

دراسة التداخلات الجزيئية لمجموعة من المركبات الحلقية السداسية مع النايتروميثان وذلك بقياس الكثافة ومعامل الانكسار عند درجة حرارة 298.15 كلفن

م.م احمد اسماعيل كنوري

م.م احمد محمد عباس الجبوري

م.م فراس حبيب عبد الرزاق الدهلكي

جامعة بغداد

جامعة ديالى - كلية التربية - الرازي

كلية التربية - ابن الهيثم

قسم الكيمياء

قسم الكيمياء

Studies of Molecular interaction for hexacyclic compound with Nitromethane by measuring densities and Refractive index in 298.15 K

Submitted by

A.T \ Ahmad Mohammad Abase aL, jobore University of Baghdad college of education Ebn Al Haytham department of chemistry

A.T\ Ahmed Esmaeel Kanore & A.T Firas Habeb Abdal Razzak

University of Diyala college of education Al Raze department of chemistry

Introduction

Nitro methane is an aprotic solvent with high polarity Which is used in a variety of applications⁽¹⁾ There is many . project between nitromethane and many kind of R - OH and Ar-OH at diffract temperature. But Less then between nitromethane and cyclic compound.

Nitromethane has been chosen as the polar component nitroalkanes are chemical compounds that are liquids at room he have reflected in their high dipole moment temperature ⁽²⁾the y and dielectric constant.

In this studied we had suggested that dipole induce dipole - and charge transfer may be happened between nitromethane and pound for the dipole pound in the cyclic compound in the other hand they have hydrogen bonding which is accuse between -N o2 grop and hydrogen in

the cyclic compound.

We suggest hexane to compact the . . Pound effect as a molecular Interaction in this work.

In this work densities as a excess molar volume and Refractive index as a (n^E) excess molar refractivity over the range of composition at atmospheric pressure and in the temperature (298.15 K) were measured from these experimental data we have obtained thermodynamic properties of this mixtures.

M.G. Santos and C. G. Losa⁽³⁾ was studied Excess volumes of 1 .1.2.2 tetrachloroethane + tetrachloroethylene and of 1 .1.2.2 tetra - chloroethane and of tetrachloroethylene with cyclohexane benzene at 303.15K this work show positive deviation from ideality in Excess molar velum for Benzine and cyclohexane and they behavior that to confirm the formation of a molecular complex.

R.K. burfat and A.J. Richard⁽⁴⁾ was measured densities and Refractive index to calculate specific volumes and of organic Liquids that is contained hexane, 1-Hexene, Cyclohexane, Cyclohexane 1.4-Cyclohexadiene, 1.3- Cyclohexadiene, Benzene and many organic Liquides in 293.15K , 295.15k

J. troncoso, C. A. Tovar, C. A. Cerdeirira, E. Corbollo, and Romani⁽²⁾ work in Temperature dependence of densities and speeds of sound of Nitromethane with butanol in the range (288.15-308.15)K they show negative and positive bivitiation in VE and speed of sound.

Chein - H. Tu , S. L. Lee. And 1. 11, pang⁽⁵⁾ work in Excess volumes and Viscosities of Binaiy Mixtures of Aliphatic Alcohols (C1 - C4) with Nitromethane at range (293.15K , 303.15K 313.15K) and show tow kind of deviation in VE , nE positive and Negative Divation

2- Experimental

Cycloheane and cyclohexane were Fisher company in purity more thatd 98% Benzene 1, 3 cyeloohexadiene and 1, 4 cycohexadiene were obtained from FLUCA in purity 99% all components were dried over molecular sieves (Aldrich, 0.3nm) Nitro methane was distilled through a glass column (23-mm 1. d and 470 - nm length, teflon mesh packing) under nitrogen. The other components were used without further purification the purity of solvents was further ascertained by measuring their densities, and refractive in dexa at 298.15K (table 1) which agreed reasonably with the corresponding literature values.

