HEAT CAPACITIES OF BINARY MIXTURES OF n-DODECANE WITH HEXANE ISOMERS *

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ABSTRACT

Volumetric heat capacities were measured for binary mixtures of n-dodecane with 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane at 298.15 K in a Picker flow microcalorimeter. The results were combined with previously published excess molar volumes to obtain excess molar isobaric heat capacities. Use of the Flory theory of mixtures to interpret the results is discussed.

INTRODUCTION

A recent paper [1] from our laboratory reported the excess molar isobaric heat capacities for mixtures of n-dodecane with n-hexane (n-C_6). As a continuation of that work, we have made similar measurements for binary mixtures of n-dodecane with each of the four isomers of n-hexane: 2-methylpentane (2-MP), 3-methylpentane (3-MP), 2,2-dimethylbutane (2,2-DMB), and 2,3-dimethylbutane (2,3-DMB). This investigation supplements our previous studies of the excess molar enthalpies and excess molar volumes of (n-dodecane + hexane isomer) mixtures [2].

EXPERIMENTAL

n-Dodecane (99 mol%) was obtained from the Aldrich Chemical Co. The hexane isomers were Research Grade reagents with purities of 99.88 mol%

TABLE 1

Densities, ρ, and molar isobaric heat capacities, $C_{p,m}$, of the component liquids at 298.15 K

Component	ρ (kg m^{-3})		$C_{p,m}$ (J K^{-1} mol^{-1})
	Observed	Literature	
n-Dodecane	745.23	745.18 [a]	375.37 [b]
2-MP	648.60	648.52 [c]	193.84 [d]
3-MP	659.79	659.76 [c]	190.77 [d]
2,2-DMB	644.47	644.46 [c]	189.14 [d]
2,3-DMB	657.10	657.02 [c]	188.77 [d]

[a] Ref. 3, see Table 23-2-(1.101)-a, dated October 31, 1976.
[b] Present work.
[c] Ref. 3, see Table 23-2-(1.201)-a, dated October 31, 1952.
[d] Adopted from ref. 6.

or more, from the Phillips Petroleum Co. The component liquids were stored over molecular sieve pellets (BDH Type 4A) and partially degassed prior to their use. Densities of the samples for the calorimetric measurements were determined at 298.15 K in a precision density meter (Anton Paar, Model DMA 02C) and are listed in Table 1, where the values compiled by the TRC [3] are given for comparison.

Mixtures were prepared by weighing, and corrections for the effect of buoyancy were included in calculating their mole fractions. The error of the mole fraction is estimated to be less than 5×10^{-5}.

Heat capacities per unit volume were obtained from comparisons between pairs of liquids flowing in the test and reference cells of a Picker micro-calorimeter. Details of the equipment and its operation have been described previously [4,5]. A temperature interval of about 1.5 K centred on 298.15 K was used. The measurements for each system followed the stepwise procedure [5] starting with the hexane isomer as the initial reference liquid. The values adopted for the molar isobaric heat capacities of the hexanes are given in Table 1, and stem from previous comparisons with n-heptane [6].

Molar isobaric heat capacities $C_{p,m}$ were obtained from the volumetric heat capacities $C_{p,m}/V_m$, using molar volumes V_m calculated from the densities of the components and our previous results for the excess molar volumes of the mixtures [2]. Excess molar isobaric heat capacities $C_{p,m}^E$ were then calculated from the relation

$$C_{p,m}^E = C_{p,m} - xC_{p,1}^* - (1-x)C_{p,2}^* \qquad (1)$$

where x is the mole fraction of n-dodecane, and $C_{p,1}^*$ and $C_{p,2}^*$ are the molar isobaric heat capacities of the pure component liquids, n-dodecane and hexane isomer respectively. The error of $C_{p,m}^E$ is estimated to be less than 0.05 J K^{-1} mol^{-1}.

