Experimental Investigation of Excess molar enthalpies of binary mixtures formed by ethyl acetate (with Cyclohexane or 1-Butanol or 1-Hexene)

Mahendra V. Guddad[1*], K. L. Shivabasappa[2], Bhausaheb L. Pangarkar[3]

[1&2]Department of Chemical Engineering, Siddaganga Institute of Technology, Tumkur, Karnataka

[2]Sir Visvesvaraya Institute of Technology, Nashik, India

[*]Corresponding Author Email: *mahe_god@rediffmail.com*

Abstract: The excess molar enthalpies of three binary systems of ethyl acetate with + Cyclohexane, + 1-Butanol, 1-Hexene have been measured at T 298.15 K and 308.15 K. The experimental results are correlated with Redlich – Kister equation. The data predicted from Redlich – Kister equation is matched with the experimental results.

Keywords: Excess Molar Enthalpies; Isothermal Calorimeter; Ethyl Acetate

I. INTRODUCTION

The excess molar enthalpies of binary mixtures formed by cyclohexane (with benzene or toluene or methanol) were presented [1]. In this work we continue our studies about the excess thermodynamic properties for binary mixtures of ethyl acetate with + Cyclohexane, + 1-Butanol, 1-Hexene have been measured at two different temperatures T 298.15 K and 308.15 K using an isothermal calorimeter. The experimental results have been fitted with Redlich – Kister equation [2]. The values obtained from standard deviation indicates with good agreement between experimental results and data predicted from polynomial equation. Excess thermodynamic properties are the essential need for the design of separation equipment.

II. EXPERIMENTAL

Van Ness and co-workers (1961) described an apparatus suitable for endothermic systems [3]. Several other calorimeters based on that original design have been reported in the literature [4-7]. Isothermal dilution calorimeters which contain a vapour space have been described [3, 8, 9] used a new isothermal calorimeter with no vapor space. [8] used an isothermal displacement calorimeter similar to the one described by Mrazek and Van Ness [3]. In the present work a static type calorimeter incorporating the design features of [1, 8, 10-12] was designed and used to measure enthalpy of mixing at 298.15 K and 308.15 K. The products used in the present work were purified by the methods suggested by Riddick, J.A and Weissberger, A. [13-14]. The purity was checked by specific gravity, refractive index and vapor phase chromatography.

An Isothermal calorimeter was used to measure excess molar enthalpies H_m^E at 298.15 ± 0.003K and 308.15 K. Details of the equipment and its operating procedure for binary system have been described previously [11,15]. Over most of the mole-fraction range, the errors of the excess molar enthalpies are estimated to be less than 0.5%.

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 110^0C with 0.1^0C 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 can 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.

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

III. RESULTS AND DISCUSSION

Excess molar enthalpies H_m^E for three binary system ethyl acetate with + Cyclohexane, + 1-Butanol, 1-Hexene have been measured at T 298.15 K and 308.15 K using an isothermal calorimeter. The experimental results of binary excess enthalpies are listed in table 1 at T 298.15 K and table 2 at T 308.15 K and shown in Figures 1-3. The experimental excess enthalpy depends on composition of the binary system were fitted to the Redlich-Kister polynomial by the method of unweighted least-squares:

Table 1: Experimental excess molar enthalpies $H_{m,12}^E$ (J mol^{-1}) at 298.15K for the binary mixtures ethyl acetate (1) + Cyclohexane (2), ethyl acetate (1) + 1-Butanol (2), ethyl acetate (1) + 1-Hexen

x_1	$H_{m,12}^E$	x_1	$H_{m,12}^E$	x_1	$H_{m,12}^E$
x_1 $(C_4H_8O_2)$ + $(1-x_1)$ C_6H_{12}					
0.05	287	0.4	1235	0.75	927
0.1	640	0.45	1206	0.8	782
0.15	786	0.505	1152	0.85	647
0.2	936	0.55	1117	0.9	510
0.25	1073	0.6	1035	0.95	364
0.3	1126	0.65	985		
0.35	1186	0.7	945		

