

Excess enthalpies for mixtures of cyclohexanone with isomeric propanols and butanols at 298·15 K

A KRISHNAIAH*, K N SURENDRANATH and
M RAMAKRISHNA

Chemical Laboratories, Sri Venkateswara University College of Engineering,
Tirupati 517 502, India

* Chemical Engineering Division, Regional Research Laboratories, Hyderabad 500 009,
India.

MS received 6 November 1987; revised 27 February 1988

Abstract. Excess enthalpies (H^E) for mixtures of cyclohexanone with propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol and 2-methyl propan-1-ol at 298·15 K have been measured over the entire composition range. All mixed endothermically with the maximum values of H^E occurring at equimole fraction. Comments about the molecular interactions contributing to the excess enthalpies of a cyclic ketone + an alcohol are made on the basis of these results.

Keywords. Calorimeter; excess enthalpy; cyclohexanone; propanol; butanol; hydrogen bonding.

1. Introduction

The thermodynamic properties of binaries containing polar and self-associated components exhibit significant deviations from ideality, arising not only from differences in size and shape but also from the possible hydrogen bonding interaction between unlike molecules. Molecular interactions between cyclohexanone (a polar component) and an aliphatic alcohol (associated in the pure state) were reported in terms of dielectric (Shanmugasundaram and Mohan 1980, 1982), ultraviolet (Shanmugasundaram and Mohan 1983) and IR (Waclawck Witold 1978) absorption studies. Excess volumes of cyclohexanone with *n*-alcohols (C₃–C₆) were reported by Rao and Naidu (1976). A search of the literature indicated that no attempt had been made to study the molecular interactions in mixtures containing cyclohexanone and aliphatic alcohols in terms of excess enthalpy data. Hence, we report here new experimental data on H^E for systems of cyclohexanone + propan-1-ol, + propan-2-ol, + butan-1-ol, + butan-2-ol and 2-methyl propan-1-ol at 298·15 K.

* For Correspondence

2. Experimental

2.1 Calorimeter

A Parr 1451 solution calorimeter was used for the present studies. The calorimeter, shown in figure 1, consists of a glass dewar mixing chamber with a rotating sample cell, a thermister probe and a specially designed temperature measuring bridge all assembled in a compact cabinet. Temperature changes can be plotted directly in Kelvin using a strip chart recorder and can be read to an accuracy of 0.001 K.

The two-piece cell which serves both as a sample holder and agitator consists of a bell which is closed with a detachable teflon dish. Liquid samples can be added to the cell from a pipette inserted through the top stem. Excellent thermal insulation is provided by a fully silvered glass dewar which serves as a mixing chamber. From 90 to 120 ml of solution can be taken in this vessel. Temperature measurements in this calorimeter are taken with a glass-sheathed thermister probe combined with a special bridge in a system designed for linear response over the range from 298.15 K to 303.15 K. Within this temperature range each 100 microvolt change in output from the bridge represents a temperature change of exactly 0.001 K. By connecting the output of the bridge to a strip chart recorder, the temperature change can be measured within an accuracy of 1%. Thus the experimental error of excess molar enthalpies H_m^E is estimated to be around 1% over the mole fraction range studied.

The operating principle of this calorimeter is very simple. The components are combined in the dewar mixing chamber and the resulting temperature change is measured with the thermister bridge. At the start of the experiment one of the

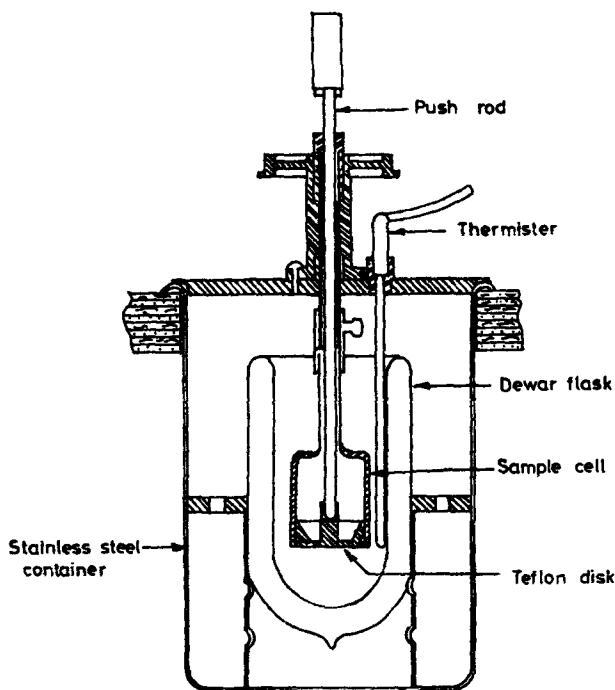


Figure 1. A schematic diagram of the calorimeter.

liquids is held in a sealed-glass rotating cell in thermal contact with the other component. When the system comes to thermal equilibrium, the contents of the rotating cell are mixed with surrounding liquid. The temperature changes due to the mixing process is sensed by the thermister and recorded on the strip chart recorder. The excess molar enthalpy, H_m^E is then calculated knowing the energy equivalent of the system by following equation.

$$H_m^E = (W_1 C_{P1} + W_2 C_{P2} + E) \Delta t/n, \quad (1)$$

where

W_i = weight of liquid i (gm), C_{P_i} = heat capacity of liquid i (joules/gm-K), E = energy equivalent of calorimeter (joules/K), (76.65 J.K^{-1}), Δt = temperature change (K), n = number of moles of mixtures.