RESULTS AND DISCUSSION

The molar isobaric heat capacity of n-dodecane at 298.15 K, determined by averaging the values derived from 18 stepwise runs, each involving an indirect comparison of n-dodecane with one of the hexane isomers, is 375.37 J K^{-1} mol^{-1}. This is in good agreement with 375.26 J K^{-1} mol^{-1} obtained in a recent investigation [7] which was carried out in a different laboratory.

Values of $C_{p,m}^E$ measured for $\{xC_{12}H_{26} + (1-x)C_6H_{14}\}$ mixtures are summarized in Table 2. The smoothing equation

$$C_{p,m}^E \ (\text{J K}^{-1} \ \text{mol}^{-1}) = x(1-x) \sum_{j=1}^{n} c_j (1-2x)^{j-1} \tag{2}$$

was fitted to each set of results by the method of least squares with all points weighted equally. Values of the coefficients c_j are listed in Table 3 together with the standard deviations s of the representations.
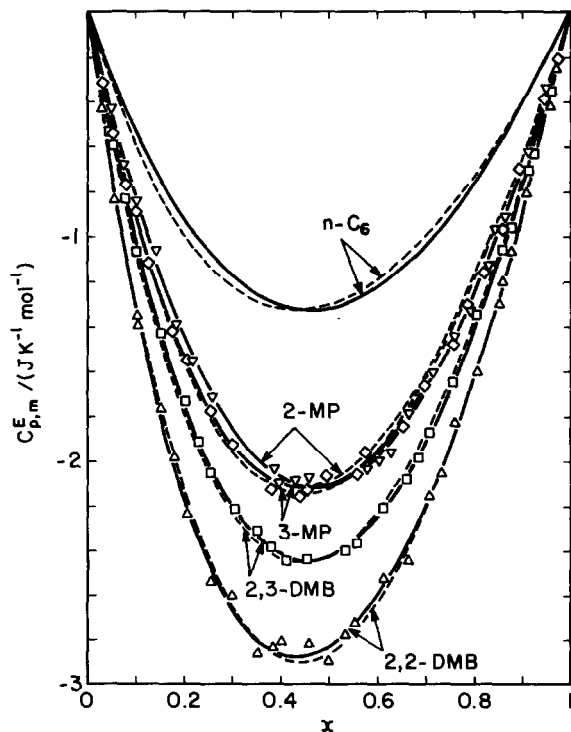

Fig. 1. Excess molar isobaric heat capacities $C_{p,m}^E$ of $xC_{12}H_{26} + (1-x)C_6H_{14}$ mixtures at 298.15 K. Experimental results: (▽) 2-MP; (◇) 3-MP; (△) 2,2-DMB; (□) 2,3-DMB. (————) calculated from eqn. (2) with coefficients from Table 3 for present results and from ref. 1 for n-C$_6$; (— — —) calculated from Flory theory with $(\partial X_{12}/\partial T)_p$ from Table 4.

TABLE 2

Excess molar isobaric heat capacities for $xC_{12}H_{26} + (1-x)C_6H_{14}$ mixtures at 298.15 K

