



Study of Physical and Spectral Properties of Quaternary System of 2,5-Hexandione + Cyclopentanol + Cyclohexanol + 3-Heptanol Mixture at 298 K

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Some physical properties (*e.g.*, density, viscosity and refractive index) of quaternary liquid mixture (2,5-hexandione + cyclopentanol + cyclohexanol + 3-heptanol) of different mole fraction of the components have been measured at 298.15 K. From the experimental density, viscosity and refractive index the values of excess volume (V^E), deviation of viscosity ($\Delta\eta$), deviation of refractive index (Δn) and excess free Gibbs energy of activation of flow (ΔG^E) have been calculated. The nature of molecular interactions between the components of liquids mixtures has been explained due to interaction parameters and excess properties. The FTIR spectrum shows a drastic change in the frequency and intensity after mixing of organic compounds at all entire range of mole fraction under study. The shift in the frequency values might be due to H-bonding or dipole-induced dipole interaction.

Keywords: Quaternary system, 2,5-Hexandione, Cyclopentanol, Cyclohexanol, 3-Heptanol, Refractive index.

INTRODUCTION

The importance of studying intermolecular interactions coincides with an ever soaring demand for the predictive equations especially for the multi liquids mixtures forms the basis of the present study. Thermodynamic and physical excess properties in coupling with thermoacoustical parameters are the importance parameters needed to show the physico-chemical characteristics of a system leading to explain of the molecular interactions occur there of. Knowledge of these parameters paves the way for important data relating to process equipments and design.

Excess properties study of solutions help to defect the formation and composition of association from interacting molecules of liquids in them.

The solute-solvent interactions of organic compounds reveal the nature of the compound to undergo hydrogen bonding, dipole change with the type of contributing groups present in the solvent [1-5].

The practical studies of quaternary liquid mixtures which measured of intensive properties such as (viscosity, density, refractive index, speed of sound and relative permittivity) reveal the importance of molecular interactions (hydrogen bonding, dipole-dipole, charge-transfer complexes, dipole-induced dipole, *etc.*) [6].

Some of the intensive properties are density, reflective index and viscosity. Recently, few equations for calculating the excess thermodynamic and other physico-chemical properties of multicomponent mixtures from the intensive properties of their various contributory of the components has been enhanced and applied to various high order component liquid systems [7,8].

Research workers have studied of densities and viscosities of quaternary liquid mixture of 1-propyl alcohol with ethyl alcohol and methyl alcohol and benzene of equal volumes of the components have been measured at 308.15, 313.15, 318.15, 323.15 and 328.15 K. We used the experimental density, viscosity and refractive index values to calculate the excess volume (V^E), excess viscosity (η^E) and excess free Gibbs energy of activation of flow (ΔG^E) values [9].

The researchers were concerned with measurement the densities, viscosities and refractive indices at different temperatures for quaternary mixtures of cyclohexane + *n*-heptane + *n*-decane + *n*-hexane and cyclohexane + 1-pentanol + 3-hexanol + *n*-hexane. From experimental values of densities, refractive indices and viscosities, the excess molar volumes, excess refractive indices and excess viscosities were determination for quaternary liquid mixtures. The Flory theory has been applied for the theoretical prediction of excess molar volume and refractive indices of quaternary liquids mixtures studied here depending on the pure component liquid parameters [10].

The main purpose of the study of excess and spectral properties is to characterize the molecular interactions in the quaternary system (2,5-hexandione + cyclopentanol + cyclohexanol + 3-heptanol).

EXPERIMENTAL

Pure samples used without further purification. The degree of purity, molar mass and the name of the supplying company for these samples were listed in Table-1.

TABLE-1
CHEMICAL MATERIALS USED WITH THEIR DEGREE OF PURITY, MOLAR MASS AND NAME OF THE SUPPLIER

Chemical material	Degree of purity (%)	Molar mass (g/mol)	Name of supplier
2,5-Hexandione	98	114.15	Merck
Cyclopentanol	99	86.13	Riedel-De Haen AG
Cyclohexanol	95	100.16	Fluka
3-Heptanol	99	116.2	Riedel-De Haen AG

