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Ministry of Higher Education and Scientific Research

Diyala University / College of Science

Department of Chemistry



**A study binary systems of
cyclohexane and some sugars
at 298.15 k-303.15 k**

Submitted to the Council of the Chemistry Department - College of Science -
Diyala University

to complete the requirements of obtaining bachelor's degree

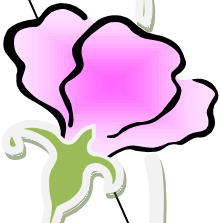
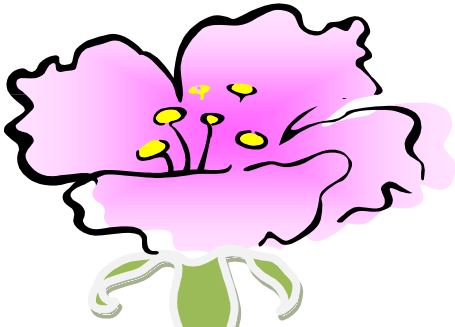
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Gifting



To whom he delivered the message with honesty. and advised the nation with sincerity.

To the Prophet of Islamic nation

..... Mohammad (peace be upon him and his family and chosen companions).

To the commander of the believers,

To the successor and the minister of the messenger of Allah,

To whom that is said "I am the city of knowledge and Ali is its gate" ,

The lion of Allah, Ali bin Abi Talib (peace be upon him).

To my first set example and my cresset which enlightens my path.

To whom God gave him the prestige and dignity.

To whom he taught me the bestowal with no price.

To whom I carry his name with a huge pride

.....My father.

To the angel of my life that pure heart in which it has seen me before her eyes did.

And her guts held me before her hands.

To whom her prayers was my life's success secret, and her compassion is my wound's balm

.....My beloved mother.

To whom their hands moved me forward towards my goals.

To whom their lovely words and favors are all over my heart.

To the most beautiful gems in my life and my God's gift to me

..... My brothers and sisters.

To whom I shared the most beautiful moments in my life with them.

To whom I am going to missand I wish they miss me too.

To my brothers in God and the one's I loved.

.....Students of Chemistry department

To whom their knowledge and their Engineering tools are given to us, to line up our random paths, to remove the obstacles and raise up towards the glory.

.....Our Professors.

To all of you, I dedicate the results of my effort.

NOOR & NOOR

1.1. General introduction:

Acknowledgement of chemical and physical properties of pure liquids and their mixtures is important both academically and industrially. Many industrial processes use mixtures of solvents and knowledge of the subject area is critical to the efficient utilization-preparation development and economic design of appropriate equipment for these processes are only possible if the chemical and physical properties of the solvent or substances to be processed are known. For this reason, the properties furthermore, many attempts have been made to correlate these data using semi-empirical or theoretical approaches considerable programs have also been made in the development of statistical theories. The calculation of physical properties using statistical theories is still not yet possible for complicated molecules such as long chain molecules, because of the range of different conformations, which can occur and the effect of these various structures on the intermolecular interactions⁽¹⁾.

The intensive properties may include density, viscosity (or fluidity) , refractive index, speed of sound and relative

permittivity. The ,practical studies of binary, ternary and quaternary mixtures reveal the importance of molecular interactions (hydrogen bonding, charge-transfer complexes, dipole- dipole, dipole-induced dipole, interstitial accommodate chain alignment ...etc.) on the physical properties of these mixtures⁽²⁾. Knowledge of the mixing properties are useful in design and simulation processes, in the synthesis of pharmaceuticals, lacquers, resins, polymers, oxygenated fuels, and paint . Some of these properties are density, reflective index, and viscosity^(3,4).

1.2. Density:

Density (ρ) refers to the mass contained within a unit volume under specified conditions' ⁽⁵⁾

$$\rho = \frac{w}{v} \dots\dots\dots [1-1]$$

Where:

(ρ) is the density of the solution.

(w) is the weight of the liquid.

(v) is the volume of the liquid, its units (cm^{-3}).

The density is one of the important physical properties which are used to distinguish between the materials with single and multi conditions. The density of the liquid materials is in the middle between the densities of solid and gases, this means that the average space between the molecules of the liquid is larger than the average space of solid and smaller than the average space of gas material .

