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Excess Enthalpies of Binary Mixtures of 1-Hexanol with Hexane Isomers at 298.15 K[†]

Fumio Kimura[‡] and George C. Benson*

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

Excess enthalpies, measured at 298.15 K in a flow microcalorimeter, are reported for binary mixtures of 1-hexanol with *n*-hexane and its four isomers.

As part of a program to study the thermodynamic properties of alcohol–hydrocarbon systems, we have determined the excess enthalpies of mixtures of 1-hexanol with *n*-hexane (n-C6), 2-methylpentane (2-MP), 3-methylpentane (3-MP), 2,2-dimethylbutane (2,2-DMB), and 2,3-dimethylbutane (2,3-DMB). As far as we are aware, only the excess enthalpies of the system 1-hexanol–*n*-hexane have been reported previously (*1*).

Experimental Section

1-Hexanol (City Chemical Co.) was purified in a preparative gas chromatograph using two columns, each 1.8 m long, connected in series and containing 10% by mass OV-17 and Apiezon L, respectively. The substrate in each column was 60–80 mesh Chromosorb W. Before its use, the 1-hexanol was stored over a molecular sieve (BDH Type 3A).

The *n*-hexane (Phillips Petroleum Co., Pure Grade) was also purified by GLC in a 1.8-m column containing 10% by mass OV-101 on Chromosorb W. The four other hydrocarbons were all Phillips Research Grade reagents with purities of 99.88 mol % or better. They were used without further purification.

Densities and refractive indexes characterizing the materials used in the calorimetric studies are given in Table I. These agree reasonably well with values from the literature (*2*, *3*).

Determinations of the molar excess enthalpy H^E were carried out in an LKB flow microcalorimeter (Model 10700-1). The output of the thermopile was measured with a Keithley 180 digital nanovoltmeter. The other auxiliary equipment and the operational procedure have been described by Tanaka et al. (*4*). A pair of piston displacement pumps was used to produce mixtures with preselected mole fractions known to better than 0.1%. Check measurements on several test systems indicate that the error of H^E is 0.5% or less over most of the mole fraction range (*4*).

Results and Discussion

The experimental values of H^E determined at 298.15 K are listed in Table II. In all cases, *x* denotes the mole fraction of 1-hexanol in the mixture. A skewed Redlich–Kister equation (*5*)

$$H^E = [x(1-x)/\{1-k(1-2x)\}] \sum_{j=1}^{n} h_j (1-2x)^{j-1} \quad (1)$$

was fitted to each set of results by the method of least squares with all points weighted equally. Values of the coefficients h_j, the skewing parameter *k* (which was also adjusted), and the standard deviation σ for the representations are summarized in Table III.

Table I. Physical Properties of Component Liquids at 298.15 K

	density, kg m^{-3}		n_D	
	measd	lit.	measd	lit.
1-hexanol	816.00	816.2 (*2*)	1.416 19	1.416 1 (*2*)
n-hexane	654.99	654.81 (*3*)	1.372 19	1.372 26 (*3*)
2-methylpentane	648.50	648.52 (*3*)	1.368 72	1.368 73 (*3*)
3-methylpentane	659.78	659.76 (*3*)	1.373 85	1.373 86 (*3*)
2,2-dimethylbutane	644.42	644.46 (*3*)	1.365 95	1.365 95 (*3*)
2,3-dimethylbutane	657.02	657.02 (*3*)	1.372 27	1.372 31 (*3*)

Table II. Experimental Results for the Molar Excess Enthalpy, H^E, of 1-Hexanol–Hexane Isomer Mixtures at Mole Fraction, *x*, of 1-Hexanol and 298.15 K

	H^E, J mol^{-1}				
x	n-C6	2-MP	3-MP	2,2-DMB	2,3-DMB
0.05	320.92	318.41	314.10	314.12	312.56
0.10	395.21	391.55	387.37	385.83	384.27
0.15	440.68	436.03	430.43	429.10	427.55
0.20	471.69	466.54	461.68	458.82	457.08
0.25	492.76	486.93	482.07	478.04	476.77
0.30	504.83	498.86	492.47	487.81	486.22
0.35	507.42	501.48	495.08	489.78	487.65
0.40	500.63	494.57	488.37	481.79	480.04
0.45	485.16	479.11	471.77	465.07	463.28
0.50	461.50	454.34	446.82	440.15	438.90
0.50	460.39	454.65	445.80	440.75	438.91
0.55	428.90	423.71	415.21	410.19	407.55
0.60	391.80	385.16	377.81	374.43	370.31
0.65	349.20	342.83	335.78	333.70	329.36
0.70	302.88	297.42	290.60	289.97	285.31
0.75	254.68	249.82	243.61	243.49	239.01
0.80	203.98	200.50	194.82	195.89	190.79
0.85	152.16	150.08	145.39	144.56	142.44
0.90	100.60	99.25	96.87	95.52	94.15
0.95	49.71	48.97	47.61	48.85	45.98

