Molecular Interaction Between Binary Mixture Of Benzene, Toluene And Acetone With Chloroderivative Of Alkane

1. C. K. Yadav, 2. Raman Gunjan, 3. Nirmal Kumar

1. Department of Chemistry B. N. Mandal University, Madhepura (BIHAR)
2. Millia Convent English School, Rambagh, Purnea
3. +2 R.P.C. High School, Purnea City, Purnea
Corresponding Author: C. K. Yadav

ABSTRACT: For study the molecular interaction between benzene, toluene, acetone and chloroderivatives of ethane the excess volume of (V^E) of mixing for those binary mixtureas a function of composition and temperature have been determined dil atometrically. V^E (excess volume) for mixture have been found to be positive in sign and depends on the temperature. The measurement have been carried out at temperature 283 K, 293 K and 303K.
Keywords: Densities, Excess volume (V^E) of mixing, Molecular Interaction, Statical Theory, Flory's theory, Benzene, Toluene, Acetone and Chloroethane

I. INTRODUCTION

Excessvolume (V^E) along with other excess thermody namic properties for binary liquid mixture have been studied in order to examine current theory of solutions and nature of molecularinteraction.

Negative values of excess volume(V^E) for benzene–diethyl lether have been reported by Rastogiet al[1]which provide strong evidence for the specific interaction between the component. The same evidence have been interpreted by studying a binary mixture of diethyl ether with toluene, O⁻, m⁻, p⁻xylene by Gupta et al[2]which gives the effect of increasing number of methyl group and their relative position in benzene ring, on the extent of molecules interaction. The present investigation provides the excess volume (V^E) of mixing as a positive deviation and hence the results have been interpreted in the light of Flory's theory[3,4],of binary mixture of smallnon–polarmolecules.Afairly good agreement has been found between theoretical & experimental value of $V^E$of binary mixture at 293K.

II. EXPERIMENTAL

Benzene and Toluene (A. R. E. Merk) wire distilled fractionally three times and stored. Chloro – derivatives of ethane were fractionally distilled thrice and stored.
Densities of purified components were compared with the value obtained from literature and worker's, these were found in general agreement to ensure their purity.

TABLE – 1(A)

Component	Temp.	Density g/ cc	
		This work	Literature Value[5–8]
Benzene	303 K	0.8678	0.8737
Toluene	303 K	–	–
Carbon Tetrachloride	303 K	0.6538	0.6-539
1, 2 - dichloroethane	303 K	1.2373	1.2373
1, 1, 2 – terichloroethane	303 K	1.2383	1.2383

TABLE - 1(B)			
Sample	**Temperature**	**Density g/cc**	
		Observed density gm/cc	**Literature value**
Acetone	303K	0.77923	0.77933
Carbon tetrachloride	303K	1.5747	1.5748
Chloroform	303K	1.4706	1.4706
Methylene Chloride	303K	1.3076	1.3076
Ethylene Chloride	303K	1.2372	1.2373

METHOD FOR MEASUREMENT OF EXCESS VOLUME

The excess volume is animportant thermodynamicpropertieswhichcanbemeasuredeith er by the indirect method of measurement of densities or by direct dilatometric measurement binary liquid mixture. Different type of dilatometer have been used by different workers[9-11]. The dilatometer construct by Rastogi et al[1]was used for the purpose on account of its superiority over other models, because the chance of leakage of volatile liquids was minimized and complete mixing of component was ensured. It consist of two closed bulbs in which liquid were introduced through the sidetube.

The working of the dilatometer had been checked by mixing measurement for mixtures of cyclohexane and carbontetrachloride at 303 K and data so obtained had been compared with that obtained by the earlier workers,[1,2]in Fig. 1. Excess volume (V^E) for the binary mixture as a function of temperature and composition were determined by a dilatometer already checked by using the following relationship:

$$V^E = q^r . \Delta h (n_1 + n_2) \qquad (1)$$

Where   r = radius of the capillary of vertical stem of dilatometer ofmixing.

Δh = change in Mg levels in the capillary on mixing measured bycathetometer. n_1+n_2=total number of moles inmixture.

III. RESULTS AND DISCUSSION

Thevalueof (V^E)of binary mixture have been recorded in TABLE–2 (V^E) data have been plotted in Fig.2. The data were fitted in the analytical equation of thetype:

$$V^E/ cc . mol^{-1}= x_1x_2[A + B (X_1 - X_2) + C (X_1-X_2)^2] \qquad (2)$$

TheconstantA,BandCalongwiththeirstandarddeviati on6V^Ecompoundbythemethodof least square have been recorded in TABLE – 3. For mole fraction $X_1$of Benzene andtoluene.

