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Excess Molar Volumes of Binary Mixtures of an Isomer of Pentanol +N-Methyl Morpholine an Interpretation in Terms of the Prigogine-Flory- Patterson Theory

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Abstract

The results of measurements of excess molar volumes V^E at 298.15 K over the whole mole fraction range for five mixtures (N-methylmorpholine + 2-pentanol; + 3-pentanol;+ 3-methyl-1-butanol; + 2-methyl-1-butanol; and 2-methyl-2-butanol) are presented. The experimental values of V^E show a negative deviation from ideal for the five sets of binary mixtures in except V^E values for mixtures of (N-methylmorpholine + 2-pentanol; and 3-pentanol) showes two structural regions. The first is positive at mole fraction $0 \leq X_2 \geq 0.25$. The second region is negative at mole fraction $0.25 \leq X_2 \geq 1$. The negativity of V^E increases in the order 2-methyl-2-butanol > 2-methyl-1-butanol > 3-methyl-1-butanol > 3-pentanol > 2-pentanol. The experimental results of V^E are compared with those predicted by the Prigogine-Flory- Petterson theory . The theory poorly predicts the experimental V^E. The experimental value of excess molar volumes V^E were fitted to the Redlich- Kister polynomial equation to derive the binary adjustable parameters and the standard deviations.

The results obtained are used to study the nature of molecular interactions in these mixtures. As far as we know, in the open literature, no study on mixtures containing N-methylmorpholine

الخلاصة

تم قياس الكثافة لمخالط ثنائية المكون من **N**- مثيل مورفالين مع ايزومرات مختلفة لكحول البنتانول عند درجة حرارة 15, 298 كلفن وعلى المدى التام من الكسور المولية.

استخدمت القياسات العملية للكثافة لحساب الحجوم المولارية الفائضة V^E الفائضة ومنها تم مناقشة التأثيرات المتبادلة لهذا النوع من المخالط.وقد فشلت نظرية فلوري لحساب القيم العملية لفائض الحجم المولي لكل الأمزجة التي تم دراستها وهذا يدل على ضعف هذه النظرية .النتائج العملية المستحصلة للحجوم الفائضة تم تطبيقها نظريا باستخدام معادلة ردلخ – كستر للحصول على ثوابت المعادلة وكذلك الانحراف القياسي عن النتائج العملية .

Introduction

Excess Thermodynamic properties of binary mixtures containing alcohol isomers have been studied extensively. These studies include the excess molar volumes$^{(1,2)}$ and the present work reports the molar excess volumes of binary mixtures of pentanol's isomers with the N-methylmorpholine as a common solvent by measured the density (ρ) over the entire composition range at 298.15 K .We have used the Prigogine- Flory- Petterson (PFP) theory to interpret the molar excess volumes of binary mixtures of N-methylmorpholine + 2-pentanol; + 3-pentanol;+ 3-methyl-1-butanol; + 2-methyl-1-butanol; and 2-methyl-2-butanol at 298.15 K over the whole mole fraction range to show that the Prigogine- Flory- Petterson (PFP) theory$^{(3-5)}$ may produce the observed volumetric behaviour for this class of mixtures.

(I) Ideal Mixture:

The ideal mixture is a hypothetical one whose properties are introduced into the thermodynamic description of real mixture as convenient standard of normal behavior. There is several definition of an ideal liquid mixture; one of the most convenient is that it is a mixture in which the chemical potentials of all components are given the equation:$^{(6-8)}$

$$\boxed{\mu_i(\rho,t,x)=\mu_i^{\circ}(\rho,t)+RT\ln x_i\text{.......................}(1)}$$

i = 1 , 2 , 3, ...

Where $\mu_i^{o}(\rho,T)$ and x$_i$ is the chemical potential and mole fraction of pure component, i, at the same pressure and temperature as the mixture being studied.

For an ideal mixture the molar function of mixing are given by the molar Gibbs function

$$\boxed{\Delta_{mix}G_m^{id}=RT[x\ln X+(1-x)\ln(1-X)]\text{....................}(2)}$$

The molar entropy

$$\boxed{\Delta_{mix}S_m^{id}=-R[x\ln X+(1-x)\ln(1-X)]\text{...................}(3)}$$

The molar enthalpy

$$\boxed{\Delta_{mix}H_m^{id}=0\text{...................}(4)}$$

The molar volume

$$\boxed{\Delta_{mix}V_m^{id}=0\text{...................}(5)}$$

For an ideal mixture the molar Gibbs energy of mixing is negative and the molar entropy of mixing is positive for any value of χ mole fraction.

