# CALCULATION OF EXCESS MOLAR VOLUMES OF SOME TERNARY LIQUID MIXTURES AT 303.15 K

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## ABSTRACT

Excess molar volumes of five ternary mixtures of 2- methoxy ethanol(1) +butyl acetate(2)+benzene(3), +toluene(3), +chlorobenzene(3), +bromobenzene(3), and +nitrobenzene(3) have been measured at 303.15K. The excess molar volume exhibited positive deviation over the entire range of composition in the systems 2-methoxy ethanol(1)+ butyl acetate(2)+ benzene(3),+toluene(3) and sigmoid behavior in the case of the remaining systems. Flory's statistical theory have been extended to predict the excess molar volumes of the five ternary mixtures at 303.15 k over a wide range of composition . An excellent agreement has been found between the experimental and theoretical excess molar volumes , both in magnitude and sign .

## INTRODUCTION

For many practical purposes it is necessary to predict the properties of a multicomponent liquid mixtures from the properties of pure components and from the data of binary systems . A sophisticated treatment of the liquid mixture is given by the refined version of the cell – model theory of Prigogine [1] , which requires various parameters for computational purposes and has poor agreement with experiment. To our knowledge few investigations have been carried out on multi – component liquid mixtures [2-9] . In most of the theories , the properties of the multicomponent system are determined with the help of the properties of their binary solutions [10,11] , but only Flory' s statistical theory [12,13] can be successfully used to predict the properties of the multicomponent system from those of pure components . Most of the work on excess molal volumes for binary system has been carried out by McGlashan and coworkers [14] , Patterson and coworkers [15,16] , Benson and coworkers [17-20], Street and coworkers [21] , and Marsh and coworkers [22-26] . The theoretical

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prediction of the excess molar volumes of multicomponent liquid systems from Flory theory has not been done so far except some work on excess heat , activity coefficient [27] , surface tension [28] and total and preferential sorption [29] in ternary systems .The excess molar volumes of ternary mixtures of hydrocarbons has received as much attention as the excess molar volumes of binary mixtures depend on the fact that all thermodynamic properties of ternary mixtures should , in principle , be determinable from the properties of the respective binary mixtures [30-33] , but after an exhaustive consultation of literature it appears to me that no body has predicted the excess molar volumes for such ternary liquid mixture using Flory' s statistical theory . In this paper five types of ternary liquid mixtures have been examined using Flory theory . These mixtures included 2-methoxyethanol(1) and butylacetate(2) as common components and aromatic hydrocarbons as noncommon components(3) .

## 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 and boilling temperatures of the components with those reported in the literature [34,35] . The measured values are included in Table (1) along with the literature values .

### (b )Measurements :

Densities were measured at 303.15 K with an Anton Paar digital densimeter (Model DMA 60/601) and controlled thermostatically with a precision of ±0.0 1 K by a (HAKKE- D1-G) temperature controller . 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$^{-1}$.

Table (1) Experimental and Literature Values of Boiling Temperature $T_b$ and Densities ρ of Pure Components at 303.15 k.

| | $T_b$ / K | | ρ / (g . cm$^{-1}$) | |
|---|---|---|---|---|
| Component | Exp. | Lit.[30,31] | Exp. | Lit.[30,31] |
| 2-Methoxyethanol | 397.6 | 397.8 | 0.95957 | 0.96024 |
| Butylacetate | 399.2 | 399.3 | 0.87123 | 0.87129 |
| Benzene | 353.0 | 353.2 | 0.86861 | 0.86863 |
| Toluene | 383.6 | 383.8 | 0.85778 | 0.85776 |
| Chlorobenzene | 404.6 | 404.8 | 1.09552 | 1.09550 |
| Bromobenzene | 428.3 | 428.5 | 1.48159 | 1.48156 |
| Nitrobenzene | 483.8 | 483.9 | 1.19347 | 1.19344 |

## RESULTS ND DISCUSSION

The excess molar volumes for the five ternary mixtures were calculated from the measured densities using the following expression [36] :

$$V^E_{123}/(cm^3.mol^{-1}) = \left[\frac{x_1M_1+x_2M_2+x_3M_3}{\rho_m}\right] - x_1v_1 - x_2v_2 - x_3v_3 \quad \ldots\ldots(1)$$

here $x_i$ and $M_i$ are respectively the mole fraction and molar mass of the pure component liquid (i). $\rho_m$ is the mixture density . $v_1$ ,$v_2$ and $v_3$ are the molar volumes of 2-methoxyethanol , butyl acetate and aromatic hydrocarbons (benzene,toluene,chlorobenzene,bromobenzene and nitrobenzene) respectively . The obtained results of $V^E_{123}$ for the five ternary mixtures are listed in Table (2) .

