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Enthalpies of Mixing of Cyclohexane with Binary Mixtures of Benzene with Toluene, *p*-Xylene & Carbon Tetrachloride

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Enthalpies of mixing of cyclohexane with title binary mixtures have been determined at 26.9°. The values have been compared with those obtained by an equation derived by Lakhanpal *et al.* [*Indian J. Chem.*, 13 (1975), 129]. It has been concluded that equation proposed by Lakhanpal *et al.* is very useful for predicting the enthalpy of mixing of a substance with a binary solvent medium from the enthalpies of corresponding binary mixtures.

DELMAS *et al.*[1] derived relation (1) for the heat of mixing

$$\triangle H_m = \frac{Z N_3 r_3 (N_1 r_1 + N_2 r_2)}{\sum_i N_i r_i} \left[\phi_1 w_{13} + \phi_2 w_{23} - \phi_1 \phi_2 w_{12} \right] \quad ...(1)$$

of a substance with a binary solvent mixture, assuming random mixing and a rigid lattice model and ignoring any ternary contacts. Equation (1) involves interchange energies, w_{ij} whose values for the respective binary mixtures are unknown. These can, however, be determined from the heats of mixing of three binary systems that constitute the ternary system. It is known, however, that interchange energies vary with concentration. It would be better, therefore, if w_{ij} in Eq. (1) are replaced by measured enthalpy changes ($\triangle H_{ij}$). This necessary modification of relation (1) was carried out by Lakhanpal *et al.*[2] who suggested Eq. (2)

$$\triangle H_m = \Phi_3 \left[\frac{x_1 + x_3}{\phi_{31}} \triangle H_{13} + \frac{x_2 + x_3}{\phi_{32}} \triangle H_{23} - (x_1 + x_2) \triangle H_{12} \right] \quad ...(2)$$

where Φ_3 is the volume fraction of component-3 and x_i are ternary mole fractions and binary enthalpies $\triangle H_{13}$, $\triangle H_{23}$ and $\triangle H_{12}$ correspond to binary volume fractions ϕ_{31}, ϕ_{32} and ϕ_{12} in the ternary mixture.

Equation (2) was used to calculate the enthalpies of some polyglycols with mixtures of dioxane + water and ethanol + water[2,3]. These values when compared with experimental values of enthalpies were found to have only a fair to moderate agreement. This was not entirely unexpected since the systems in question consisted of a long chain component and were highly polar in nature. Equation (2) should, however, give better results for non-polar systems, some of which have been studied in this work.

Materials and Methods

Cyclohexane, benzene, toluene, *p*-xylene and carbon tetrachloride were purified by standard methods and their purity was checked by comparing their densities and refractive indices with the literature values.

Enthalpies of mixing were determined at 26.9° with an isothermal phase change calorimeter using purified diphenyl ether as the dilatometric fluid.

Results and Discussion

Binary systems — Enthalpies of mixing ($\triangle H_{12}$) of cyclohexane + benzene, + toluene, + carbon tetrachloride and that of benzene + toluene, + carbon tetrachloride at 26.9° (300.05*K*) have been determined over the entire concentration range. The experimental data have been fitted[4] to Eqs. (3) and (4),

$$\triangle H_{12} = x_1 x_2 \left[A_0 + A_1 (x_1 - x_2) + A_2 (x_1 - x_2)^2 \right] \quad ...(3)$$

TABLE 1 — CO-EFFICIENTS AND STANDARD ERRORS FOR LEAST SQUARE ANALYSIS OF ENTHALPY DATA FOR VARIOUS BINARY SYSTEMS ACCORDING TO EQUATION (2)

Binary systems	A_0	A_1	A_2	σ	Δ
Cyclohexane+benzene	770.09	—65.15	35.34	6.44	6.83
Cyclohexane+toluene	573.34	—73.90	77.87	0.69	0.12
Cyclohexane+CCl_4	150.87	—32.83	56.62	1.29	0.85
Benzene+toluene	60.35	1.46	—35.29	0.92	1.53
Benzene + CCl_4	114.43	—6.02	4.79	1.14	0.96

TABLE 2 — CO-EFFICIENTS AND STANDARD ERRORS FOR LEAST SQUARE ANALYSIS OF ENTHALPY DATA FOR VARIOUS BINARY SYSTEMS ACCORDING TO EQUATION (3)