Table 1: Continue next page

x_1 ($C_4H_8O_2$) + (1- x_1) $C_4H_{10}O$					
0.05	315	0.4	1538	0.75	1248
0.1	578	0.45	1614	0.8	1072
0.15	730	0.505	1625	0.85	856
0.2	1156	0.55	1619	0.9	668
0.25	1272	0.6	1603	0.95	384
0.3	1384	0.65	1562		
0.35	1493	0.7	1464		
x_1 ($C_4H_8O_2$) + (1- x_1) C_6H_{12}					
0.05	243.25	0.4	793.15	0.75	623.42
0.1	375.32	0.45	827.34	0.8	556.12
0.15	437.63	0.505	821.36	0.85	472.83
0.2	536.24	0.55	817.56	0.9	363.81
0.25	618.56	0.6	788.23	0.95	219.54
0.3	726.42	0.65	747.35		
0.35	753.82	0.7	683.45		

Table 2: Experimental excess molar enthalpies $H^E_{m,12}$ (J mol^{-1}) at 308.15K for the binary mixtures ethyl acetate (1) + Cyclohexane (2), ethyl acetate (1) + 1-Butanol (2), ethyl acetate (1) + 1-Hexene (2)

x_1	$H^E_{m,12}$	x_1	$H^E_{m,12}$	x_1	$H^E_{m,12}$
x_1 ($C_4H_8O_2$) + (1-x_1) C_6H_{12}					
0.05	356	0.4	1436	0.75	1036
0.1	726	0.45	1395	0.8	872
0.15	905	0.505	1312	0.85	730
0.2	1084	0.55	1268	0.9	584
0.25	1243	0.6	1178	0.95	435
0.3	1304	0.65	1120		
0.35	1372	0.7	1068		
x_1 ($C_4H_8O_2$) + (1- x_1) $C_4H_{10}O$					
0.05	356	0.4	1613	0.75	1291
0.1	628	0.45	1686	0.8	1112
0.15	783	0.505	1698	0.85	893
0.2	1215	0.55	1687	0.9	704
0.25	1332	0.6	1661	0.95	417
0.3	1446	0.65	1615		
0.35	1560	0.7	1512		
x_1 ($C_4H_8O_2$) + (1- x_1) C_6H_{12}					
0.05	156.45	0.4	753.21	0.75	614.74
0.1	263.56	0.45	806.45	0.8	548.32
0.15	323.45	0.505	803.24	0.85	461.02
0.2	445.36	0.55	806.32	0.9	354.25

Table 2: Continue next page

0.25	543.26	0.6	775.56	0.95	212.46
0.3	657.63	0.65	732.56		
0.35	681.23	0.7	672.56		

$$H^E_{m,12}\, Jmal^{-1} = \sum_{k=1}^{n} h_k\, (1-2x_1)^{k-1} \qquad (1)$$

The coefficient h_k of Eq. (1) and the standard deviation σ of Eq. (2) calculated for the three constituent binary mixtures are tabulated in Table 3.

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n}\left(H^E_{exp,i} - H^E_{cal,i}\right)^2}{n}} \qquad (2)$$

