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Research Article

## Excess Molar Enthalpies of mixing of sec- or tert-Butyl chloride with Aromatic hydrocarbons at the temperature 308.15 K

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### ABSTRACT

Excess molar enthalpies of mixing for sec- or tert-butyl chloride + benzene or toluene or o- or m- or p-xylene have been determined experimentally as a function of mole fraction over the whole composition range at 308.15 K.  $H_m^E$  were measured by a 2-drop calorimeter. The data have been analyzed qualitatively in terms of specific electron donor- acceptor type interactions and the interruption of the molecular order of the pure component in the mixture. The observed data of enthalpies of mixing for these binary mixtures are also analyzed in terms of Flory theory. The Flory theory gave poor agreement between experimental and calculated values.

**Keywords:** Excess molar enthalpy, sec-butyl chloride, tert- butyl chloride, aromatic hydrocarbon, Flory theory

### INTRODUCTION

The study of thermodynamic excess properties of liquid mixtures has been a qualitative and quantitative way to provide information about molecular structure and intermolecular forces in liquid mixtures. The excess thermodynamic properties of a liquid mixture may be considered to be made up of two parts; one corresponds to the breaking of like forces between the molecules in the pure component and the formation of new interactions between the components of the mixture<sup>1-6</sup>. An aromatic hydrocarbon are the potential electron donors and with the alkyl halide form charge transfer complexes due to interaction of  $\pi$  electron cloud of the aromatic ring with the empty 'd' orbital of the halogen in alkyl halide<sup>7-14</sup>. Following our

systematic study of thermodynamic properties of binary liquid mixtures containing butyl chloride + benzene or toluene, o- or m- or p- xylene<sup>15-17</sup>, In this paper we are reporting  $H_M^E$  of sec- or tert butyl chloride (A) + benzene, toluene, o- or m- or p- xylene (B) at 308.15K to understand the nature of molecular interactions in these binary mixtures.

## EXPERIMENTAL

Sec-or tert-butyl chlorides, benzene, toluene, o-, m-, p- xylenes (Fluka) were purified by standard procedure<sup>18</sup>. The purity of the sample was checked by densities and refractive indices measurements at  $298.15 \pm 0.01$  K as described earlier<sup>19</sup> and the values are agreed with in  $0.00005 \text{ g.cm}^{-3}$  with the literature value<sup>20</sup> as shown in the **Table-1**.

**Table- 1: Densities ( $\rho$ ) and refractive indices ( $n_D$ ) of the pure components at  $T = 298.15$  K**

material	$\rho/\text{Kg}\cdot\text{m}^{-3}$		$n_D$	
	exptl.	ref. 18	exptl.	ref. 18
sec-butyl chloride	867.71	867.67	1.3943	1.3942
tert-butyl chloride	836.07	836.10	1.3826	1.3828
benzene	873.65	873.60	1.4980	1.4979
toluene	862.22	862.19	1.4940	1.4941
o-xylene	875.92	875.94	1.5031	1.5029

The excess molar enthalpies as a function of composition were measured by using 2-drop calorimeter (model, 4600) supplied by the calorimetry Science corporation (CSC) USA as described by Dimple *et al*<sup>21</sup>. The estimated uncertainty of the measured  $H_m^E$  values is  $\pm 1$  %.

## RESULTS

The  $H_m^E$  data for the binary mixtures of sec- or tert- butyl chloride (A) + benzene or toluene or o- or m- or p- xylenes (B) as a functions of composition at 308.15 K are reported in the **Table-2** and shown graphically in the **Fig.1 And Fig. 2**.

The equation:

$$H_m^E / (\text{Jmol}^{-1}) = x_A x_B [H_0 + H_1(x_A - x_B) + H_2(x_A - x_B)^2] \quad (1)$$

has been fitted to the data, where the coefficient  $H_0$ ,  $H_1$  and  $H_2$  are adjustable parameters. These parameters are evaluated by the method of least squares and are given together with the standard deviation  $\sigma(H_m^E)$  in **Table-3**.

