Enthalpy of Mixing of Some Hydrocarbon–Alcohol and Hydrocarbon–Nitroalkane Mixtures at 25°C

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The enthalpy of mixing of 1-hexanol with benzene, 2-methyl-2-butanol with benzene, toluene, and 1,3,5-trimethylbenzene, and of nitroethane and 2-nitropropane with *n*-hexane, cyclohexane, methylcyclohexane, and 2,2,4-trimethylpentane was measured at 25°C with a microflow calorimeter with a reproducibility of better than 1%.

Reported in this paper is the enthalpy of mixing of several nonpolar plus polar component binary solutions. The alcohol-hydrocarbon mixtures measured were 1-hexanol with benzene, and 2-methyl-2-butanol with benzene, toluene, and 1,3,5-trimethylbenzene. The nitroalkane–hydrocarbon mixtures measured were nitroethane and 2-nitropropane with *n*-hexane, cyclohexane, methylcyclohexane, and 2,2,4-trimethylpentane. For some of the same solutions we have measured excess Gibbs energy (*14*), temperature and composition of liquid-liquid immiscibility (*4*), and density and surface tension (*15*).

Experimental

Calorimeter. The flow microcalorimeter was constructed by Trowbridge and coworkers (*2, 5*) from a mixing and flow system with thermopile purchased from the Beckman Instrument Co., Palo Alto, Calif. Features described by Monk and Wadso (*12*) and Sturtevant and Lyons (*17*) were incorporated. The flow system and thermopile are inside an insulated brass submarine immersed in a well-insulated water bath thermostated to ±0.02°C by a remote pumping regulator. The signal from the thermopile is monitored by a microvolt meter (Model 150-B, Keithly Instruments, Cleveland, Ohio) and displayed on a recorder. Two syringe drive pumps (Harvard Apparatus Co., Millis, Mass.) fitted with gas tight syringes (Hamilton Co., Reno, Nev.) deliver the component liquids to the thermopile by way of Teflon tubing.

The viscous flow heat correction was measured by pumping some of the mixtures back through the calorimeter after the initial mixing experiment. The effect changed little with the flow rates of 1.4×10^{-3} to 2.2×10^{-1} ml min^{-1} used in these experiments. The viscous flow heat correction amounted to only 0.7–0.1% of the measured heat of mixing.

The calorimeter was calibrated by carrying out several neutralization experiments between sodium hydroxide and hydrochloric acid solutions. Values of the enthalpy of neutralization and dilution were taken from Hale et al. (*6*) and Vanderzee and Swanson (*18*). Hexane–cyclohexane and benzene–cyclohexane were used as test systems. The enthalpy of mixing results smoothed by the excess properties equation are given in Table I. The *n*-hexane–cyclohexane enthalpies of mixing agree with the average deviation of 0.5% from accepted values (*10, 11, 13, 17*). Values of the enthalpy of mixing of the benzene–cyclohexane system agree with an average deviation of $0.2–0.4_5$% with workers' values reported in the critical evaluation of Stokes et al. (*16*). All measurements were carried out at 25.00° ± 0.02°C.

Chemicals. The source, purification, refractive index, and density of the chemicals used in this study are summarized in Table II. The values agree well with accepted literature values.

Results and Discussion

The enthalpy of mixing (cal mol^{-1}) at 11–15 mole fractions for each of the twelve systems is given in Table III.

The data were fitted to the excess properties equation

$$H^E \text{ (cal mol}^{-1}) = X_1 X_2 \sum_{n=0}^{n} A_n (X_1 - X_2)^n$$

where X_1 and X_2 are mole fractions, A_n are empirical constants, and n is an integer. Values of the constants in the excess properties smoothing equation along with the standard deviation, σ_{ave}, and maximum deviation, σ_{max}, determined by least-squares analysis, are given in Table IV.

Hydrocarbon alcohol systems. The enthalpy of mixing at 0.5 mole fraction, $H_{0.5}{}^E$, the maximum enthalpy of mixing, $H_{\text{max}}{}^E$, and the corresponding hydrocarbon mole fraction were computed from the smoothing equations. The values are ($H_{0.5}{}^E/H_{\text{max}}{}^E/X_{1\ \text{max}}$) 273/287/0.63, 374/382/0.58, 330/337/0.58, and 321/330/0.61 for 1-hexanol with benzene, and 2-methyl-2-butanol with benzene, toluene, and 1,3,5-trimethylbenzene, respectively. A value of 253 cal mol^{-1} for $H_{0.5}{}^E$ has been reported for the benzene–1-hexanol system (*3*). The $H_{\text{max}}{}^E$ values occur at hydrocarbon-rich mole fractions which are typical of other hydrocarbon–alcohol heat of mixing data (*3*).