$OV^E$was calculated by the equation :

$$OV^E/ cc . mol^{-1}= [\sum(\Delta V^E)^2(m - n)]^{1}/_{2}\ldots\ldots\ldots\ldots\ldots\ldots.\ldots \qquad (3)$$

WhereΔV^Eisthedeviationintheobservedvalueofexce ssvolumefromthatcalculatedfrom equation(2).

Temperature dependent V^Eequation for binary system mentioned above have been recorded in TABLE – 4. The last column includes dV^E/ dl for equimolar binary system.

We would now discuss the results for the thermodynamic excess function (volume excess andexcessadiabaticcompressibilities)inthelightofthe oriesofsolutionsinceLatticemodeltheory explains that no volume change on mixing, should occur in our investigation but as we have first component benzene and toluene which is according to conformal theory of thesolution.

A polar and semi – polar liquid on the other hand conformal theory of solution, a polar and semi – polar liquid, on the other hand second component (ethyl chloride, 1, 2 – dichloroethane, 1, 1, 2 – trichloroethane) are also polar solvent. So, our results predicts that there are positive deviation in excess volume V^Eas well as in excess adiabatic

compressibilities (K_S^E).
We are unaware of any previous volume change on mixing data which could compare with the present result for the mixture's , volume change on mixing V^E values are found to be positive over the whole composition range for all the studied system. The plot of V^E and K_S^E against X_1 are slightly skewed towards the highmolefractionofbenzeneandtoluene.TheVEvalue sforequimolar mixture are found to vary in the followingorder:

Toluene < Benzene VS ethylchloride, 1, 2, - dichloroethane and 1, 1, 2 – trichloroethane. It seems that the variation in volume change on mixing V^E and K_S^E values of this mixture is due to the cumulative effect and polarisibility of the first and second component respectively. $\boxed{X_1 = 0.5}$

Specificinteractionoftheelectrondonoracce ptortypebetweenchloroethaneandaromatic hydrocarbon and the disruption n in the orientation order of the pure component as V^E values for all the presentmixtureare positive,thecontributionfactor.Itisassumethatenergy associatedwithorientational order for all pure aromatic hydrocarbon is of the same order than the variation in V^E of these mixture will due to the variation in magnitude of specific interaction in these mixture.

The electron donating power of he benzene will increase with the introduction of a methyl group in the ring as in toluene. Consequently electron donor acceptor interaction will also increases and the V^E and K^E values for toluene mixture should less than those of benzene mixture. Our experimental results supports this conjecture.
Since in these mixture the shapes and sizes of the two components are different and chloro
– alkanes are slightly polar molecule, it as though worth while to examine our data in the term of "Statistical theory of Flory" which takes into consideration the shapes and sizes of the molecules. According to Flory theory[1,2], VE for a binary mixture arte given by:
$$V^E = V^E_{calc}[X_1 V_1^* + X_2 V_2^*] \quad \dots\dots\dots\dots\dots\dots\dots \quad (4)$$

Examination of the TABLE – 2 shows that the Flory's theory correctly predict the sign and to someextentmagnitudeofV^Evaluesforallthemixtures. Thusitcouldbeconcludedthat theFlory's theory is able to predict value change on mixing V^E quitereasonably.   For   equimolarmixture,mixture ofbenzene.Toluenewiththechloroethane.Thedeviati oniscalculatedformvaluechangeonmixing(V^E)value sfromtheexperimentalvaluesarenearly48%to77%.T

hese values are reasonably good a greement exceptin case of benzene where the deviation are probably due to the errors in different parameters obtained fromliterature[9].
Value change on mixing V^E can be expressed in terms of Sachez and Lacomees theory's[10-11] as
$$V^E = [1/_{Pmix} - (\phi_1 V_1 + \phi_2 V_2) Y_{mix} V_{mix}^*] \quad (5)$$

Allthetermintheaboveequationhavethesamesignific antandtheparametersforbenzene, toluene and the other component were taken from theliterature[9].
The calculated value for the various mixture shows a reasonably good agreement with the corresponding experimentalvalueat which is shown in a TABLE –3.

V^Evaluesshowsfineragreementwithcorresp ondingexperimentalvalues insomecaseseven   the sign ischanged.
The effect of temperature rise is to cause thermal expansion which is observed in the rising trends of excess compressibility which confirms that the strength of interaction decreases with the rise in temperature. Due to thermal expansion the inter – atomic distance increases and perusal of the sign and the magnitude of different parameter. The average strength of molecular interaction becomes weaker with rise in temperature in both the system.

