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Study of Heats Of Mixing Of Binary Liquid Mixtures

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Abstract : *Studies of heats of reactions of binary liquid mixtures are given a considerable importance in understanding the nature of molecular interactions. Such studies mainly help to know the enthalpies of liquid mixtures. The present study deals with design of a simple embedded based system for measuring heat-of mixing of binary liquid mixtures. The system consists of two units, cell assembly and data acquisition system. One of the components of the binary mixture is taken into the cell, other component is injected in to the cell through appropriate mechanical arrangement. The reaction on mixing causes the thermal changes which are sensed by the thermal sensor, that can be measured up to $10^{-4o}C$. The entire unit is interfaced to LPC 2366 ARM based controller (A less power consumption device made by philips). The ARM controller sends the data to the Personal Computer through the serial port and software is developed to calculate enthalpy values. A comparison of the results obtained with the literature data showed good agreement. The designed system can be used as an alternative for the measuring heats of mixing of binary liquid mixtures. The paper deals with the design aspects both hardware and software features of the system.*

Keywords - *liquids, mixtures, ARM Processor, embedded*

I. INTRODUCTION

Heat of mixing data for binary liquid systems is useful for both chemists and engineers to know the nature of the solutions and design the heat transfer equipment (heat exchangers). As the data of the non ideal systems are very limited and the effect of temperature are very rarely has been investigated. Based on heat transfer theory, the relations between the heat effect generated and the quantity measured in the calorimeter known as the heat balance equation is established, which expresses the change of temperature directly as a function of the heat produced in a calorimeter and is applied to design different types of calorimeters. A number of calorimeter is available micro to macro and simple to complex in design. The calorimeters are differed by their principle, heat flow calorimeter, Benson et. al.[1] Picker flow calorimeter, Fortier and Benson[2] in this type of calorimeter excess heat capacities of mixtures of non-electrolytes were determined from volumetric heat capacity. Steady state and composition scanning differential flow micro calorimeters by Patrick Picker et. al.[3,4] They developed two different flow micro calorimeters, one is of the adiabatic type and can be used to measure **ΔT** mixing for liquid phase reactions, and other can be operated under either adiabatic or isothermal conditions and serves for either gas or liquid phase investigations. The available commercial calorimeters like Parr[5,6] and ITC are sophisticated and very costly. Hence an attempt is made to design adiabatic micro calorimeter which is simpler and versatile for a rapid and fairly accurate measurement of exothermic and endothermic heats of mixing for binary liquid mixtures. The proposed system shows a new approach which is attached with all the advantages of any embedded based system in speed and compatibility. These measurements assume a great significance because of diversified applications of these measurements in industries and R&D purposes.

II. MATERIALS AND METHODS

The chemicals used in the present work Carbon tetrachloride, n-hexane, Cyclohexane , Dimehyl formamide, methyl-tert-butylethane (MTBE), Chlorobenzene, Nitrobenzene, Carbontettachloride are obtained from M/s Fulka Ltd.,Bombay. Benzene (Spectroscopic grade) was obtained from M/s SD Fine Chemicals, Boisar, India. Dimethoxyethane are obtained from SD Fine Chemicals, Boisar, India The chemicals used here are used without any further purification. methyl-isobutyl ketone, methyl-ethylketone obtained from BDH Ltd., and dried over 4A molecular sieves for 4 – 5 days and purified by fractional distillation. Pure component properties used to calculate excess enthalpies such as molecular weight, density and heat capacity are collected and tabulated in Table 1. Measured density, boiling point and refractive index of the the compounds and compared with literature values reported by Riddick et al[7] and Ian M. Smallwood[8] to ensure the purity of the compounds. The data is tabulated in Table2. From Table2, it is found that the measured properties are in good agreement with literature values[9,10]. The purity of the compounds are checked and further confirmed by GC, a single sharp peak. The vibrator, Nokia 1100 (range is 500 milli volts to one volt) is used as a device to stir the mixture inside the cell, the ARM7TDMI based LPC2366 controller (NXP Philips), 12V and 2Amp stepper motor similar to that used in HP printer, constant current source REF200 and 5 kΩ thermistor are purchased from local electronic shop, Ahmedabad, India. Micro syringe (Borosil) of 10 ml capacity, Dewar flask (Eagle) of 20 ml capacity are obtained from Ahmedabad, India. Insulating materials is Polytherific foam (PUF) from M/s Bharathi Refrigeration systems from Ahmedabad, India.

The heats of mixing is calculated using the equation.

$$H^E = -\Delta T\left(w_1 C_{P1} + w_2 C_{P2} + C.C\right)$$

Where ΔT temperature difference, w is weight and C_P is heat capacity of the components, C.C is cell constant. Suffixes represent components 1 and 2 respectively. The pure component data is collected from literature is tabulated in Table2.