The excess Gibbs energy of mixing has been reported on the three systems benzene–1-hexanol, benzene–2-methyl-2-butanol, and toluene–2-methyl-2-butanol (*14*). When corrected from 30° to 25°C and combined with the present enthalpy of mixing results, we find that only the benzene–1-hexanol solutions show a negative entropy of mixing at the high alcohol concentrations. In general, the overall thermodynamic behavior of the hydrocarbon alcohol solutions appears to be consistent with the patterns presented and discussed by Brown et al. (*3*).

Table I. Test Systems. Smoothed Values of Enthalpy of Mixing from Excess Properties Equation

Mole fraction cyclohexane	Enthalpy of mixing, cal mol^{-1}, 25°C	
	n-Hexane(1)–cyclohexane(2)	Benzene(1)–cyclohexane(2)
0.05	7.84	39.46
0.10	15.15	73.78
0.20	28.20	128.20
0.30	38.98	165.21
0.40	47.07	186.12
0.50	51.93	192.94
0.60	52.96	176.05
0.70	49.43	158.58
0.80	40.47	120.09
0.90	24.61	67.00
0.95	13.57	35.31
Std error	0.12	0.59
Max dev	0.16	0.82

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It is of interest to compare trends seen in the enthalpy of mixing of equimolar mixtures of hydrocarbon–alcohol solutions with trends observed in hydrocarbon solutions of other polar molecules. The alcohol solutions have a higher enthalpy of mixing at 25°C with benzene than with *n*-hexane, which is consistent with the viewpoint (*1*, *3*) that more hydrogen bonds are broken in benzene solution than in hexane solutions. Another trend is seen in the enthalpy of mixing of alcohols with aromatic hydrocarbons. For a given alcohol the excess enthalpy at 25°C decreases as more alkyl groups are substituted on the benzene ring. Typical are the results of 2-methyl-2-butanol in benzene, toluene, and 1,3,5-trimethylbenzene reported here. Neither of these trends appears to be true for nonhydrogen-bonded polar liquids such as nitroalkanes, acetonitrile, and dimethylsulfoxide. The 2-nitropropane has an excess enthalpy of 350 cal mol^{-1} in *n*-hexane, whereas it is 14 cal mol^{-1} with benzene (*7*). The simple nitroalkanes show over twice the enthalpy of mixing in 1,3,5-trimethylbenzene than they show with benzene (*7*).

Hydrocarbon nitroalkane solutions. Two of the hydrocarbon–nitroethane solutions are partially miscible at the temperature of the enthalpy measurement. Their upper consolute solution temperatures are 32.4°C (*4*) for the *n*-hexane–nitroethane and 29.8°C for the 2,2,4-trimethylpentane–nitroethane solution (*19*).

The excess properties equation parameters for these two systems in Table IV are intended to apply only to the miscible regions at 25°C.

A zero-order lattice theory has been applied by Kehiaian et al. (*8*) to obtain surface interchange enthalpies. The interchange enthalpies have successfully reproduced the enthalpies of mixing of ethers with aliphatic and aromatic hydrocarbons. Kertes and Grauer (*9*) have extended the calculation to amine nitrogen containing compounds in mixtures with hydrocarbons.

Although the present data are somewhat limited to establish a completely consistent value of an interchange enthalpy of the nitro group with an alkane or cycloalkane segment, we have derived a value which reproduces our results to within 5%. Contact surface areas of 0.875, 0.750, and 2.125 were assigned the CH_3, CH_2, and NO_2 groups, respectively. The interchange enthalpy between methyl and nitro groups and methylene and nitro groups was assumed to be the same. The alkane–nitro group interchange enthalpy found to be consistent with our measurements is 1350 ± 65 cal mol^{-1}. This compares with interchange enthalpy values of 2380 ± 12 and 3600 ± 170 cal mol^{-1} for alkane–ether oxygen (*8*) and alkane–amine nitrogen (*9*) segments, respectively.