The liquids were mixed due to a different mole fraction of components and kept in well-stoppered bottles to ensure good thermal equilibrium. The densities and viscosities of the pure liquids (2,5-hexandione, cyclopentanol, cyclohexanol and 3-heptanol) and their mixtures were measured by using density bottle and Oswald's viscometer at 298 K, respectively. The viscometer was put for 30 min in the water-bath under thermostatically controlled [11] to obtain constant temperature. The measurements of flow time of the pure liquid and their mixtures by the viscometer were made at least three times for each pure liquid and liquids mixtures at 298 K studied. The average of three readings of time of flow of each liquid or mixture were used in determining the corresponding viscosity, whereas the densities of the liquids and liquid mixtures were determined using the formula:

$$\text{Density} = \frac{\text{Mass of liquid or liquid mixture}}{\text{Volume of density bottle}}$$

Refractive index of the pure component liquids and quaternary liquid mixtures was measured at 298.15 K using an Abbe refractometer (Tafesa) by the reflection method using sodium line ($\lambda = 5893 \text{ \AA}$) with a precision of the reading (± 0.0002). In all measurements for this study, the temperature was kept constant with in $\pm 0.01 \text{ K}$ using as Chott-Gerate (T1150) ther-

mostat water bath and a Hewlett-Packard model 201 a quartz thermometer.

The FTIR spectrum of the quaternary liquids mixtures at different mole fraction range were recorded in the frequency range $4000\text{--}400 \text{ cm}^{-1}$ employing Shimadzu model 1800 FTIR spectrometer.

RESULTS AND DISCUSSION

Measured value of the densities, viscosity and refractive index of the pure compounds and quaternary mixtures 2,5-hexandione + cyclopentanol + cyclohexanol + 3-heptanol at 298.15 K are listed in Tables 2 and 3.

TABLE-2
EXPERIMENTAL VALUES OF DENSITY (ρ), VISCOSITY (η) AND REFRACTIVE INDEX (n) FOR PURE SUBSTANCES AT 298.15 K

Pure substances	$\rho \text{ (g/cm}^3\text{)}$	$\eta \text{ (mpoise)}$	$n \text{ (cm}^3\text{/mol}^{-1}\text{)}$
2,5-Hexandione	1.02228	1.2845	1.454
Cyclopentanol	0.94384	5.7817	1.4321
Cyclohexanol	1.00012	23.4868	1.4645
3-Heptanol	0.81973	4.0569	1.424

The excess molar volume, deviation of viscosity and deviation of refractive index were calculated from density, viscosity and refractive index measurements according to the following eqns. 1-3 [12-14]:

$$V^E = \frac{(x_1 M_1 + x_2 M_2 + x_3 M_3 + x_4 M_4)}{\rho_{\text{mix}}} - \frac{(x_1 M_1)}{\rho_1} - \frac{(x_2 M_2)}{\rho_2} - \frac{(x_3 M_3)}{\rho_3} - \frac{(x_4 M_4)}{\rho_4} \quad (1)$$

$$\Delta\eta_{\text{mix}} = \eta_{\text{mix}} - x_1 \eta_1 - x_2 \eta_2 - x_3 \eta_3 - x_4 \eta_4 \quad (2)$$

$$n^E = n_{\text{mix}} - x_1 n_1 - x_2 n_2 - x_3 n_3 - x_4 n_4 \quad (3)$$

where x_1 , M_1 , ρ_1 and η_1 are the mole fraction, molar mass, density and viscosity of pure component (1), respectively. x_2 , M_2 , ρ_2 and η_2 are the mole fraction, molar mass, density and viscosity of pure component (2) respectively, x_3 , M_3 , ρ_3 and η_3 are the mole fraction, molar mass, density and viscosity of pure component (3) respectively. x_4 , M_4 , ρ_4 and η_4 are the mole fraction, molar mass, density and viscosity of pure component (4) respectively. ρ_{mix} and η_{mix} are density and viscosity of ternary mixture, respectively.

TABLE-3
VALUES OF DENSITY (ρ) VISCOSITY (η), REFRACTIVE INDEX (n), EXCESS VOLUME (V^E), DEVIATION OF VISCOSITY ($\Delta\eta$), DEVIATION OF REFRACTIVE INDEX (Δn) AND ACTIVATION OF FREE GIBB'S ENERGY FOR QUATERNARY SYSTEM OF 2,5-HEXANDIONE (x_1) + CYCLOPENTANOL (x_2) + CYCLOHEXANOL (x_3) + 3-HEPTANOL (x_4) at 298.15 K

