STATISTICAL THERMODYNAMICS AND EXCESS MOLAR VOLUMES OF SOME TERNARY AND QUATERNARY LIQUID MIXTURES AT 298.15 K.

Eman T.Kareem , Department of Chemisty , Colleg of Education (Ibn – Al – Haitham) , University of Baghdad ,
P.O.Box 4150 , Baghdad , Iraq .

ABSTRACT :-

The statistical mechanical concept of Flory has been extended for the theoretical prediction of excess molar volume of ternary and quaternary solutions assuming two-body interactions . The validity of the developed expressions has been tested for four ternary solutions and quaternary solutions .Surprisingly , the agreement between theory and experiment was found to be quite satisfactory for the excess molar volume in both sign and value.

الثرموديناميك الاحصائي والحجوم المولاريه الفائضه لبعض المحاليل ثلاثيه ورباعيه المكون عند 298,15 كلفن .

ايمان طالب كريم ، قسم الكيمياء ، كليه التربيه (ابن الهيثم) ، جامعه بغداد ،ص.ب.(4150)
العراق ، بغداد ، الاعظميه–ساحه عنتر .

الخلاصه : –

مفاهيم الميكانيك الاحصائي لنظريه فلوري تم توسيعها في هذا البحث لتتنبئا نظريا بالحجوم المولاريه الفائضه للمحاليل ثلاثيه ورباعيه المكون بافتراض حصول تداخلات بين مكونين اثنين من مكونات المحلول . تم اختبار صحه هذا التعبير الموسع لنظريه فلوري على اربعه محاليل ثلاثيه المكون ومحلول اخر رباعي المكون وكانت النتائج التي حصل عليها مطابقه تماما للنتائج العمليه للحجوم المولاريه الفائضه في الاشاره والقيمه .

INTRODUCTION :-

The scarcity of experimental data on the excess molar volume of ternary and quaternary liquid systems has hampered the theoretical developments in the field of thermodynamics of multicomponent systems . However, a considerable amount of experimental work on the excess molar volume of ternary liquid systems has been done and is still in progress [1-16] .Lately, [17,18] a general equation for estimating the excess thermodynamic and other physicochemical properties of multicomponent systems from the observed properties of their various contributory binary combinations of the components has been developed and applied to various multicomponent liquid systems . The Flory – Patterson theory [19-22] has been extended to ternary solutions includingn organic liquids , liguified gases and metal alloys for the computation of surface tension [23] , ultrasonic velocity [24] , viscosity [8,17,18,25] activity coefficient , and heat of mixing [1] . It appears that a theoretical prediction of the excess molar volume of ternary and quaternary liquid systems using the statistical mechanical theory of Flory has not been made so far . The present paper deals with the extension of Flory's statistical theory to ternary and quaternary liquid systems for the prediction of excess molar volume using thermal expansivity and isothermal compressibility of the pure liquid components as the desired parameter . The authenticity of the proposed method has been tested on four ternary liquid systems and one quaternary liquid system .

EXPERIMENTAL :-

(a) Materials :-

All the chemicals used were supplied by Fluka AG (Buchs,Switzerland) and Aldrich Chemical Company Inc.(Milwaukee , U.S.A) . The purities of all substances were better than 99.95 mass % as found by GLC analysis . The purity of the chemicals was checked by comparing the densities of the components with those reported in the literature [26,27] , the measured values are 0.76975, 1.58421, 0.87361 and 0.65508 $g.cm^{-3}$ at 298.15K for n-hexadecane , carbontetrachloride, benzene and n-hexane, while the literature values are : 0.77070, 1.58409, 0.87357 and 0.65503 $g.cm^{-3}$ respectively .