The molar function of mixing for a binary mixture [xA+(1-x)B], where x denotes the molar function of A,are defined by :

(II) Molar Mixing Functions

$$\Delta_{mix} X_m = X_m - xX_A^* - (1-x)X_B^* \text{.........................}(6)$$

Where X_m is the molar quantity of a binary mixture [XA+(1-x)B] at the temperature T and pressure P and where X^*_A and X^*_B are the molar quantities of the pure substances A and B at the same temperature and pressure. X denotes any extensive quantity such as G, H, S or V.

Excess partial molar quantities can be written as the difference between the partial molar quantities for the non-ideal mixture and those of an ideal mixture.

It has become customary to use instead of the molar function of mixing $\Delta_{mix}X_m$, the excess molar function(9):

(III) Excess Function

$$X_m^E = \Delta_{mix} X_m - \Delta_{mix} X_m^{id} \text{.............}(7)$$

so that "excess" means excess over ideal.

Thermodynamic function like Gibbs energy, molar polarization, entropy and enthalpy and excess molar volume are used by workers(10,11)) in investigating the orientation of molecular dipoles and molecular interaction in binary and ternary mixture in polar- polar, polar-non polar liquids . Payne and Theodorou(12) have suggested that the excess function are more useful than the thermodynamic functions in interpreting the molecular interactions in such binary mixtures . The miscibility between the two liquids in a mixture is maximum when the molecular interaction between them is more.

The present paper studies the binary mixtures containing a common solvent one of morpholine derivatives(13-15). We present here new experimental data on density, ρ , and of N-methylmorpholine and 2-pentanol; 3-pentanol; 3-methyl-1-butanol; 2-methyl-1-butanol; and 2-methyl-2-butanol as co-solvent at temperature 298.15 K. This system is particularly chosen in view of its importance in chemical engineering design processes and polymer processing industries(16).

Experimental

Materials

The 2-pentanol, 3-pentanol, 3-methyl-1-butanol, 2-methyl-1-butanol, 2-methyl-2-butanol and N-methylmorpholine (pure grade) were obtained from Aldrich. N-methylmorpholine was purified as previously described(15).All solvents were checked by gas liquid chromatographic analysis, density. All binary mixtures were prepared over the whole mole fraction range $0<\chi_2<1$ using Sartorius balance (precision $1x10^{-4}$) and air tight stoppered bottles. The more volatile component liquid was directly poured into the bottle. The second component liquid was injected into the bottle through the stopper by means of a syringe. This procedure hindered any vapour loss and contamination. The mole fraction x_i of component liquid i in the binary mixture was calculated liquid in the binary mixture was calculated from the following relation:

$$x_i = \frac{W_i/M_i}{W_i/M_i + W_j/M_j} \text{............(8)}$$

where W_i, M_i are the weight and the molecular weight of the component liquid i. The possible error in the mole fraction is estimated to be lower than $2x10^{-4}$.

The uncertainty in the mole fraction was ± 2×10^{-5}.

Measurements:

Densities were measured with a digital precision system DMA 60/602 (Anton Paar). Details of the system and the calibration procedure were adequately covered in previous work(13). The reproducibility of density measurements was ± 3×10^{-5}g. cm^{-3} .

For all measurements, a Schott-Gerate CT 1150 thermostat was used at a constant digital temperature control of ±0.01 K at the desired temperature.

Results and Discussion

The experimental results of density, ρ of pure liquids and binary mixtures of N-methylmorpholine and 2-pentanol; 3-pentanol; 3-methyl-1-butanol; 2-methyl-1-butanol; and 2-methyl-2-butanol at 298.15 K are presented in Table 1. Excess molar volumes, V^E for binary mixtures have been calculated from the following equations(17).

$$V^E / cm^3 mol^{-1} = \left[(x_1 M_1 + x_2 M_2)/\rho\right] - (x_1 M_1/\rho_1) + (x_2 M_2/\rho_2) \text{..........(9)}$$

where

χ_1 , χ_2 : mole fractions of liquids 1 and 2 .
M_1 ,M_2: molar masses of liquids 1 and 2 .
ρ_1 , ρ_2 : density of liquids 1 and 2 .
ρ : density of mixture .