TABLE – 2
Experimental Excess Volume V^E at Temperature 293 K

Expt.	Mole fraction of Benzene	Volume Excess V^E/ cc / mole	Deviation from the equation (Table 5.1 cc / mole)
Benzene + Ethyl Chloride			
1.	0.1516	0.215	+ 0.004
2.	0.4016	0.514	– 0.015
3.	0.5429	0.590	– 0.005
4.	0.7957	0.415	– 0.003
5.	0.9394	0.0301	– 0.020
Benzene + 1, 2 – Dichloroethane			
1.	0.2875	0.176	– 0.001
2.	0.3508	0.281	– 0.005
3.	0.4636	0.276	+ 0.1015
4.	0.5027	0.293	+ 0.001
5.	0.7917	0.210	– 0.006
6.	0.8291	0.169	+ 0.005
Benzene + 1, 1, 2 – Trichloroethane			
1.	0.2245	0.385	+ 0.016
2.	0.4522	0.621	– 0.067
3.	0.5143	0.631	– 0.025
4.	0.8011	0.380	– 0.0003
5.	0.8816	0.241	+ 0.004

TABLE – 2 (Contd…)
Experimental Excess Volume V^E at Temperature 293 K

Expt.	Mole fraction of Toluene	Volume Excess V^E/ cc / mole	Deviation from the equation (Table 5.1 cc / mole)
Benzene + Ethyl Chloride			
1.	0.1596	0.215	+ 0.004
2.	0.3142	0.514	– 0.015
3.	0.5429	0.590	– 0.005
4.	0.6925	0.415	– 0.003
5.	0.8416	0.0301	– 0.020
6.	0.8915	0.214	– 0.002
Toluene + Ethyl Chloride			
1.	0.1596	0.241	+ 0.001
2.	0.3142	0.421	– 0.004
3.	0.5429	0.569	– 0.005
4.	0.6925	0.415	– 0.003
5.	0.8416	0.301	– 0.020
6.	0.8915	0.214	– 0.002
Toluene + 1, 2, - Dichloroethane			
1.	0.2516	0.194	– 0.002
2.	0.3926	0.254	+ 0.015
3.	0.4824	0.380	+ 0.005
4.	0.6124	0.364	+ 0.004
5.	0.7916	0.210	– 0.006
6.	0.8496	0.184	– 0.004
Toluene + 1, 1, 2, - Trichloroethane			
1.	0.2250	0.192	– 0.004
2.	0.3841	0.252	+ 0.001
3.	0.5215	0.391	– 0.004

|			
4.	0.6524	0.291	+ 0.002
5.	0.7941	0.215	+ 0.003
6.	0.8616	0.182	– 0.005

TABLE – 3
Value of Constants A, B and C of Binary Mixtures and Standard DeviationsV^E at Temperature 293 K

Mixture	A	B	C	oV^E/ cc mol^{-1}
Benzene + Ethyl Chloride	0.8715	0.1145	+ 0.2693	0.8146
Benzene + 1, 2, Dichloroethane	-0.6816	0.1477	– 0.0124	0.6172
Benzene + 1, 1, 2, Trichloroethane	-0.5789	0.2398	– 0.3373	0.6182
Toluene + Ethyl Chloride	0.5451	1.0162	– 0.7530	0.3069
Toluene + 1, 2, Dichloroethane	-0.2937	1.2494	– 0.3333	0.2518
Toluene + 1, 1, 2, Trichloroethane	-0.2013	0.8782	+ 0.0043	0.2036

LIST OF SYMBOLS

V^E	=	Excess Value
V^*I	=	Characteristics volume of pure component
ϕ	=	Segment fraction of component
$\Theta \sigma V^E$ Standard deviation		Site function of component
K_S^E	=	Excess Compressibilities
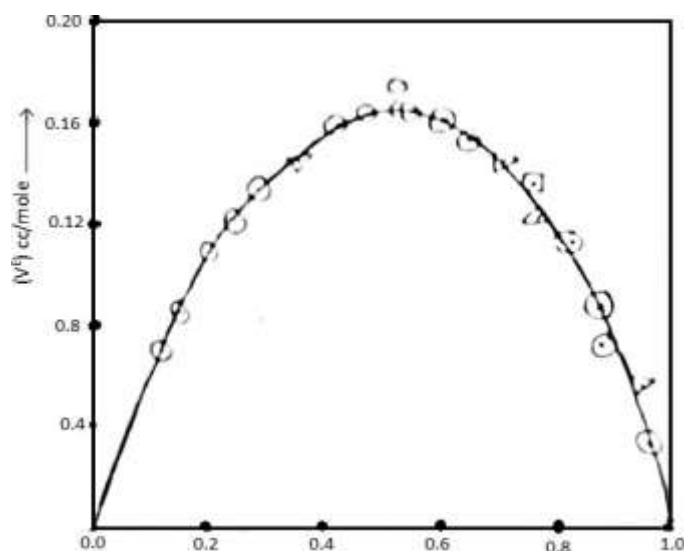
(Fig. 1)

