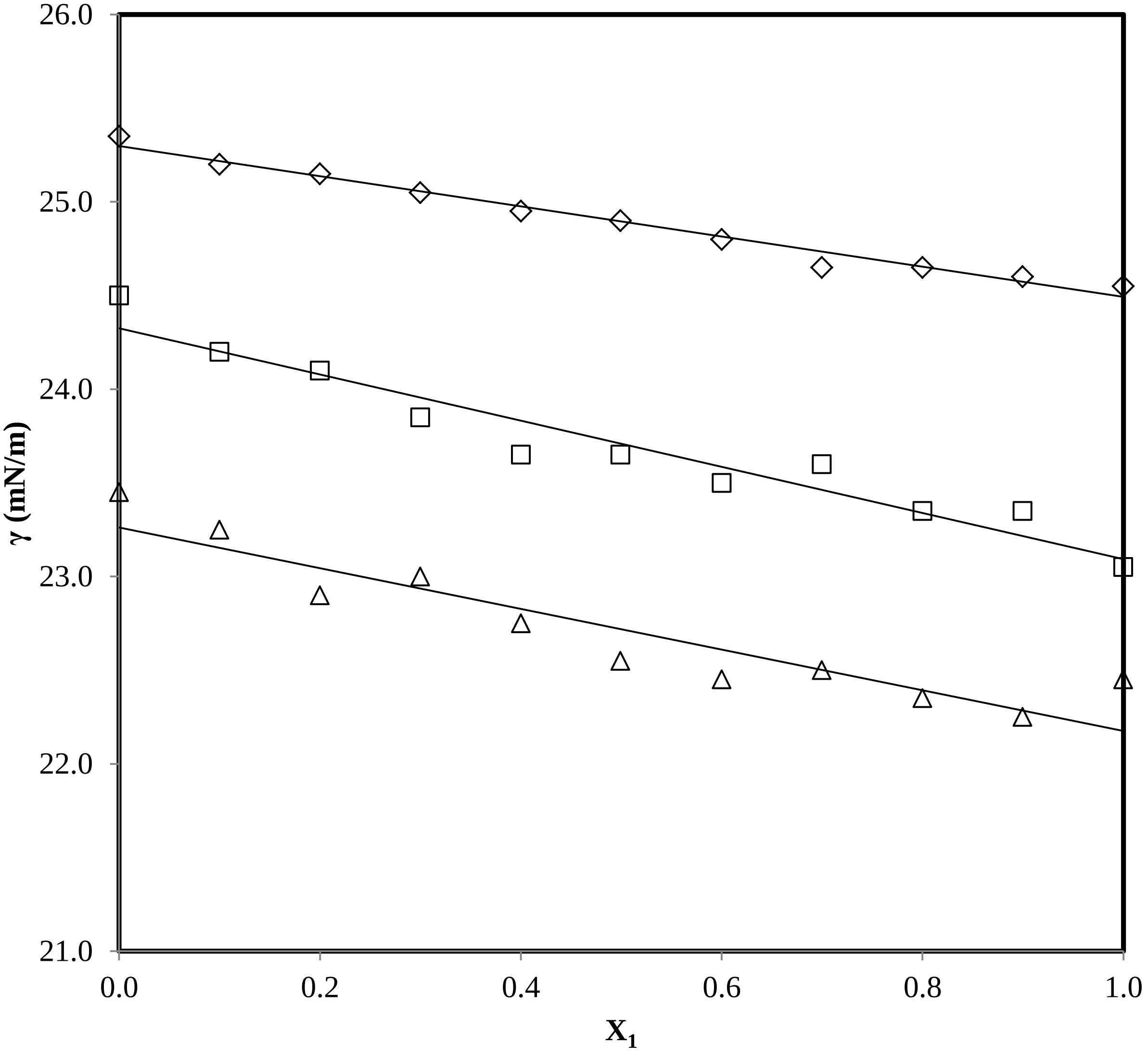

Figure 3.7 Surface tension against mole fraction for the ethyl acetate (1) and methyl acetate (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K.

3.1.2 Effect of chain length of alkyl acetates on surface tension of cyclohexanone mixtures

An increase in the number of C atoms in the alkyl chain of n-alkyl acetates causes a decrease in the surface tension of the mixtures across the whole composition (Figure 3.8, Figure 3.9 and Figure 3.10). This is thought to be due to the decreasing polarizability of the acetate as the length of the alkyl chain increases, leading to a decrease in the dipole-dipole interactions between the molecules [5].

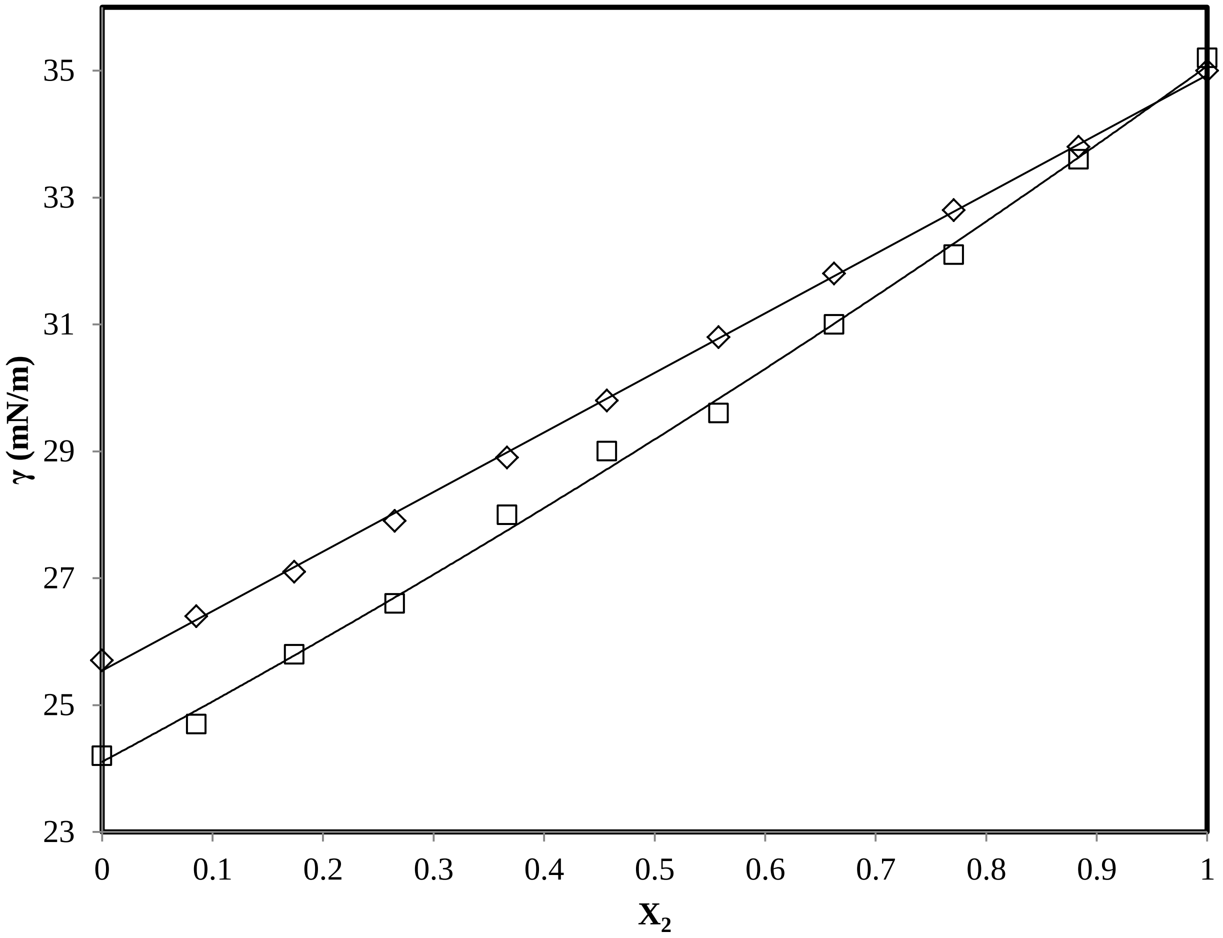

Figure 3.8 Surface tension against mole fraction for cyclohexanone (2) + methyl acetate (◇) and ethyl acetate (□) at T= 298.15K

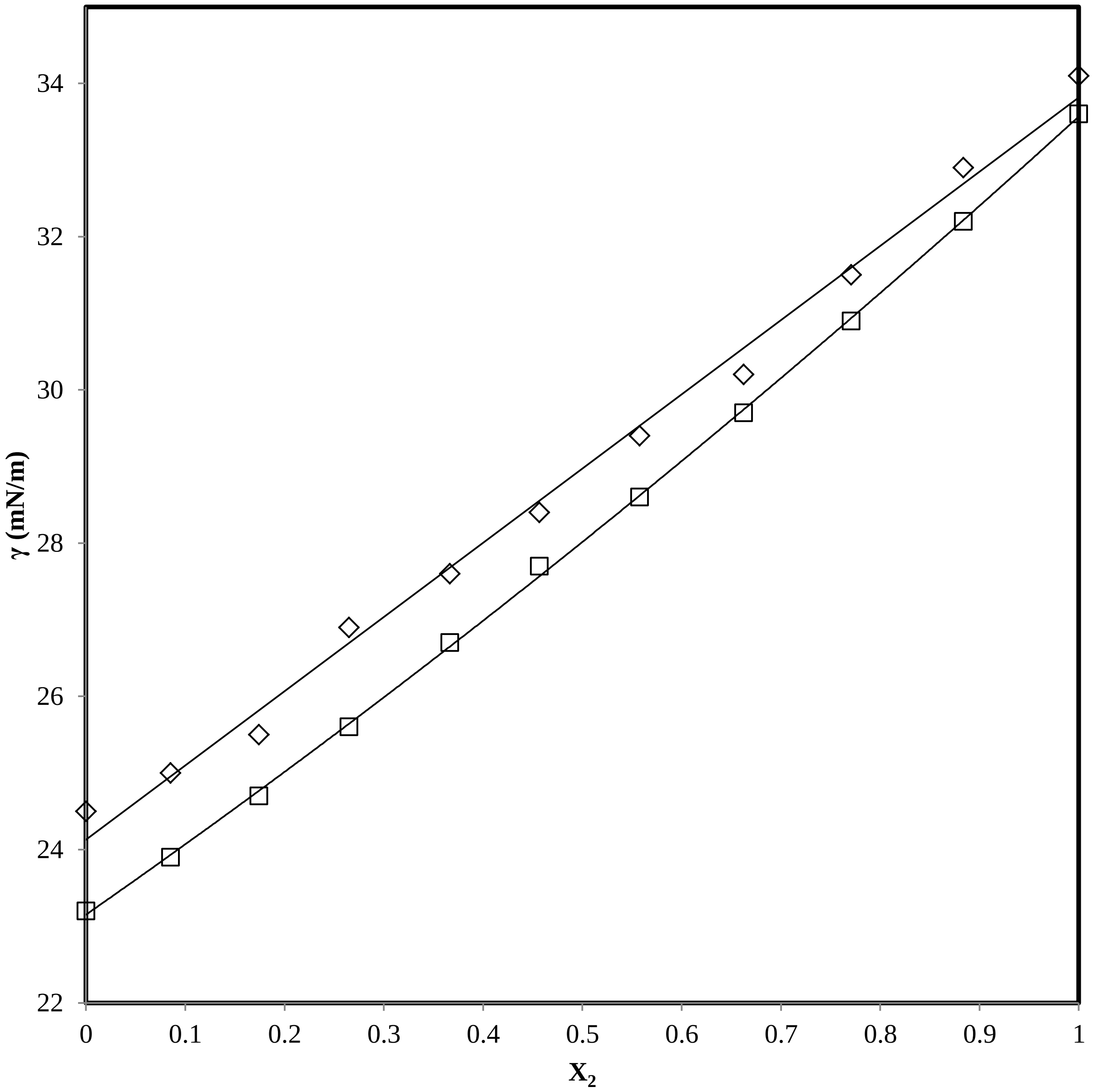

Figure 3.9 Surface tension against mole fraction for cyclohexanone (2) + methyl acetate (◇) and ethyl acetate (□) at T= 308.15K

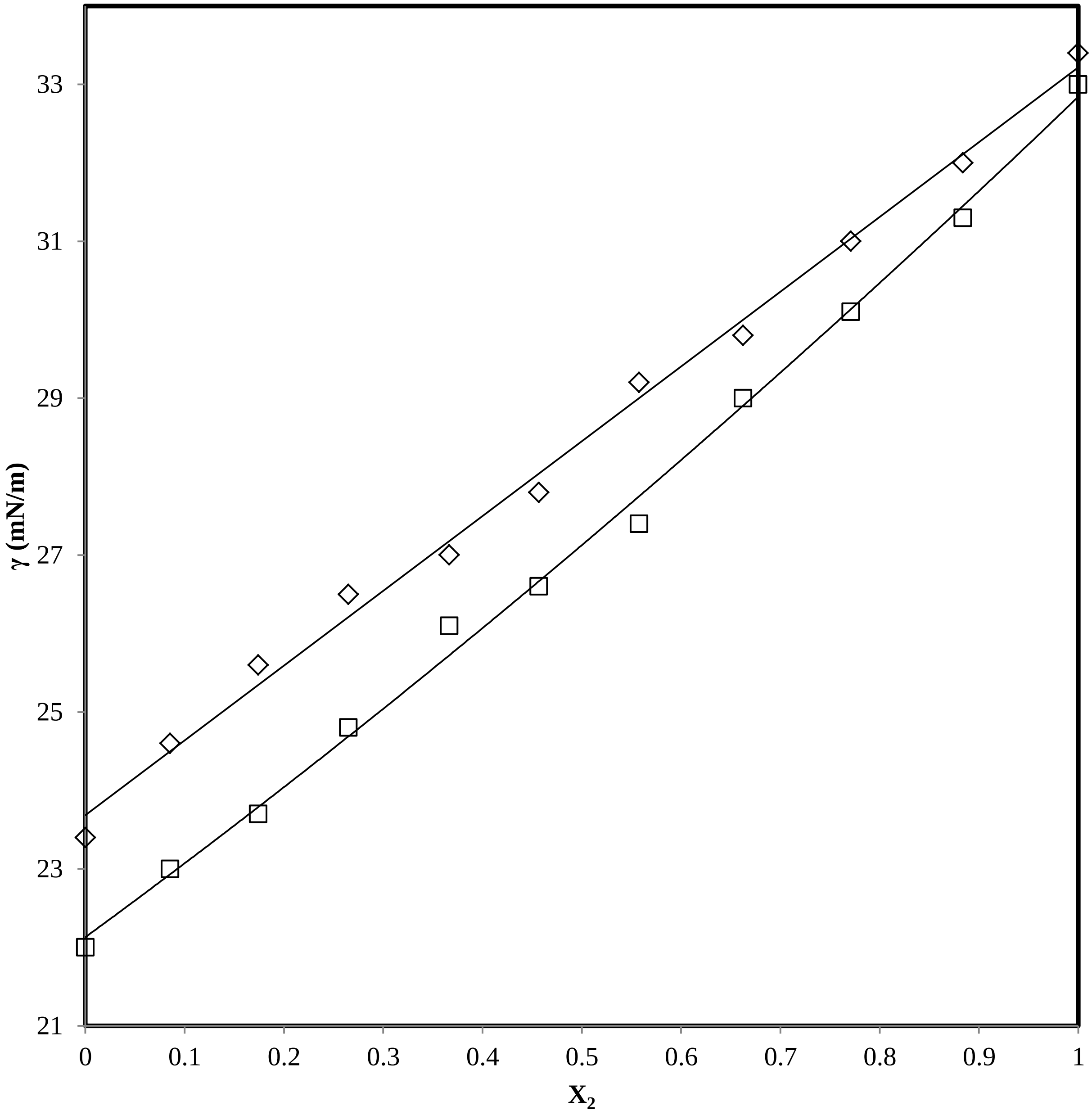

Figure 3.10 Surface tension against mole fraction for cyclohexanone (2) + methyl acetate (◇) and ethyl acetate (□) at T= 318.15K

3.1.3 Effect of different classes of ketones on surface tension of methyl acetate mixtures

When a comparison is made between mixtures containing various ketones but the same n-alkyl acetate, the trends are as shown in Figure 3.11, Figure 3.12 and Figure 3.13. The different classes show that the bulky molecules interact weakly with the methyl acetate molecules at the surface observed by the nonlinear trend of surface tension with change in mole fraction. Acetone, which has a value of surface tension close to that of methyl acetate, shows stronger interactions at the surface.

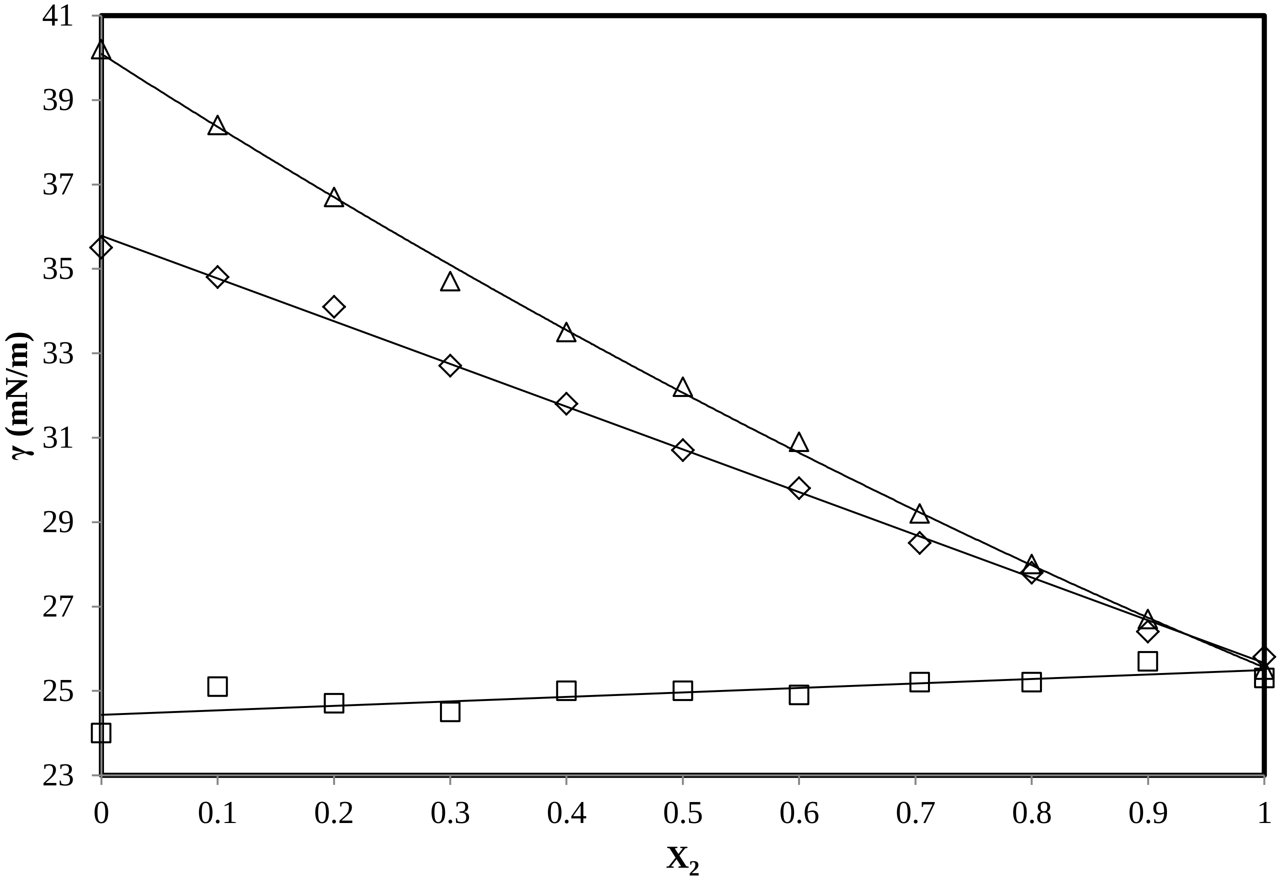

Figure 3.11 Surface tension against mole fraction for methyl acetate (2) + cycloheptanone (◇), acetone (□) and acetophenone (△) at T=298.15K

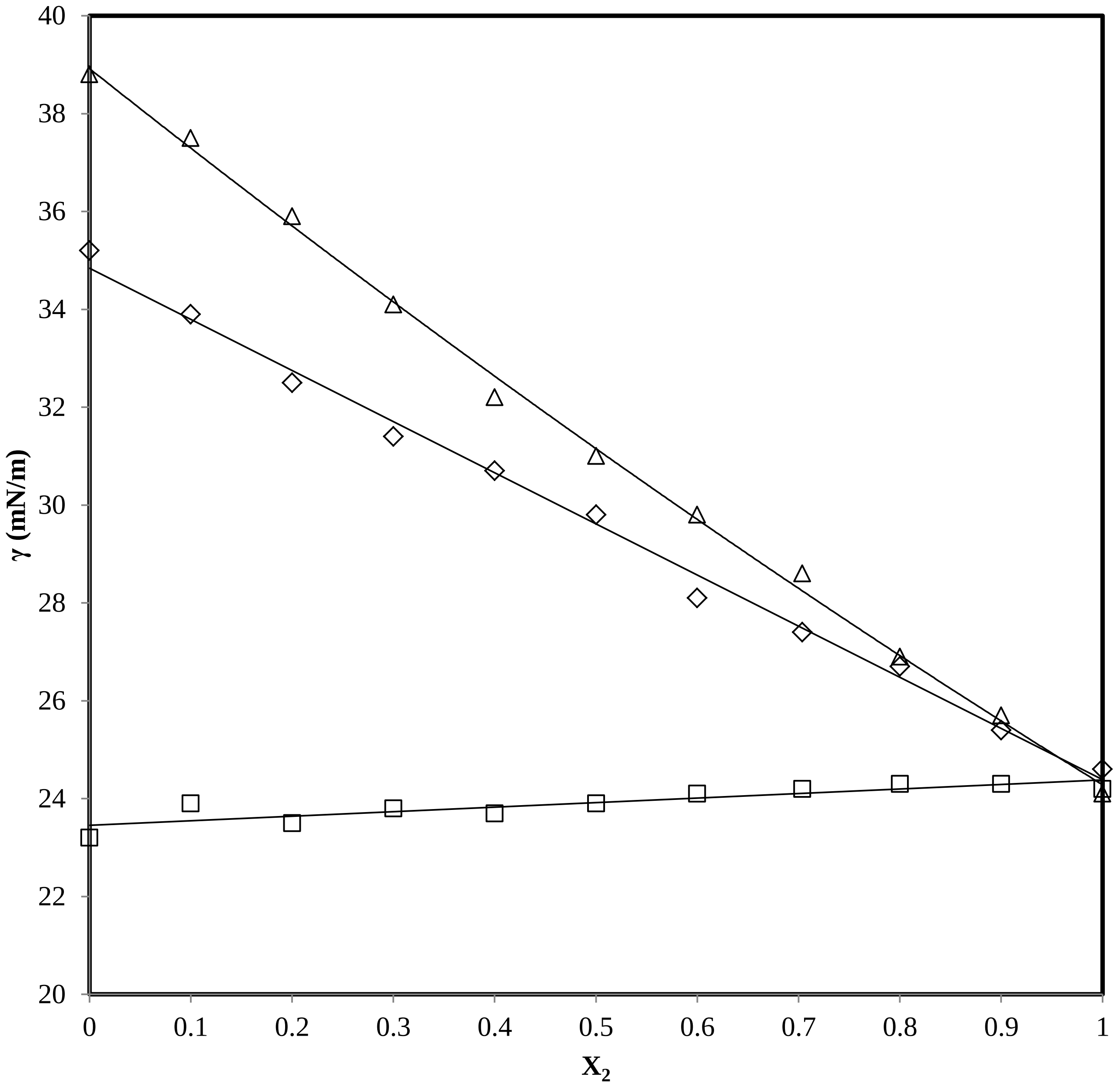

Figure 3.12 Surface tension against mole fraction for methyl acetate (2) + cycloheptanone (◇), acetone (□) and acetophenone (△) at T=308.15K

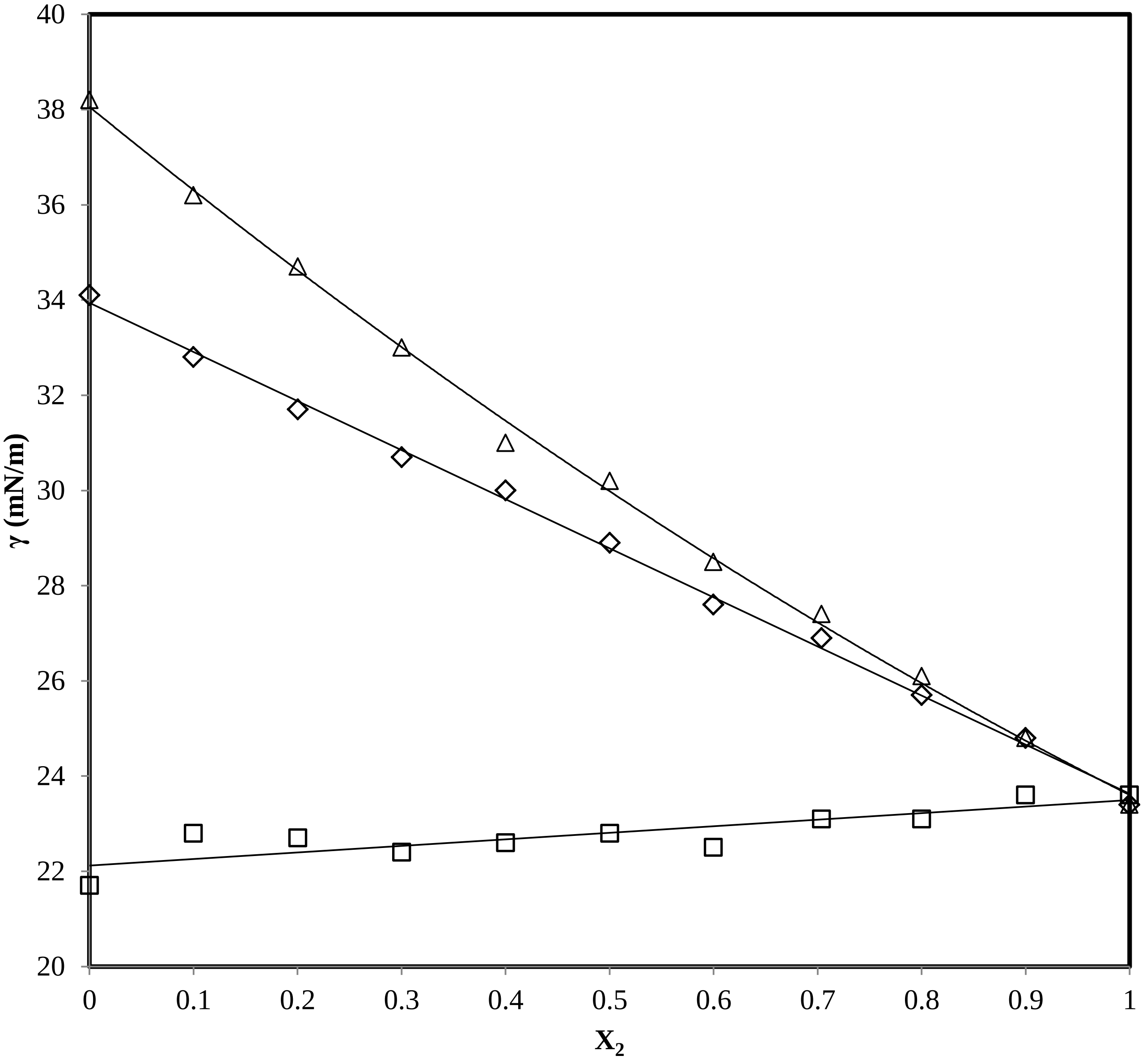

Figure 3.13 Surface tension against mole fraction for methyl acetate (2) + cycloheptanone (◇), acetone (□) and acetophenone (△) at T=318.15K

3.2 Surface Tension Deviations

3.2.1 Unfitted Δγ

A sample calculation of the surface tension from equation 4 is tabulated below in Table 3.2 for the methyl acetate (1) and cyclohexanone (2) mixtures, using the equation:

$$\Delta\gamma = \gamma - (X_1\gamma_1 + X_2\gamma_2)$$

Where γ is the surface tension of the mixture, γ_1 is the surface tension of pure component 1 and equals 25.7 mN/m, γ_2 = 35.0 mN/m is the surface tension of pure component 2.

Table 3.2 Calculated surface tension deviations for the methyl acetate (1) and cyclohexanone (2) system at temperature 298.15K.