The alkane–nitro segment interchange enthalpy, $h_{an}^* = 1350 \pm 65$ cal mol^{-1}, can be used to estimate the enthalpy of mixing of alkane–nitroalkane solutions. First, one calculates the molar interchange enthalpy, h^*, which takes the form $h^* = \alpha_{2n}^2 h_{an}^*$ when one assumes methyl and methylene segments have the same interaction enthalpy with the nitro segment and a zero interchange enthalpy with each other. In the equation, α_{2n} is the fraction of the contact surface of the nitroalkane component owing to the nitro segment. It is calculated from the contact surface areas given in the paragraph above by the relation $\alpha_{2n} = q_{2n}/q_2$ where q_{2n} is the contact surface owing to the nitro segment and q_2 is the total contact surface of the nitroalkane. The enthalpy of mixing is

$$H^E = q_1 q_2 \frac{X_1 X_2}{q_1 X_1 + q_2 X_2} \cdot h^*$$

where q_1 is the alkane total contact surface, q_2 is the nitroalkane total contact surface, X_1 and X_2 are the respective mole fractions, and h^* is the molar interchange enthalpy.

We have recently measured values of 66.2 and 14.2 cal

Table II. Source Purification and Physical Properties of Solution Components

Compound	Refractive index, $n^{25}D$	Density, g ml^{-1}, 30°C	Source and purification
1-Hexanol	1.41675	0.81264	Eastman practical, dried over $CaSO_4$, distilled from over CaH_2
2-Methyl-2-butanol (*t*-pentyl alcohol)	1.4022	0.79975	Eastman practical, dried over $CaSO_4$, distilled from over CaH_2
Nitroethane	1.38950	1.03450	Matheson Coleman & Bell practical, dried over $CaSO_4$, distilled 57°, 97 mm Hg
2-Nitropropane	1.39235	0.97730	Eastman practical, dried over $CaSO_4$, distilled 67°, 132 mm Hg
n-Hexane	1.37240	0.65038	Fisher 99 mol % certified, distilled from over CaH_2
Cyclohexane	1.42350	0.76898	Phillips research grade, Lot S-402, 99.5 mol %
Methylcyclohexane	1.42055	0.76051	Matheson Coleman & Bell practical, treated with concd H_2SO_4, water, $CaSO_4$, and distilled from over CaH_2
2,2,4-Trimethylpentane (isooctane)	(1) 1.38905 (2) 1.38910	0.68344	(1) Phillips research grade, 99.98 mol %. (2) Fisher, 99 mol % certified, distilled from over CaH_2
Benzene	(2) 1.49800	0.86838	(1) Phillips research grade, 99.91 mol %. (2) Phillips 99 mol % pure, treated with concd H_2SO_4, water, $CaSO_4$, and distilled from CaH_2
Toluene	1.49405	0.8576	Phillips 99 mol % pure, distilled from over CaH_2
1,3,5-Trimethylbenzene (mesitylene)	1.49610	0.8560	Eastman practical, dried over $CaSO_4$, distilled from over sodium

mol^{-1} for the enthalpy of mixing of equimolar mixtures ($H_{0.5}{}^E$) of nitroethane and of 2-nitropropane with benzene, respectively (*7*). When these values are compared with the enthalpy of mixing of nitroalkanes with aliphatic hydrocarbons, the enthalpy of mixing of nitroethane with cyclohexane is six times more endothermic than mixing nitroethane with benzene, and the enthalpy of mixing of 2-nitropropane with *n*-hexane and cyclohexane is 25 times more endothermic than mixing 2-nitropropane with benzene. These trends are of much greater magnitude and of opposite direction than those observed for alcohol–hydrocarbon mixtures (*3*). The result suggests that either benzene is not nearly as effective in breaking up hydrogen-bonding association in alcohols or that there is a contribution from a process that is much more exothermic between aromatic hydrocarbon and nitroalkane than the interaction between aromatic hydrocarbon and alcohol.

