Experimental Study to Predict the Excess Thermal Properties for Ternary Systems of Toluene with Normal Alkanes at Various Temperatures

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Abstract:

This study is concerned with the prediction and calculation of thermodynamic properties for ternary mixtures of Toluene with n-alkanes. An experimental database was established for this purpose, the database consists of density and dynamic viscosity for three mixtures.Densities and dynamic viscosities have been measured for the ternary systems of

(Toluene + n-hexane + n-decane, Toluene + n- hexane + n- dodecane, and Toluene + n- hexane + n- hexadecane) over the entire range of mole fraction at temperatures 293.15, 308.15, and 323.15 K and atmospheric pressure by using Anton Paar SVM 3000. Densities, kinematic viscosities, excess volume, excess viscosities and excess activation energies of viscous flow were reported for ternary mixtures of toluene + n-hexane + n-decane + n-dodecane + hexadecane at difference temperatures and mole fraction range to understand the effect of both carbon atom number and temperature.

Keywords: Excess properties, Density, Viscosity, Alkanes, Liquid ternary mixtures.

Introduction:

Liquid viscosity and liquid density are key properties in the design of oil extraction and processing. Knowledge of the viscosity of pure liquids and mixtures is important for practical and theoretical purposes. The viscosity of liquid mixtures is an invaluable data for the chemical engineer in the design and optimization of industrial processes. The liquid solutions are often more easily dealt with through properties that measure their deviation, not from ideal gas behavior, but from ideal solution behavior. The excess function is a measure of deviation from the ideal behavior of the mixture, and found to be highly sensitive towards molecular interactions between the component molecules of liquid mixture. The sign and magnitude of these excess functions from ideal depends on the strength of interaction between unlike molecule(Dikko et al 2014, and Smith et al. 2005).

Knowledge of thermodynamic and transport properties of multicomponent liquid systems is essential in many industrial applications. Experimental viscosity data and methods for the estimation of viscosities of multicomponent mixtures are not only of theoretical but also of great practical interest. Although a number of predictive equations are available for estimating thermodynamic excess properties (excess volume, excess enthalpy and excess activation energy) of multicomponent system, such methods are rarely used for viscosity (Morrison and Boyd, 1973).

However, many empirical or semi-empirical equations can correlate viscosity data of binary mixtures using several adjustable parameters. The literature of correlations of flow properties for ternary and multicomponent liquid mixtures is rather limited. Recently, the empirical and semi-empirical equations for binary mixtures were extended to ternary mixtures by introducing a ternary parameter; also, new models have been developed for the prediction of viscosities of mixtures. Some of them are based on a molecular approach, while others are based on the group contribution concept. The first type of modules require binary interaction parameters for each binary system present in the multicomponent mixture, but no ternary (or higher) constants are generally needed. Ternary mixture has been studied in second part literature(Dominguez, et al., 2000).

The possible existence of two or more liquid phases simultaneously must frequently be considered in process applications of phase equilibrium if limited miscibility occurs unexpectedly, it can be a serious disadvantage; for example, two phase pumping the capacity and efficiency are both adversely affected in distillation columns when two liquid phases exit internally. When two liquid phases occur in process flow streams, extra process steps are required to either keep them well mixed if separation is

not desired or to allow them to settle when phase separation is desired. If limited liquid phase miscibility is expected, however, advantage can be taken of it in process design liquid-liquid extraction is a powerful separation method based entirely on limited liquid miscibility and the high selectivity of the phases between carious components (Arenosa et al., 1972).

In distillation the overhead product may have limited miscibility after condensation. The liquid phase separation properly considered in design and then gives an additional highly selective stage of separation. If isotropic distillation is used, an additional component not present in the feed stream is added to enhance the relative volatility of the key components. Since this extra component (called the entrained) must subsequently be separated from the product, limited liquid miscibility is highly desirable (Barbe, and Patterson, 1980).

The mathematical treatment of liquid-liquid equilibrium is in many ways more complex than that of vapor-liquid equilibrium. The primary reason for the difficulty is that neither phase is ever an ideal solution. Indeed, if an ideal solution exists in the liquid phase, there can never be more than a single liquid phase formed. The excess volume and viscosity of binary mixtures of toluene and n-alkanes were discussed in terms of Flory Patterson theory and the absolute rate and free volume theories. The high and positive excess viscosity (μ^E)and excess activation energy of viscous flow (ΔG^{*E}) for large n-alkanes were attributed to the orientation order in the pure n-alkanes (Alonsu et al., 1983).

Density and viscosities of ternary liquid mixtures of water, methanol, ethanol have been measured at different temperature. From these data the values of various properties, excess volume, excess viscosity, and excess

Gibb's free energy of activation of flow have been determined by (Dikko and Alkasim 2014).

Many works carried out for predicting the excess thermodynamic properties (Vega et al. 1999, Visak et al. 2000, Tourino et al. 2005, Iuloan et al. 2006, Rathore et al. 2006, Vadamalar et al. 2009, EzhilPavai et al. 2011, Dikio et al. 2012, and Dopazo et al 2014), but the mixtures of this work have not been studied so far at such conditions. Knowledge of thermodynamic properties is essential for the proper design of industrial processes, chemical engineering and also for optimizing thermodynamic model/theories development. It is hoped that the present work would help in availability of experimental data for some unknown mixtures to understand its behavior.

