ENTHALPY OF MIXING AND HEAT OF VAPORIZATION OF ETHYL ACETATE WITH BENZENE AND TOLUENE AT 298.15 K AND 308.15 K

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Abstract - The present work was carried out in two phases. First, enthalpy of mixing was measured and then the heat of vaporization for the same mixtures was obtained. The data are useful in the design of separation equipments. From the various designs available for the experimental determination of enthalpy of mixing, and heat of vaporization, the apparatus was selected, modified and constructed. The apparatus of enthalpy of mixing was tested with a known system Benzene – i-Butyl Alcohol and the data obtained was in very good agreement with literature values. Experiments were then conducted for mixtures of Ethyl Acetate with Benzene and Toluene. The experimental data was fitted to the standard correlations and the constants were evaluated. Heat of vaporization data were obtained from a static apparatus and tested for accuracy by conducting experiments with a known system Benzene – n-Hexane and the data obtained were found to be in agreement with literature values. Experiments were then conducted to measure heat of vaporization for the mixtures of Ethyl Acetate with Benzene and Toluene. Using experimental data of enthalpy of mixing from the first phase, and heat capacity data, the heat of vaporization were calculated.
Keywords: Enthalpy of Mixing; Heats of Vaporization; Ethyl Acetate; Benzene and Toluene.

INTRODUCTION

Enthalpy of mixing refers to the change in the enthalpy per mole of solution formed when pure components are mixed at the same temperature and pressure. Enthalpy effects on mixing of liquids are quite large and of considerable importance especially for the design of absorption and distillation columns. In the present work a static type calorimeter incorporating the design features of Tanaka *et.al.* (1972), Patel (1974), Rao and Viswanath (1973)

and Nirguna Babu (2003) was designed and used to measure enthalpy of mixing at 298.15 K and 308.15 K.

Heat of Vaporization is the amount of heat required to change a unit amount of liquid at bubble point (saturated liquid) to a vapor at its dew point (saturated vapor). Heat of vaporization data is useful for heat load determination in distillation columns. The design features of Dana (1925) were incorporated in the construction of the calorimeter adopted for the present study.

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EXPERIMENTAL

Apparatus

In the present work two types of setups were used to generate data for enthalpy of mixing and heat of vaporization, as described below.

The schematic diagram of the calorimeter used for the measurement of enthalpy of mixing is shown in Figure 1. It consists of a cylindrical Dewar flask of inner diameter 55 mm and 113.7 mm height. The space between the wall of the calorimeter and the jacket is evacuated to 10^{-4} mm Hg. The total volume is 270 cc. The top section of the calorimeter has provisions for inserting transducer AD590 (temperature sensing device), nichrome heater, a stirrer and two openings to feed two liquid components. The stirrer used is of paddle type. There are two paddles fixed equidistant and placed at 15 mm from the bottom as suggested by Uhl and Gray (1967) and Robert H Perry *et al* (1998). The stirrer passes through teflon joint with O-ring seal. Transducer AD590 and nichrome heater are inserted through B-14 ground glass joints. Two B-14 joints

are provided on the sides of the calorimeter to feed the two liquid components that are in the jacketed burettes. A capillary tube of 85 mm height and 0.1 mm diameter is fused to the top section of the calorimeter as shown in Figure 1, to eliminate the pressure build up in the calorimeter and conduct the experiment at atmospheric pressure. A transducer AD590 with an accuracy of ± 0.1 ^{0}C embedded in the glass tube is used as the temperature-sensing device. A digital multi meter with accuracy of 0.001mA is connected to the transducer and used for temperature measurement. The entire unit is kept in a water bath, whose temperature is maintained by a thermostat with 0.1 ^{0}C accuracy. The heater consists of a nichrome wire coil of 1.5 Ω resistance fused to enameled copper wire ends. A power pack supplies controlled power to the heater. A 0.01 sec. accuracy electronic digital watch is used to measure the time.

A fractional h.p. motor is used for stirring through a speed regulator. Water from the constant temperature water bath is circulated through the jackets of the burettes fixed on the calorimeter with the help of another fractional h.p. pump.

