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RESEARCH ARTICLE

SOME THERMOPHYSICAL PROPERTIES FOR QUATERNARY SYSTEMS OF N.M.MORPHOLINE, WITH ALKANES AND ALCOHOLS AT FOUR TEMPERATURES

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ABSTRACT

This research reports measurement the densities ρ , and refractive indices, Y_D , for the systems of (N.M. Morpholine + n-nanone + n-octane + n-heptane) and (N.M. Morpoline + 1-nanonal + 1-octanol + n-heptane) over the rang of temperatures (293.15k – 323.15k). From experimental data of densities, and refractive indices, the excess molar volumes, V^E , and excess refractive indices Y_D^E , were calculated for quaternary systems. The excess function results for these systems were observed rocking between positive and negative deviation from ideality depending on molecular interaction in these system. The Flory theory has been extended for the theoretical prediction of excess molar volumes of quaternary systems studied here depending on the pure component liquid parameters. The theory predicted the volumetric behavior and magnitudes of, V_{1234}^E , well.

Refractive indices for quaternary system studied in this work can be predicted by using different refractive indices mixing rules, found good agreement between the experimental and predicted values of the refractive indices for the quaternary system studied here.

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INTRODUCTION

Computer-stimulated calculation and neutron-scattering experiments (Sirger *et al.*, 1979; Klein and Mcdonald 1979) have been insight into the relations between molecular structure and macroscopic behavior. Considerable progress has also been made in the development statistical the cories over recent years (Kohler *et al.*, 1979; Clancy and Gubbins 1978). The calculation of physical properties using a computer statistical theory is still not yet possible for complicated molecules such as long-chain hydrocarbons, because of the range of different conformations which can occur and the effects of there various structures on the intermolecular interaction (Zeidler 1980). The partical studies quaternary mixtures reveal the importance of molecular interaction (hydrogen bonding, charge-transfer complexes, dipole-dipole, dipole-induced dipole, interstitial accommodate chain alignment....etc.) on the physical properties of these mixtures (Blumenhine *et al.*, 1966). Knowledge of the mixing properties are useful in design and simulation processes, in the synthesis of pharmaceuticals, lacquers, resins, polymers, oxygenated fuels, and paint (Wei and Rowley 1994; Vogal 1993). Some of these properties are density refractive index and viscosity. 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 (Salman 2001).

Experimental

(A) (Materials):

All the chemical used were supplied by Fluka AG (Buchs, Switzerland) and Aldrich chemical company Inc. (Milwankee., U.S.A). The purities of all substances were better than 99.95% mass as found by G/C analysis. The purity of the chemicals was checked by comparing the densities, refractive indices and viscosities of the components with those reported in the literature (Kareem 2002; Domanska *et al.*, 1999; Tamura *et al.*, 2000; Krishnalah and Viswanth 1991; Aminabhau and Gopalkrishna 1994).

(B) Measurements

1- Densities-Measurements

Densities were measured at 293.15, 303.15, 313.15 and 323.15k with an Anton paar digital densimeter (Model DMA 60/601) and controlled thermostatically with a precision of $\pm 0.01k$ by a (HAKKE-DI-G) temperature controller Densities were measured with a precision of $2 \times 10^{-5} \text{ g.cm}^{-3}$. The maximum uncertainty in the excess molar volumes is expected to be less than $3 \times 10^{-3} \text{ cm}^3.\text{mol}^{-1}$.

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Refractive Indices Measurements

Refractive index, n_D of the pure component liquids and quaternary mixtures were measured at 293.15, 303.15, 313.15, and 323.15k using an Alb refractometer (Tafesa) by the reflection method using sodium line ($\lambda = 5893\text{\AA}$) with a precision of the reading of ± 0.0002 . In all refractive indices measurements. The temperature was kept constant within ± 0.01 k using as Chott-Gerate (T 1150) thermostat water bath, and a Hewlett-packard model 201 Aquartz thermometer.

RESULTS

Experimental results of the densities, ρ_{1234} of the quaternary mixtures N-Methyl Morpholine + n-nonane + n-octane + n-heptane and N-Methyl Morpholine + 1-nonanol + 1-octanol + n-heptane at (293.15, 303.15, 313.15, and 323.15k) are listed in Table (1). The excess molar volumes for quaternary mixtures studied here were calculated from the measured densities using the following equation (Lorenzana *et al.*, 1991).

$$V_{1234}^E / \text{cm}^3 \cdot \text{mol}^{-1} = \left[\frac{X_1 M_1 + X_2 M_2 + X_3 M_3 + X_4 M_4}{\rho_{1234}} \right] - \left[X_1 \frac{M_1}{\rho_1} + X_2 \frac{M_2}{\rho_2} + X_3 \frac{M_3}{\rho_3} + X_4 \frac{M_4}{\rho_4} \right] \dots (1)$$

Where $X_{(1,2,3,4)}$, $M_{(1,2,3,4)}$ and $\rho_{(1,2,3,4)}$ are respectively the mole fraction, molar mass and density of the pure component liquid (1,2,3,4) ρ_{1234} is the density mixture. The experimental results of V_{1234}^E are listed in Table (3) and plotted as a function of the mole fraction X_1, X_2, X_3 , and X_4 for the four components at four temperatures in Figures (1,2). The statistical concept of Flory theory has been extended for the theoretical prediction of excess molar volume of the quaternary mixture assuming two body interactions (G. and Hamer 1935). The excess molar volumes (V^E) calculated directly from characteristic and reduced volumes and the segment fraction using thermal expansion coefficient (α) of the pure four component liquids, and using the equations.

$$V^E = (X_1 V_1^* + X_2 V_2^* + X_3 V_3^* + X_4 V_4^*) [V - (w_1 V_1 + w_2 V_2 + w_3 V_3 + w_4 V_4)] \dots (2)$$

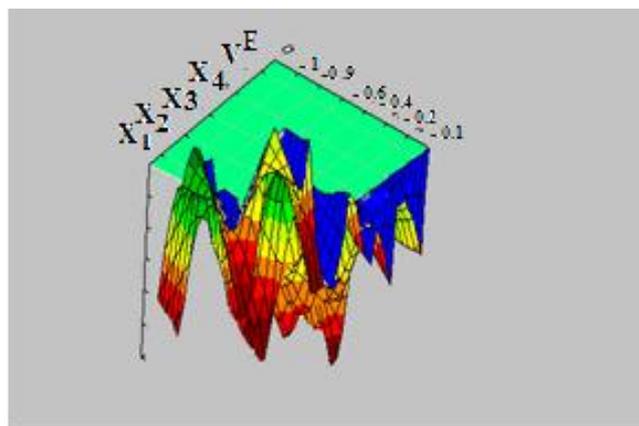
Table 1. Experimental values of the densities (ρ) for quaternary system at four temperatures