The density of most liquids decreases on increases temperature. As the liquid is expanded when it is heated,

so its volume increases , then its density decreases specific temperature the density of different liquids are clearly different when considering the relative forces between the molecules. Whenever this force is large, molecules become closer to each other which make density larger .^(6,7)

1.3. Ideal Mixture:

The ideal mixture is a hypothetical one whose properties are introduced into the thermodynamic description of real mixture as convenient standard of normal behavior. There are several definitions of an ideal liquid mixture, one of the most convenient is that it is a mixture in which the chemical potentials of all components are given by the equation:

$$\mu_i(P, T, X) = \mu_i^\circ (P, T) + RT \ln x_i \dots\dots\dots [1-2]$$

$$i=1,2,3,\dots\dots\dots$$

where $\mu_i^\circ (P, T)$ and X_i is the chemical potential and mole fraction of pure component, i , at same pressure and temperature as the mixture being studied.

For an ideal mixture, the molar function of mixing are

given by the molar Gibbs function:

$$\Delta_{\text{mix}} G_m^{id} = RT[X \ln X + (1-X) \ln(1-X)] \dots \dots \dots [1-3]$$

The molar entropy

$$\Delta_{\text{mix}} S_m^{id} = R[-X \ln X + (1-X) \ln(1-X)] \dots \dots \dots [1-4]$$

The molar enthalpy

$$\Delta_{\text{mix}} h_m^{id} = 0 \dots \dots \dots [1-5]$$

The molar volume

$$\Delta_{\text{mix}} v_m^{id} = 0 \dots \dots \dots [1-6]$$

For an ideal mixture the molar Gibbs energy of mixing is negative and the molar entropy of mixing is positive for any value of X mole fraction⁽⁸⁾.

1.4. Molar mixing functions:

The molar function of mixing for a binary mixture [xA+(1-x)B] where X denotes the molar function of A, are defined by:

$$\Delta_{\text{mix}} X_m = X_m - xX_A^* - (1-x)X_B^* \dots \dots \dots [1-7]$$

Where X_m is the molar quantity of binary mixture [XA+(1-X)B] at the temperature T and pressure P and where X_A^* and X_B^* are the molar quantities of the pure substances A and B at same temperature and pressure. X denotes any extensive quantity such as Gibbs free energy (G), enthalpy (H), entropy (S), or volume (V)⁽⁸⁾.

1.5.Excess Function:

Excess partial molar quantities can be written as the difference between the partial molar quantities for the non-ideal mixture and those of an ideal mixture.

It has become customary to use instead of the molar function of mixing $\Delta_{\text{mix}} X_m$, the excess molar function

$$X_m^E = \Delta_{\text{mix}} X_m - \Delta_{\text{mix}} X_m^{\text{id}} \dots \dots \dots [1-8]$$

So that "excess" means excess over ideal.

Thermodynamic function like Gibbs energy, molar polarization, entropy and enthalpy and excess molar volume are used by workers⁽⁹⁻¹¹⁾, in investigating the orientation of molecular dipoles and molecular interaction in binary and ternary mixture in polar-polar, polar-non polar liquids. Payne and Theodorou⁽¹²⁾ have suggested that the excess function are more useful than the thermodynamic functions in interpreting the molecular interactions in such binary mixtures. The miscibility between the two liquids in a mixture is maximum when the molecular interaction between them is more.

1.6. Theories of solution pertaining to volume change on mixing:

Thermodynamic properties of mixtures are most readily determined by experiments carried out under conditions of constant pressure⁽¹³⁾. Yet, most theories of solutions yield thermodynamic properties at constant volume.

The conversion from one set of conditions to the other utilizes the volume change on mixing. Several different theories⁽¹⁴⁾ for mixing at constant volume are possible.

1.7. Corresponding state approaches:

Pitzer⁽¹⁵⁾ is has usually been credited with the formulation of the corresponding states approach in terms of molecular interaction. Many Workere⁽¹⁶⁻²⁰⁾ applied the molecular corresponding state equation to liquid mixtures. Longuet- Higgins⁽²¹⁾ conformal solution equation for volume changes on mixing reduced in the first order to the regular solution equation.

