Experimental study on the calorimetric data of cyclohexanol with alkanols (C₁–C₄) and correlation with the Wilson, NRTL and UNIQUAC models at T = 300 K

Hosseinali Zarei [*], Elahe Parvini, Mahboobe Behroozi

Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran

A B S T R A C T

Excess molar enthalpies, H_m^E for the binary mixtures of cyclohexanol with methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol and butan-2-ol have been calculated from calorimetric data at T = 300 K and atmospheric pressure. Calorimetric measurements were performed with a Parr 1455 solution calorimeter. All the binary mixtures show endothermic behaviour over the entire range of compositions. The H_m^E values become more positive with increasing the steric factors. With increasing the chain length of the alkanols, the H_m^E values become less positive. The maximum H_m^E values were observed about 0.4–0.6 mole fraction of cyclohexanol. The results were interpreted on the basis of the polarity, size and shape of alkanols. The experimental data were correlated by the Redlich–Kister equation and three thermodynamics models (Wilson, NRTL and UNIQUAC).

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1. Introduction

Non-ideal mixtures are very interesting from the thermodynamic point of view due to their peculiar behaviour. Excess thermodynamic properties such as excess molar enthalpy, H_m^E, provide useful information about structure and molecular interactions of the components in mixtures. The H_m^E data can be used for the evolution of thermodynamic models for describing the behaviour of solutions [1–6]. Binary mixtures of associated hydroxyl compounds can be provided for the above purposes. Furthermore, these compounds are very important in chemical, physical, and biological processes because of their ability to form hydrogen bonds [7].

Binary mixtures of two alcohols show small deviations from ideal behaviour. A number of studies have been performed on the excess molar enthalpy, H_m^E, of binary mixtures of two linear alcohols [8–15]. A literature survey shows that very few reports have been reported on H_m^E data of binary mixture of cyclic alcohols with linear alcohols [2]. Cyclic and linear alcohols are associated through the hydrogen bond in the pure state as well as in mixtures. The degree of association in alkanols containing cyclic alkyl group is very low due to steric factors [16]. In this study, excess molar enthalpy, H_m^E, have been calculated for {cyclohexanol + alkanols (C₁–C₄)} from calorimetric measurements at T = 300 K. The experimental H_m^E data were correlated with Redlich–Kister equation. The data have also been analyzed in terms of three thermodynamic models (Wilson, NRTL and UNIQUAC).

2. Experimental

2.1. Materials

All pure components were purchased from Merck. Purity grade, densities and refractive indices of the chemical substances are reported in table 1 [17–23]. Also, the corresponding literature values of the chemicals are given in table 1. The agreement between the experimental and literature values is good. Just before the measurements, all the pure substances were degassed with a bath ultrasonic cleaner.

2.2. Apparatus and procedure

Binary mixtures were prepared by weighing the components with an electronic balance (AB 204-N Mettler) precise to $\pm 1 \cdot 10^{-7}$ kg. The uncertainty of the mole fraction was less than $\pm 1 \cdot 10^{-4}$. The values of density of pure components and their binary mixtures were determined using an Anton Paar digital vibrating u-tube densimeter (model DMA 4500) with an accuracy of $\pm 5 \cdot 10^{-2}$ kg · m^{-3} whose cell temperature was controlled within ± 0.01 K, with a solid-state thermostat. Calibration of the instrument was performed by double distilled water and dry air at the beginning of each series of measurements. An Abbé refractometer (model DR-A1) with an uncertainty of ± 0.0002 was applied for refractive index n_D, measurements for pure components. The uncertainty of the temperature measurement was ± 0.1 K.

Calorimetric measurements were carried out by a Parr 1455 solution calorimeter in an isolated room at T = 300 K and

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TABLE 1
Purity grade, density ρ, and refractive index n_D^{25}, of pure components at T = 303.15 K and UNIQUAC structural parameters q_i.

Component	Mass fraction purity	$\rho \cdot 10^{-3}/\text{kg} \cdot \text{m}^{-3}$		n_D^{25}		q_i
		Exp.	Lit.	Exp.	Lit.	
Cyclohexanol	0.99	0.94136	0.94152[a]	1.4632	1.46477[b]	3.512[h]
Methanol	0.998	0.78187	0.78185[b]	1.3255	1.32652[b]	1.432[i]
Ethanol	0.998	0.78082	0.78069[c]	1.3580	1.35941[b]	1.972[i]
Propan-1-ol	0.998	0.79553	0.79548[d]	1.3821	1.3837[b]	2.512[i]
Propan-2-ol	0.995	0.77671	0.77666[e]	1.3741	1.3752[b]	2.508[i]
Butan-1-ol	0.998	0.80198	0.80192[f]	1.3962	1.39479[b]	3.052[i]
Butan-2-ol	0.99	0.79858	0.79866[e]	1.3940	1.39488[g]	3.048[i]

[a] Reference [17].
[b] Reference [18].
[c] Reference [19].
[d] Reference [20].
[e] Reference [21].
[f] Reference [22].
[g] Reference [23].
[h] Reference [30].
[i] Reference [31].

