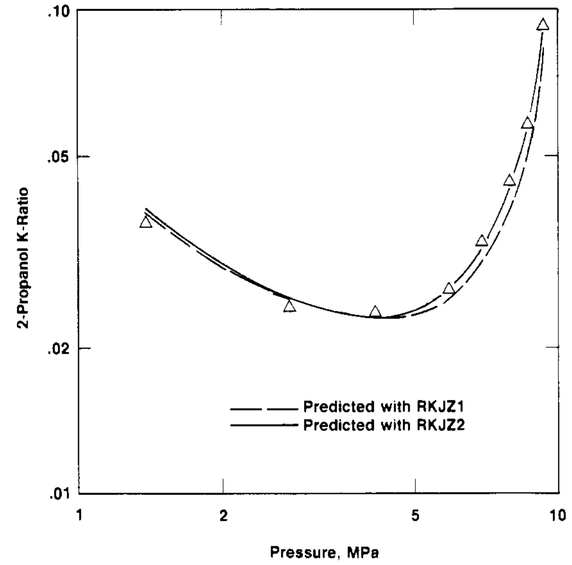

Figure 5. Experimental vapor-liquid ratio of mole fractions for 2-propanol (*K* ratio) at 62 °C.

D	binary molecular size-related parameter
i	*i*th component property
j	*j*th component property
K	equilibrium vapor/liquid ratio of mole fractions (*K* ratio)
m	mixture property
x	mole fraction

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Registry No. 2-Propanol, 67-63-0; carbon dioxide, 124-38-9.

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Excess Enthalpies of Binary Mixtures of *n*-Decane with Hexane Isomers

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Calorimetric measurements of excess enthalpies are reported for each of the five mixtures (*n*-decane–an isomeric hexane) at 298.15 K. The results for equimolar mixtures, together with previously published results for other (*n*-alkane–isomeric hexane) mixtures, are well correlated in terms of the acentric factors of the *n*-alkanes.

Currently we are studying the variations in the excess thermodynamic properties of binary mixtures which result from isomeric changes in one of the components. In this regard, we have been investigating systems formed by mixing an *n*-alkane with the five isomeric hexanes: *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). Previous papers have reported excess enthalpies for mixtures of each of these isomers with *n*-heptane (*1*), *n*-octane (*2*), and *n*-dodecane (*3*). The present paper describes a similar study of (*n*-decane–isomeric hexane) mixtures.

Excess enthalpies of (*n*-decane–*n*-C6) mixtures have been studied several times in the past (*4*–*6*), but we are unaware of previous measurements on any of the other mixtures.

Experimental Section

Excess molar enthalpies H_m^E were determined at 298.15 K in an LKB flow microcalorimeter. Details of the equipment and its operation have already been described (*1*, *7*). For most of the measurements, the error in the determination of H_m^E is estimated to be less than 0.5%. However, it may be somewhat higher for small H_m^E (<10 J mol^{-1}).

The component liquids were obtained from the Phillips Petroleum Co. and were used without further purification. The *n*-decane was Pure Grade with a purity of at least 99 mol %. The isomeric hexanes were Research Grade with purities exceeding 99.9 mol %. At 298.15 K, the densities (in kg m^{-3}) of the samples used for the calorimetric measurements were as

Table I. Experimental Results for the Excess Molar Enthalpy, H_m^E, of (*n*-Decane–Isomeric Hexane) Mixtures at Mole Fraction, *x*, of *n*-Decane and 298.15 K