1. Jacketed Burette
2. Stop Cock
3. O - Ring Teflon Joint
4. Side Capillary
5. B - 14 Ground Joint
6. Transducer AD590
7. Heater
8. Vacuum Space
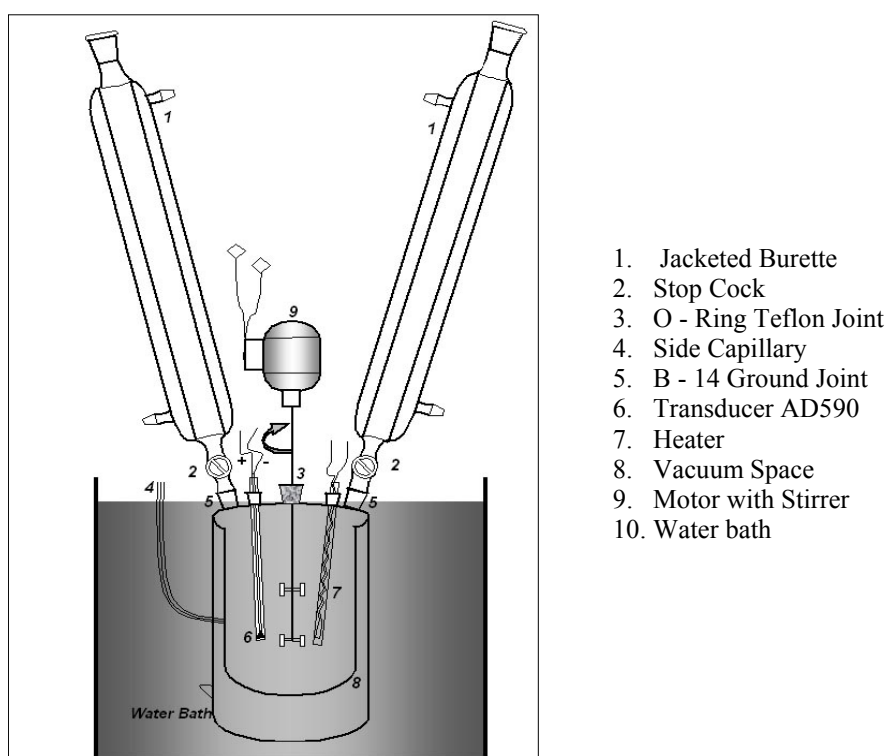9. Motor with Stirrer
10. Water bath

Figure 1: Schematic diagram of the Calorimeter for Measurement of Enthalpy of Mixing

Figure 2 shows the diagram of the apparatus used to measure heat of vaporization by Rao and Viswanath (1973) with few modifications. The calorimeter is enclosed in a jacket and the annular space is evacuated to 10^{-4} mm Hg. The heating element inside the calorimeter is a nichrome wire fused to tungsten wire leads. The vapors from the calorimeter are condensed and collected in the liquid meter. When the liquid meter is filled with the condensate, the liquid is automatically siphoned into the pre heater. This siphoning device permits a close cycle of operation. The vapor line between the calorimeter and the condenser is heated 1^0C above the boiling point to prevent any partial condensation

and downward flow of condensate. The pre heater consists of a three-liter flask and an external heater. The liquid in the pre heater is well stirred by means of a stirrer introduced through an O-ring seal. The black dots in the diagram represent heating elements. The liquid from the pre heater flows by gravity into the calorimeter and the flask surrounding it.