Table (1). Comparison of measured densities, and Refractive Indices of pure components with literature values at 298.15K

Compound	$\rho/\text{g.cm}^{-3}$		n_D	
	This work	Lit	This work	Lit
Nitromethane	1.13102	1.13128 ⁽⁶⁾	1.3899	1.3924 ⁽⁶⁾
Cyclohexane	0.77391	0.7736 ⁽⁷⁾	1.4252	1.4249 ⁽⁸⁾
Cyclohexene	0.80642	0.8061 ⁽⁹⁾	1.4458	1.4461 ⁽⁹⁾
1,3-cyclohexadiene	0.82753	0.8272 ⁽¹⁰⁾	1.4779	1.4776 ⁽¹¹⁾
1,4-cyclohexadiene	0.83328	0.8333 ⁽¹¹⁾	1.4737	1.4734 ⁽¹¹⁾
Benzene	0.87392	0.8736 ⁽¹²⁾	1.5017	1.5020 ⁽⁹⁾

All dried liquids were boiled to remove dissolved air solutions of different composition were prepared by mass in a 25.cm³ Erlenmeyer Flask provided with a joint stopper using a mettle AB₂OA balance with an uncertainty of $\pm 0.1\text{mg}$.

3. Results and Discussion

The uncertainty in the mole fraction is $\pm 5 \times 10^{-5}$ Densities were measured using a DMA - 58 vibrating - tube centimeter (Ant or paar Graz/ Austria) with stated uncertainty of $+0.00002 \text{ g} \cdot \text{C m}^{-3}$.

The temperature in the measuring cell was regulated to $\pm 0.01\text{K}$ the uncertainty of the density measurements was less than $\pm 0.001 \text{ g} \cdot \text{cm}^{-3}$. Refractive Index (no) were measured for the pure component and for mixture to the five system in diffract mole fraction at 298.15K and by using sodium line ($\lambda = 5893 \text{ \AA}$) in Refractometer types (Tafesa) in accuracy not less than (± 0.0004) in all the measurement, the Temperature is constant at (298.15K) by using the water bath from schott - Gerate CT 1 1 50 Thermostat and that is contains thermometer hewlett - Packard - model 201 Aquartz Thermometer. To get high accuracy we are used distill water and methanol to chide the Refractive Index in (298.15K) and that is lead to good result for the measurement

The experimental densities, and excess molar volume for all of the binary mixtures are given tables (2) the molar excess volumes, V^E , have been calculated from density data according to the equation

$$V^E = (X_1 M_1 + X_2 M_2) / \rho - (X_1 M_1 / \rho_1) - (X_2 M_2 / \rho_2) \dots \dots (1)$$

Where p is the density of the mixture and X_1 , p_1 , M_1 , X_2 , p_2 and M_2 , are the mole fractions, densities, and molecular weights of pure components (1) and (2) respectively. The Deviation from Refractivity (n^E) is given by

$$n^E = n_{mix} - (X_1 n_1 + X_2 n_2) \dots \dots (2)$$

Where (N_{mix}) is the Refractive Index for the mixture, n_1 , n_2 Refractive Index for the pure component Nitromethan (X_1) and cyclohexane, cyclohexane, 1,3 cyclo hexadiene, 1,4 cyclohexadiene and Benzene (X_2), X_1 , X_2 the mole fraction for Nitromethan and another cyclic compound respectively. The

mole fraction (X_1) and Refractive Index Deviation from Refractivity for all binary mixtures are given in tables (3).

Table (2): Experimental Densities (ρ) and Excess molar Volume and mole fraction, Refractive index (n_D) and Diviation from Refractivity (n^E) for Nitromethan (X_1) and cyclohexane (X_2), Cyclohexene (X_2), 1,3 cyclohexadiene (X_2) 1,4 cyclohexdiene (X_2), Benzene (X_2) at 298.15K.