The basic assumption of any corresponding state theory is that the intermolecular potential energy is due to central forces only and has the same form for all pair interactions. The theory is characterized by parameters. $-E$, the energy of a molecular pair at its equilibrium distance, and σ , the collision diameter. For substances which obey the principle of corresponding states a plot of reduced volume $(V/N\sigma^3)$ against the reduced temperature (KT/E) at fixed value of the reduced pressure $(P\sigma^3/E)$ should give the same curve not only for the pure substances A and B, but for A-B mixtures, each of which has suitably averaged E and σ value appropriate to its composition. Usually the Leunard - Jones interaction

potential is used along with the Lorentz-Berthelot combining rules of the A-B interactions.

$$\sigma_{AB} = (1/2)(\sigma_{AA} + \sigma_{BB}) \dots \dots [1-9]$$

and

$$E_{AB} = (E_{AA} E_{BB})^{1/2} \dots \dots [1-10]$$

Kohler⁽²²⁾ does not use the geometric mean rule but develops an equation based on the dispersion forces formula but which does not require acknowledgment of ionization potential for systems with components of similar electronic structure there is little difference between the interaction energies given by Kohler's equations and the geometric mean.

1.8. Literature survey :

The literature indicated to many researches and studies concerned with the thermo dynamic properties of binary mixtures containing hydrocarbons have been studied extensively from both the experimental and theoretical point⁽²³⁻³⁰⁾. Gomez - Ibanez and liu⁽²³⁾ measured the excess volumes for cyclohexane the hexane and n - dodecane at 288.15k, 298.15k and 308.15k using

apycnometer. The experimental results were compared with these predicted from theories of solution resulting in qualitative but not quantitative agreement and these systems are independent of the temperature.

Goateset al⁽²⁹⁻³⁰⁾ measured the excess volumes with the vibrating tube densimeter for cyclohexane + n - hexane, + n -heptane + n - octane + n - nonane, and + n - decane and for n -hexane + n - heptane, + n - octane, + n - nonane, and + n - decane at 283.15k, 298.15k, and 303.15 k. The excess volume increases regularly with the increasing size of the alkyl group of the hydrocarbon.

These studies include the excess molar volumes, excess Gibbs free energy and excess enthalpies⁽³¹⁻³⁸⁾. Recently the excess molar volumes of ternary and quaternary mixtures containing hydrocarbon are reported in the literature⁽³⁹⁻⁴⁴⁾.

Aminabhavi et al.⁽³⁷⁻³⁸⁾, determined the excess molar volumes for the binary mixtures of cyclohexane with hexane, heptane, octane, nonane, dodecane, tridecane, tetradecane and pentadecane at (298.15k, 303.15k and 308.15 k) the results of excess molar volume are

comparable with the available published results at 298.15k.

Shukla et al.⁽⁴⁵⁾, tested the validity for the statistical mechanical concept of Flory for the theoretical prediction of excess volume for three quaternary mixtures containing *n* - alkanes, and they found excellent agreement both in sign and magnitude with experimental values for these systems.

Al-Dujali, A.H.⁽⁴⁶⁾ and Awwad, A.M. excess molar volumes of binary mixtures of an isomer of pentanol + an *n* - alkane at 288.15k, 298.15k, 308.15k and 315.15k. The excess molar volumes V^E of binary mixtures of pentan - 1 - o1 + *n* - hexane, pentan - 2 - o1 + *n* - hexane, pentan - 3 - o1 + *n* - hexane, pentan - 1 - o1 + *n* - decane, pentan - 2 - o1 + *n* - decane, pentan 3 - o1 + *n* - decane were determined from precise density measurement over the whole mole fraction range and at 288.15k, 298.15k, 308.15k and 318.15k in the case of the (pentan 1 - o1 + *n* - hexane) system, V^E volumes are negative excess for mole fraction of less than 0.1 where they become positive V^E volumes are positive over the whole mole fraction

range and all temperatures studied for pentan-2-ol + n-hexane, pentane-3-ol + n-hexane. Pentan-1-ol + n-decane, pentane-2-ol + n-decane + pentan-3-ol + n-decane.

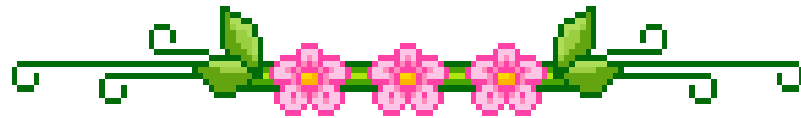
Mier et al.⁽⁴⁷⁻⁴⁸⁾ have studied the excess molar heat capacities C_{pm}^E and excess molar volumes V_m^E of all possible binary and Ternary mixtures from $[x_1 \text{CH}_3(\text{CH}_2)_5\text{CH}_3 + x_2 \text{CH}_3\text{C}(\text{CH}_3)_2\text{-CH}_2\text{-CH}(\text{CH}_3)\text{CH}_3 + x_3 \text{CH}_3\text{C}(\text{CH}_3)_2\text{OC}_2\text{H}_5 + (1-x_1 - x_2 - x_3) \text{C}_2\text{H}_5\text{OH}] \dots(1)$, The experimental results are compared with values calculated for the binary results using Colville's extended Kohler's equation⁽¹⁾.