Table III. Enthalpy of Mixing, H^E, Cal Mol^{-1}, 25.0°C

X_2	H^E	X_2	H^E	X_2	H^E	X_2	H^E
Benzene(1)–1-hexanol(2)		Benzene(1)–2-methyl-2-butanol(2)		Toluene(1)–2-methyl-2-butanol(2)		1,3,5-Trimethylbenzene(1)–2-methyl-2-butanol(2)	
0.0634	149.84	0.0719	182.37	0.0619	159.23	0.1080	223.86
0.0870	179.82	0.0981	223.14	0.1143	226.15	0.1454	253.67
0.1566	233.91	0.1317	265.20	0.1534	261.96	0.2497	310.06
0.2067	261.43	0.1754	304.15	0.2027	292.43	0.3179	326.19
0.2674	280.88	0.2295	339.67	0.2626	316.14	0.3950	331.96
0.3383	289.38	0.2944	365.26	0.3328	331.09	0.4776	325.61
0.4163	287.23^a	0.3688	380.59	0.4112	336.31	0.5605	307.94^a
0.4987	270.58	0.4491	381.09^a	0.4936	331.05^a	0.6401	280.94
0.5822	243.03	0.5321	365.30	0.5761	311.54	0.7136	248.20
0.6613	206.43	0.6143	333.51	0.6556	277.05	0.7780	211.58
0.7329	165.94	0.6906	292.09	0.7280	237.46	0.8307	173.51
0.7928	129.76	0.7582	246.92	0.7894	195.31	0.9053	106.59
0.8826	75.18	0.8143	200.85	0.8398	158.59	0.9307	81.25
		0.8957	122.48	0.9113	96.16		
n-Hexane(1)–nitroethane(2)		Cyclohexane(1)–nitroethane(2)		Methylcyclohexane(1)–nitroethane(2)		2,2,4-Trimethylpentane(1)–nitroethane(2)	
0.1110	223.53	0.0935	195.81	0.1085	207.03	0.0740	163.44
0.1952	313.45	0.1258	240.60	0.1912	293.29	0.1008	203.21
0.2540	337.45	0.2196	327.09	0.2492	333.20	0.1361	245.90
0.3230	^{b}	0.2833	355.85	0.3177	361.53	0.1800	295.20
0.4008	^{b}	0.3560	381.37	0.3948	378.64	0.2343	330.75
0.4837	^{b}	0.4354	396.20	0.4774	386.99	0.3008	360.85
0.5675	^{b}	0.5194	402.13	0.5613	383.28	0.3760	^{c}
0.6468	^{a,b}	0.6021	396.15^a	0.6410	371.06^a	0.4578	^{c}
0.7186	^{b}	0.6794	371.65	0.7134	345.18	0.5418	^{c}
0.7815	307.01	0.7480	331.35	0.7772	306.41	0.6235	^{c}
0.8342	263.73	0.8055	282.11	0.8306	259.64	0.6980	^{a,c}
0.8758	208.91	0.8905	181.55	0.8729	209.52	0.7632	^{c}
0.9079	160.54	0.9409	106.49	0.9057	162.90	0.8186	281.47
0.9507	91.94			0.9305	125.43	0.8639	235.66
						0.8988	188.49
						0.9460	110.66
n-Hexane(1)–2-nitropropane(2)		Cyclohexane(1)–2-nitropropane(2)		Methylcyclohexane(1)–2-nitropropane(2)		2,2,4-Trimethylpentane(1)–2-nitropropane(2)	
0.1212	198.19	0.1378	218.33	0.0880	152.79	0.1101	176.68
0.2125	275.31	0.1823	256.86	0.1185	189.32	0.1482	222.46
0.2746	309.51	0.2382	294.20	0.2083	266.36	0.1959	257.17
0.4261	348.29	0.3804	346.20	0.2696	301.29	0.2544	296.47
0.5099	349.21	0.4623	354.79	0.3408	327.69	0.3233	324.11
0.5921	334.70^a	0.5453	346.90^a	0.4201	342.72	0.4001	342.44
0.6693	308.22	0.6259	323.57	0.5036	340.56	0.4830	350.12
0.7393	268.25	0.7009	286.27	0.5860	329.76^a	0.5657	340.70
0.8481	181.60	0.7672	244.02	0.6637	302.75	0.6468	316.64^a
0.8865	143.48	0.8219	199.55	0.7344	263.91	0.7202	282.80
0.9386	82.75	0.8658	159.99	0.7954	221.70	0.7822	242.81
				0.8448	177.71	0.8341	199.38
				0.9139	106.53	0.8757	159.64
						0.9076	124.88
						0.9507	70.57

[a] Enthalpy value corresponding to one-half volume fraction. [b] Formed partially miscible liquid-liquid mixtures on mixing. Enthalpy values were 341, 343, 342, 342, 340, and 334 cal mol^{-1}. [c] Formed partially miscible liquid-liquid mixtures on mixing. Enthalpy values were 355, 350, 343, 333, 322, and 316 cal mol^{-1}.