**Table- 2: Experimentally measured excess molar enthalpies of mixing for sec- or tert butyl chloride (A) + aromatic hydrocarbon (B) mixtures at 308.15 K.**

Mole fraction, $x_A$	$H_m^E$ (J mol <sup>-1</sup> )	Mole fraction, $x_A$	$H_m^E$ (J mol <sup>-1</sup> )
sec-butyl chloride (A) + benzene (B)			
0.1054	4.1	0.5155	11.4
0.2154	7.2	0.6172	10.4
0.3227	9.6	0.7095	8.5
0.4174	11	0.8225	5.6
sec-butyl chloride (A) + toluene (B)			
0.1445	-346.6	0.4428	-285.7
0.2017	-387.8	0.5218	-231.2
0.2545	-395.2	0.6144	-173.1
0.3344	-363.8	0.7277	-122.3
0.3835	-330.8	0.8215	-78.4
sec-butyl chloride (A) + o-xylene (B)			
0.1075	-283.1	0.4814	-322.4
0.2112	-418.7	0.5814	-247.2
0.2527	-432.8	0.6272	-214.1
0.3025	-432.6	0.7318	-142.8
0.3376	-427.1	0.8415	-81.8
0.4217	-374.1		
sec-butyl chloride (A) + m-xylene (B)			
0.1058	-342.5	0.4827	-357.6
0.1635	-458.6	0.5715	-276.5
0.2116	-502.8	0.6114	-241.9
0.2554	-512.3	0.7341	-150.4
0.3025	-508.8	0.8595	-68.9
0.4114	-423.2		
sec-butyl chloride (A) + p-xylene (B)			
0.1154	-410.1	0.4545	-401.6
0.2155	-556.4	0.5217	-328.7
0.2648	-564	0.6315	-230.1
0.3047	-542.1	0.7219	-152.4
0.3535	-497.8	0.8873	-64.3
0.4155	-442.5		
tert-butyl chloride (A) + benzene (B)			
0.1052	-186.4	0.4215	-69.8
0.1625	-218.6	0.5158	-8.8
0.2114	-226.4	0.6278	29.8
0.2655	-206.2	0.7352	32.5
0.3213	-159.5	0.8589	12.8
0.3585	-121.6	1.0000	0
tert-butyl chloride (A) + toluene (B)			
0.1115	-476.8	0.4155	-334.2
0.1635	-538.5	0.5275	-198.4
0.2152	-558.9	0.6245	-118.3

0.2685	-538.2	0.7215	-72.2
0.3145	-488.8	0.8155	-52.9
0.3517	-424.4	0.8972	-42.1

tert-butyl chloride (A) + o-xylene (B)

0.1125	-446.2	0.4245	-368.2
0.1774	-555.8	0.5255	-233.5
0.2375	-578.3	0.6272	-128.2
0.2842	-559.7	0.7117	-75.0
0.3314	-514.9	0.8328	-42.8
0.3817	-426.1		

tert-butyl chloride (A) + m-xylene (B)

0.1145	-472.2	0.3742	-477.7
0.1745	-578.2	0.4115	-410.6
0.2015	-604.5	0.5214	-253.6
0.2324	-617.5	0.6177	-142.8
0.2871	-596.1	0.7115	-89.0
0.3282	-552.8	0.8218	-44.1

tert-butyl chloride (A) + p-xylene (B)

0.1125	-476.5	0.3517	-547.9
0.1715	-608.2	0.4085	-462.5
0.1975	-635.5	0.5175	-283.8
0.2316	-642.1	0.6115	-160.8
0.2865	-628.3	0.7114	-90.2
0.3151	-608.8	0.8454	-32.7