Table (2) Experimental and Theoretical Prediction of Excess MolarVolumes for 2-Methoxyethanol(1)+Butyl Acetate(2)+Aromatic Hydrocarbons(3) at 303.15 K .

| $X_2$ | $X_3$ | $V^E_{123}$ exp. | $V^E_{123}$ Flory |
|---|---|---|---|
| 2- Methoxyethanol (1) + Butyl Acetate (2) + Benzene (3) | | | |
| 0.7730 | 0.1348 | 0.3043 | 0.3042 |
| 0.7097 | 0.1968 | 0.3880 | 0.3881 |
| 0.5566 | 0.3449 | 0.5291 | 0.5291 |
| 0.4918 | 0.4275 | 0.4887 | 0.4889 |
| 0.4291 | 0.4914 | 0.4971 | 0.4972 |
| 0.2684 | 0.6603 | 0.4011 | 0.4011 |
| 0.1944 | 0.6995 | 0.4944 | 0.4945 |
| 0.1062 | 0.8140 | 0.2932 | 0.2933 |
| 0.0326 | 0.8921 | 0.1751 | 0.1752 |
| 2-Methoxyethanol (1) + Butyl Acetate (2) + Toluene (3) | | | |
| 0.7985 | 0.0457 | 0.1960 | 0.1960 |
| 0.7074 | 0.1750 | 0.2042 | 0.2043 |
| 0.5911 | 0.2746 | 0.2534 | 0.2533 |
| 05432 | 0.4164 | 0.0198 | 0.0199 |
| 0.4457 | 0.5027 | 0.0420 | 0.0422 |
| 0.2497 | 0.6570 | 0.1264 | 0.1265 |
| 0.2238 | 0.6821 | 0.1130 | 0.1131 |
| 0.1000 | 0.7996 | 0.1055 | 0.1055 |
| 0.0206 | 0.8462 | 0.1372 | 0.1374 |
| 2-Methoxyethanol (1) + Butyl Acetate (2) + Chlorobenzene (3) | | | |
| 0.7676 | 0.0229 | 0.1950 | 0.1952 |
| 0.6988 | 0.1305 | 0.1188 | 0.1189 |
| 0.5440 | 0.2572 | 0.0702 | 0.0703 |
| 0.5484 | 0.3405 | 0.0776 | 0.0776 |
| 0.5427 | 0.4119 | -0.2203 | -0.2202 |
| 0.4526 | 0.4814 | -0.2097 | -0.2098 |
| 0.2248 | 0.6408 | -0.0702 | -0.0701 |
| 0.2044 | 0.6664 | -0.0651 | -0.0651 |
| 0.0445 | 0.8061 | 0.1133 | 0.1132 |
| 2-Methoxyethanol (1) + Butyl Acetate (2) + Bromobenzene (3) | | | |
| 0.7316 | 0.0987 | 0.3483 | 0.3480 |
| 0.6663 | 0.1736 | 0.3864 | 0.3865 |
| 0.5703 | 0.2892 | 0.3181 | 0.3182 |
| 0.5983 | 0.3689 | -0.1387 | -0.1389 |
| 0.4093 | 0.5777 | -0.2433 | -0.2433 |
| 0.2862 | 0.6053 | 0.0620 | 0.0620 |
| 0.2029 | 0.6478 | 0.0712 | 0.0713 |
| 0.0249 | 0.8145 | 0.1404 | 0.1405 |
| 0.0136 | 0.8330 | 0.1547 | 0.1546 |
| 2-Methoxyethanol (1) + Butyl Acetate (2) + Nitrobenzene (3) | | | |
| 0.7382 | 0.1142 | 0.4266 | 0.4266 |
| 0.6834 | 0.1491 | 0.5791 | 0.5790 |
| 0.5947 | 0.3060 | 0.1411 | 0.1411 |
| 0.5341 | 0.3882 | -0.0490 | -0.0493 |
| 0.4138 | 0.5178 | -0.1563 | -0.1562 |
| 0.3220 | 0.6290 | -0.2526 | -0.2526 |
| 0.1997 | 0.6865 | -0.0837 | -0.0838 |
| 0.0517 | 0.8097 | 0.0104 | 0.0105 |
| 0.0158 | 0.8430 | 0.0927 | 0.0927 |