X1- N- Methyl Morpholine+ x2- n- Nonane+ x3- n-Octane + x4- n-Heptane							
X1	X2	X3	X4	293.15 k (ρ) ($\text{g}\cdot\text{cm}^{-3}$)	303.15 k (ρ) ($\text{g}\cdot\text{cm}^{-3}$)	313.15 k (ρ) ($\text{g}\cdot\text{cm}^{-3}$)	323.15 k (ρ) ($\text{g}\cdot\text{cm}^{-3}$)
0.2394	0.0000	0.4911	0.2695	0.89210	0.84652	0.80121	0.7834
0.0000	0.5913	0.3653	0.0434	0.94352	0.88324	0.78319	0.7585
0.1216	0.4669	0.0000	0.4115	1.06513	0.97782	0.76501	0.7211
0.3915	0.3332	0.2016	0.0737	1.13662	1.05724	0.84516	0.7899
0.4277	0.2009	0.2661	0.1053	0.79031	0.75128	0.70578	0.6882
0.5634	0.0921	0.3072	0.0373	0.82336	0.79099	0.76759	0.7159
0.6087	0.0000	0.3799	0.0114	0.84618	0.82096	0.79232	0.7329
0.0000	0.4011	0.4934	0.1055	0.91004	0.87344	0.84493	0.7753
0.4453	0.3237	0.0000	0.231	0.98745	0.92112	0.89321	0.8342
0.3559	0.2811	0.1908	0.1722	1.01199	0.99541	0.93766	0.8894
0.2731	0.2193	0.1114	0.3962	1.19219	1.01234	0.99248	0.9119
0.1835	0.1504	0.0762	0.5899	1.22035	1.13958	1.06670	0.9856

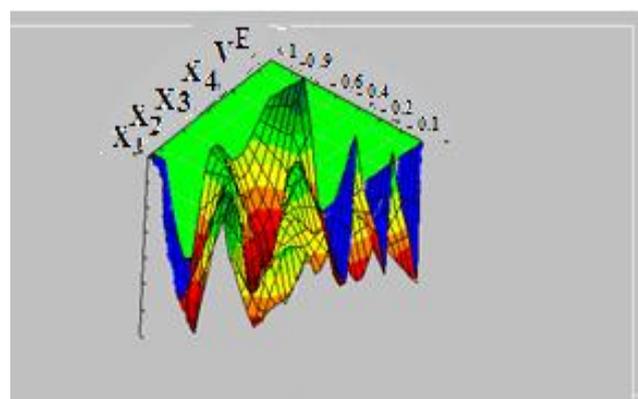
X1- N- Methyl Morpholine+ x2- 1- Nonanol+ x3-1-Octanol + x4- n-Heptane							
X1	X2	X3	X4	293.15 k (ρ) ($\text{g}\cdot\text{cm}^{-3}$)	303.15 k (ρ) ($\text{g}\cdot\text{cm}^{-3}$)	313.15 k (ρ) ($\text{g}\cdot\text{cm}^{-3}$)	323.15 k (ρ) ($\text{g}\cdot\text{cm}^{-3}$)
0.5343	0.0951	0.3219	0.0487	0.94113	0.89745	0.82152	0.79227
0.7013	0.0127	0.1201	0.1659	0.99025	0.94416	0.87284	0.84376
0.8201	0.0000	0.0423	0.1376	1.08156	0.97838	0.91393	0.88617
0.0000	0.5851	0.0000	0.4149	1.21298	1.09329	0.99756	0.94298
0.2917	0.5133	0.0991	0.0959	0.85349	0.80970	0.78676	0.73680
0.4775	0.3015	0.1176	0.1034	0.89592	0.84660	0.83649	0.79669
0.5927	0.2406	0.1653	0.0014	0.93814	0.89512	0.87430	0.83580
0.7158	0.0979	0.1800	0.0063	1.00128	0.97225	0.91410	0.87651
0.9463	0.0000	0.0000	0.0537	1.06263	1.00197	0.97541	0.91232
0.0000	0.6553	0.1537	0.191	1.18574	1.10453	1.00032	0.95131
0.0329	0.4966	0.0928	0.3777	1.20361	1.16311	1.00781	0.99080
0.1214	0.3712	0.0344	0.473	1.26462	1.20470	1.10373	1.00123

Table 2. Parameters for the pure liquids according to the Flory Theory at 303.15k

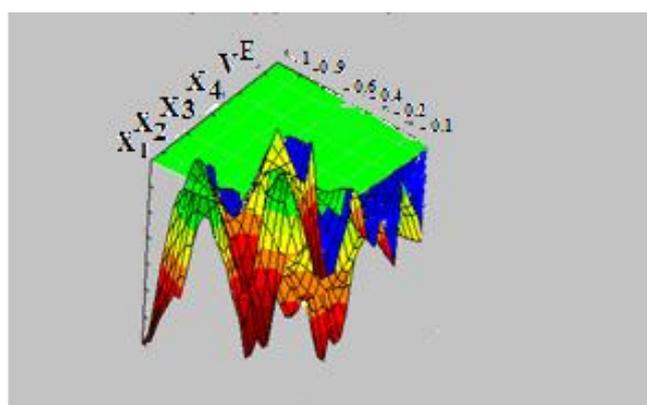
Liquid	$V/\text{cm}^3 \cdot \text{mol}^{-1}$	$V^*/\text{cm}^3 \cdot \text{mol}^{-1}$	\tilde{V}	T^*/k	\tilde{T}	$P^*/\text{J}\cdot\text{cm}^{-3}$	$\alpha \times 10^{-3}/\text{k}^{-1}$	S^*/A^{-1}
N.M.M.	101.39	91.94	1.2006	6054.00	0.0492	402	0.779	1.121
n-Heptane	147.480	104.191	1.297	6453.00	0.0640	432	1.235	1.02
n-Nonane	159.312	119.281	1.289	4753.57	0.062	435	1.203	1.01
n-Octane	163.519	127.689	1.281	4824.43	0.0618	439	1.1165	0.99
1-Nonanol	123.012	138.009	1.575	5549.16	0.088	557	1.1189	0.63
1-Octanol	145.302	138.448	1.593	5528.06	0.076	552	1.194	0.86