γ (mN/m)	**X_1**	**X_2**	**$X_1\gamma_1$**	**$X_2\gamma_2$**	**$(X_1\gamma_1 + X_2\gamma_2)$**	**Δγ (mN/m)**
35.0	0	1	0	35.0	35.0	0
33.8	0.1163	0.8837	2.99	30.9	33.9	-0.1
32.8	0.2292	0.7708	5.89	27.0	32.9	-0.1
31.8	0.3376	0.6624	8.68	23.2	31.9	-0.1
30.8	0.4422	0.5578	11.4	19.5	30.9	-0.1
29.8	0.5432	0.4568	14.0	16.0	29.9	-0.1
28.9	0.6334	0.3666	16.3	12.8	29.1	-0.2
27.9	0.7351	0.2649	18.9	9.27	28.2	-0.3
27.1	0.8259	0.1741	21.2	6.09	27.3	-0.2
26.4	0.9147	0.0853	23.5	2.99	26.5	-0.1
25.7	1	0	25.7	0	25.7	0

Table 3.3 Surface tension deviations for the methyl acetate (1) and cyclohexanone (2) mixtures at these different temperatures

Mole fraction of 1, X1	**Surface tension deviation, Δγ (mN/m)**		
	T=298.15K	**T=308.15K**	**T=318.15K**
0	0	0	0
0.1163	-0.1	-0.1	-0.2
0.2292	-0.1	-0.4	-0.1
0.3376	-0.1	-0.7	-0.2
0.4422	-0.1	-0.5	0.2
0.5432	-0.1	-0.5	-0.2
0.6334	-0.2	-0.4	-0.1
0.7351	-0.3	-0.1	0.5
0.8259	-0.2	-0.7	0.5
0.9147	-0.1	-0.3	0.3
1	0	0	0

3.2.2 Fitting Δγ on the Redlich-Kirster polynomial

Surface tension deviations were fitted to Redlich-Kirster polynomial and the least-squares values for the coefficients A_k were obtained

$$\Delta\gamma = x_i\, x_j \sum_{k=0}^{n} A_k\, (x_i - x_j)^k$$

In the case of (methyl acetate + cyclohexanone) binary mixture, the deviations from the ideal behaviour are minimal especially at the lower temperature, which indicate that the interactions between the component molecules are strong (see Figure 3.14). At higher temperature, the interactions are expected to weaken due to increase in kinetic energy within the system.

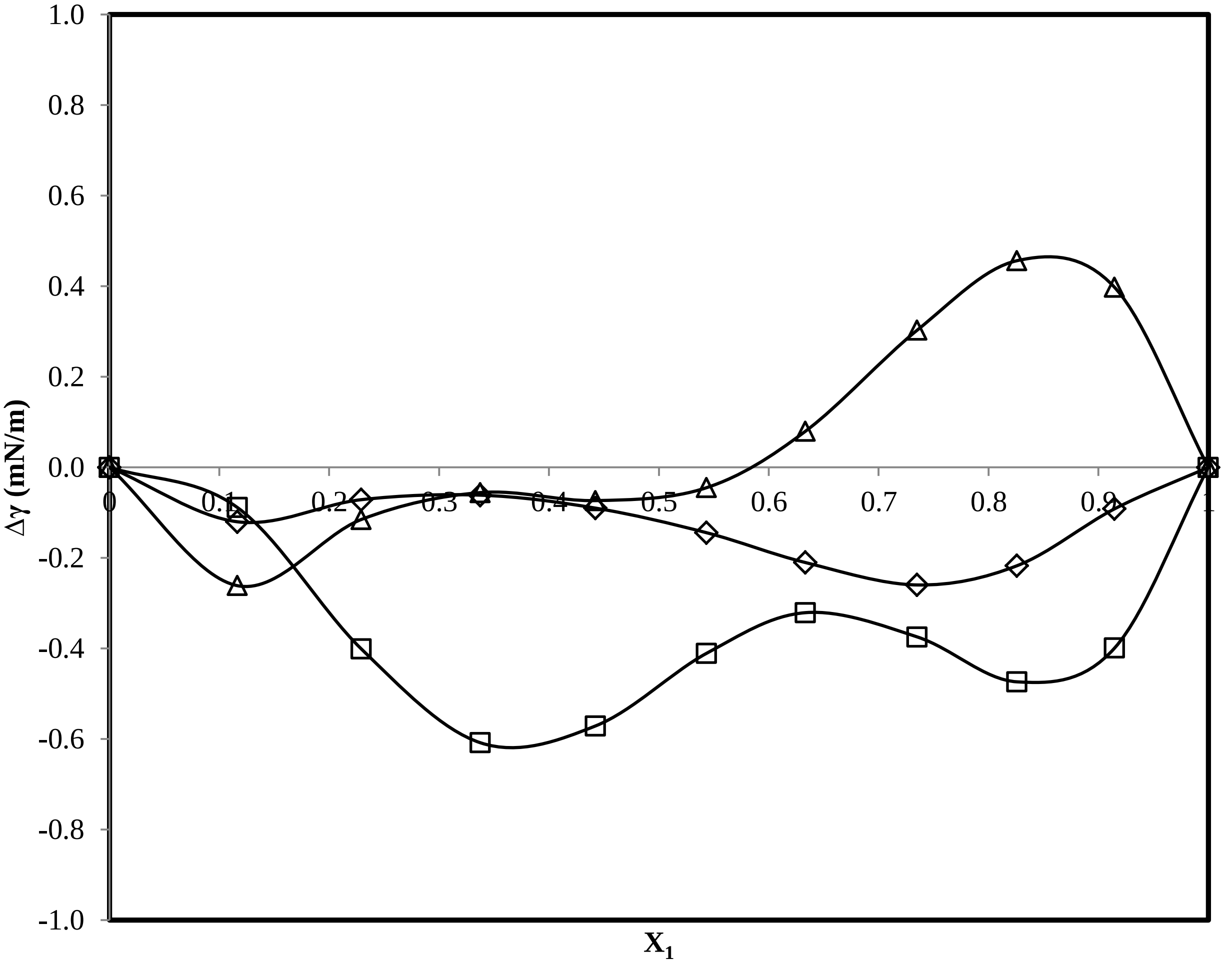

Figure 3.14 Surface tension deviation against mole fraction for methyl acetate (1) and cyclohexanone (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K.

The ethyl acetate-cyclohexanone system shows negative surface tension deviations across all temperatures which indicates that the component with the lower surface tension is preferentially expelled to the surface phase [5], [6] (see Figure 3.15). Therefore, in this mixture the mole fraction of ethyl acetate is greater in the surface phase than it is in the bulk. The largest deviation occurs in (X_1 =0.3-0.4).

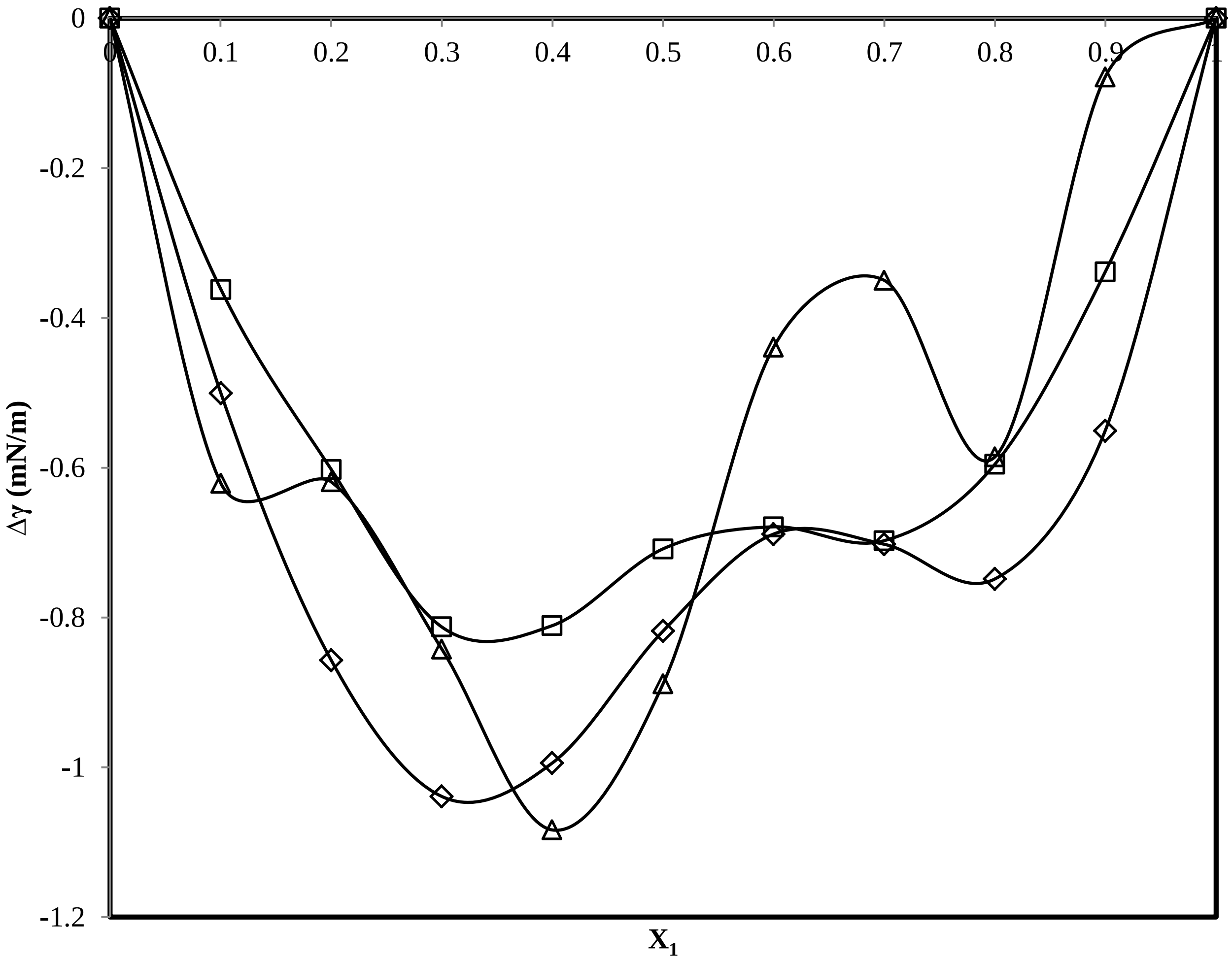

Figure 3.15 Surface tension deviations against mole fraction for the ethyl acetate (1) and cyclohexanone (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K.

For the cycloheptanone-methyl acetate mixture, (Figure 3.16) shows almost ideal behavior for X_1 range: 0.3-0.6. This indicates strong dipole-dipole interactions between the components at the interface.

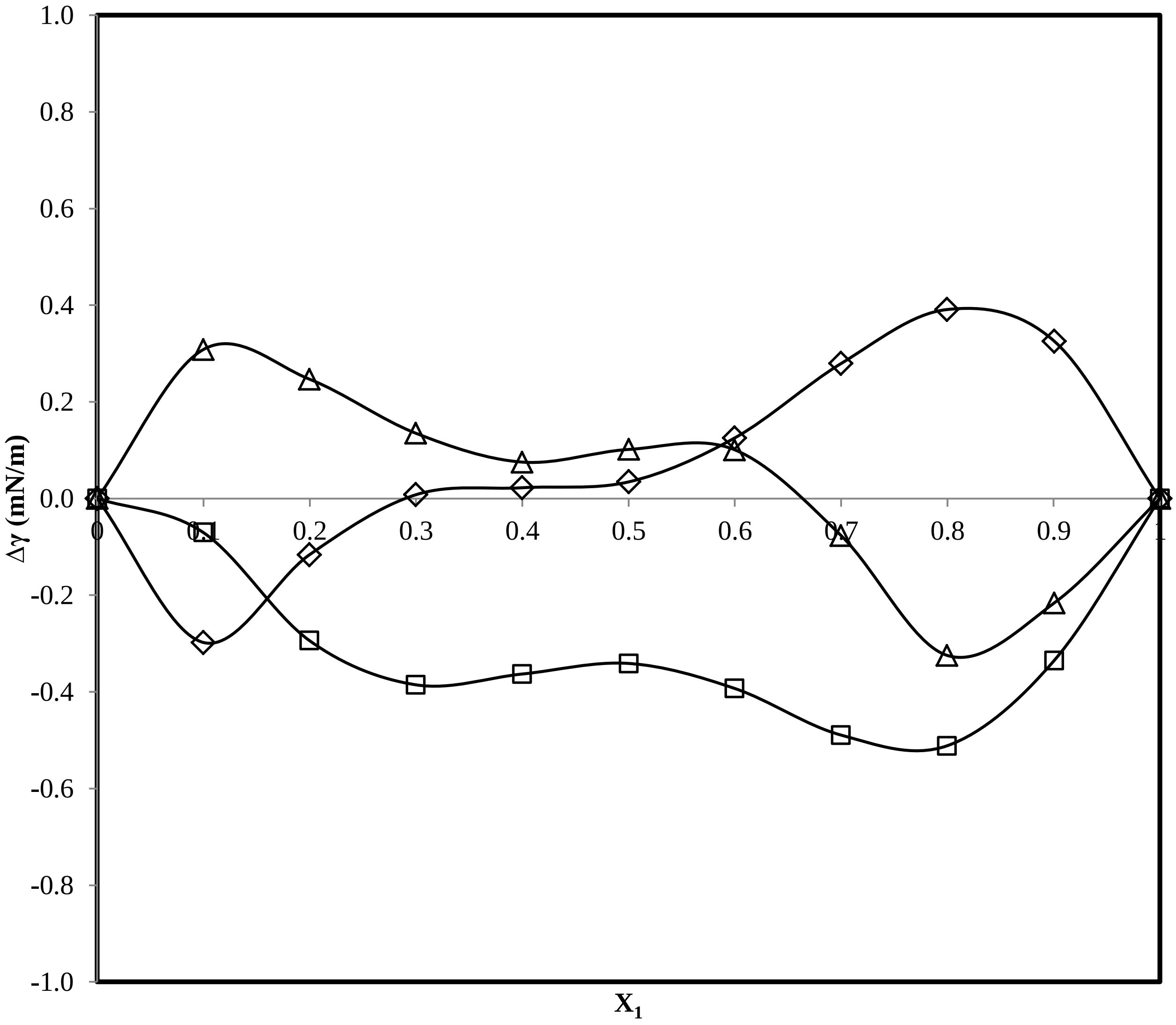

Figure 3.16 Surface tension deviation against mole fraction for cycloheptanone (1) and methyl acetate (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K

For acetophenone- ethyl acetate mixture, the deviations from ideality are negative and relatively large, indicating weak interactions and a greater tendency of the component with the lower surface tension to be expelled from the bulk to the surface (see Figure 3.17). Therefore, solute-solute interactions are dominant at the surface. This behavior is observed for all the temperatures studied with the largest negative deviation occurring at the intermediate temperature, 308.15K.

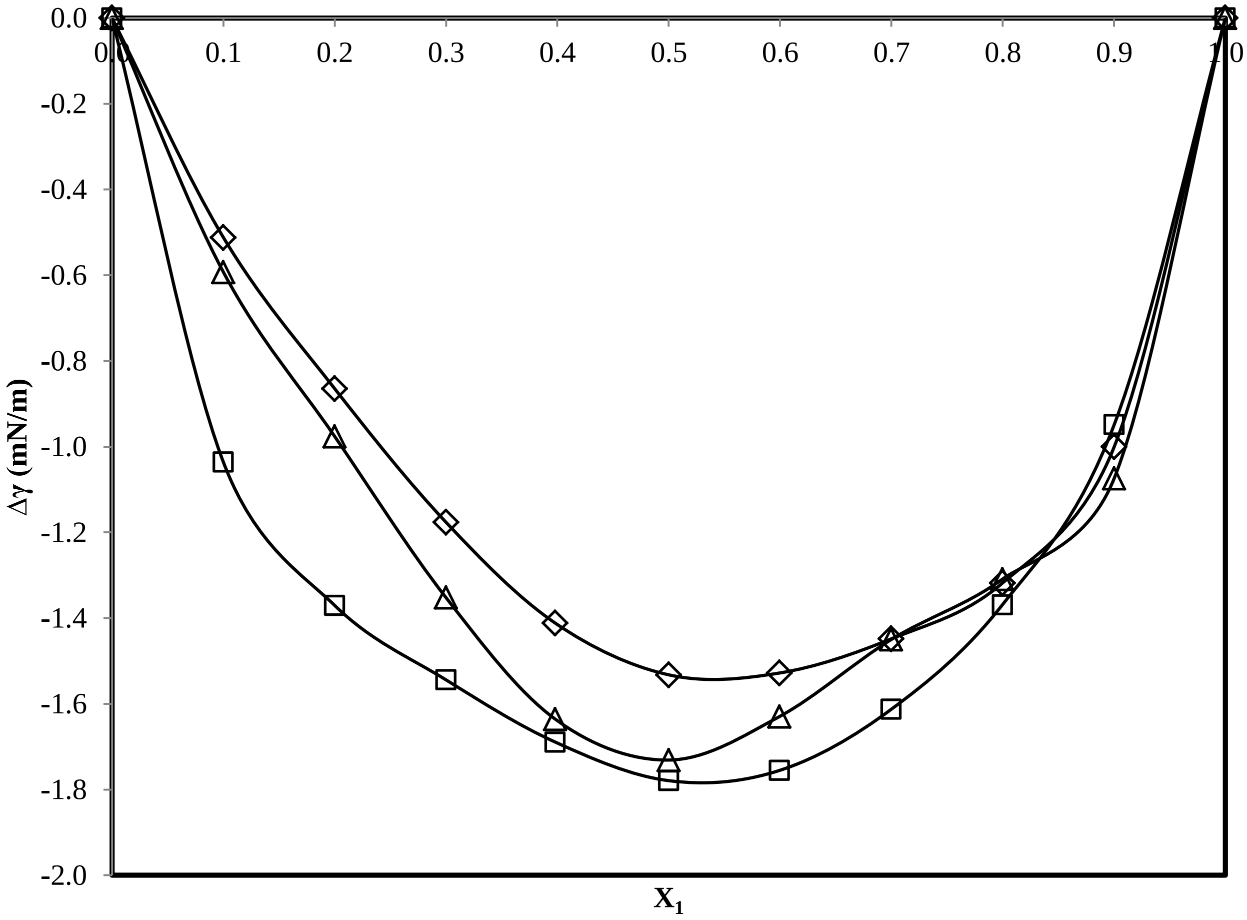

Figure 3.17 Surface tension deviation against mole fraction for acetophenone (1) and ethyl acetate (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K.

The ethyl acetate - methyl acetate mixture, (Figure 3.18) shows minimal deviations from ideal behaviour, indicating strong molecular interactions, that is solute-solvent. This is to be expected given their similar structures. At the highest temperature small but significant negative deviations are observed, this is probably due to an increase in temperature which weakens the cohesive forces within the system.

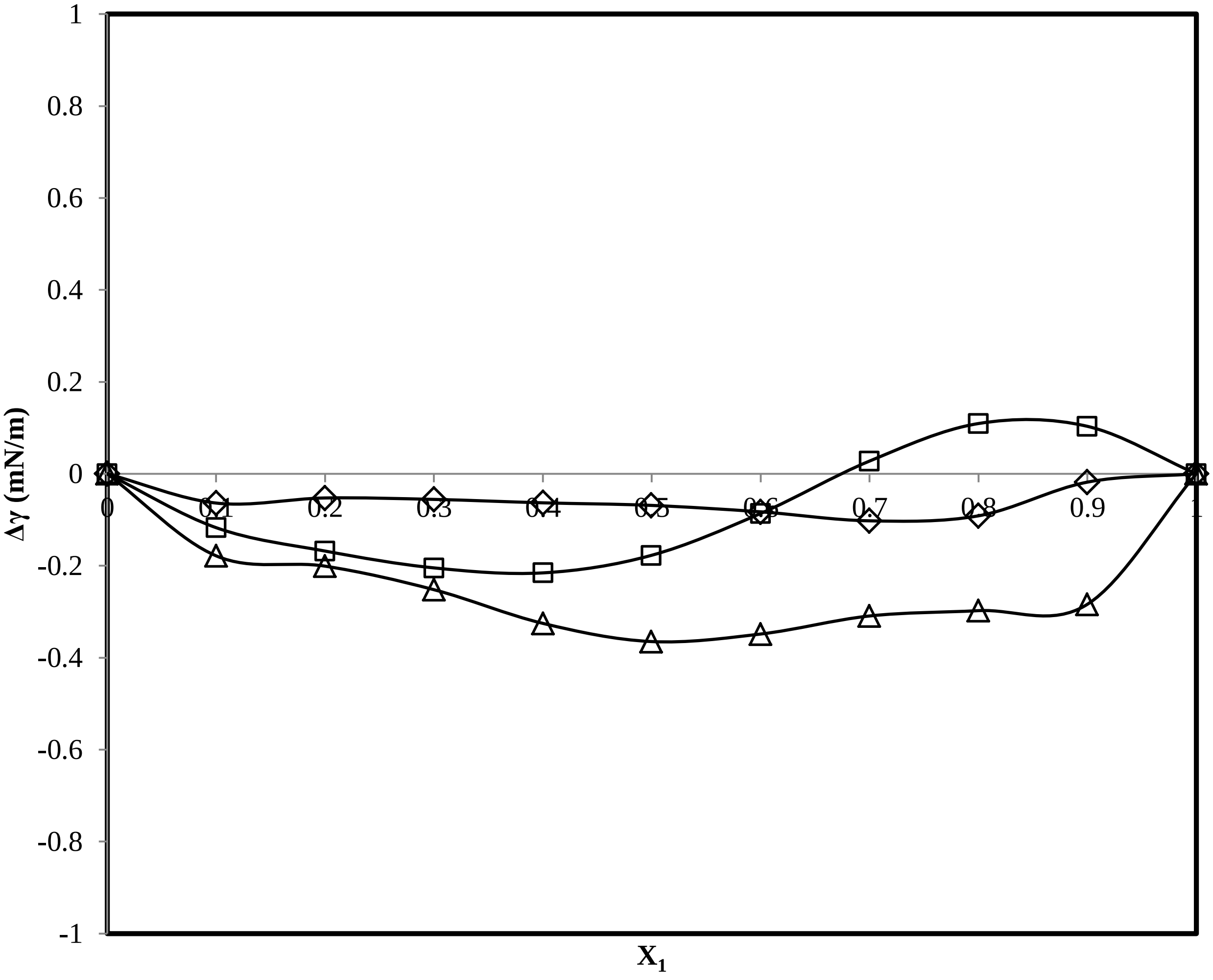

Figure 3.18 Surface tension deviation against mole fraction for ethyl acetate (1) and methyl acetate (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K.

3.3 Temperature Dependence of Surface Tension (Surface Entropy)

Figure 3.19 to Figure 3.25 show the variation of surface entropy with mole fraction for the various systems studied. In general plots of surface entropy versus mole fraction gave negative deviations although a high degree of scatter in experimental points was observed. For the (ethyl acetate + methyl acetate) binary system (Figure 3.25), a relatively smooth S^S vs X_1 plot was generated giving rise to a minimum at about X_1 = 0.7, which is very close to V_m^E vs X_1 minima at which the maximum molecular interactions occur. However, the plot for $\Delta\gamma$ vs X_1 indicated the maximum in the same region only at 308K.

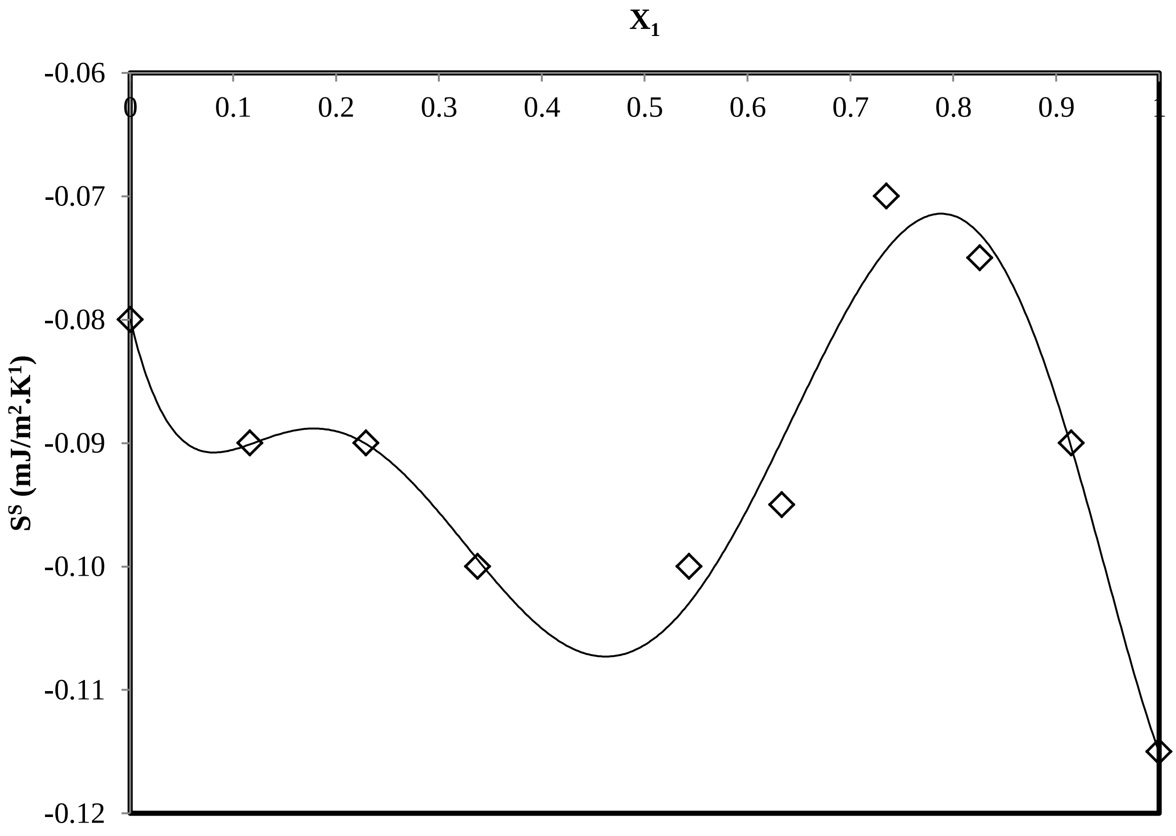

Figure 3.19 Surface entropy against mole fraction for methyl acetate (1) and cyclohexanone (2) mixtures

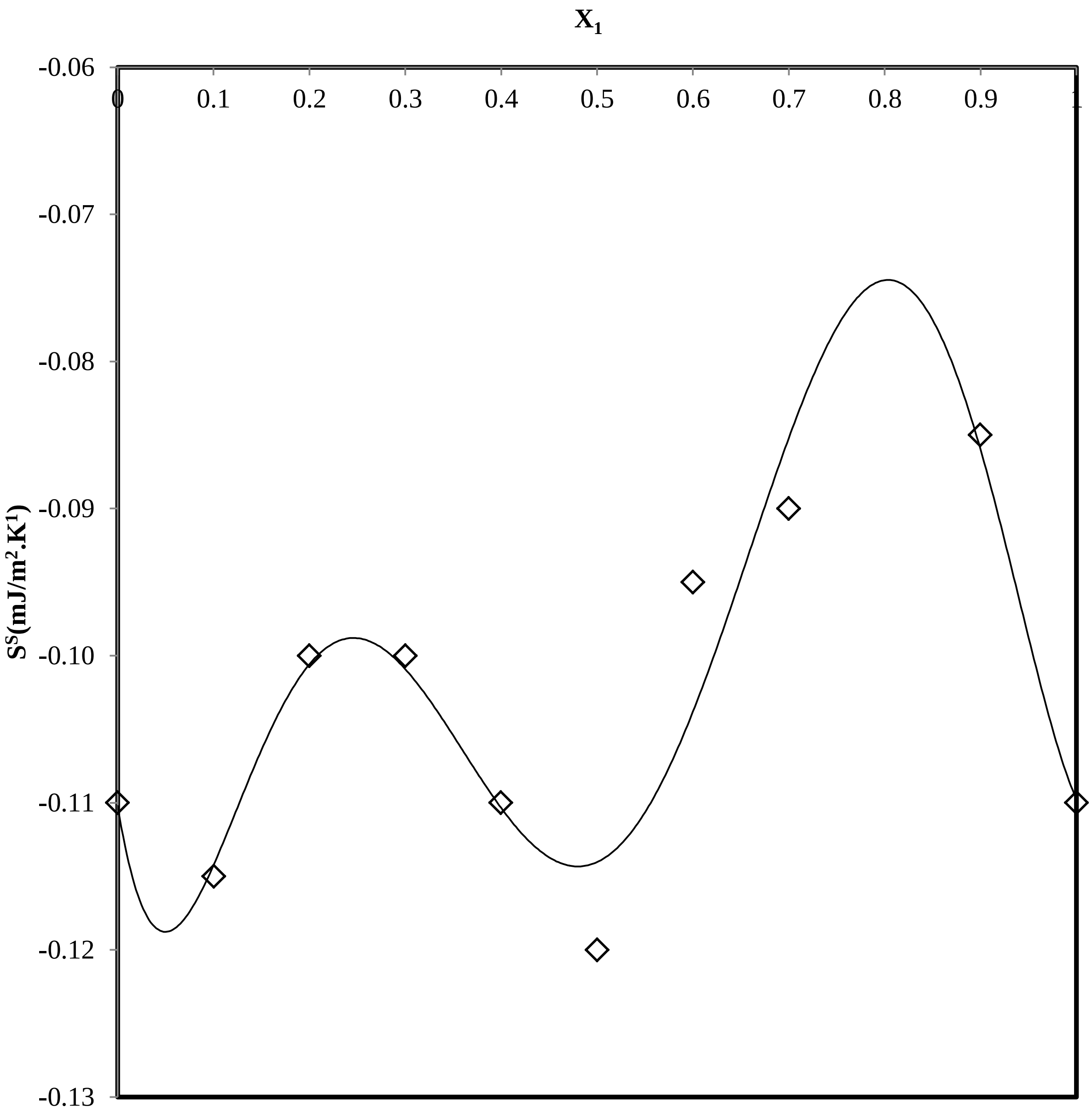

Figure 3.20 Surface entropy against mole fraction for ethyl acetate (1) and cyclohexanone (2) mixtures