Table 1 Properties of pure components from literature value

Sl. No.	Name of he compound	Molecular weight	Density g/cc	Cp, Cal/ mol/°C	Chemical Formula	References
1	DMF	73	0.945	36	$C_4H_{10}O_2$	5
2	MIBK	100	0.801	46	$C_6H_{12}O$	
3	MEK	72	0.805	38	$C_4H_{10}O$	
4	MTBE	88	0.741	44.8	$C_5H_{12}O$	
5	Benzene	78	0.790	31	C_6H_6	
6	Chloro Benzene	113	1.106	35	C_4H_5cl	
7	Nitro benzene	123	1.204	44	$C_6H_5NO_2$	
8	Hexane	86	0.659	42.0	C_6H_{14}	
9	Cyclo hexane	84	0.778	36.4	C_6H_{12}	
10	Ethanol	46	0.789	27	C_6H_5O	
11	Water	18	0.998	18	H_2O	
12	Carbon tetrachloride	154	1.580	32	CCl_4	

Table 2 Comparison of properties of pure components

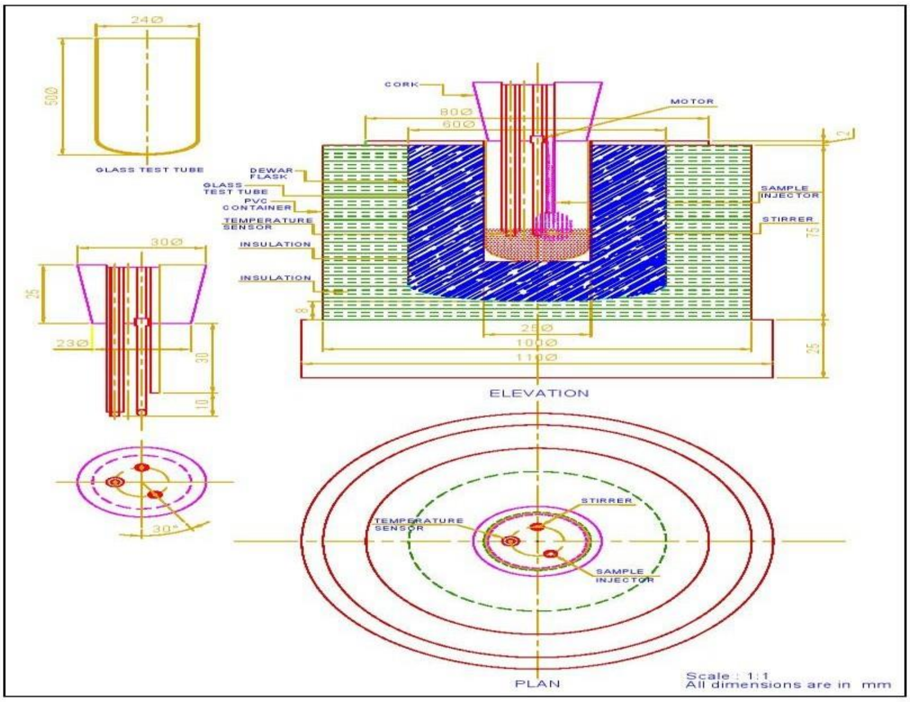
Sl. No.	Name of the compound	Density g/cc		Boiling point, °C		Refractive Index		Ref.
		Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	
1	DMF	0.9453	0.945	152.6	153	1.4276	1.427	5
2	MIBK	0.8007	0.801	116.3	116	1.3945	1.394	
3	MEK	0.8039	0.805	79.8	80	1.3772	1.377	
4	MTBE	0.7402	0.741	55.2	55	1.3686	1.369	
5	Benzene	0.7896	0.790	79.8	80	1.4978	1.498	
6	ChloroBenzene	1.1062	1.106	131.7	132	1.5236	1.523	
7	Nitro benzene	1.2038	1.204	210.8	211	1.5488	1.550	
8	Hexane	0.6578	0.659	69.4	69	1.3725	1.372	
9	Cyclo hexane	0.7782	0.778	80.6	81	1.4242	1.424	
10	Ethanol	0.7886	0.789	78.2	78	1.3586	1.359	
11	Water	0.9982	0.998	99.8	100	1.3323	1.332	
12	Carbon tetrachloride	1.5796	1.580	75.6	76	1.4592	1.459	

III. APPARATUS

The calorimeter was designed to operate adiabatically and to allow the heats of mixing at room temperature to determine for the entire composition range. The designed system consists of two units. One is calorimeter cell assembly and other is data acquisition system. The Cell design is as shown in fig.1.

The cell assembly consists of a test cell of 10 ml capacity inserted in a Dewar flask, which is insulated with Polytherific foam material about 2 mm thickness. One of the components of binary mixture is taken into the test cell and other component is added by means of dispensing unit. The dispensing unit consist of 12 V stepper motor, gear rod, coupling and micro syringe. Syringe is taken and attached to a gear rod. Stepper motor is plugged to a 12 V power supply and interfaced to LPC 2366 ARM controller. The syringe is connected to a feed tube at one end and the other end is kept in to the cell inside Dewar flask. A 5 kΩ thermistor was taken. The thermistor is a glass covered probe with a resistance of 5 kΩ at room temperature was sealed in the end of a piece of glass tubing which carried the leads a out of the calorimeter. One of the lead is connected to constant current source REF200 and the other lead is grounded to the power supply. The thermistor is inserted in the solution. Thermistor senses the temperature changes produced on adding second component to the other component which was held in the calorimeter cell. The sensed voltages are sent to the ADC channle2 of the port pin 24 of ADC of LPC 2366 ARM controller and data is acquired from the PC through the serial port .A tiny DC motor is taken and the leads are taken out and plugged to 900 mV power supply. A small glass tube is taken and bended at the edge to act this as a stirrer. The glass tube is fixed to the tip of the motor. Stirrer runs at a very low speed, so that the heat produced due to the stirrer is negligible. Here the designed tiny stirrer will not produce any frictional heat while stirring.