Experimental Section:
   1. Materials:

The anhydrous grade n-hexane, n-dodecane, hexadecane and n-decane were obtained from Sigma-Aldrich. The claimed mole fraction purity for these chemicals was greater than 99%. The purity of all samples was ascertained by comparing the values of their measured their measured densities and viscosities with their literature values at 298.15 K. The determined densities and viscosities of pure components agree well with literature values and given in Table (1).

   2. Apparatus and procedure:

A calibration of measuring density and kinematic viscosity by using reference compounds. The purities of the compounds were checked by determining their densities and refractive index at 298.15 K, which were reasonably in accordance with values found in the literature Table (2). The pure components were degassed ultrasonically and dried over molecular

sieves type 4A $^1/_{16}$ in. Precautions were taken such as using samples recently prepared and reducing to a minimum the vapor space in the vessels to avoid preferential evaporation during manipulation error and the subsequent composition errors. Densities and dynamic viscosities have been measured for the ternary systems at different temperatures and atmospheric pressure by using Anton Paar SVM 3000.The experiments have been done in Petroleum Research Center.

Table (1) Densities and Kinematic viscosities of the pure components at 308.15 K in the literatures (Wu et al.1999,and Kumar et al., 1981) and this work.

	$\rho\ (g/cm^3)$		$\nu\ (cSt)$	
Component	Literatures	This work	Literature	This work
n-hexane	0.6906	0.6872	0.4495	0.4428
n-decane	0.7185	0.7185	1.0305	1.0306
n-dodecane	0.7080	0.7082	1.7215	1.7212
n-hexadecane	0.7608	0.7610	3.4925	3.4927
Toluene	0.8534	0.8537	0.6479	0.6477

Table (2) The refractive index (n) at 25°C in the literatures (Reddy, and PrabhakaraRao, 1985) and this work.

	Refractive index (n)	
Component	Literatures	This work
n-hexane	1.37225	1.37227
n-decane	1.49415	1.49414

3. Data analysis:

The study was done to get the excess thermodynamic properties data experimentally for toluene + n-hexane, + n-decane, + n-dodecane, + n-hexadecane mixtures in the binary system. However the study was under

taking three different temperatures 293.15 K, 308.15 K, and 323.15 K for each mixture.

The excess molar volume(V^E), excess viscosity(μ^E), and the excess activation energy (G^{*E}) of viscous flow were calculated from the following equations respectively (Dikko and Alkasim 2014):

$$V_m^E = \frac{\sum_{i=1}^n x_i Mwt}{\rho_m} - \sum_{i=1}^n \frac{x_i Mwt}{\rho_i} \qquad (1)$$

$$\mu^E = ln\mu_m - \sum_{i=1}^n x_i\mu_i \qquad (2)$$

$$G^{*E} = RT(ln\mu_m V_m - \sum_{i=1}^n x_i ln(\mu_i V_i)) \qquad (3)$$

Results and Discussion:

It has been noticed from this study that excess volumes, excess viscosities and excess activation energies change wherever degrees of temperature change as shown in the results and experimental data which has been collected.

The excess molar volume for the ternary mixtures (Toluene + n-hexane + n-decane, Toluene + n- hexane + n-dodecane, and Toluene+ n-hexane + n-hexadecane) have been noticed that positive and increase with increasing of temperature and number of carbon atoms. It can be seen from this study that excess volumes, excess viscosities and excess activation energies change wherever degrees of temperature change as shown in the results which has been collected. For example in Figure (1) the excess volume for mixture (n-hexane + n-decane + toluene) system is negative signal at 293.15 K and it increases by the increasing of the toluene quantity and also in increasing the temperature the change becomes obvious in the

excess volume as it is quite clear at 323.15 K (Dikio et al. 2012, Finkers et al 2011, and Patil et al. 2011) .

It can be seen here the carbon atoms has a clear effect on n-alkane when dissolved with toluene. The compounds have carbon atoms less than 12, the excess volume signal was negative at 293.15 K such as n-hexane and n-decane while the other n-alkane were mostly in positive and it increase by the increase of carbon atoms.

The excess viscosity of viscous flow were calculated from Equation (2) was negative for lower (n<12) and positive for longer n-alkanes (n > 12). The viscosity deviations for all ternary systems are negative over the entire composition range. In fact, negative deviations in viscosity are observed which regularly increase as the size or viscosity of the n-alkane is increased. This reveals that the strength of specific interaction is not the only factor influencing the viscosity deviation of liquid mixtures. The molecular size and shape of the components also play an equally important role (Pavai et al. 2011, Rathore et al. 2006, Iulian et al 2006, and Dopazo et al 2014).

The excess activation energy for ternary system mixtures, it was positive for all the ternary mixtures and all studied temperature and compositions.The predicted dynamic viscosity for the ternary systems of n-alkane + toluene at 293.15 K, 308.15 K, and 323.15 K mild smoothly without distinct extremes from the values of pure toluene to that of n-alkanes. In some cases, it has been noticed un smoothly curves that leads to the un stability of the system and that's meaning the mass transfer still occurred in between the molecules (Dikko et al. 2014, Sameti et al 2011, Vadamalar et al. 2009, and Visak et al 2000).

