Study of Volumetric, Viscometric and Thermodynamics Behavior of Binary and Ternary Systems for 2,5 Hexandione with Some Alcohol Cyclic at Different Temperatures

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Summary: The density and viscosity of binary and ternary mixtures of 2,5 Hexandione with cyclopentanol and cyclohexanol were measured at 298.15, 303.15, 308.15 and 313.15 K, from using this data (density and viscosity) the excess molar volume V^E, Viscosition deviation $\Delta\eta$ and activation excess parameters ΔG^{*E}, ΔH^{*E} and ΔS^{*E} have been calculated. The results were fitted by Redlich-Kister equations. Negative and positive deviations are obtained for both the binary and ternary Systems at temperatures under study. This expose that the presence of intermolecular interactions in the binary and ternary mixtures.

Keywords: 2,5 Hexandione ; Binary mixtures; Ternary system; Density; Viscosity.

Introduction

Many engineering and technological problems require quantitative data on the density and viscosity of liquid mixtures. So the interest of the properties of liquid-liquid mixtures enable the important information for the characterization of the interactions between components and applications in chemical and biochemical industry [1-3].

Multi component excess molar properties, necessary for process design, are normally estimated from binary and ternary mixing values. The model of thermo physical properties of mixed solvent has received increasing attention as important tool both at the molecular level and for practical applications [4]. So the thermodynamic functions of non-electrolyte solutions are major in the process containing heat transfer, chemical separation, fluid flow and mass transfer. in addition, thermodynamic functions of binary and ternary mixtures play important role in study of specific interactions have deviations from ideality arising not only from change in molecular shape and size, but also due to structural changes [5]. Alcohols made as simple examples of industrially important amphiphilic materials which exist in the liquid phase which may be due to hydrogen bonding of their O–H group. Alcohols have both a proton acceptor and a proton donor groups. It is expected that there will be a good degree of H-bonding produce self-association in the pure phase in addition to mutual association in their binary systems [6, 7].

A survey of literatures of binary system which reported the Molar excess volumes and ultrasonic velocities were determined for the systems cyclopentanol + cyclohexanol, cyclopentanol + cycloheptanol, and cyclohexanol + cycloheptanol at 25ºC. Values of the adiabatic compressibilities were calculated from the experimental results [8], The viscosity and density of binary mixtures cyclohexanol + 2- heptanone, cyclohexanol + 2-hexanone and ternary mixture cyclohexanol + 2-hexanone + 2-heptanone have been measured at the range of temperatures (293.15, 303.15 and 313.15K). The excess molar volume and excess viscosity of binary mixtures cyclohexanol + 2-hexanone, cyclohexanol + 2- heptanone and ternary mixture cyclohexanol+ 2-heptanone + 2-hexanone were also calculated over the range of temperatures (293.15, 303.15 and 313.15K). and the results were fitted to Redlich-kister-type polynomial equation [9].

In order to understand specific intermolecular interactions between 2,5 hexandione with cyclopentanol or cyclohexanol mixtures (binary and ternary systems, the density and viscosity measurements for these systems at 298.15, 303.15, 308.15 and 313.15 K have been studied.

Experimental

The chemical materials that were used in this research with their degree of purity, molar mass and the name of the supplying company as shown in Table-1.

Table-1: The 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

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Different known compositions were prepared. The binary and ternary liquid mixtures in stopper measuring volume flasks (50 ml). The density and viscosity were measured as a function of composition of the binary and ternary liquid mixtures of 2,5 Hexandione with cyclopentanol and cyclohexanol respectively at 298.15, 303.15, 308.15 and 313.15 K. The density was determined using a density bottle (10 ml). The weight of the samples was determined using an electronic digital balance (Model: Shimadzu AX-200) with an accuracy of ± 0.0001 mg. An Ubbelohde Viscometer (12ml) was used for the viscosity measurement and an efflux time was determined using a digital clock to within ±0.01sec, An electronic digital operated constant temperature bath (RAAGA Industries) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the certain temperature with an accuracy of ± 0.01 K. The average was three readings

Each solution was taken to calculate both density and viscosity.

Results and Discussions

For binary system

$$V^E = \frac{(x_1M_1 + x_2M_2)}{\rho_{mix}} - \frac{(x_1M_1)}{\rho_1} - \frac{(x_2M_2)}{\rho_2} \qquad 1$$

The experimental values of density, viscosity and the calculated values of excess volume and viscosity deviation from equations (1, 2) for the two binary liquid systems at 298.15, 303.15,308.15 and 313.15 K are given in Table-2 and 3. The excess volume of binary mixtures is calculated by

where x_1, M_1 and ρ_1 are the mole fraction, molar mass and density of component (1) respectively . x_2, M_2 and ρ_2 are the mole fraction, molar mass and density of component (2) respectively. ρ_{mix} is the density of mixture. Viscosity deviation of binary mixtures are determined by :

$$\Delta\eta = \eta_{mix} - x_1\eta_1 - x_2\eta_2 \qquad 2$$

where x_1, x_2 , $\eta_1$and η_2 are the mole fraction and the viscosities of pure components respectively. η_{mix} is the viscosity of the mixture [10], the change of excess parameter with the mole fraction of 2,5 Hexandione (x_1) at 298.15, 303.15, 308.15 and 313.15 K are plotted in Fig 1-4.

Table-2: Values of density (ρ), viscosity (η), Excess volume (V^E), and viscosity deviations (Δη), for Binary System of 2,5 Hexandione (x_1) with cyclopentanol (x_2) at different temperatures.