x_1	x_2	x_3	$\rho \text{ (g/cm}^3\text{)}$	$\eta \text{ (mpoise)}$	n	$V^E \text{ (cm}^3\text{/mol)}$	$\Delta\eta \text{ (mpoise)}$	$n^E \text{ (cm}^3\text{/mol}^{-1}\text{)}$	$\Delta G^* \text{ (J mol}^{-1}\text{)}$
0.0452	0.1927	0.4800	0.90074	7.8335	1.4440	3.230	-5.757	-0.0024	2500.6
0.1422	0.3034	0.3579	0.91420	4.6671	1.4429	3.265	-6.474	-0.0023	2322.2
0.2262	0.4171	0.2443	0.92839	3.3786	1.4413	3.215	-5.518	-0.0028	2061.2
0.3225	0.5154	0.1306	0.94389	2.5973	1.4405	3.180	-3.992	-0.0026	1565.1
0.3612	0.5495	0.0358	0.94187	2.1174	1.3480	2.787	-2.582	-0.0927	1276.9
0.2734	0.4742	0.1787	0.93654	2.8698	1.4402	3.045	-4.719	-0.0031	1815.0
0.1863	0.3645	0.2995	0.92265	3.8753	1.4430	3.162	-6.112	-0.0017	2182.7
0.0903	0.2542	0.4178	0.90942	5.6468	1.4441	2.980	-6.717	-0.0016	2287.7
0.0289	0.1635	0.4532	0.89194	7.1783	1.4457	2.776	-5.885	0.0012	2268.1

The excess molar volume V^E and viscosity deviations ($\Delta\eta$) and excess refractive index (Δn) for quaternary mixture are listed in Table-2 and plotted as a function of the mole fraction x_1 , x_2 , x_3 and x_4 for the four components at 298 K in Figs. 1-3.

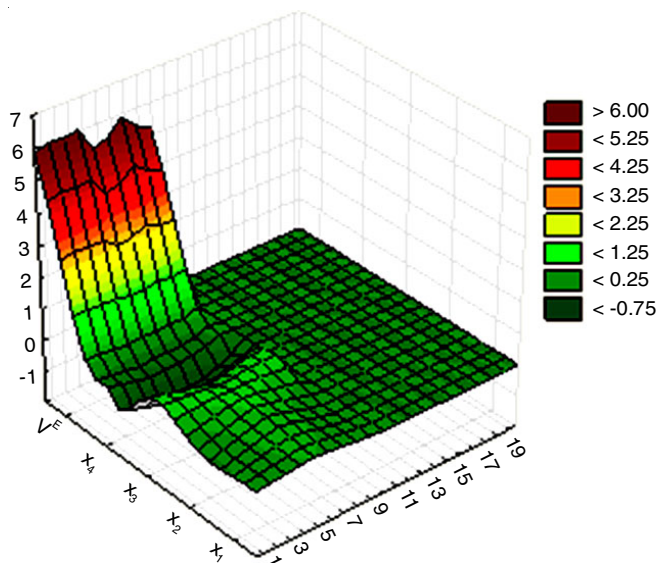


Fig. 1. Excess molar volumes V^E for quaternary system versus x_1 2,5-hexandione + x_2 cyclopentanol + x_3 cyclohexanol + x_4 3-heptanol at 298.15 K

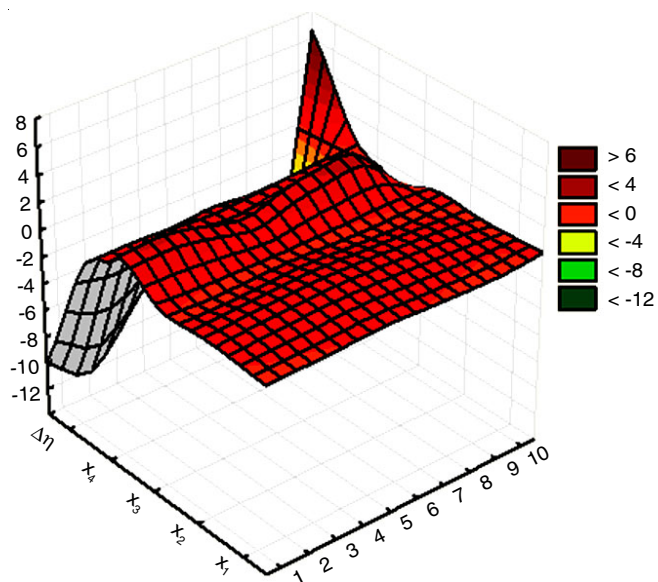


Fig. 2. Deviation of viscosity ($\Delta\eta$) for quaternary system versus x_1 2,5-hexandione + x_2 cyclopentanol + x_3 cyclohexanol + x_4 3-heptanol at 298.15 K

