

Experimental Investigation of Excess molar enthalpies of binary mixtures formed by cyclohexane with (benzene or toluene or methanol)

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Abstract

The experimental excess enthalpy data are useful in the design of separation equipments. From the various designs available for the experimental determination of enthalpy of mixing, the apparatus was selected, modified and constructed. The apparatus of enthalpy of mixing was tested with a known system and the data obtained was in very good agreement with literature values. The excess molar enthalpies are reported for three binary systems formed by mixing cyclohexane with +benzene, + toluene, methanol have been measured at T 298.15 K and 308.15 K using an isothermal calorimeter. The experimental results are correlated with polynomial equations.

Keywords: Excess molar enthalpies; isothermal calorimeter; cyclohexane

Introduction

This work continues our studies about the excess thermodynamic properties for binary mixtures. Excess enthalpy data for the mixtures composed of organic compounds are essential both in theory and practice. Researches on these thermodynamic properties are useful in the design of separation and it provides full understanding of the liquid mixture behaviour. Heat of mixing of mixtures over the whole composition range are useful for a full understanding of their thermodynamic and transport properties, as well as for practical chemical engineering purposes. Enthalpy effects on mixing of liquids are quite large and of considerable importance especially for the design of absorption and distillation columns [1].

Experimental

Van Ness and co-workers (1961) described an apparatus suitable for endothermic systems [2]. A number of other calorimeters based on that original design have been reported in the literature [3-6]. Isothermal dilution calorimeters which contain a vapour space have been described [2,7,8] used a new isothermal calorimeter with no vapor space. [7] used an isothermal displacement calorimeter similar to the one described by Mrazek and Van Ness [2]. In the present work a static type calorimeter incorporating the design features of

[1,7,9-11] 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. [12-13]. 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 ± 0.003 K and 308.15 K. Details of the equipment and its operating procedure for binary system have been described previously [1]. 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°C with 0.1°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.

Results and discussion

Excess molar enthalpies H_m^E for three binary system cyclohexane (1) + benzene (2), cyclohexane (1) + toluene (2), cyclohexane (1) + methanol (2) have been measured at T

298.15 K and 308.15 K using an isothermal calorimeter. 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 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 un weighted least-squares.

Table 1 Experimental excess molar enthalpies $H_{m,12}^E$ (J mol⁻¹) at 298.15K for the binary mixtures cyclohexane (1) + benzene (2), cyclohexane (1) + toluene (2), cyclohexane (1) + methanol (2)

x_1	$H_{m,12}^E$	x_1	$H_{m,12}^E$	x_1	$H_{m,12}^E$
$x_1 (C_6H_{12}) + (1-x_1) C_6H_6$					
0.05	165.25	0.4	703.47	0.75	547.46
0.1	283.48	0.45	726.57	0.8	467.81
0.15	357.93	0.505	742.28	0.85	394.23
0.2	437.73	0.55	754.67	0.9	297.64
0.25	538.12	0.6	723.15	0.95	167.62
0.3	623.34	0.65	694.23		
0.35	668.36	0.7	634.61		
$x_1 (C_6H_{12}) + (1-x_1) CH_3OH$					
0.05	173.64	0.4	437.73	0.75	475.64
0.1	286.34	0.45	442.56	0.8	457.84
0.15	367.45	0.505	453.78	0.85	436.25
0.2	393.78	0.55	448.73	0.9	346.25
0.25	408.67	0.6	464.67	0.95	273.45
0.3	423.17	0.65	473.56	0.975	183.64
0.35	428.97	0.7	498.13		
$x_1 (C_6H_{12}) + (1-x_1) C_6H_5CH_3$					
0.05	37.86	0.4	145.67	0.75	108.96
0.1	53.67	0.45	147.35	0.8	93.67
0.15	71.62	0.505	152.72	0.85	80.42
0.2	98.56	0.55	150.68	0.9	63.46
0.25	115.67	0.6	139.67	0.95	46.32
0.3	123.61	0.65	125.53	0.975	36.28
0.35	138.23	0.7	116.2		

$$H_{m,12}^E / J mol^{-1} = \sum_{k=1}^n h_k (1 - 2x_1)^{k-1} \quad (1)$$

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.

$$\sigma = \sqrt{\frac{\sum_{i=1}^n (H_{exp,i}^E - H_{cal,i}^E)^2}{n}} \quad (2)$$

Table 2 Experimental excess molar enthalpies $H_{m,12}^E$ (J mol⁻¹) at 308.15K for the binary mixtures cyclohexane (1) + benzene (2), cyclohexane (1) + toluene (2), cyclohexane (1) + methanol (2)