1-9 Aim of this study

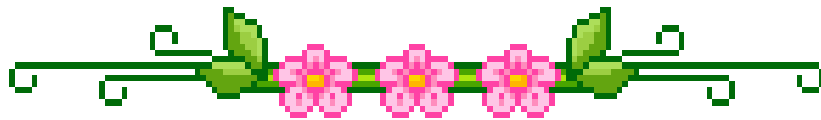
The academic and technological importance of hydrocarbons and sugars their mixtures lead us in this work to investigate excess properties of the binary system mixtures containing cyclohexane and some

sugar The aim of this study is

To get a complete picture on molecular interactions of these mixtures.



chapter two



2.1 Materials :

The chemical materials in this research were reported in table (2-1) with some physical properties and supplies of all chemicals used in this study.

Table (2-1), the chemical materials used in this research and some physical properties.

<i>Substance</i>	<i>Source</i>	<i>M.W</i>	<i>Purity</i>	<i>M.P</i>
<i>Cyclohexane</i>	<i>BDH</i>	<i>84.16</i>	<i>99.9%</i>	<i>6-5 C°</i>
<i>D- Glucose</i>	<i>BDH</i>	<i>182.18</i>	<i>99.9%</i>	<i>146C°</i>
<i>D- lactose</i>	<i>BDH</i>	<i>342.30</i>	<i>99.9%</i>	<i>202.8 C°</i>
<i>D- furactose</i>	<i>BDH</i>	<i>181.15</i>	<i>99.9%</i>	<i>100-104 C°</i>

*These materials were involved in the preparation of the different mixtures used for binary,. It is useful to mention that no additional purifying procedure were done these materials. These materials were kept over the molecular sieves (union carbide 4A) to becom dry before their use. Measurement of density (**p**), of the pure compounds were*

done and the data obtained were compared with the standard values, mentioned in the literatures as shown in table(2-2), This table shows that the results were compatible with these in the literatures and this proves the high standards of our measuring equipments.

Table (2.2): Experimental and Literature Values of Densities ρ , pure component at 298.15k.

<i>Liquid</i>	$P_{obs.}$	$P_{Lit...}$
<i>Cyclohexane</i>	0.816	0.773
<i>Glucose</i>	1.54	1.66
<i>lactose</i>	1.53	1.62
<i>fructose</i>	1.54	1.65

Obs. = observed , Lit. = Literature (87 - 99)

2.2 Mixtures preparation :

All binary, mixtures over the whole mole fraction range $0 < x < 1$ were prepared by mass on a single pan mettler balance (sartorius) in with accuracy of ± 0.0001 g and air tight stoppered bottle pure component liquids were taken separately in glass stoppered bottles. The required volume of each volatile liquid was weighted and transferred directly into an air tight stoppered bottle.

The charged bottle was closed and weighted. The second, and third preparation component liquid was injected to in the bottle through the stopper by means of a syringe respectively. This procedure hindered any vapor loss and contamination. In the preparation of different binary, care was taken to ensure that the same procedure was adopted throughout the present work.

The mole fraction X_i of component liquid (i) in the binary, mixtures was calculated using the following equation:

$$X_i = (W_i / M_i) / \sum_{x=i,j,k,l}^m (W_s / M_s) \dots \dots \dots [2-1]$$

Where :-

W_i and M_i are, respectively the weight in gram and the molecular weight of the component liquid ith. The calculated mole fraction was accurate to $\pm 1 \times 10^{-4}$

2.3.Mode of action

The dissolve (15gm) of glucose in (75 ml) of water .

the system component from two materials (glucose and cyclohexane).

the mixing of materials according to the table (2-3)

. **table (2.3): explaine how to mix materials the reaction .**

No . sample	A1 (ml)	A2 (ml)
1	5	0
2	4.5	0.5
3	4	1
4	3.5	1.5
5	3	2
6	2.5	2.5
7	2	3
8	1.5	3.5
9	1	4
10	0.5	4.5

where

A1= The volume of the first material .