T/K	x_1	ρ (g/cm^3)	η(mpoise)	V^E(cm^3/mol)	Δη(mpoise)
	1.0000	1.02228	1.2846	0.0000	0.000
	0.8828	1.02096	1.3050	-0.6808	-0.507
	0.7646	1.01526	1.3578	-0.9210	-0.986
	0.6531	1.01168	1.4941	-1.3588	-1.351
	0.5420	1.00898	1.7345	-1.9008	-1.610
298.15	0.4393	1.00530	1.9518	-2.2998	-1.854
	0.3453	1.00324	2.2820	-2.8056	-1.947
	0.2548	1.00164	2.7876	-3.3379	-1.848
	0.1630	0.97005	3.4071	-1.0836	-1.642
	0.0777	0.95494	4.0500	-0.3669	-1.383
	0.0000	0.94384	5.7818	0.0000	0.000
	1.0000	1.01768	1.2266	0.0000	0.000
	0.8828	0.99183	1.2100	1.9842	-0.432
	0.7646	0.97107	1.2198	3.3559	-0.840
	0.6531	0.95784	1.2985	3.8810	-1.156
	0.5420	0.94513	1.3859	4.3019	-1.462
303.15	0.4393	0.94505	1.5195	3.3449	-1.691
	0.3453	0.94264	1.7498	2.7199	-1.794
	0.2548	0.94150	2.1224	1.9815	-1.741
	0.1630	0.94009	2.6915	1.2522	-1.497
	0.0777	0.93865	3.4997	0.5798	-0.991
	0.0000	0.93695	4.7655	0.0000	0.000
	1.0000	1.01018	1.0767	0.0000	0.000
	0.8828	0.97772	1.1563	2.8226	-0.272
	0.7646	0.96416	1.1667	3.4335	-0.615
	0.6531	0.94685	1.2251	4.4854	-0.891
	0.5420	0.94539	1.3753	3.6664	-1.074
308.15	0.4393	0.94134	1.5087	3.2002	-1.248
	0.3453	0.93672	1.6012	2.8536	-1.437
	0.2548	0.93472	1.8500	2.2361	-1.459
	0.1630	0.93435	2.2730	1.4265	-1.311
	0.0777	0.93399	2.8466	0.6730	-0.993
	0.0000	0.93352	4.0726	0.0000	0.000
	1.0000	1.00910	0.9591	0.0000	0.000
	0.8828	0.97109	1.0432	3.4219	-0.211
	0.7646	0.95444	1.0476	4.3403	-0.504
	0.6531	0.94235	1.1092	4.7316	-0.723
	0.5420	0.94019	1.2541	3.9276	-0.858
313.15	0.4393	0.93555	1.3254	3.4686	-1.045
	0.3453	0.93270	1.4925	2.8724	-1.114
	0.2548	0.93186	1.7081	2.0787	-1.126
	0.1630	0.92943	1.9855	1.4344	-1.080
	0.0777	0.92818	2.4736	0.7197	-0.807
	0.0000	0.92768	3.4756	0.0000	0.000

Table-3: Values of density (ρ) ,viscosity (η), Excess volume (V^E) and viscosity deviations (Δη), for binary System of 2,5 Hexandione (x_1) with cyclohexanol (x_2) at 298.15, 303.15,308.15 and 313.15 K

T/K	x_1	ρ (g/cm^3)	η(mpoise)	V^E(cm^3/mol)	Δη(mpoise)
	1.0000	1.02228	1.2846	0.0000	0.000
	0.9040	1.01968	1.6697	0.0730	-1.746
	0.7880	1.01684	1.5507	0.1216	-4.440
	0.6884	1.01432	1.7487	0.1664	-6.452
	0.5867	1.01148	2.1685	0.2346	-8.291
298.15	0.4824	1.00840	3.0790	0.3158	-9.696
	0.3870	1.00578	4.3684	0.3634	-10.524
	0.2868	1.00314	6.9952	0.3960	-10.122
	0.1928	1.00190	10.7881	0.2944	-8.415
	0.0854	1.00130	18.4465	0.0917	-3.143
	0.0000	1.00012	23.4868	0.0000	0.000
303.15	1.0000	1.01768	1.2266	0.0000	0.000
	0.9040	1.01510	1.3364	0.0697	-1.288
	0.7880	1.01178	1.4381	0.1688	-2.875
	0.6884	1.00882	1.6393	0.2592	-4.123
	0.5867	1.00558	1.9756	0.3683	-5.268
	0.4824	1.00272	2.3899	0.4239	-6.372
	0.3870	0.99980	2.7590	0.5011	-7.391
	0.2868	0.99822	3.7170	0.4201	-7.892
	0.1928	0.99664	6.0299	0.3507	-6.947
	0.0854	0.99590	10.2159	0.1576	-4.326

Table-3 continue

	0.0000	**0.99534**	**15.7844**	**0.0000**	**0.000**
	1.0000	**1.01018**	**1.0767**	**0.0000**	**0.000**
	0.9040	**1.00930**	**1.2396**	**-0.0972**	**-0.888**
	0.7880	**1.00896**	**1.3096**	**-0.2967**	**-2.088**
	0.6884	**1.00706**	**1.4532**	**-0.2949**	**-3.035**
	0.5867	**1.00270**	**1.7146**	**-0.0376**	**-3.888**
308.15	**0.4824**	**0.99912**	**2.0683**	**0.1222**	**-4.676**
	0.3870	**0.99324**	**2.2036**	**0.5398**	**-5.585**
	0.2868	**0.99202**	**3.1808**	**0.4420**	**-5.705**
	0.1928	**0.99082**	**4.6774**	**0.3533**	**-5.237**
	0.0854	**0.99060**	**7.6416**	**0.1290**	**-3.450**
	0.0000	**0.98994**	**12.0262**	**0.0000**	**0.000**
	1.0000	**1.00910**	**0.9591**	**0.0000**	**0.000**
	0.9040	**1.00636**	**1.1603**	**-0.1012**	**-0.548**
	0.7880	**1.00348**	**1.1961**	**-0.2786**	**-1.418**
	0.6884	**1.00020**	**1.2632**	**-0.3482**	**-2.129**
	0.5867	**0.99684**	**1.4826**	**-0.4255**	**-2.704**
313.15	**0.4824**	**0.99338**	**1.7724**	**-0.5103**	**-3.228**
	0.3870	**0.98830**	**1.8284**	**-0.3880**	**-3.917**
	0.2868	**0.98292**	**2.8447**	**-0.2636**	**-3.683**
	0.1928	**0.97824**	**4.2244**	**-0.1947**	**-3.037**
	0.0854	**0.97290**	**6.7182**	**-0.1272**	**-1.382**
	0.0000	**0.96790**	**8.7671**	**0.0000**	**0.000**

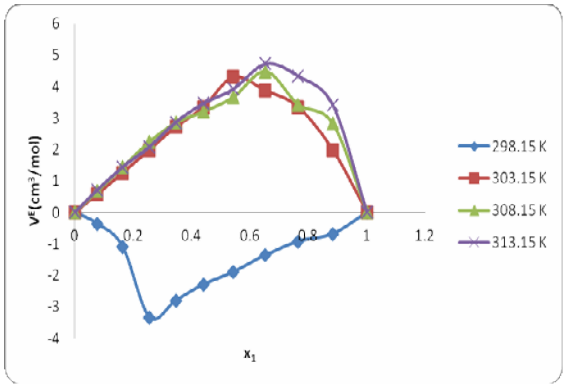

Fig. 1: Excess molar volume (V^E) of 2,5 hexandione with cyclopentanol mixture at different temperatures.