It can see from this results the change which occurs in excess volume from negative to positive is due to the integration of molecules and

divergence within them. This is because the molecules approached each other and attracted each other in other words occurrence of decreasing in the original volume and in the original viscosity before dissolving the two compounds. When the sign is positive this indicates that the molecules become apart and discordant that leads to volume increase (Vega et al. 1999).
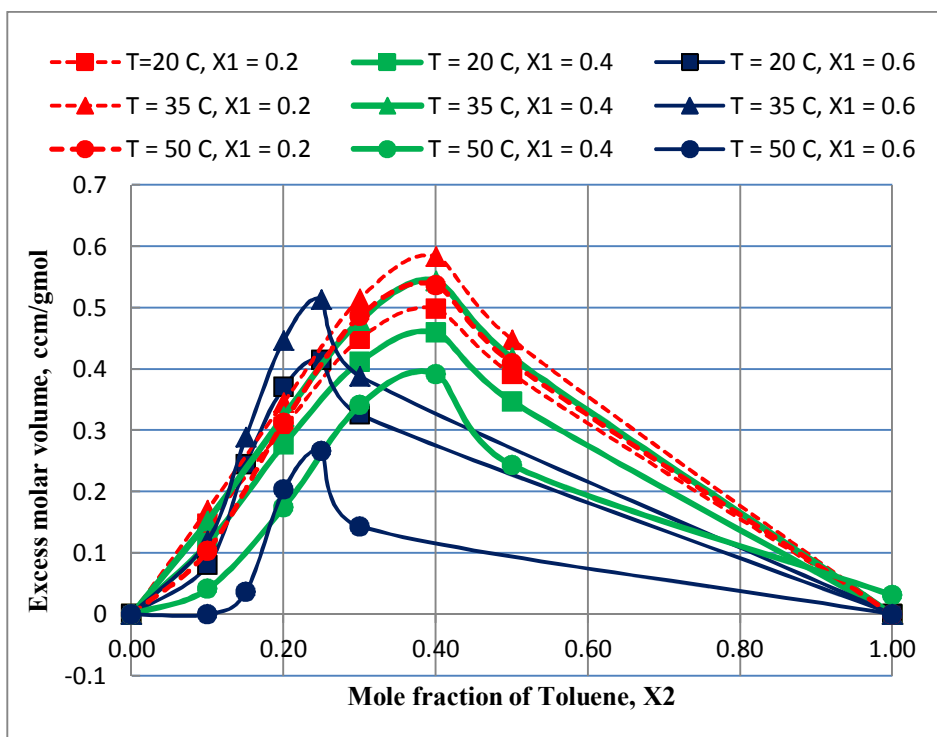

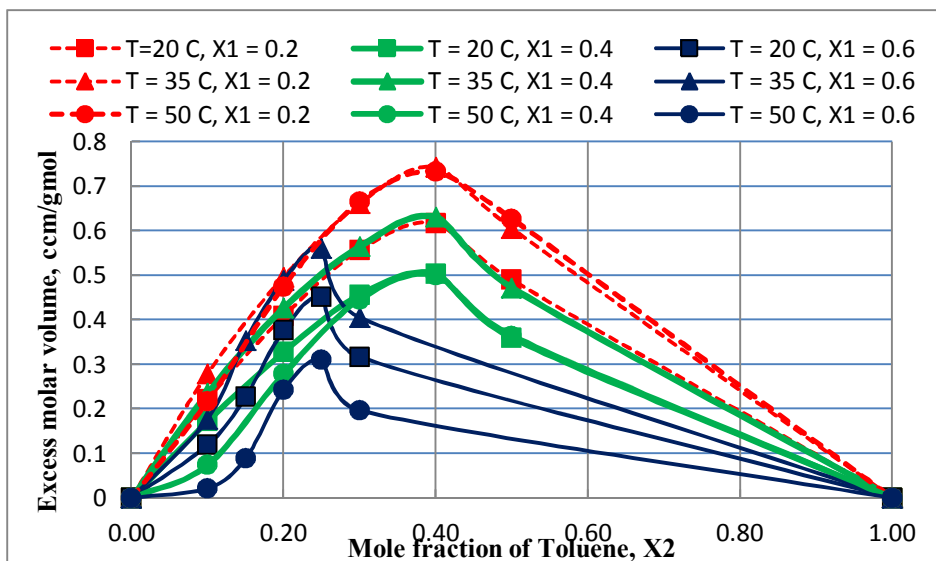**Figure (1) Excess molar volume (cm³/gmol) for ternary mixture X1 n-Hexane + X2 n Decane +X3 Toluene at different temperatures**