Fig 1 Calorimeter Design



IV. EXPERIMENTAL PROCEDURE

The designed specification of calorimeter used for the measurement of heat of mixing for binary liquid mixtures is as shown in Fig.1. First data point is obtained by taking known quantity (5 ml) of component 1 into test cell and the 0.5 ml of component 2 is added through dispensing unit. A Vibrator is used to provide uniform distribution of the component 2 into component 1 in the cell. The temperature change is recorded at every 5 seconds. Experiment is stopped after reaching thermal equilibrium, i.e., no temperature change. 0.5 ml of component 2 is added to the mixture (5.5 ml) in the cell. The temperature change is recorded at every 5 seconds and stopped after reaching thermal equilibrium. The procedure is repeated till total amount of component 2 added is 5 ml with a 0.5 ml increment. . The temperature difference (ΔT) is obtained by plotting time vs. temperature. Up to 50% weight percent range is covered in this way. To obtain the data over entire composition range, the procedure is repeated by interchanging components 2 and 1, by taking 5 ml of component 2 in the cell and added component 1 in the increments of 0.5 ml.

V. RESULTS AND DISCUSSIONS

The designed calorimeter is tested with a number of binary systems.

Table 3A Determination of cell constants using Cyclo Hexane + n-Hexane system

Mole fraction X1	Temp diff DT	H^E, ca/g Expt	Lit	Diff	Cell const. Diff/ DT
0.1085	-0.0988	0.1988	2.3047	2.1060	21.3199
0.1958	-0.0589	0.1139	1.3839	1.2700	21.5664
0.2675	-0.0714	0.1501	1.6880	1.5380	21.5415
0.3275	-0.0964	0.2188	2.2971	2.0782	21.5661
0.3784	-0.1207	0.2945	2.8867	2.5922	21.4734
0.4221	-0.1389	0.3625	3.3584	2.9959	21.5644
0.4601	-0.1519	0.4221	3.6979	3.2758	21.5635
0.4934	-0.1599	0.4715	3.9204	3.4489	21.5625
0.5228	-0.1643	0.5122	4.0481	3.5359	21.5178
0.5490	-0.1642	0.5396	4.1030	3.5634	21.7014
0.5490	-0.1640	0.5613	4.1030	3.5417	21.5956
0.5750	-0.1661	0.5402	4.1010	3.5608	21.4378
0.6035	-0.1645	0.5071	4.0346	3.5275	21.4452
0.6349	-0.1597	0.4650	3.8862	3.4212	21.4257
0.6699	-0.1503	0.4120	3.6385	3.2264	21.4673
0.7089	-0.1363	0.3503	3.2776	2.9273	21.4791
0.7527	-0.1171	0.2812	2.8032	2.5220	21.5304
0.8023	-0.0959	0.2138	2.2488	2.0350	21.2275
0.8589	-0.0738	0.1529	1.7249	1.5720	21.3011
0.9241	-0.0656	0.1209	1.5116	1.3907	21.2090
					429.4956
			Average Value		21.4748

Table 3B Determination of cell constants using Benzene + CCl4 system

mole fraction X1	temp dif DT	Qmix , cal/g Expt.	Lit.	Diff	Diff/DT
0.9080	-0.0237	0.0411	0.554664	-0.51356	21.66934
0.8315	-0.0426	0.080877	0.995101	-0.91422	21.46067
0.7669	-0.0576	0.118819	1.356356	-1.23754	21.48502
0.7116	-0.0698	0.155455	1.659999	-1.50454	21.55507
0.6638	-0.0810	0.193709	1.920077	-1.72637	21.31319
0.6220	-0.0897	0.229178	2.146178	-1.917	21.37839
0.5851	-0.0974	0.264939	2.345107	-2.08017	21.35696
0.5524	-0.1036	0.298827	2.521859	-2.22303	21.45784
0.5231	-0.1095	0.333726	2.680204	-2.34648	21.43627
0.4968	-0.1142	0.366933	2.823053	-2.45612	21.50718
0.0898	-0.0221	0.039784	0.518298	-0.47851	21.65221
0.1649	-0.0404	0.07907	0.943367	-0.8643	21.39349
0.2285	-0.0560	0.118393	1.300488	-1.18209	21.10883
0.2831	-0.0680	0.154438	1.606293	-1.45185	21.35081
0.3305	-0.0792	0.192308	1.872179	-1.67987	21.21049
0.3720	-0.0880	0.227491	2.106235	-1.87874	21.34937
0.4086	-0.0950	0.2605	2.314384	-2.05388	21.61982
0.4413	-0.1020	0.295708	2.501076	-2.20537	21.62126
0.4705	-0.1099	0.335864	2.669737	-2.33387	21.23633
0.4968	-0.1106	0.355366	2.823053	-2.46769	22.31182
					429.4744
		Average value			21.4772