Power is supplied to the calorimeter heater from a very well regulated DC power source of not more than 0.1% ripple. This DC power unit is connected to AC power supply through a voltage stabilizer of 3% ripple. The DC power unit supplies up to a maximum of 300 Volts and 5 amperes. The power is measured with calibrated voltmeter and ammeter.
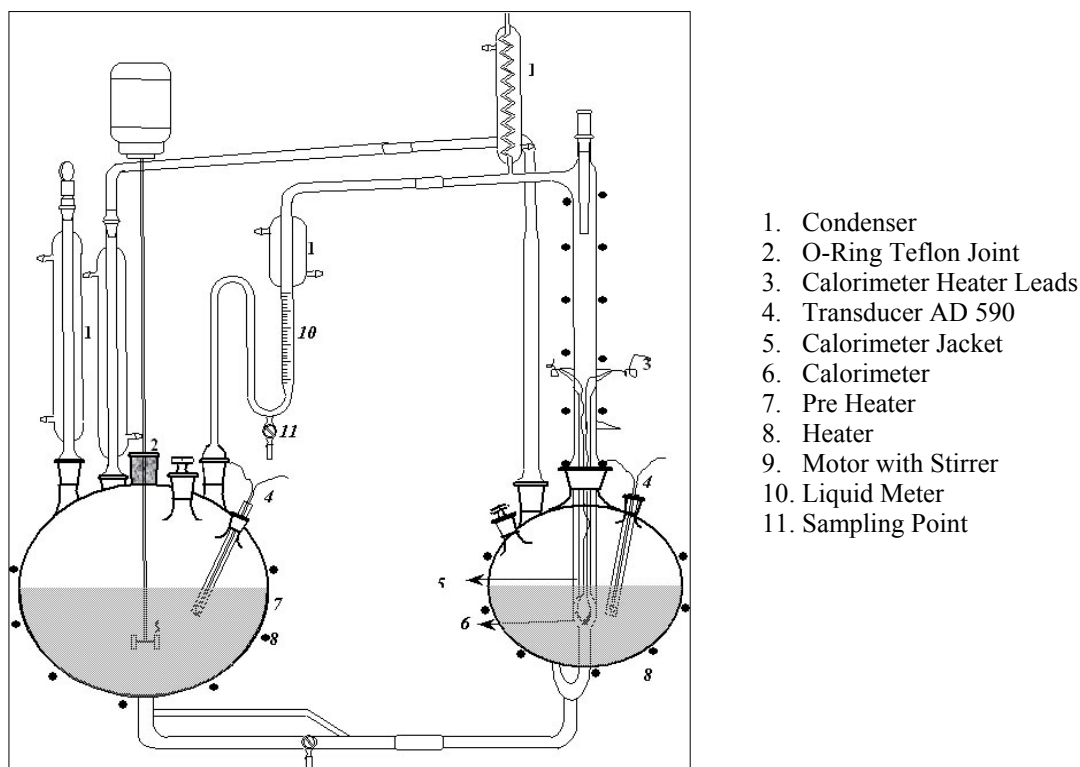

1. Condenser
2. O-Ring Teflon Joint
3. Calorimeter Heater Leads
4. Transducer AD 590
5. Calorimeter Jacket
6. Calorimeter
7. Pre Heater
8. Heater
9. Motor with Stirrer
10. Liquid Meter
11. Sampling Point

Figure 2: Calorimeter for Measurement Enthalpy of vaporization

Procedure

The procedures for the two types of setups used are given below.

a) Procedure for Measurement of Enthalpy of Mixing

The calorimeter is immersed in the constant temperature water bath. The liquids whose enthalpy of mixing is to be determined are taken in jacketed burettes. Long stemmed thermometers of range -10 to 110 ^{0}C with 0.1^{0}C accuracy are used to measure the temperatures of the liquids in the jacketed

burettes. The temperature of the water bath is maintained at the desired value at which the enthalpy of mixing is to be measured.

When the temperature of the liquids in both burettes equals that of the constant temperature bath, T_0, a known amount of liquid (1) from one of the burettes is run down into the calorimeter. Stirring is started and continued till the end of the experiment. Then, from the second burette, a known amount of liquid (2) is run down into calorimeter so that the total volume of both liquids is 270 ml. The temperature T_1 in the calorimeter is registered by means of transducer AD590. The liquid in the calorimeter is allowed to cool to the original

temperature T_0, and the heater is switched on and heating is continued till the liquid attains the temperature T_1. The current through the heater, the potential drop across it and the heating time of the mixture are all recorded. Finally, the liquids are emptied from the calorimeter.

The same procedure is repeated for different volume ratios of the two liquids, always keeping the total volume of 270 ml.

b) Procedure for Measurement of Heat of Vaporization Measure

About 2100 CC of liquid mixture of known composition is taken in the pre heater. The liquid is heated to about 2^0C below its bubble point. The calorimeter heater is switched on and the voltage is adjusted to about 7.26 volts. The vapor line heater-voltage is adjusted to prevent the re-condensation of saturated vapor from the calorimeter. Steady state is reached in about 3 to 4 hours depending on the boiling point of the mixture. At steady state, the composition of samples drawn from the liquid meter is constant and equal to that of the feed mixture. The time required to fill the meter with condensate is also constant.

Purification and Analysis

The products used in the present work were purified by the methods suggested by Riddick and Bunger (1970) and also Weissberger (1949). The purity was checked by specific gravity, refractive index and vapor phase chromatography.