Nitromethane (X_1) + cyclohexane (X_2)				
X_1	ρ gm cm ⁻³	n_D	V^E	n^E
0.0759	0.78786	1.4233	0.0081	0.00081
0.1482	0.802222	1.4214	0.0151	0.00153
0.2119	0.815867	1.4196	0.0184	0.00197
0.3098	0.838793	1.4166	0.0305	0.00239
0.3851	0.858256	1.4144	0.047	0.0028
0.4719	0.883125	1.4118	0.0619	0.00335
0.5684	0.91436	1.4096	0.0759	0.00454
0.6491	0.94388	1.4080	0.09065	0.00573
0.7164	0.971275	1.4075	0.1179	0.00866
0.7813	1.000708	1.4068	0.1035	0.009218
0.8615	1.042167	1.4043	0.07519	0.00952
0.9206	1.077042	1.4003	0.0481	0.00762
0.9614	1.10363	1.3952	0.0185	0.00402

Nitromethane (X_1) + cyclohexane (X_2)				
X_1	ρ gm cm ⁻³	n_D	V^E	n^E
0.0711	0.819029	1.4425	0.0075	0.00077
0.1384	0.831794	1.4395	0.0143	0.00151
0.1974	0.84374	1.43649	0.0176	0.00179
0.2875	0.86338	1.4318	0.0297	0.00218
0.3501	0.878156	1.4285	0.043	0.00241
0.4383	0.900839	1.4242	0.0592	0.00318
0.5815	0.943305	1.4174	0.073	0.00429
0.6549	0.968165	1.4144	0.087	0.00548
0.7491	1.004074	1.4119	0.0951	0.0082
0.8311	1.039608	1.4079	0.0994	0.0089
0.8837	1.065057	1.4052	0.091	0.0091
0.9413	1.095706	1.4006	0.072	0.0078
0.9804	1.118925	1.3948	0.0271	0.0041

Nitromethane (X ₁) + 1,3 cyclohexadiene (X ₂)				
X ₁	ρ gm cm ⁻³	n _D	V ^e	n ^e
0.0474	0.835625	1.4742	0.01205	0.00053
0.1285	0.85031	1.4679	0.0326	0.00131
0.2048	0.865203	1.4614	0.049	0.00155
0.2851	0.882216	1.4547	0.0563	0.00194
0.372	0.902389	1.44722	0.0519	0.00206
0.4319	0.917426	1.4424	0.0476	0.00259
0.5285	0.943953	1.4351	0.034	0.0038
0.6118	0.969495	1.4287	0.0103	0.00465
0.6748	0.990466	1.4242	0.002	0.0057
0.7372	1.013305	1.4182	- 0.029	0.0052
0.8163	1.044612	1.41016	- 0.0378	0.0041
0.8815	1.073018	1.40336	- 0.0391	0.00304
0.9714	1.116329	1.3946	- 0.0127	0.0022

Nitromethane (X ₁) + 1,4 cyclohexadiene (X ₂)				
X ₁	ρ gm cm ⁻³	n _D	V ^e	n ^e
0.0806	0.849977	1.46758	0.0074	0.00064
0.1612	0.867561	1.46165	0.01398	0.00146
0.2298	0.88333	1.456013	0.01711	0.00157
0.3165	0.90428	1.44915	0.0276	0.00198
0.3839	0.92141	1.44375	0.041	0.00223
0.4619	0.94235	1.43795	0.054	0.00296
0.5209	0.95904	1.43345	0.0615	0.00341
0.6117	0.986087	1.4270	0.084	0.0046
0.7164	1.02063	1.42047	0.0965	0.0068
0.7871	1.044641	1.41614	0.103	0.0084
0.8319	1.061196	1.41298	0.0985	0.009
0.9063	1.090405	1.40535	0.0793	0.0076
0.9638	1.11494	1.39663	0.0365	0.0037

Nitromethane (X ₁) + Benzene (X ₂)				
X ₁	ρ gm cm ⁻³	n _D	V ^e	n ^e
0.0816	0.88683	1.4968	0.02085	0.00431
0.1582	0.899739	1.4895	0.03917	0.0055
0.2048	0.908033	1.4842	0.0487	0.0054
0.2844	0.923138	1.4746	0.05239	0.0047
0.326	0.931578	1.46915	0.045	0.0039
0.3912	0.945889	1.46096	0.042	0.003
0.4519	0.958952	1.45348	0.04106	0.00231
0.5485	0.982473	1.44207	0.0271	0.0017
0.6492	1.009617	1.43031	0.0101	0.0012
0.7296	1.033578	1.42066	- 0.00918	0.000531
0.8043	1.057727	1.40057	- 0.0195	- 0.0002
0.8612	1.077717	1.4048	- 0.0347	- 0.0006
0.9318	1.10396	1.3971	- 0.025	- 0.0004