No adiabatic calorimeter is fully adiabatic, some heat will be lost by the sample to the sample holder. A mathematical correction factor, known as the cell constant, can be used to adjust the calorimetric result to account for these heat losses. Every calorimeter has a unique calorimeter constant. It may be calculated by applying a known amount of heat to the calorimeter and measuring the calorimeter's corresponding change in temperature. The calorimeter constant is then calculated by dividing the change in enthalpy (ΔH) by the change in temperature (ΔT). In our study we have determined calorimeter constant from the experiment results with the literature values for two different binary systems, cyclo alkane and normal chain alkane system, i.e.,

cyclohexane + n-Hexane and aromatic and chlorinated alkanes, i.e., Benzene + Carbontetrachloride (CCl4)[11]. Average value of the differences between experimental and literature values over the entire composition range was taken as the cell constant. It was found that the cell constant for both the systems is similar. The results are tabulated in Table 3A and Table 3B. The detailed calculation procedure is given in Appendix A.
The recorded temperature values are smoothened for finding the temperature difference (ΔT) values and the enthalpy calculations done by using the C++ program.

Appendix A

Steps to calculate the cell constant

The pure component data, molecular weight, heat capacity and density are collected from the literature.
Cyclohexane (1) + n-Hexane (2)

Component	Molecular weight	Heat capacity	Density (g/cc)
		(cal/g. K)	
Cyclohexane	84.61	0.43251	0.7785
n-Hexane	86.18	0.48735	0.6548

First Data Point

Weight of 5 ml of component 1 (w1) = 5 x 0.7785 = 3.8925 g
Weight of 0.5 ml of component 2 (w2)= 0.5x 0.6548 = 0.3274 g
Weight fraction = w1/(w1+w2)
= 3.8925/(3.8925+0.3274)= 0.9224

Mole fracton of component 1, $X1 = \frac{w1/MW1}{\left(w1/MW1 + w2/MW2\right)} = \frac{3.8925/84.611}{\left(3.8925/84.611 + 0.3274/86.18\right)} = 0.9241$

Average molecular weight = x1*MW1 + (1-X1)*MW2
= 0.9241x84.61 + (1-0.9241)*86.18
= 84.3133
Totals Moles in the mixture = Moles of component 1 (n1) + Moles of component 2 (n2)
= w1/MW! + w2/MW2
= 3.8925/84.61 + 0.3274/86.18
= 0.0501

$Q_1 = 0.0$
Q_2, (cal/g k) = -ΔT(w1cp1 + w2cp2) T
$Q_2 = -(-0.0656\times(3.8925 \times 0.43251 + 0.3274 \times 0.48735))$
= 0.1209
$Q_{Mixt} = Q_1 + Q_2 = 0 + 0.1190 = 0.1190$ Cal/g K
Qmix, (Lit value)= 1.5116
Difference = Qmix, (Expt) - Qmix(Lit)
= 0.1209 - 1.5116
= - 1.3907Cell Constant = Difference / ΔT
= - 1.3907/(-0.0656)
= 21.2090

Second Data Point

Weight of 5.5 ml mixture = 3.8925 + 0.3274 = 4.2199 g
Weight of 0.5 ml component2 = 0.3274 g
Step wise calculation of weight of each component in the mixture:
Step 1: weight of mixture x weight fraction of component 1/average molecular weight of mixture (as in data point 1)
Weight of component 1 = 4.2199 x 0.9224 = 3.8925 g
Weight of component 2 in the mixture= 4.2199 x (1-0.9224) = 0.3274 8
Total weight of component 2 for second point = weight in the mixture and added weight
= 0.3274 +0 .3274 = 0.6548 g
Weight fraction = 3.8925/(3.8925 + 0.6548)
= 0.8560
Mole fraction = 3.8925/84.16 +0.6548/86.18 = 0.8589

Average molecular weight = 0.8589 x 84.61 + (1-0.8589) x 86.18 = 84.4450
Total moles = 3.8925/84.61 + 0.6548/86.18 = 0.0538
Q1 is the heat of mixing
Q1 = Q_{Mixt} of data point 1 x weight fraction of component1/average molecular weight
Q1 = 0.1209 x 0.9224/84.3133
= 0.0051
Q_2, (cal/g k) = -ΔT(w1cp1 + w2cp2)
= - (-0.0738 x (3.8925 x 0.43251 + 0.3274 x 0.48735))
= 0.1478
Q_{mix} = 0.0051 + 0.1478 = 0.1529 cal/g K
Qmix, (Lit value)= 1.7249
Difference = Qmix, (Expt) - Qmix(Lit)
= 0.1529 - 1.7249 = - 1.5720
Cell Constant = Difference / ΔT
= - 1.5720/(-0.0738)
= 21.301