Figure (2) Excess molar volume (cm³/gmol) for ternary mixture X1 n-Hexane + X2 n-Dodecane + X3 Toluene at different temperatures
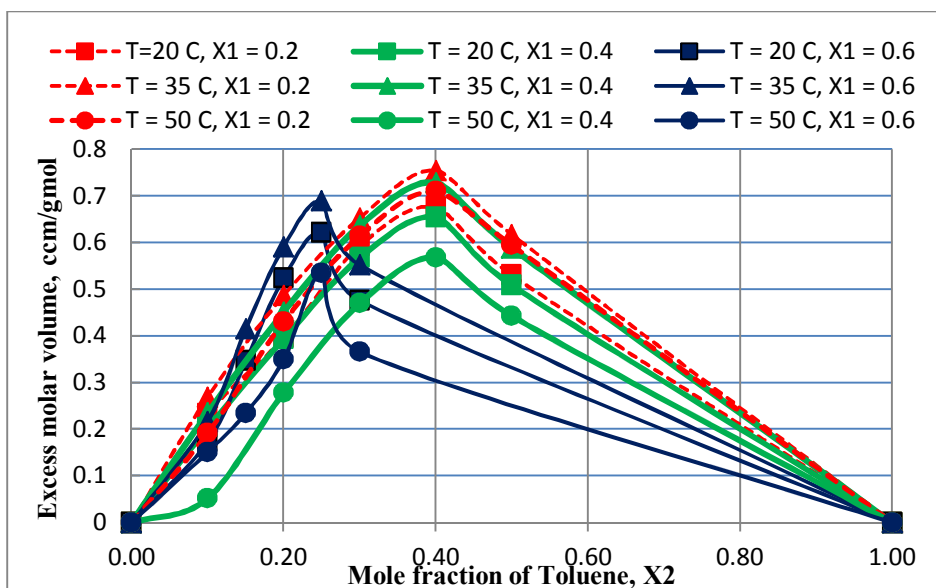
Figure (3) Excess molar volume (cm³/gmol) for ternary mixture X1 n-Hexane + X2 n-Hexadecane + X3 Toluene at different temperatures