Measurements :-

Densities were measured at 298.15 K with an Anton Paar digital densimeter (Model DMA 60/601) and controlled thermostatically with a precision of ± 0.01 K by a (HAKKE-DI-G) temperature controller . The operational was described elsewhere [28] . Densities were measured with a precision of $2x10^{-5}$ $g.cm^{-3}$. The maximum uncertainty in the excess molar volumes is expected to be less than $3x10^{-3}$ $cm^3.mol^{-1}$.

RESULTS AND DISCUSSION :-

Ternary Mixtures :-

The reduced equation of state derived from the resulting partition function is given by

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{1/3}}{\tilde{V}^{1/3} - 1} - \frac{1}{\tilde{V}\tilde{T}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where $\tilde{P}$,$\tilde{V}$ and $\tilde{T}$ are the reduced pressure , volume and temperature , respectively .

The reduced equation of state at zero pressure is

$$T^* = \frac{T}{\tilde{T}} = \frac{T\tilde{V}^{4/3}}{\tilde{V}^{1/3} - 1} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

and

$$\tilde{V}^{1/3} = \left(\frac{\alpha T}{3(1+\alpha T)} + 1 \right) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

where α is the coefficient of thermal expansion at P=0 . While predicting the surface tension of ternary liquid mixtures, Pandey and Pant [23] extended Flory theory and defined an element (or segment) as an arbitrary chosen portion of the molecule , and again defined the segment fractions of molecule by the relations

$$\psi_2 = \frac{X_2}{\left[X_2 + X_3 \left(\frac{V_3^*}{V_2^*} \right) + X_1 \left(\frac{V_1^*}{V_2^*} \right) \right]} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

$$\psi_3 = \frac{X_3}{\left[X_3 + X_2 \left(\frac{V_2^*}{V_3^*} \right) + X_1 \left(\frac{V_1^*}{V_3^*} \right) \right]} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

$$\psi_1 = [1-\psi_2-\psi_3] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

where ψ_i and V_i^* are the segment fraction and the characteristic volume of component (i) . In the light of the above relations , the excess molar volumes of ternary mixture can be obtained using the equation

$$\tilde{V} - \tilde{V}_0 = \tilde{V}^E = \frac{V^E}{X_1 V_1^* + X_2 V_2^* + X_3 V_3^*} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

where $\tilde{V}_0$ is the ideal reduced volume given by

$$\tilde{V}_0 = \psi_1 \tilde{V}_1 + \psi_2 \tilde{V}_2 + \psi_3 \tilde{V}_3 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

Substitution of eqn(8) into eqn(7) gives the excess molar volume of the ternary liquid system which can be written as

$$V^E = \left(X_1 V_1^* + X_2 V_2^* + X_3 V_3^* \right) [\, \tilde{V} - (\psi_1 \tilde{V}_1 + \psi_2 \tilde{V}_2 + \psi_3 \tilde{V}_3)] \ldots\ldots(9)$$

where V^E is the excess molar volume and $\tilde{V}$ is the reduced volume of the ternary liquid mixture . Assuming the volume reduction parameters of the ternary mixtures to be linear in mole fraction , one obtains

$$\tilde{V} = \frac{V}{X_1 V_1^* + X_2 V_2^* + X_3 V_3^*} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(10)$$

where V is the molar volume of the liquid mixture , given by :

$$V = \frac{M_1 X_1 + M_2 X_2 + M_3 X_3}{\rho_m} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

where M_i is the molecular weight of component , ρ_m is the density of the mixture .By using the equation of state parameters of pure liquids , Table (1) and applied the above equations(9-11) , we calculated the excess molar volumes for the four ternary mixtures studied here . Table (2) presents the theoretical predication of V^E_{123} values with experimental values for comparison for the four

ternary mixtures . The maximum percent average deviation is less than 0.97 % , which means that Flory theory for predicting the excess molar volumes of ternary mixtures studied here are quite reasonable , as evident from this excellent agreement in both sign and magnitude .We conclude that Flory theory is applicable to binary mixtures and could be extended to mulitcomponent liquid mixtures based on the pure component liquid parameters .