The reliability of the apparatus and of the method is established by measuring excess enthalpies of a standard system, cyclohexane + n -hexane, throughout the concentration range at 298.15 K. Our results are in agreement with those obtained by the standard equation (Stokes and Marsh 1972). The data are given in table 1.

2.2 Materials

All the chemicals used in this work were purified by the standard methods described in the literature (Riddick and Bunger 1970). Cyclohexanone (BDH) was dried over anhydrous sodium sulphate for two days and fractionally distilled. Alcohols were dried by refluxing with fused calcium oxide and fractionally distilled. The purity of the samples was checked by comparing the measured densities and boiling points of the purified samples with those reported in the literature (Riddick and Bunger 1970; Timmermans 1965).

3. Results and discussion

Values of the molar excess enthalpies, H^E are given in table 2 for cyclohexanone + propan-1-ol, + propan-2-ol, + butan-1-ol, + butan-2-ol

Table 1. Calculated (Stokes–March equation) and experimental enthalpies for the system, cyclohexane (1) + n -hexane (2) at 298.15 K

x_1	H_{calc}^E (J mol ⁻¹)	H_{expt}^E (J mol ⁻¹)
0.0864	55.9	55.3
0.1435	89.2	88.3
0.2124	125.3	126.9
0.2578	146.3	148.1
0.3453	180.2	178.6
0.4037	197.7	199.8
0.5562	221.0	223.4
0.6199	219.6	217.4
0.6635	214.2	216.5
0.7495	191.3	188.8
0.8539	137.5	139.2
0.9463	60.4	59.8

Table 2. Excess enthalpies of cyclohexanone with alcohols at 298.15 K. x is the mole fraction of cyclohexanone.

x	H^E (J/mol)	x	H^E (J/mol)
<i>Cyclohexanone + propan-1-ol</i>			
0.0673	396.6	0.5025	1226.4
0.1258	631.5	0.6250	1180.4
0.1955	857.7	0.7083	1067.6
0.2575	1011.3	0.7842	902.0
0.3304	1147.7	0.8794	575.2
0.3869	1214.5	0.9397	297.9
<i>Cyclohexanone + propan-2-ol</i>			
0.0843	528.8	0.5587	1400.3
0.1504	829.3	0.6078	1361.3
0.2122	1038.0	0.6674	1264.6
0.2669	1173.4	0.7404	1111.6
0.3404	1306.9	0.8427	760.6
0.4028	1386.9	0.9413	307.2
<i>Cyclohexanone + butan-1-ol</i>			
0.0850	434.4	0.5389	1281.9
0.1560	713.0	0.5978	1267.4
0.2246	928.4	0.6740	1200.4
0.2829	1066.8	0.7451	1075.9
0.3448	1185.5	0.8199	823.0
0.4015	1262.0	0.9204	383.1
<i>Cyclohexanone + butan-2-ol</i>			
0.0711	375.5	0.5267	1400.4
0.1511	726.3	0.5802	1381.5
0.2303	989.8	0.7061	1219.8
0.2959	1145.7	0.7772	1045.3
0.3654	1278.4	0.8493	797.1
0.4186	1343.7	0.9179	482.8
<i>Cyclohexanone + 2-methyl propan-1-ol</i>			
0.0573	234.5	0.5160	1104.7
0.1091	451.3	0.6433	1085.2
0.1958	748.7	0.7216	973.8
0.2647	911.5	0.7696	869.6
0.3286	1035.6	0.8457	657.9
0.3886	1124.2	0.9247	389.2

and + 2-methyl propan-1-ol at 298.15 K and graphically represented in figure 2. The results for each mixture were fitted with the smoothing function

$$H^E/J \text{ mol}^{-1} = x(1-x) \sum_{i=0}^3 h_i (2x-1)^i \quad (2)$$

by the method of least-squares with each point weighted equally. x represents the mole fraction of cyclohexanone. Values of the coefficients h_i and the percentage of standard deviation, $\% \sigma(H^E)$ representing the fit of each set of results are given in table 3. For all the mixtures, the excess enthalpies at 298.15 K are positive and the H^E vs. mole fraction curves are symmetrical.