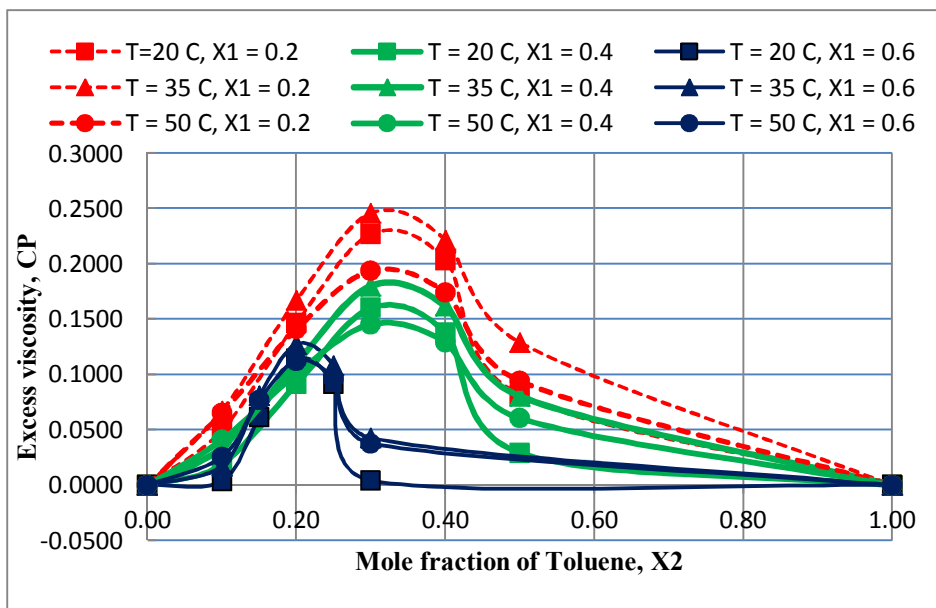
Figure (4) Excess viscosity (CP) for ternary mixture X1 n-Hexane + X2 n-decane + X3 Toluene at different temperatures
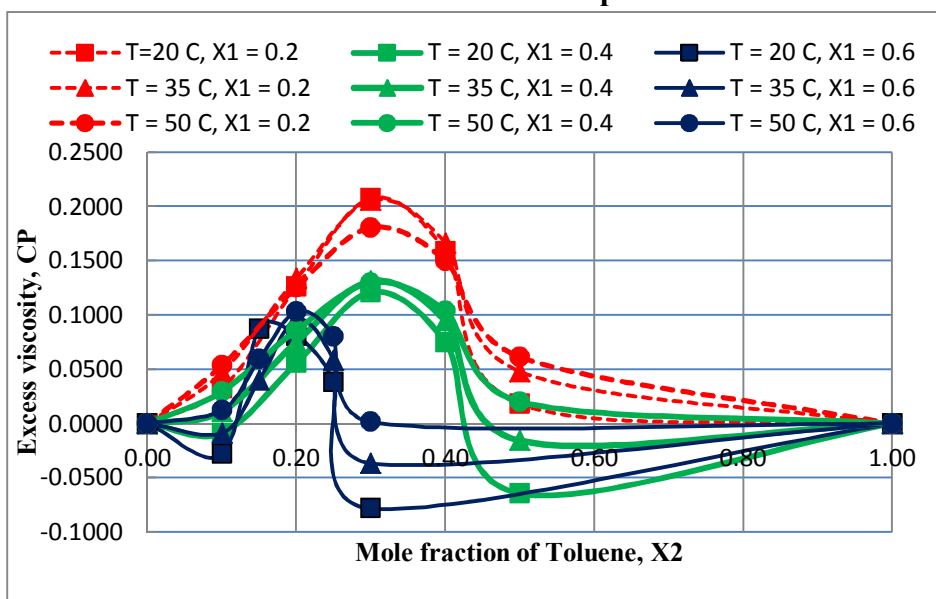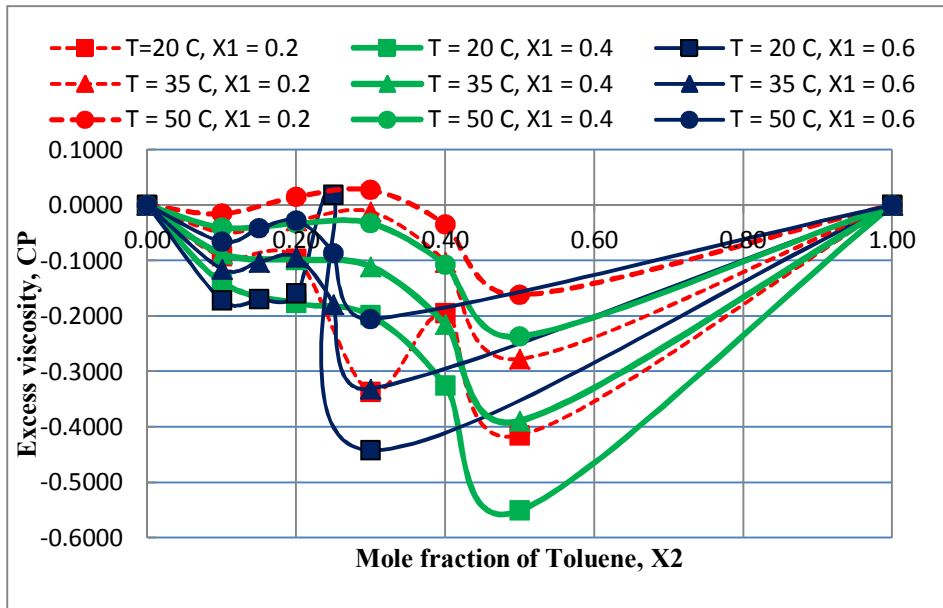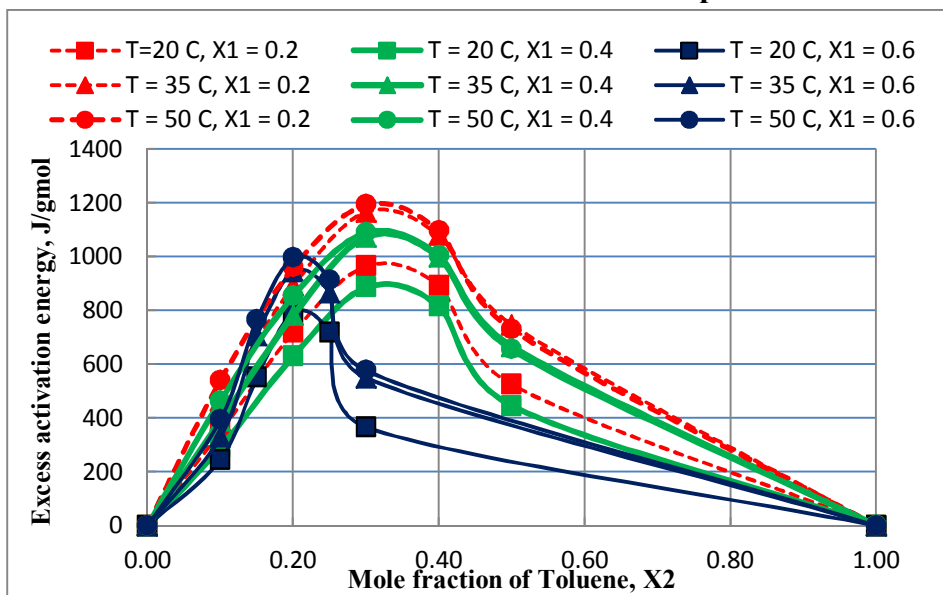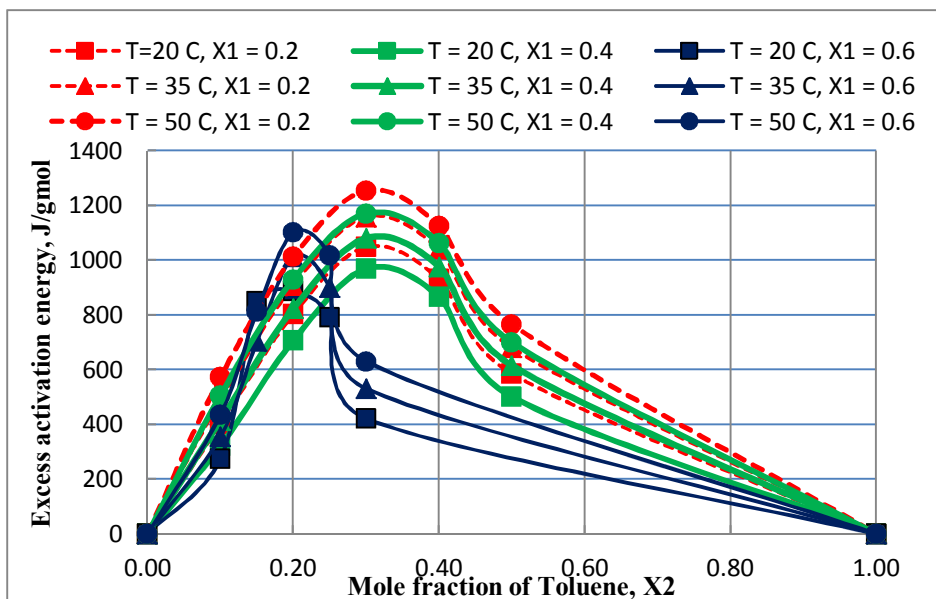