Table (1)-Parameters for the Pure Component Liquids According to the Flory Theory at 298.15 K .

Component	M / g.mol^{-1}	V / Cm^3.mol^{-1}	α x10^{-3}/ K^{-1}	V	V* / Cm^3.mol^{-1}
n-Hexadecan	226.450	293.789	0.868	1.220	240.823
Carbontetrachlorid	153.823	97.107	1.217	1.291	75.242
Benzene	78.115	89.422	1.227	1.292	69.192
n-Hexane	86.178	131.534	1.390	1.322	99.459

Table (2) – Experimental and Theoretical Prediction of Exess Molar Volumes for the Four Ternary Mixtures at 298.15 K .

X_2	X_3	V^E_{123} exp.	V^E_{123} Flory
n-Hexadecane(1)+Carbon tetrachloride(2)+Benzene(3)			
0.2860	0.2651	0.8543	0.8542
0.2780	0.4697	0.9421	0.9420
0.4474	0.2880	0.8357	0.8355
0.4100	0.4349	0.7162	0.7160
0.6257	0.2259	0.5974	0.5976
0.1453	0.7922	0.4283	0.4285
0.3242	0.6088	0.4452	0.4450
0.5477	0.3819	0.3991	0.3989
0.7648	0.1629	0.3490	0.3488
0.2817	0.3865	0.9282	0.9281
0.3805	0.4123	0.8376	0.8377
0.2240	0.6697	0.6161	0.6160
n-Hexadecane(1)+Carbon tetrachloride(2)+n-Hexane(3)			
0.2910	0.2493	0.1025	0.1024
0.3465	0.3649	0.0347	0.0347
0.4576	0.2556	0.2442	0.2440
0.2122	0.5879	-0.2109	-0.2110
0.4855	0.3347	0.1485	0.1483
0.1824	0.7279	-0.1162	-0.1160
0.4337	0.4819	0.0341	0.0343
0.6400	0.2810	0.1889	0.1890
0.8002	0.1234	0.2343	0.2344

0.3706	0.2390	0.1873	0.1870
0.4277	0.3378	0.0882	0.0883
0.2691	0.5965	-0.1550	-0.1549
n-Hexadecane(1)+Benzene(2)+n-Hexane(3)			
0.2836	0.1849	0.4544	0.4545
0.3586	0.3457	0.2931	0.2930
0.4941	0.2368	0.6257	0.6255
0.2552	0.5598	0.1162	0.1160
0.4706	0.3421	0.4778	0.4776
0.7030	0.1413	0.7590	0.7589
0.2580	0.6616	0.2025	0.2024
0.4724	0.4519	0.4243	0.4240
0.6666	0.2627	0.5087	0.5088
0.8205	0.1109	0.4967	0.4965
0.4657	0.3105	0.4881	0.4879
0.3120	0.5599	0.1888	0.1889
Carbon tetrachloride(1)+n-Hexane(2)+Benzene(3)			
0.1195	0.1639	0.1435	0.1433
0.1531	0.3127	0.2176	0.2178
0.2210	0.2072	0.2524	0.2524
0.1237	0.5193	0.2209	0.2210
0.4249	0.1579	0.2452	0.2450
0.2414	0.5667	0.3467	0.3466
0.4133	0.3891	0.3583	0.3580
0.5706	0.1750	0.2741	0.2741
0.1482	0.2187	0.2355	0.2353
0.1965	0.3392	0.2032	0.2033
0.4557	0.2228	0.2897	0.2899
0.1371	0.6214	0.2109	0.2110

Quaternary Mixture :-

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 [28].The excess molar volumes (V^E_{1234}) calculated directly from characteristic and reduced volumes and the segment fraction using thermal expansion coefficient (α) of the pure four component liquids , Table (1) and using the equation :

$$V^E=(X_1V^*_1+X_2V^*_2+X_3V^*_3+X_4V^*_4)[\tilde{V}-(\psi_1\tilde{V}_1+\psi_2\tilde{V}_2+\psi_3\tilde{V}_3+\psi_4\tilde{V}_4] \quad \ldots\ldots\ldots(12)$$