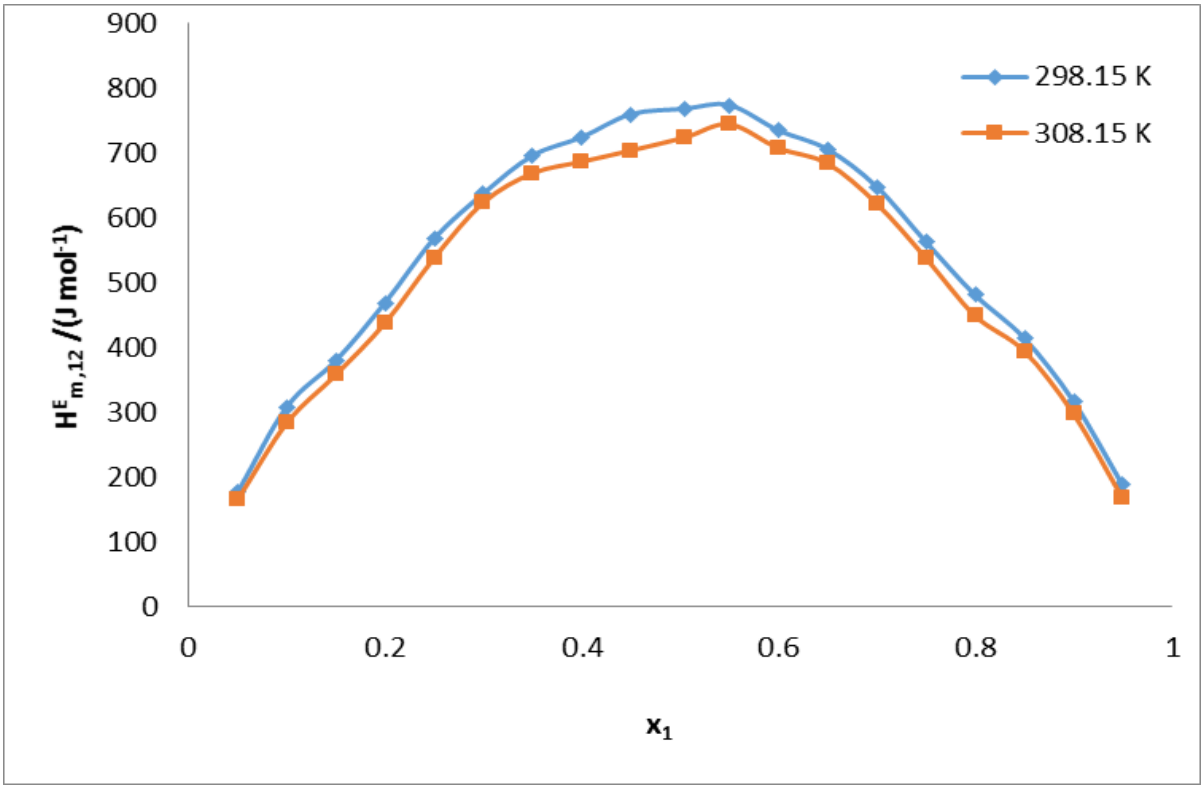

Figure 1: Enthalpy of mixing for ethyl acetate (1) + Cyclohexane (2) system.