The obtained results of V^E for the mixture of N-methylmorpholine + 2-pentanol,+ 3-pentanol,+ 3-methyl-1-butanol,+ 2-methyl-1-butanol and 2-methyl-2-butanol at 298.15 K are presented in Table 1 .

The excess molar volumes V^E for the binary mixtures of N-methylmorpholine ,+ 2-pentanol ,+ 3-pentanol are show two structural regions exist over the entire composition range. In the first, the 2-pentanol and 3-pentanol regions $0 \leq \chi_2 \geq 0.25$, this shows a positive deviation, from ideal as shown in Fig. 1. This behavior may be explained qualitatively:

(i) Strong self – association in 2-pentanol, 3-pentanol through hydrogen bonding .

(ii) Steric effect of methyl group connected to nitrogen atom with lone pairs of electrons in N-methylmorpholine prevent any molecular interactions between the hydroxyl group of , 3-pentanol and the lone pair of electrons on the nitrogen atom .

(iii) Added 2-pentanol, 3-pentanol to N-methylmorpholine enhances the N-methylmorpholine structure.

In the second regions of 2-pentanol and 3-pentanol $0.25 \leq \chi_2 \geq 1$ and The excess molar volumes V^E for the binary mixtures of N-methylmorpholine ,+ 3-methyl-1-butanol; 2-methyl-1-butanol; and 2-methyl-2-butanol shows a negative deviation, from ideal as shown in Fig. 1. This behavior due to a strong hydrogen bonding between the hydroxyl groups of alcohols and the lone pair of electrons on the nitrogen atom and destroying the self-association in alcohols leading to give negative V^E . It seems that the methyl group has no effect on the molecular interactions between the solvent and co-solvent. Each set of results was fitted to the Redlich-Kister equation(18-20).

$$V^E(cm^3 mol^{-1}) = x(1-x)\sum_{i=0}^{n} A_i(1-2x)^i \quad \textbf{..........(10)}$$

The corresponding coefficients A_i are given in table 2, together with standard deviation (σV^E) defined as :

$$\sigma V^E = \left(\sum_{i=1}^{n}(V^E_{\exp} - V^E_{theor})^2 / (N-n)\right)^{1/2} \quad \textbf{.................(11)}$$

Where N is the number of data points and n is the number of coefficients. Where χ is the mole fraction of pentanol isomers.

Theoretical Prediction of Excess Molar Volumes – Flory Theory

The excess molar volumes for all binary mixtures studied here were predicted using the theory of Flory(3-5,21). According to Flory, molecule in liquid is considered to be made up of segments each having a 'hard core' volume v^* but occupying an effective volume $\tilde{v}$ in the liquid. The reduced volume

$$\tilde{v} = v_i / v_i^* \text{..........}(12)$$

For pure liquid i was calculated from thermal expansion coefficient according to Flory formula

$$\tilde{v}_i = [(1+4/3\alpha_i T)/(1+\alpha_i T)]^3 \text{........}(13)$$

Where α_i is the coefficient of thermal expansion calculated from measured densities ρ_i at two temperatures

$$\alpha_i = (\ln\rho_2 - \ln\rho_1)/(T_2 - T_1) \text{...........}(14)$$

The characteristic pressure P* and temperature T* are obtained from the relation

$$P_i^* = \alpha_i T \tilde{v}_i^2 / K_{Ti} \text{............}(15)$$

K_{Ti} being the isothermal compressibility and

$$T_i^* = T_i / \tilde{T}_i \text{..........}(16)$$

Where at zero pressure the reduced volume and temperatures satisfy the reduced equation of state.

$$\tilde{T}_i = (\tilde{v}_i^{1/3} - 1)/\tilde{v}_i^{4/3} \text{ ....}(17)$$

The reduced temperature appropriate for a mixture of two components (indicated by subscripts 1 and 2) at mole fraction x is

$$\tilde{T} = (\phi_1 P_1^* \tilde{T}_1 + \phi_2 P_2^* \tilde{T}_2)/(\phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \theta_2 X_{12}) \text{.......}(18)$$