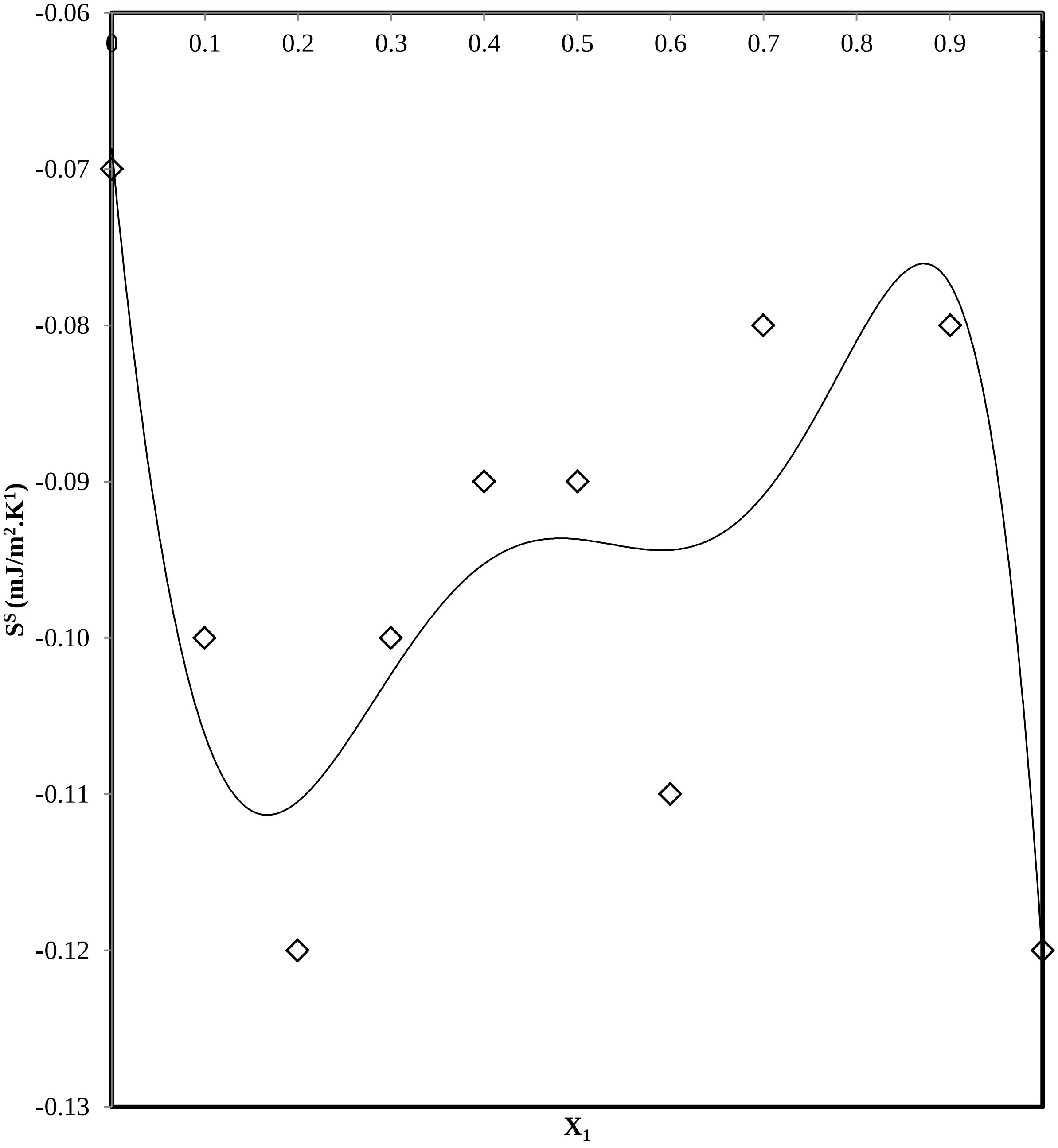

Figure 3.21 Surface entropy against mole fraction for cycloheptanone (1) and methyl acetate (2) mixtures

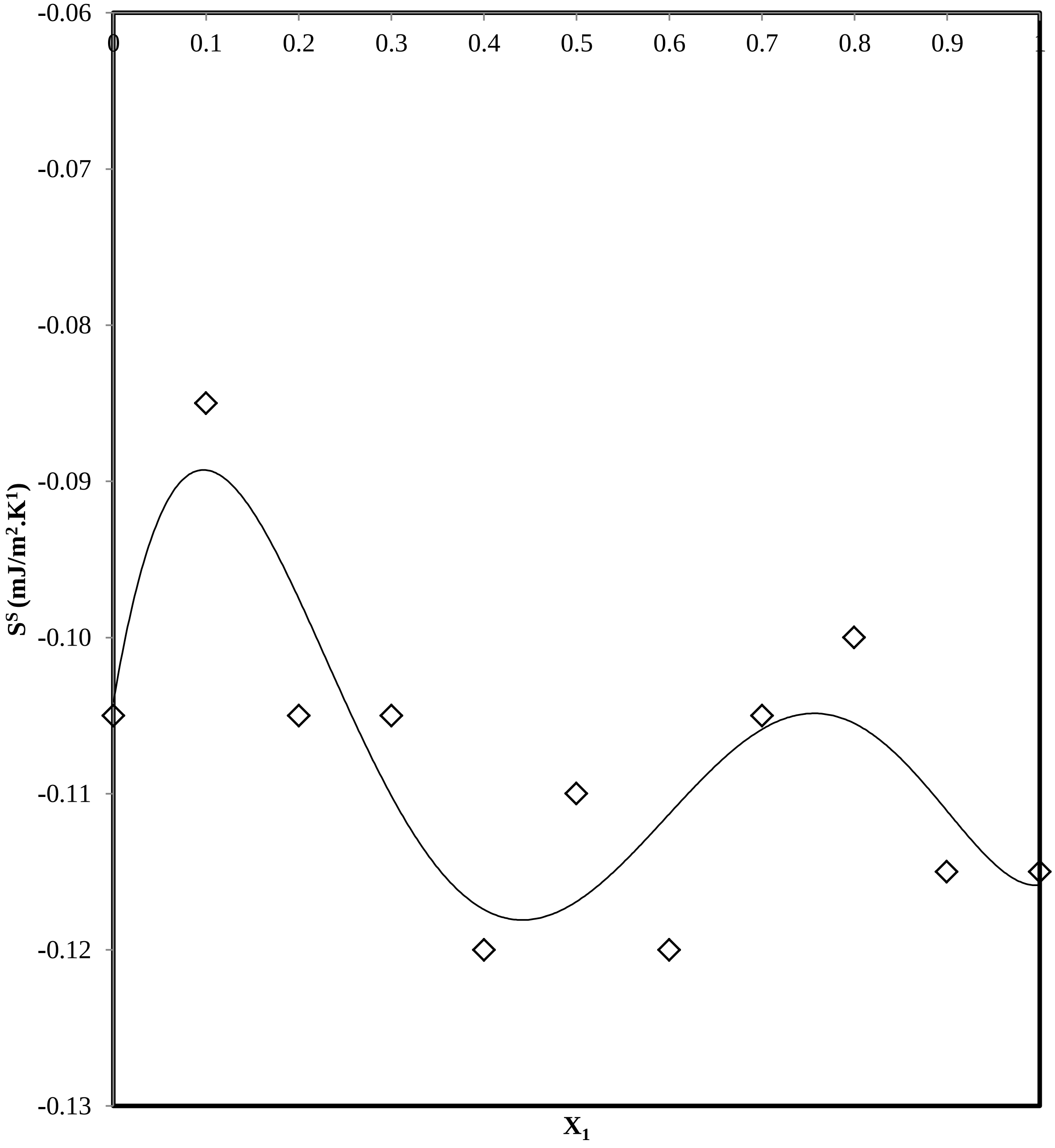

Figure 3.22 Surface entropy against mole fraction for acetone (1) and methyl acetate (2) mixtures

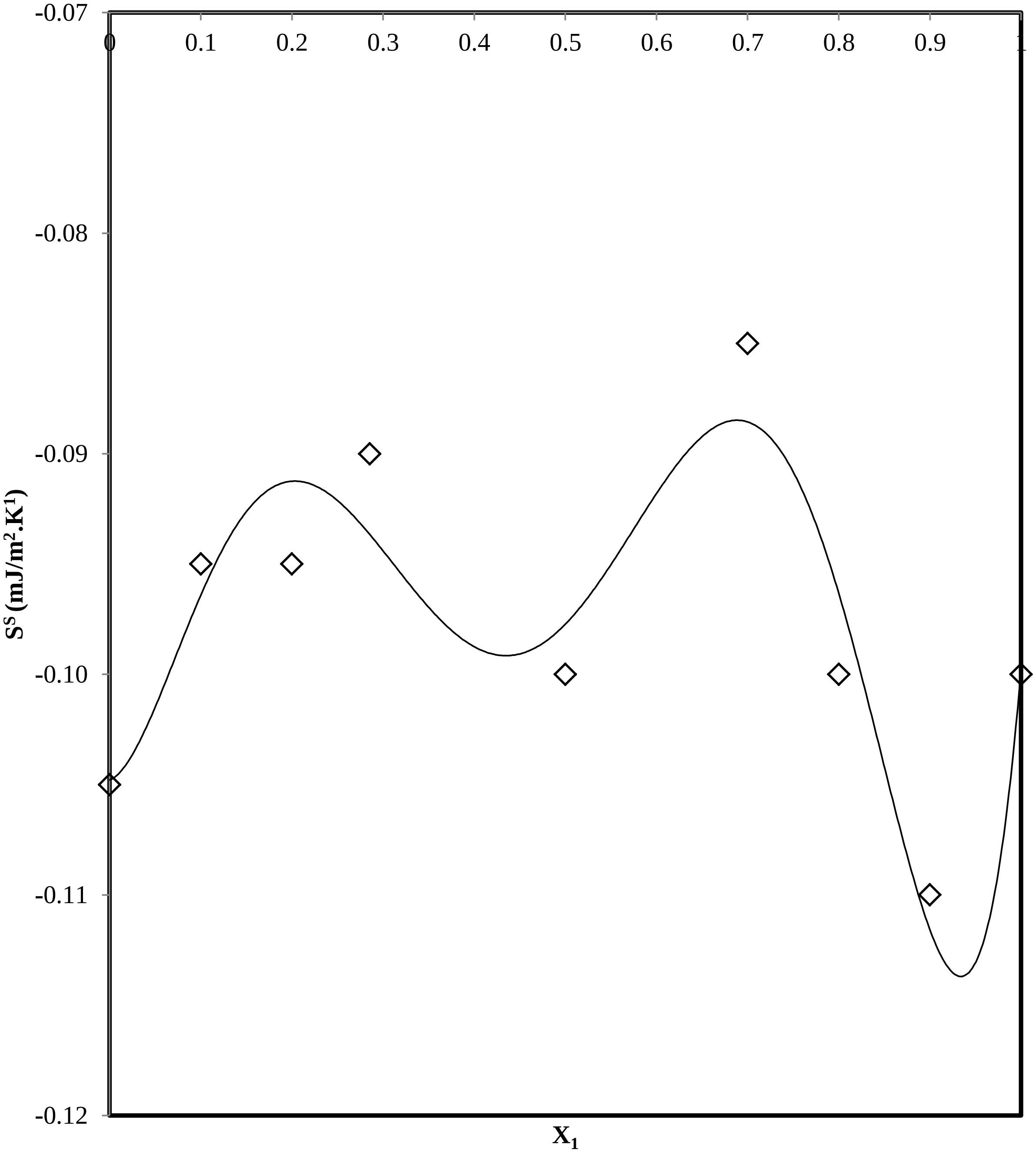

Figure 3.23 Surface entropy against mole fraction for acetophenone (1) and methyl acetate (2) mixtures

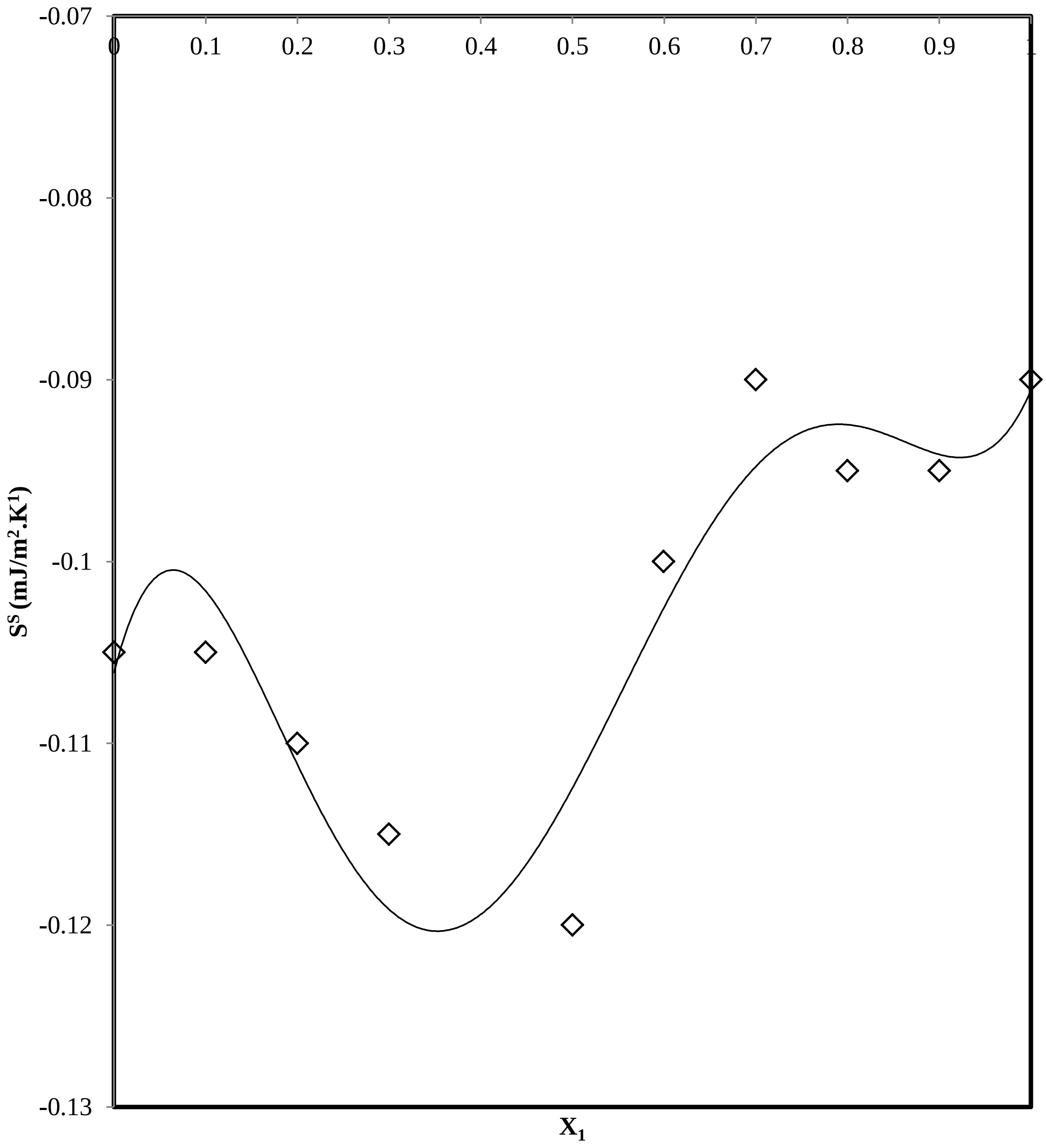

Figure 3.24 Surface entropy against mole fraction for acetophenone (1) and ethyl acetate (2) mixtures

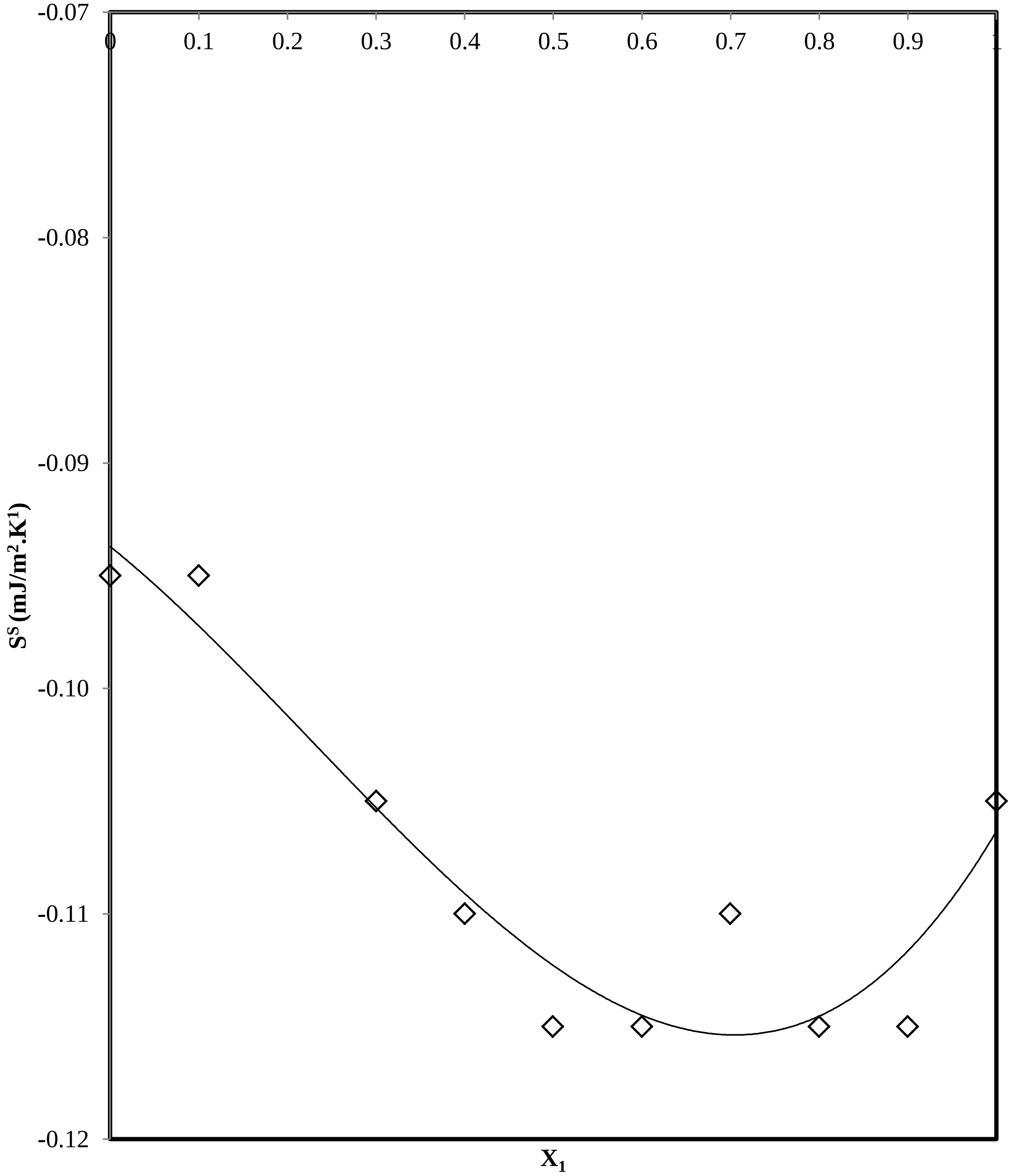

Figure 3.25 Surface entropy against mole fraction for ethyl acetate (1) and methyl acetate (2) mixtures

3.4 Excess Molar Volumes

Figure 3.26, Figure 3.27 and Figure 3.28 show the variation of the excess molar volume, (V_m^E) data as a function of x_1 for (methyl acetate + cyclohexanone), (methyl acetate + acetone) and (methyl acetate + acetophenone) systems at temperatures of 298.15, 308.15 and 318.15 K respectively. Positive values for V_m^E data were observed for the three systems. Positive V_m^E values indicate presence of dispersive intermolecular interactions due to the loosening of molecular parking in each of the binary systems, which leads to the observed volume expansion.

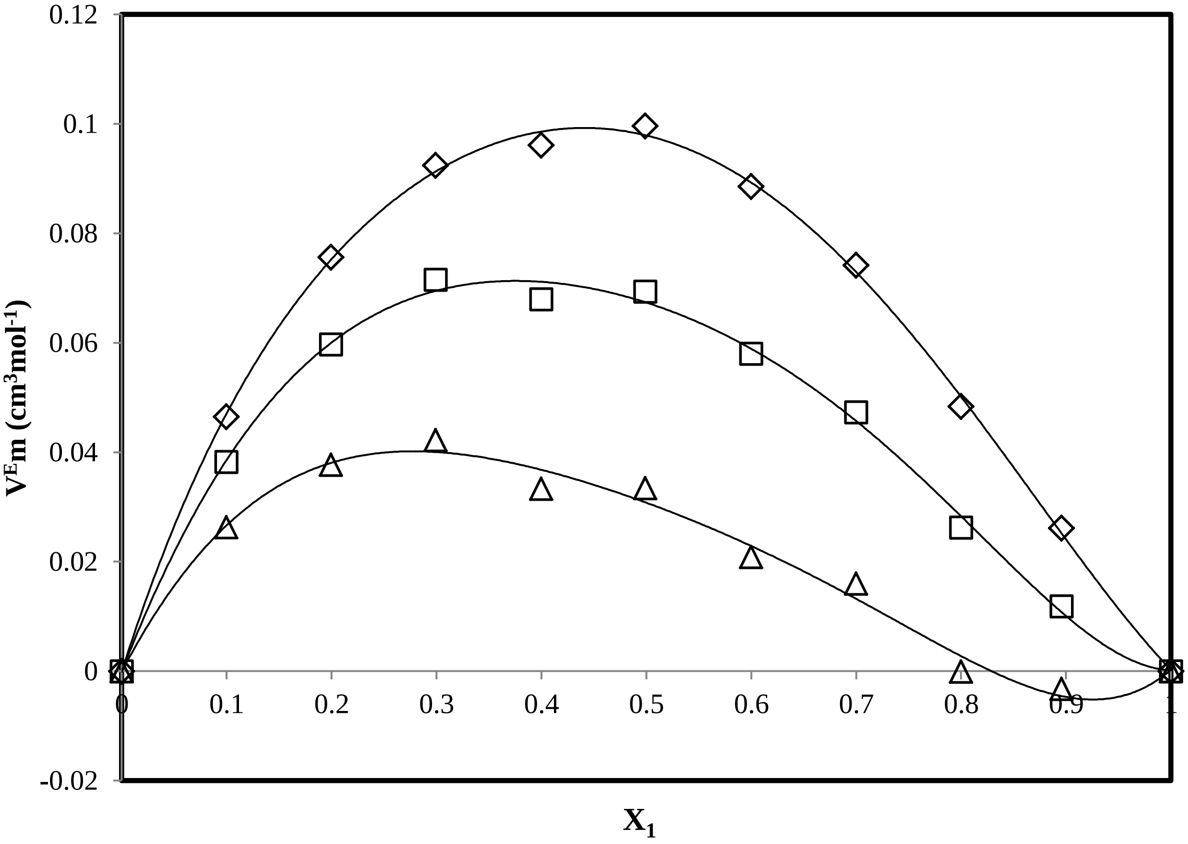

Figure 3.26 Excess molar volume against mole fraction for methyl acetate (1) and cyclohexanone (2) mixtures at various temperatures: (◇) 2980.15K, (□) 308.15K and (△) 318.15K

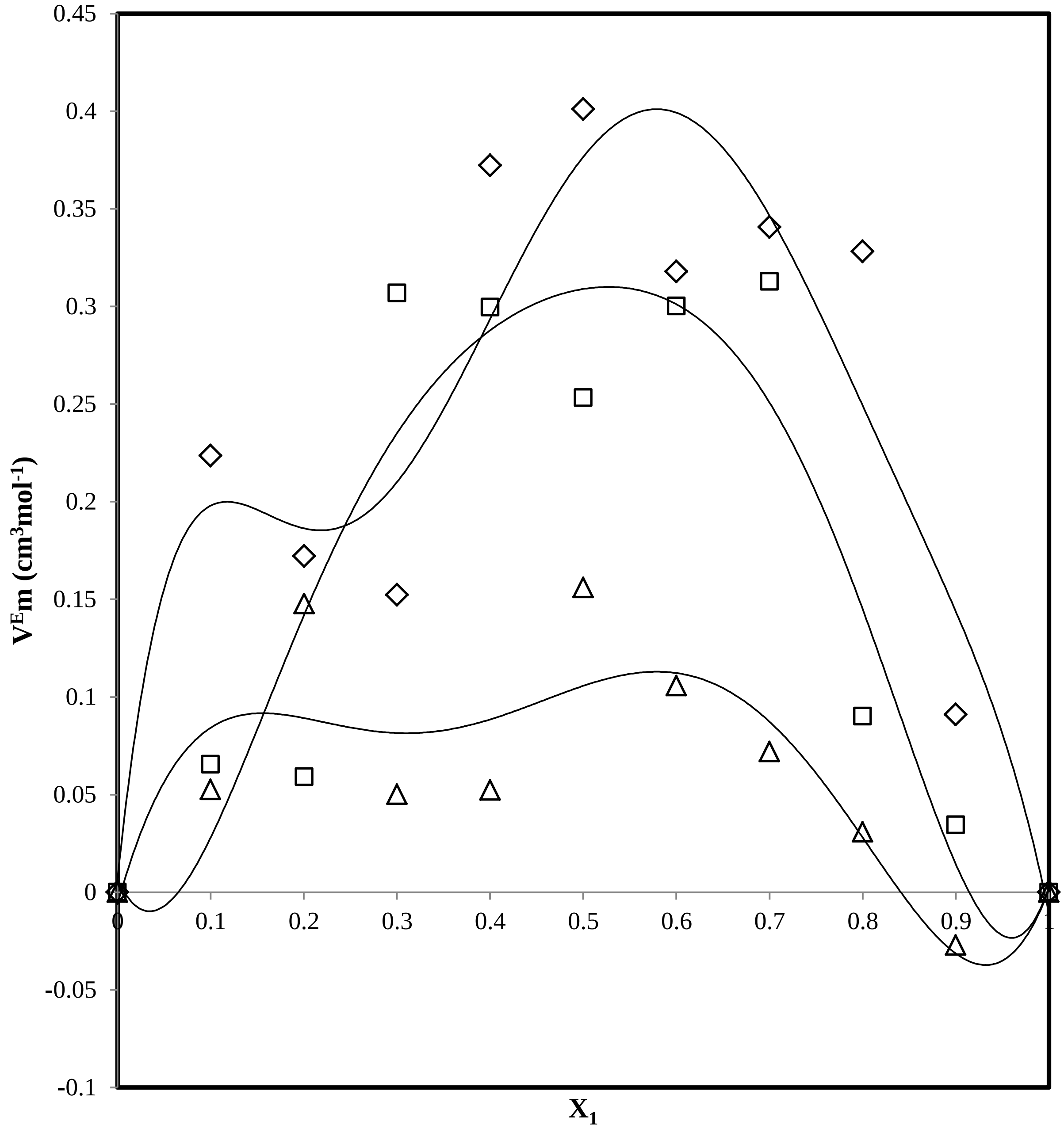

Figure 3.27 Excess molar volume against mole fraction for acetone (1) and methyl acetate (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K

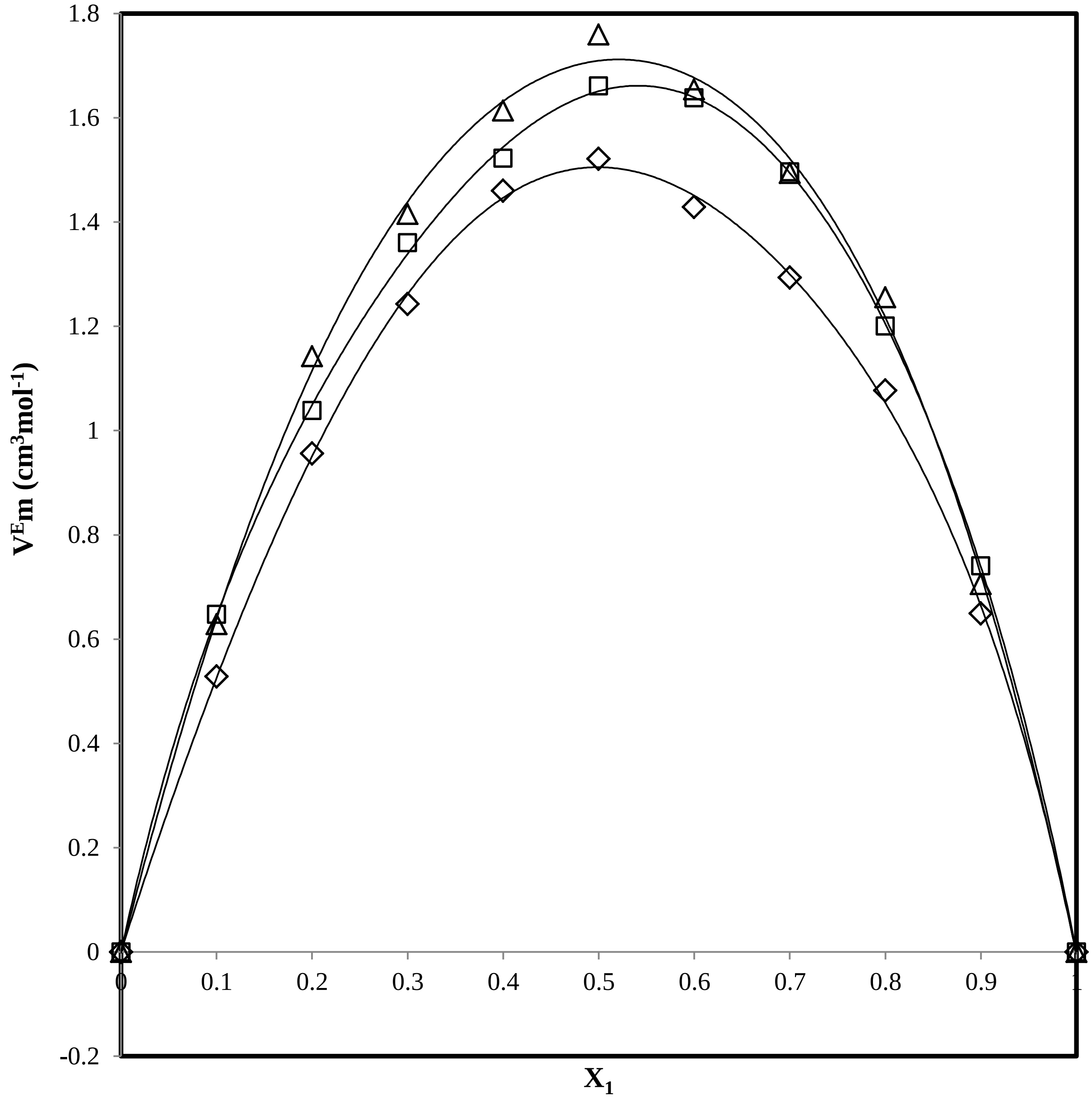

Figure 3.28 Excess molar volume against mole fraction for acetophenone (1) and methyl acetate (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K

For (ethyl acetate + cyclohexanone) binary system (Figure 3.29), the V_m^E *vs* x_1 plots showed sigmoidal behaviour, with positive deviation in the x_1 range: 0 – 0.25, 0 – 0.13, 0 – 0.05 and negative deviation in x_1 range 0.25 – 1, 0.13 – 1, 0.05 – 1 at temperatures of 298, 308 and 318K respectively.