Where ψ_i is the segment fraction of component (i) . V^*_i and $\tilde{V}_i$ are the characteristic and reduced volume of component (i) , respectively . $\tilde{V}$ is the reduced volume of quaternary mixture which obtained by the following equation

$$\tilde{V} = \frac{V}{X_1V_1^* + X_2V_2^* + X_3V_3^* + X_4V_4^*} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(13)$$

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

$$V = \frac{X_1M_1 + X_2M_2 + X_3M_3 + X_4M_4}{\rho_m} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(14)$$

By using the equation of state parameters of pure liquids , Table (1) and applied equations (12-14) , we calculated the excess molar volumes for the quaternary mixture studied here . Table (3) presents the theoretical predication of V^E_{1234}values with experimental values for comparison for quaternary mixture . A careful perusal of Table(3) leads to the inference that the theoretical excess molar volume has been found to exhibit excellent agreement both in sign and magnitude with experimental values for the quaternary mixture studied here , Thus it may be concluded that the expressions of Flory' s statistical theory obtained here for predicting the excess molar volume of quaternary liquid mixture is quite reasonable and valid , as evident from their excellent agreement in both sign and magnitude .

Table(3)Experimental and Theoretical Predictionof Excess Molar Volumes for the Quaternary Mixture n-Hexadecane(1)+ Carbon tetrachloride(2)+Benzene(3) +n-Hexane(4) at 298.15 K.

X_2	X_3	X_4	V^E_{1234} exp.	V^E_{1234} Flory
0.1432	0.1108	0.1681	0.2019	0.2018
0.1728	0.1939	0.2063	0.3923	0.4020
0.2877	0.2944	0.2131	0.5010	0.5099
0.5529	0.1503	0.1250	0.5028	0.5026
0.1345	0.5734	0.1354	0.6633	0.6634
0.1855	0.1562	0.4642	0.0991	0.0898
0.3986	0.2776	0.1942	0.4876	0.4877
0.3568	0.3490	0.1789	0.4762	0.4760
0.2700	0.2672	0.3310	0.3440	0.3441
0.2856	0.3697	0.2417	0.4553	0.4550
0.2304	0.4075	0.2576	0.4783	0.4782
0.3656	0.2579	0.2708	0.3990	0.3989
0.1559	0.6857	0.1085	0.4204	0.4187
0.0967	0.7809	0.0848	0.3775	0.3777
0.2098	0.5662	0.1592	0.4702	0.4701
0.5369	0.2370	0.1599	0.3511	0.3489
0.0674	0.8460	0.0712	0.2349	0.2347
0.3385	0.3326	0.2580	0.3801	0.3779
0.2243	0.4281	0.2823	0.4303	0.4305
0.6744	0.1523	0.1284	0.2498	0.2604
0.4056	0.4717	0.0938	0.2880	0.2879
0.4077	0.2382	0.2868	0.3422	0.3424
0.2565	0.2394	0.4354	0.2873	0.2870
0.7538	0.1170	0.1012	0.1788	0.1805

The study of the excess molar volume leads to the two important structural aspects that can be assessed by the relation

$V^E = V^E_{size} + V^E_{int.}$ ……(15)

V^E_{size} is associated with the size difference of molecules while $V^E_{int.}$ with the interaction forces between molecules . Theoretical studies of the molecular

interactions in ternary and quaternary liquid mixtures are very complicated due to the involvement of two- or three- and four-body effects . However , in the multicomponent system it appears that the contributions of two- or three- and four-body interactions are less efficient and contribute very little to the energy of systems under investigation . That is why the results obtained by considering two-body interactions are found to be excellent .

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