Where X_{12} is a constant characterizing the difference in the energy of species 1 and 2. The segment or hard – core volume fraction, ϕ_i is defined by

$$\phi_1 = (1-\phi_2) = x_1 v_1^* / (x_1 v_1^* + x_2 v_2^*) \text{.......}(19)$$

And the surface fraction

$$\theta_2 = (1-\theta_1) = \theta_2 S_2 / (\phi_1 S_1 + \phi_2 S_2) \text{.......}(20)$$

S being the molecular surface /volume ratio in the absence of a value for X_{12} (e.g. from measured values of excess heats of mixing)

$\tilde{T}$ For the solution is given by equation 18 which, taking $X_{12} = 0$ reduces to

$$\tilde{T} = (\phi_1 P_1^* \tilde{T}_1 + \phi_2 P_2^* \tilde{T}_2)/(\phi_1 P_1^* + \phi_2 P_2^*) ....(21)$$

Excess molar volumes were there calculated from the following equation

$$VE = \frac{\left(x_1 V_1^* + x_2 V_2^*\right)\left(\phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2\right)^{7/3}\left(\tilde{T} - T^\circ\right)}{4/3 - (\phi_1 V_1 + \phi_2 V_2)} ....(22)$$

Where

$$T^\circ = [(\phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2)^{1/3} - 1]/(\phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2)^{4/3} ....(23)$$

The parameters of the pure component liquids molar volume, V, thermal expansion coefficient, α, characteristic volume, v^*, characteristic temperature, T^*, reduced volume, $\tilde{v}$ and reduced temperature $\tilde{T}$ were calculated from equations (12-23) are parmeterued for computing the excess molar volumes V^E of the binary mixtures in this study are listed in Table 3. Predicted V^E values and the experimental values over the entire composition range at 298.15 K are listed in Table 4 with the experimental data. We observed poor a agreement between the experimental values and the predicted ones. The theory fails to predict the excess molar volumes of polar – polar mixtures. This indicates that Flory theory did not take in account the polarity effect in these mixtures.

Table (1). Experimental Values of the density (ρ) and Excess molar volume (V^E) of χ_1 N-methylmorpholine and χ_2 Isomeric pentanols mixtures at 298 K .

χ_2	ρ/ g.cm^{-3}	V^E / cm^{3}mol^{-1}	χ_2	ρ/ g.cm^{-3}	V^E / cm^{3}mol^{-1}
χ_1 N-methylmorpholine + χ_2 2-pentanol			χ_1 N-methylmorpholine + χ_2 3-pentanol		
0.00000	0.91625	0.0000	0.00000	0.91625	0.0000
0.02911	0.91191	0.1399	0.02939	0.91205	0.1189
0.04421	0.90966	0.2121	0.04401	0.91007	0.1650
0.07720	0.95745	0.2504	0.07739	0.90589	0.2299
0.16584	0.89581	0.2800	0.1579	0.89645	0.2018
0.25398	0.88776	0.0802	0.25439	0.88791	0.0566
0.41397	0.87308	-0.2866	0.41465	0.87270	-0.2477
0.61901	0.85256	-0.5648	0.62021	0.85170	-0.4712
0.80090	0.83155	-0.4655	0.80179	0.83062	-0.3549
0.90899	0.81826	-0.2989	0.90990	0.81769	-0.2372
0.93999	0.81445	-0.2518	0.94309	0.81343	-0.1614
0.96000	0.81183	-0.1990	0.96281	0.81082	-0.1053
0.97730	0.80946	-0.1399	0.97781	0.80883	-0.0622
0.98649	0.80843	-0.1390	0.98650	0.80778	-0.0511
0.98990	0.80774	-0.0979	0.98933	0.80747	-0.0519
1.00000	0.80590	0.0000	1.00000	0.81591	0.0000

Table (1) cont.