x_1	$H_{m,12}^E$	x_1	$H_{m,12}^E$	x_1	$H_{m,12}^E$
$x_1 (C_6H_{12}) + (1-x_1) C_6H_6$					
0.05	165.25	0.4	686.16	0.75	537.62
0.1	283.48	0.45	703.45	0.8	448.61
0.15	357.93	0.505	723.64	0.85	394.23
0.2	437.73	0.55	743.81	0.9	297.64
0.25	538.12	0.6	707.12	0.95	167.62
0.3	623.34	0.65	683.42		
0.35	668.36	0.7	621.57		
$x_1 (C_6H_{12}) + (1-x_1) CH_3OH$					
0.05	162.14	0.4	411.23	0.75	447.84
0.1	220.54	0.45	418.24	0.8	426.51
0.15	343.16	0.505	425.42	0.85	407.56
0.2	373.96	0.55	431.12	0.9	283.86
0.25	371.14	0.6	440.37	0.95	218.94
0.3	387.46	0.65	450.46	0.975	143.84
0.35	401.35	0.7	464.25		
$x_1 (C_6H_{12}) + (1-x_1) C_6H_5CH_3$					
0.05	36.43	0.4	128.76	0.75	94.35
0.1	51.36	0.45	135.42	0.8	81.46
0.15	68.12	0.505	142.34	0.85	67.32
0.2	84.65	0.55	131.64	0.9	48.34
0.25	96.78	0.6	123.43	0.95	34.62
0.3	106.45	0.65	114.42	0.975	30.46
0.35	118.56	0.7	105.34		

Conclusion

The experimental determination of excess molar enthalpy values for three binary 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 the most of the composition range, the errors of the excess molar enthalpies 5 %.

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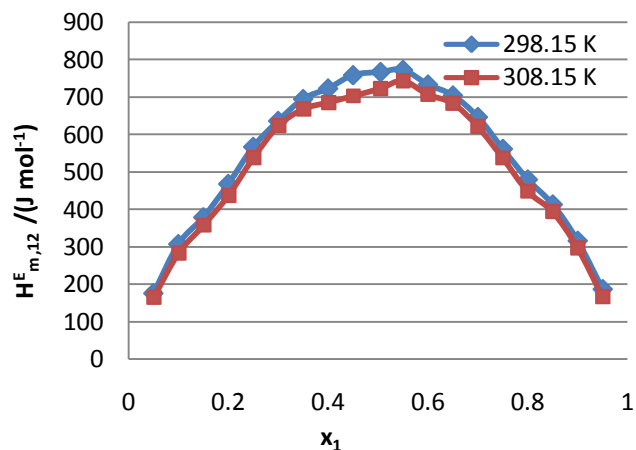


Figure 1: Enthalpy of mixing for cyclohexane (1) - Benzene (2) system

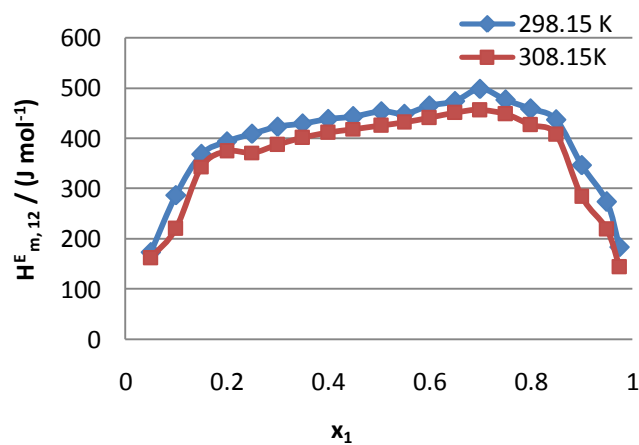


Figure 2: Enthalpy of mixing for cyclohexane (1) - Toluene (2) system.

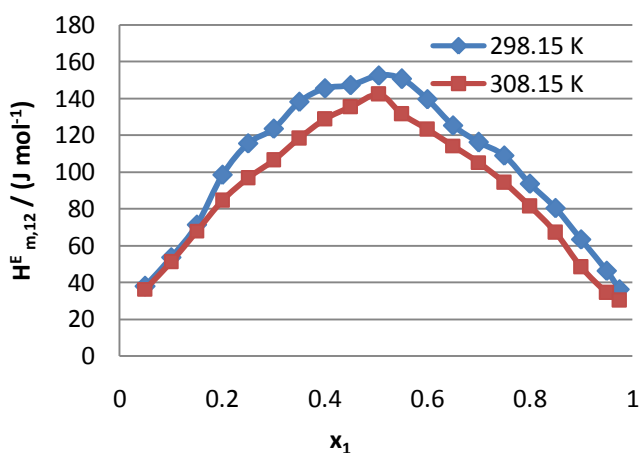


Figure 3: Enthalpy of mixing for cyclohexane (1) – methanol (2) system.

Table 3 Parameters h_k and standard deviations σ for the representation of $H_{m,12}^E$ 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	$\sigma / J mol^{-1}$
298.15	(Cyclohexane + benzene)	3105.219	-39.0518	-965.185	-107.845	2205.068	0.34
308.15	(Cyclohexane + benzene)	3015.72	-149.056	-869.524	55.07913	1684.273	0.54
298.15	(Cyclohexane + Toluene)	1812.289	-210.699	1655.016	-595.166	2120.399	0.48
308.15	(Cyclohexane + Toluene)	1699.904	-305.24	1852.081	-258.249	801.9138	0.52
298.15	(Cyclohexane + methanol)	585.0825	104.7014	84.06362	-297.084		0.211
308.15	(Cyclohexane + methanol)	524.325	38.20897	27.25812	-76.2953		0.21

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