A2= The volume of the second material .

record the weight of the volumetric bottle it empty , after addition ,lucose and after addition cyclohexane .

where

W0= weight volnmetric bottle which is empty .

W1= weight glucose.

W2= weight cyclohexane.

was calculated number of moles and mole fraction by the equation

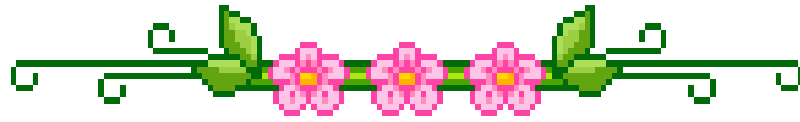
$$x_1 = \frac{n_1}{n_1 + n_2}$$

$$1 - x_1 = x_2$$

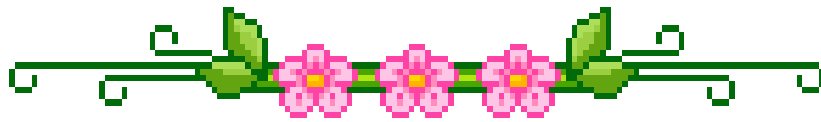
$$n_1 = \frac{w_1}{Mw. t_1} , \quad n_2 = \frac{w_2}{Mw. t_2}$$

and calculated excess molar volume VE by equation

$$V^E (\text{cm}^3 \cdot \text{mol}^{-1}) = \frac{x_1 m_1 + x_2 m_2}{\rho_m} - \frac{x_1 m_1}{\rho_1} + \frac{x_2 m_2}{\rho_2}$$



chapter three



3.1 Results :

3.1.1 Densities (p):

Experimental results of the densities of pure component liquids and the binary mixtures cyclohexane + some *sugar* at 298.15k, 303.15k are listed in table (3-1).

3.1.2 Excess molar volumes, (V_{12}^E):

The excess molar volumes for binary mixtures were calculated from the measured densities using the following expression⁽¹⁰³⁾.

$$V_{12}^E / \text{cm}^3 \cdot \text{mol}^{-1} = \left[\frac{x_1 M_1 + x_2 M_2}{\rho_m} \right] - \left[x_1 \frac{M_1}{\rho_1} + x_2 \frac{M_2}{\rho_2} \right] \dots \dots \dots [3 - 1]$$

Where X_1 , M_1 and ρ_1 are respectively the mole fraction molar mass and density of component (1). X_2 , M_2 and ρ_2 are the mole fraction, mol are mass and density of component (2). ρ_m is the mixture density. The equation [3-1] may be written as:

$$V_{12}^E / \text{cm}^3 \cdot \text{mol}^{-1} = \frac{X_1 M_1 + X_2 M_2}{\rho_m} - X_1 V_1 - X_2 V_2 \dots \dots \dots [3 - 2]$$

Where V_1 and V_2 are the molar volume of liquid 1 and 2.

The obtained results of V_{12}^E are listed in table (3-3) plotted as a function of the mole fraction X_1 at 298.15K - 303.15K (3.1) .

The experimental excess molar volume V_{12}^E ,for cyclohexane Glucose , Lactose and furactose system is negative from ideality at low mole fractions of Glucose .

3.2.Discassion

The experimental excess molar volume V_{12}^E for cyclohexane + some sugars is negative from ideality at Low mole fraetum at 298.15 and 303.15K . This sugyests that globular molecule cyclohexane disturbing the orientational order in. cyclohexane and hydrogen bonding intraction in sugar and result less packed structure . It seems that in addition to the above discussed molecular interactions, the size and molar volume of cyclohexane and sugar could increasc the devation from ideatity with increasing the molar volume of cyclohexane and some sugars .

Figure (3.1) Excess molar volumes V^E versus X_1 for cyclohexane + X₂ Glucose 298.15 K , 303.15K