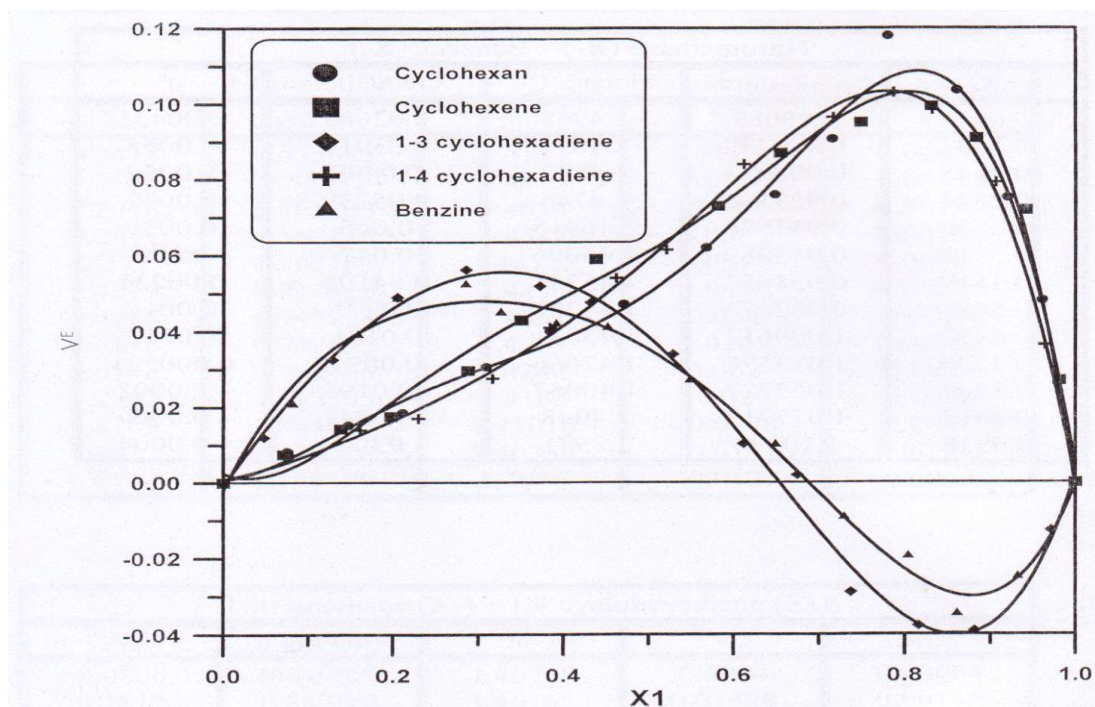


Figure (1): Excess molar volume for the binary mixture of nitromethane (X_1) with cyclohexane, cyclohexene, 1-3 cyclohexadiene, 1-4 cyclohexadiene and benzene at 298.15°K.