Figure (5) Excess viscosity (CP) for ternary mixture X1 n-Hexane + X2 n-Dodecane + X3 Toluene at different temperature

Figure (6) Excess viscosity (CP) for ternary mixture X1 n-Hexane + X2 n-Hexadecane + X3 Toluene at different temperatures

Figure (7) Excess activation energy (J/gmol) for ternary mixture X1 n-Hexane + X2 n-decane + X3 Toluene at different temperatures

Figure (8) Excess activation energy (J/gmol) for ternary mixture X1 n-Hexane + X2 n-Dodecane + X3 Toluene at different temperatures
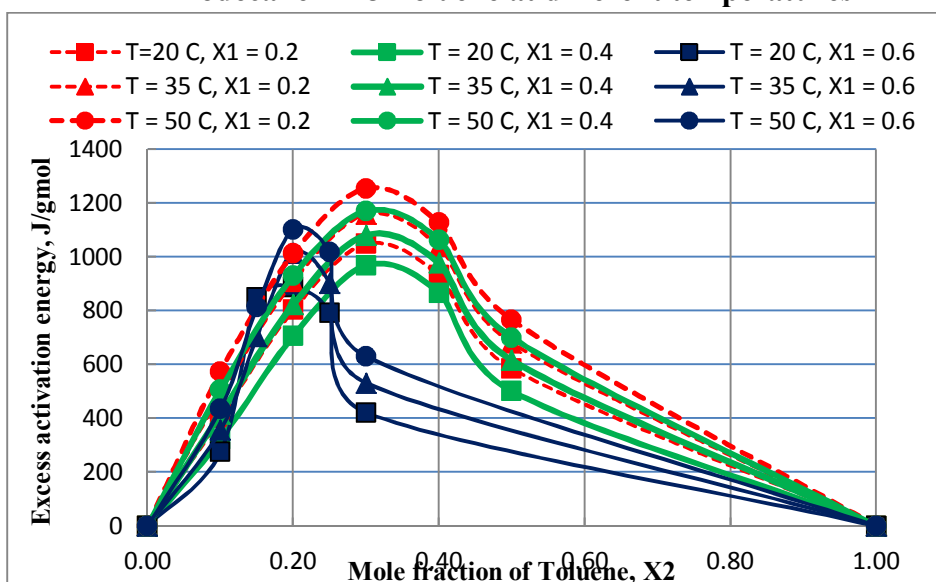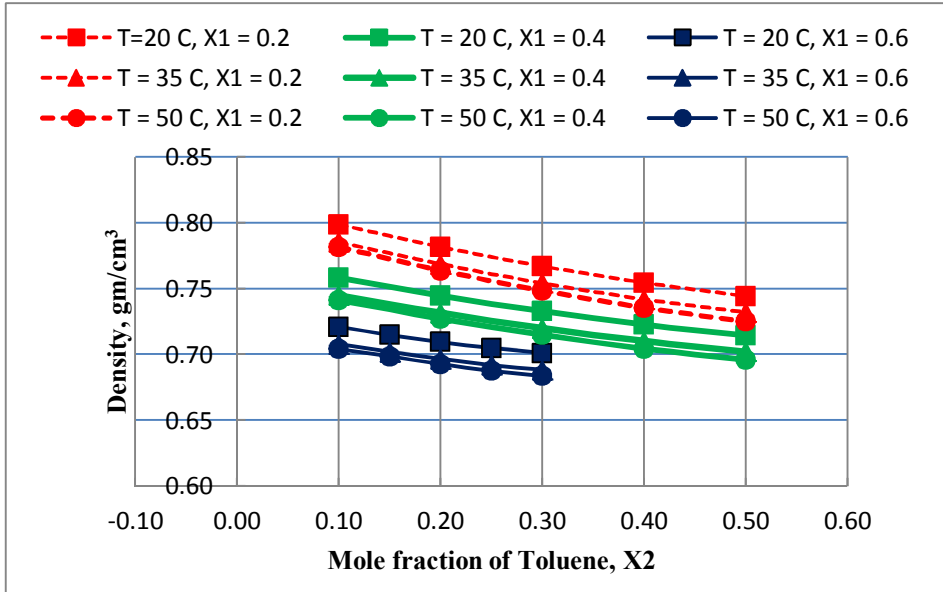

Figure (9) Excess activation energy (J/gmol) for ternary mixture X1 n-Hexane + X2 n-Hexadecane + X3 Toluene at different temperatures