Table III. Coefficients, Skewing Factor, and Standard Deviation for Least-Squares Representations of H^E for 1-Hexanol–Hexane Isomer Mixtures at 298.15 K by Eq 1

hexane isomer	h_1	h_2	h_3	h_4	h_5	k	σ
n-C6	1842.95	−666.0	−685.5	86.1	224.7	0.9633	0.47
2-MP	1817.99	−634.4	−701.0	61.9	274.6	0.9612	0.55
3-MP	1787.00	−596.1	−706.6	42.4	273.7	0.9618	0.55
2,2-DMB	1763.83	−620.8	−616.2	52.2	157.9	0.9687	0.74
2,3-DMB	1754.88	−581.9	−670.8	49.1	216.4	0.9649	0.45

The results for 1-hexanol–*n*-hexane mixtures are plotted in Figure 1. It can be seen that our findings agree reasonably well with the earlier but less extensive measurements by Brown et al. (*1*). The skewed parabolic curve for H^E, with a maximum occurring in the 1-hexanol-dilute region (near $x = 0.35$), is typical of the results for all of the systems studied. Over most of the mole fraction range, these fall in the order:

n-C6 > 2-MP > 3-MP > 2,2-DMB > 2,3-DMB

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[‡] NRCC Research Associate, 1980.

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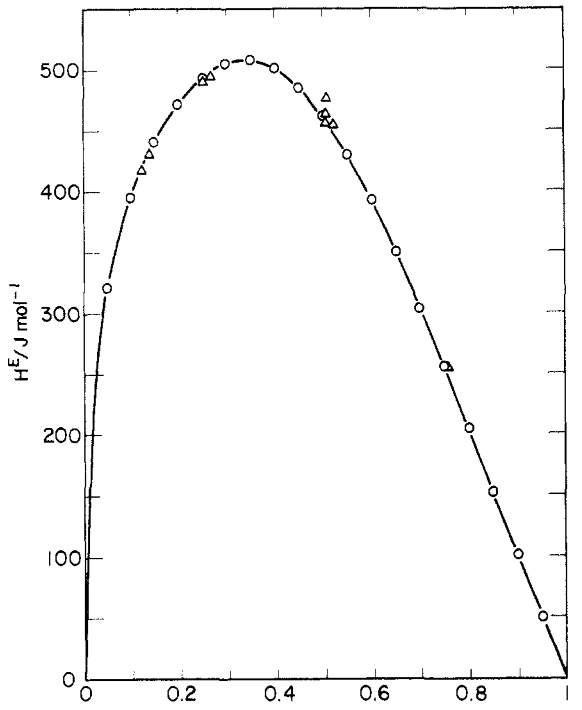

Figure 1. Molar excess enthalpy, H^E, of 1-hexanol-*n*-hexane mixtures at mole fraction, *x*, of 1-hexanol and 298.15 K: (O) present work; (Δ) Brown et al. (*1*). Curve is least-squares representation of our results by eq 1.

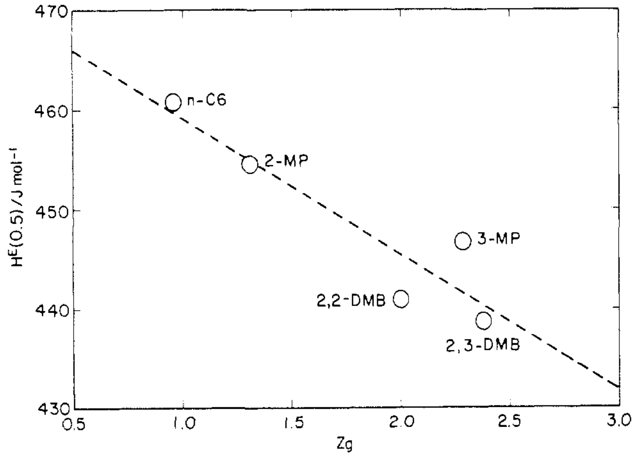

Figure 2. Plot of $H^E(0.5)$, the molar excess enthalpy of an equimolar 1-hexanol-hexane isomer mixture, against Z_g, the mean number of gauche conformations of the isomer: (- - -) least-squares line with coefficient of correlation = −0.92.

The maximum difference between the curves for n-C6 and 2,3-DMB is ~22 J mol^{-1}.

Qualitatively, the excess enthalpies of 1-hexanol-hexane isomer mixtures arise from changes in the extent of the interactions between the groups (i.e., hydroxyl and hydrocarbon) comprising the molecules. In this regard, it is evident from the present results that the interactions of the various hexane isomers must be very similar. The small excess enthalpies reported for n-C6-2,2-DMB mixtures ($H^E(0.5) \approx 6.8$ J mol^{-1} (*6*)) lend support to this view. Thus the excess enthalpies of the present systems are attributable primarily to the disruption of interactions between the hydroxyl groups of 1-hexanol molecules when the hexane isomer is added. Figure 2 shows that there is a roughly linear correlation (coefficient of correlation = −0.92) between the values of H^E for equimolar mixtures and Z_g, the mean number of gauche conformations of the branched alkane molecule (*7*, *8*). It therefore appears that the effectiveness of the isomer to disrupt the H bonds between alcohol molecules decreases as the ability to assume a larger number of conformations increases.

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Glossary

h_1, h_2, ..., h_j	coefficients in representation of molar excess enthalpy by eq 1
H^E	molar excess enthalpy, J mol^{-1}
k	skewing parameter in eq 1
n	number of coefficients in eq 1
n_D	refractive index for sodium light
x	mole fraction of 1-hexanol
Z_g	mean number of gauche conformations of hexane isomer

Greek Letters

σ	standard deviation

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