Third Data Point

Weight of mixture (6ml) = 4.2199 + 0.3274 = 4.5473 g
Weight of component 1 in the mixture = 4.5473 x 0.8560 = 3.8925
Weight of component 2 in the mixture = 4.5473 x (1-0.8560) = 0.6548
Total weight of component 2 for second point = weight in the mixture and added weight
= 0.6548 + 0.3274 = 0.9822 g
Weight fraction = 3.8925/(3.8925 + 0.9822)
= 0.7985
Mole fraction = 3.8925/84.16 +0.9822/86.18 = 0. 8023
Average molecular weight = 0.7985 x 84.61 + (1-0.7985) x 86.18) = 84.5594
Total moles = 3.8925/84.61 + 0.9822/86.18 = 0.0576
Q1 = Q_{Mixt} of data point 2 x weight fraction of component1/average molecular weight
Q1 = 1.529 x 0.8560/84.4450
= 0.065
Q_2, (cal/g k) = -ΔT(w1cp1 + w2cp2 + E)
= -(-0.09486 x (3.8925 x 0.43251 + 0.9822 x 0.48735))
= 0.2073
Q_{mix} = 0.0065 + 0.2073 = 0.2138 cal/g K
Qmix, (Lit value)= 2.488
Difference = Qmix, (Expt) - Qmix(Lit)
= 0.2138 – 2.488 = - 2.035
Cell Constant = Difference / ΔT
= - 2.035/(-0.0959)
= 21.2275
The procedure is followed for all data points and taken average value. Which is 21.4739

The step wise calculation procedure is presented in Appendix B. The graphs on mole fraction vs. enthalpy of binary liquid mixtures are drawn using excel sheet.

The measured values of Excess enthalpies using the designed calorimeter for various systems are compared with the literature values. In this study MTBE with substitute compounds are taken and tabulated below.

Appendix B

The pure component data, molecular weight, heat capacity and density is collected from the literature.
Methyl Tertiary Buty Ethane (MTBE)(1)_+ Benzene (2)

Component	Molecular weight	Heat capacity		Density (g/cc)
		cal/mol K	(cal/g. K)	
MTBE	88.15	44.79	0.5081	0.7410
Benzene	78.00	31.00	0.3974	0.8675

First data point

Weight of 5 ml of component 1 (w1) = 5 x 0.741 = 3.702g

Weight of 0.5 ml of component 2 (w2)= 0.5x 0.8675= 0.4338 g

Weight fraction = w1/(w1+w2)

= 3.702/(3.702+0.4338) = 0.8951

Mole fracton of component 1, $X1 = \frac{w1/MW1}{\left(w1/MW1 + w2/MW2\right)} = \frac{3.702/88.15}{\left(3.702/88.15 + 0.4338/78\right)} = 0.8831$

Average molecular weight = x1*MW1 + (1-X1)*MW2

= 0.8831x88.15 + (1-0.8831)*78

= 87.0

Totals Moles in the mixture = Moles of component 1 (n1) + Moles of component 2 (n2)

= w1/MW! + w2/MW2

= 3.702/88.15 + 0.4388/78

= 0.0476

$Q_1 = 0.0$

Q_2, (cal/g k) = $-\Delta T(w1cp1 + w2cp2 + E)$

where E = cell constant = 21.4739

$Q_2 = -(-0.06457\times(3.8925 \times 0.43251 + 0.3274 \times 0.48735 + 21.4739))$

= 0.5530

$Q_{Mixt} = Q_1 + Q_2 = 0 + 0.0553 = 0.05530$ Cal/g K

$Q_{Mixt,}$ (Cla/mol K) = $Q_{Mixt,}$ (Cla/g K) /total moles = 0.0553/0.0476

= 11.6825

Q_{Mixt} = 11.6825x 4.186 = 48.9771 J/mol K

Second Data Point

Weight of 5.5 ml mixture = 4.1358 g

Weight of 0.5 ml component2 = 0.4388 g

Step wise calculation of weight of each component in the mixture:

Step 1: weight of mixture x weight fraction of component 1/average molecular weight of mixture(as in data point 1)

Weight of component 1 = 4.1358 x 0.8951/87 = 3.702 g

Weight of component 2 in the mixture= 4.1358 – 3.702 + 0.4338 = 8.8675 g

Total weight of component 2 for second point = weight in the mixture and added weight

= 4.1358 – 3.702 + 0.4338 = 0.8675 g

Weight fraction = 3.702/(3.702+0.8675)

= 0.8102

Mole fraction = $\frac{3.702/88.15}{\left(3.702/88.15 + 0.8675/78\right)} = 0.7906$

Average molecular weight = 0.7906x88.15 + (1-0.7906)*78

= 86.0

Total moles = 3.702/88.15 + 0.8675/78

= 0.531

Q1 is the heat of mixing

Q1 = Q_{Mixt} of data point 1 x weight fraction of component1/average molecular weight

Q1 = 0.533*0.8951/87

= 0.0235

Q_2, (cal/g k) = $-\Delta T(w1cp1 + w2cp2 + E)$

= -(3.702*0.5081+0.8675*0.3974+ 21.4739))

= 0.9926

Q_{mix} = 0.0235 + 0.9926 cal/g K

= 1.0162

$Q_{Mixt,}$ (Cla/mol K) = $Q_{Mixt,}$ (Cla/g K) /total moles = 1.0162/0.0531 = 19.1303

Q_{Mixt} =4.186* 19.1303 = 80.0796 J/mol K

The procedure is followed for all data points.