Binary systems	A'_0	A'_1	A'_2	σ'	Δ'
Cyclohexane+benzene	776.76	—138.65	37.69	1.53	0.53
Cyclohexane+toluene	573.06	—78.55	78.53	0.61	0.11
Cyclohexane+CCl_4	150.16	—40.62	58.09	1.19	0.79
Benzene+toluene	60.25	7.58	—35.91	0.70	1.17
Benzene+CCl_4	114.43	—0.96	4.07	1.05	0.88

$$\triangle H_{12} = \phi_1\phi_2\left[A_0 + A_1(\phi_1-\phi_2) + A_2(\phi_1-\phi_2)^2\right] \quad \ldots(4)$$

and the values for co-efficients A_n and A_n along with standard errors σ, σ' and percent errors $\triangle$, $\triangle'$ are reported in Tables 1 and 2. It is seen that in conformity with our earlier conclusion[4] Eq. (4) gives a better representation of experimental data. This is particularly true for cyclohexane + benzene system in which σ value is far greater than σ'. σ can, however, be scaled down at the cost of adding another term to Eq. (3). Our $\triangle H_{12}$ values at 0.5 mol fraction and at 26.9° have been compared with the corresponding literature data at 25° in Table 3. It may be seen that, in general, our experimental values compare very well with the corresponding literature values, thus certifying the accuracy of our results. Enthalpies of mixing data for the binary systems cyclohexane + *p*-xylene and benzene + *p*-xylene (required in this work) have been reported earlier[4].

Ternary systems — Heats of mixing of cyclohexane (component 3) with 1–2 binary mixtures of benzene + toluene, benzene + *p*-xylene and benzene + carbon tetrachloride have been determined at 26.9° and the data are recorded in Table 4. In each of the above systems, components 1 and 2 have been mixed in the ratio of 20 : 80, 50 : 50 and 80 : 20 by weight. As expected, $\triangle H_m$ values depend on the (i) composition of 1–2 mixture and (ii) the heats of mixing of 1–3 and 2–3 binary systems (see Fig. 1, as a typical

TABLE 3 — COMPARISON OF OUR HEATS OF MIXING DATA WITH LITERATURE VALUES AT 0.5 MOLE FRACTION

Binary systems	$\triangle H_{12}$ at 0.5 mole fraction (cal./mole)			
	Literature values at 25°C			This work at 26.9°
Cyclohexane + benzene	192.4[5],	191.2[6,7],	191.4[8]	192.0
Cyclohexane + toluene	142.7[9],	142.4[10],		143.0
Cyclohexane + CCl_4	35.0[11],	40.2[12],	38.0[13],†	37.8
Benzene + toluene	16.3[9],	16.0[14],	14.0[15]	15.1
Benzene + CCl_4	26.0[12],	27.6[6],	27.8[7], 29.6[16],‡	28.6

†at 20°
‡at 35°

TABLE 4 — COMPARISON OF EXPERIMENTAL AND THEORETICAL VALUES OF $\triangle H_m$ FOR THE SOLUTIONS OF CYCLOHEXANE IN VARIOUS BINARY MIXTURES