RESULTS AND DISCUSSIONS

Initially the enthalpy of mixing of a known system (Benzene – i-Butyl Alcohol) was measured at 298.15 K and 308.15 K. All data were taken at the local atmospheric pressure of 689 mm Hg.

The enthalpy of mixing was calculated using the formula.

$$\Delta H_{m,Experimental} = \frac{EIt}{\dfrac{V_1 \rho_1}{M_1} + \dfrac{V_2 \rho_2}{M_2}} \qquad (1)$$

Obtained data were in close agreement with Perrin (1981) values found in literature with average absolute deviations of 0.0157 and 0.0189, and maximum deviations of 0.024683 and 0.03003 at 298.15 K and 308.15 K respectively.

The experiments were then conducted with the unknown systems, Ethyl Acetate with Benzene and Toluene, at 298.15 K and 308.15 K. All experiments

were conducted at 298.15 K and 308.15 K since there was no appreciable change in the enthalpy of mixing values beyond 308.15 K. Also the liquids start vaporizing at higher temperatures. The experimental data obtained are given in Tables 1 and 2 and shown in Figures 3 and 4. That enthalpy of mixing data was then fitted to the standard equation of the type

$$\frac{\Delta H_{m,Calculated}}{x_1 x_2} = A_0 + A_1(2x_1 - 1) +$$

$$A_2(2x_1 - 1)^2 + A_3(2x_1 - 1)^3 \qquad (2)$$

where A_0, A_1, A_2, and A_3 are constants and evaluated using regression analysis.

Using the following relation percentage deviation was calculated.

$$\frac{\Delta H_{m,Experimental} - \Delta H_{m,Calculated}}{\Delta H_{m,Experimental}} \cdot 100 \qquad (3)$$

The calculated values of enthalpy of mixing and the deviations obtained for the two systems are also given in Tables 1 and 2.

In a second phase, experiments were conducted following the procedure explained above to obtain the heat of vaporization data for Ethyl Acetate with Benzene and Toluene systems using the equation (4). The latent heat is given by

$$\Delta H_{Experimental}^V = \frac{EItM_{Ave}}{\rho V} \qquad (4)$$

$$\Delta H_{Calculated}^V = \sum \left[L_i(T_d)x_i + \int_{T_b}^{T_d} C_{Pi} x_i dT \right] +$$

$$\Delta H_{m,Experimental}(T_d)x_i \qquad (5)$$

The heats of vaporization were calculated using equation (5). The data required in the equation for the calculation are VLE data, heat of vaporization data and enthalpy of mixing values at boiling point. Since there was no variation in ΔH_m values beyond 308.15 K, the ΔH_m data at 308.15 K were used instead of at boiling point in the present calculations. The calculated values are compared with the experimental values and are given in the Table 4 along with heat of vaporization values at dew point. The data required at dew point were calculated using Watson (1943) relation and the deviations were found to be less than 5% as shown in Figures 5 and 6.

Table 1: Experimental Values of Enthalpy of Mixing for Ethyl Acetate (1) + Benzene (2)

x_1	$\Delta H_{m,Expt}$/ J. mol^{-1}	$\Delta H_{m, Calculated}$/ J. mol^{-1}	% Deviation	x_1	$\Delta H_{m,Expt}$/ J. mol^{-1}	$\Delta H_{m, Calculated}$/ J. mol^{-1}	% Deviation
Temperature 298.15 K							
0.0509	21.6017	21.6259	-0.1120	0.5309	104.9595	105.0328	-0.0698
0.1017	40.6771	40.6682	0.0219	0.5781	102.1298	102.1850	-0.0541
0.1338	51.4105	51.3846	0.0506	0.6252	97.4701	97.4892	-0.0196
0.1659	61.1445	61.1069	0.0615	0.6733	90.8746	90.8415	0.0363
0.2121	73.4218	73.3790	0.0584	0.7213	82.4512	82.3588	0.1121
0.2583	83.6840	83.6495	0.0413	0.7702	72.0401	71.8939	0.2029
0.3030	91.7177	91.7018	0.0173	0.8191	59.8125	59.6409	0.2869
0.3476	97.9291	97.9383	-0.0094	0.8690	45.5176	45.3799	0.3025
0.3930	102.4066	102.4430	-0.0355	0.9188	29.4161	29.4136	0.0087
0.4384	105.0615	105.1211	-0.0567	0.9594	14.9958	15.2137	-1.4532
0.4847	105.9239	105.9975	-0.0694				
Temperature 308.15 K							
0.0509	27.26286	27.2576	0.0194	0.5309	119.4267	119.3933	0.0280
0.1017	50.79362	50.7877	0.0116	0.5781	114.9148	114.8755	0.0342
0.1338	63.77904	63.7792	-0.0003	0.6252	108.4332	108.3956	0.0347
0.1659	75.36046	75.3684	-0.0106	0.6733	99.91803	99.8909	0.0272
0.2121	89.63594	89.6541	-0.0203	0.7213	89.59309	89.5842	0.0100
0.2583	101.1824	101.2063	-0.0236	0.7702	77.35039	77.3646	-0.0183
0.3030	109.8477	109.8711	-0.0213	0.8191	63.48207	63.5174	-0.0557
0.3476	116.1584	116.1755	-0.0147	0.8690	47.80099	47.8454	-0.0929
0.3930	120.2591	120.2651	-0.0049	0.9188	30.69378	30.7195	-0.0839
0.4384	122.1246	122.1167	0.0065	0.9594	15.7993	15.7755	0.1505
0.4847	121.8304	121.8083	0.0181				