MOLE FRACTION OF CARBON TETRA CHLORIDE
Excess volumes of mixing for cyclobuxane + carbon tetra chloride

⊙   This work, 30^{0}C

Δ   Gupta & Yadav, 30^{0}C (Ref 2) Rastogi & Yadav, 30^{0}C (Ref.1)
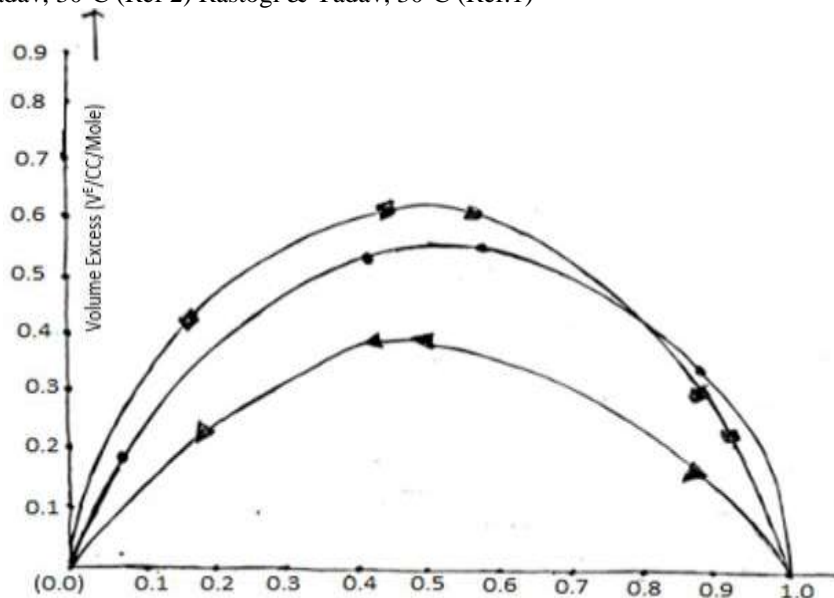

Fig 1 (a)

Nature of graph obtained at 293 K
Benzene + Ethylecloride
Benzene + 1, 2 - Dicholoroethane
Benzene + 1, 2 –Trichloroethane (X1)   Mole Fraction of ethylcholorid
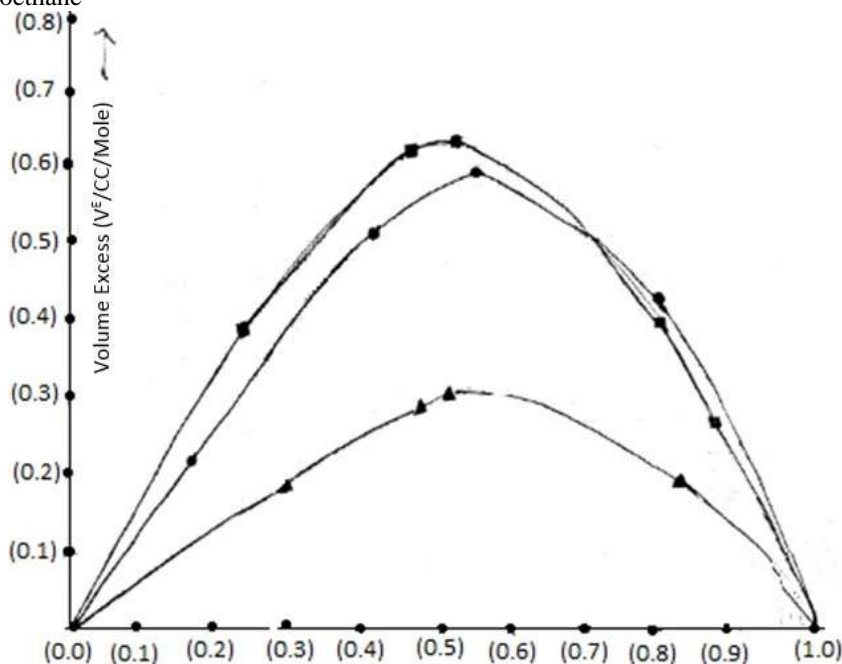1, 2 ■ Dichloroethane
1, 1, 2 – Trichoroethane