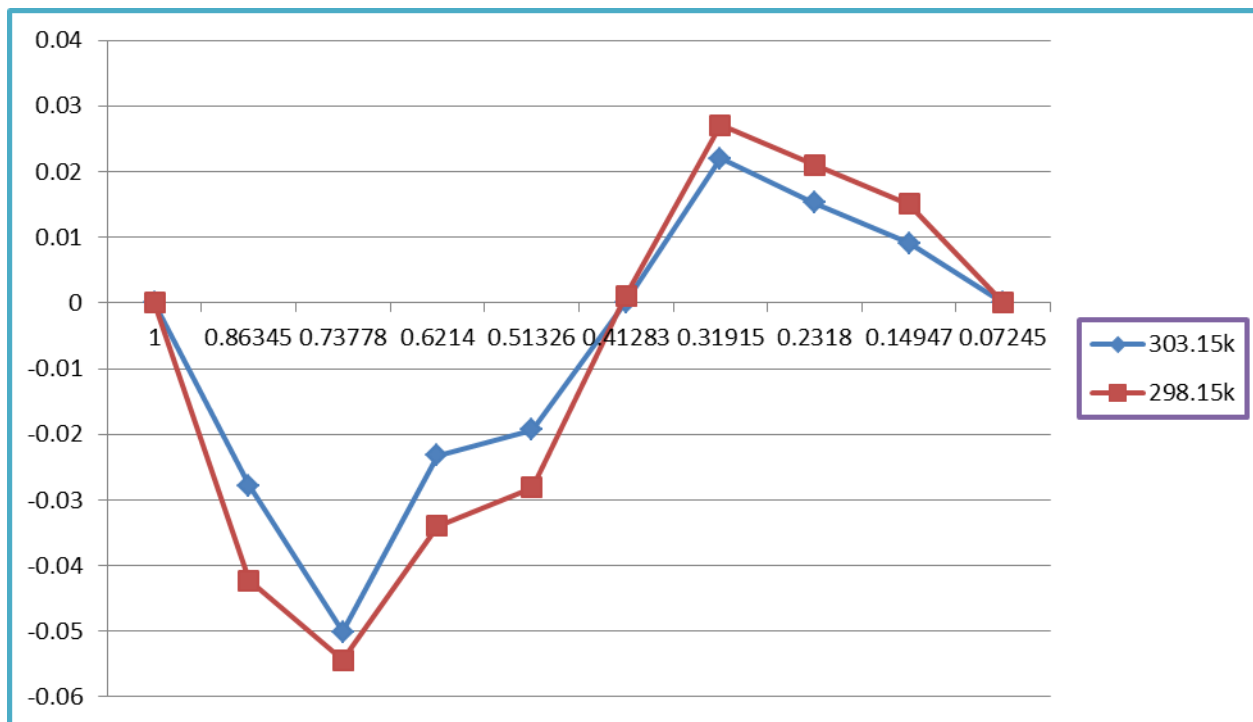
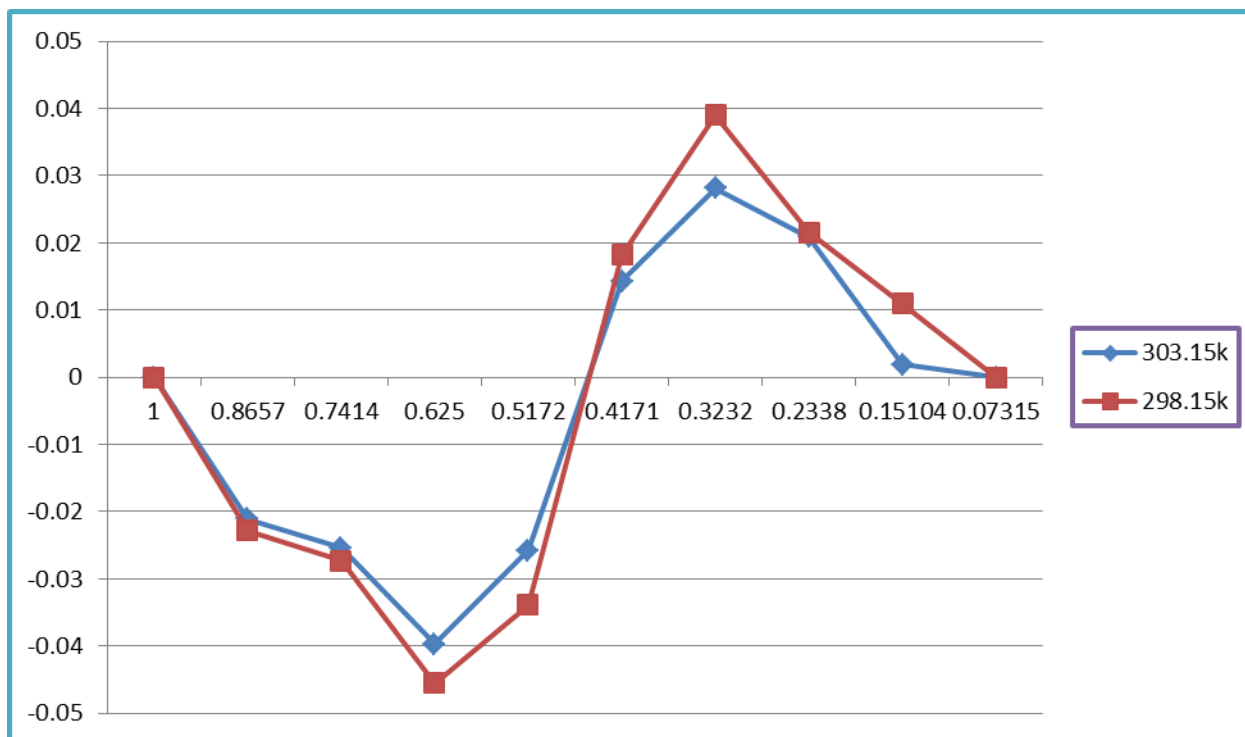