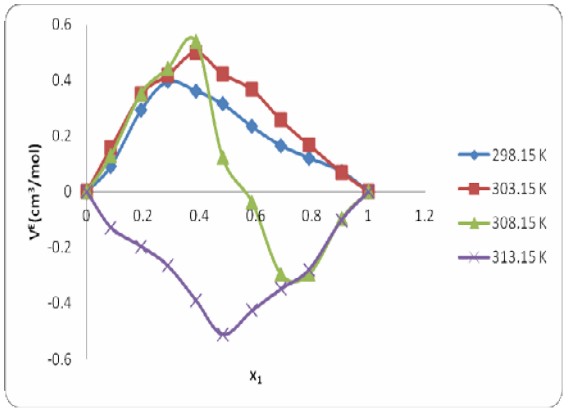

Fig. 2: Excess molar volume (V^E) of 2,5 Hexandione with cyclohexanol mixture at different temperatures.

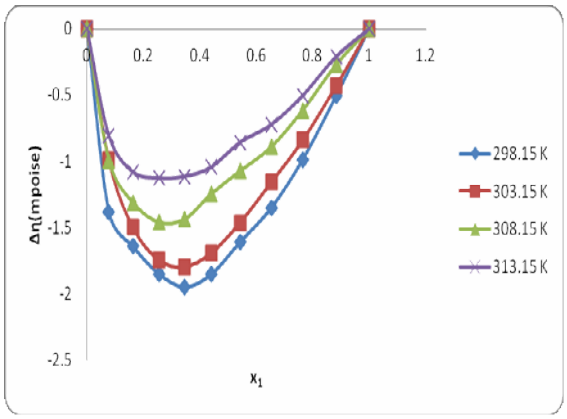

Fig. 3: Viscosity deviations and (Δη) of 2,5 hexandione with cyclopentanol mixture at different temperatures.

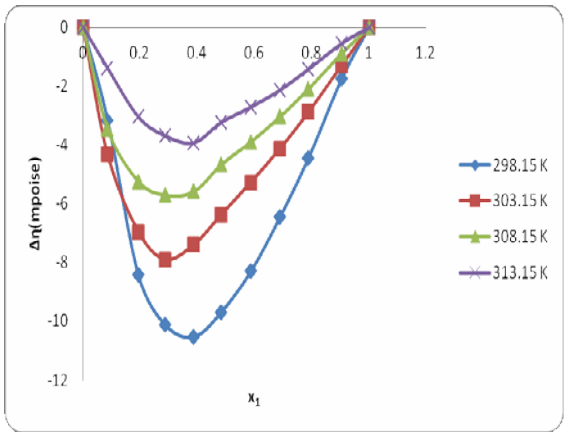

Fig. 4: Viscosity deviations and (Δη) of 2,5 hexandione with cyclohexanol mixture at different temperatures.

According to [11] V^E is a function of many opposing effects (physical, chemical and structural). physical effects represents a positive contribution to V^E, the chemical or specific intermolecular interactions (such as hydrogen bond interaction, dipole–dipole/dipole-induced–dipole interaction, formation of charge transfer complexes, *etc.*) represents a negative contributions to V^E . Therefore, the actual volume variation would based on the relative force of these effects.

Moreover, the V^E values decrease with increasing temperatures of the 2,5 hexandione + cyclohexanol mixture, which leading of increase in intermolecular interactions between the component molecules with arising temperature, which is probably due the greater thermal agitation that ultimately increases the mutual fitting of the mixing components to some extent at higher temperatures.while we were observing opposite behavior for hexandione + cyclopentanol mixture.

Fig. 1, Table-2 show the V^E values for 2,5 Hexandione are negative (strong interaction) over the entire mole fraction of cyclopentanol at lower temperatures while the values V^E parameter become positive (weak interaction) with increasing temperature.on other hand Fig. 2, Table-3 show the V^E values for 2, 5 Hexandione are positive (waek interaction) over the entire mole fraction of cycloHexanol at lower temperatures while the values V^E parameter become negative (strong interaction) with increasing temperature This is because 2,5 Hexandione and cycloalkanols are associated [12]. The observed V^E may be analyzed in terms of many effects, which may be classified into physical, chemical and geometrical contributions [13, 14]. In the present investigation the positive deviations of V^E have been attributed to dispersive forces that show weak molecular interaction between the different molecules, while the negative deviations of V^E have been attributed to interactive forces (Hydrogen bonding) that show strong molecular interaction between the unlike molecules for both binary system under study. in other word The above mentioned order indicates the formation of transition complex with formation of new hydrogen bonds between the unlike molecules in the liquid mixtures [15].

The values of Δη, the sign and the extent of deviation of this property from ideality depend on the force of interaction between different molecules. The excess viscosity refers to strength of the molecular interaction between the molecules. For systems where dispersion, induction and dipolar forces which are applied by the values of excess viscosity are found to be negative, the large negative values of excess viscosity for all the systems can be refered to the presence of the dispersion, induction, and dipolar forces between the components [16].

For both binary systems It is seen from the Table-2 and 3, Fig 3 and 4 that the curves for Δη values are negative over the entire mole fraction of the cycloalkanols at 298.15 , 303.15, 308.15 and 313.15 K temperatures .These excess parameters at a particular mole fraction of the cycloalkanols becomes less negative with increase of temperature. The negative Δη may be refered to the existence of dispersion and dipolar forces between different molecules and related to the difference in size and shape of the molecules. Increase of temperature disturbs here to and homo-association of the molecules which increases fluidity of the liquid. Values of Δη are more at higher temperature, providing additional evidence for the existence of interactions of weak magnitude like dipole-induced dipole type between components of liquid mixtures [17].