Table IV. Constants for Excess Properties Equation, Standard Error, and Maximum Error, Cal Mol^{-1}, 25.0°C

Mixture	A_0	A_1	A_2	A_3	A_4	σ_{ave}	σ_{max}
Benzene(1)–1-hexanol(2)	1091.0	493.8	−12.3	604.5	898.4	3.28	6.5
Benzene(1)–2-methyl-2-butanol(2)	1494.3	388.6	277.8	539.8	605.2	1.63	2.6
Toluene(1)–2-methyl-2-butanol(2)[a]	1320.3	333.6	248.7	567.5	690.1	0.57	0.7
Toluene(1)–2-methyl-2-butanol(2)[b]	1322.2	327.8	226.3	596.4	749.8	2.95	6.3
1,3,5-Trimethylbenzene(1)–2-methyl-2-butanol(2)	1286.9	310.3	489.0	563.4	467.3	2.49	4.3
n-Hexane(1)–nitroethane(2)[c]	1341.8	−32.8	1990.3	402.9	−1199.5	2.08	5.3
Cyclohexane(1)–nitroethane(2)	1608.7	−66.0	738.5	514.9	...	1.19	2.4
Methylcyclohexane(1)–nitroethane(2)	1545.6	−19.3	894.5	261.7	−204.0	1.04	1.6
2,2,4-Trimethylpentane(1)–nitroethane(2)[d]	1560.8	−19.3	937.7	201.8	...	1.86	3.5
n-Hexane(1)–2-nitropropane(2)	1399.5	113.5	323.7	308.0	163.9	0.78	0.9
Cyclohexane(1)–2-nitropropane(2)	1412.4	159.9	228.5	298.5	264.2	1.04	1.7
Methylcyclohexane(1)–2-nitroethane(2)	1371.4	127.9	320.8	292.5	79.1	1.09	2.1
2,2,4-Trimethylpentane(1)–2-nitropropane(2)	1393.9	102.1	345.3	200.4	120.0	1.44	3.3

[a] Excludes measurements at mole fractions of 0.0619 and 0.9133. [b] Includes all measurements. [c] For liquid miscible ranges of 0.0–0.3 and 0.78–1.0 mole fraction nitroethane. [d] For liquid miscible ranges of 0.0–0.3 and 0.82–1.0 mole fraction nitroethane.

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Excess Gibbs Free Energies and Heats of Mixing for Binary Systems Ethyl Acetate with Methanol, Ethanol, 1-Propanol, and 2-Propanol

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Isothermal vapor-liquid equilibrium data for the methanol–ethyl acetate, ethyl acetate–ethanol, ethyl acetate–1-propanol, and ethyl acetate–2-propanol systems are presented at 55°C. Heat of mixing data are also obtained for the ethyl acetate–1-propanol system at 25°, 35°, and 45°C and for the other systems at 25° and 35°C. A simultaneous fit of the excess Gibbs free energies and heats of mixing is successfully represented by the Wilson equation whose energy parameter differences are assumed to be a quadratic function of temperature.

As part of a continuing study of thermodynamic properties of binary alcohol mixtures including such solvents as esters and ketones, vapor-liquid equilibrium data at 55°C for the four binary systems, methanol–ethyl acetate, ethanol–ethyl acetate, ethyl acetate–1-propanol, and ethyl acetate–2-propanol, were measured by a Scatchard still. The experimental data are compared with those of other investigations (*4, 6*) using the Wilson equation. Heat of mixing data are presented for the ethyl acetate–1-propanol system at 25°, 35°, and 45°C and for the other three systems at 25° and 35°C. Both excess Gibbs free energies and heat of mixing data are simultaneously correlated by the Wilson equation whose energy parameter differences are given by a quadratic function of temperature.

Experimental Procedure

Materials purchased for experimental work were of chemically pure grade. The alcohols used were mainly purified by fractional distillation in a glass column packed with McMahon packings. The alcohols were first treated with drying materials: methanol (anhydrous calcium sulfate), ethanol (calcium oxide), and propanols (copper sulfate anhydride). Ethyl acetate was purified according

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