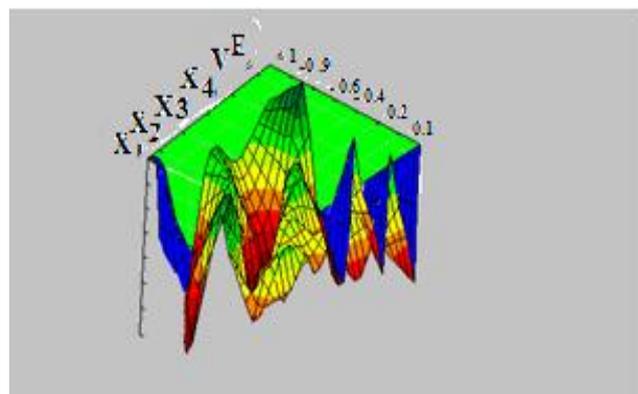
1-a



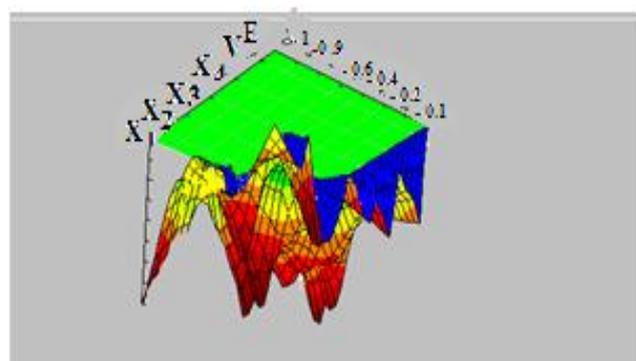
2-a



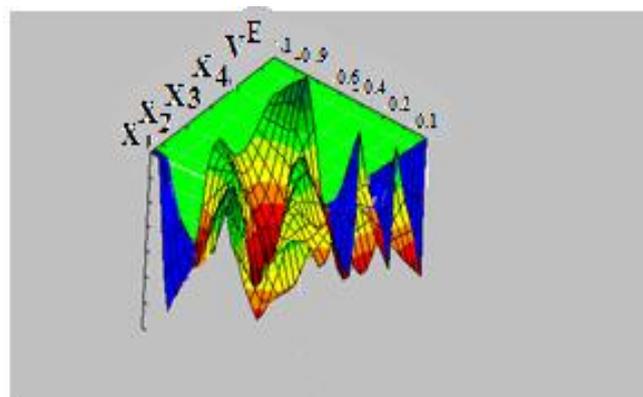
1-b



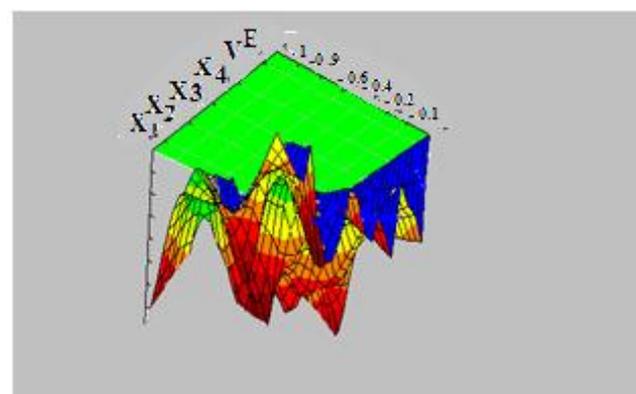
2-b



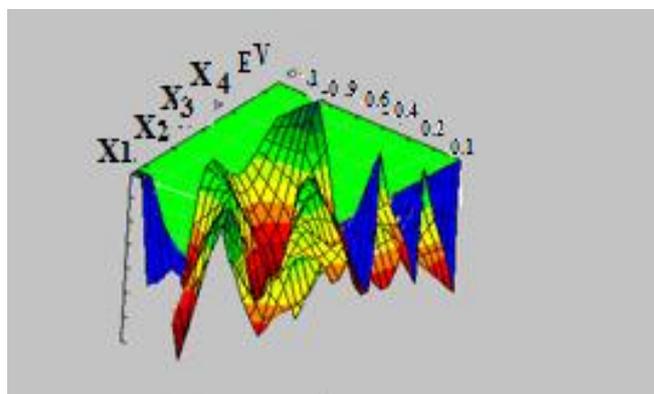
1-c



2-c



1-d



2-d

Figure 1. Excess molar volumes V^E_{1234} for quaternary system versus X_1 N.M.M + X_2 n-Nonane + X_3 n-Octane X_4 n-heptane at (1-a) 293.15k,(1-b) 303.15k, (1-c) 313.15k, and (1-d)323.15 K

Figure 2. Excess molar volumes V^E_{1234} for quaternary system versus X_1 N.M.M + X_2 1-Nonanol + X_3 1-Octanol + X_4 n-heptane at (2-a) 293.15k,(2-b) 303.15k, (2-c) 313.15k, and (2-d)323.15 K

Table 3. Experimental and theoretical prediction of (v^E) for quaternary system

X1- N- Methyl Morpholine+ x2- n- Nonane+ x3- n-Octane + x4- n-Heptane									
X1	X2	X3	X4	293.15 k	303.15 k	303.15 k	313.15 k	323.15 k	
				$V^E_{(Cm^{-3}.mol^{-1})}$	$V^E_{exp.(Cm^{-3}.mol^{-1})}$	$V^E_{pred.(Cm^{-3}.mol^{-1})}$	$V^E_{(Cm^{-3}.mol^{-1})}$	$V^E_{(Cm^{-3}.mol^{-1})}$	
0.2394	0.0000	0.4911	0.2695	-0.7003	-0.6925	-0.6019	-0.6905	-0.7048	
0.0000	0.5913	0.3653	0.0434	-0.9832	-1.0130	-1.0098	-1.0593	-1.0905	
0.1216	0.4669	0.0000	0.4115	-0.9232	-0.8867	-0.8255	-0.7068	-0.6708	
0.3915	0.3332	0.2016	0.0737	-0.6851	-0.7107	-0.6559	-0.7166	-0.7271	
0.4277	0.2009	0.2661	0.1053	-0.5759	-0.5947	-0.5733	-0.6124	-0.6270	
0.5634	0.0921	0.3072	0.0373	-0.5069	-0.5356	-0.5062	-0.5612	-0.5725	
0.6087	0.0000	0.3799	0.0114	-0.4801	-0.5105	-0.4910	-0.5335	-0.5486	
0.0000	0.4011	0.4934	0.1055	-0.9571	-0.9788	-0.9630	-1.0232	-1.0367	
0.4453	0.3237	0.0000	0.231	-0.6124	-0.6135	-0.6071	-0.6382	-0.6220	
0.3559	0.2811	0.1908	0.1722	-0.6934	-0.7209	-0.7057	-0.7401	-0.7442	
0.2731	0.2193	0.1114	0.3962	-0.8713	-0.7823	-0.7800	-0.8083	-0.7644	
0.1835	0.1504	0.0762	0.5899	-1.0169	-0.9737	-0.9609	-0.9454	-0.8840	