Table 4 Comparison of H^E values for MTBE + Benzene system

Mole fraction	Temp diff.	H^E, ca/g		% dev	% Abs. dev
X1	DT	Expt.	Lit.		
0.0702	-0.0377	61.66723	65.7224	-6.58	6.58
0.1312	-0.0656	101.4375	103.1158	-1.65	1.65
0.1847	-0.0833	121.8941	124.9320	-2.49	2.49
0.2320	-0.0969	134.7273	137.8477	-2.32	2.32
0.2741	-0.1135	150.273	145.4869	3.18	3.18
0.3118	-0.1106	140.068	149.8851	-7.01	7.01
0.3458	-0.1242	150.5544	152.2232	-1.11	1.11
0.3766	-0.1213	141.2712	153.2092	-8.45	8.45
0.4047	-0.1260	141.1457	153.2811	-8.60	8.60
0.4303	-0.1312	141.7238	152.7191	-7.76	7.76
0.4563	-0.1264	155.8413	151.5737	2.74	2.74
0.4856	-0.1215	156.2761	149.6136	4.26	4.26
0.5190	-0.1056	143.4629	146.5411	-2.15	2.15
0.5573	-0.0918	132.8393	141.9060	-6.83	6.83
0.6017	-0.0850	130.5302	135.0060	-3.43	3.43
0.6537	-0.0727	120.0582	124.7196	-3.88	3.88
0.7157	-0.0646	113.819	109.2392	4.02	4.02
0.7906	-0.0419	80.07923	85.7189	-7.04	7.04
0.8831	-0.0235	48.67686	50.1959	-3.12	3.12
					86.62
Percent Average Deviation (PAAD)					4.56%

Table 5 Comparison of H^E values for MTBE + Chlorobenzene System

mole fraction	temp dif	HE, Expt	HE, Lit.	% dev	% Abs. dev
X1	DT	Cla/g	Cla/g		
0.0788	0.0385	-71.64272	-66.9476	6.55	6.55
0.1460	0.0864	-148.0908	-143.055	3.40	3.40
0.2041	0.1247	-200.8032	-210.02	-4.59	4.59
0.2549	0.1794	-272.6966	-264.025	3.18	3.18
0.2995	0.1985	-285.8596	-305.821	-6.98	6.98
0.3391	0.2549	-349.1017	-337.345	3.37	3.37
0.3744	0.2623	-342.6953	-360.589	-5.22	5.22
0.4062	0.2921	-365.1651	-377.279	-3.32	3.32
0.4349	0.3147	-377.281	-388.817	-3.06	3.06
0.4609	0.3571	-411.4704	-396.311	3.68	3.68
0.4872	0.3069	-384.2116	-400.949	-4.36	4.36
0.5166	0.2915	-385.3712	-402.623	-4.48	4.48
0.5499	0.2976	-414.3931	-399.995	3.47	3.47
0.5876	0.2741	-404.0098	-391.151	3.18	3.18
0.6310	0.2304	-361.9965	-373.34	-3.13	3.13
0.6813	0.1900	-320.8879	-342.619	-6.77	6.77
0.7403	0.1668	-301.8436	-293.525	2.76	2.76
0.8104	0.1168	-228.0132	-219.373	3.79	3.79
0.8953	0.0582	-122.1843	-115.891	5.15	5.15
					80.45
	PAAD				4.23%

Table 6 Comparison of H^E values for MTBE + Nitro Benzene system

mole fraction	temp dif	H^E, Expt.	H^E, Lit.	% dev	% Abs. dev
0.0790	-0.03460	64.9066	57.12924	11.982	11.982
0.1465	-0.05047	88.6246	83.18271	6.140	6.140
0.2047	-0.05184	85.5674	93.53545	-9.312	9.312
0.2555	-0.06652	103.5125	95.70375	7.544	7.544
0.3002	-0.06061	89.4404	93.53582	-4.579	4.579
0.3399	-0.06734	94.4018	89.08179	5.635	5.635
0.3753	-0.06627	88.6210	83.47089	5.811	5.811
0.4070	-0.05681	72.6937	77.34162	-6.394	6.394
0.4357	-0.05516	67.6311	71.06154	-5.072	5.072
0.4618	-0.04823	61.6576	64.84383	-5.168	5.168
0.4881	-0.04726	61.8176	58.15572	5.924	5.924
0.5175	-0.03460	47.8459	50.24988	-5.024	5.024
0.5507	-0.02999	43.0956	40.93145	5.022	5.022
0.5885	-0.02176	32.4054	30.00963	7.393	7.393
0.6318	-0.00983	15.3460	17.36053	-13.128	13.128
0.6821	-0.00280	3.9234	3.0949	21.116	21.116
0.7409	0.00670	-13.1272	-12.0003	8.584	8.584
0.8110	0.01315	-26.4091	-25.2766	4.288	4.288
0.8956	0.01474	-31.0094	-28.9053	6.785	6.785
		PAAD			144.9 7.6%