Generally The values of V^E and Δη are negative and positive and become more negative for all the mixtures under study over the whole mole fraction range and show a increasing tendency with increasing size of alchole cyclic molecules.

The excess Gibbs free energy of activation of viscous flow was calculated from equation (3) and recorded in Table-4.

$$\Delta G^{*E} = RT[\ln(\eta_{mix}V_{mix}) - (x_1 \ln \eta_1 V_1) - (x_2 \ln \eta_2 V_2)] \quad 3$$

where R is the universal constant of gases, T is the absolute temperature, V_1 and V_2 are the molar volumes of component 1 and 2, x_1 and x_2 represents the mole fraction of component 1 and 2. η_1, η_2 and η_{mix} are the viscosity of component 1 and 2 and mixture respectively, V_{mix} was calculated from equation (4) below.

$$V_{mix} = \frac{x_1 M_1 + x_2 M_2}{\rho_{mix}} \quad 4$$

where x_1 and x_2 acts the mole fraction of component 1 and 2, (ρ_{mix}) the density of mixture. The plots of excess Gibbs free energy of activation of viscous flow against mole fraction at 298.15, 303.15, 308.15 and 313.15 K for 2,5 Hexandione +cyclopentanol and 2,5 Hexandione +cyclohexanol mixtures are presented in Fig 5 and 6 respectively.

Table-4: The excess free energy ΔG^{*E} of 2,5 Hexandione with cyclopentanol and cyclohexanol mixture at different temperatures

ΔG^{*E} (J.mol^{-1}) of 2,5 Hexandione +cyclopentanol				
x_1	298.15 K	303.15 K	308.15 K	313.15 K
1.0000	0.00	0.00	0.00	0.00
0.8828	487.16	527.35	778.39	850.56
0.7646	599.40	646.52	890.19	971.95
0.6531	659.54	692.41	919.80	1020.66
0.5420	711.54	602.71	934.45	1066.83
0.4393	600.73	454.80	802.20	847.29
0.3453	520.33	372.05	520.78	719.82
0.2548	470.99	337.65	369.11	546.53
0.1630	377.64	293.74	245.98	292.03
0.0777	77.83	211.86	68.74	109.23
0.0000	0.00	0.00	0.00	0.00
ΔG^{*E} (J.mol^{-1}) of 2,5 Hexandione +cyclohexanol				
x_1	298.15 K	303.15 K	308.15 K	313.15 K
1.0000	0.00	0.00	0.00	0.00
0.9040	744.95	408.98	606.43	802.83
0.7880	225.27	355.57	539.58	737.92
0.6884	64.94	308.80	456.68	580.71
0.5867	10.40	272.58	405.31	565.31
0.4824	166.07	119.10	281.63	470.28
0.3870	284.60	-194.55	-200.42	-55.73
0.2868	561.48	-262.25	-57.18	348.14
0.1928	685.19	75.01	67.28	558.51
0.0854	742.08	205.13	144.10	636.24
0.0000	0.00	0.00	0.00	0.00

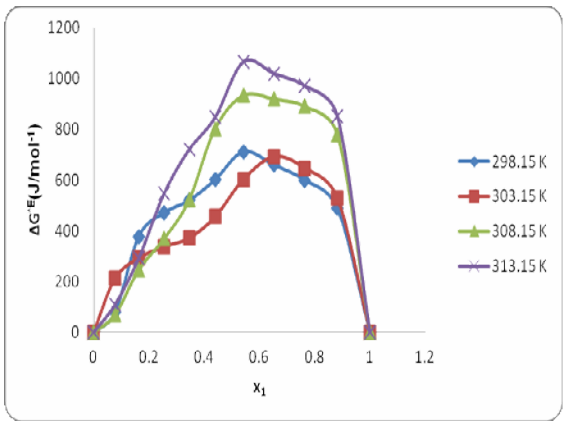

Fig. 5: Excess Gibb's free energy (ΔG^{*E}) of 2,5 hexandione with cyclopentanol mixture at different temperatures.

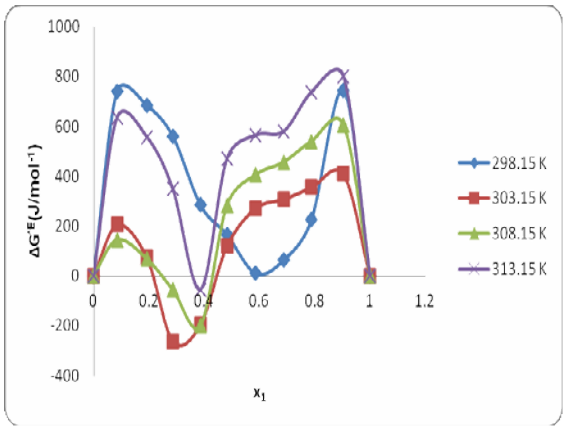

Fig. 6: Excess Gibb's free energy (ΔG^{*E}) of 2,5 hexandione with cyclohexanol mixture at different temperatures.

Excess properties give important data about the molecular interactions and macroscopic behavior of liquid mixtures which can be used to examine and indicate thermodynamic models for determinig and predicting fluid phase equilibria. The magnitude of ΔG^{*E} acts the strength of interaction between different molecules. From Table-4 and Figure. 5 shows the excess Gibbs free energy of activation of viscous flow for 2,5 hexandione with cyclopentanol or cyclohexanol binary systems were found to be positive over whole mole fraction while we found to be negative in sshort range of mole fraction for 2,5 hexandione with cyclohexanol binary system so the positive ΔG^{*E} may be attributed to specific interactions like hydrogen bonding and charge transfer while negative values may be ascribed to the dominance of dispersion force, And ΔG^{*E} values increased with increase in temperature. The positive values of excess Gibbs free energy of activation of viscous flow indicate the presence of specific and strong interactions in the systems under investigation [18-20].

The Eyring viscosity relation [21] yields the following equation for the free energy of viscous flow (ΔG^{*E}):

$$\eta = (hN/V)\exp(\Delta G^{*E}/RT) \qquad 5$$

where h is Planck's constant, N is Avogadro's number and the other symbols have their usual meanings. Rearranging Equation (5) and putting $\Delta G^{*E} = \Delta H^{*E} - T\Delta S^{*E}$, one obtains the relation:

$$R \ln(\eta V / hN) = \Delta H^{*E} / T - \Delta S^{*E} \qquad 6$$

Thus , the linear regressions of R ln (ηV/hN) against (1/T) could give the values of enthalpy (ΔH^{*E}) and entropy (ΔS^{*E}) of activation of viscous flow from the slope and negative intercept, respectively.The values of ΔH^{*E}, ΔS^{*E} values as given in Table-5 of the 2,5 hexandione with alcholecyclic binary systems mixtures.