X1- N- Methyl Morpholine+ x2- 1- Nonanol+ x3- 1-Octanol + x4- n-Heptane									
X1	X2	X3	X4	293.15 k	303.15 k	303.15 k	313.15 k	323.15 k	
				$V^E_{(Cm^{-3}.mol^{-1})}$	$V^E_{exp.(Cm^{-3}.mol^{-1})}$	$V^E_{pred.(Cm^{-3}.mol^{-1})}$	$V^E_{(Cm^{-3}.mol^{-1})}$	$V^E_{(Cm^{-3}.mol^{-1})}$	
0.5343	0.0951	0.3219	0.0487	-0.3657	-0.3937	-0.3815	-0.4084	-0.4211	
0.7013	0.0127	0.1201	0.1659	-0.3467	-0.3628	-0.3566	-0.3565	-0.3563	
0.8201	0.0000	0.0423	0.1376	-0.3155	-0.3221	-0.3090	-0.3220	-0.3220	
0.0000	0.5851	0.0000	0.4149	-0.8832	-0.8327	-0.8300	-0.7983	-0.7831	
0.2917	0.5133	0.0991	0.0959	-0.4708	-0.4893	-0.4742	-0.5122	-0.5193	
0.4775	0.3015	0.1176	0.1034	-0.4014	-0.4200	-0.4198	-0.4433	-0.4495	
0.5927	0.2406	0.1653	0.0014	-0.3406	-0.3743	-0.3653	-0.3974	-0.4122	
0.7158	0.0979	0.1800	0.0063	-0.2889	-0.3232	-0.3150	-0.3430	-0.3542	
0.9463	0.0000	0.0000	0.0537	-0.2225	-0.2518	-0.2410	-0.2653	-0.2632	
0.0000	0.6553	0.1537	0.191	-0.7160	-0.7198	-0.7044	-0.7203	-0.7326	
0.0329	0.4966	0.0928	0.3777	-0.8338	-0.8373	-0.8293	-0.7746	-0.7938	
0.1214	0.3712	0.0344	0.473	-0.9004	-0.8878	-0.8713	-0.8525	-0.7947	

Table 4. Experimental values of the refractive indices (n_D) for quaternary system at four temperatures

X1- N- Methyl Morpholine+ x2- n- Nonane+ x3- n-Octane + x4- n-Heptane									
X1	X2	X3	X4	293.15 k	303.15 k	313.15 k	323.15 k		
				n_D	n_D	n_D	n_D		
0.2394	0.0000	0.4911	0.2695	1.3927	1.3813	1.3721	1.3677		
0.0000	0.5913	0.3653	0.0434	1.3979	1.3951	1.3788	1.3739		
0.1216	0.4669	0.0000	0.4115	1.4054	1.3997	1.3809	1.3797		
0.3915	0.3332	0.2016	0.0737	1.4147	1.4007	1.3923	1.3867		
0.4277	0.2009	0.2661	0.1053	1.3809	1.3801	1.3737	1.3658		
0.5634	0.0921	0.3072	0.0373	1.3834	1.3829	1.3798	1.3714		
0.6087	0.0000	0.3799	0.0114	1.3912	1.3887	1.381	1.3785		
0.0000	0.4011	0.4934	0.1055	1.4102	1.3912	1.3892	1.3827		
0.4453	0.3237	0.0000	0.231	1.4189	1.4044	1.3951	1.3891		
0.3559	0.2811	0.1908	0.1722	1.4222	1.4084	1.4012	1.3949		
0.2731	0.2193	0.1114	0.3962	1.4264	1.4133	1.408	1.3998		
0.1835	0.1504	0.0762	0.5899	1.4298	1.4196	1.4159	1.4053		

X1- N- Methyl Morpholine+ x2- 1- Nonanol+ x3-1-Octanol + x4- n-Heptane									
X1	X2	X3	X4	293.15 k	303.15 k	313.15 k	323.15 k		
				n_D	n_D	n_D	n_D		
0.5343	0.0951	0.3219	0.0487	1.4015	1.3909	1.3822	1.3661		
0.7013	0.0127	0.1201	0.1659	1.4089	1.4041	1.3945	1.372		
0.8201	0.0000	0.0423	0.1376	1.4107	1.4067	1.4001	1.3794		
0.0000	0.5851	0.0000	0.4149	1.4213	1.4184	1.4077	1.3856		
0.2917	0.5133	0.0991	0.0959	1.3826	1.3709	1.3682	1.3531		
0.4775	0.3015	0.1176	0.1034	1.3889	1.3776	1.3735	1.3604		
0.5927	0.2406	0.1653	0.0014	1.3954	1.382	1.3789	1.3693		
0.7158	0.0979	0.1800	0.0063	1.4076	1.3897	1.3813	1.3737		
0.9463	0.0000	0.0000	0.0537	1.4142	1.3947	1.3869	1.3799		
0.0000	0.6553	0.1537	0.191	1.4187	1.4028	1.3923	1.3887		
0.0329	0.4966	0.0928	0.3777	1.4207	1.4174	1.4078	1.3946		
0.1214	0.3712	0.0344	0.473	1.4298	1.4237	1.4194	1.4033		

Where $W_1, W_2, W_3, \text{and } W_4$ are the segment fractions of components 1,2,3 and 4 and defined by the relations:

$$w_1 = (1 - w_2 - w_3 - w_4) \dots\dots(3)$$

$$w_2 = X_2 / [X_2 + X_3 \left(\frac{V_3^*}{V_2^*}\right) + X_4 \left(\frac{V_4^*}{V_2^*}\right) + X_1 \left(\frac{V_1^*}{V_2^*}\right)] \dots\dots(4)$$

$$w_3 = X_3 / [X_3 + X_4 \left(\frac{V_4^*}{V_3^*}\right) + X_1 \left(\frac{V_1^*}{V_3^*}\right) + X_2 \left(\frac{V_2^*}{V_3^*}\right)] \dots\dots(5)$$

$$w_4 = X_4 / [X_4 + X_1 \left(\frac{V_1^*}{V_4^*}\right) + X_2 \left(\frac{V_2^*}{V_4^*}\right) + X_3 \left(\frac{V_3^*}{V_4^*}\right)] \dots\dots(6)$$

V in equation (2) is the reduced volume of quaternary mixture which is obtained by the following equation:

$$V = V / (X_1 V_1^* + X_2 V_2^* + X_3 V_3^* + X_4 V_4^*) \dots\dots(7)$$

Where V is the molar volume of the mixture, given by:

$$V = (X_1 M_1 + X_2 M_2 + X_3 M_3 + X_4 M_4) / \rho_m \dots\dots(8)$$

Where ρ_m is the density of the mixture.