Figure (3.2) Excess molar volumes V^E versus X_1 for cyclohexane + X₂ furactose 298.15 K , 303.15K



**Figure (3.3) Excess molar volumes V_E versus X_1 for
cyclohexane + X2 lactose 298.15 K , 303.15K**

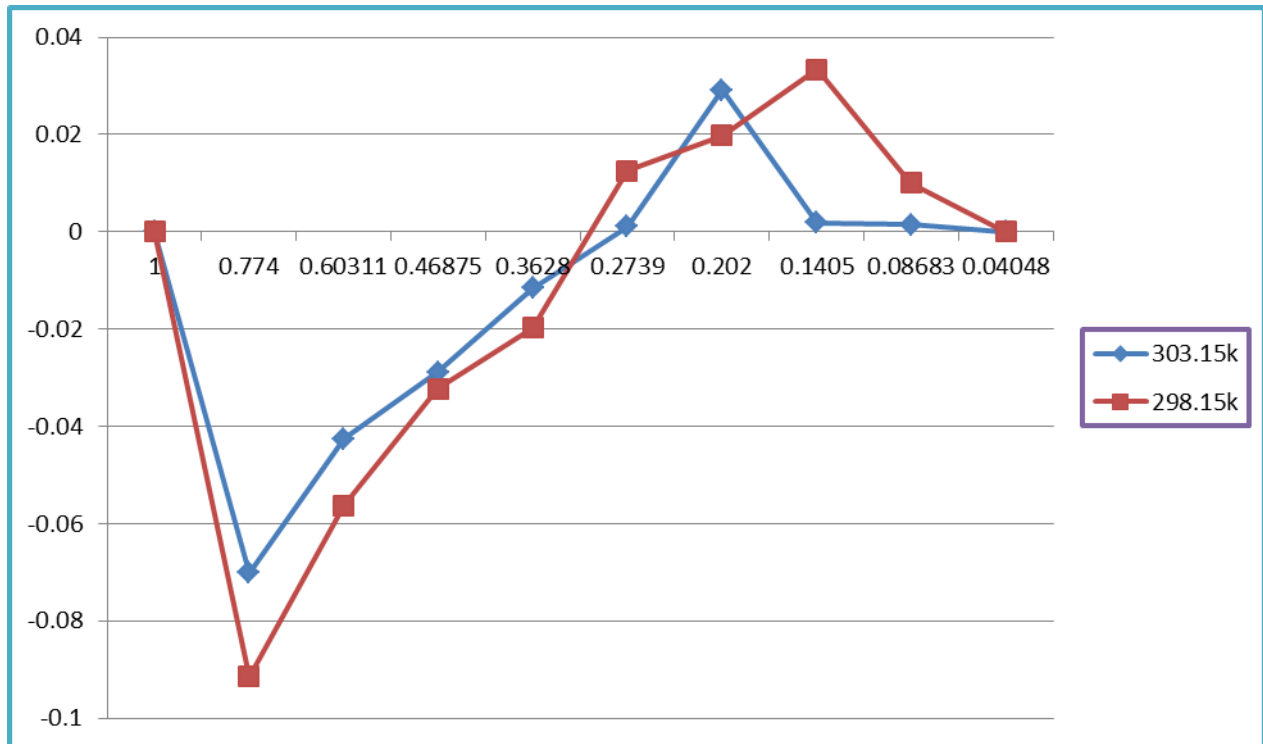


Table (3.1) Experimental values of the densities (ρ) and excess molar volumes (V_{12}^E) for binary mixtures of two temperatures.