χ_2	ρ/ g.cm^{-3}	V^E / cm^{3}mol^{-1}	χ_2	ρ/ g.cm^{-3}	V^E / cm^{3}mol^{-1}
χ_1 N-methylmorpholine + χ_2 3-methyl 1-butanol			χ_1 N-methylmorpholine + χ_2 2-methyl-1-butanol		
0.00000	0.91625	0.0000	0.00000	0.91625	0.0000
0.04397	0.91253	-0.1395	0.04111	0.91540	-0.3999
0.10399	0.90651	-0.2182	0.10115	0.91139	-0.6304
0.19311	0.90078	-0.7300	0.19415	0.90522	-1.0124
0.29419	0.89291	-1.1520	0.29544	0.89905	-1.5035
0.39346	0.88571	-1.6399	0.39355	0.89416	-2.1208
0.49874	0.87679	-2.0100	0.49791	0.88806	-2.6779
0.60100	0.86681	-2.2144	0.60461	0.87782	-2.7777
0.69888	0.85530	-2.1712	0.69791	0.86675	-2.6119
0.80059	0.84088	-1.8119	0.80048	0.85208	-2.1208
0.90166	0.82345	-1.0383	0.90441	0.83384	-1.1799
0.95038	0.81400	-0.5145	0.96000	0.82361	-0.6025
0.96311	0.81146	-0.3670	0.96511	0.82185	-0.4407
0.97081	0.80933	-0.2700	0.97101	0.82039	-0.3289
0.97991	0.80818	-0.1801	0.97959	0.81875	-0.2306
1.00000	0.80460	0.0000	1.00000	0.81491	0.0000

Table (1) cont.

χ_2	ρ/ g.cm^{-3}	V^E / cm^{3}mol^{-1}
χ_1 N-methylmorpholine + χ_2 2-methyl 2-butanol		
0.00000	0.91625	0.0000
0.03998	0.9146	-0.3291
0.10401	0.91293	-0.9601
0.1888	0.90398	-1.4909
0.29181	0.89717	-1.7854
0.39311	0.89037	-2.0800
0.49871	0.88284	-2.5933
0.60100	0.87391	-2.9011
0.69888	0.86331	-2.9515
0.80059	0.85023	-2.7491
0.90166	0.83291	-1.9905
0.95011	0.81963	-0.9631
0.96341	0.81451	-0.4799
0.97011	0.81276	-0.3440
0.97891	0.81042	-0.1611
1.00000	0.80690	0.0000

Table (2). Polynomial Coefficients and Standard Deviations σ, Obtains for Fits of Eqn. 10 to the V^E Composition Data for the binary Systems at 298.15 K.

system	A_o	A_1	A_2	A_3	σ
χ_1 N-methylmorpholine + χ_2 2-pentanol	-1.752	2.599	2.327	2.934	0.27
χ_1 N-methylmorpholine + χ_2 3-pentanol	-1.518	2.108	2.337	1.972	0.21
χ_1 N-methylmorpholine + χ_2 3-methyl-1-butanol	-8.169	6.136	1.332	-1.629	0.79
χ_1 N-methylmorpholine + χ_2 2-methyl-1-butanol	-10.261	7.095	0.339	-4.508	0.95
χ_1 N-methylmorpholine + χ_2 2-methyl-2-butanol	-10.312	8.099	-7.118	-4.511	1.02

Table (3). Parameters of the pure liquids according to the Flory theory at 298.15 K.

Liquid	$V/Lmol^{-1}$	$\alpha\times10^3$ (K^{-1})	V^*	T^* (K)	$\tilde{v}$ / $Lmol^{-1}$	$\tilde{T}\times10^2$
N-methylmorpholine	110.370	0.777	91.956	6061.5	1.192	4.785
2-pentanol	109.382	1.012	87.490	5196.1	1.293	6.347
3-pentanol	108.041	1.036	86.080	5129.9	1.267	5.999
3-methyl-1-butanol	109.558	0.878	89.644	5633.4	1.110	3.086
2-methyl -1-butanol	108.174	0.745	90.670	6226.7	1.616	9.152
2-methyl -2-butanol	109.240	1.170	85.240	4813.6	1.250	5.745

Table (4). Excess molar volume (V^E) from Experimental and the predicted by Flory Theory.