x	H_m^E/J mol^{-1}	x	H_m^E/J mol^{-1}	x	H_m^E/J mol^{-1}	x	H_m^E/J mol^{-1}	x	H_m^E/J mol^{-1}
n-Decane–*n*-C6		*n*-Decane–2-MP		*n*-Decane–3-MP		*n*-Decane–2,2-DMB		*n*-Decane–2,3-DMB	
0.0498	2.16	0.0540	8.70	0.0501	7.70	0.0502	15.87	0.0500	9.41
0.0999	4.26	0.1004	15.53	0.1001	14.66	0.1001	29.38	0.1001	17.54
0.1502	6.31	0.1506	22.21	0.1504	20.73	0.1500	41.08	0.1503	24.67
0.2002	8.13	0.2006	27.93	0.2007	26.16	0.1500	41.11	0.2001	30.85
0.2498	9.86	0.2507	32.90	0.2287	28.63	0.2001	50.66	0.2502	36.01
0.2998	11.38	0.3003	36.88	0.2500	30.50	0.2499	58.41	0.2997	40.04
0.3501	12.55	0.3514	40.10	0.3001	34.22	0.2998	64.67	0.3497	43.17
0.4004	13.57	0.4027	42.43	0.3498	37.03	0.3500	69.01	0.3997	45.33
0.4491	14.21	0.4506	43.77	0.3992	39.11	0.4001	71.92	0.4493	46.48
0.5000	14.61	0.5033	44.41	0.4502	40.17	0.4496	73.55	0.5004	46.88
0.5495	14.77	0.5512	43.91	0.5007	40.67	0.4982	73.36	0.5014	46.73
0.5991	14.44	0.6012	42.52	0.5494	40.17	0.5509	71.98	0.5498	46.03
0.6500	13.95	0.6507	40.33	0.5968	38.98	0.5996	69.02	0.6001	44.51
0.6996	12.95	0.7005	37.31	0.6493	36.74	0.6500	64.64	0.6494	41.87
0.7501	11.76	0.7505	33.23	0.6997	34.02	0.6996	59.06	0.6999	38.64
0.8000	10.07	0.8001	28.27	0.7494	30.16	0.7499	52.74	0.7495	34.30
0.8497	8.09	0.8502	22.52	0.8009	25.64	0.7992	44.34	0.7995	29.22
0.8998	5.67	0.8880	17.40	0.8503	20.54	0.8497	35.03	0.8500	23.01
0.9502	2.96	0.9567	7.03	0.9000	14.43	0.8999	24.44	0.8984	16.42
				0.9500	7.66	0.9494	12.78	0.9610	6.44

Table II. Coefficients, h_j, and Standard Deviation, *s*, for Representations of H_m^E by Eq 1

	hexane isomer				
	n-C6	2-MP	3-MP	2,2-DMB	2,3-DMB
h_1	58.61	177.32	162.42	293.43	187.14
h_2	-9.87	-2.28	1.51	30.98	9.20
h_3	-4.77	-5.35	-1.63	8.99	
h_4				6.34	
s	0.04	0.08	0.07	0.14	0.09

follows: *n*-decane, 726.16; *n*-C6, 654.91; 2-MP, 648.77; 3-MP, 659.80; 2,2-DMB, 644.48; 2,3-DMB, 657.12. These are in reasonable agreement with the values complied by the Thermodynamic Research Center (*8*).

Results and Discussion

The experimental values of H_m^E for (*n*-decane–isomeric hexane) mixtures at 298.15 K are given in Table I. In all cases, *x* is the mole fraction of *n*-decane. The smoothing function

$$H_m^E/(\mathrm{J\ mol^{-1}}) = x(1-x)\sum_{j=1}^{n} h_j(1-2x)^{j-1} \qquad (1)$$

was fitted to each set of results by the method of least squares with all points assigned equal weight. The values of the coefficients h_j obtained from the analysis are listed in Table II along with the standard deviation of the representation. Plots of the experimental results and their representation by eq 1 are shown in Figure 1.

As already mentioned, there have been several previous calorimetric studies of (*n*-decane–*n*-C6) mixtures. The measurements by McGlashan and Morcom (*4*) were carried out at 293.15 K and are not directly comparable to our results. More recently, values of H_m^E at 298.15 K were reported by Marsh et al. (*5*), and by Heintz and Lichtenthaler (*6*). As shown in Figure 1, our results fall consistently between these two sets. Thus, at $x = 0.5$, the smoothed values of H_m^E are 14.35 (*5*), 14.65 (present work), and 15.15 (*6*) J mol^{-1}.