Table 2: Experimental Values of Enthalpy of Mixing for Ethyl Acetate (1) – Toluene (2)

| x_1	$\Delta H_{m,Expt}$/ J. mol^{-1}	$\Delta H_{m, Calculated}$/ J. mol^{-1}	% Deviation	x_1	$\Delta H_{m,Expt}$/ J. mol^{-1}	$\Delta H_{m, Calculated}$/ J. mol^{-1}	% Deviation
Temperature 298.15 K							
0.0598	9.0322	8.9895	0.4729	0.5111	84.5645	84.4895	0.0886
0.1195	19.2744	19.3045	-0.1559	0.5573	88.0498	87.9761	0.0838
0.1587	26.4989	26.5515	-0.1985	0.6029	89.8047	89.7435	0.0681
0.1979	33.9540	34.0130	-0.1737	0.6485	89.6618	89.6237	0.0426
0.2462	43.2434	43.2932	-0.1150	0.6935	87.4428	87.4346	0.0094
0.2945	52.3948	52.4224	-0.0528	0.7384	82.9422	82.9664	-0.0292
0.3327	59.3481	59.3534	-0.0089	0.7827	76.0719	76.1241	-0.0686
0.3708	65.9142	65.8961	0.0276	0.8269	66.5726	66.6403	-0.1017
0.4178	73.2745	73.2297	0.0611	0.8618	57.0902	57.1543	-0.1123
0.4648	79.5970	79.5322	0.0814	0.8967	45.7418	45.7815	-0.0868
				0.9484	25.3061	25.2555	0.1998
Temperature 308.15 K							
0.0598	12.4352	12.3871	0.3870	0.5573	101.6667	101.5857	0.0797
0.1195	25.5624	25.5974	-0.1370	0.6029	102.9086	102.8421	0.0646
0.1587	34.4180	34.4784	-0.1756	0.6485	102.0343	101.9937	0.0398
0.1979	43.3013	43.3687	-0.1557	0.6935	98.8860	98.8788	0.0073
0.2462	54.0769	54.1335	-0.1048	0.7384	93.2549	93.2837	-0.0309
0.2945	64.4186	64.4501	-0.0490	0.7827	85.0805	85.1402	-0.0702
0.3327	72.1077	72.1140	-0.0088	0.8269	74.0927	74.1692	-0.1032
0.3708	79.2327	79.2127	0.0253	0.8618	63.3097	63.3818	-0.1139
0.4178	87.0434	86.9937	0.0570	0.8967	50.5518	50.5964	-0.0882
0.4648	93.5593	93.4876	0.0767	0.9484	27.8359	27.7798	0.2015
0.5111	98.4724	98.3897	0.0840				
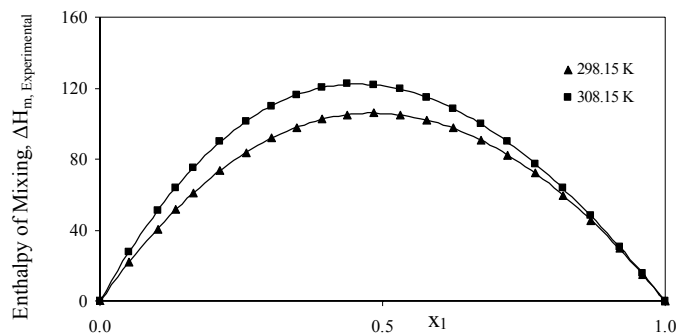
Figure 3: Enthalpy of mixing for Ethyl Acetate (1) - Benzene (2) system.
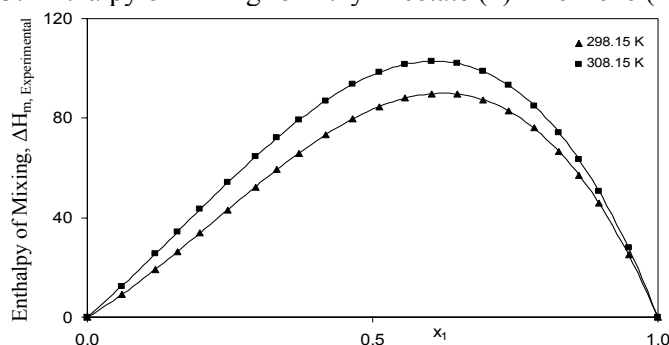