% of benzene in the binary mixtures	80		50			20		
ϕ_3	$\triangle H_m$ (cal/mole)		ϕ_3	$\triangle H_m$ (cal/mole)		ϕ_3	$\triangle H_m$ (cal/mole)	
	Obs.	Calc.		Obs.	Cald		Obs	Cald.
				BENZENE + TOLUENE				
0.0514	29.9	29.4	0.0401	22.0	22.3	0.0802	41.7	42.5
0.1178	70.9	68.2	0.1099	58.3	59.6	0.1419	68.0	70.5
0.2690	136.0	135.1	0.1962	97.0	97.6	0.2191	105.5	106.8
0.3195	152 5	151.3	0.3126	136 5	137.6	0.3378	134.5	133.3
0.4688	180.0	182.9	0.4256	160.0	163.0	0.4665	154.7	153.1
0.5497	190.2	187.6	0 5729	168.8	172.7	0.5880	153.7	153.9
0.6173	181.4	182.5	0.6634	162.3	162.4	0.6728	144.7	144.3
0.7329	153.2	156.1	0.7388	140.0	141.9	0.7917	112.3	114.4
0.8836	78 5	82.7	0.9018	62.2	62.8	0.8932	65.1	67.1
0.9585	32.0	33.8	0.9613	24.5	25.2	0 9605	25.4	25.5
				BENZENE + *p*-XYLENE				
0.0953	56.0	53.0	0.0416	20.0	20.0	0.0476	20.0	20.6
0.1799	98.4	95.7	0.1135	55.0	55.2	0.1114	46.0	46.2
0.3083	147.5	143.6	0.2656	117.0	114.8	0.2265	91.0	90.1
0.3963	165.7	165.1	0.3878	148.0	146.4	0.3418	122.0	120.5
0.5180	176.0	180.5	0.5212	163.1	159.6	0.4561	144.3	141.9
0.5884	174.1	178.8	0 6046	156.3	157.2	0.5505	145.0	142.5
0.7795	134.5	135.3	0.7458	124.9	125.5	0.6965	126.4	122.6
0.8814	82.7	81.4	0.8481	88.5	86.8	0.7945	97.7	96.4
0.9083	68.4	64.4	0.9253	48.0	49.0	0.8997	56.0	54.8
0.9586	32.0	32.3	0.9598	25.5	25.3	0.9636	22.1	22.4
				BENZENE + CARBON TETRACHLORIDE				
0.0561	30.0	30.5	0.0394	16.0	16.4	0.0489	13.0	14.1
0.2138	99.0	103.9	0.1065	43.8	44.2	0.2132	52.0	51.3
0.3452	145.0	145 3	0.2570	95.5	92.6	0.2887	66.0	64.5
0.4073	159.1	160.0	0 3832	124.0	120.4	0.4387	85.8	81.6
0.5024	172.0	171.5	0.4932	136.0	133.8	0.6409	82.5	82.5
0.6950	157.5	156.1	0.5869	134.5	134.4	0.7226	74.0	73.3
0.8797	76.0	80.8	0.6791	123.0	124.8	0.7997	61.6	61.5
0.8884	70.9	74.7	0.7916	97.0	98.6	0.8835	40.0	40.0
0.9354	45.0	46.8	0.9085	49.6	50.8	0.9561	18.0	17.3

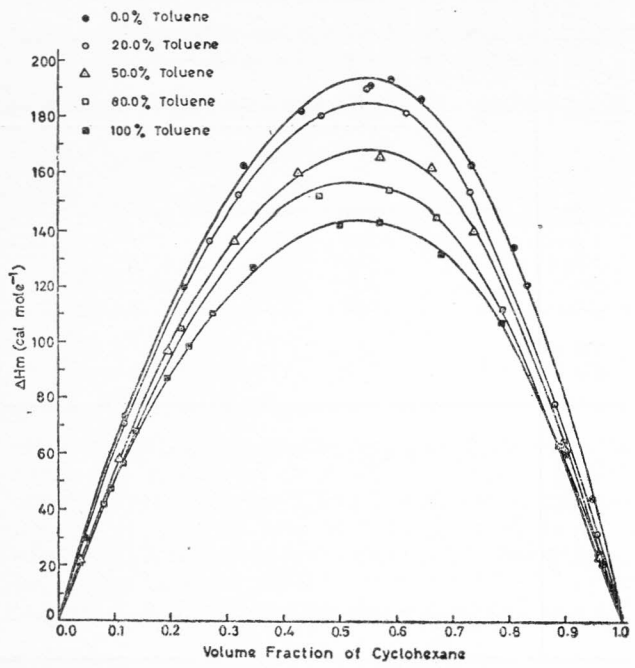

Fig. 1 — Plot of $\triangle H_m$ vs volume fraction of cyclohexane for cyclohexane—benzene—toluene system.

case). Theoretical values of $\triangle H_m$ have been calculated from Eq. (2) and these have been compared with the (smoothened) experimental values in Table 4. It is satisfying to note that the two sets of values agree with one another almost quantitatively. A small number of observed deviations fall within the range of $\pm 5.0\%$, and may be entirely attributed to experimental uncertainties. It may, therefore, be concluded that Eq. (2) is extremely useful for predicting the heats of mixing of a substance with a binary solvent medium from such data on the corresponding binary mixtures. This is particularly true for non-polar systems. It may also be concluded that ternary contacts, if any, between the three components do not contribute significantly to the total heat of mixing of a ternary mixture.

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