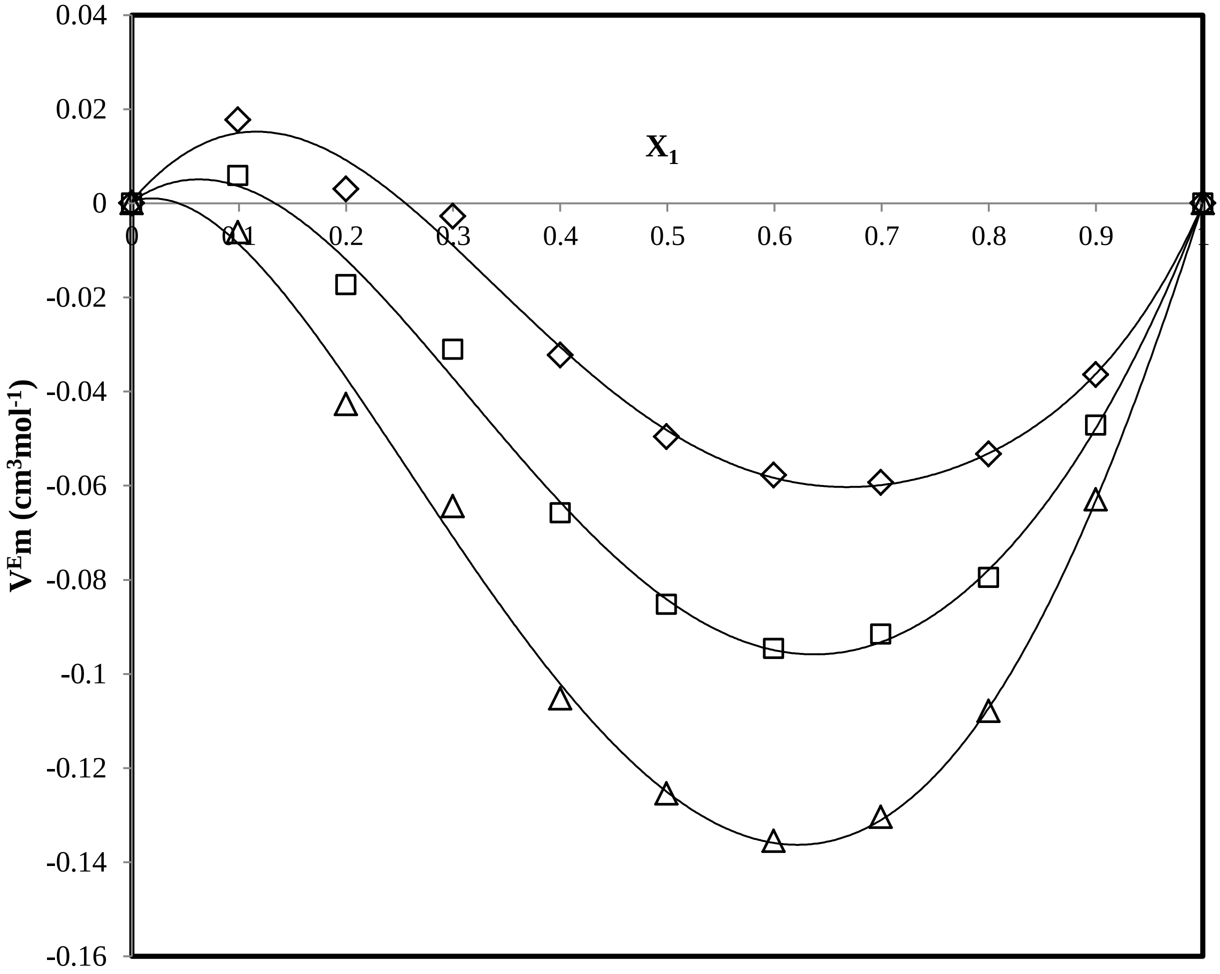

Figure 3.29 Excess molar volume against mole fraction for ethyl acetate (1) and cyclohexanone (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K

The V_m^E *vs* x_1 data for (cycloheptanone + methyl acetate), (acetophenone + ethyl acetate) and (ethyl acetate + methyl acetate) binary systems (Figure 3.30, Figure 3.31 and Figure 3.32) show negative deviations at the three temperatures investigated. Since for each of the three binary mixtures, weak van der Waals intermolecular interactions exist between the molecules, negative excess molar volume values observed for arise mainly from unlike component free volume differences, which is a measure of the geometrical interstitial accommodation.

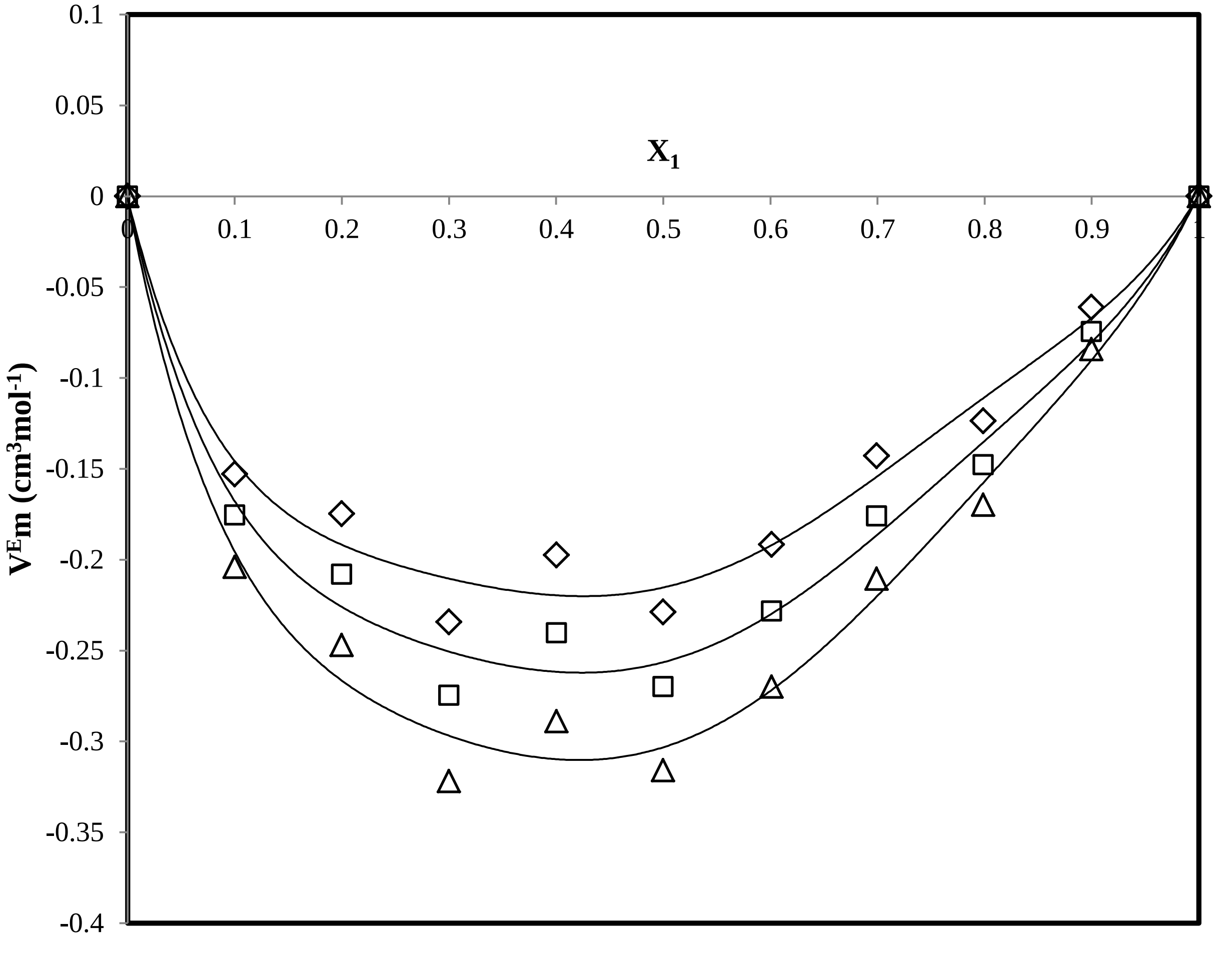

Figure 3.30 Excess molar volume against mole fraction for cycloheptanone (1) and methyl acetate (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K

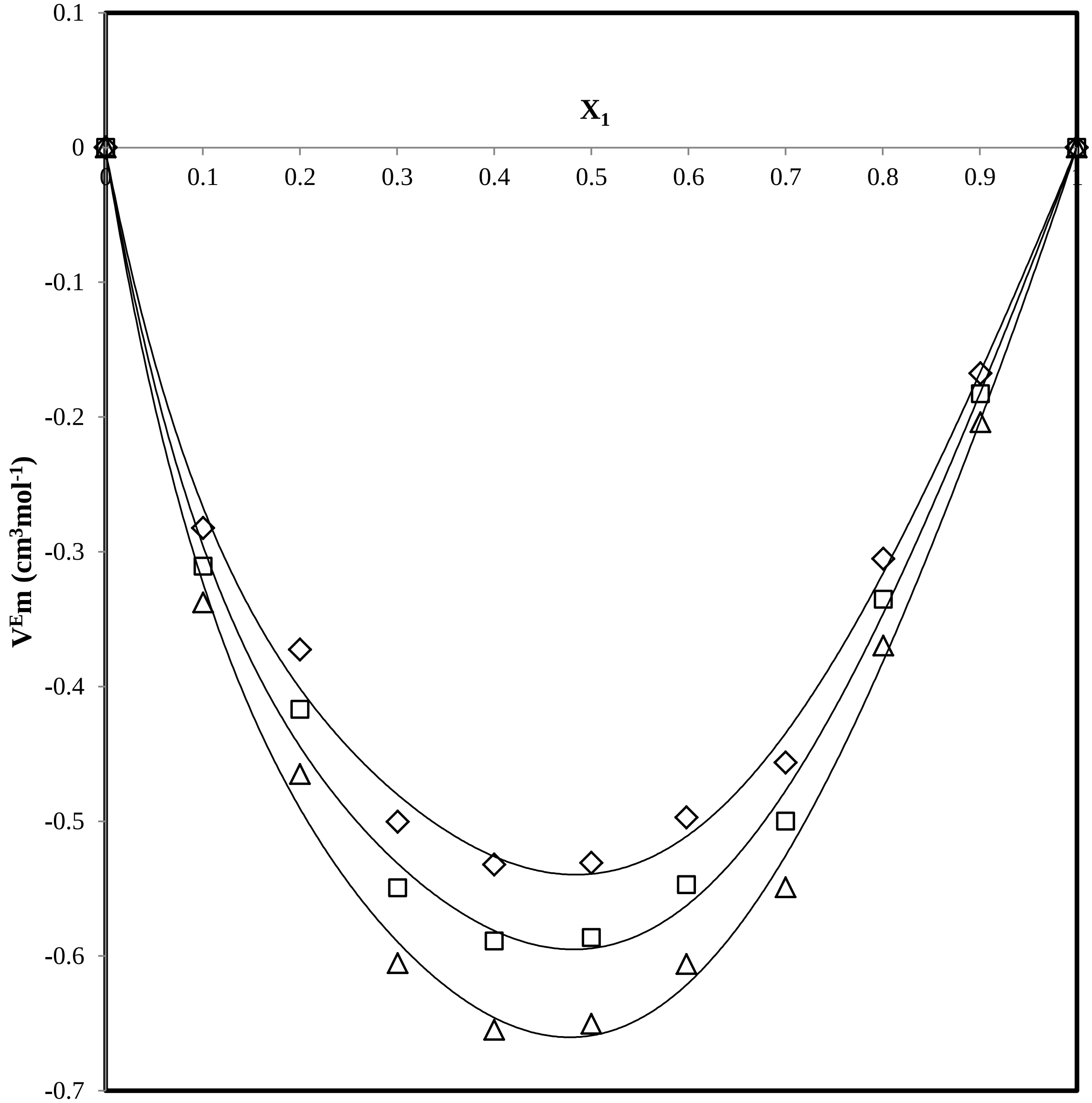

Figure 3.31 Excess molar volume against mole fraction for acetophenone (1) and ethyl acetate (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K

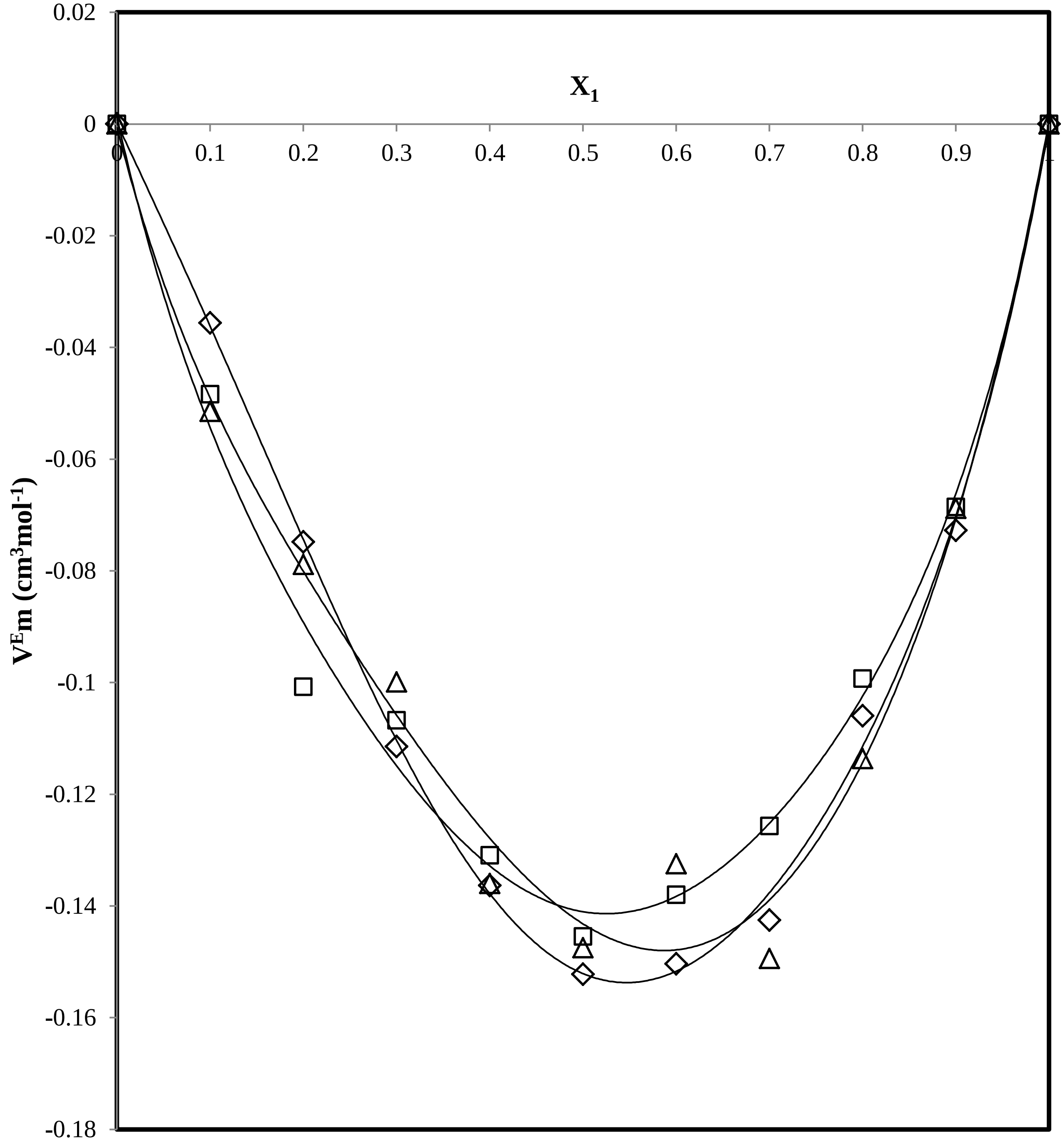

Figure 3.32 Excess molar volume against mole fraction for ethyl acetate (1) and methyl acetate (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K

The temperature dependence of V_m^E in general provides understanding of the structural behavior between molecules of the two components of each binary mixture. Figure 3.26, Figure 3.27, Figure 3.29, Figure 3.30, Figure 3.31 and Figure 3.32 show that for each binary mixture the algebraic value of V_m^E over the entire x_1 range decreases (become more negative) with increase in temperature. In general the increase in temperature would promote increased molecular motion which would lead to a decrease in the intermolecular interactions which would decrease close molecular packing and an increase in algebraic excess molar volume values. The observed volume contraction suggest that the expansion in the volume of the system caused by an increase in temperature, results in a more favourable geometrical interstitial accommodation of molecules of each component into the expanded free volume of the liquid structures. For (acetophenone + methyl acetate) binary system Figure 3.28, increase in temperature resulted in increase in the absolute value V_m^E due to the predominance of dispersive interactions and Brownian motion over geometrical effects.

3.5 Density and Prediction of Surface tension

The density decreased linearly with increase in concentration of the acetates in all the systems with acetates and ketones, at all temperatures studied. This can be seen in Figure 3.33 - Figure 3.39.

3.5.1 Fitted density plots

The experimental values of density for each system were fitted to the following polynomial expression.

$$\rho = \sum_{k=0}^{n} B_k {x_1}^k$$

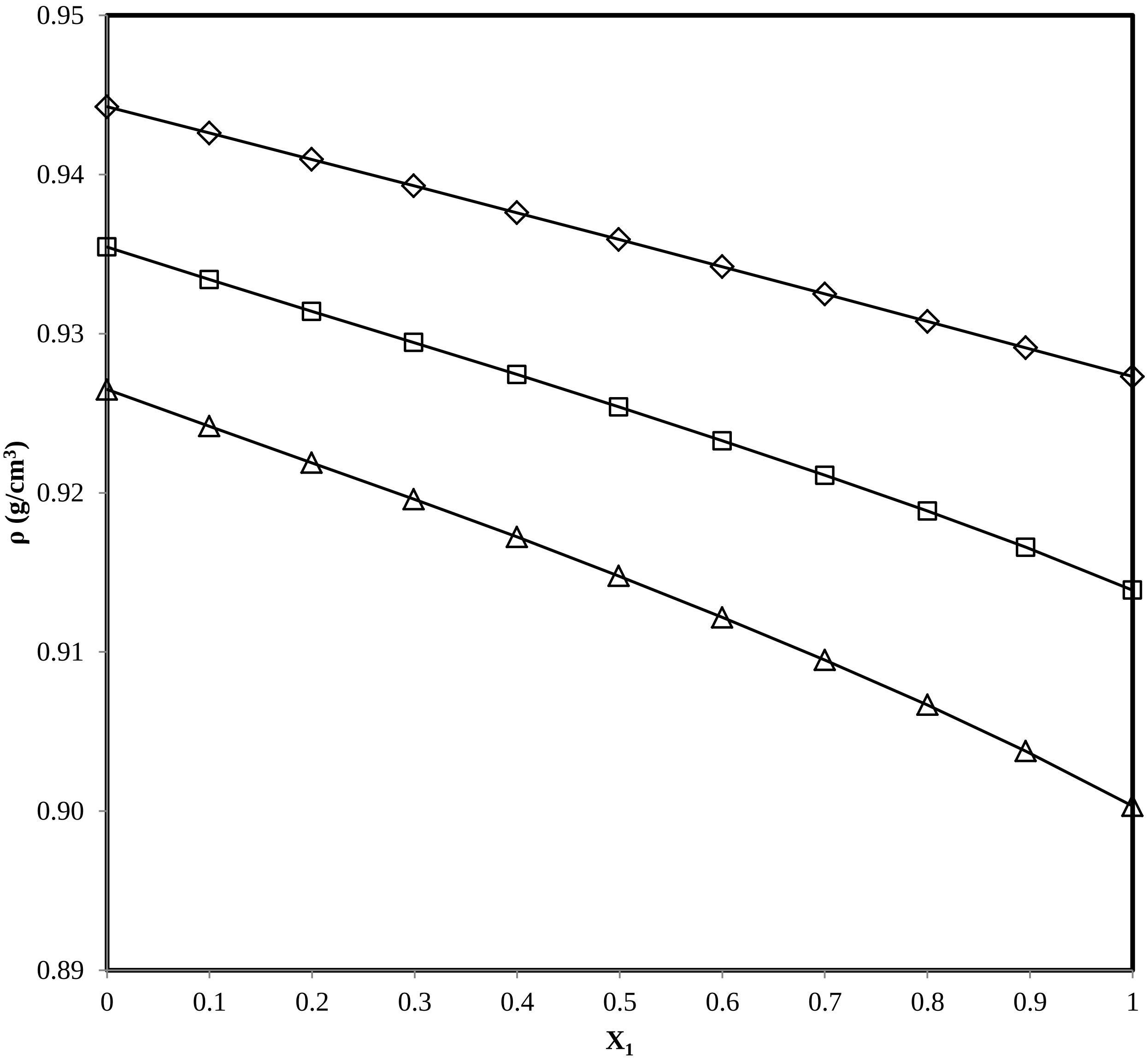

Figure 3.33 Density against mole fraction for the methyl acetate (1) and cyclohexanone (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K.

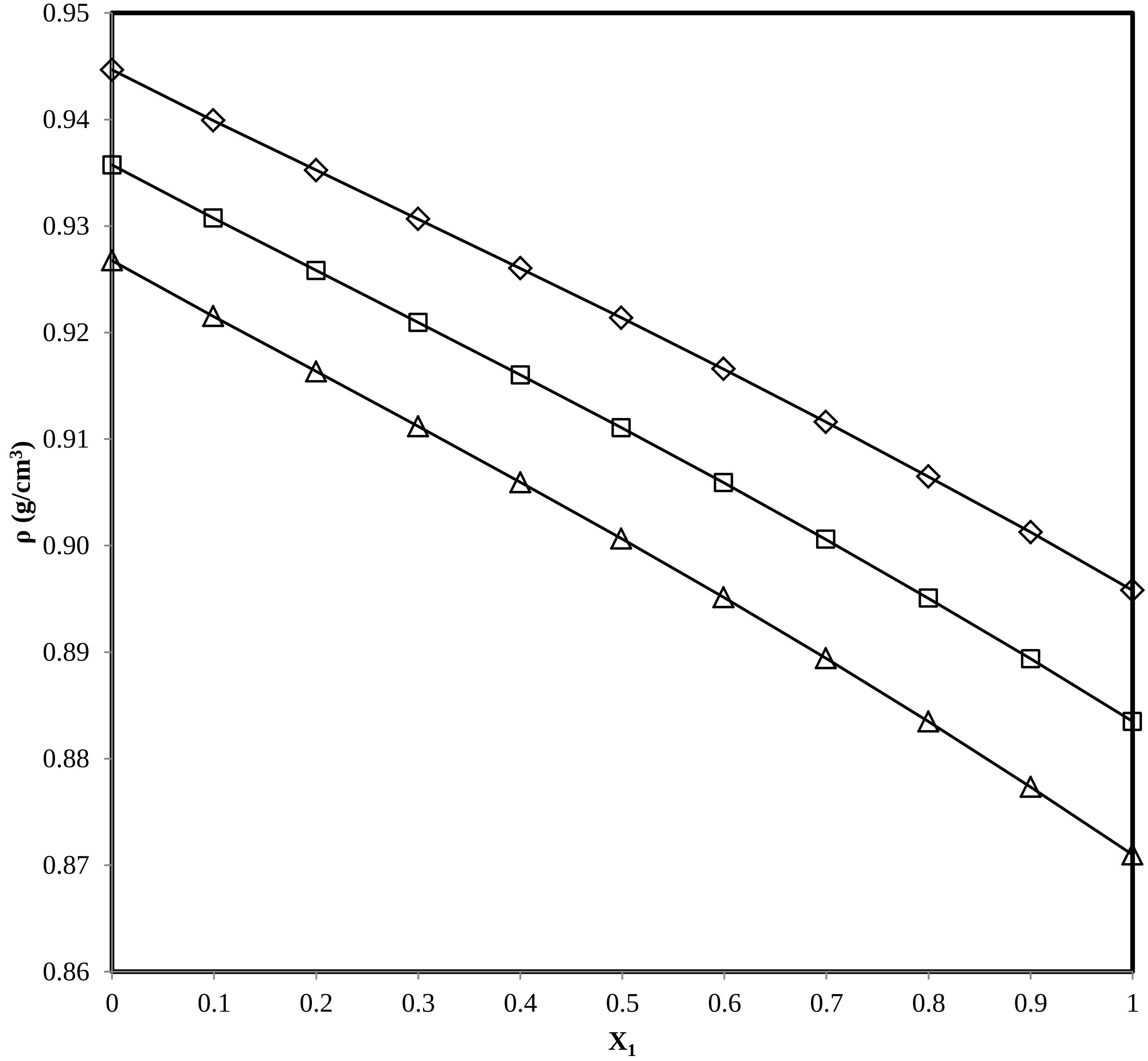

Figure 3.34 Density against mole fraction for the ethyl acetate (1) and cyclohexanone (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K.