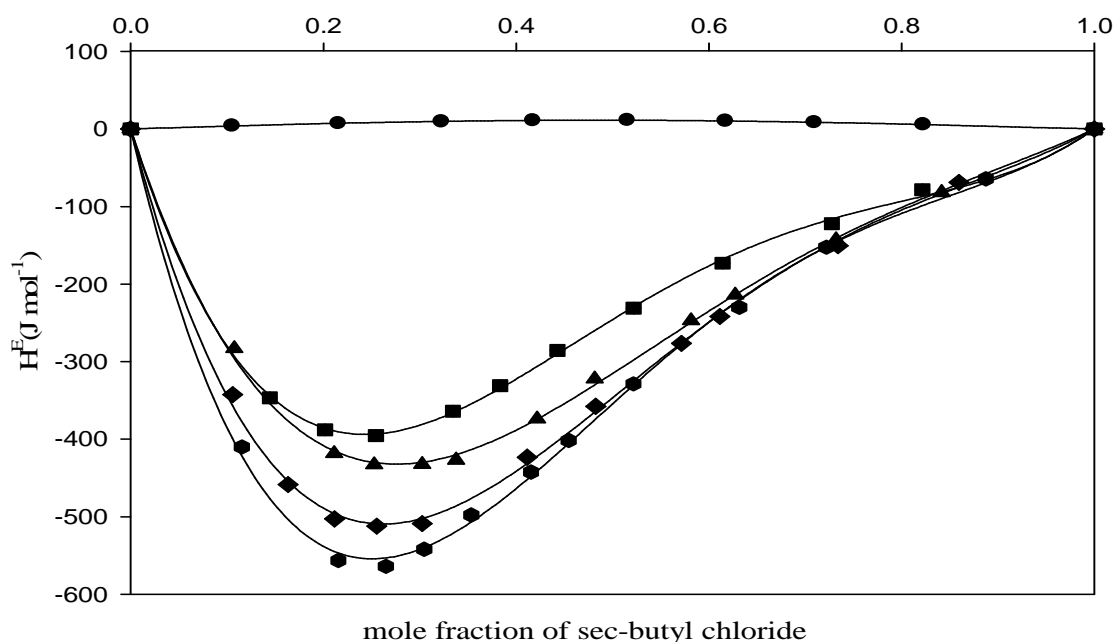


Fig. 1: Experimentally measured  $H^E_{mL}$  at 308.15 K for sec-butyl chloride + benzene(●) or toluene(■) or o-xylene(▲) or m-xylene(◆) or p-xylene(●)