Fig 1 (a)

Mole Fraction of Benzene Nature of the graph Obtained at 293 K

●   Benzene +Ethylecloride
Benzene + 1, 2 - Dicholoroethane
Benzene + 1, 2 – Trichloroethane $(X1)$ = Mole Fraction of Benzene
$(X2)$= Mole fraction of ethyle Cholorid
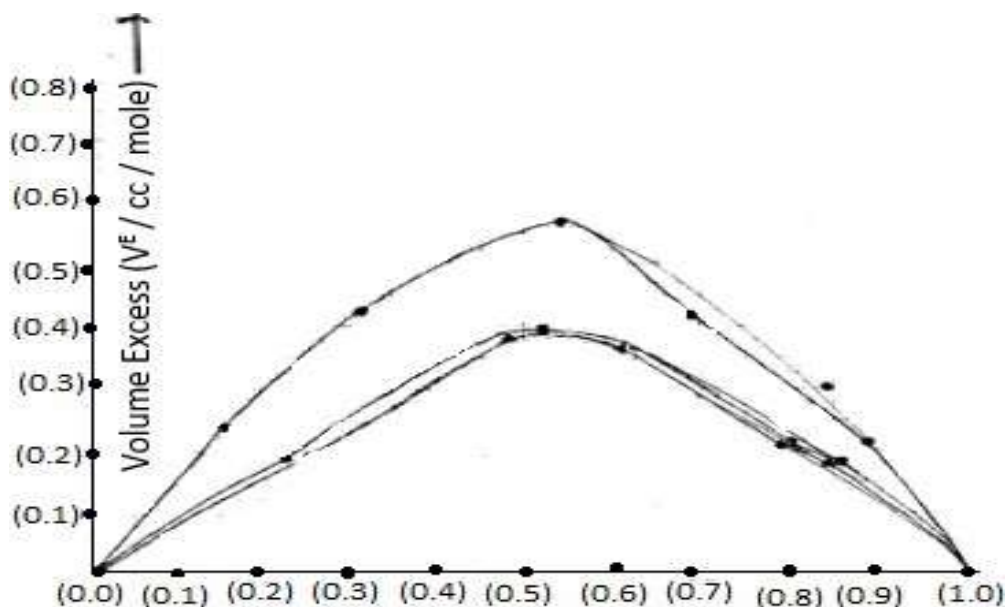1, 2 – Dicholoroethane, 1, 1, 2 – Tricholoroethane

Fig 1 (b) Mole Fraction ofToluene

Nature of the Graph Obtained at 293 K

●   Toluene +Ethylecloride
Toluene + 1, 2 - Dicholoroethane
Toluene + 1, 1, 2 – Trichloroethane (X_1) = Mole Fraction of Toluene
(X_2)= Mole fraction of Ethyle Choloride
1, 2 – Dicholoroethane, 1, 1, 2 – Tricholoroethane

IV. ACKNOWLEDGEMT

REFERENCES

1.	Rastogi,R.P.,JaganNath&Yadava,R.B.	Ind.J.Chem.8,541(1970)
2.	Gupta,A.K.&Yadav,C.K.	A.J.Chem.Vol.9,No.1112–121(1997)
3.	Flory,P.J.	J.Am.Chem.Soc.87,1833(1965)
4.	Abe,A.,Flory,P.J.	Ibid,87,1883(1965)
5.	Yadav,C.K.	Ph.D.ThesisL.N.M.U.(1988)
6.	Jain,D.V.S.,North,A.M.&RichardA.Parthrick	J.Chem.Soc.Trans.Faraday1,70,1292(1974)

7.	Timmermans	J.PhysicoChemicalConstantofPureorganiccompounds.ElsevierPublishingCo.(1950)
8.	StaveleyandMissBelthy	J.Chem.Soc.,406(1952)
9.	Balescu,R.	Bull.Acad.P.Belg.Sc.41,1242(1955)
10.	Forbe,R.J.andMuroe,W.R.	Trams.FaradaySoc.61,2120(1965)
11.	Mathot,V.andSimon,M.	Adv.Chme.Phy.11,117(1963)
12.	Randov, A. Bartov sk L. Hovorka, t. p. Jik, P. Poncarzov, M. Bartovsk	Worldwide Science Org. (1 Jan 2010)
13.	Alexander Apeiblat	J. of molecular liquid volume, 130 issues 1-3, page 132