Figure 4: Enthalpy of mixing for Ethyl Acetate (1) - Toluene (2) system.

Table 3: Coefficients of Equation (2) for liquid mixtures

Sl No	Systems	T / K	Coefficients				Percentage Average Absolute Deviation
			A_0	A_1	A_2	A_3	
1	Ethyl Acetate (1) + Benzene (2)	298.15	-0.0768	452.19	-509.54	57.134	0.0896
		308.15	0.0009	574.12	-752.29	178.23	0.0299
2	Ethyl Acetate (1) + Toluene (2)	298.15	0.0942	134.21	264.81	-398.98	0.0973
		308.15	0.1072	195.00	193.90	-388.86	0.0896

Table 4: Experimental and Calculated values of Heat of Vaporization

x_1	T_b / K	T_d / K	$\Delta H^v{}_{,\,Experimental.}$ / J. mol^{-1}	$\Delta H^v{}_{,\,Calculated}$ / J. mol^{-1}	% Deviation
		Ethyl Acetate (1) + Benzene (2)			
0.0000	353.12	353.12	30675.00	30674.55	0.0000
0.0160	353.02	353.04	30674.72	30685.44	-0.0349
0.0270	352.96	352.99	30674.48	30691.80	-0.0565
0.0600	352.78	352.83	30673.55	30709.45	-0.1170
0.1360	352.39	352.48	30670.18	30742.15	-0.2347
0.1600	352.27	352.37	30668.76	30750.24	-0.2657
0.2300	351.95	352.06	30663.70	30767.94	-0.3400
0.3000	351.65	351.76	30657.30	30777.24	-0.3913
0.3590	351.42	351.53	30650.89	30778.91	-0.4177
0.4220	351.19	351.29	30643.06	30774.80	-0.4299
0.4410	351.13	351.22	30640.51	30772.42	-0.4305
0.5280	350.87	350.93	30627.71	30755.20	-0.4163
0.5870	350.71	350.76	30618.02	30737.96	-0.3917
0.6970	350.48	350.50	30597.91	30695.13	-0.3177
0.7740	350.36	350.37	30582.34	30657.84	-0.2469
0.8340	350.29	350.29	30569.39	30625.20	-0.1825
0.8410	350.29	350.29	30567.84	30621.20	-0.1746
0.8570	350.27	350.27	30564.25	30611.94	-0.1560
0.9120	350.24	350.24	30551.56	30578.76	-0.0890
0.9500	350.23	350.24	30542.49	30554.73	-0.0401
1.0000	350.25	350.25	30530.17	30530.17	0.0000