Table-5: The activation excess parameter $\Delta H^{*E}$and ΔS^{*E} of 2,5 Hexandione with cyclopentanol and cyclohexanol mixture at different temperatures.

2,5 Hexandione + cyclopentanol			2,5 Hexandione + cyclohexanol		
x_1	ΔH^{*E}	ΔS^{*E}	x_1	ΔH^{*E}	ΔS^{*E}
1.0000	0	0	1.0000	0	0
0.8828	8542.6	-192.5	0.9040	17476.9	-164.3
0.7646	9755.2	-188.6	0.7880	12865.5	-179.5
0.6531	11272.4	-184.0	0.6884	16279.6	-169.1
0.5420	11962.8	-182.5	0.5867	19135.1	-161.2
0.4393	14746.4	-173.9	0.4824	27231.3	-136.5
0.3453	17709.5	-165.0	0.3870	43223.5	-85.2
0.2548	21513.1	-153.7	0.2868	43498.4	-87.5
0.1630	25695.6	-141.5	0.1928	46600.6	-80.8
0.0777	24737.3	-146.3	0.0854	50311.6	-72.8
0.0000	0	0	0.0000	0	0

Table-5 showed that the ΔH^{*E} values are positive, the ΔS^{*E} values are negative for all the studied binary mixtures throughout the entire composition range, and show a increase in ΔH^{*E} and an opposite trend in ΔS^{*E} values with mole fraction x_1 of 2,5 Hexandione. It has been suggested earlier. The enthalpy of activation of viscous flow may be regarded as a measure of the degree of cooperation between the species participating in the viscous flow. In a highly structured liquid, there will be a considerable degree of order; hence, for cooperative movement of the entities, a large heat of activation is required for the flow process. Thus the ΔH^{*E} values indicate that the ease of formation of activated species necessary for viscous flow. This behavior is also supported by negative values of ΔS^{*E} for the mixtures [22]. The excess properties Y^E (excess volume

,deviation viscosity, activiation free Gibbes energy) are fitted by the method of nonlinear least squares to a Redlich kister type polynomial [23]**:**

$$Y^E = x_1 x_2 \sum A_i (x_1 - x_2)^i \qquad 7$$

where x_1 is the mole fraction of 2,5Hexandione , x_2 is the mole fraction of cyclopentanol or cyclohexanol, A_i are adjustable parameters obtained by a least squares method, and J is the degree of the polynomials. The coefficients A_i were obtained by fitting Equation (7) to the experimental results using least-squares regression method with all points weighted equally.

$$\sigma Y^e = \sqrt{\frac{\sum (Y^E_{obs} - Y^E_{cal})}{(n-m)}} \qquad 8$$

In each case the optimum number of coefficients A_i was determined from an examination of the change of standard deviation as calculated by:

where n acts the number of experimental values and m represents the number of coefficients in fitting the data.

Table-6: Estimated parameter of Excess molar volume Function for binary mixtures at different temperatures.

V^E /(cm^3.mol^{-1}) 2,5hexandion+cyclohexanol				
T/K	**A_0**	**A_1**	**A_2**	**σ**
298	**1.2543**	**-1.0133**	**0.0010**	**0.045**
303	**1.7327**	**-1.0481**	**-0.4318**	**0.017**
308	**0.6523**	**-3.6741**	**-0.9339**	**0.030**
313	**-1.7946**	**-0.2000**	**1.0065**	**0.049**
V^E /(cm^3.mol^{-1})	**2,5hexandion+cyclopentanol**			
T/K	**A_0**	**A_1**	**A_2**	**σ**
298	**-9.3322**	**6.8516**	**2.3729**	**0.174**
303	**15.2936**	**7.9818**	**-2.8614**	**0.077**
308	**14.5722**	**9.5611**	**5.7847**	**0.020**
313	**15.3203**	**13.3988**	**9.8089**	**0.027**

Table-7: Estimated parameter of Deviation viscosity Function for binary system mixtures at different temperatures.

Δη /(mpoise) 2,5hexandion+cyclohexanol				
T/K	**A_0**	**A_1**	**A_2**	**σ**
298	**-39.1504**	**21.7143**	**4.1857**	**0.213**
303	**-25.2474**	**23.1531**	**-15.1845**	**0.072**
308	**-18.5698**	**17.7583**	**-12.1439**	**0.044**
313	**-13.3725**	**9.4566**	**-0.2332**	**0.112**
Δη /(mpoise) 2,5hexandion+cyclopentanol				
T/K	**A_0**	**A_1**	**A_2**	**σ**
298	**-6.7090**	**5.1113**	**-5.2872**	**0.115**
303	**-6.1974**	**4.8221**	**-3.4454**	**0.055**
308	**-4.5902**	**4.6973**	**-4.4221**	**0.069**
313	**-3.6873**	**3.6981**	**-3.5350**	**0.069**

The standard deviations between our experimental binary data and estimated values were determined from eqution 8, and the results are listed in Tables-5 to 7). It is found that for the solution of the third degree polynomial, the agreement between the experimental values and the calculated ones is satisfactory. The derived parameters A_0, A_1, A_2 and σ are presented in Table-6 to 8 a good agreement was found in between Redlich-Kister parameters the solution of the third degree polynomial obtained with V^E, Δη and ΔG^{*E}.The Redlich kister equation provided the best results to the experimental data with the standard deviations of for the 2,5 hexanedione + cyclohexanol ($V^E > 0.01$, $\Delta\eta > 0.04$, $\Delta G^{*E} > 2$) than 2,5 hexanedione + cyclopentanol ($V^E > 0.02$, $\Delta\eta > 0.05$, $\Delta G^{*E} > 0.8$) at different temperatures under study.

Table-8: Estimated parameter of Excess and Deviation Function for mixtures at different temperatures.