The excess free Gibbs energy of activation of viscous flow was calculated from eqn. 4 and recorded in Table-3 [15].

$$\Delta G^{*E} = RT[\ln(\eta_{\text{mix}} V_{\text{mix}}) - (x_1 \ln \eta_1 V_1) - (x_2 \ln \eta_2 V_2) - (x_3 \ln \eta_3 V_3) - (x_4 \ln \eta_4 V_4)] \quad (4)$$

where T is the absolute temperature, R is the universal constant of gases, V_1 , V_2 , V_3 and V_4 are the molar volumes of component 1, 2, 3 and 4, x_1 , x_2 , x_3 and x_4 represents the mole fraction of component 1, 2, 3 and 4. The V_{mix} is obtained from eqn. 5 below. η_1 , η_2 , η_3 , η_4 and η_{mix} are the viscosity of component 1, 2, 3, 4 and mixture, respectively.

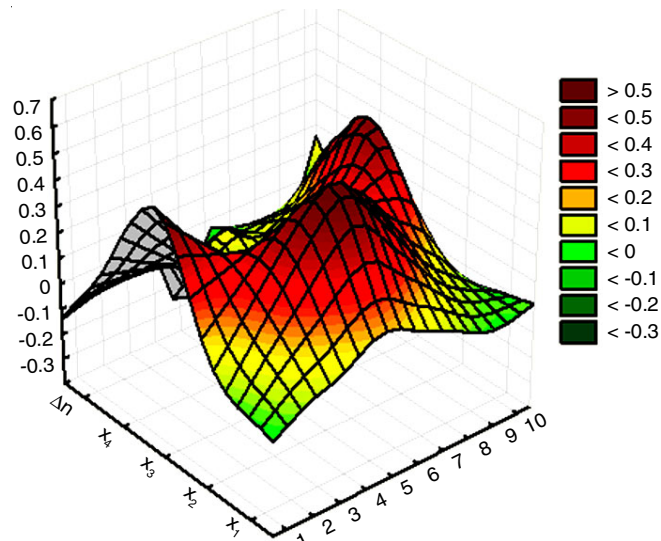


Fig. 3. Deviation of refractive index (Δn) for quaternary system versus x_1 2,5-hexandione + x_2 cyclopentanol + x_3 cyclohexanol + x_4 3-heptanol at 298.15 K

$$V_{\text{mix}} = \frac{x_1 M_1 + x_2 M_2 + x_3 M_3 + x_4 M_4}{\rho_{\text{mix}}} \quad (5)$$

where x_1 , x_2 , x_3 and x_4 represents the mole fraction of component 1, 2, 3 and 4, (ρ_{mix}) the density of mixture. The plot between excess free Gibbs energy of activation of viscous flow (ΔG^{*E}) and mole fractions (x_1 , x_2 , x_3 , x_4) at 298.15 K for 2,5-hexandione + cyclopentanol + cyclohexanol mixtures are presented in Fig. 4.

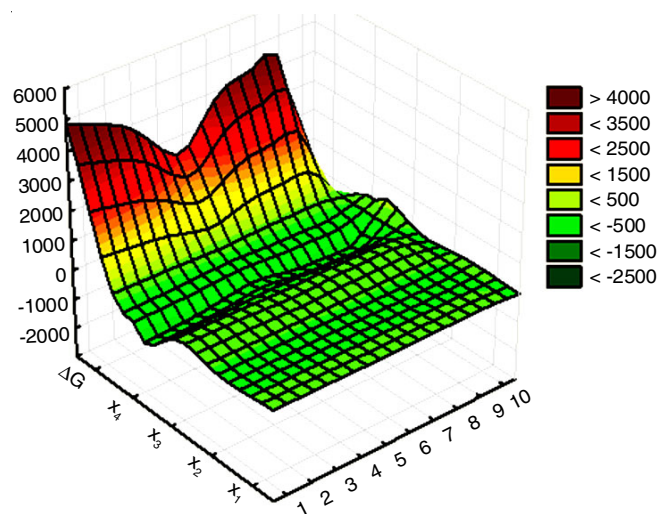


Fig. 4. Activation of free Gibbs energy (ΔG^*) for quaternary system versus x_1 2,5-hexandione + x_2 cyclopentanol + x_3 cyclohexanol + x_4 3-heptanol at 298.15 K