χ_2	V^E(exp.)	V^E(ther.)	χ_2	V^E(exp.)	V^E(ther.)
χ_1 N-methylmorpholine + χ_2 2-pentanol			χ_1 N-methylmorpholine + χ_2 3-pentanol		
0.00000	0.0000	0.0000	0.00000	0.0000	0.0000
0.02911	0.1399	0.0241	0.02939	0.1189	0.0233
0.04421	0.2121	0.0153	0.04401	0.1650	0.0131
0.07720	0.2504	-0.0065	0.07739	0.2299	-0.0090
0.16584	0.2800	-0.0592	0.1579	0.2018	-0.0631
0.25398	0.0802	-0.1052	0.25439	0.0566	-0.1090
0.41397	-0.2866	-0.1681	0.41465	-0.2477	-0.1671
0.61901	-0.5648	-0.2000	0.62021	-0.4712	-0.1790
0.80090	-0.4655	-0.1682	0.80179	-0.3549	-0.1062
0.90899	-0.2989	-0.1111	0.90990	-0.2372	-0.0121
0.93999	-0.2518	-0.0890	0.94309	-0.1614	0.0271
0.96000	-0.1990	-0.0733	0.96281	-0.1053	0.0532
0.97730	-0.1399	-0.0580	0.97781	-0.0622	0.0740
0.98649	-0.1390	-0.0500	0.98650	-0.0511	0.0862
0.98990	-0.0979	-0.0472	0.98933	-0.0519	0.0911
1.00000	0.0000	0.0000	1.00000	0.0000	0.0000

Table (4) cont.

χ_2	**V^E(exp)**	**V^E(ther)**	χ_2	**V^E(exp)**	**V^E(ther)**
χ_1 N-methylmorpholine + χ_2 3-methyl 1-butanol			χ_1 N-methylmorpholine + χ_2 2-methyl-1-butanol		
0.00000	0.0000	0.0000	0.00000	0.0000	0.0000
0.04397	-0.1395	0.0390	0.04111	-0.3999	0.0511
0.10399	-0.2182	0.0342	0.10115	-0.6304	0.0611
0.19311	-0.7300	0.0271	0.19415	-1.0124	0.0762
0.29419	-1.1520	0.0211	0.29544	-1.5035	0.0933
0.39346	-1.6399	0.0180	0.39355	-2.1208	0.1112
0.49874	-2.0100	0.0180	0.49791	-2.6779	0.1280
0.60100	-2.2144	0.0222	0.60461	-2.7777	0.1461
0.69888	-2.1712	0.0260	0.69791	-2.6119	0.1622
0.80059	-1.8119	0.0352	0.80048	-2.1208	0.1800
0.90166	-1.0383	0.0480	0.90441	-1.1799	0.1980
0.95038	-0.5145	0.0555	0.96000	-0.6025	0.2081
0.96311	-0.3670	0.0581	0.96511	-0.4407	0.2090
0.97081	-0.2700	0.0590	0.97101	-0.3289	0.2100
0.97991	-0.1801	0.0611	0.97959	-0.2306	0.2111
1.00000	0.0000	0.0000	1.00000	0.0000	0.0000

Table (4) cont.

χ_2	**V^E(exp)**	**V^E(ther)**
χ_1 N-methylmorpholine + χ_2 2-methyl 2-butanol		
0.00000	0.0000	0.0000
0.03998	-0.3291	-0.0170
0.10401	-0.9601	-0.1132
0.1888	-1.4909	-0.2266
0.29181	-1.7854	-0.3511
0.39311	-2.0800	-0.4490
0.49871	-2.5933	-0.5211
0.60100	-2.9011	-0.5500
0.69888	-2.9515	-0.5242
0.80059	-2.7491	-0.4222
0.90166	-1.9905	-0.1990
0.95011	-0.9631	-0.0351
0.96341	-0.4799	0.0181
0.97011	-0.3440	0.0464
0.97891	-0.1611	0.0862
1.00000	0.0000	0.0000