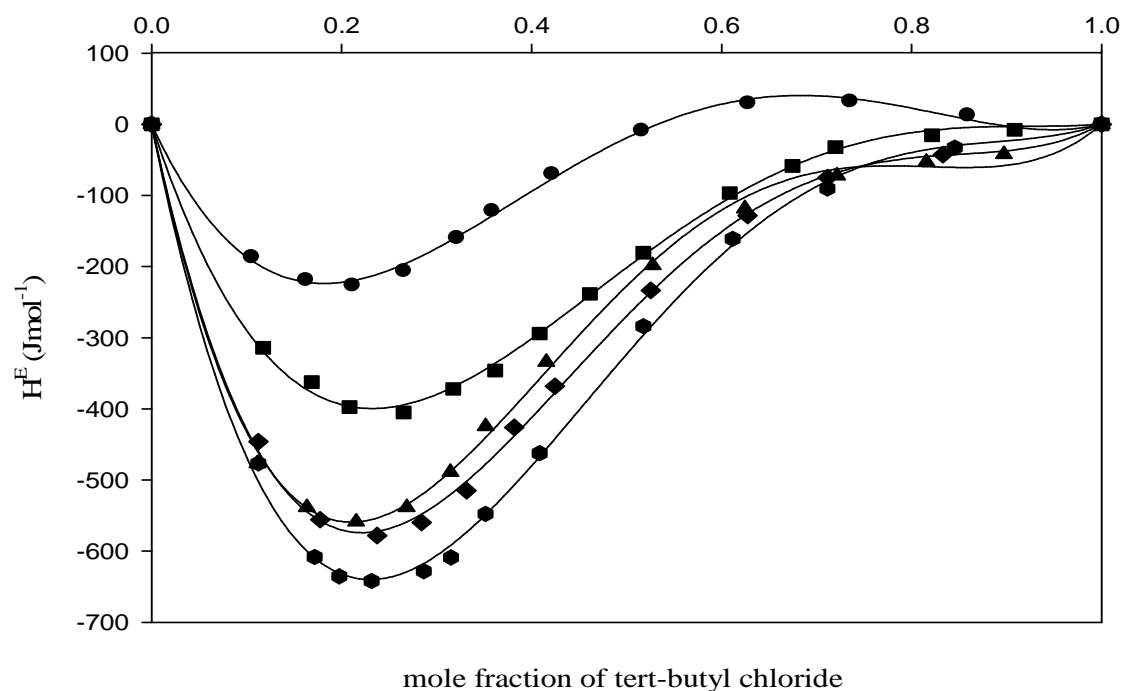


Fig. 2: Experimentally measured  $H_m^E$  at 308.15 K for tert- butyl chloride + benzene(●) or toluene(■) or o-xylene(▲) or m-xylene(◆) or p-xylene(●)

Table-3: Values of adjustable parameter  $H_0$ ,  $H_1$  and  $H_2$  of eqn. (1) and standard deviation,  $\sigma(H_m^E)$  ( $\text{J mol}^{-1}$ ) of the molar excess enthalpies of various binary mixtures at 308.15 K

System	$H_0$	$H_1$	$H_2$	$\sigma H_m^E$
SBC + benzene	45.0	-3.1	-10.9	0.1
SBC + toluene	-983.3	1521.8	-1424	4.6
SBC + o-xylene	-1262.3	1599.5	-918.2	5.6
SBC+ m-xylene	-1387	2002.6	-1300.9	7.3
SBC+ p-xylene	-1418.6	2236.6	-1678.4	7.8
TBC + benzene	-76.7	1276.2	-1519.6	5.8
TBC + toluene	-909.7	2601.4	-2831.7	11.2
TBC + o-xylene	-1079.1	2723.3	-2363.7	8.8
TBC+ m-xylene	-1168.7	2886.9	-2417	11.0
TBC+ p-xylene	-1292.9	3087.7	-2243.5	11.7

## DISCUSSION AND CONCLUSION

Excess molar enthalpy of mixing plots show negative values for all the mixtures (except butyl chloride + benzene mixtures).  $H_m^E$  values for sec-butyl chloride + benzene mixture are found to be positive but very less in magnitude and  $H_m^E$  values for tert butyl chloride + benzene mixture changes its sign from negative to positive. All curves are skewed towards the low mole fraction of butyl chloride.

At mole fraction 0.3 of the butyl chloride in mixtures, values were found to vary in the following order: sec- butyl chloride (SBC) + benzene > + toluene > + o-xylene > + m-xylene > + p-xylene and for tert-butyl chloride (TBC) + benzene > + m-xylene > + toluene > + o-xylene > + p-xylene.

$H_m^E$  data can be explained qualitatively if it is assumed that electron donor- acceptor type interactions exists between sec- or tert- butyl chloride with aromatic hydrocarbons ( behave as electron donor) and there is a disruption in the favorable orientational order in the pure components of the mixture when they are mixed. Both of these factors play a dominant role in deciding the sign of  $H_m^E$ . In the case of SBC + benzene mixtures, the positive values of  $H^E$  over the whole composition range suggest that the energy released by electron donor acceptor (EDA) interactions is less than the energy gained by the system due to disruption of the orientational order of pure components. When a methyl group is introduced in benzene (as in toluene), the electron density of  $\pi$ - electron increases and EDA interactions becomes stronger and this leads to a negative value of  $H_m^E$ . The introduction of two methyl groups in benzene (as in xylenes), further enhance these interactions and yield more negative values of  $H_m^E$ .