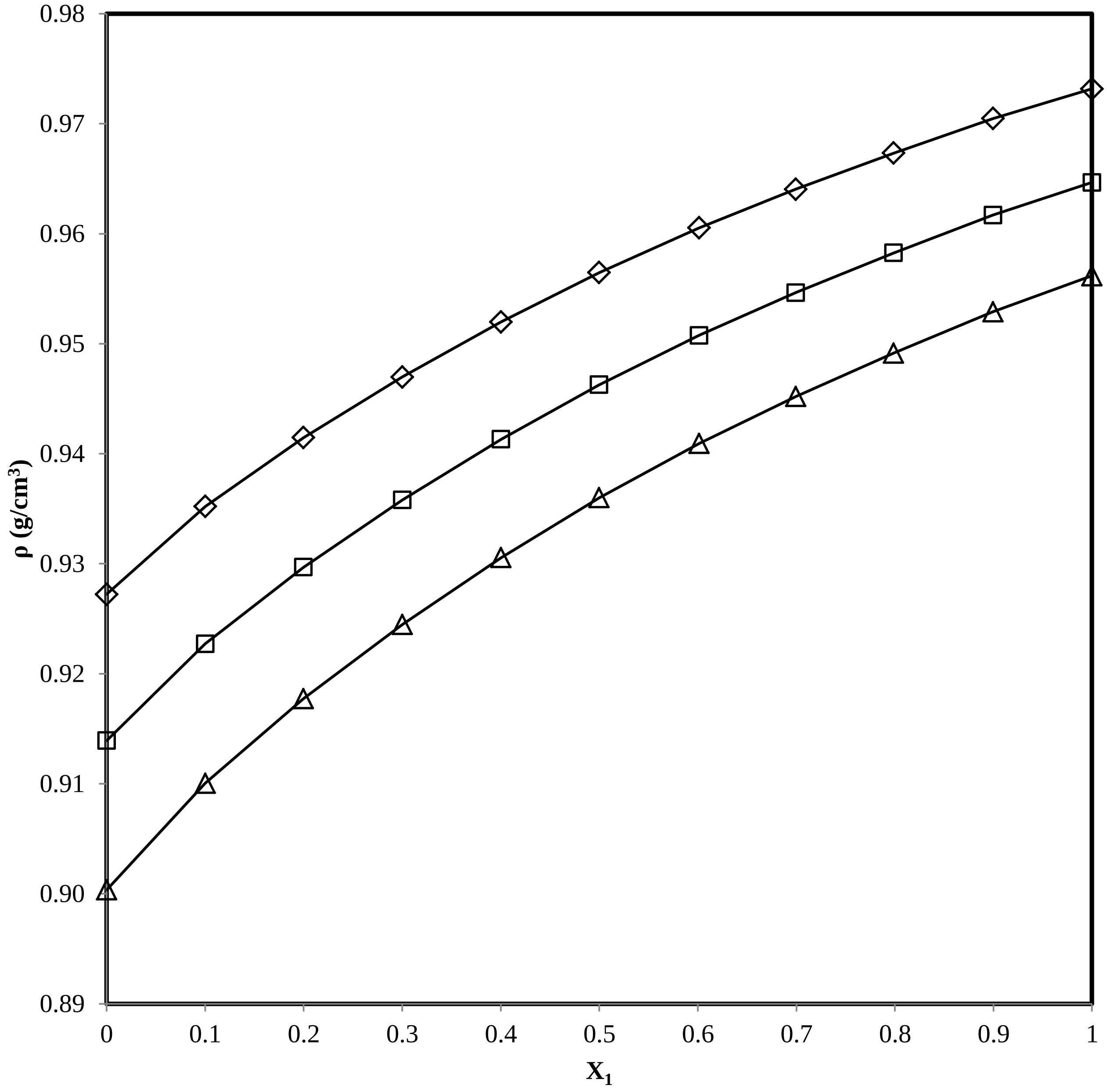

Figure 3.35 Density against mole fraction for the cycloheptanone (1) and methyl acetate (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K.

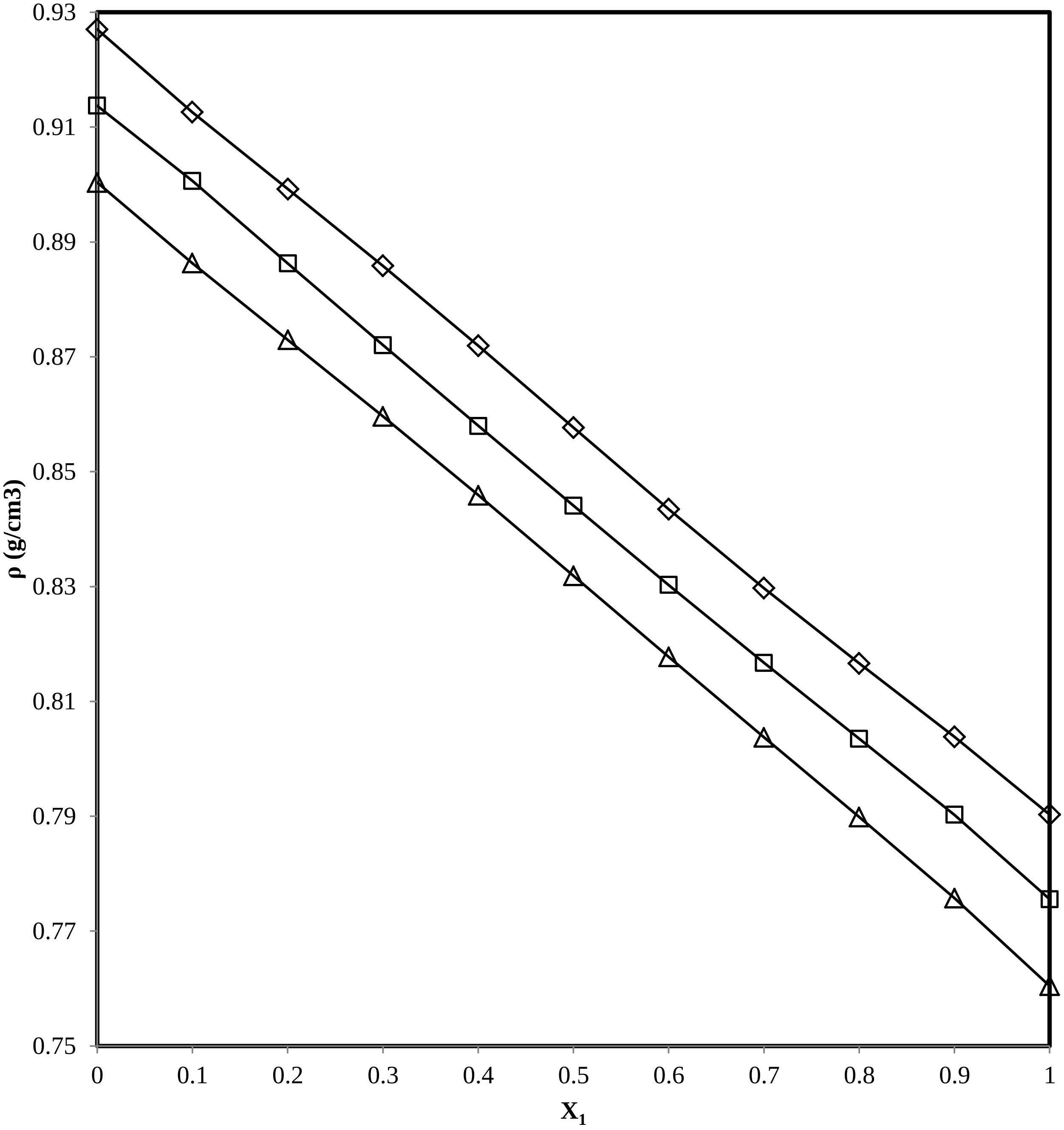

Figure 3.36 Density against mole fraction for the acetone (1) and methyl acetate (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K.

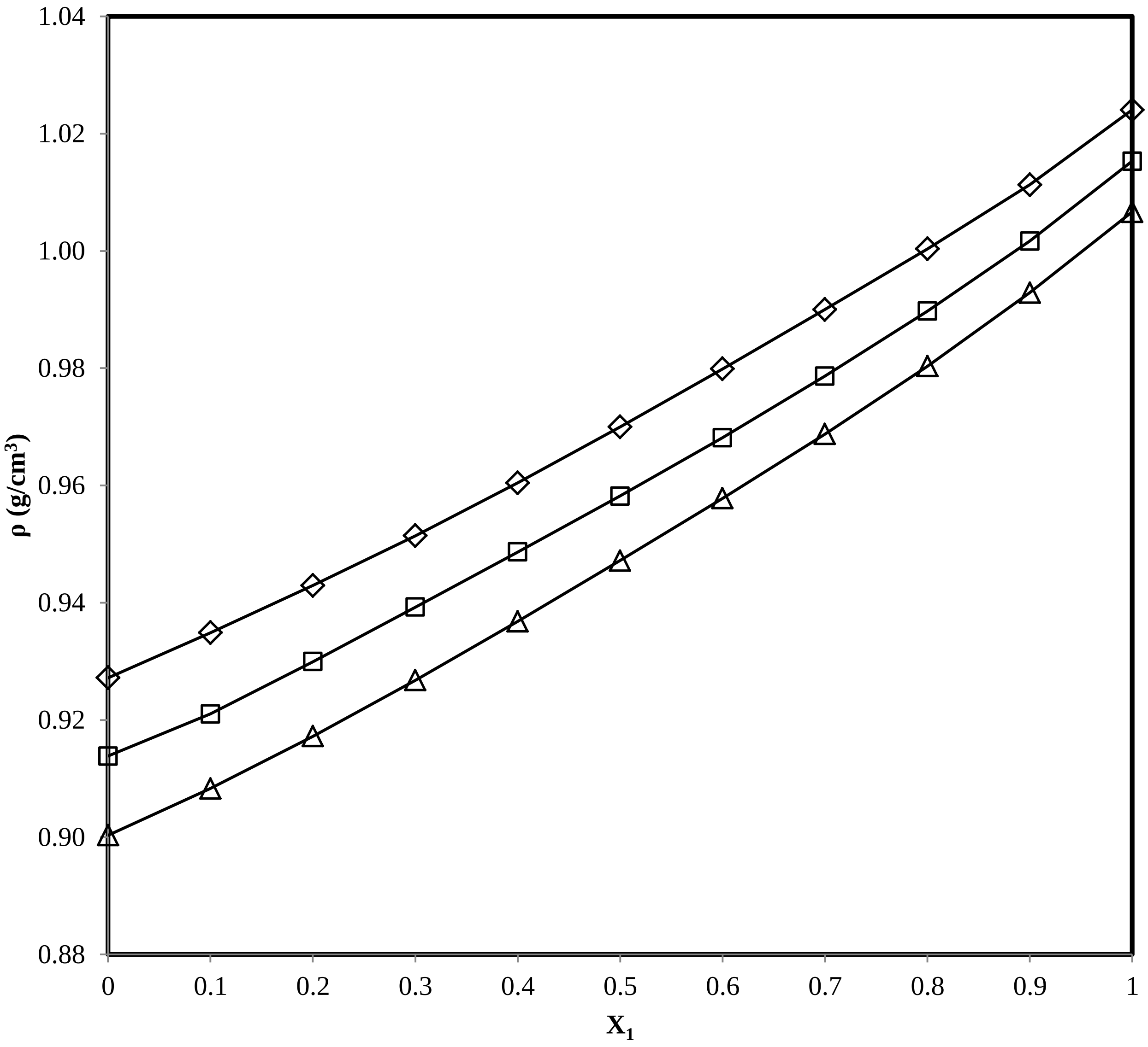

Figure 3.37 Density against mole fraction for the acetophenone (1) and methyl acetate (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K.

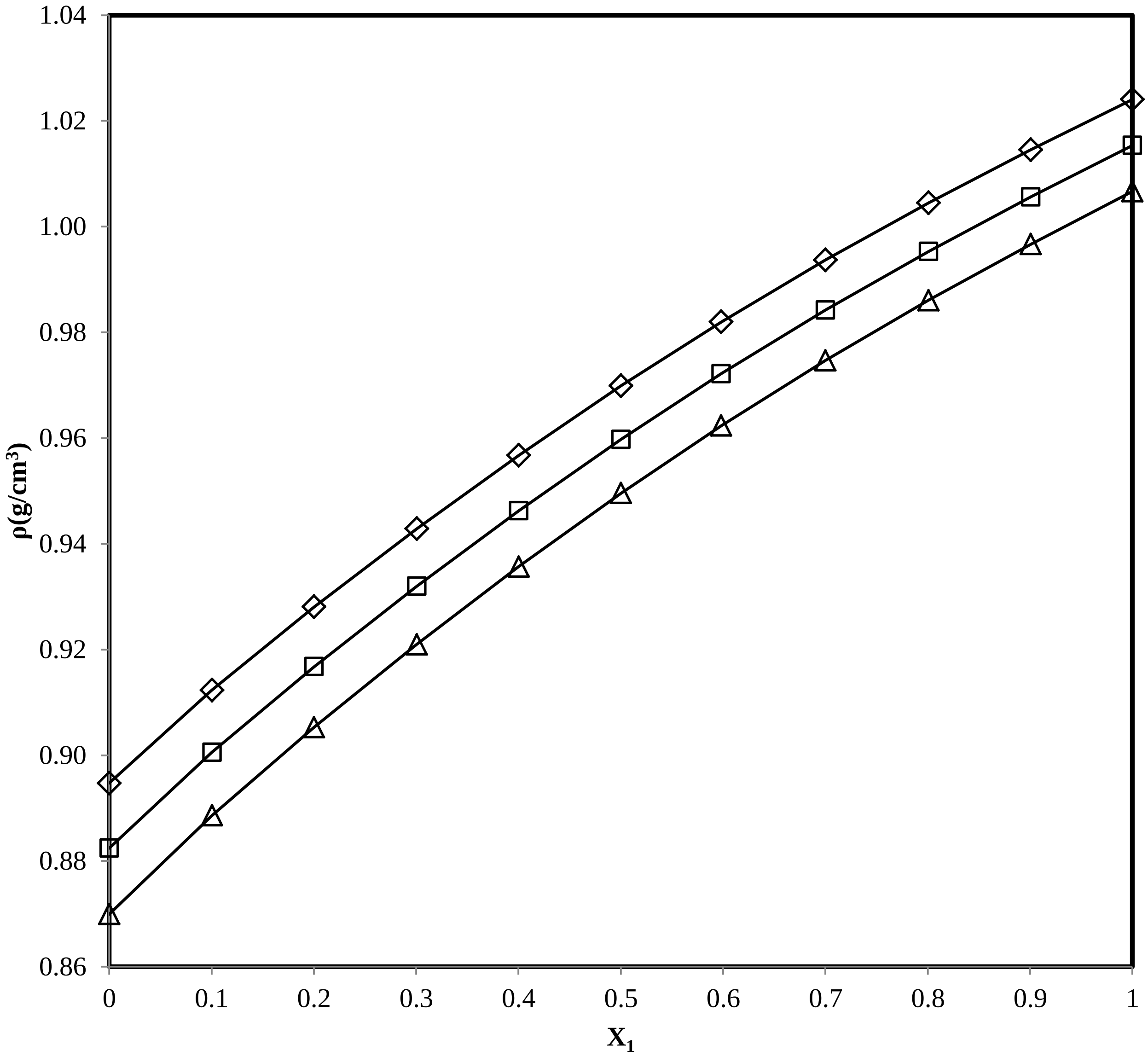

Figure 3.38 Density against mole fraction for the acetophenone (1) and ethyl acetate (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K

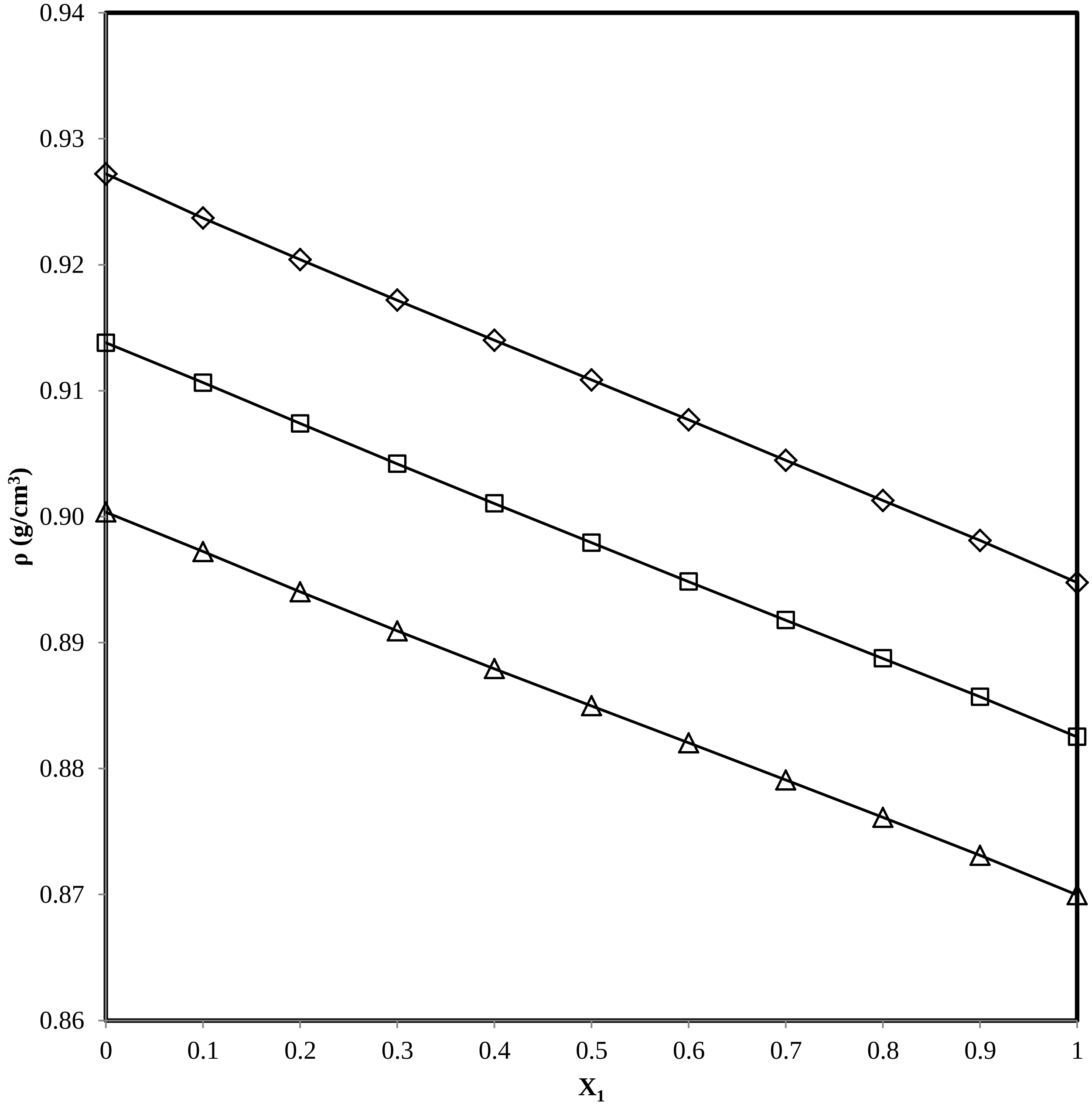

Figure 3.39 Density against mole fraction for the ethyl acetate (1) and methyl acetate (2) mixtures at various temperatures: (◇) 298.15K, (□) 308.15K and (△) 318.15K

3.5.2 Comparison of experimental and calculated Surface Tension

The value of the Parachor for a pure sample was calculated by using the Sudgen's equation below, to be used in the prediction of the surface tensions of mixtures.

$$[P] = \gamma^{\frac{1}{4}} \frac{M}{\rho}$$

Where; [P] is the parachor-characteristic of any liquid substance, γ is the surface tension of a pure substance, M is the molar mass and ρ is the density of the pure substance. The values of surface tension and density used in these calculations were taken from literature sources shown in Table 3.4.

Table 3.4 Calculated and expected values of the Parachor for the substances used in the study calculated using the literature values of surface tension and density

Substance	**Calculated [P]**	**Expected [P]**	**Literature Surface Tension (mN/m) at 298.15K**	**Literature Density (g/cm^3) at 298.15K**
Methyl acetate	178.3	180.2[66]	24.79[35], 24.7[51], 24.54[52]	0.9273[53], 0.9244[54], 0.932[55]
Ethyl acetate	217.8	216.8[67]	23.93[35], 23.2[51], 23.24[52]	0.89468[53], 0.902[56]
Acetophenone	294.1	293.8[67]	39.0[51], 38.95[52]	1.02081[53], 1.03[57], 1.033[58]
Acetone	160.9	161.5[67]	23.0[51], 23.04[52], 23.1[59]	0.79032[31], 0.791[60], 0.78458[61]
Cyclohexanone	251.2	252.2[67]	34.4[51], 34.37[52]	0.94644[31], 0.9421[62]
Cycloheptanone	286.99	288.0[67]	34.05[52]	0.951[63][64]

The surface tension of mixtures was calculated from the following equation;

$$\gamma = \left\{[P_1]\frac{x_1}{M_1} + [P_2]\frac{1 - x_1}{M_2}\right\}^4 \rho^4$$

Where; ρ is the density of the mixture.

The mean relative standard deviations were calculated as follows to compare the experimental and predicted surface tension values.

$$MRSD = 100 * \left[\frac{1}{N}\sum_i \left(\frac{\gamma_{i,exp} - \gamma_{i,cal}}{\gamma_{i,exp}}\right)^2\right]^{\frac{1}{2}} \qquad (10)$$

Where; $\gamma_{i,exp}$ is the experimental surface tension, $\gamma_{i,cal}$ is the calculated surface tension of the *i*th mole fraction. *N* is the number of experimental values.

The experimental and predicted surface tension values have good agreement in terms of the trend of surface tension with change in mole fraction (see Figure 3.40 - Figure 3.44 and Figure 3.46) except for the (acetophenone-ethyl acetate) system (see Figure 3.45). As the temperature is increased for most of the systems, it is observed that the predicted and experimental values diverge and the mean relative standard deviations are above 5%. This may be because the assumption made here about parachor being temperature-independent is not strictly valid [68].

Methyl acetate + cyclohexanone system

Temp (K)	MRSD (%)
298.15	2.4
308.15	2.8
318.15	5.5

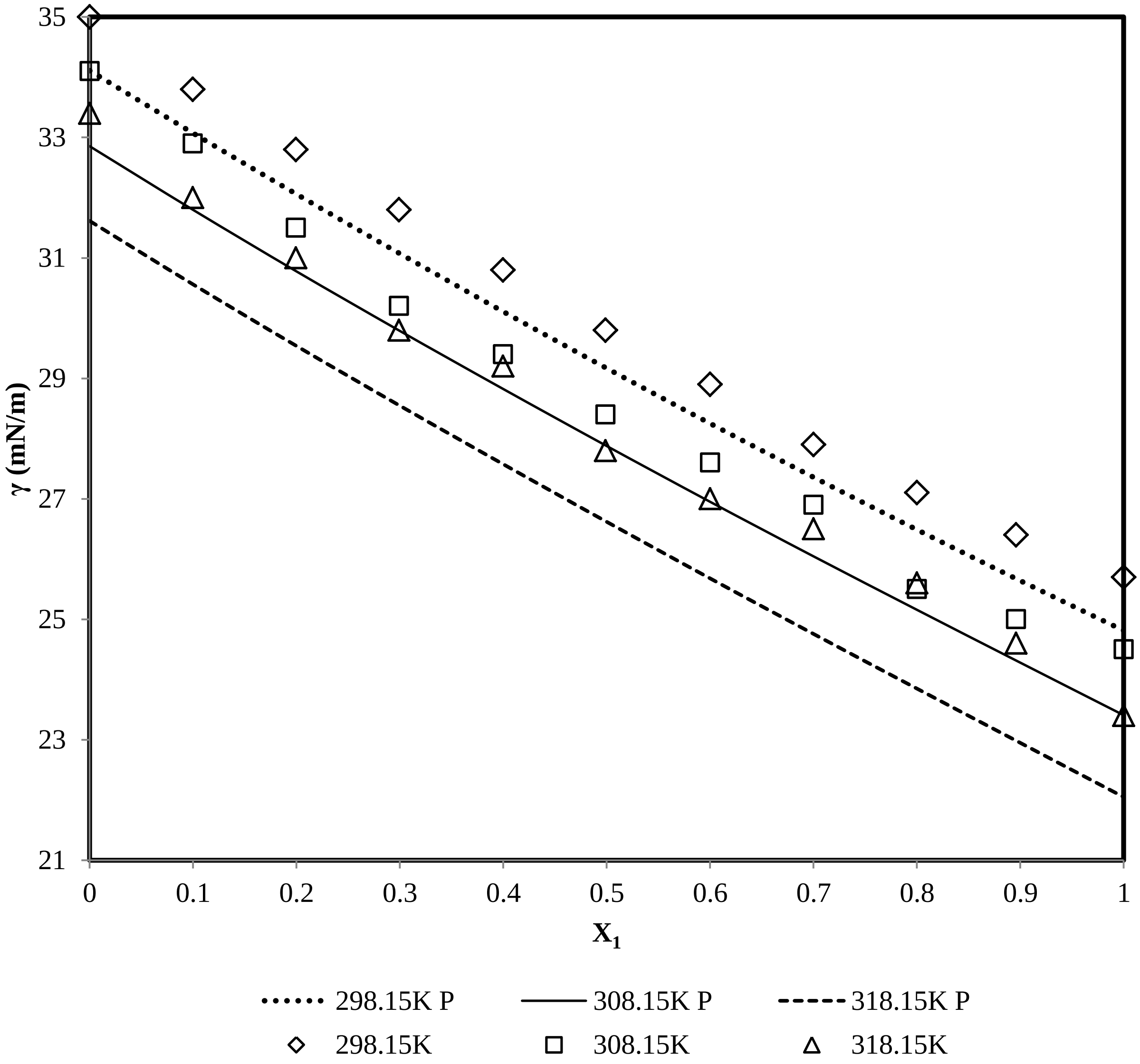

Figure 3.40 The predicted and experimental surface tension against mole fraction for methyl acetate (1) and cyclohexanone (2) mixtures at various temperatures. The smooth lines are predicted and the points are experimental

Ethyl acetate + cyclohexanone system

Temp (K)	**MRSD (%)**
298.15	1.2
308.15	1.0
318.15	2.3

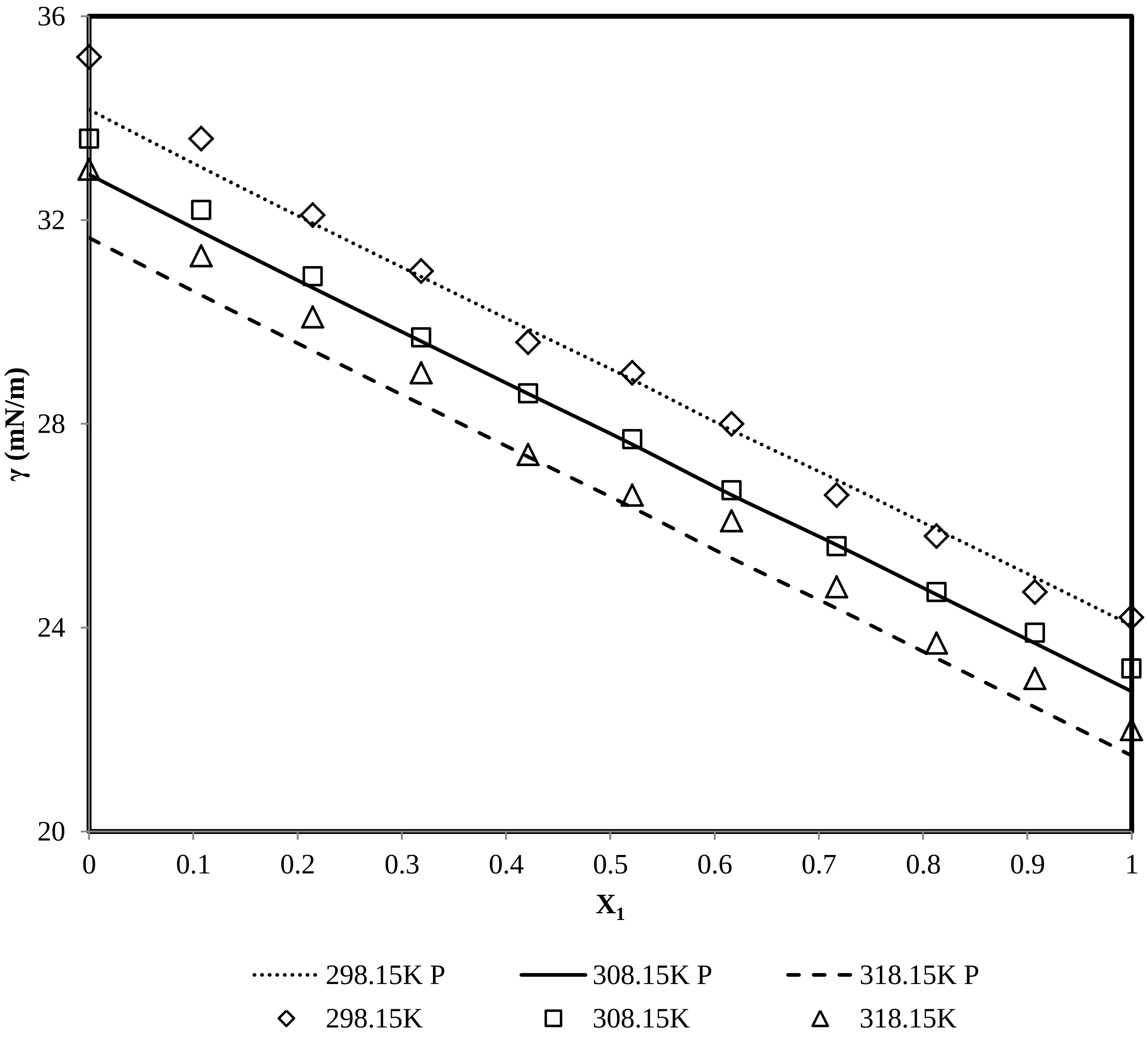

Figure 3.41 The predicted and experimental surface tension against mole fraction for ethyl acetate (1) and cyclohexanone (2) mixtures at various temperatures. The smooth lines are predicted and the points are experimental