By using the equation of state parameters of pure liquids, table (2) applied equations (2-8), we calculated the excess molar volume for the quaternary mixtures studied here. Table (3) present the theoretical prediction of V^E values at 303.15k with experimental values for comparison for quarter nary mixtures studied here. The maximum percent average deviation is less than 0.92% which means that Flory theory for predicting the excess molar volumes of quaternary mixtures studied here is quite reasonable, as evident from this excellent agreement in both sign and magnitude. Experimental results of refractive indices of quaternary mixtures studied here at (293.15, 303.15, 313.15 and 323.15) k are listed in Table (4). Excess refractive indices for quaternary mixtures at (293.15, 303.15, 313.15 and 323.15) k were calculated from measurements of the refractive indices of the mixture and the pure liquids by equation (9) (Lam *et al.*, 1974).

$$n^E = n_{D,m} - \sum_{s=i,j,k} X_s n_{D,s} \dots\dots(9)$$

The obtained result are listed in Table (5) and a plotted as a function of mole fraction X_1, X_2, X_3 and X_4 for the four components at four temperatures in Figures (3,4). Many equations were proposed using mixing rules for the analysis of the Data for quaternary mixtures. In order to check their validity, the measured refractive indices of mixtures were compared with that calculated from different equations. Arago and Biot (Ritzoulis *et al.*, 2000) attempts to describe the refractive properties of the solutions using the following equation:

$$n = W_1 n_1 + W_2 n_2 \dots\dots(10)$$

Where n, n_1 and n_2 are the refractive indices of mixtures component 1 and 2 respectively, W_1 and W_2 are the volume fraction of the respective components in the mixture. Gladstone and Dale (24) formulated the following relation:

$$n - 1 = W_1(n_1 - 1) + W_2(n_2 - 1) \dots\dots(11)$$

This may be reduced to equation (10) if one assumes volume additively (no change in volume on mixing). Lorentz and Lorenz (Ritzoulis *et al.*, 2000) gave more commonly used mixing rule in the analysis of refractive index:

$$\frac{n^2 - 1}{n^2 - 2} = W_1 \left[\frac{n_1^2 - 1}{n_1^2 + 2} \right] + W_2 \left[\frac{n_2^2 - 1}{n_2^2 + 2} \right] \dots\dots(12)$$

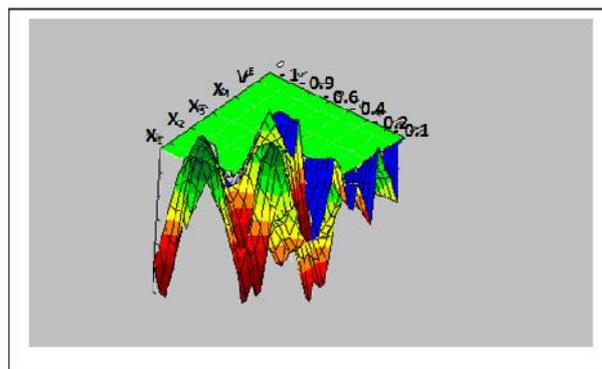
Wiener (Ritzoulis *et al.*, 2000) derived an equation that may be applied to isotropic bodies of spherical and symmetrical shape and that is valid for binary system is volume additively is assumed.

$$\frac{n^2 - n_1^2}{n^2 + 2n_1^2} = W_2 \left[\frac{n^2 - n_1^2}{n^2 + 2n_1^2} \right] \dots\dots(13)$$

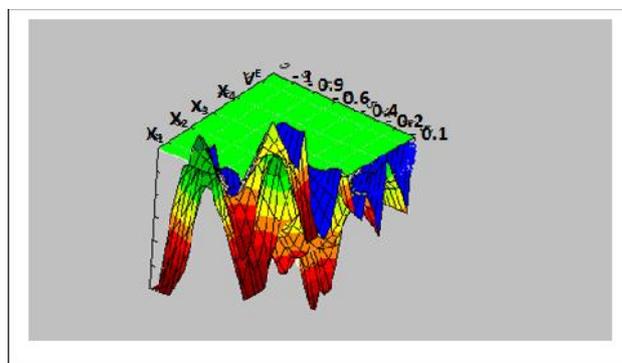
Helaler *et al.* (Ritzoulis *et al.*, 2000) derived an equation by summing the equivalent of the light scattering equations of Debye and Kayleigh, in the form:

$$\frac{n - n_1}{n_1} = \frac{3}{2} W_2 \left[\frac{(n_2 / n_1) - 1}{(n_2 / n_1) + 2} \right] \dots\dots(14)$$

The calculated refractive indices from these equations are listed in Table (6) for quaternary mixtures studied here at (293.15, 303.15, 313.15, and 323.15)k. We found good agreement between the experimented data and the calculated.