Table-3 and Fig. 1 show the variation in excess molar volume as a function of the mole fraction of 2,3-hexandione + alkanols in these system. The values of excess molar volume were positive in this study and decreased with increasing concentrations of 2,3-hexandione. This was due to the weakening of the hydrogen bonding interaction between 2,3-hexandione and alcohols (cyclopentanol + cyclohexanol + 3-heptanol) and also due to the dissociation of alkanol molecules. The observed

TABLE-4
CHARACTERISTIC PEAKS OF FT-IR SPECTRA FOR PURE COMPOUNDS
(2,5-HEXANDIONE, CYCLOPENTANOL, CYCLOHEXANOL AND 3-HEPTANOL)

Number peak	2,5-Hexandione	Cyclopentanol	Cyclohexanol	3-Heptanol
1	451.34	408.91	435.50	449.41
2	522.71	447.49	680.87	507.28
3	742.59	673.16	889.18	580.57
4	966.34	993.34	966.34	783.10
5	1157.29	1070.49	1066.64	968.27
6	1359.82	1166.93	1316.74	1460.11
7	1708.93	1340.53	1450.47	1714.72
8	2362.80	1450.47	1712.79	2364.73
9	2929.87	1710.86	2929.87	2929.87
10	–	2362.80	3358.07	3338.78
11	–	2954.95	3747.69	3728.40
12	–	3340.91	–	–

positive value for excess molar volume also suggests that the 2,3-hexandione - alkanol association is weaker than the alkanol - alkanol interactions [12].

The deviations viscosity may be explicated on the following factors. (1) The variation in shape and size of the component molecules and the loss of dipolar association to a decrease in viscosity; (2) specific interactions between unlike molecules such as charge transfer complexes and H-bond formation may cause rise in viscosity of liquid mixtures rather than in pure liquid. The former effect produces negative in excess viscosity and latter effect produces positive in excess viscosity. Positive values of $\Delta\eta$ are indicative of strong interactions whereas negative values indicate weaker interactions [16].

The magnitude of deviation of viscosity ($\Delta\eta$), the sign and extent of deviation of this property from ideality depends on the strength of interaction between difference molecules. the excess viscosity gives the strength of the molecular interaction between interacting liquid molecules, from Table-3 and Fig. 2 we observed the negative values of excess viscosity for system under study can be attributed to the presence of the dispersion to the existence of dispersion and dipolar forces between difference molecules and related to the variation in size and shape of the molecules [17,18].

From Table-3 and Fig. 3 we found the negative deviations in Δn values which refer to weak interactions between the liquids of the mixture which agreement with results of excess volume and deviation of viscosity [19].

From Table-3 and Fig. 4. The positive values of ΔG^E may be due to the size effect of the liquid mixtures [20] and may be considered. a reliable measure to detect the presence of interaction between the liquids molecules. The positive values of ΔG^E can be seen in quaternary liquids mixture where specific interactions (hydrogen bonding) between the molecules are dominant. For a strong hydrogen bond donor mixing cosolvents-specific donor-acceptor interactions may probably produce stable stoichiometric complexes which are formed in competition with the simultaneous disruption of the structures of both the pure solvents [13,21]. This behaviour has been lead to the fact that the O-H bond moment of these associates are increased through mutual induction. Depending on the above, taking into account all these assumptions, we can attribute the observed deviations of all these effects.

The FT-IR spectra of pure compounds and quaternary liquids mixtures at different ranges of mole fraction are also studied. The key IR data of pure compounds (2,5-hexandione, cyclopentanol, cyclohexanol and 3-heptanol) are shown in Table-4.

From the FT-IR spectra of compounds before and after mixing, we observed that the all the peaks after mixing were changed relative in position indicated the weak molecular interaction such as H-bonding, dipole-dipole between C-H, C=O groups of 2,5-hexandione with C-H, OH of all alcohol (cyclopentanol, cyclohexanol, 3-heptanol) leading to the vibrational band shifts slightly towards a higher or lower frequency at different mole fraction of compounds under study, inter molecular hydrogen bonding gives rise to broad bands. So it confirms the 2,5-hexandione and alcohol are participated in inter molecular hydrogen bonding. The change of intensity is also an argument in favour of complex formation between 2,5-hexandione with cyclopentanol, cyclohexanol and 3-heptanol [22].

Conclusion

From experimental values of density, viscosity and refractive index we obtained on excess molar volume, deviation of viscosity and deviation of refractive index and these results gives a weak molecular interaction such as H-bonding and dipole-dipole interaction. These results agreement with The FTIR spectra of compounds after mixing (quaternary system).

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