Figure (10) Density (gm/cm³) for ternary mixture X1 n-Hexane + X2 n-decane + X3 Toluene at different temperatures
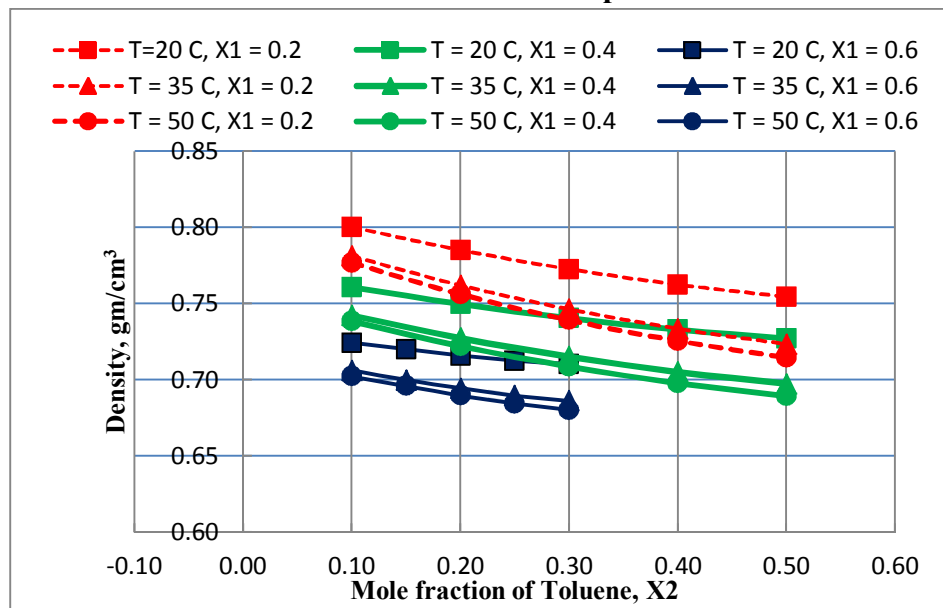

Figure (11) Density (gm/cm³) for ternary mixture X1 n-Hexane + X2 n-Dodecane + X3 Toluene at different temperatures
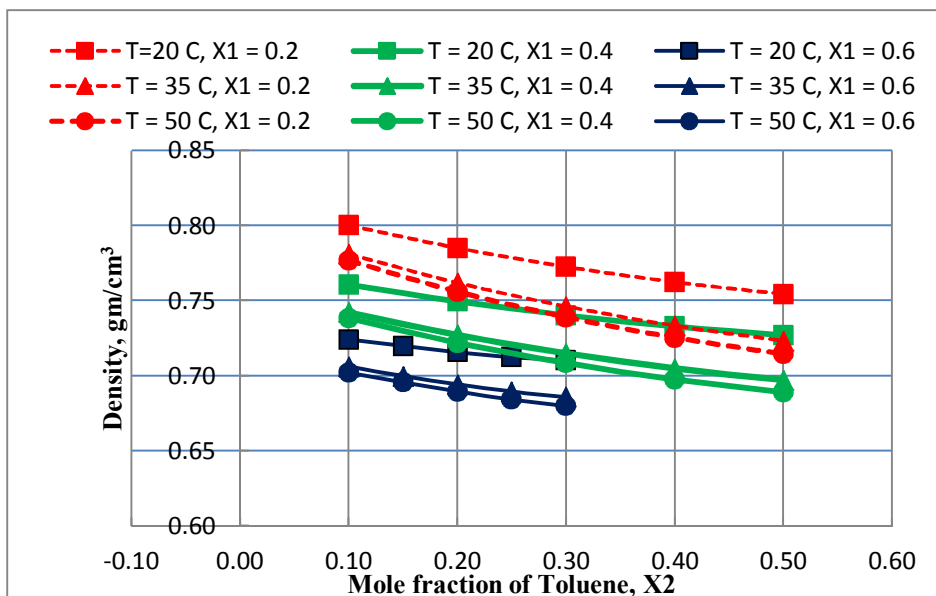
Figure (12) Density (gm/cm³) for ternary mixture X1 n-Hexane + X2 n-Hexadecane + X3 Toluene at different temperatures
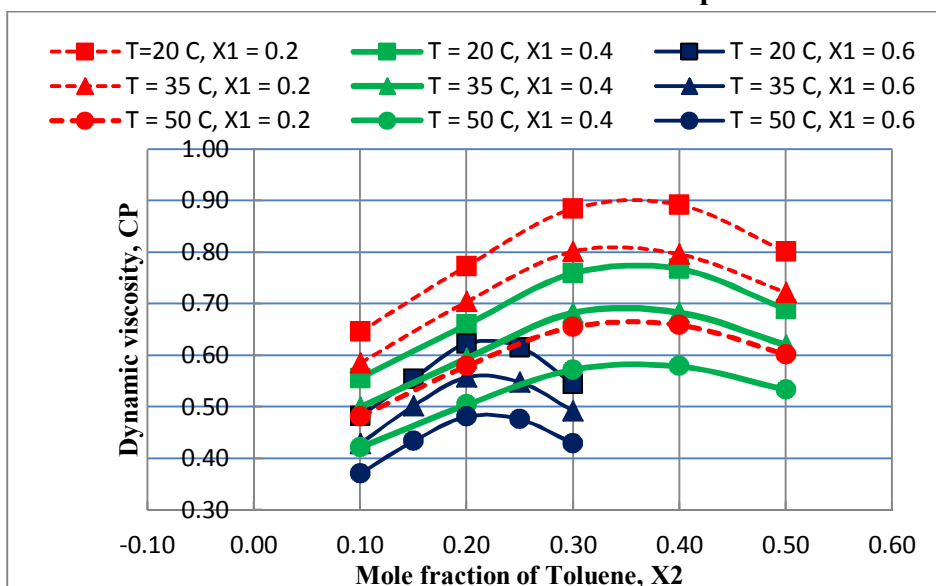