The magnitude of H_m^E for the five systems decreases in the order 2,2-DMB > 2,3-DMB > 2-MP > 3-MP > n-C6. This is the same as found for (*n*-dodecane–isomeric hexane) mixtures but differs from the order of the curves for mixtures containing shorter *n*-alkanes. For (n-C_hH_{2h+2}–isomeric hexane) mixtures with h = 6, 7, 8, 10, and 12, the order of the curves is preserved with the exception of the position of the curve for 2,3-DMB. In the latter case, the magnitude of H_m^E tends to increase relative to the other curves as the chain length of the *n*-alkane

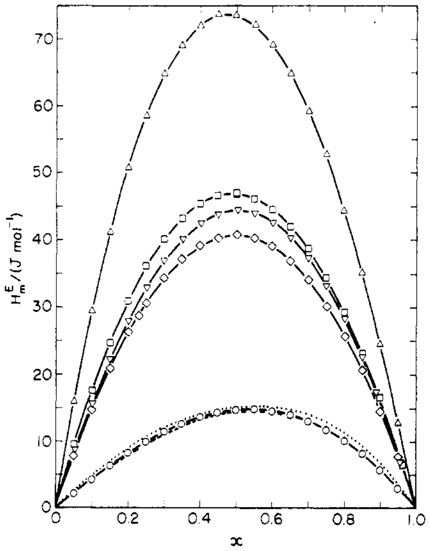

Figure 1. Excess molar enthalpy, H_m^E, of (*n*-decane–isomeric hexane) mixtures at 298.15 K and mole fraction, *x*, of *n*-decane: (○) *n*-C6; (▽) 2-MP; (◇) 3-MP; (△) 2,2-DMB; (□) 2,3-DMB. Curves (—) calculated from eq 1. Smoothed results for (*n*-decane–*n*-C6) mixtures from the literature: (---) Marsh et al. (*5*); (···) Heintz and Lichtenthaler (*6*).

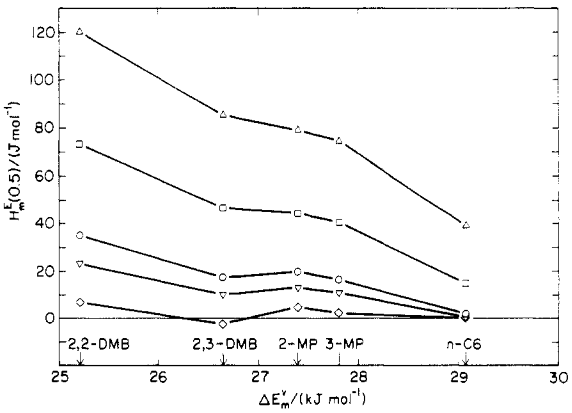

Figure 2. Excess molar enthalpy, $H_m^E(0.5)$, of equimolar binary mixtures of *n*-alkanes C_hH_{2h+2} (h = 6, 7, 8, 10, 12) with hexane isomers at 298.15 K plotted against the molar energy of vaporization, ΔE_m^v, of the isomer at 298.15 K: (◇) h = 6, Lam et al. (*9*) and Ott et al. (*10*); (▽) h = 7, Kimura et al. (*1*); (○) h = 8, Hamam et al. (*2*); (□) h = 10, present work; (△) h = 12, Hamam et al. (*3*). Points for the same *n*-alkane are joined by lines.