ΔG^{*E} /(J.mol^{-1}) 2,5hexandion+cyclohexanol				
T/K	**A_0**	**A_1**	**A_2**	**σ**
298	**66.34**	**-1941.13**	**10337.67**	**3.74**
303	**46.07**	**2474.44**	**3817.59**	**3.03**
308	**537.87**	**3267.54**	**4389.57**	**2.79**
313	**1016.03**	**1801.40**	**9395.30**	**3.33**
ΔG^{*E} /(J.mol^{-1})	**2,5hexandion+cyclopentanol**			
T/K	**A_0**	**A_1**	**A_2**	**σ**
298	**2607.44**	**1118.47**	**1167.34**	**1.67**
303	**2099.70**	**1838.20**	**2674.26**	**1.47**
308	**3323.22**	**3188.22**	**1121.79**	**1.50**
313	**3815.27**	**3007.37**	**1409.63**	**0.84**

For Ternary system

The excess molar volume and viscosity deviations were calculated from density and viscosity measurements according to the following equations (9, 10) [24, 25].

$$V^E = \frac{(x_1M_1 + x_2M_2 + x_3M_3)}{\rho_{mix}} - \frac{(x_1M_1)}{\rho_1} - \frac{(x_2M_2)}{\rho_2} - \frac{(x_3M_3)}{\rho_3} \qquad 9$$

$$\Delta\eta = \eta_{mix} - x_1\eta_1 - x_2\eta_2 - x_3\eta_3 - \qquad 10$$

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. P_{mix} and η_{mix} are the density and viscosity of the ternary mixture respectively.

The excess molar volume V^E and viscosity deviations (Δη) for ternary mixture are listed in Table-9 and plotted as a function of the mole fraction x_1, x_2 and x_3 for the three components at four different temperatures in Fig. 7 and 8.

Table-9: Values of density (ρ) viscosity (η), Excess volume (V^E) and viscosity deviations (Δη) for ternary System of 2,5 Hexandione (x_1) + cyclopentanol (x_2) + cycloHexanol (x_3) at different temperatures

T/K	x_1	x_2	ρ (g/cm^3)	η(mpoise)	V^E(cm^3/mol)	Δη(mpoise)
	0.6504	0.1491	0.95878	1.8169	5.4636	-4.591
	0.5542	0.2691	0.95488	1.8418	4.9222	-4.576
	0.4953	0.3810	0.95455	1.9677	4.1259	-3.776
	0.4396	0.4777	0.95160	2.0230	3.7127	-3.246
298.15	0.4004	0.5545	0.95034	2.1129	3.2747	-2.666
	0.3131	0.4560	0.94815	2.6893	3.8116	-5.773
	0.2213	0.3396	0.94756	4.4245	4.2661	-8.137
	0.1290	0.2278	0.94599	7.4183	4.8001	-9.170
	0.0414	0.1182	0.94535	14.2467	5.2350	-6.227
	0.6504	0.1491	0.95348	1.5346	5.5602	-3.139
	0.5542	0.2691	0.95056	1.5863	4.8725	-3.165
	0.4953	0.3810	0.94890	1.6955	4.1954	-2.680
	0.4396	0.4777	0.94874	1.9530	3.4461	-2.168
303.15	0.4004	0.5545	0.94829	2.0496	2.9017	-1.795
	0.3131	0.4560	0.94467	2.3693	3.6178	-3.833
	0.2213	0.3396	0.94372	3.5242	4.1383	-5.297
	0.1290	0.2278	0.94353	5.7937	4.5450	-5.602
	0.0414	0.1182	0.94256	9.7258	5.0409	-4.153
	0.6504	0.1491	0.94931	1.3331	5.3518	-2.386
	0.5542	0.2691	0.94662	1.3670	4.6791	-2.451
	0.4953	0.3810	0.94384	1.4728	4.1611	-2.100
	0.4396	0.4777	0.93913	1.5016	3.9476	-1.912
308.15	0.4004	0.5545	0.94210	1.6741	3.0351	-1.557
	0.3131	0.4560	0.93993	2.0989	3.6002	-2.872
	0.2213	0.3396	0.93946	2.9571	4.0715	-3.945
	0.1290	0.2278	0.93809	4.5075	4.6146	-4.294
	0.0414	0.1182	0.93846	7.7892	4.9644	-2.843
	0.6504	0.1491	0.94446	1.2668	5.3043	-1.633
	0.5542	0.2691	0.94182	1.3092	4.6093	-1.707
	0.4953	0.3810	0.94076	1.3808	3.9479	-1.503
	0.4396	0.4777	0.93707	1.4456	3.6596	-1.361
313.15	0.4004	0.5545	0.93815	1.6011	2.9987	-1.105
	0.3131	0.4560	0.93524	1.9025	3.2891	-2.007
	0.2213	0.3396	0.93420	2.5628	3.4261	-2.680
	0.1290	0.2278	0.93198	3.5752	3.6752	-2.979
	0.0414	0.1182	0.93455	5.3585	3.3964	-2.460

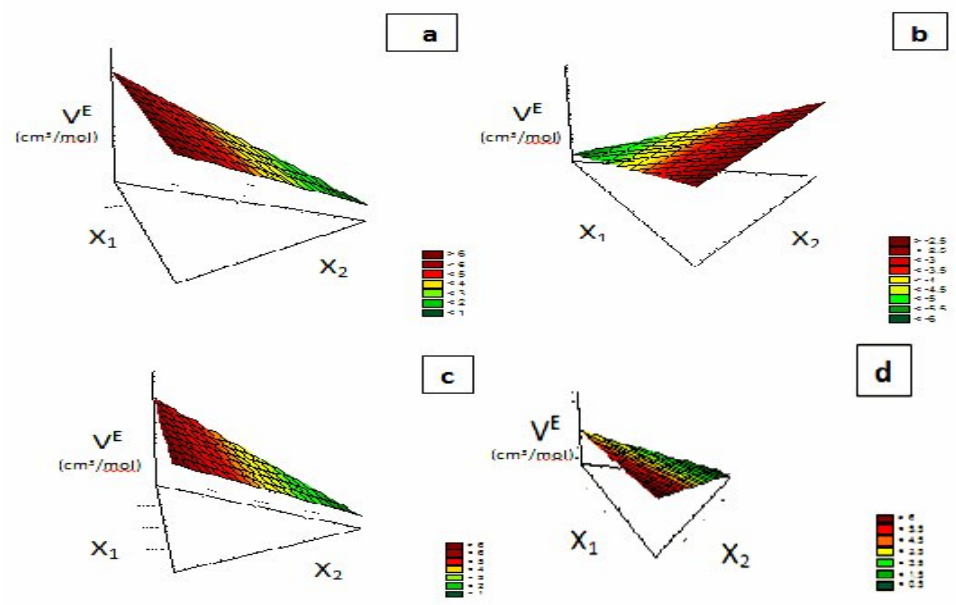

Fig (7): Excess molar volumes V^E for ternary system (x_1 2,5 hexandione + x_2 cyclopentanol + x_3 cyclohexanol) at (a) 298.15K, (b) 303.15K, (c) 308.15K, and (d) 318.15K.