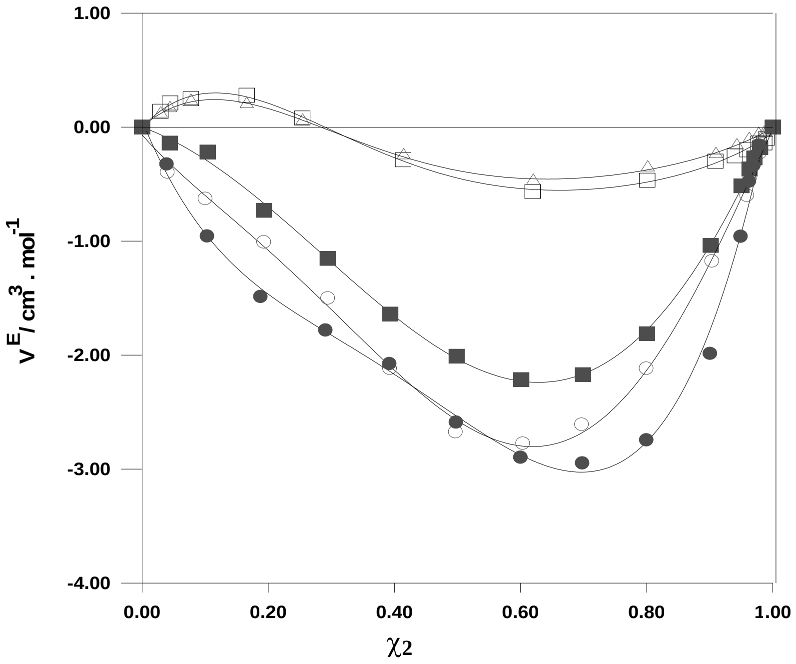

Fig. 1- Excess molar volumes V^E, at 298.15 K versus χ_2, the mole fraction of Isomeric Pentanols: (□) 2-pentanol;(Δ) 3-pentanol;(■) 3-methyl-1- butanol; (○) 2-methyl-1-butanol; and (●) 2-methyl-2-butanol.

References

1- G.C.Franchini, A.Mrchetti, L.Tassie and G.Tosi, ***J. Chem. Soc. Faraday Trans. I,*** 1988, **84**, 4427.

2- G.C.Franchini, A.Mrchetti,C.Parti, L.Tassie and G.Tosi, ***J. Chem. Soc. Trans. I***, 1989, **85**, 1697.

3- P. J. Flory, ***J.Am. Chem. Soc***., 1965, **87**, 1833.

4- T. A. Salman Ph.D.Thesis, University of Al- Nahreen, College of Science (2001).

5- H. T. Van and D. J. Patterson, ***J. Soln. Chem.***, 1982, **11**, 793.

6- E. Brandstat, V. George and A. Kolbe, ***J. Mol. Liq.***, 1985, **31**, 107 .

7- B. B.Swain and G. S. Roy, ***Jpn,. J. Apl. Phys.***, 1986, **25**, 209.

8- S. Tripathy, B. B. swain, ***Chem. Papers.***, 1991, **45**, 3210.

9- A.M.Awwad and E. I. Allos, ***J. Solution Chem.***, 1987, **16(6)**, 465.

10- A. M. Awwad ;S.F. Al-Modifai and K. A. Jbara, ***J. Chem. Thermoldyn.,*** 1985, **17** 105.

11- S.F. Al-Modifai, A. M. Awwad and K. A. Jbara, ***Thermochemical Acta***, 1985, **84**, 33.

12- R. Payne, I, Theodorou, ***J. Phys. Chem.,*** 1972, **76**, 2892.

13- S.F. Al-Azzawi, and A. M. Awwad , ***J. Chem. Eng. Data***, 1990, **35**, 411.

14- A. H. Al-Dujali; A. A. Yassen and A. M. Awwad , ***J. Chem. Eng. Data***, 2000, **45**,647.

15- S. F. Aghamiri, H. Modarress and G. A. mansoor, ***J. Phys. Chem.***, 2001, **14**, 105.

16- H. Shekaari and H. Modarress, ***J of Sci Islamic Repuplic of Iran***, 2003, **14 (2)**, 133.

17- E. Jimenez, C. Franjo and M. I. Pazandrade , ***J. Chem. Eng. Data***, 1997, **42**, 262 .

18- A. M. Awwad, A. H. Al-Dujali and H. A. Salman, ***J. Chem. Eng. Data***, 2002, **47**, 421.

19- A. H. Al-Dujali; A. M. Awwad and H. A. Salman , ***Iraqi J. Sci***., 2001, **42**, 33.

20- W . L Weng, ***J. Chem. Eng.***, 2000, **45**, 606.

21- A. M. Awwad and K. A. Jbara, ***Fluid Phase Equilibria***, 1989, **47**, 95.