Cycloheptanone + methyl acetate system

Temp (K)	MRSD (%)
298.15	4.5
308.15	4.1
318.15	3.8

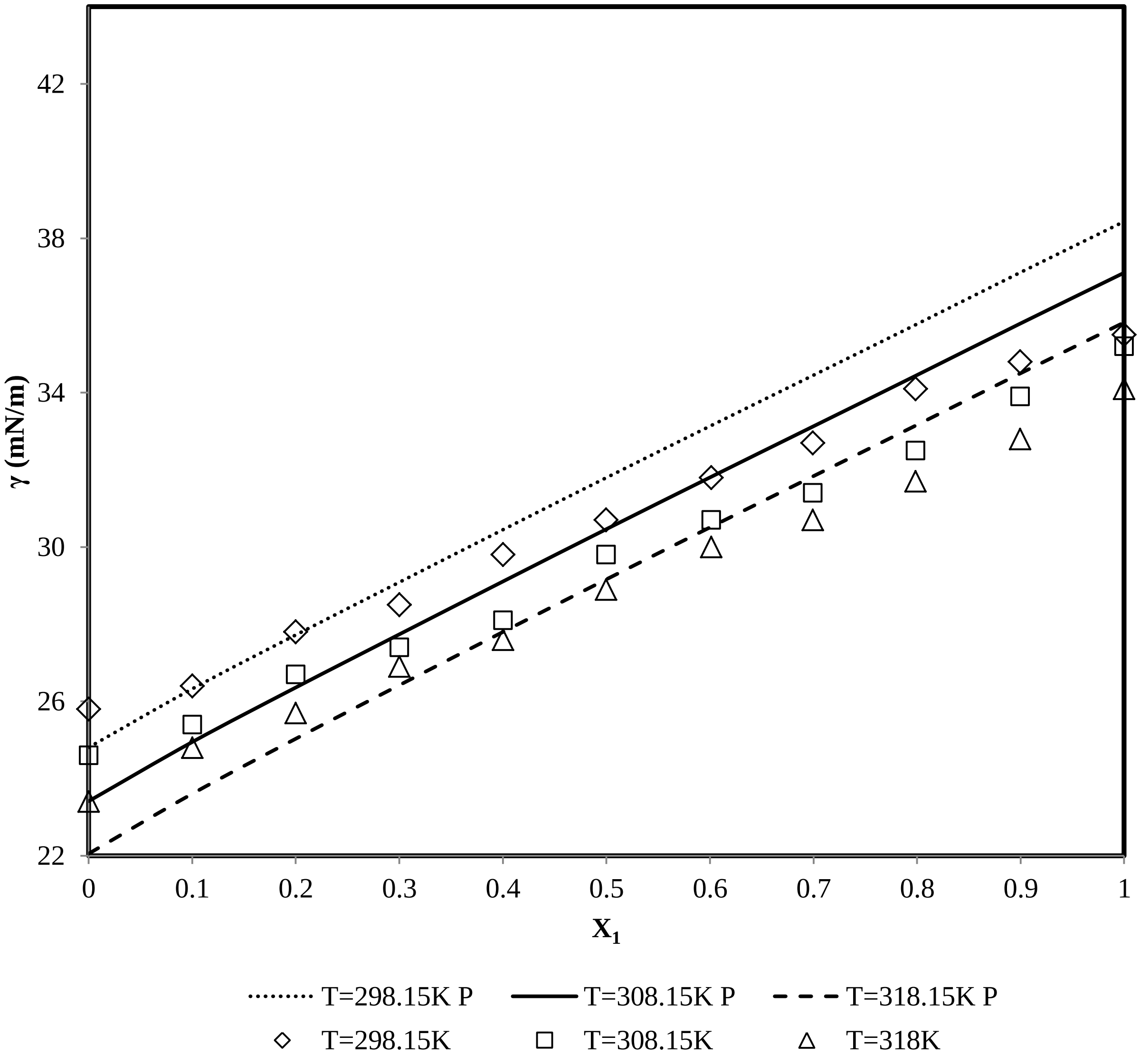

Figure 3.42 The predicted and experimental surface tension against mole fraction for cycloheptanone (1) and methyl acetate (2) mixtures at various temperatures. The smooth lines are predicted and the points are experimental

Acetone + methyl acetate system

Temp (K)	MRSD (%)
298.15	3.6
308.15	5.5
318.15	6.8

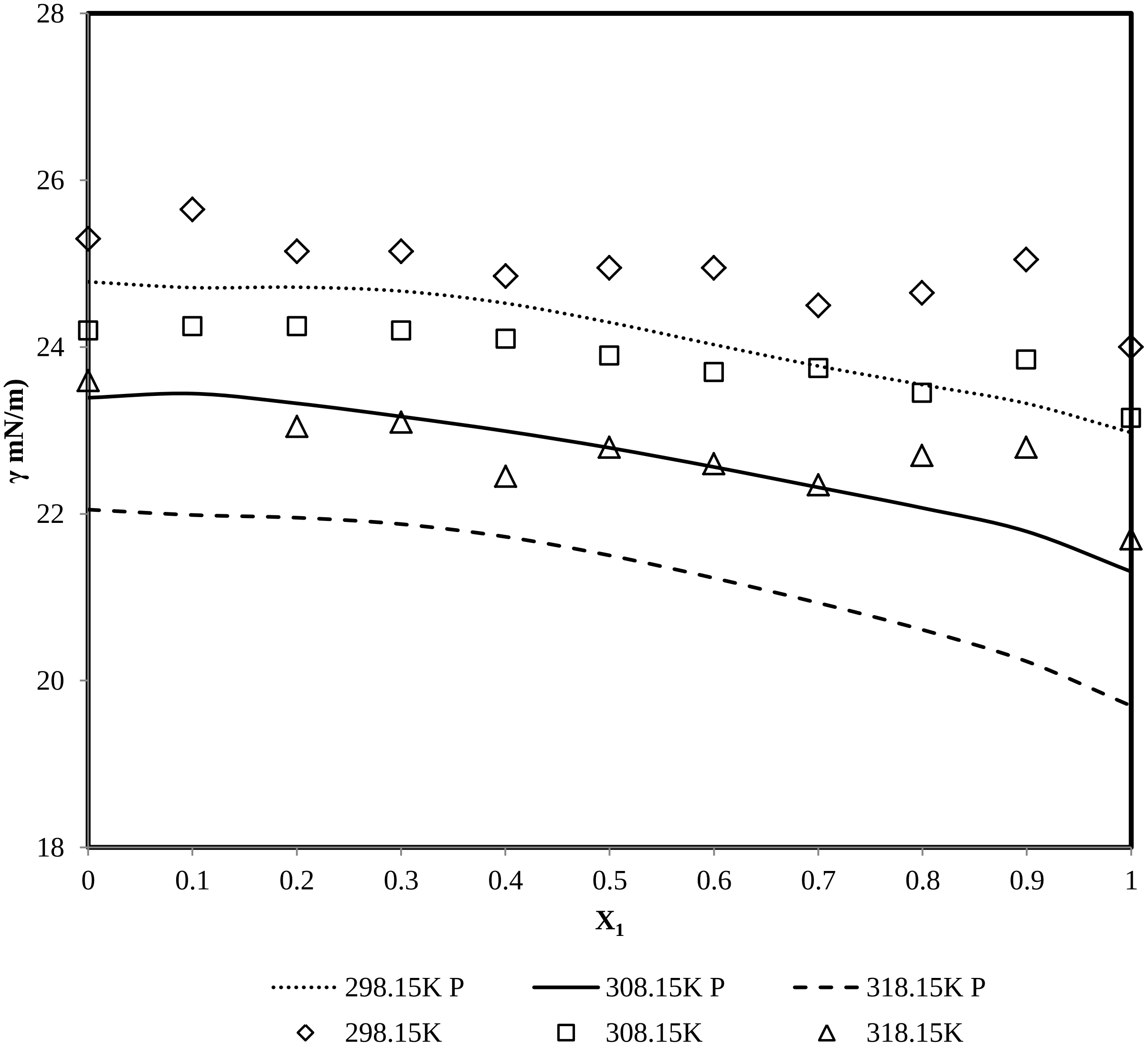

Figure 3.43 The predicted and experimental surface tension against mole fraction for acetone (1) and methyl acetate (2) mixtures at various temperatures. The smooth lines are predicted and the points are experimental

Acetophenone + methyl acetate system

Temp (K)	MRSD (%)
298.15	3.3
308.15	4.8
318.15	5.6

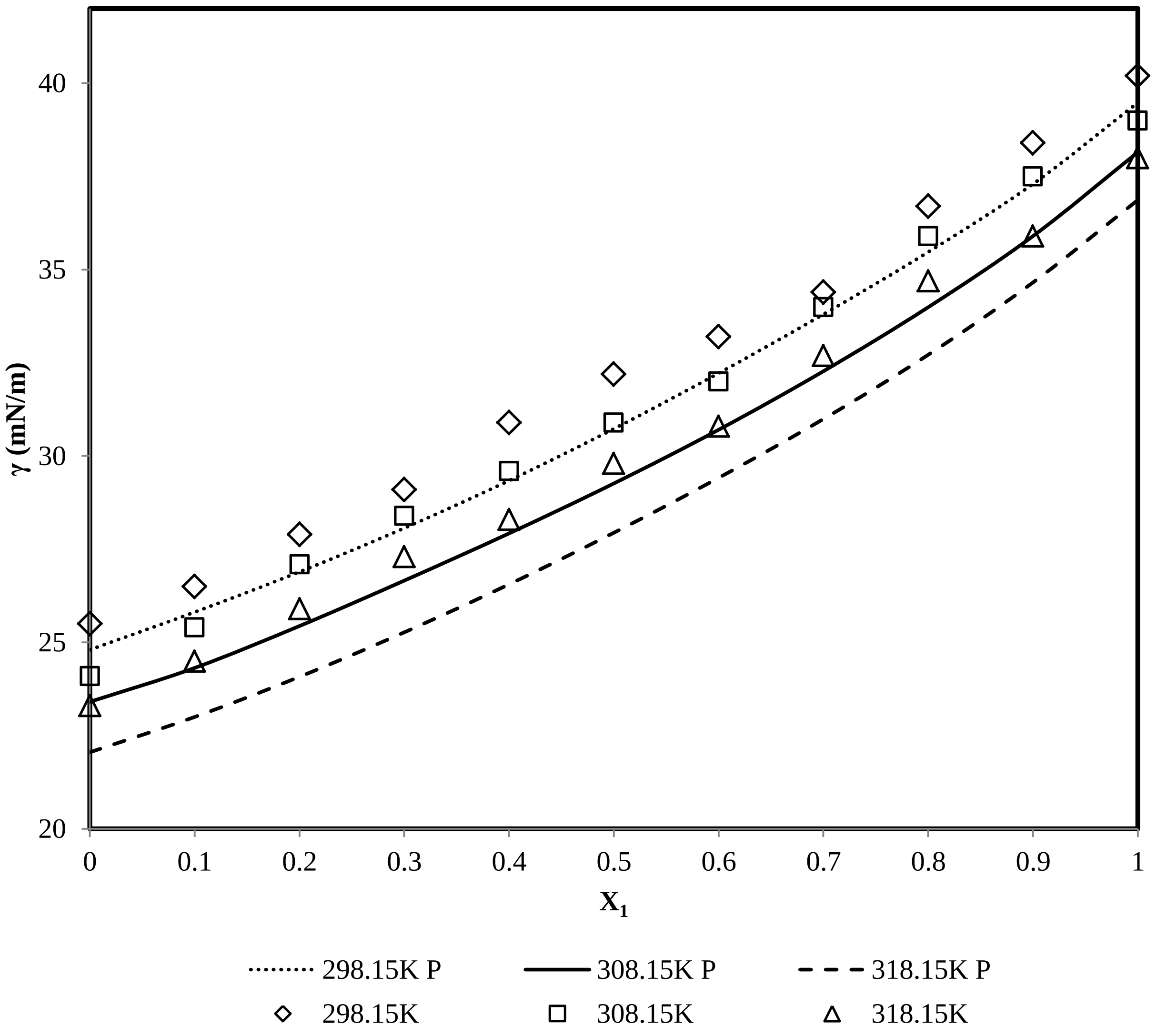

Figure 3.44 The predicted and experimental surface tension against mole fraction for acetophenone (1) and methyl acetate (2) mixtures at various temperatures. The smooth lines are predicted and the points are experimental

Acetophenone + ethyl acetate system

Temp (K)	MRSD (%)
298.15	4.3
308.15	4.7
318.15	3.4

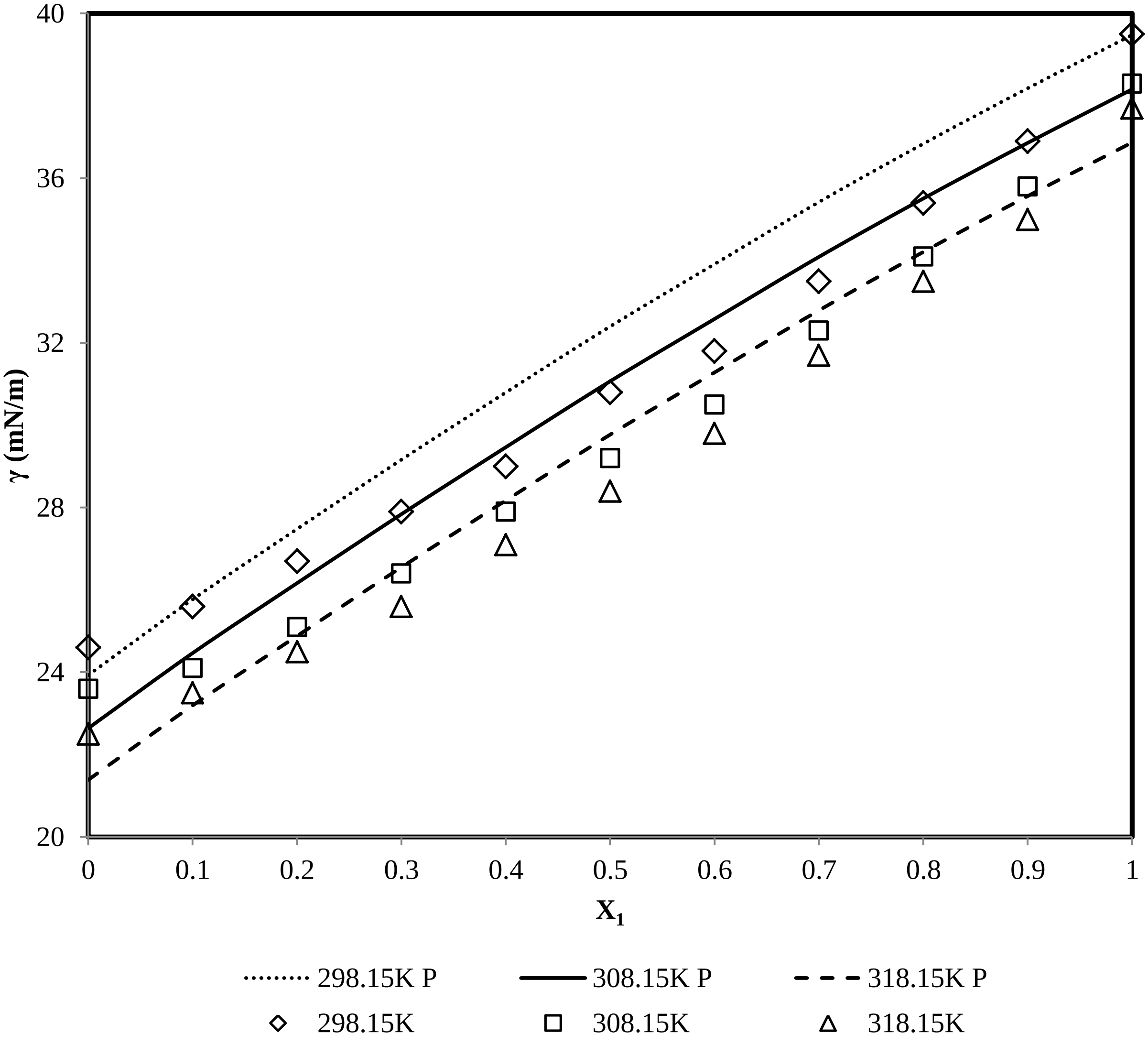

Figure 3.45 The predicted and experimental surface tension against mole fraction for acetophenone (1) and ethyl acetate (2) mixtures at various temperatures. The smooth lines are predicted and the points are experimental

Ethyl acetate + methyl acetate system

Temp (K)	MRSD (%)
298.15	1.7
308.15	2.5
318.15	4.0

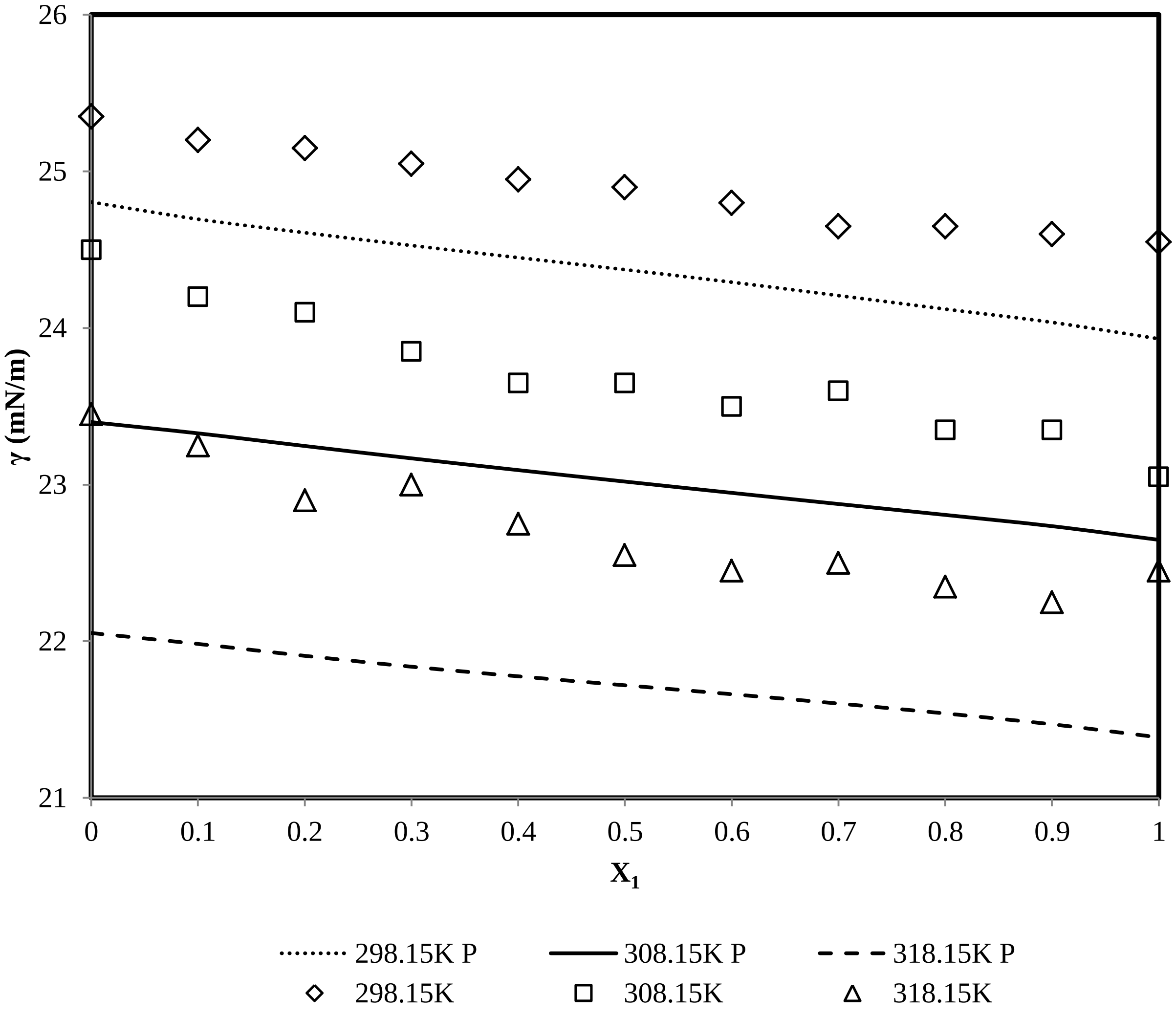

Figure 3.46 The predicted and experimental surface tension against mole fraction for ethyl acetate (1) and methyl acetate (2) mixtures at various temperatures. The smooth lines are predicted and the points are experimental

CHAPTER 4

4.0 CONCLUSION

Surface tension and density were measured for the seven systems; methyl acetate (1) + cyclohexanone (2), ethyl acetate (1) + cyclohexanone (2), cycloheptanone (1) + methyl acetate (2), acetone (1) + methyl acetate (2), acetophenone (1) + methyl acetate (2), acetophenone (1) + ethyl acetate (2) and ethyl acetate (1) + methyl acetate (2) systems. A linear trend of surface tension with varying mole fraction was observed for the (methyl acetate – cyclohexanone), (cycloheptanone – methyl acetate), (acetone – methyl acetate) and (ethyl acetate – methyl acetate) binary mixtures. A linear change of the surface tension with increasing mole fraction of the solute indicates strong molecular interactions between the solute and solvent molecules.

On the other hand, a nonlinear trend indicates that the components are distributed differently between the bulk and the surface. The component with the lower surface tension tends to be expelled to the surface. This trend was observed for the following mixtures; (ethyl acetate – cyclohexanone), (acetophenone – methyl acetate) and (acetophenone – ethyl acetate) systems.

From the surface tension deviations calculated, the system that showed the smallest deviation from the ideal behavior ($\Delta\gamma = 0$) was the (ethyl acetate – methyl acetate) mixture, indicating that the intermolecular interactions (dipole-dipole) between the components are the strongest. This is to be expected given the similarity in their structures. The maximum deviation at all the temperatures studied was exhibited by (acetophenone - ethyl acetate) mixture. This indicates that the interface is richer in ethyl acetate, which is the component with the lower surface tension. The other system showing an appreciable negative deviation is ethyl acetate and cyclohexanone. In this case also, ethyl acetate is preferably expelled to the interface. The deviation shown by the (cyclohexanone - methyl acetate) mixture is smaller than the corresponding mixture containing ethyl acetate in place of methyl acetate. This is a reflection of slightly higher surface tension of methyl acetate compared to ethyl acetate, and subsequently a smaller tendency to be expelled to the surface.

For the (cycloheptanone - methyl acetate) mixture, the deviation is somewhat lower than the (cyclohexanone - methyl acetate) mixture. This reflects the higher value of the surface tension of cyclohexanone and consequently a smaller difference between the surface tensions of the two components of the (cycloheptanone - methyl acetate) mixture.

The surface entropies of the systems under study were all negative and mostly indicated orderly molecular arrangement at the x_1 =0.5 at the surface. For the (ethyl acetate – cyclohexanone) and (acetophenone – ethyl acetate) systems, the surface tension deviations ($\Delta\gamma$) were negative and also showed the minima at x_1 = 0.5 which confirmed that the surface is homogenous and has an orderly arrangement.

Excess molar volumes (V_m^E) obtained from the experimental density values were negative for (ethyl acetate - cyclohexanone), (cycloheptanone – methyl acetate), (acetophenone – ethyl acetate) and (ethyl acetate – methyl acetate) systems. This arises mainly from the difference in the free volume of the unlike component. The solute-solvent interactions are strong between the molecules in the bulk region of these systems. For the (methyl acetate - cyclohexanone), (acetone – methyl acetate) and (acetophenone – methyl acetate) systems the values of (V_m^E) were found to be positive. This indicates that there is presence of dispersive intermolecular interactions due to the loosening of molecular parking in each of the binary systems which then leads to the observed volume expansion.

Surface tension was predicted using the measured density of the mixtures using the Sudgen’s model, given by equation (8). The density values were fitted to a Redlich-Kister polynomial expression, according to equation (9). The predicted and experimental surface tension showed good agreement as the mean relative standard deviations, (MRSD) were below 5% for most systems.