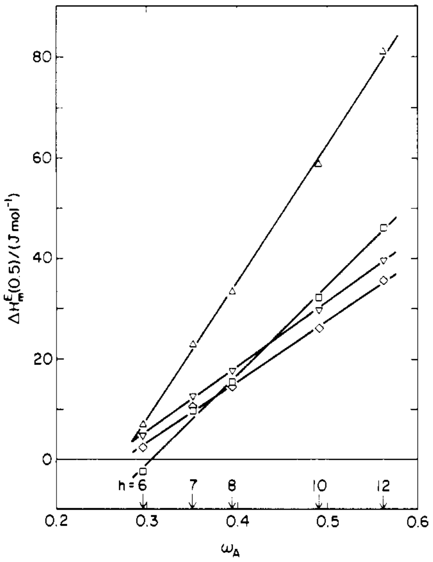

Figure 3. Difference, $\Delta H_m^E(0.5)$, between the excess molar enthalpies at 298.15 K for equimolar binary mixtures of *n*-alkanes C_hH_{2h+2} (h = 6, 7, 8, 10, 12) with hexane isomers and of the same *n*-alkanes with *n*-C6, plotted against the acentric factor, ω_A, of the *n*-alkane: (▽) 2-MP; (◇) 3-MP; (△) 2,2-DMB; (□) 2,3-DMB (see Figure 2 for sources of the enthalpy data).

increases. For h = 6, 7, 8, and 12 it was noted (*1*, *2*) that the excess molar enthalpies H_m^E (0.5) of equimolar mixtures exhibit a parallel (although nonlinear) behavior when plotted against the molar energies of vaporization ΔE_m^v of the isomers at 298.15 K, as calculated from their molar enthalpies of vaporization (*8*). Figure 2 shows that the points for the present mixtures with *n*-decane (h = 10) follow a similar behavioral pattern.

In Figure 3 $\Delta H_m^E(0.5)$, defined as the difference between $H_m^E(0.5)$ for an equimolar mixture of an *n*-alkane with a hexane isomer (*1-3*, *9*, *10*) and $H_m^E(0.5)$ for an equimolar mixture of the same *n*-alkane with *n*-C6, is plotted against the acentric factor ω_A of the *n*-alkane (*11*). The nearly linear variation observed previously (*2*) is still evident after the addition of the points representing the present results. The line for 2,3-DMB crosses those for 2-MP and 3-MP, illustrating the shifting relative behavior mentioned above.

Glossary

ΔE_m^v	molar energy of vaporization (of hexane isomer), kJ mol^{-1}
h_i	coefficient in eq 1
H_m^E	excess molar enthalpy, J mol^{-1}
s	standard deviation for least-squares fit of H_m^E, J mol^{-1}
x	mole fraction of *n*-alkane
ω_A	acentric factor of *n*-alkane

Registry No. *n*-C_6, 110-54-3; 2-MP, 107-83-5; 3-MP, 96-14-0; 2,2-DMB, 75-83-2; 2,3-DMB, 79-29-8; *n*-decane, 124-18-5.

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Aqueous Solubilities and Enthalpies of Solution of *n*-Alkylbenzenes

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Aqueous solubilities of a homologous series of five liquid *n*-alkylbenzenes, ethylbenzene through *n*-hexylbenzene, were measured in the range 7-45 °C with an automated coupled-column liquid chromatographic apparatus. Standard molar free energies, enthalpies, and heat capacity changes for the solution process were evaluated by the least-squares method of Clarke and Glew and combined with published vaporization data in order to calculate the corresponding quantities for the hydration process (g → aq). The methylene increments for free energy, enthalpy, and entropy of hydration in this series are close to those that have been determined for *n*-alkanes.

Introduction

Low-molecular-weight *n*-alkylbenzenes are hydrophobic liquids that are useful for studying the effects of alkyl chain length on the thermodynamics of the aqueous solution process. The aqueous solubilities of these compounds are conveniently measured by a coupled-column liquid chromatographic method (*1*, *2*), with the benzene moiety providing the chromophore required for UV detection. The solubilities are so low that saturated solutions are nearly ideal dilute solutions; thus accurate enthalpies and entropies of solution can in principle be obtained from the temperature dependence of the solubility. The solubility data can be combined with vaporization data available in the literature in order to calculate thermodynamic properties of the gas-to-water transfer process which is of fundamental importance in understanding hydrophobic interactions.

The aqueous solubilities of benzene and the lower *n*-alkylbenzenes each display a minimum near room temperature (*3*).

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