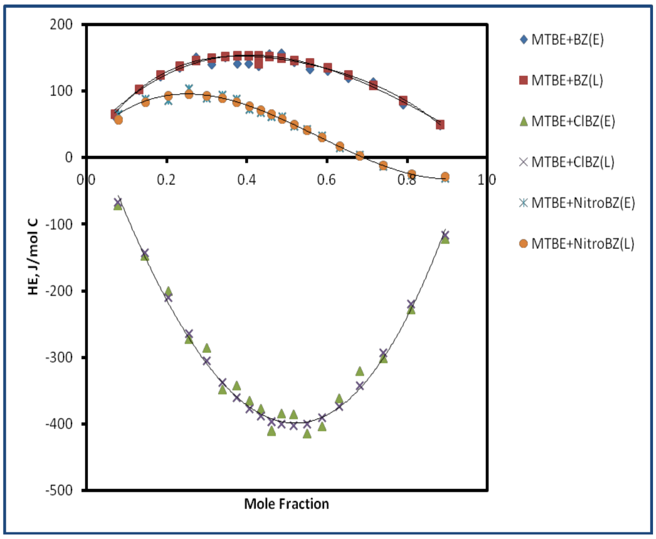


Fig 2: MTBE + Benzene substituted compounds

The comparison for three binary systems methyl tertiary butyl ether (MTBE) with benzene, chlorobenzene and Nitrobenzene[12] is as shown in the figure 2. From the Tables 4 – 6, it is observed that the excess enthalpy values for MTBE and benzene are positive (156.3, 153.3 and 48.7, 50.2 maximum and minimum values for experimental and literature values respectively). The percent average absolute deviation (PAAD) calculated using eqn. (2) is 4.6%. For MTBE and chlorobenzene, it is negative with -76.6, -66.9 and -414.4, -402.6 maximum and minimum values for experimental and literature values respectively and PAAD is 4.3%. The values for nitrobenzene are positive to negative with a PAAD of 7.6%. The maximum and minimum values for experimental and literature are 103.5 , 3.9 & -31.0. The higher percent deviation (7.6%) is due to the small values of excess enthalpies.

Table 7 Comparison of H^E values for DMF + MIBK System

mole fraction	temp dif	H^E, Expt.	H^E , Lit.	% dev	% Abs. dev
0.1038	-0.0291	46.469	44.616	3.99	3.99
0.1880	-0.0559	81.993	87.315	-6.49	6.49
0.2578	-0.0832	112.791	107.080	5.06	5.06
0.3165	-0.0954	120.398	116.434	3.29	3.29
0.3667	-0.1002	118.366	122.495	-3.49	3.49
0.4099	-0.1112	123.542	127.564	-3.25	3.25
0.4477	-0.1289	135.242	131.977	2.41	2.41
0.4809	-0.1419	141.294	135.551	4.06	4.06
0.5103	-0.1414	134.135	138.101	-2.96	2.96
0.5366	-0.1584	143.336	139.564	2.63	2.63
0.5626	-0.1405	144.914	139.975	3.41	3.41
0.5914	-0.1182	129.089	138.935	-7.63	7.63
0.6232	-0.1257	139.480	135.671	2.73	2.73
0.6587	-0.1040	121.933	129.232	-5.99	5.99
0.6984	-0.1028	124.170	118.633	4.46	4.46
0.7432	-0.0846	106.351	103.220	2.94	2.94
0.7942	-0.0597	79.388	83.368	-5.01	5.01
0.8527	-0.0446	61.985	61.195	1.28	1.28
0.9205	-0.0280	40.099	38.678	3.54	3.54
					74.63
			PAAD		3.93%

Table 8 Comparison of H^E values for DMF + MEK System

Mole fraction	temp dif	H^E, Expt.	H^E, Lit.	% dev	% Abs. dev
0.1391	-0.0756	162.723	139.003	14.58	14.58
0.2443	-0.1179	221.623	215.641	2.70	2.70
0.3265	-0.1432	242.307	257.387	-6.22	6.22
0.3926	-0.1758	270.856	285.953	-5.57	5.57
0.4469	-0.2085	295.428	309.162	-4.65	4.65
0.4923	-0.2407	316.253	328.827	-3.98	3.98
0.5308	-0.2850	349.362	345.031	1.24	1.24
0.5639	-0.2916	335.523	357.669	-6.60	6.60
0.5926	-0.3190	346.031	366.825	-6.01	6.01
0.6178	-0.3683	378.277	372.783	1.45	1.45
0.6423	-0.3156	355.885	376.137	-5.69	5.69
0.6689	-0.3442	398.299	376.385	5.50	5.50
0.6978	-0.3284	392.669	371.922	5.28	5.28
0.7293	-0.2970	368.535	360.660	2.14	2.14
0.7637	-0.2685	345.255	340.054	1.51	1.51
0.8016	-0.2258	303.091	307.351	-1.41	1.41
0.8434	-0.1958	271.337	260.136	4.13	4.13
0.8899	-0.1316	190.022	196.987	-3.67	3.67
0.9417	-0.0794	116.019	116.019	0.00	0.00
					82.32
			PAAD		4.33%