Continuation Table 4

| x_1	T_b / K	T_d / K	ΔH^v, Experimental / J. mol^{-1}	ΔH^v, Calculated / J. mol^{-1}	% Deviation
		Ethyl Acetate (1) + Toluene (2)			
0.0000	383.01	382.97	33872.00	33872.00	0.0000
0.0210	382.58	381.82	33779.58	33959.03	-0.5312
0.0320	382.35	380.87	33732.29	33997.07	-0.7849
0.0480	382.01	379.94	33664.86	34048.01	-1.1381
0.1070	380.69	376.46	33429.06	34192.04	-2.2824
0.1750	379.03	372.80	33179.67	34276.44	-3.3055
0.2700	376.50	368.51	32863.72	34258.71	-4.2448
0.2830	376.14	368.02	32822.88	34244.75	-4.3319
0.3650	373.73	365.09	32575.23	34097.15	-4.6720
0.4520	370.98	362.22	32325.35	33836.32	-4.6743
0.5980	365.97	358.16	31911.91	33189.68	-4.0041
0.6560	363.84	356.55	31742.04	32870.51	-3.5551
0.7150	361.61	355.25	31561.92	32515.01	-3.0197
0.7730	359.34	354.14	31375.01	32138.88	-2.4346
0.8350	356.84	352.91	31161.44	31711.70	-1.7658
0.8910	354.52	351.80	30953.72	31307.19	-1.1419
0.9220	353.21	351.39	30831.80	31076.91	-0.7950
0.9540	351.84	350.81	30700.21	30835.23	-0.4398
0.9700	351.15	350.60	30632.10	30713.06	-0.2643
1.0000	349.94	349.94	30500.00	30500.00	0.0000
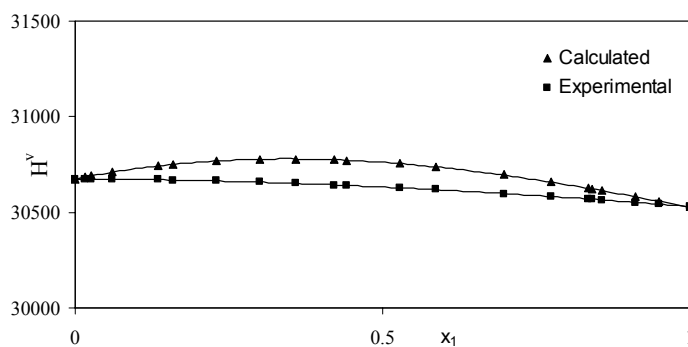
Figure 5: Comparison of experimental and calculated data of Enthalpy of Vaporization for Ethyl Acetate (1) - Benzene (2) system.
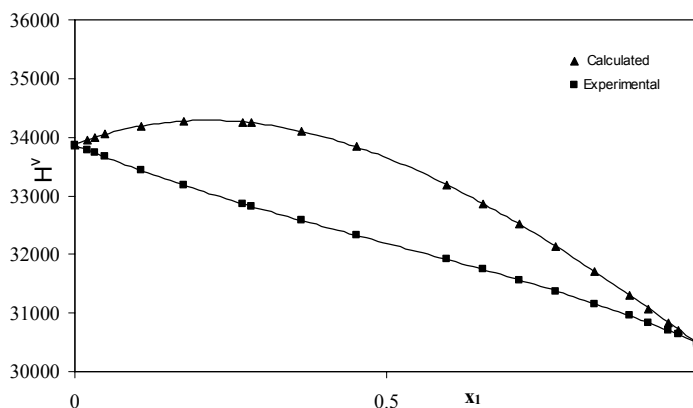

Figure 6: Comparison of experimental and calculated data of Enthalpy of Vaporization for Ethyl Acetate (1) - Toluene (2) system.

CONCLUSIONS

The enthalpy of mixing and heat of vaporization were measured experimentally for the systems Ethyl Acetate with Benzene and Toluene and from the data obtained it can be concluded that the apparatus employed for both determinations can be used for any unknown systems.

ACKNOWLEDGEMENT

The authors thank the management of Siddaganga Institute of Technology – Tumkur - Karnataka - India, for their financial support

NOMENCLATURE

Ai	Constants in enthalpy equation	$J.\,mole^{-1}$
A, B	Constants in density equation	(-)
Cpi	Ideal gas specific heat of pure component	$J.\,mole^{-1}.\,K^{-1}$
E	Potential drop across the heater	milli volts
I	Current	milli amperes
Li	Heat of vaporization of pure component	$J.\,mole^{-1}$
M	Molecular weight	(-)
T	Time	seconds
T_b, T_d	Bubble point and dew point temperatures	K
V	Volume of components	m^3
x	Mole fraction	
ΔH_m	Enthalpy of mixing	$J.\,mole^{-1}$
ΔH^V	Heat of vaporization	$J.\,mole^{-1}$
ρ	Density	$kg.\,m^{-3}$

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