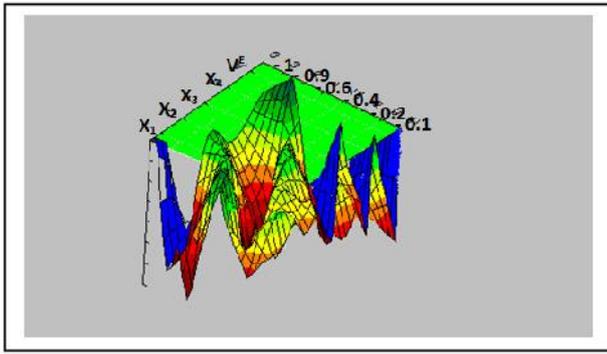


3-a

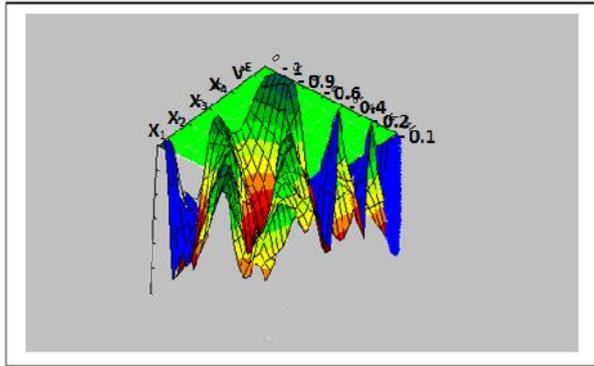


3-b

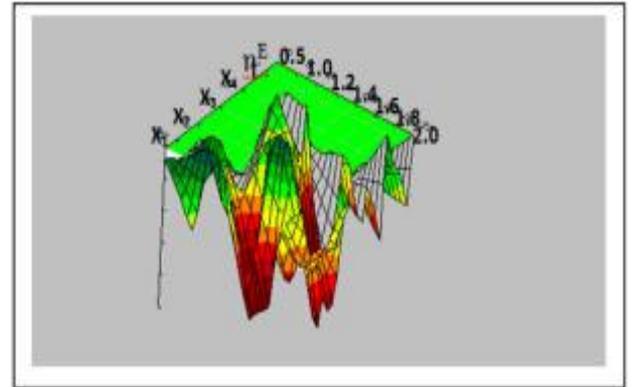
Figure 3. Excess molar volumes V_{1234}^E for quaternary system versus X_1 N.M.M + X_2 n-Nonane + X_3 n-Octane + X_4 n-heptane at 303.15k (3-a) V_{flory}^E , (3-b) V_{exp}^E .



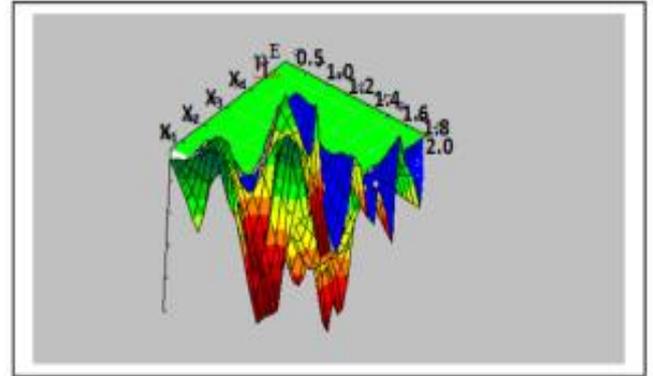
4-a



4-b



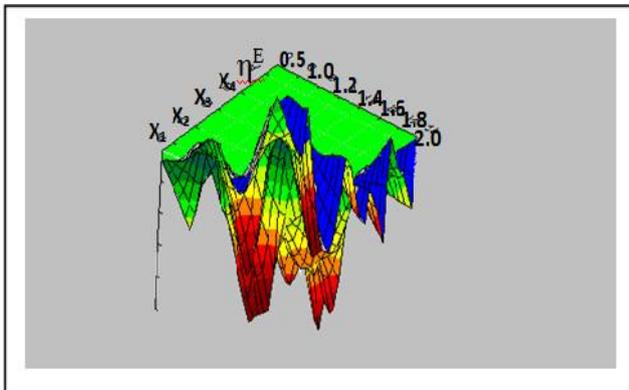
5-c



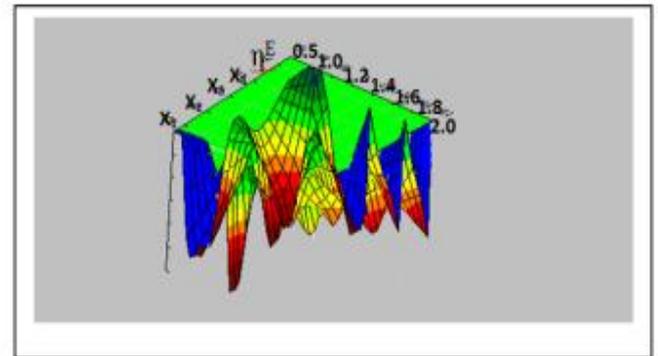
5-d

Figure 4. Excess molar volumes V_{1234}^E for quaternary system versus X_1 N.M.M + X_2 1-Nonanol + X_3 1-Octanol + X_4 n-heptane at 303.15k (4-a) V_{flory}^E , (4-b) V_{exp}^E .

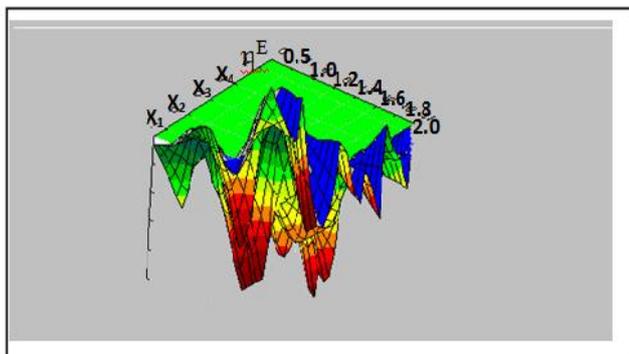
Figure 5. Excess refractive indices n^E for quaternary system versus X_1 N.M.M + X_2 n-Nonane + X_3 n-Octane + X_4 n-heptane at (5-a) 293.15k, (5-b) 303.15k, (5-c) 313.15k, and (5-d) 323.15k