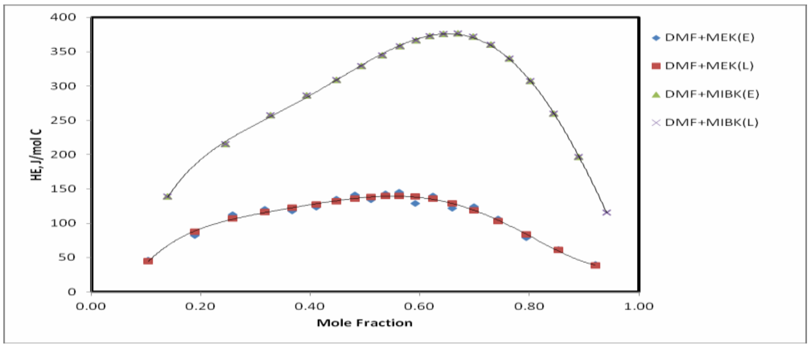


Fig.3: DMF with ketones

Similar observation were made (Tables7, 8) with dimethyl formamide(DMF) with methyl ethyl ketone (MEK) and mehyl isobutyl ketone (MIBK)[13] systems. The PAAD are 3.9 % and 4.3% for DMF + MEK and DMF+MIBK respectively. From the figs.2 and 3, it can be seen that the experimental values are in good agreement with literature values.

Table 9 Experimental values of H^E for DME + Benzene System

Mole fraction	temp dif	H^E, Expt.	H^E, Lit.	% dev	% Abs. dev
0.0950	-0.1013	201.26	197.705	1.766	1.766
0.1735	-0.0958	174.28	189.773	-8.890	8.890
0.2395	-0.0956	161.37	160.594	0.481	0.481
0.2957	-0.1003	158.1	142.251	10.025	10.025
0.3442	-0.0912	136.77	134.310	1.798	1.798
0.3865	-0.1034	144.62	132.089	8.665	8.665
0.4236	-0.1023	137.16	132.161	3.644	3.644
0.4565	-0.0976	125.33	132.721	-5.897	5.897
0.4858	-0.1018	124.22	133.028	-7.091	7.091
0.5121	-0.1095	127.82	132.911	-3.983	3.983
0.5121	-0.1086	126.16	132.911	-5.351	5.351
0.5384	-0.0946	115.82	132.377	-14.296	14.296
0.5675	-0.0983	125.7	131.442	-4.568	4.568
0.6000	-0.1101	144.37	130.395	9.680	9.680
0.6363	-0.0997	137.33	130.095	5.269	5.269
0.6774	-0.0965	139.2	132.326	4.938	4.938
0.7241	-0.088	135.98	140.051	-2.994	2.994
0.7777	-0.1034	166.91	156.547	6.209	6.209
0.8400	-0.0982	169.25	179.709	-6.180	6.180
0.9130	-0.1023	179.57	177.836	0.966	0.966
					112.690
					5.63%

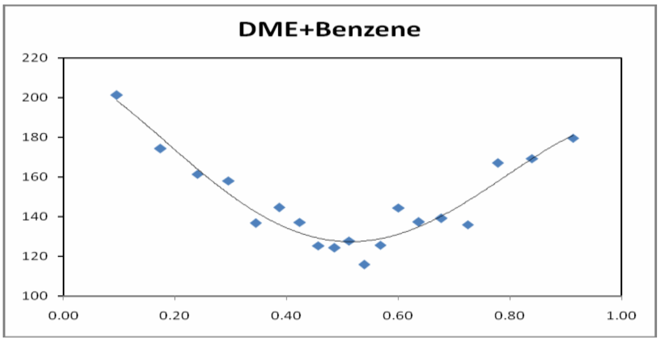


Fig. 4 DME + Benzene

The binary mixtures for Dimethoxyethane(DME) +Benzene set of results was fitted by the flowing equation to calculate the enthalpy.

$$H^E(j/mol) = 3553.1(x_1-x_2)^4 - 159.31(x_1-x_2)^3 + 221.25(x_1-x_2)^2 - 10.094(x_1-x_2) + 532.07 \quad (2)$$

Excess enthalpy data is generated for a binary system dimethoxyethane and benzene at room temperature. Fig. 4 represents the experimental data and polynomial equation (2). The data along with the calculated values using equation (2) is reported in Table 8. The percet average absolute deviation over the entire composition range is 4.3%.

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