x	$C_{p,m}^E$ (J K^{-1} mol^{-1})	x	$C_{p,m}^E$ (J K^{-1} mol^{-1})	x	$C_{p,m}^E$ (J K^{-1} mol^{-1})	x	$C_{p,m}^E$ (J K^{-1} mol^{-1})	x	$C_{p,m}^E$ (J K^{-1} mol^{-1})
n-Dodecane + 2-MP									
0.04821	−0.428	0.21698	−1.554	0.45608	−2.071	0.71406	−1.603	0.84242	−0.964
0.07363	−0.676	0.25757	−1.712	0.57783	−2.033	0.75776	−1.442	0.86267	−0.907
0.10059	−0.838	0.38471	−2.033	0.60302	−1.994	0.79061	−1.330	0.91162	−0.619
0.14110	−1.059	0.39472	−2.095	0.62681	−1.959	0.83031	−1.125	0.94734	−0.333
0.18326	−1.390	0.42826	−2.081	0.66412	−1.786				
n-Dodecane + 3-MP									
0.02953	−0.315	0.17458	−1.418	0.43801	−2.154	0.65309	−1.842	0.85760	−0.966
0.05138	−0.541	0.20533	−1.551	0.45472	−2.126	0.69607	−1.661	0.89395	−0.696
0.07824	−0.764	0.25535	−1.774	0.49416	−2.061	0.75497	−1.479	0.94405	−0.388
0.09867	−0.887	0.30084	−1.923	0.55595	−2.059	0.78418	−1.300	0.97192	−0.208
0.12510	−1.114	0.38108	−2.126	0.57445	−1.957	0.81983	−1.154		
n-Dodecane + 2,2-DMB									
0.02913	−0.430	0.20524	−2.241	0.45818	−2.822	0.70655	−2.153	0.85835	−1.201
0.05478	−0.837	0.25512	−2.543	0.49814	−2.893	0.73236	−2.055	0.87672	−1.067
0.10081	−1.359	0.29824	−2.604	0.53395	−2.778	0.75891	−1.827	0.90732	−0.806
0.10345	−1.395	0.35293	−2.863	0.55201	−2.723	0.80488	−1.604	0.95693	−0.423
0.15258	−1.764	0.38302	−2.837	0.61110	−2.525	0.85141	−1.301	0.97172	−0.256
0.17976	−1.984	0.40131	−2.808	0.66296	−2.443				
n-Dodecane + 2,3-DMB									
0.04538	−0.531	0.22966	−1.915	0.40990	−2.446	0.65953	−2.082	0.85948	−1.055
0.05409	−0.593	0.25405	−2.053	0.45422	−2.438	0.68400	−1.977	0.87629	−0.959
0.07872	−0.829	0.30370	−2.216	0.53231	−2.398	0.70807	−1.864	0.91331	−0.701
0.10053	−1.066	0.35157	−2.309	0.55744	−2.363	0.75410	−1.646	0.92291	−0.626
0.15269	−1.430	0.37987	−2.382	0.61163	−2.208	0.80379	−1.349	0.96088	−0.349
0.20253	−1.730								

TABLE 3

Coefficients, c_j, and standard deviation, s, for least-squares representations of $C_{p,m}^E$ for $x C_{12}H_{26} + (1 - x)C_6H_{14}$ mixtures at 298.15 K by eqn. (2)

| | n-Dodecane + | | | |
	2-MP	3-MP	2,2-DMB	2,3-DMB
c_1	− 8.436	− 8.417	− 11.315	− 9.693
c_2	− 1.055	− 1.594	− 2.871	− 1.740
c_3		− 0.848	− 1.582	− 0.567
s	0.032	0.026	0.044	0.021

The experimental results and their representations by eqn. (2) are plotted in Fig. 1. Also shown is a curve for (n-dodecane + n-C_6) mixtures calculated from the smoothing function reported by Kumaran et al. [1].

We are not aware of any directly comparable studies of (n-dodecane + hexane isomer) mixtures. However, values of $C_{p,m}^E$ for (n-heptane + hexane isomer) mixtures are available [8]. For both sets of systems, $C_{p,m}^E$ is negative and the curves fall in the same order, although the curves from the present study for 2-MP and 3-MP are nearly the same, within their experimental uncertainties. The differences between the results for the two sets of systems reflect the greater dissimilarity of the component molecules. Thus the magnitude of $C_{p,m}^E$ for a (n-dodecane + hexane isomer) mixture is larger than that of the corresponding mixture with n-heptane, and the curves for the mixtures with n-dodecane are slightly more asymmetric than those with n-heptane.