Figure (13) Dynamic Viscosity for ternary mixture X1 n-Hexane + X2 n-decane+ X3 Toluene at different temperatures
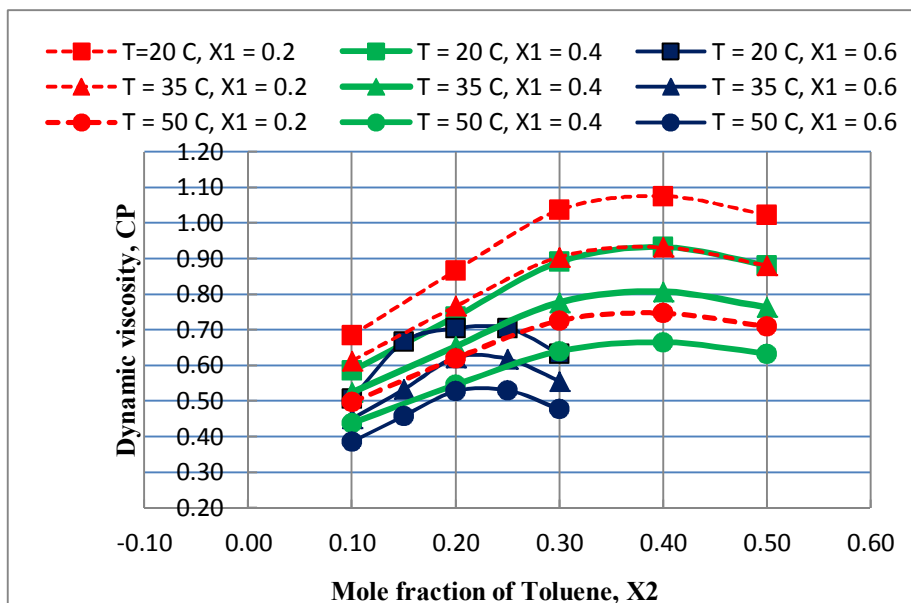
Figure (14) Dynamic Viscosity for ternary mixture X1 n-Hexane + X2 n-Dodecane + X3 Toluene at different temperatures
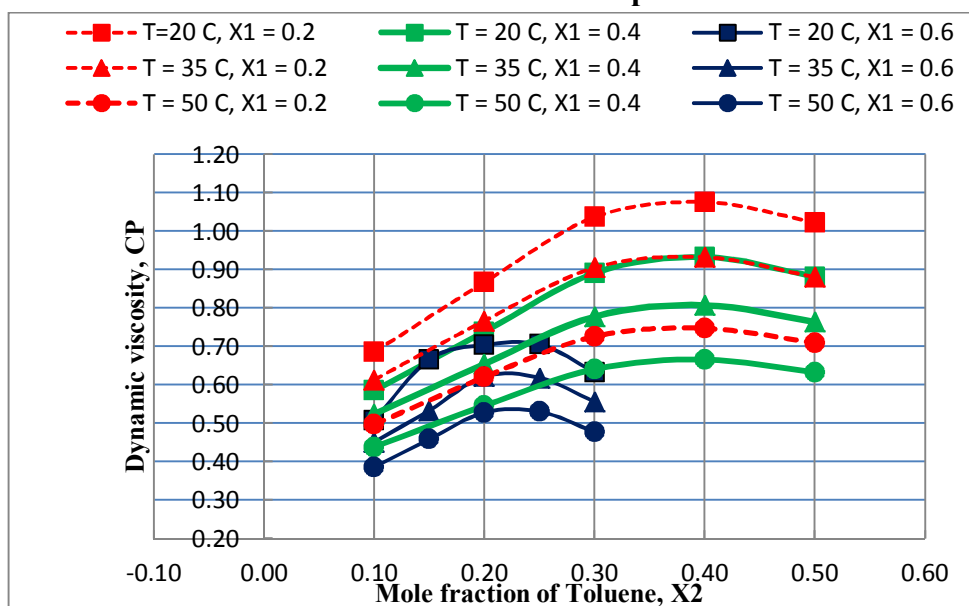

Figure (15) Dynamic Viscosity for ternary mixture X1 n-Hexane + X2 n-Hexadecane + X3 Toluene at different temperatures

Conclusion:

It can be concluded that the change which occurs in excess volume from negative to positive is due to the integration of molecules and divergence within them also excess volumes and excess viscosities with negative sign, this is because the molecules approached each other and attracted each other as well. In other words occurrence of decreasing in the original volume and in the original viscosity before dissolving the three compounds. When the sign is positive this indicates that the molecules become apart and discordant that leads to volume increase. The thermodynamic properties of the solutions for systems were different when the temperature and carbon atom number changed.

Nomenclature:

M^E	= Molar excess property
M	= Molar property
V	= Molar volume
G	= Molar Gibbs free energy
V^E	= Molar excess volume
μ^E	= Excess viscosity
G^{*E}	= Molar excess activation energy
x_i	= Mole fraction of pure compound i
R	= Universal gas constant
μ_m &	= Viscosity of mixture and pure component i
μ_i	respectively
ρ_m&ρ_i	= Density of mixture and pure component i respectively
V_i	= the volume of pure component i
Mw	= Molecular weight of the pure compound

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