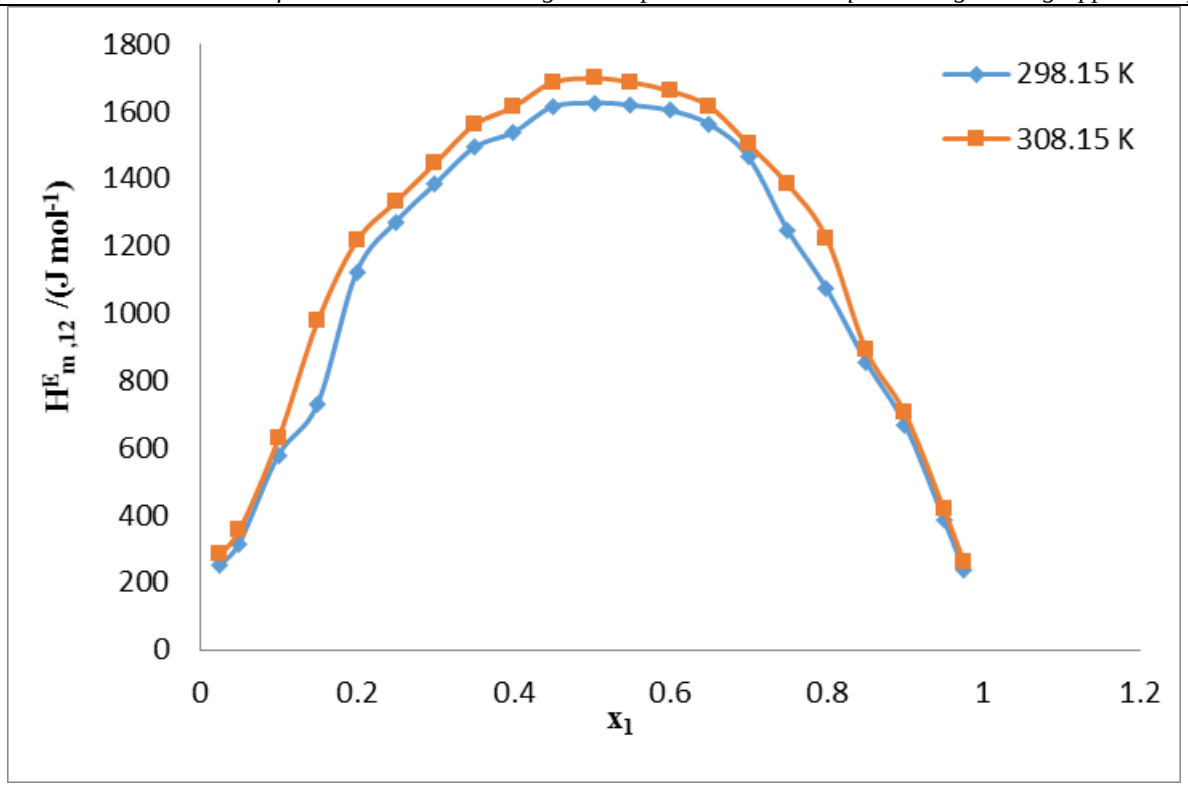

Figure 2: Enthalpy of mixing for ethyl acetate (1) + 1-Butanol (2) system.

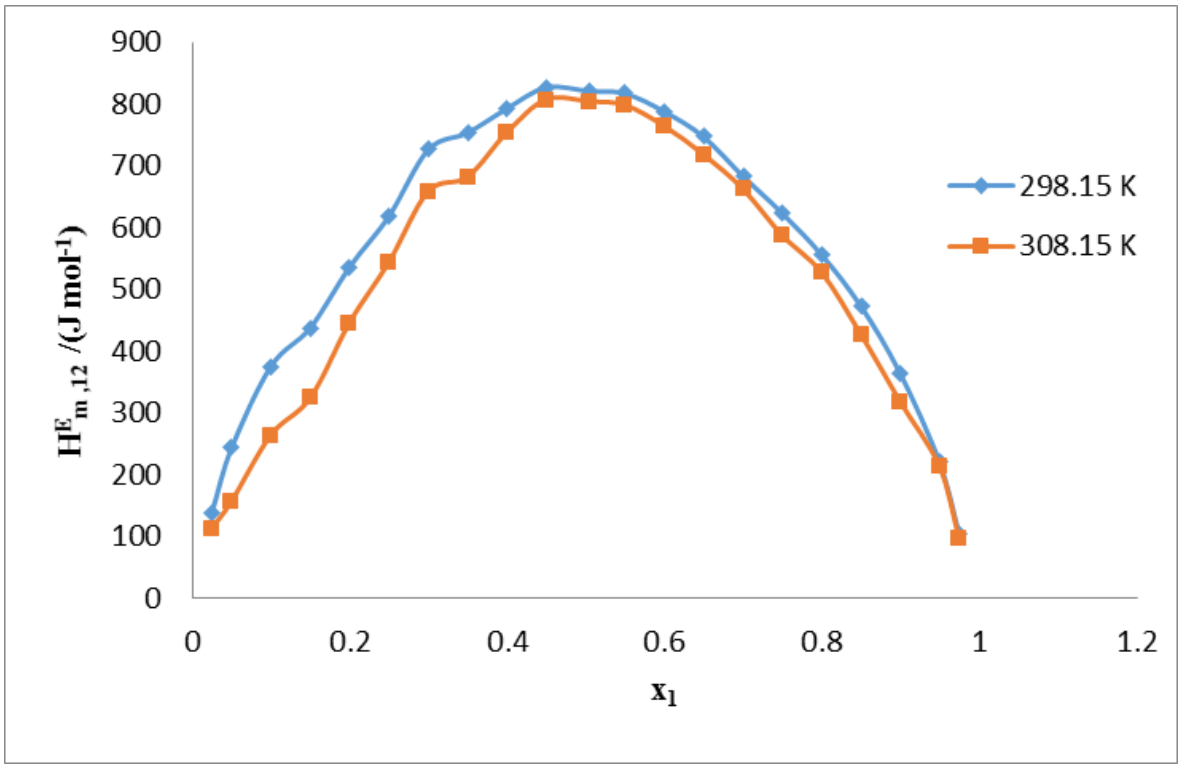

Figure 3: Enthalpy of mixing for ethyl acetate (1) + 1-Hexene (2) system.