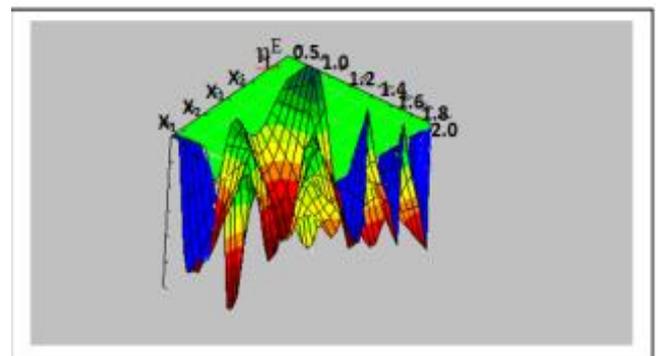
5-a



6-a



5-b



6-b

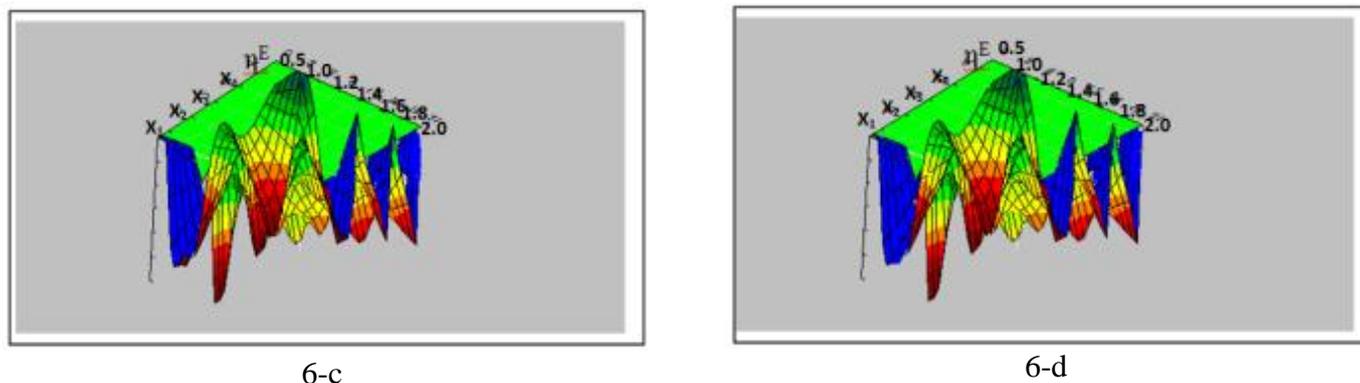


Figure 6. Excess refractive indices n^E for quaternary system versus X_1 N.M.M+ X_2 1-Nonanol + X_3 1-Octanol + X_4 n-heptane at (6-a) 293.15k, (6-b) 303.15k, (6-c) 313.15k, and (6-d) 323.15k.

Table 5. Experimental values of excess refractive indices (n^E) for quaternary system at four temperatures

X1- N- Methyl Morpholine+ x2- n- Nonane+ x3- n-Octane + x4- n-Heptane							
X1	X2	X3	X4	293.15 k n^E	303.15 k n^E	313.15 k n^E	323.15 k n^E
0.2394	0.0000	0.4911	0.2695	-0.0183	-0.2790	-0.0358	-0.0388
0.0000	0.5913	0.3653	0.0434	-0.0034	-0.0794	-0.0189	-0.0225
0.1216	0.4669	0.0000	0.4115	0.0007	-0.0080	-0.0200	-0.0198
0.3915	0.3332	0.2016	0.0737	-0.0111	-0.0282	-0.0302	-0.0340
0.4277	0.2009	0.2661	0.1053	-0.0459	-0.0380	-0.0498	-0.0560
0.5634	0.0921	0.3072	0.0373	-0.0525	-0.0529	-0.0530	-0.0595
0.6087	0.0000	0.3799	0.0114	-0.0474	-0.0482	-0.0546	-0.0552
0.0000	0.4011	0.4934	0.1055	0.0107	-0.0078	-0.0067	-0.0120
0.4453	0.3237	0.0000	0.231	-0.0085	-0.0182	-0.0288	-0.0330
0.3559	0.2811	0.1908	0.1722	0.0004	-0.0082	-0.0172	-0.0218
0.2731	0.2193	0.1114	0.3962	0.0130	-0.0125	-0.0019	-0.0086
0.1835	0.1504	0.0762	0.5899	0.0250	-0.0282	0.0145	0.0053

X1- N- Methyl Morpholine+ x2- 1- Nonanol+ x3-1-Octanol + x4- n-Heptane							
X1	X2	X3	X4	293.15 k n^E	303.15 k n^E	313.15 k n^E	323.15 k n^E
0.5343	0.0951	0.3219	0.0487	-0.0451	-0.0541	-0.4394	-0.0755
0.7013	0.0127	0.1201	0.1659	-0.0384	-0.0416	0.0136	-0.0701
0.8201	0.0000	0.0423	0.1376	-0.0420	-0.0444	0.0822	-0.0680
0.0000	0.5851	0.0000	0.4149	0.00697	0.0059	0.0704	-0.0244
0.2917	0.5133	0.0991	0.0959	-0.0552	-0.0653	-0.0712	-0.0801
0.4775	0.3015	0.1176	0.1034	-0.0543	-0.0640	-0.0864	-0.0779
0.5927	0.2406	0.1653	0.0014	-0.0560	-0.0678	-0.2963	-0.0770
0.7158	0.0979	0.1800	0.0063	-0.0474	-0.0638	-0.3197	-0.0762
0.9463	0.0000	0.0000	0.0537	-0.0466	-0.0645	0.0032	-0.0754
0.0000	0.6553	0.1537	0.191	-0.0053	-0.0195	0.0227	-0.0310
0.0329	0.4966	0.0928	0.3777	0.0040	0.0025	0.3883	-0.0176
0.1214	0.3712	0.0344	0.473	0.0170	0.0128	0.6913	-0.0049

Table 6. The predicted refractive indices (n_D) for quaternary system at four temperatures

X1- N- Methyl Morpholine+ x2- n- Nonane+ x3- n-Octane + x4- n-Heptane							
X1	X2	X3	X4	293.15 k $n_{D, pred}$	303.15 k $n_{D, pred}$	313.15 k $n_{D, pred}$	323.15 k $n_{D, pred}$
0.2394	0.0000	0.4911	0.2695	1.3920	1.3800	1.3715	1.3665
0.0000	0.5913	0.3653	0.0434	1.3965	1.3935	1.3770	1.3725
0.1216	0.4669	0.0000	0.4115	1.4030	1.3970	1.3800	1.3785
0.3915	0.3332	0.2016	0.0737	1.4135	1.3995	1.3905	1.3855
0.4277	0.2009	0.2661	0.1053	1.3795	1.3790	1.3715	1.3645
0.5634	0.0921	0.3072	0.0373	1.3805	1.3805	1.3790	1.3705
0.6087	0.0000	0.3799	0.0114	1.3890	1.3865	1.365	1.3780
0.0000	0.4011	0.4934	0.1055	1.4090	1.3900	1.3880	1.3810
0.4453	0.3237	0.0000	0.231	1.4170	1.4020	1.3945	1.3875
0.3559	0.2811	0.1908	0.1722	1.4200	1.4055	1.4000	1.3930
0.2731	0.2193	0.1114	0.3962	1.4250	1.4115	1.4070	1.3925
0.1835	0.1504	0.0762	0.5899	1.4275	1.4180	1.4130	1.4035