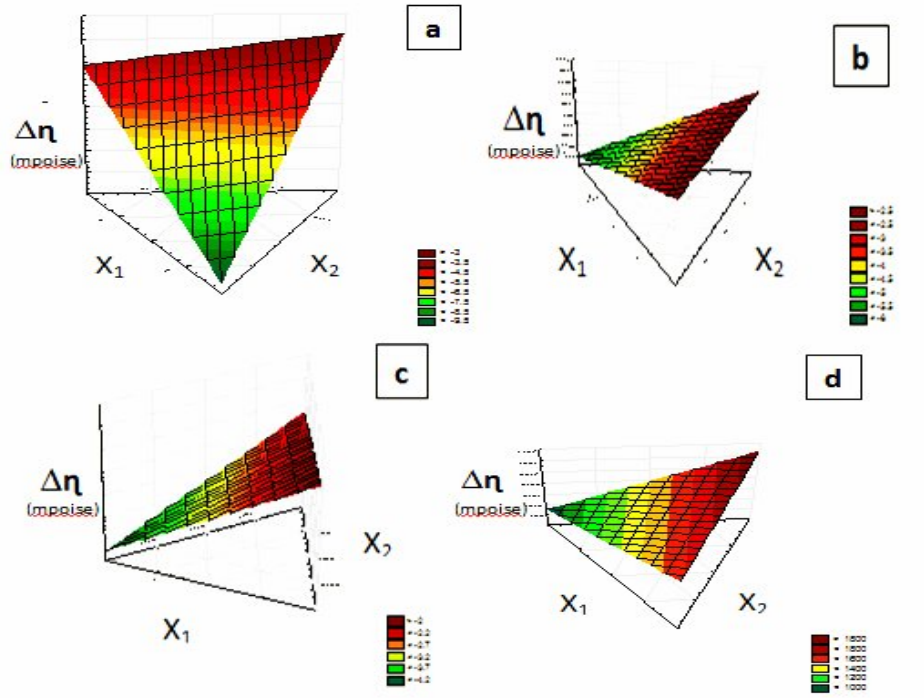

Fig (8): Viscosity deviations (Δη) for ternary system (x_1 2,5 hexandione + x_2 cyclopentanol + x_3 cyclohexanol) at (a) 298.15K, (b) 303.15K, (c) 308.15K, and (d) 318.15K.

Fig. 7 show that the excess molar V^E is a positive deviation over the whole composition range at 298.15, 303.15 308.15 and 313.15K. Further, these values are decreases with rising of temperature in system under study. For some ternary liquid mixtures, there is the negative excess free volume which refers to decrease as the strength of the interaction between the different molecules increases although they do not parallel with the excess compressibilities. The values of V^E are the resultant of contributions from many opposing effects**.** These may be divided arbitrarily into these kinds, namely, chemical, physical and structural contributions, physical contributions, which are non-specific interactions between the real species present in the mixture, contribute a positive term to V^E. The chemical or specific intermolecular interactions and structures (interstitial accommodation) contribute negative value V^E. In the present study the positive contribution of V^E show the existence of dispersive forces between the component molecules of the mixtures. Further from the obtained behavior of V^E with rising of temperature suggests the strength of interaction get strongest [11].

While Fig. 8 show viscosity deviations (Δη) for ternary mixtures studied here is a negative deviation over the whole composition range at (298.15, 303.15, 308.15 and 313.15K). This suggests that the ternary mixtures are not ideal in terms of component binaries, indicating that the third component modifies the nature and degree of molecular interaction between 2,5hexandione with alchoholcyclic mixtures.

The excess Gibbs free energy of activation of viscous flow was calculated from equation (11) and recorded in Table-10.

$$\Delta G^{*E} = RT[\ln(\eta_{mix}V_{mix}) - (x_1 \ln \eta_1 V_1) - (x_2 \ln \eta_2 V_2) - (x_3 \ln \eta_3 V_3)] \quad 11$$

where R is the universal constant of gases, T is the absolute temperature, V_1, V_2 and V_3 are the molar volumes of component 1, 2 and 3, x_1, x_2 and x_3 represents the mole fraction of component 1,2 and 3. The V_{mix} is obtained from equation (12) below. η_1, η_2, η_3 and η_{mix} are the viscosity of component 1 ,2 ,3 and mixture respectively.

$$V_{mix} = \frac{x_1M_1 + x_2M_2 + x_3M_3}{\rho_{mix}} \quad 12$$

where x_1, x_2 and x_3 represents the mole fraction of components 1, 2 and 3, (p_{mix}) the density of mixture. The plots of excess Gibbs free energy of activation of viscous flow against mole fraction at 298.15, 303.15, 308.15 and 313.15 K for 2,5 Hexandione +cyclopentanol + cycloHexanol mixtures are presented in Fig. 9.