X₁ Cyclohexane + X₂ Glucose			
X₁ 303.15K	X₂ 303.15K	ρ (g.cm³) 303.15k	V_{12}^E (cm³.mol⁻¹) 303.15k
1	0	1.046	0.000
0.86345	0.13655	1.02	- 0.0278
0.73778	0.26222	0.994	- 0.0501
0.6214	0.3786	0.968	- 0.0232
0.51326	0.48674	0.942	- 0.0193
0.41283	0.58717	0.916	0.0001
0.31915	0.68085	0.89	0.0220
0.2318	0.7682	0.864	0.0153
0.14947	0.85053	0.838	0.0091
0.07245	0.92755	0.812	0.000

X₁ Cyclohexane + X₂ Glucose			
X₁ 298.15K	X₂ 298.15K	ρ (g.cm³) 298.15k	V_{12}^E (cm³.mol⁻¹) 298.15k
1	0	1.05	0.0000
0.8633	0.1367	1.024	- 0.0423
0.7376	0.2624	0.998	- 0.0544
0.62118	0.37882	0.972	- 0.0340
0.5132	0.4868	0.946	- 0.0281
0.4126	0.5874	0.92	0.0011
0.31855	0.68145	0.894	0.0271
0.2313	0.7687	0.868	0.0210
0.14937	0.85063	0.842	0.0151
0.072398	0.92602	0.816	0.0000

Table (3.2) Experimental values of the densities (ρ) and excess molar volumes (V_{12}^E) for binary mixtures of two temperatures.

X₁ Cyclohexane + X₂ fuructose			
X₁ 303.15K	X₂ 303.15K	ρ (g.cm³) 303.15k	V_{12}^E (cm³.mol⁻¹) 303.15k
1	0	1.06	0.000
0.8657	0.1343	1.033	- 0.0211
0.7414	0.2586	1.005	- 0.0254
0.625	0.375	0.978	- 0.0397
0.5172	0.4828	0.95	- 0.0258
0.4171	0.5829	0.923	0.0143
0.3232	0.6768	0.896	0.0281
0.2338	0.7662	0.868	0.0209
0.15104	0.84896	0.841	0.0019
0.07315	0.92685	0.813	0.000

X₁ Cyclohexane + X₂ fuructose			
X₁ 298.15K	X₂298.15K	ρ (g.cm³) 298.15k	V_{12}^E (cm³.mol⁻¹) 298.15k
1	0	1.064	0.0000
0.865	0.135	1.237	- 0.0228
0.7405	0.2595	1.009	- 0.0273
0.625	0.375	0.982	- 0.0455
0.5176	0.4824	0.954	- 0.0339
0.4159	0.5841	0.927	0.0182
0.3223	0.6777	0.9	0.0390
0.2346	0.7654	0.872	0.0215
0.1517	0.8483	0.845	0.0110
0.07358	0.92649	0.817	0.000

Table (3.3) Experimental values of the densities (ρ) and excess molar volumes (V_{12}^E) for binary mixtures of two temperatures.

X₁ Cyclohexane + X₂ lactose			
X₁ 303.15K	X₂ 303.15K	ρ (g.cm³) 303.15k	V_{12}^E (cm³.mol⁻¹) 303.15k
1	0	1.064	0.000
0.774	0.226	1.036	- 0.0701
0.60311	0.39689	1.008	- 0.0426
0.46875	0.53125	0.981	- 0.0288
0.3628	0.6372	0.953	- 0.0116
0.2739	0.7261	0.925	0.0011
0.202	0.798	0.897	0.0292
0.1405	0.8595	0.869	0.0019
0.08683	0.91317	0.842	0.0015
0.04048	0.95952	0.814	0.000

X₁ Cyclohexane + X₂ lactose			
X₁ 298.15K	X₂ 298.15K	ρ (g.cm³) 298.15k	V_{12}^E (cm³.mol⁻¹) 298.15k
1	0	1.068	0.000
0.7734	0.2266	1.04	- 0.0915
0.6034	0.3966	1.012	- 0.0562
0.47028	0.52972	0.985	- 0.0323
0.36335	0.63665	0.957	- 0.0197
0.2756	0.7244	0.929	0.0126
0.2023	0.7977	0.901	0.0198
0.1402	0.8598	0.873	0.0334
0.08085	0.71315	0.846	0.0101
0.04056	0.9594	0.818	0.000

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