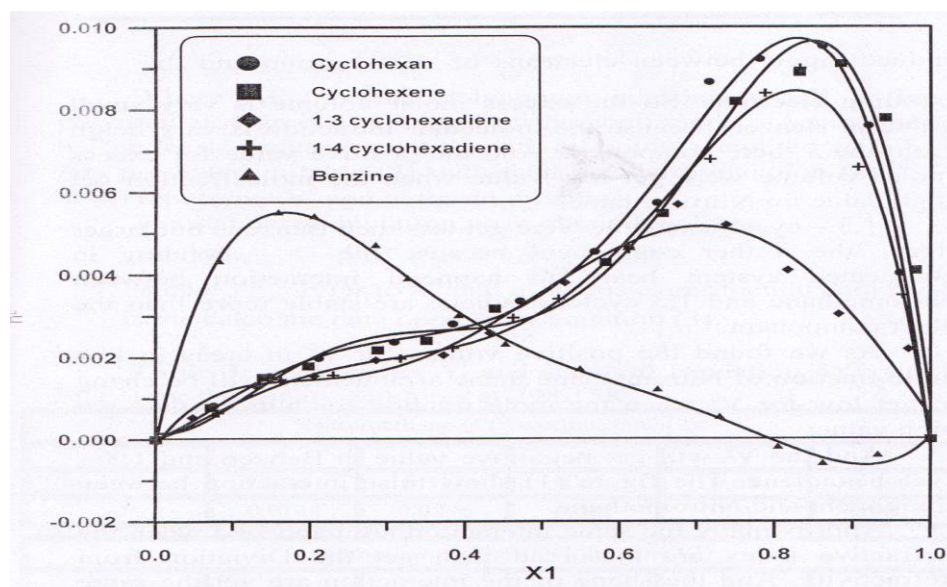


Figure (2): Excess molar refractivity for the binary mixture of nitromethane (X1) with cyclohexane, cyclohexane, 1-3 cyclohexadiene, 1-4 cyclohexadiene and benzene at 298.150K.

In the system studied, excess molar volume are get positive value in all component with Nitromethane but the area of positive value is defrant from component to ather in this arrangement Cyclohexane) cyclohexane cyclohexadiene) 1,3 cyclohexadiene) Benzene Thise arrengmt happened because molecular infraction was depend in these system in dipole - dipole and dipole

induce dipole between electrons of -N o2 group and the - bonding electrons. So the excess molar volume is vary small value in Benzen because the molecular infraction is vary heigh from the a there component. And the positive value for excess molar volume were get low value when the mole fraction get high value for Nitromethane.

1 ,3 - cyclohexadiene were get less then Benzene but larger than the a the: component because the- bonding in conjugated system heals to happens interaction between Nitromethane and 1,3 cyclohexadiene are stable more than the ather component.

As we found the positive volume in VE in creas in low mole fraction of Nitromethane thane arrangement will be chang to get low for VE when the mole fraction for Nitromethan get high value.

And the VE will get negations value in Benzen and 1,3 - cyclohexadiene. The figure (1) show these interaction between component and Nitromethan'e.

Approximatly the same interaction are happened when the Refractive index are masuread than get the Diviation from Refractivity. And the shape of the interaction are get the same size and shape from VE. the figure (2) show this interaction in this work we found the positive VE in low mole fraction of Nitromethane than it will be decreases in high value of mole oration of Nitromethane and it will be get negative shape in 1,3 cyclohexadiene and Benzene and for the same cause of molecular interaction Dipole - dipole.

that is happened between (NO2) group and (11 - bonding) in the component respectively.

Data on derived densities and Refractive Index at 298.15K are given in table (2). The results of VE and nE for each mixture are fitted tothe reddish- Kister (14) polynom ial equation of the form

$$\gamma(x) = X_1 X_2 \sum_{i=1}^n A_i (X_1 - X_2)^i \dots \dots (3)$$

Where A_i , is the polynomial coefficient and is the polynomial degree. The values of the coefficients , A , obtained by the least – squares method with all points weighted equally. Are presented in table (4) with their standard deviation $(\delta)^{(15)}$, $Y(x)$ represents V^E and n^E for all mixtures.

The standard deviation were obtained by form

$$\delta = \left[\sum (\gamma_{\text{expt}}^E - \gamma_{\text{calc}}^E)^2 / (m - n) \right]^{1/2} \dots \dots (4)$$

Where γ_{expt}^E refer to V^E and n^E that is experimental data and γ_{calc}^E is the calculate data optained by equation (3).

Table 3: coefficients A_i and standard Deviation $\delta Y(x)$ of Eq (3) for the Binary Mixtures at 298.15K

Nitromethane (1) + cyclohexane (2)					
Y(x)	A_0	A_1	A_2	A_3	δ
$V^E / \text{cm}^3 \text{mol}^{-1}$	0.26	0.512	0.456	0.08	0.0091
n^E	0.0148	0.0296	0.075	0.56	0.0012

Nitromethane (1) + cyclohexene (2)					
Y(x)	A_0	A_1	A_2	A_3	δ
$V^E / \text{cm}^3 \text{mol}^{-1}$	0.248	0.5	0.459	0.075	0.012
n^E	0.0152	0.0231	0.067	0.053	0.001

Nitromethane (1) + 1,3 cyclohexadiene (2)					
Y(x)	A_0	A_1	A_2	A_3	δ
$V^E / \text{cm}^3 \text{mol}^{-1}$	+0.14	- 0.246	- 0.3	- 0.09	0.0071
n^E	0.014	- 0.022	0.06	- 0.045	0.00103