CHAPTER 5

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APPENDICES

SURFACE TENSION TABLES

A1: Surface tension for ethyl acetate (1) and cyclohexanone (2) at these various temperatures

Mole fraction of 1, X_1	**Surface tension, γ (mN/m)**		
	T = 298.15K	**T = 308.15K**	**T = 318.15K**
0	35.2	33.6	33.0
0.1003	33.6	32.2	31.3
0.2000	32.1	30.9	30.1
0.3000	31.0	29.7	29.0
0.3997	29.6	28.6	27.4
0.5000	29.0	27.7	26.6
0.5999	28.0	26.7	26.1
0.6998	26.6	25.6	24.8
0.7999	25.8	24.7	23.7
0.8997	24.7	23.9	23.0
1	24.2	23.2	22.0

A2: Surface tension for cycloheptanone (1) and methyl acetate (2) at these various temperatures

Mole fraction of 1, X_1	**Surface tension, γ (mN/m)**		
	T=298.15K	**T=308.15K**	**T=318.15K**
0	25.8	24.6	23.4
0.09977	26.4	25.4	24.8
0.1997	27.8	26.7	25.7
0.2999	28.5	27.4	26.9
0.4000	29.8	28.1	27.6
0.5003	30.7	29.8	28.9
0.5999	31.8	30.7	30.0
0.7000	32.7	31.4	30.7
0.7997	34.1	32.5	31.7
0.9006	34.8	33.9	32.8
1	35.5	35.2	34.1

A3: Surface tension for acetone (1) and methyl acetate (2) at three various temperatures

Mole fraction of 1, X_1	**Surface tension, γ (mN/m)**		
	T=298.15K	**T=308.15K**	**T=318.15K**
0	25.3	24.2	23.6
0.1000	25.7	24.3	23.6
0.2002	25.2	24.3	23.1
0.3000	25.2	24.2	23.1
0.4002	24.9	24.1	22.5
0.4997	25.0	23.9	22.8
0.6000	25.0	23.7	22.6
0.7001	24.5	23.8	22.4
0.7994	24.7	23.5	22.7
0.8995	25.1	23.9	22.8
1	24.0	23.2	21.7

A4: Surface tension for acetophenone (1) and methyl acetate (2) at these various temperatures

Mole fraction of 1, X_1	**Surface tension, γ (mN/m)**		
	T=298.15K	**T=308.15K**	**T=318.15K**
0	25.5	24.1	23.4
0.1001	26.7	25.7	24.8
0.2000	28.0	26.9	26.1
0.2853	29.2	28.6	27.4
0.4001	30.9	29.8	28.5
0.5000	32.2	31.0	30.2
0.6000	33.5	32.2	31.0
0.6999	34.7	34.1	33.0
0.8000	36.7	35.9	34.7
0.9000	38.4	37.5	36.2
1	40.2	38.8	38.2

A5: Surface tension for acetophenone (1) and ethyl acetate (2) at these various temperatures

Mole fraction of 1, X_1	**Surface tension, γ (mN/m)**		
	T=298.15K	**T=308.15K**	**T=318.15K**
0	24.6	23.6	22.5
0.1000	25.6	24.1	23.5
0.2000	26.7	25.1	24.5
0.2999	27.9	26.4	25.6
0.3980	29.0	27.9	27.1
0.5000	30.8	29.2	28.4
0.5994	31.8	30.5	29.8
0.6999	33.5	32.3	31.7
0.7997	35.4	34.1	33.5
0.9002	36.9	35.8	35.0
1	39.5	38.3	37.7

A6: Surface tension for ethyl acetate (1) and methyl acetate (2) at these various temperatures

Mole fraction of 1, X_1	**Surface tension, γ (mN/m)**		
	T = 298.15K	**T = 308.15K**	**T = 318.15K**
0	25.4	24.5	23.5
0.1000	25.2	24.2	23.3
0.1999	25.2	24.1	22.9
0.3000	25.1	23.9	23.0
0.4001	25.0	23.7	22.8
0.4994	24.9	23.7	22.6
0.6001	24.8	23.5	22.5
0.6997	24.7	23.6	22.5
0.7999	24.7	23.4	22.4
0.8998	24.6	23.4	22.3
1	24.6	23.1	22.5

REDLICH-KIRSTER POLYNOMIALS

For surface tension deviations, A_k

A7: Methyl acetate + cyclohexanone mixture

Temp (K)	**Coefficients, A_k**							
	A0	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**	**A7**
298	-0.4712	1.1407	-1.8339	1.0948	1.1174	-6.2782	-0.5081	2.6709
308	-1.9290	-3.3750	-1.4199	13.9035	0.2875	-7.0988		
318	-0.2782	-0.6439	4.9059	-6.5883	-4.8527			

A8: Surface tension deviations for the methyl acetate (1) and cyclohexanone (2) mixtures at these various temperatures

X1	**Surface tension deviation, $\Delta\gamma$ (mN/m)**		
	T=298.15K	**T=308.15K**	**T=318.15K**
0	0	0	0
0.1163	-0.1	-0.1	-0.3
0.2292	-0.1	-0.4	-0.1
0.3376	-0.1	-0.6	-0.1
0.4422	-0.1	-0.6	-0.1
0.5432	-0.1	-0.4	0.0
0.6334	-0.2	-0.3	0.1
0.7351	-0.3	-0.4	0.3
0.8259	-0.2	-0.5	0.5
0.9147	-0.1	-0.4	0.4
1	0	0	0

A9: Ethyl acetate + cyclohexanone

Temp (K)	Coefficients, Ak						
	A0	A1	A2	A3	A4	A5	A6
298	-3.2727	-3.6270	-5.9484	11.4564	3.0581	-8.1950	
308	-2.8337	-1.6502	-7.5181	7.2616	19.8950	-7.7189	-16.7414
318	-3.5547	-8.3375	11.5948	42.7001	-53.0602	-55.6112	53.4142

A10: Surface tension deviations for the ethyl acetate (1) and cyclohexanone (2) mixtures at these various temperatures

X1	Surface tension deviation, $\Delta\gamma$ (mN/m)		
	T=298.15K	T=308.15K	T=318.15K
0	0	0	0
0.1003	-0.5	-0.4	-0.6
0.2000	-0.9	-0.6	-0.6
0.3000	-1.0	-0.8	-0.8
0.3997	-1.0	-0.8	-1.1
0.5000	-0.8	-0.7	-0.9
0.5999	-0.7	-0.7	-0.4
0.6998	-0.7	-0.7	-0.3
0.7999	-0.7	-0.6	-0.6
0.8997	-0.6	-0.3	-0.1
1	0	0	0

A11: Cycloheptanone + methyl acetate

Temp (K)	**Coefficients, Ak**						
	A0	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
298	0.1377	-0.9066	4.5407	-4.1215	-7.0350	-1.9289	
308	-1.3646	0.2098	-5.5172	2.5568	6.4286		
318	0.4060	-0.8542	-0.6384	15.2643	-8.9960	-12.8406	15.9747

A12: Surface tension deviations for the cycloheptanone (1) and methyl acetate (2) mixtures at these various temperatures

X1	**Surface tension deviation, Δγ (mN/m)**		
	T=298.15K	**T=308.15K**	**T=318.15K**
0	0	0	0
0.09977	-0.3	-0.1	0.3
0.1997	-0.1	-0.3	0.2
0.2999	0.0	-0.4	0.1
0.4000	0.0	-0.4	0.1
0.5003	0.0	-0.3	0.1
0.5999	0.1	-0.4	0.1
0.7000	0.3	-0.5	-0.1
0.7997	0.4	-0.5	-0.3
0.9006	0.3	-0.3	-0.2
1	0	0	0

A13: Acetone + methyl acetate

Temp (K)	**Coefficients, Ak**						
	A0	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
298	2.2445	-2.5119	-18.9084	15.6576	65.9317	-36.3311	-10.3250
308	1.2955	-0.6739	7.5559	26.3378	-35.0749	-54.5655	59.0036
318	-0.1531	-1.9480	-2.9850	-2.8069	28.4755	-18.1937	

A14: Surface tension deviations for the cycloheptanone (1) and methyl acetate (2) mixtures at these various temperatures

X1	**Surface tension deviation, Δγ (mN/m)**		
	T=298.15K	**T=308.15K**	**T=318.15K**
0	0	0	0
0.1000	0.2	0.1	0.1
0.2002	0.3	0.3	0.0
0.3000	0.3	0.3	-0.2
0.4002	0.2	0.3	-0.1
0.4997	0.1	0.3	0.0
0.6000	0.2	0.2	0.1
0.7001	0.4	0.1	0.2
0.7994	0.6	0.2	0.5
0.8995	0.6	0.5	0.9
1	0	0	0

A15: Acetophenone + methyl acetate

Temp (K)	Coefficients, Ak						
	A0	A1	A2	A3	A4	A5	A6
298	-3.0369	10.0810	-4.5177	-36.2174	4.7983	28.9263	
308	-3.2289	7.2109	16.7258	-21.9668	-22.8087	13.4146	2.5593
318	-3.7172	4.1982	2.2350	-4.9283			

A16: Surface tension deviations for the acetophenone (1) and methyl acetate (2) mixtures at these various temperatures

X1	Surface tension deviation, Δγ (mN/m)		
	T=298.15K	T=308.15K	T=318.15K
0	0	0	0
0.1001	0.2	-0.1	-0.1
0.2000	0.3	0.1	-0.2
0.2853	0.3	0.1	-0.3
0.4001	0.2	-0.2	-0.6
0.5000	0.1	-0.5	-0.9
0.6000	0.2	-0.6	-0.9
0.6999	0.4	-0.4	-0.8
0.8000	0.6	0.0	-0.6
0.9000	0.6	0.2	-0.4
1	0	0	0

A17: Acetophenone + ethyl acetate

Temp (K)	Coefficients, Ak				
	A0	A1	A2	A3	A4
298	-6.1291	1.0250	0.1833	3.7082	-5.8427
308	-7.1169	0.7436	-1.2853	-2.0996	-7.5478
318	-6.9246	-0.3421	3.3272	5.7647	-10.9075

A18: Surface tension deviations for the acetophenone (1) and ethyl acetate (2) mixtures at these various temperatures

X1	Surface tension deviation, $\Delta\gamma$ (mN/m)		
	T=298.15K	T=308.15K	T=318.15K
0	0	0	0
0.1000	-0.5	-1.0	-0.6
0.2000	-0.9	-1.4	-1.0
0.2999	-1.2	-1.5	-1.4
0.3980	-1.4	-1.7	-1.6
0.5000	-1.5	-1.8	-1.7
0.5994	-1.5	-1.8	-1.6
0.6999	-1.4	-1.6	-1.4
0.7997	-1.3	-1.4	-1.3
0.9002	-1.0	-0.9	-1.1
1	0	0	0

A19: Ethyl acetate + methyl acetate

Temp (K)	**Coefficients, Ak**						
	A0	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
298.15	-2.2257	-4.9186	8.7090	16.1708	-25.8896	-17.9737	14.7847
308.15	-2.0533	-0.2766	2.0889	3.6617	-5.3551		
318.15	-0.0134	0.8189	0.6482	-0.3565	-0.1976	-3.3802	

A20: Surface tension deviations for the acetophenone (1) and ethyl acetate (2) mixtures at these various temperatures

X1	**Surface tension deviation, Δγ (mN/m)**		
	T=298.15K	**T=308.15K F**	**T=318.15K**
0	0	0	0
0.1000	-0.1	-0.1	-0.2
0.1999	-0.1	-0.2	-0.2
0.3000	-0.1	-0.2	-0.3
0.4001	-0.1	-0.2	-0.3
0.4994	-0.1	-0.2	-0.4
0.6001	-0.1	-0.1	-0.3
0.6997	-0.1	0.0	-0.3
0.7999	-0.1	0.1	-0.3
0.8998	0.0	0.1	-0.3
1	0	0	0

For density, B_k

A21: Methyl acetate + cyclohexanone mixture

Temp (K)	**Coefficients, Bk**							
	A0	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**	**A7**
298.15	0.9443	-0.01645	-0.0005054					
308.15	0.9354	-0.01999	-0.01239	0.1008	-0.3133	0.4625	-0.3306	0.09150
318.15	0.9265	-0.02245	-0.01367	0.0998	-0.3145	0.4672	-0.3361	0.09354

A22: Ethyl acetate + cyclohexanone

Temp (K)	**Coefficients, Bk**							
	A0	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**	**A7**
298.15	0.9447	-0.04997	0.03042	-0.1302	0.3346	-0.5011	0.3826	-0.1152
308.15	0.9357	-0.05166	0.01968	-0.07051	0.1578	-0.2286	0.1725	-0.05143
318.15	0.9268	-0.05468	0.02833	-0.1181	0.2670	-0.3564	0.2455	-0.06740

A23: Cycloheptanone + methyl acetate

Temp (K)	**Coefficients, Bk**						
	A0	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
298.15	0.9272	0.0937	-0.1780	0.4498	-0.7035	0.5544	-0.1705
308.15	0.9139	0.1026	-0.1858	0.4542	-0.7011	0.5490	-0.1682
318.15	0.9003	0.1129	-0.1999	0.4779	-0.7276	0.5631	-0.1707

A24: Acetone + methyl acetate

Temp (K)	**Coefficients, Bk**						
	A0	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
298.15	0.9270	-0.1563	0.1611	-0.4692	0.5413	-0.2138	
308.15	0.9137	-0.1168	-0.2052	0.7347	-1.3007	1.1372	-0.3875
318.15	0.9003	-0.1482	0.1040	-0.2934	0.3168	-0.1038	-0.01525

A25: Acetophenone + methyl acetate

Temp (K)	**Coefficients, Bk**							
	A0	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**	**A7**
298.15	0.9272	0.07542	0.01832	-0.03444	0.1797	-0.2687	0.1265	
308.15	0.9138	0.05507	0.2228	-0.6441	0.9430	-0.6033	0.06864	0.05925
318.15	0.9003	0.07245	0.0910	-0.2387	0.5719	-0.8682	0.6869	-0.2091

A26: Acetophenone + ethyl acetate

Temp (K)	**Coefficients, Bk**						
	A0	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
298.15	0.8947	0.1878	-0.1530	0.3079	-0.4346	0.3012	-0.07998
308.15	0.8824	0.1939	-0.1615	0.3276	-0.4618	0.3191	-0.08437
318.15	0.8699	0.1995	-0.1651	0.3390	-0.4899	0.3486	-0.09529

A27: Ethyl acetate + methyl acetate

Temp (K)	**Coefficients, Bk**							
	A0	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**	**A7**
298.15	0.9272	-0.03779	0.03989	-0.1745	0.4622	-0.6839	0.5159	-0.1543
308.15	0.9138	-0.03048	-0.01703	0.06732	-0.1191	0.1024	-0.03439	
318.15	0.9004	-0.03018	-0.01860	0.08027	-0.1364	0.1076	-0.03310	

MEAN RELATIVE STANDARD DEVIATIONS (MRSD)

$$MRSD = 100 * \left[\frac{1}{N}\sum_{i}\left(\frac{\gamma_{i,exp} - \gamma_{i,cal}}{\gamma_{i,exp}}\right)^2\right]^{\frac{1}{2}}$$

Where; $\gamma_{i,exp}$ is the experimental surface tension, $\gamma_{i,cal}$ is the calculated surface tension of the i^{th} mole fraction.

N is the number of experimental data

Let;

A = $(\gamma_{exp}-\gamma_{cal})/\gamma_{exp}$

B = Σ (A^2)

C = (1/N)*B

N = 11

A28: The mean relative standard deviation of the experimental and calculated surface tension values of methyl acetate + cyclohexanone mixtures at temperature 298.15K

X1	**γcal**	**γexp**	**(γexp-γcal) /γexp**	**A^2**	**B**	**C**	**C^(1/2)**	**MRSD (%)**
0	34.1	35.0	0.02543	0.0006468				
0.09981	33.1	33.8	0.02148	0.0004615				
0.1996	32.1	32.8	0.02246	0.0005045				
0.2992	31.1	31.8	0.02267	0.0005139				
0.3998	30.1	30.8	0.02241	0.0005024				
0.4990	29.2	29.8	0.02089	0.0004366	0.00640	0.000582	0.0241	2.4
0.6000	28.3	28.9	0.02243	0.0005030				
0.7001	27.4	27.9	0.01943	0.0003777				
0.8001	26.5	27.1	0.02261	0.0005112				
0.8959	25.7	26.4	0.02749	0.0007559				
1	24.8	25.7	0.03450	0.001190				

A29: The mean relative standard deviation of the experimental and calculated surface tension values of methyl acetate + cyclohexanone mixtures at temperature 308.15K

X1	**γcal**	**γexp**	**(γexp-γcal) /γexp**	**A^2**	**B**	**C**	**C^(1/2)**	**MRSD (%)**
0	32.9	34.1	0.03652	0.001333				
0.09981	31.8	32.9	0.03342	0.001117				
0.1996	30.8	31.5	0.02285	0.0005219				
0.2992	29.8	30.2	0.01338	0.0001791				
0.3998	28.8	29.4	0.01954	0.0003819				
0.4990	27.9	28.4	0.01806	0.0003263	0.00834	0.000758	0.0275	2.8
0.6000	27.0	27.6	0.02351	0.0005527				
0.7001	26.0	26.9	0.03179	0.001011				
0.8001	25.2	25.5	0.01345	0.0001808				
0.8959	24.3	25	0.02736	0.0007487				
1	23.4	24.5	0.04459	0.001988				

A30: The mean relative standard deviation of the experimental and calculated surface tension values of methyl acetate + cyclohexanone mixtures at temperature 318.15K

X1	**γcal**	**γexp**	**(γexp-γcal) /γexp**	**A^2**	**B**	**C**	**C^(1/2)**	**MRSD (%)**
0	31.6	33.4	0.05347	0.002859				
0.09981	30.6	32.0	0.04492	0.002018				
0.1996	29.5	31.0	0.04702	0.002211				
0.2992	28.6	29.8	0.04181	0.001748				
0.3998	27.6	29.2	0.05559	0.003091				
0.4990	26.6	27.8	0.04215	0.001777	0.0327	0.00298	0.0546	5.5
0.6000	25.7	27.0	0.04892	0.002393				
0.7001	24.8	26.5	0.06579	0.004329				
0.8001	23.8	25.6	0.06841	0.004680				
0.8959	23.0	24.6	0.06565	0.004310				
1	22.0	23.4	0.05774	0.003334				

A31: the mean relative standard deviation of the experimental and calculated surface tension values of ethyl acetate + cyclohexanone mixtures at temperature 298.15K

X1	**γcal**	**γexp**	**(γexp-γcal) /γexp**	**A^2**	**B**	**C**	**C^(1/2)**	**MRSD (%)**
0	34.2	35.2	0.0293	0.000858				
0.1077	33.0	33.6	0.0168	0.000282				
0.2146	31.9	32.1	0.00503	0.0000253				
0.3187	30.9	31.0	0.00362	0.0000131				
0.4212	29.9	29.6	-0.00880	0.0000774				
0.5212	28.9	29.0	0.00457	0.0000209	0.00162	0.000148	0.0121	1.2
0.6163	27.9	28.0	0.00436	0.0000190				
0.7173	26.9	26.6	-0.0112	0.000126				
0.8129	25.9	25.8	-0.00509	0.0000259				
0.9074	25.0	24.7	-0.0115	0.000133				
1	24.0	24.2	0.00652	0.0000426				

A32: The mean relative standard deviation of the experimental and calculated surface tension values of ethyl acetate + cyclohexanone mixtures at temperature 308.15K

X1	**γcal**	**γexp**	**(γexp-γcal) /γexp**	**A^2**	**B**	**C**	**C^(1/2)**	**MRSD (%)**
0	32.9	33.6	0.0210	0.000440				
0.1077	31.8	32.2	0.0135	0.000181				
0.2146	30.7	30.9	0.0075	0.0000556				
0.3187	29.6	29.7	0.0027	0.00000728				
0.4212	28.6	28.6	0.0003	0.0000000883				
0.5212	27.6	27.7	0.0038	0.0000141	0.00117	0.00011	0.0103	1.0
0.6163	26.6	26.7	0.0036	0.0000130				
0.7173	25.6	25.6	-0.0008	0.000000706				
0.8129	24.6	24.7	0.0021	0.00000435				
0.9074	23.7	23.9	0.0087	0.0000755				
1	22.7	23.2	0.0195	0.000380				

A33: The mean relative standard deviation of the experimental and calculated surface tension values of ethyl acetate + cyclohexanone mixtures at temperature 318.15K

X1	**γcal**	**γexp**	**(γexp-γcal) /γexp**	**A^2**	**B**	**C**	**C^(1/2)**	**MRSD (%)**
0	31.7	33.0	0.0408	0.00167				
0.1077	30.5	31.3	0.0247	0.000611				
0.2146	29.4	30.1	0.0221	0.000490				
0.3187	28.4	29.0	0.0212	0.000450				
0.4212	27.4	27.4	0.0017	0.00000284				
0.5212	26.4	26.6	0.0092	0.0000842	0.00571	0.00052	0.0228	2.3
0.6163	25.4	26.1	0.0283	0.000801				
0.7173	24.4	24.8	0.0171	0.000292				
0.8129	23.4	23.7	0.0127	0.000162				
0.9074	22.4	23.0	0.0245	0.000602				
1	21.5	22.0	0.0233	0.00054				

A34: The mean relative standard deviation of the experimental and calculated surface tension values of cycloheptanone + methyl acetate mixtures at temperature 298.15K

X1	**γcal**	**γexp**	**(γexp-γcal) /γexp**	**A^2**	**B**	**C**	**C^(1/2)**	**MRSD (%)**
0	24.8	25.8	0.0386	0.00149				
0.1001	26.3	26.4	0.0029	0.00000837				
0.1999	27.7	27.8	0.0029	0.00000855				
0.3001	29.1	28.5	-0.0206	0.000425				
0.4003	30.5	29.8	-0.0218	0.000476				
0.4999	31.8	30.7	-0.036	0.00127	0.0219	0.00199	0.045	4.5
0.6012	33.1	31.8	-0.042	0.00179				
0.6993	34.4	32.7	-0.053	0.00284				
0.7987	35.8	34.1	-0.049	0.00237				
0.8996	37.1	34.8	-0.066	0.00441				
1	38.4	35.5	-0.083	0.00683				

A35: The mean relative standard deviation of the experimental and calculated surface tension values of cycloheptanone + methyl acetate mixtures at temperature 308.15K

X1	**γcal**	**γexp**	**(γexp-γcal) /γexp**	**A^2**	**B**	**C**	**C^(1/2)**	**MRSD (%)**
0	23.4	24.6	0.0483	0.00234				
0.1001	24.9	25.4	0.01787	0.000319				
0.1999	26.4	26.7	0.0129	0.000166				
0.3001	27.7	27.4	-0.0123	0.000151				
0.4003	29.1	28.1	-0.0359	0.00129				
0.4999	30.5	29.8	-0.0222	0.00049	0.0187	0.00170	0.041	4.1
0.6012	31.8	30.7	-0.036	0.00133				
0.6993	33.1	31.4	-0.055	0.00300				
0.7987	34.4	32.5	-0.060	0.00356				
0.8996	35.8	33.9	-0.056	0.00310				
1	37.1	35.2	-0.054	0.00293				

A36: The mean relative standard deviation of the experimental and calculated surface tension values of cycloheptanone + methyl acetate mixtures at temperature 318.15K

X1	**γcal**	**γexp**	**(γexp-γcal) /γexp**	**A^2**	**B**	**C**	**C^(1/2)**	**MRSD (%)**
0	22.1	23.4	0.0576	0.00332				
0.1001	23.6	24.8	0.0482	0.00232				
0.1999	25.0	25.7	0.0261	0.000683				
0.3001	26.4	26.9	0.0178	0.000319				
0.4003	27.8	27.6	-0.0073	0.0000527				
0.4999	29.2	28.9	-0.0090	0.0000811	0.0157	0.00143	0.038	3.8
0.6012	30.5	30	-0.017	0.000304				
0.6993	31.8	30.7	-0.037	0.00135				
0.7987	33.1	31.7	-0.046	0.00208				
0.8996	34.5	32.8	-0.052	0.00268				
1	35.8	34.1	-0.050	0.00254				

A37: The mean relative standard deviation of the experimental and calculated surface tension values of acetone + methyl acetate mixtures at temperature 298.15K

X1	**γcal**	**γexp**	**(γexp-γcal) /γexp**	**A^2**	**B**	**C**	**C^(1/2)**	**MRSD (%)**
0	24.8	25.3	0.0205	0.000419				
0.1000	24.7	25.7	0.0365	0.00134				
0.2002	24.7	25.2	0.0172	0.000295				
0.3000	24.7	25.2	0.0191	0.000363				
0.4002	24.5	24.9	0.0131	0.000171				
0.4997	24.3	25.0	0.0262	0.000686	0.0141	0.00128	0.0358	3.6
0.6000	24.0	25.0	0.0369	0.00136				
0.7001	23.8	24.5	0.0297	0.000882				
0.7994	23.5	24.7	0.0447	0.00200				
0.8995	23.3	25.1	0.0689	0.00475				
1	23.0	24.0	0.0427	0.00183				

A38: The mean relative standard deviation of the experimental and calculated surface tension values of acetone + methyl acetate mixtures at temperature 308.15K

X1	**γcal**	**γexp**	**(γexp-γcal) /γexp**	**A^2**	**B**	**C**	**C^(1/2)**	**MRSD (%)**
0	23.4	24.2	0.0334	0.00111				
0.1000	23.4	24.3	0.0333	0.00111				
0.2002	23.3	24.3	0.0382	0.00146				
0.3000	23.2	24.2	0.0427	0.00182				
0.4002	23.0	24.1	0.0460	0.00211				
0.4997	22.8	23.9	0.0464	0.00215	0.0330	0.00300	0.0547	5.5
0.6000	22.6	23.7	0.0480	0.00231				
0.7001	22.3	23.8	0.0603	0.00364				
0.7994	22.1	23.5	0.0588	0.00346				
0.8995	21.8	23.9	0.0864	0.00746				
1	21.3	23.2	0.0796	0.00633				

A39: The mean relative standard deviation of the experimental and calculated surface tension values of acetone + methyl acetate mixtures at temperature 318.15K

X1	**γcal**	**γexp**	**(γexp-γcal) /γexp**	**A^2**	**B**	**C**	**C^(1/2)**	**MRSD (%)**
0	22.1	23.6	0.0657	0.00431	0.0510	0.00464	0.0681	6.8
0.1000	22.0							
0.2002	22.0	23.1	0.0476	0.00226				
0.3000	21.9	23.1	0.0530	0.00280				
0.4002	21.7	22.5	0.0323	0.00104				
0.4997	21.5	22.8	0.0569	0.00324	0.0510	0.00464	0.0681	6.8
0.6000	21.2	22.6	0.0606	0.00368				
0.7001	20.9	22.4	0.0635	0.00403				
0.7994	20.6	22.7	0.0920	0.00847				
0.8995	20.2	22.8	0.113	0.0127				
1	19.7	21.7	0.0923	0.00852				

A40: The mean relative standard deviation of the experimental and calculated surface tension values of acetophenone + methyl acetate mixtures at temperature 298.15K

X1	**γcal**	**γexp**	**(γexp-γcal) /γexp**	**A^2**	**B**	**C**	**C^(1/2)**	**MRSD (%)**
0	24.8	25.5	0.0274	0.00075				
0.1001	25.8	26.5	0.0260	0.00068				
0.2000	26.9	27.9	0.0361	0.00130				
0.2853	28.1	29.1	0.0356	0.00127				
0.4001	29.3	30.9	0.0505	0.00255				
0.5000	30.7	32.2	0.0457	0.00209	0.0121	0.00110	0.0332	3.3
0.6000	32.2	33.2	0.0295	0.00087				
0.6999	33.8	34.4	0.0174	0.0003				
0.8000	35.5	36.7	0.0335	0.00112				
0.9000	37.3	38.4	0.0287	0.00083				
1	39.5	40.2	0.0180	0.00032				

A41: The mean relative standard deviation of the experimental and calculated surface tension values of acetophenone + methyl acetate mixtures at temperature 308.15K

X1	**γcal**	**γexp**	**(γexp-γcal) /γexp**	**A^2**	**B**	**C**	**C^(1/2)**	**MRSD (%)**
0	23.4	24.1	0.0289	0.000834				
0.1001	24.3	25.4	0.0428	0.00183				
0.2000	25.4	27.1	0.0612	0.00375				
0.2853	26.7	28.4	0.0614	0.00377				
0.4001	27.9	29.6	0.0566	0.00320				
0.5000	29.3	30.9	0.0530	0.00281	0.0256	0.00232	0.0482	4.8
0.6000	30.7	32	0.0406	0.00164				
0.6999	32.3	34	0.0508	0.00258				
0.8000	34.0	35.9	0.0532	0.00283				
0.9000	35.9	37.5	0.0427	0.00182				
1	38.1	39	0.0218	0.000477				

A42: The mean relative standard deviation of the experimental and calculated surface tension values of acetophenone + methyl acetate mixtures at temperature 318.15K

X1	**γcal**	**γexp**	**(γexp-γcal) /γexp**	**A^2**	**B**	**C**	**C^(1/2)**	**MRSD (%)**
0	22.1	23.3	0.0536	0.00288				
0.1001	23.0	24.5	0.0614	0.00377				
0.2000	24.1	25.9	0.0703	0.00495				
0.2853	25.3	27.3	0.0744	0.00554				
0.4001	26.6	28.3	0.0616	0.00379				
0.5000	27.9	29.8	0.0624	0.00390	0.0350	0.00318	0.0564	5.6
0.6000	29.4	30.8	0.0451	0.00203				
0.6999	31.0	32.7	0.0523	0.00273				
0.8000	32.7	34.7	0.0572	0.00328				
0.9000	34.7	35.9	0.0347	0.00120				
1	36.9	38	0.0299	0.000894				

A43: The mean relative standard deviation of the experimental and calculated surface tension values of acetophenone + ethyl acetate mixtures at temperature 298.15K

X1	**γcal**	**γexp**	**(γexp-γcal) /γexp**	**A^2**	**B**	**C**	**C^(1/2)**	**MRSD (%)**
0	23.9	24.6	0.0273	0.000746				
0.09992	25.8	25.6	-0.00647	0.0000419				
0.2003	27.5	26.7	-0.0293	0.000857				
0.3000	29.2	27.9	-0.0452	0.00204				
0.4002	30.8	29.0	-0.0619	0.00384				
0.5000	32.4	30.8	-0.0519	0.00269	0.0208	0.00189	0.0435	4.3
0.6000	33.9	31.8	-0.0664	0.00441				
0.7000	35.4	33.5	-0.0573	0.00328				
0.8000	36.8	35.4	-0.0405	0.00164				
0.9000	38.2	36.9	-0.0348	0.00121				
1	39.5	39.5	0.000571	0.000000327				

A44: The mean relative standard deviation of the experimental and calculated surface tension values of acetophenone + ethyl acetate mixtures at temperature 308.15K

X1	**γcal**	**γexp**	**(γexp-γcal) /γexp**	**A^2**	**B**	**C**	**C^(1/2)**	**MRSD (%)**
0	22.6	23.6	0.0408	0.00166				
0.09992	24.5	24.1	-0.0150	0.000226				
0.2003	26.2	25.1	-0.0425	0.00181				
0.3000	27.8	26.4	-0.0545	0.00297				
0.4002	29.5	27.9	-0.0562	0.00316				
0.5000	31.1	29.2	-0.0639	0.00409	0.0242	0.00220	0.0469	4.7
0.6000	32.6	30.5	-0.0682	0.00465				
0.7000	34.1	32.3	-0.0554	0.00306				
0.8000	35.5	34.1	-0.0412	0.00170				
0.9000	36.9	35.8	-0.0295	0.000872				
1	38.2	38.3	0.00373	0.0000139				

A45: The mean relative standard deviation of the experimental and calculated surface tension values of acetophenone + ethyl acetate mixtures at temperature 318.15K

X1	**γcal**	**γexp**	**(γexp-γcal) /γexp**	**A^2**	**B**	**C**	**C^(1/2)**	**MRSD (%)**
0	21.4	22.5	0.0496	0.00246				
0.09992	23.2	23.5	0.0132	0.000174				
0.2003	24.9	24.5	-0.0156	0.000245				
0.3000	26.5	25.6	-0.0370	0.00137				
0.4002	28.2	27.1	-0.0396	0.00157				
0.5000	29.8	28.4	-0.0482	0.00233	0.0130	0.00118	0.0344	3.4
0.6000	31.3	29.8	-0.0497	0.00247				
0.7000	32.8	31.7	-0.0343	0.00118				
0.8000	34.2	33.5	-0.0211	0.000446				
0.9000	35.6	35	-0.0161	0.000260				
1	36.9	37.7	0.0221	0.000489				