X1- N- Methyl Morpholine+ x2 - 1- Nonanol+ x3-1-Octanol + x4- n-Heptane

X1	X2	X3	X4	293.15 k	303.15 k	313.15 k	323.15 k
0.5343	0.0951	0.3219	0.0487	$n_{D, pred}$ 1.4005	$n_{D, pred}$ 1.3900	$n_{D, pred}$ 1.3815	$n_{D, pred}$ 1.3655
0.7013	0.0127	0.1201	0.1659	1.4075	1.4025	1.3940	1.3710
0.8201	0.0000	0.0423	0.1376	1.4095	1.4050	1.3995	1.3785
0.0000	0.5851	0.0000	0.4149	1.4190	1.4175	1.4065	1.3850
0.2917	0.5133	0.0991	0.0959	1.3815	1.3700	1.3675	1.3525
0.4775	0.3015	0.1176	0.1034	1.3880	1.3760	1.3720	1.3595
0.5927	0.2406	0.1653	0.0014	1.3930	1.3815	1.3780	1.3685
0.7158	0.0979	0.1800	0.0063	1.4065	1.3890	1.3805	1.3730
0.9463	0.0000	0.0000	0.0537	1.4130	1.3935	1.3860	1.3790
0.0000	0.6553	0.1537	0.191	1.4175	1.4010	1.3915	1.3880
0.0329	0.4966	0.0928	0.3777	1.4200	1.4150	1.4075	1.3940
0.1214	0.3712	0.0344	0.473	1.4285	1.4230	1.4185	1.4025

DISCUSSION

The experimental excess molare volumes V_{1234}^E for the quaternary mixtures studied here at (293.15, 303.15, 313.15, and 323.15) k are rocking between N.M.M. + n-Nonane + n-Octane + n-Heptane and N.M.M. + 1-Nonanol + 1-Octanol + n-Heptane. The negative value of V^E means a strong molecular interaction among the mixture components also the values of this interaction decreases with increasing mole fraction of N-methyl morpholine (NMM), this molecules seems to be a globular molecule in comparison with other three molecules which are linear alkans so that the strength of attraction comes from the tendency of alkanic molecules to pack well with each other, here the globular NMM molecules acts to perturbate this packing and that will move away the alkanic chains from each other the result is the decrease of whole interaction strength as we see from V^E values of high mole fraction of NMM. The Calculated value of V^E at 303.15K according to Flory theory are in agreement with the values predicted experimentally, we think that the disappearance of large deviations from theoretical model is due for non existing of strong orientational forces among solution component molecules so and for the same reason the deviations of y^E values were smaller than a theoretical model with increasing the values of V^E and y^E show a random behavior which attributed to complexity of the composition of this system. The excess refractive indices n^E behavior for the quaternary system studied here show a similar volumetric behavior, Table (5) and Figures (5). Refractive indices for quaternary system studied in this work can be predicted by using different refractive indices mixing rules and presented in Table (6). The researcher found good agreement between the experimental and the predicted values of the refractive indices for quaternary system studied here.

REFERENCES

- Aminabhau T.M., and B. Gopalkrishna, J. Chem. Eng. Data, 39,529, (1994).
- Barbe M. and D. Patterson, J. Sol. Chem., 9,753, (1980).
- Barbosa E.F.G., S.M.C. Sousa, M.C.S. Santos and I.M.S. Lamperia, Phys. Chem., 3,556, (2001).
- Benson G.B.C., S. Murakami, V. T. Lam and J. Singh, Can.J. Chem., 48,211, (1970).
- Blumenhine R.L., W.H. Fortune, and P.G. Seuis, J. Chem. Eng. Data, 11,406, (1966).
- Clancy P. and Gubbins K.E., Disc. Faraday Soc., 66,116, (1978).
- Domanska U., J. Lachwa and P. Morawski, J. Chem. Eng. Data, 44,974, (1999).
- G. and W. J. Hamer, J. Chem. Soc., 57,1805, (1935).
- Heric E.L. and B.M. Coursey, J. Chem. Eng. Data, 17, (41-44), (1972).
- Jones D.E.G., I.A. Weeks and G.C. Benson, Can. J. Chem., 47,281, (1971).
- Kareem E.T., PhD. Thesis. Baghdad University (2002).
- Klein M.L. and McDonald I.R., J. Chem. Phys., 71,298, (1979).
- Kohler F., Quirke N. and Perram J. W., J. Chem. Phys., 71,4128, (1979).
- Krishnah A. and D.S. Viswanth, J. Chem. Eng. Data, 36,317, (1991).
- Lam V.T., P. Picker, D. Patterson and P. Tancrede, J. Chem., Soc. Faraday Trans., 2,70,1465, (1974).
- Lorenzana M.T., E. Jimenez, J. L. Legoido, J. Ferradez and M.I. Andrade, Phys. Chem. Lig., 24,13, (1991).
- Riddic J.A. and W.B. Bunger "Techniques of Chemistry" 2, Organic Solvents. 5th Ed. Wiley-Interscience, New York (1985).
- Ritzoulis G., D. Missopolinon, S. Doulami, and C. Panayioton, J. Chem. Eng. Data, 45,638, (2000).
- Salman H.E., PhD. Thesis "Density, refractive index, dielectric constant, and excess property of binary mixtures containing sulfolane and N-methyl morpholine" Saddam University (2001).
- Salman T.A., Journal for Science, Al-Nahrain University (2008).
- Shukla R.K., Shukla A.K. and Pandey J.D., J. Phys. Chem., 93,4627, (1989).
- Sirger K., Singer J.V.L. and Tayler A.J., Mol. Phys., 37, 1239, (1979).
- Tamura K., N. Morishita and T. Yamada, J. Chem. Eng. Data, 45,555, (2000).
- Tu. C.H., S.L. Lec and I.H. Peng, J. chem. Eng. Data, 46,151, (2001)
- Vogal E., Fluid phase Equilibrium, 88, 227, (1993).
- Weast C. R., Hand book of chemistry and physics, "Chemical Rubber" company, cleveland and OH, 6th Ed. (1984).
- Wei I. C. and R.L. Rowley, J. Chem. Eng. Data, 49,332, (1994).
- Zeidler M., Angew. Chem. Int. Ed. Engl., 19,697, (1980).