Nitromethane (1) + 1,4 cyclohexadiene (2)					
Y(x)	A_0	A_1	A_2	A_3	δ
$V^E / \text{cm}^3 \text{mol}^{-1}$	0.232	0.46	0.3	0.06	0.0065
n^E	0.0128	0.02	0.06	+ 0.05	0.00046

Nitromethane (1) + Benzene (2)					
Y(x)	A_0	A_1	A_2	A_3	δ
$V^E / \text{cm}^3 \text{mol}^{-1}$	0.136	- 0.34	- 0.15	- 0.05	0.0051
n^E	0.0065	- 0.016	0.03	- 0.04	0.0003

ABSTRACT :

In this work molecular infraction was found and measured by using density and refractive index for the binary mixture of Nitromethane (X1) and some cyclic compound (cyclohexane, cyclohexane, 1-3 cyclohexadiene, 1-4 cyclohexadiene, benzene) in 298.15K. by the density and refractive index we calculate the excess molar quantities in excess molar volume and deviation from refractivity. The clear molecular infraction that is hapend in this work dipole - dipole. for all the results we fited it by using the squar method and calculate the standard deviation by using the Redlik - kister equation

الخلاصة:-

بأستخدام قياسات الكثافة ومعامل الانكسار عند درجة حرارة 298.15 كلفن في نظام مكون من النايتروميثان مع بعض المركبات الحلقية السداسية (سايكلوهكسان، سايكلوهكسين، 1-3 سايكلوهكساديين، 4-1 سايكلوهكساديين، بنزين) امكن حساب الحجم المولي الفائض وانحراف الانكسار المولي الفائض لكل الانظمة .

وجد ان نوع التداخل الحاصل في هذه الانظمة هو من نوع دايبول - دايبول القيم المستحصلة عمليا تم معايرتها بأستخدام طريقة المربعات الصغرى وبأستخدام معادلة Ridick-kister ومنها تم الحصول على معاملات المعادلة متعددة الحدود والانحراف المعياري .

Refrance;

1 - C. H. Tu, S. L. Lee and 1. H. pang J. Chem.. Eng Data 46, 1 51 - 155, 2001.

2- J. Tron coso, C. A. tovor, C. A. cerdeirina, and L. Romani, J. Chem. Eng. Data 46, 312 - 316, 2001

- 3- M. G. Santos and C. G. Losa J. Chem.. Thermodynamics 7, 293 - 297 (1975).
- 4- R. K. Burkat and A. J. Richard, J. Chem. Thermodynamics 7, 271, 277 (1975).
- 5- Chein - H. Tu, S. L. Lee and I. H. Pang, J. Chem. Eng Data, 46, 151 - 155, 2001.
- 6- (9) Riddick, A; Bunger, W. B; Sakano, T. K. Organic Solvents physical properties and Method of purification, 4th ed Wiley - Interscience : New York, 1986.
- 7- (b) Weast, R. G.; Hand book of Chemistry and physics, 50th Ed. The chemical rubber company Cleveland. - 70, C-255 (1969).
- 8- (c) Fowles, E. H. J. Warren, F. L. J. Chem. soc., 3221 (1931).
- 9- (d) Forziati, A. F, Camin, D. L. ; Rossini, F. D. J. Res. Natl. Bur. Stand., 45, 406 (1950).
- 10- (e) Crossley, A. W. J. Chem.. soc., 85, (1904).
- 11- (f) Beilsteins Handbuch der Organischen Chemie, vol 5, sup 2, p. 79 (1943).
- 12- (j) Wibaut, J. P., Heak, F. A. Rec. Trav. Chim., 67, 85 (1948).
- 13- (h) Wood, S. E. ; Langermann; Bastion, R. J. Chem. Phys. 32, 1389 (1960).
- 14- Redlich. O.; Kister, A. T. Algebraic Representation of the thermodynamic properties and the classification of solutions. Ind. Eng. Chem.. 40, 345 - 348 (1948).
- 15- W. L. Wing. J. Chem.. Eng. Data, 45, 607, (2000)