A46: The mean relative standard deviation of the experimental and calculated surface tension values of ethyl acetate + methyl acetate mixtures at temperature 298.15K

X1	**γcal**	**γexp**	**(γexp-γcal) /γexp**	**A^2**	**B**	**C**	**C^(1/2)**	**MRSD (%)**
0	24.8	25.0	0.0079	0.0000617				
0.09997	24.7	24.9	0.0082	0.0000679				
0.1999	24.6	25.0	0.0157	0.000245				
0.3000	24.5	24.9	0.0150	0.000224				
0.4001	24.4	24.8	0.0141	0.000200				
0.4994	24.4	24.8	0.0172	0.000297	0.00313	0.00028	0.0169	1.7
0.6001	24.3	24.7	0.0165	0.000272				
0.6997	24.2	24.5	0.0119	0.000143				
0.7999	24.1	24.7	0.0235	0.000550				
0.8998	24.0	24.6	0.0229	0.000525				
1	23.9	24.5	0.0232	0.000539				

A47: The mean relative standard deviation of the experimental and calculated surface tension values of ethyl acetate + methyl acetate mixtures at temperature 308.15K

X1	**γcal**	**γexp**	**(γexp-γcal) /γexp**	**A^2**	**B**	**C**	**C^(1/2)**	**MRSD (%)**
0	23.4	24.6	0.0488	0.00238				
0.09997	23.3	24	0.0280	0.000785				
0.1999	23.2	23.9	0.0273	0.000747				
0.3000	23.2	23.6	0.0183	0.000336				
0.4001	23.1	23.3	0.00890	0.0000792				
0.4994	23.0	23.4	0.0163	0.000264	0.00668	0.000608	0.0247	2.5
0.6001	22.9	23.3	0.0151	0.000229				
0.6997	22.9	23.6	0.0307	0.000940				
0.7999	22.8	23.2	0.0170	0.000288				
0.8998	22.7	23.1	0.0158	0.000250				
1	22.6	23.1	0.0196	0.000384				

A48: The mean relative standard deviation of the experimental and calculated surface tension values of ethyl acetate + methyl acetate mixtures at temperature 318.15K

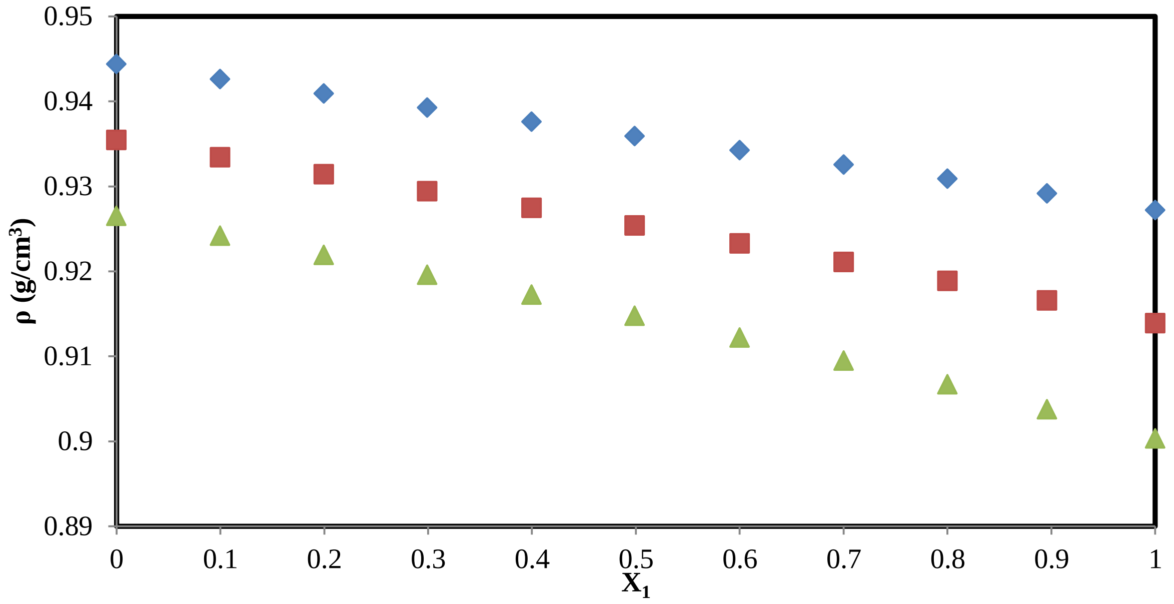
X1	**γcal**	**γexp**	**(γexp-γcal) /γexp**	**A^2**	**B**	**C**	**C^(1/2)**	**MRSD (%)**
0	22.1	23.4	0.0576	0.00332				
0.09997	22.0	23.3	0.0565	0.00320				
0.1999	21.9	22.8	0.0392	0.00153				
0.3000	21.8	22.8	0.0422	0.00178				
0.4001	21.8	22.6	0.0365	0.00133				
0.4994	21.7	22.4	0.0304	0.000925	0.0174	0.00159	0.0398	4.0
0.6001	21.7	22.2	0.0242	0.000588				
0.6997	21.6	22.3	0.0313	0.000979				
0.7999	21.5	22.3	0.0341	0.00116				
0.8998	21.5	22.0	0.0241	0.000581				
1	21.4	22.4	0.0453	0.00205				

DENSITY VALUES

Before fitting into the Redlich-Kirster polynomial

A49: Showing density measurements at various temperatures of 298.15K, 308.15K and 318.15K for methyl acetate (1) and cyclohexanone (2) mixtures**.**

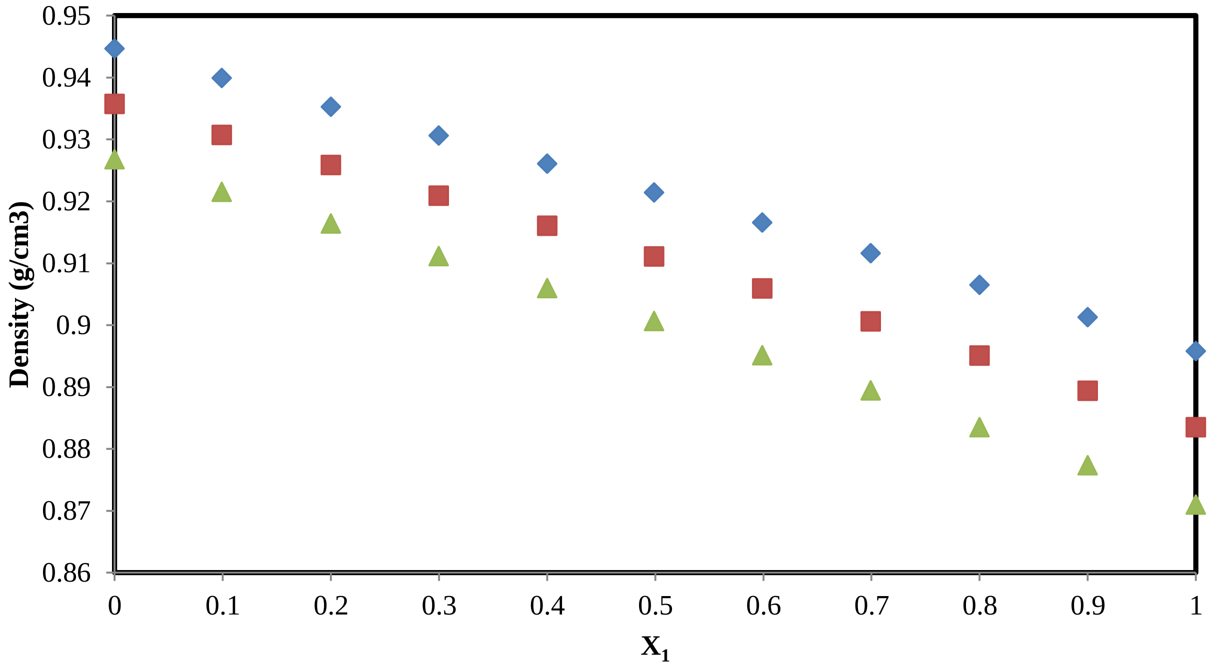
	Density (g/cm^3)		
X_1	**T=298.15K**	**T=308.15K**	**T=318.15K**
0	0.94436	0.93545	0.92649
0.09981	0.94258	0.93340	0.92418
0.1996	0.94088	0.93141	0.92190
0.2992	0.93922	0.92942	0.91958
0.3998	0.93759	0.92746	0.91725
0.4990	0.93590	0.92538	0.91475
0.6000	0.93424	0.92328	0.91220
0.7001	0.93254	0.92108	0.90946
0.8001	0.93087	0.91887	0.90669
0.8959	0.92915	0.91657	0.90376
1	0.92719	0.91388	0.90032



A50: Density against mole fraction for the methyl acetate (1) and cyclohexanone (2) mixtures at various temperatures: ◆ 298.15K, ■ 308.15K and ▲ 318.15K.

A51: Showing density measurements at various temperatures of 298.15K, 308.15K and 318.15K for ethyl acetate (1) and cyclohexanone (2) mixtures.

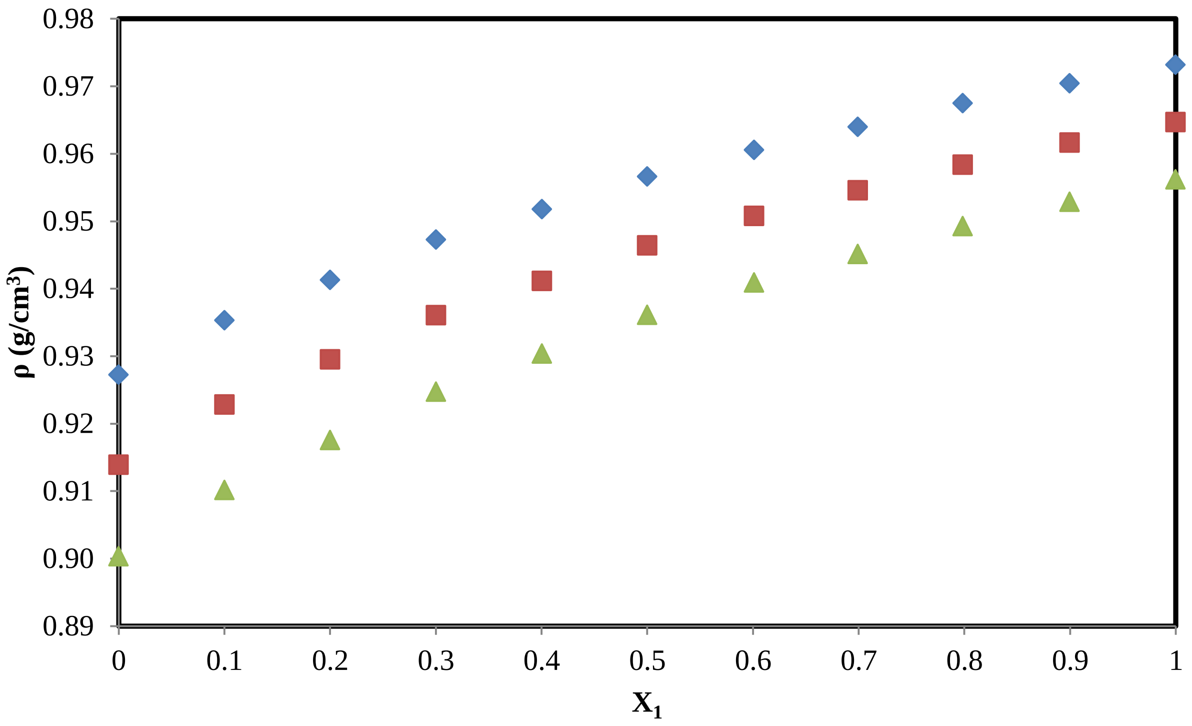
	DENSITY (g/cm^3)		
X_1	**T=298.15K**	**T=308.15K**	**T=318.15K**
0	0.94467	0.93574	0.92677
0.0991	0.93990	0.93074	0.92152
0.2000	0.93529	0.92586	0.91639
0.2998	0.93060	0.92090	0.91114
0.4001	0.92605	0.91605	0.90598
0.4991	0.92140	0.91108	0.90066
0.5992	0.91656	0.90591	0.89514
0.6994	0.91160	0.90057	0.88943
0.7999	0.90650	0.89508	0.88350
0.9001	0.90126	0.88937	0.87734
1	0.89580	0.88349	0.87099



A52: Density against mole fraction for the ethyl acetate (1) and cyclohexanone (2) mixtures at various temperatures: ◆ 298.15K, ■ 308.15K and ▲ 318.15K.

A53: Showing density measurements at various temperatures of 298.15K, 308.15K and 318.15K for cycloheptanone (1) and methyl acetate (2) mixtures.

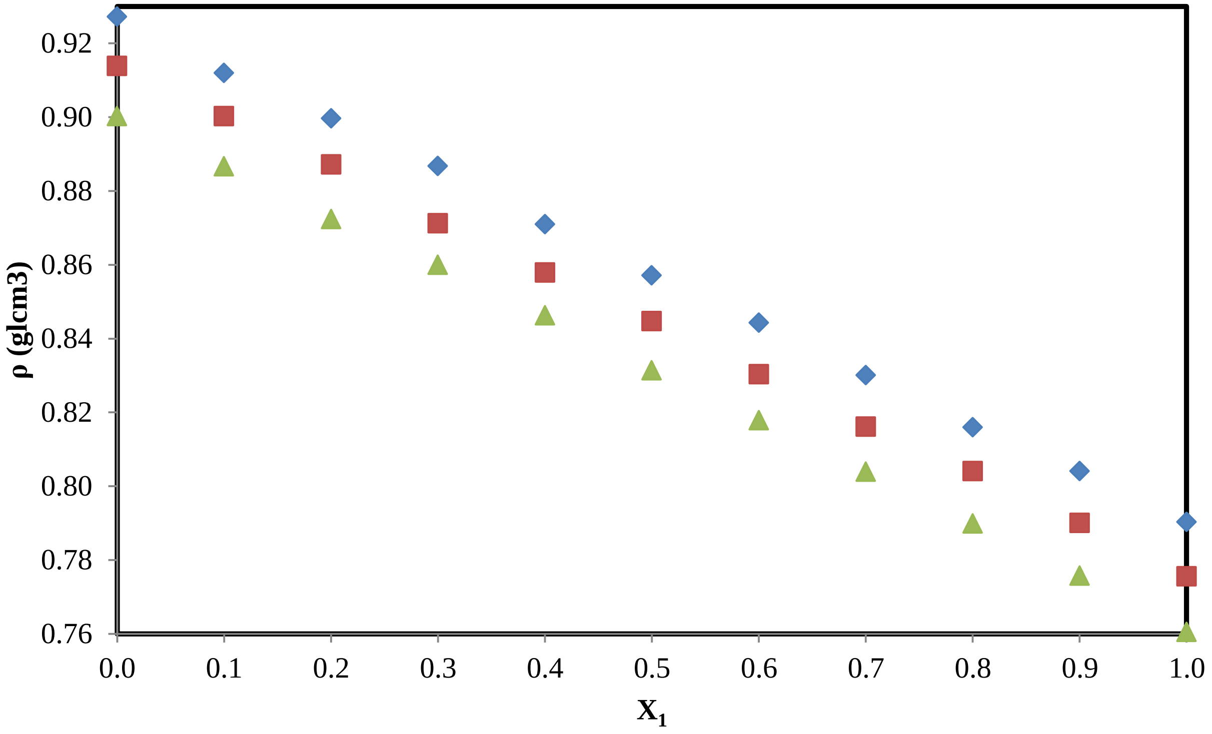
	DENSITY (g/cm^3)		
X_1	**T=298.15K**	**T=308.15K**	**T=318.15K**
0	0.92721	0.9139	0.90033
0.1001	0.93528	0.9228	0.91014
0.1999	0.94128	0.92949	0.91754
0.3001	0.94723	0.93604	0.92473
0.4003	0.95176	0.94111	0.93036
0.4999	0.9566	0.9464	0.93612
0.6012	0.96052	0.95074	0.94091
0.6993	0.96394	0.95455	0.94511
0.7987	0.96745	0.95838	0.94926
0.8996	0.97041	0.96164	0.95284
1	0.97318	0.96467	0.95619



A54: Density against mole fraction for the cycloheptanone (1) and methyl acetate (2) mixtures at various temperatures: ◆298.15K, ■ 308.15K and ▲ 318.15K.

A55: Showing density measurements at various temperatures of 298.15K, 308.15K and 318.15K for acetone (1) and methyl acetate (2) mixtures

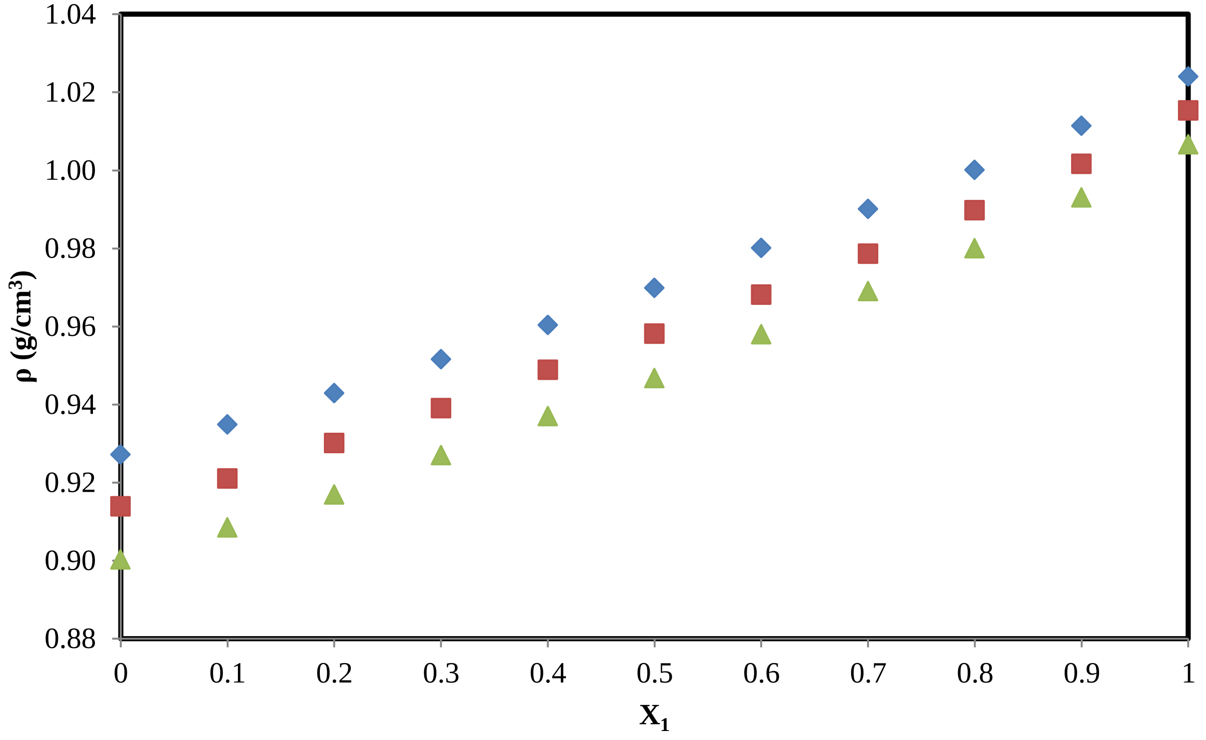
	Density (g/cm^3)		
X_1	**T=298.15K**	**T=308.15K**	**T=318.15K**
0	0.9272	0.9138	0.90027
0.09992	0.91194	0.90021	0.88664
0.2003	0.89959	0.88717	0.87231
0.3000	0.88675	0.87122	0.85995
0.4002	0.87093	0.85782	0.84625
0.5000	0.85711	0.84468	0.83134
0.6000	0.84428	0.83029	0.81781
0.7000	0.83004	0.81605	0.80389
0.8000	0.81595	0.80406	0.78982
0.9000	0.80404	0.79005	0.77569
1	0.79027	0.77557	0.76047



A56: Density against mole fraction for the acetone (1) and methyl acetate (2) mixtures at various temperatures: ◆ 298.15K, ■ 308.15K and ▲ 318.15K.

A57: Showing density measurements at various temperatures of 298.15K, 308.15K and 318.15K for acetophenone (1) and methyl acetate (2) mixtures

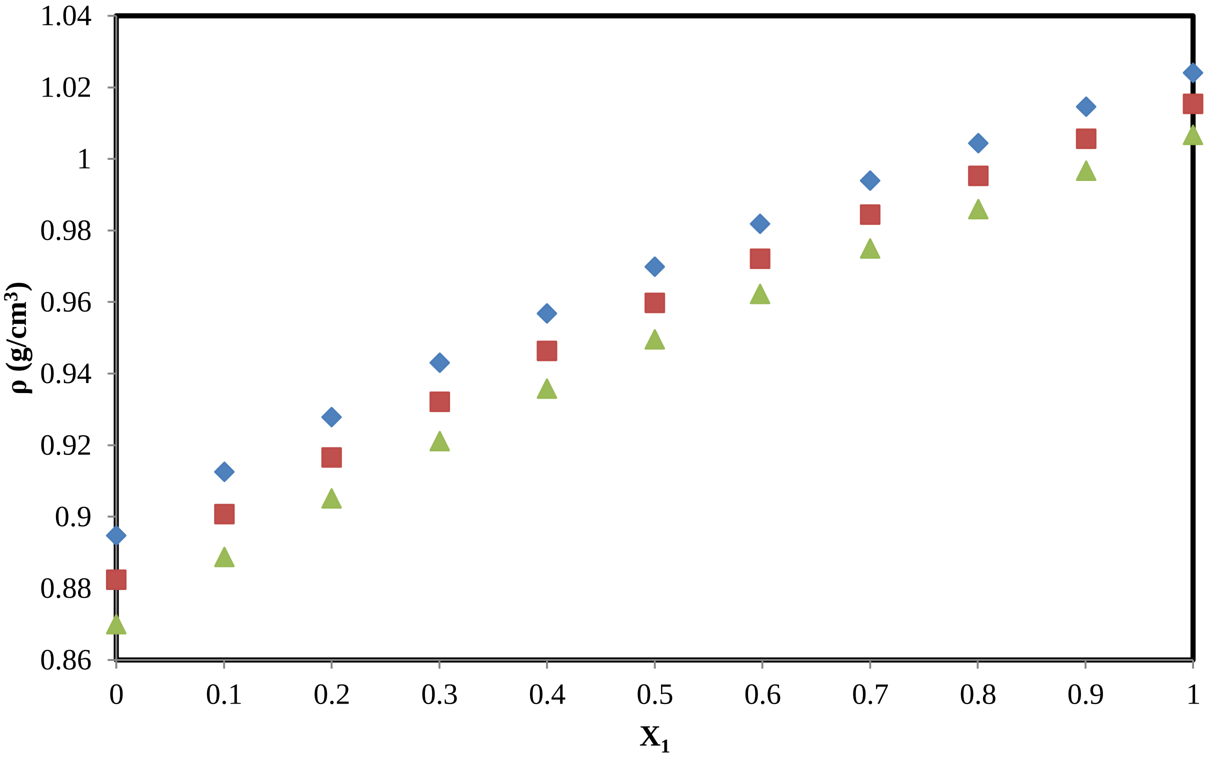
	Density (g/cm^3)		
X_1	**T=298.15K**	**T=308.15K**	**T=318.15K**
0	0.92719	0.91385	0.90031
0.1000	0.93487	0.92098	0.90843
0.2001	0.94289	0.93008	0.91694
0.3000	0.95161	0.93905	0.92702
0.4000	0.96031	0.94884	0.93701
0.4999	0.96982	0.95809	0.94671
0.5999	0.98009	0.96816	0.95798
0.7000	0.99007	0.97862	0.96901
0.8000	1.00012	0.98976	0.98001
0.9000	1.01142	1.00166	0.99301
1	1.02401	1.01531	1.00663



A58: Density against mole fraction for the acetophenone (1) and methyl acetate (2) mixtures at various temperatures: ◆298.15K, ■ 308.15K and ▲ 318.15K.

A59: Showing density measurements at various temperatures of 298.15K, 308.15K and 318.15K for acetophenone (1) and ethyl acetate (2) mixtures**.**

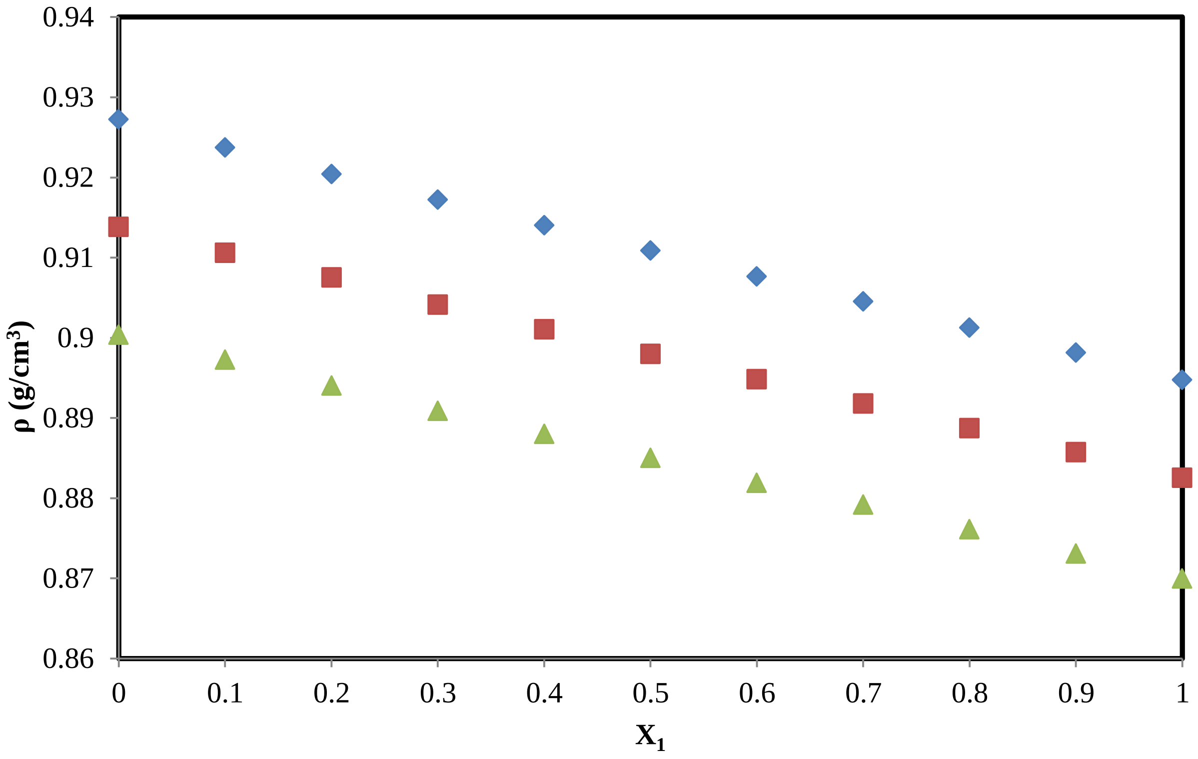
	Density (g/cm^3)		
X_1	**298.15k**	**308.15k**	**318.15k**
0	0.89471	0.8824	0.86992
0.1005	0.91247	0.9007	0.88874
0.2002	0.9278	0.91651	0.90508
0.3006	0.94304	0.93213	0.92112
0.4002	0.95679	0.94631	0.93576
0.5002	0.96982	0.9597	0.94952
0.5981	0.98185	0.97205	0.96221
0.7001	0.9939	0.98443	0.97491
0.8007	1.00439	0.9952	0.98597
0.9007	1.01456	1.00563	0.9967
1	1.02404	1.01537	1.00667



A60: Density against mole fraction for the acetophenone (1) and ethyl acetate (2) mixtures at various temperatures: ◆298.15K, ■ 308.15K and ▲ 318.15K

A61: Showing density measurements at various temperatures of 298.15K, 308.15K and 318.15K for ethyl acetate (1) and methyl acetate (2) mixtures

	Density (g/cm^3)		
X_1	**T=298.15K**	**T=308.15K**	**T=318.15K**
0	0.92721	0.91381	0.90035
0.1001	0.9237	0.91057	0.89724
0.2000	0.92039	0.90752	0.89402
0.3000	0.91719	0.90411	0.89087
0.4000	0.914	0.90103	0.888
0.5000	0.91085	0.89798	0.88501
0.6000	0.90765	0.89484	0.88189
0.7000	0.90452	0.89178	0.87919
0.8000	0.90124	0.88871	0.87612
0.9000	0.89812	0.88572	0.87309
1	0.89476	0.88251	0.86997



A62: Density against mole fraction for the ethyl acetate (1) and methyl acetate (2) mixtures at various temperatures: ◆ 298.15K, ■ 308.15K and ▲ 318.15K