As effect of shape and branching of molecule is concerned, tert-butyl chloride is more symmetrical molecule and thus it will interact strongly than sec- butyl chloride with aromatic hydrocarbons, thus produces more negative  $H_m^E$  values.

## FLORY STATISTICAL THEORY

We examined our data in light of statistical mechanical theory by Flory<sup>22, 23</sup> which takes in to consideration the shape and size of the molecule. According to this theory  $H_m^E$  is given by:

$$H_m^E = x_A P_A^* V_A^* (\tilde{V}_A^{-1} - \tilde{V}_{cal}^{-1}) + x_B P_B^* V_B^* (\tilde{V}_A^{-1} - \tilde{V}_{cal}^{-1}) + x_A V_A^* \theta_B \chi_{AB} \tilde{V}_{cal}^{-1} \quad (2)$$

Where  $x_A$  and  $x_B$  and  $V_A^*$  and  $V_B^*$  denote the mole fractions and characteristic volume of components A and B respectively of the binary mixtures.  $\tilde{V}_{cal}^E$  is given by

$$\tilde{V}_{cal}^E = \tilde{V}_o^{7/3} [4/3 - \tilde{V}_o^{1/3}]^{-1} [\tilde{T} - \tilde{T}_o] \quad (3)$$

Where  $\tilde{V}_o$ ,  $\tilde{T}$  and  $\tilde{T}_o$  are the ideal reduced volume, reduced temperature and the ideal reduced temperature of the mixture defined by the following equations

$$\tilde{V}_o = \phi_A \tilde{V}_A + \phi_B \tilde{V}_B \quad (4)$$

$$\tilde{T}_o = (\tilde{V}_o^{\frac{1}{3}} - 1) / \tilde{V}_o^{4/3} \quad (5)$$

$$\tilde{V}_A = [1 + \alpha_A (T/3) / (1 + \alpha_A T)]^3 \quad (6)$$

$$V_A^* = \tilde{V}_A / \tilde{V}_B \quad (7)$$

$$\phi_A = 1 - \phi_B = N_A V_A^* / (N_A V_A^* + N_B V_B^*) \quad (8)$$

The equations have the same significance as has been described by Flory,  $\alpha$  is the coefficient of volume expansion of the pure component. The reduced temperature,  $\tilde{T}$  of the mixture is given by

$$\tilde{T} = \phi_A P_A^* \tilde{T}_A + \phi_B P_B^* \tilde{T}_B / \phi_A P_A^* + \phi_B P_B^* (1 - \phi_A \theta_B \chi_{AB} / \phi_A P_A^* + \phi_B P_B^*)^{-1} \quad (9)$$

Where  $P_A^*$  is a characteristic pressure defined by

$$P_A^* = \alpha_A T \tilde{V}_A^2 / (K_T)_A \quad (10)$$

Where  $(K_T)_A$  denotes the isothermal compressibility, is a fair potential and  $\theta_B$  is the site fraction given by

$$\theta_B = x_B / (x_B + x_A \gamma_A S_A / \gamma_B S_B) \quad (11)$$

Where  $S_A$  denotes the contact sites in each segment of a molecule, considered to be made up of  $\gamma_A$  segments. To calculate  $\gamma_A S_A / \gamma_B S_B$ , it is assumed that the number of contact sites  $\gamma_A S_A$  per molecule is proportional to the surface area of a sphere of the same core volume. Thus

$$(\gamma_A S_A / \gamma_B S_B) = (V_A^* / V_B^*)^{2/3} \quad (12)$$

The reduced temperature  $\tilde{T}$  of the mixture is dependent on the adjustable parameter  $\chi_{AB}$ , which could be evaluated from the knowledge of some other excess function of the system. We have evaluated this parameter by using the experimental values of  $V^{E16, 17}$  at  $x_A = 0.5$  of the mixtures. These values of  $\chi_{AB}$  are given in Table 4 along with the  $H^E$  values at  $x_A = 0.1, 0.3, 0.5, 0.7, 0.9$ .