Table-10: The excess activation free energy ΔG^{*E} of 2,5 Hexandione + cyclopentanol + cyclohexanol mixture at different temperatures

ΔG^{*E} (J.mol^{-1}) of 2,5 Hexandione +cyclopentanol+cyclohexanol					
x_1	x_2	298.15 K	303.15 K	308.15 K	313.15 K
0.6504	0.1491	1185.2	1130.1	1199.7	1505.8
0.5542	0.2691	1185.6	1199.8	1250.0	1578.0
0.4953	0.3810	1268.4	1282.3	1346.6	1602.2
0.4396	0.4777	1130.8	1420.3	1179.4	1488.8
0.4004	0.5545	997.8	1289.6	1184.1	1471.9
0.3131	0.4560	1197.5	1382.5	1543.3	1776.1
0.2213	0.3396	1378.5	1455.3	1544.5	1747.7
0.1290	0.2278	1178.6	1338.6	1301.7	1356.9
0.0414	0.1182	913.4	865.4	955.2	709.3

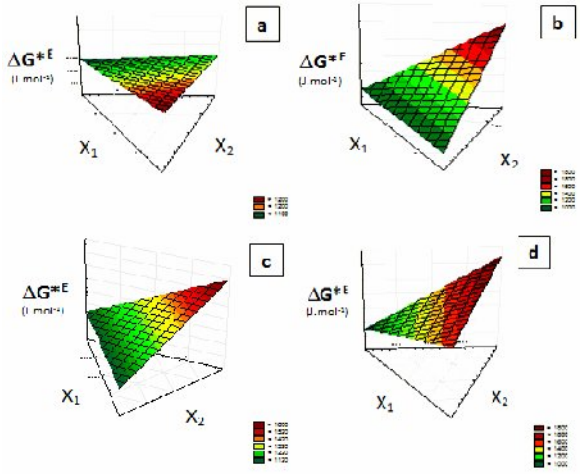

Fig. 9: Excess free Gibbes energy (ΔG^{*E}) for ternary system x_1 2,5hexandion + x_2 cyclopentanol + x_3 cyclohexanol at (a) 298.15K, (b) 303.15K, (c) 308.15K, and (d) 318.15K.

From Table-10 we found the change of excess Gibbs energy (ΔG^{*E}) for the ternary liquid system are positive in all the temperatures and increase with mole fraction of 2,5 hexandione . the positive values of excess Gibbs energy values may be refered to specific interactions such as charge transfer and hydrogen bonding are dominant [26].

From a plotting of the previous equation (6) the ΔH^{*E} and ΔS^{*E} for ternary system are calculated and recorded in Table-11.

Table-11: The activation excess parameter ΔH^{*E} and ΔS^{*E} of 2,5 Hexandione + cyclopentanol + cyclohexanol mixture at different temperatures

2,5 Hexandione + cyclopentanol + cyclohexanol			
x_1	x_2	ΔH^{*E}	ΔS^{*E}
0.6504	0.1491	18252.0	-162.7
0.5542	0.2691	17533.6	-165.0
0.4953	0.3810	17944.3	-164.0
0.4396	0.4777	18831.9	-161.5
0.4004	0.5545	15332.5	-173.4
0.3131	0.4560	17280.4	-168.7
0.2213	0.3396	27437.3	-138.7
0.1290	0.2278	37075.9	-110.8
0.0414	0.1182	48337.0	-78.4

From Table-11 we were observed for ternary mixture with increase in mole fraction of 2,5 hexandione enthalpy change decreases but entropy change increases ,these behavior is similar with behavior for two binary systems.

The excess properties Y^E (excess volume, deviation viscosity,activiation free Gibbes energy) are fitted by the method of nonlinear least squares to a Redlich kister type polynomial (13) [23]:

$$Y^E = E_1 x_1 x_2 + E_2 x_1 x_3 + E_3 x_2 x_3 \qquad 13$$

where x_1, x_2 and x_3 are the mole fraction of 2,5 Hexandione, cyclopentanol and cyclohexanol respectively, E_1, E_2 and E_3 are adjustable parameters for polynomials equation which obtained by a least squares method. In each case the optimum number of coefficients E_i was determined from an examination of the variation of standard deviation for ternary system as calculated by previous equation (6).

Table-12: Estimated parameter of Excess and Deviation Function for 2,5hexandion + cyclopentanol + cyclohexanol mixtures at different temperatures

V^E /(cm^3.mol^{-1})				
T/K	E_1	E_2	E_3	σ
298	8.8801	27.1179	15.6552	0.542
303	7.8552	29.6208	13.2376	0.532
308	9.0770	26.3384	14.4361	0.530
313	9.6879	28.8593	5.8915	0.444
Δη /(mpoise)				
T/K	E_1	E_2	E_3	σ
298	-2.7223	-19.8941	-45.9944	0.376
303	-2.4330	-14.1324	-28.4021	0.318
308	-2.8779	-10.2984	-20.6904	0.249
313	-2.0408	-6.1639	-15.6336	0.283
ΔG^{*E} /(J.mol^{-1})				
T/K	E_1	E_2	E_3	σ
298	3488.59	4885.86	4768.58	5.166
303	4613.54	3086.33	5989.37	4.543
308	4051.83	4235.20	6075.78	4.245
313	5355.01	6184.80	4858.57	1.252

The standard deviations between our experimental ternary system data and estimated values were determined from eqution 8, and the results are listed in Table-12. The Redlich kister equation provided the good results to the experimental data with the standard deviations of 2,5 hexanedione + cyclopentanol + cyclohexanol (V^E > 0.4, Δη > 0.2, ΔG^{*E} > 1) at different temperatures under study.

Conclusion

In this work excess molar volume ,divation viscosity ,excess thermodynamics parameters (free Gibbes energy, enthalpy and entropy) were calculated from experimental densities and viscosities for binary

and ternary systems at 298.15 , 303.15 ,308.15 and 313.15 K . The results are shown that:

1. The V^E values for binary mixture of 2,5 Hexandione + cyclopentanol is negative and become positive (less interaction)with increase of temperature over the entire concentration range. But we observed reversal behavior for 2,5Hexandione + cyclohexanol due to hydrogen bonding of components in the mixtures. On the other hand The V^E values for ternary mixture is positive (less interaction) with increase of temperature.
2. The $\Delta\eta$ values for all binaries and ternary mixtures of are negative (more interaction) with increase of temperature over the entire mole fraction of 2,5 hexandione range.
3. Both binaries and ternary systems have positive ΔH^{*E} and negative ΔS^{*E} values, show decrease in ΔH^{*E} and reverse trend in ΔS^{*E} values with mole fraction x_1 of 2,5 hexandione. This indicates that the formation of activated species necessary for viscous flow is difficult for 2,5hexandione in Ternary system or with cyclopentanol mixtures and becomes more easily with cyclohexanol mixture.
4. The experimental values of V^E, $\Delta\eta$ and ΔG^{*E} correlated well with the Redlich-Kister equation and for the binaries systems better than ternary system.

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