TABLE 2
Excess molar enthalpy H_m^E, for the binary mixtures of (cyclohexanol + alkanols) at T = 300 K.

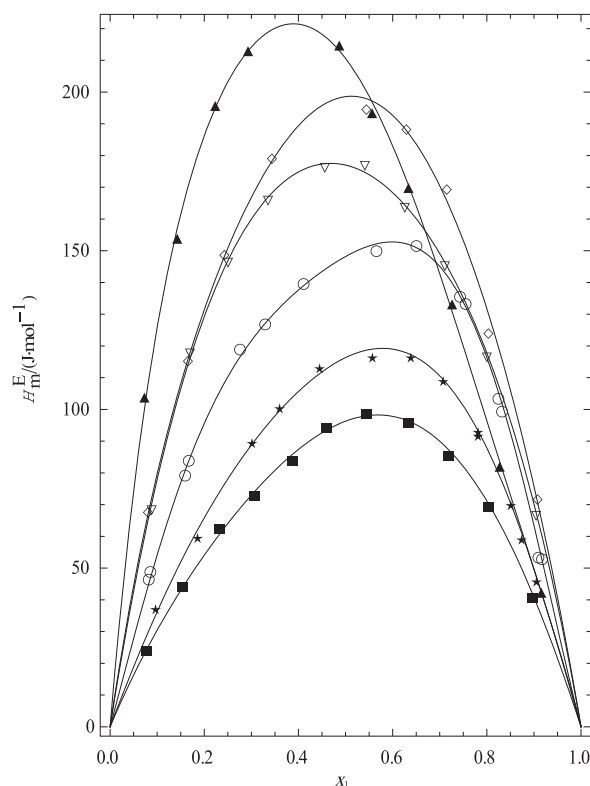| x_1	$H^E/(\text{J} \cdot \text{mol}^{-1})$	x_1	$H^E/(\text{J} \cdot \text{mol}^{-1})$
{cyclohexanol(1) + methanol(2)}			
0.0742	104.1	0.5587	193.8
0.1422	153.9	0.6333	170.0
0.2234	196.0	0.7266	133.2
0.2948	213.5	0.8274	82.2
0.4871	214.9	0.9162	42.4
{cyclohexanol(1) + propan-1-ol(2)}			
0.0808	24.4	0.5470	98.9
0.1568	44.5	0.6359	96.4
0.2326	63.1	0.7223	85.9
0.3085	73.1	0.8063	69.6
0.3888	84.3	0.9010	40.9
0.4614	94.6		
{cyclohexanol(1) + butan-1-ol(2)}			
0.0976	37.4	0.7119	109.1
0.1867	59.9	0.7842	92.2
0.3025	89.5	0.7850	93.5
0.3622	100.7	0.8549	70.5
0.4484	113.3	0.8747	59.1
0.5609	116.8	0.9059	46.2
0.6402	116.8		
{cyclohexanol(1) + ethanol(2)}			
0.0883	68.6	0.5436	177.2
0.1688	118.2	0.6255	163.7
0.2501	146.8	0.7119	145.4
0.3370	165.9	0.8026	116.9
0.4560	176.4	0.9062	67.1
{cyclohexanol(1) + propan-2-ol(2)}			
0.0817	67.8	0.6326	188.7
0.1653	115.5	0.7173	169.4
0.2454	149.1	0.8036	124.5
0.3436	179.3	0.9097	72.1
0.5462	194.9		
{cyclohexanol(1) + butan-2-ol(2)}			
0.0831	46.8	0.6512	151.7
0.0874	48.9	0.7441	135.8
0.1613	79.3	0.7557	133.6
0.1704	84.1	0.8271	103.5
0.2787	118.9	0.8352	99.7
0.3304	127.3	0.9129	53.5
0.4131	139.8	0.9201	53.1
0.5657	150.2		

FIGURE 1. Plot of excess molar enthalpy against mole fraction for the following binary mixtures at T = 300 K: {cyclohexanol(1) + alkanols(2)}, ▲, methanol; ▽, ethanol; ■, propan-1-ol; ◇, propan-2-ol; ✳, butan-1-0l; ○, butan-2-ol. The solid lines represent the values calculated from the Redlich–Kister equation.

cibility of the components was tested before the measurements. Components in each system were miscible completely over the entire composition range. More details of the procedures and apparatus have been explained previously [24,25].

3. Results and discussion

The experimental H_m^E values for six binary mixtures of cyclohexanol with alkanols (C$_1$–C$_4$) were calculated from calorimetric data

atmospheric pressure. The temperature in the calorimetric measurements can be read to an uncertainty ±0.002 K. The uncertainty of the H_m^E values was estimated to be ±1 · 10^{-2} J · mol^{-1}. The mis-