The excess enthalpies are influenced by two opposing effects: (1) absorption of heat due to depolymerization of self-associated alcohols by cyclohexanone and

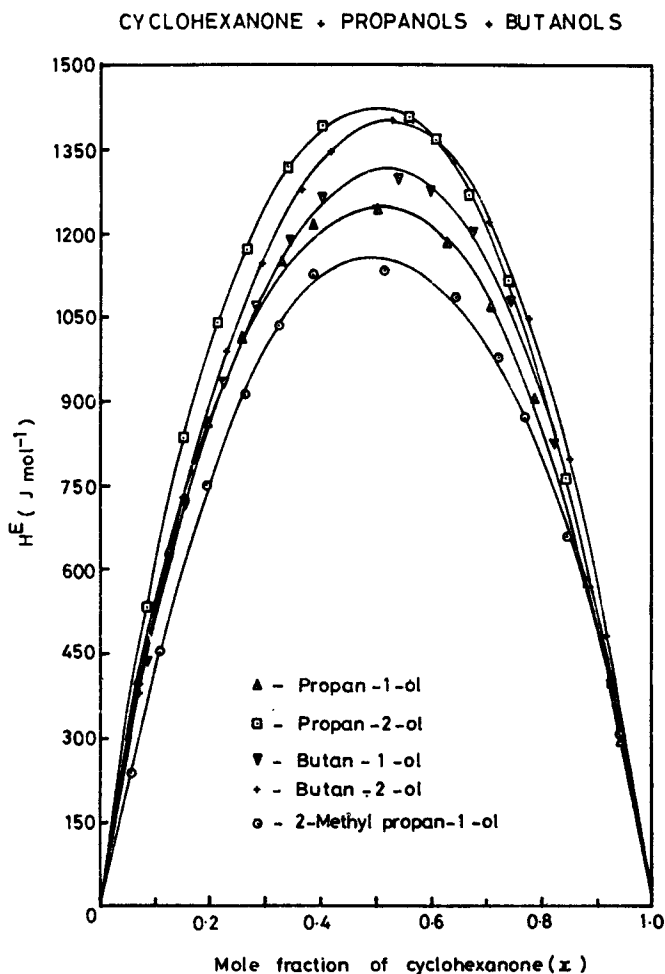


Figure 2. Excess enthalpies (H^E) are plotted against mole fraction (x) of cyclohexanone.

Table 3. Coefficients and percentage of standard deviation, $\% \sigma(H^E)$ for least squares representation of H^E .

System	h_0	h_1	h_2	h_3	$\% \sigma(H^E)$
Cyclohexanone + propan-1-ol	4988.84	1588.41	1076.53	-914.03	1.70
Cyclohexanone + propan-2-ol	5699.98	-60.74	795.85	-995.77	0.47
Cyclohexanone + butan-1-ol	5249.68	331.60	621.41	-337.59	1.41
Cyclohexanone + butan-2-ol	5586.05	414.11	678.72	24.57	0.43
Cyclohexanone + 2-methyl propan-1-ol	4623.24	-185.17	561.94	1149.11	2.16

reduction in dipole-dipole interactions between ketone molecules; (2) liberation of heat as a result of possible hydrogen bonding interaction between the carbonyl group of the ketone and the hydroxyl function of the alcohol. The actual values of H^E would depend upon the relative strength of the two opposing effects. The

positive experimental H^E values suggest that the former effect is stronger than the latter. Our observations are in line with those reported by Neumann and Weber (1963) for cyclohexanone + cyclohexanol.

The lower positive values of H^E for the cyclohexane – propan-1-ol system than for that containing propan-2-ol indicates that propan-1-ol interacts more strongly than propan-2-ol. This may be attributed to the steric hindrance of the methyl group in propan-2-ol. In the case of the systems containing butanols H^E falls in the order,

butan-2-ol > butan-1-ol > 2-methyl propan-1-ol.

This trend may be explained on the basis of steric and electromeric effects. When the alkyl group of the alcohol becomes more and more branched, the effect of interaction is more and more sterically hindered and the positive H^E values should be in the order

butan-2-ol > 2-methyl propan-1-ol > butan-1-ol.

But in contrast the observed H^E values suggest the stronger interaction in the system, cyclohexanone + 2-methyl propan-1-ol than that containing butan-1-ol. This may be due to the electromeric effect predominating over the steric effect in the system, cyclohexanone + 2-methyl propan-1-ol.

Acknowledgement

We are thankful to Dr. Asad Ali Khan, Chemical Engineering Division, Regional Research Laboratory, Hyderabad, for providing the facilities to carry out this work.

One of the authors (AK) is thankful to the University Grants Commission, New Delhi, for National Associateship Award.

References

- Neumann S and Weber U V 1963 *J. Prakt. Chem.* **19** 206
Rao M V P and Naidu P R 1976 *J. Chem. Thermodyn.* **8** 96
Riddick J A and Bunger W B 1970 *Organic solvents* 3rd edn. (New York: Interscience) vol. 2
Shanmugasundaram V and Mohan R 1980 *Bull. Soc. Chim. Belg.* **89** 409
Shanmugasundaram V and Mohan R 1982 *Bull. Soc. Chim. Belg.* **91** 885
Shanmugasundaram V and Mohan R 1983 *J. Indian Chem. Soc.* **60** 298
Stokes R H and Marsh K N 1972 *Annu. Rev. Phys. Chem.* **23** 65
Timmermans J 1965 *Physico-chemical constants of pure organic compounds* (Amsterdam: Elsevier) vol. 1
Waclawck Witold 1978 *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **26** 135