Table 3: Parameters h_k and standard deviations σ for the representation of $H^E_{m,12}$ at 298.15K and 308.15 K by Eq. (1)

T /K	System (1+2)	h_1	h_2	h_3	h_4	h_5	σ /J mol^{-1}
298.15	ethyl acetate (1) + cyclohexane (2)	4743	-2253	359.6	3680	3441	0.41
308.15	ethyl acetate (1) + cyclohexane (2)	5460	-2677	-90.97	4126	4858	0.43
298.15	ethyl acetate (1) + 1-butanol (2)	6710	-42.33	-1075	964	2229	0.53
308.15	ethyl acetate (1) + 1-butanol (2)	6831	-157.1	1290	867	118.1	0.46
298.15	ethyl acetate (1) + 1-hexene (2)	3340	-139.3	-1136	381	3678	0.47
308.15	ethyl acetate (1) + 1-hexene (2)	3273	-107.6	-2107	-641.6	3413	0.38

IV. CONCLUSIONS

The experimental determination of excess molar enthalpy values for three binaries at 298.15K and 308.15K has been performed by means of isothermal calorimeter. The heats of mixing values for binary systems studied are endothermic in nature and over most of the composition range, the errors of the excess molar enthalpies 5 %.

Conflict of interest: The authors declare that they have no conflict of interest.

Ethical statement: The authors declare that they have followed ethical responsibilities

REFERENCES

[1]. Mahendra Guddad, K. L. Shivabasappa, Bhausaheb L. Pangarkar, International Journal of Engineering Research and Technology, ISSN 0974-3154 Volume 10, Number 1, 285-288, 2017.
[2]. Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. Ind. Eng. Chem., 40, 345-348, 1948.
[3]. R. V. Mrazek and H. C. Van Ness, Amer. Inst. Chem. Engineers J. 7, 190, 1961.
[4]. D. R. Winterhalter and H. C. Van Ness, J. Chem. and Eng. Dara, 11, 189, 1966.
[5]. C. G. Savini, D. R. Winterhalter, L. H. Kovach, and H. C. Van Ness, J. Chem. and Eng. Data, 11, 40, 1966.
[6]. R. H. Stokes, K. N. Marsh, and R. P. Tomlins, J. Chem. Thermodynamics, I, 211, 1969.
[7]. B. Murakami and G. C. Benson, J. Chem. Thermodynamics, 1, 559, 1969.
[8]. R. Tanaka, S. Murakami, and R. Fujishiro, Bull. Chem. SOC. Japan, 45, 2107, 1972.
[9]. J. J. Christensen, J. W. Gardner, D. J. Eatough, R. M. Izatt, P. J. Watts, and R. M. Hart, Rev. Sci. Instr, 44, 481,1973.
[10]. Patel, H.R., Ph.D. Thesis, Department of Chemical Engineering, Indian Institute of Science, Bangalore, India, 1974.
[11]. Rao Y.J., and Viswanath D. S, J.Chem .Eng. Data, 18, 49, 1973.
[12]. Nirguna Babu. P, Ph.D. Thesis, Department of Chemical Engineering, Siddaganga Institute of Technology, Tumkur – 572103 – India, 2003.
[13]. Riddick, J.A., Bunger, W. S., Techniques of Chemistry, Organic Solvents, Vol. II, 3e, Wiley-Interscience, NY, 1970.
[14]. Weissberger, A., Editor, Techniques of Organic Chemistry, Vol I, Interscience, NY, 1949.
[15]. K. L. Shivabasappa, P. Nirguna Babu and Y. Jagannadha Rao, Braz. J. of Chem. Eng., 25, 167, 2008.

This volume is dedicated to Late Sh. Ram Singh Phanden, father of Dr. Rakesh Kumar Phanden.