The results given in Table (2) indicate that $V^E_{123}$ are sigmoid in all the systems except for 2-methoxyethanol (1) + butyl acetate (2) + benzene (3) , +toluene (3) where $V^E_{123}$ are positive over the entire range of composition . This suggests that the ternary mixtures are not ideal in terms of constituent binaries , indicating that the third component modifies both the nature and degree of interaction between 2-methoxyethanol + butyl acetate . The statistical concept of Flory theory has been extended for the theoretical prediction of excess molar volume of the ternary mixture assuming tow-body interactions [37] . The excess molar volumes ($V^E$) calculated directly from characteristic and reduced volumes and the segment fraction using thermal expansion coefficient ($\alpha$) of the pure three component liquids , Table (3) and using the equation :

$$V^E = (x_1v^*_1+x_2v^*_2+x_3v^*_3)\,[\tilde{v}-(\varphi_1\tilde{v}_1+\varphi_2\tilde{v}_2+\varphi_3\tilde{v}_3] \quad \ldots\ldots(2)$$

Where $\varphi_1$ , $\varphi_2$ and $\varphi_3$ arethe segment fractions of components 1,2 and 3 . $v^*_i$ and $\tilde{v}_i$ are the characteristic and reduced volume , respectively . $\tilde{v}$ is the reduced volume of ternary mixture which obtained by the following equation : -

$$\tilde{v} = \frac{V}{x_1V_1 + x_2V^*_2 + x_3V^*_3} \quad \ldots\ldots(3)$$

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

$$V = \frac{x_1M_1 + x_2M_2 + x_3M_3}{\rho_m} \quad \ldots\ldots(4)$$

By using the equation of state parameters of pure liquids , Table (3) and applied equations (2-4) , I calculated the excess molar volumes for the five ternary mixtures studied here . Table (2) presents the theoretical predication of $V^E_{123}$ values with experimental values for comparison for the five ternary mixtures . The maximum percent average deviation , given by $[\Sigma d_i/n]^{1/2}$ where $d=100[(V_{exp.}-V_{Flory})/V_{exp.}]$ and n is the number of observations .It is less than 0.98 % , 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 . I conclude that Flory theory is applicable to binary mixtures and could be extended to multicomponent liquid mixtures based on the pure component liquid parameters .

Table (3) Parameters for the Pure Liquids According to the Flory Theory at 303.15 K from Literature [13,34,35,38].

| Liquid | $V/cm^3.mol^{-1}$ | $V^*/cm^3.mol^{-1}$ | $T^*/K$ | $\alpha x10^{-3}/K^{-1}$ | $\tilde{v}$ | $\tilde{T}$ |
|---|---|---|---|---|---|---|
| 2-Methoxyethanol | 79.275 | 63.117 | 5209 | 1.025 | 1.256 | 0.0582 |
| Butylacetate | 114.929 | 89.300 | 4835 | 1.178 | 1.287 | 0.0627 |
| Benzene | 89.937 | 69.236 | 4715 | 1.240 | 1.299 | 0.0643 |
| Toluene | 107.417 | 84.848 | 5078 | 1.071 | 1.266 | 0.0597 |
| Chlorobenzene | 102.801 | 81.719 | 5182 | 1.033 | 1.258 | 0.0585 |
| Bromobenzene | 105.981 | 84.447 | 5218 | 1.019 | 1.255 | 0.0581 |
| Nitrobenzene | 103.170 | 82.142 | 5209 | 1.025 | 1.256 | 0.0582 |

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# حساب الحجوم المولاريه الفائضه لبعض المحاليل ثلاثيه المكون عند ٣٠٣،١٥كلفن

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**الخلاصه**

تم قياس الحجوم المولاريه الفائضه عند ٣٠٣،١٥ كلفن لخمسه محاليل ثلاثيه المكون ٢-ميثوكسي ايثانول (١)+بيوتيل استيت (٢)+بنزين (٣),+تلوين (٣),+كلوروبنزين (٣),+بروموبنزين (٣) و +نتروبنزين (٣).اظهرت الحجوم المولاريه الفائضه انحرافا موجبا للمحاليل ٢-ميثوكسي ايثانول (١)+بيوتيل استيت (٢)+بنزين (٣) و +تلوين (٣) اما باقي المحاليل فكان سلوكها مغاير لذلك . نظريه فلوري تم تطويرها لتتنبئا بحساب الحجوم المولاريه الفائضه للمحاليل ثلاثيه المكون المدروسه هنا عند ٣٠٣،١٥ كلفن قد وجد هنالك تطابقا ممتازا بين القيم العمليه والنظريه للحجوم المولاريه الفائضه في القيمه والاشاره .