The parameters of the pure components were evaluated by using physical properties like heat of vaporization and isothermal compressibilities values reported in literature<sup>20, 24</sup>.

An examination of **Tables- 4** shows that agreement is poor between the experimental and the calculated values by Flory's theory. Generally, Flory theory is applicable to those mixtures, where only physical interactions are present. In our mixtures, most probably EDA type interactions are present; therefore the agreement between the experimental and calculated values is poor. Another reason for failure of theory may be due to the approximate values of  $\alpha$  and  $K_T$  of some of the pure components were used to calculate the  $H_m^E$  values.  $\alpha$  and  $K_T$  were calculated from the coefficient of volume expansion and from the solubility parameters of pure components respectively.

**Table- 4:** Comparison of the measured  $H_m^E$  values for sec- or tert- butyl chloride (A) + aromatic hydrocarbon (B) at 308.15 K with their corresponding  $H_m^E$  values evaluated from Flory theory.

mole fraction( $x_A$ )	$H_m^E$ (J mol <sup>-1</sup> )	
	Experimental	Flory
sec-butyl chloride (A) + benzene (B)		
	$\chi_{AB} = -0.2472$	
0.1	3.9	-2.0
0.3	9.1	-4.6
0.5	11.3	-5.4
0.7	8.5	-4.5
0.9	2.9	-1.8
sec-butyl chloride (A) + toluene (B)		
	$\chi_{AB} = -0.7652$	
0.1	-282.2	-9.3
0.3	-380.4	-22.3
0.5	-245.2	-27.2
0.7	-125.9	-23.4
0.9	-64.5	-10.2
sec-butyl chloride (A) + o-xylene (B)		
	$\chi_{AB} = 0.2008$	
0.1	-266.3	-6.0
0.3	-433.2	-15.6
0.5	-308.5	-20.4
0.7	-166.3	-18.8
0.9	-50.4	-8.8
sec-butyl chloride (A) + m-xylene (B)		
	$\chi_{AB} = 6.5801$	
0.1	-333.0	44.8
0.3	-511.6	106.9
0.5	-345.2	130.0
0.7	-172.7	111.7
0.9	-49.5	48.9
sec-butyl chloride (A) + p-xylene (B)		
	$\chi_{AB} = 2.0417$	
0.1	-369.9	8.0
0.3	-546.4	19.5
0.5	-353.5	22.9
0.7	-164.7	19.0



	0.9	-59.8	8.0
tert-butyl chloride (A) +benzene (B)	$\chi_{AB} = 1.2493$		
	0.1	-183.3	7.8
	0.3	-173.9	17.1
	0.5	-17.7	19.8
	0.7	39.6	16.0
	0.9	2.7	6.6
tert-butyl chloride (A) + toluene (B)	$\chi_{AB} = 7.2370$		
	0.1	-439.7	49.1
	0.3	-507.5	114.1
	0.5	-222.0	135.3
	0.7	-78.3	113.4
	0.9	-37.3	48.5
tert-butyl chloride (A) + o-xylene (B)	$\chi_{AB} = 14.8540$		
	0.1	-413.1	103.6
	0.3	-547.1	245.7
	0.5	-267.3	297.6
	0.7	-81.5	254.7
	0.9	-27.5	111.3
tert-butyl chloride (A) + m-xylene (B)	$\chi_{AB} = 20.0757$		
	0.1	-439.7	146.8
	0.3	-589.4	350.2
	0.5	-283.7	426.6
	0.7	-95.7	367.1
	0.9	-25.1	161.3
tert-butyl chloride (A) + p-xylene (B)	$\chi_{AB} = 13.6708$		
	0.1	-422.5	94.6
	0.3	-622.3	225.4
	0.5	-311.9	274.0
	0.7	-93.2	235.3
	0.9	-20.3	103.2

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