Analysis of the results in terms of the Flory theory of mixtures [8,9] followed the course described recently for (n-heptane + hexane isomer) mixtures [10]. Differentiation of the Flory expression for the excess molar enthalpy [8] with respect to temperature T leads to the relation

$$C_{p,m}^E = - \left(x_1 p_1^* V_1^* / \tilde{v}_1^2 \right)(\partial \tilde{v}_1 / \partial T)_p - \left(x_2 p_2^* V_2^* / \tilde{v}_2^2 \right)(\partial \tilde{v}_2 / \partial T)_p$$
$$+ (1/\tilde{v}^2)[x_1 p_1^* V_1^* + x_2 p_2^* V_2^* - x_1 V_1^* \theta_2 X_{12}](\partial \tilde{v}/\partial T)_p$$
$$- (x_1 V_1^* \theta_2 / \tilde{v}^2)(\partial X_{12}/\partial T)_p \tag{3}$$

where in the present application, the subscripts 1 and 2 refer to n-dodecane and a hexane isomer, respectively. The characteristic pressures p^*, molar volumes V^*, and temperatures T^* for the components can be calculated from their physical properties (molar volume, isobaric thermal expansivity, and isothermal compressibility) as outlined by Abe and Flory [9]. In eqn. (3), $\tilde{v}$ denotes the reduced volume (V_m/V^*), and the derivatives $(\partial \tilde{v}/\partial T)_p$ can be evaluated from Flory's equation of state [8]. θ_2 is the site fraction for species 2, and assuming that the molecules are approximately spherical

$$\theta_2 = x_2 / \left[x_2 + x_1 (V_1^* / V_2^*)^{2/3} \right] \tag{4}$$

TABLE 4

Interchange energy parameters, X_{12}, and their temperature coefficients, $(\partial X_{12}/\partial T)_p$, both at 298.15 K, and the corresponding values of the parameters X_{12}^{∞} and T_u in eqn. (4) for (n-dodecane + hexane isomer) mixtures.

	X_{12} [a] (J cm^{-3})	$(\partial X_{12}/\partial T)_p$ (J cm^{-3} K^{-1})	X_{12}^{∞} (J cm^{-3})	T_u (K)
n-C$_6$	2.0422	−0.02749	0.4074	239
2-MP	3.2076	−0.05230	0.5472	247
3-MP	3.0034	−0.05563	0.4605	252
2,2-DMB	4.4466	−0.07707	0.7209	250
2,3-DMB	3.2283	−0.06715	0.4482	257

[a] Ref. 2.

In Flory's original formulation, the interchange energy parameter X_{12} was considered to be independent of T. However our previous work [10] shows that it is necessary to treat X_{12} as a function of T, since the last term in eqn. (3) can be relatively significant. Heintz and Lichtenthaler [11] also considered X_{12} to be dependent on T, and assumed that its variation could be represented by the equation

$$X_{12}(T) = X_{12}^{\infty}T/(T - T_u) \qquad (5)$$

where X_{12}^{∞} is the limiting value of $X_{12}(T)$ for $T \rightarrow \infty$, and T_u is a fictive transition temperature for the disruption of some ordered structure.

Values of p^*, V^*, and T^* for the pure components were taken from ref. 2, where their sources are indicated. The values of X_{12}, determined to give least-squares fits between the experimental and theoretical excess molar enthalpy curves for (n-dodecane + hexane isomer) mixtures [2], were also adopted. Eqn. (3) was then fitted to the representations of the $C_{p,m}^{E}$ results by eqn. (2), using a least-squares procedure in which $(\partial X_{12}/\partial T)_p$ was adjusted. The values of $(\partial X_{12}/\partial T)_p$, obtained in this way, are listed in Table 4 where the corresponding results for X_{12}^{∞} and T_u are also given.

The broken curves in Fig. 1, calculated from eqn. (4) using the values of $(\partial X_{12}/\partial T)_p$ from Table 4, agree well with the curves representing the smoothed experimental results. If $(\partial X_{12}/\partial T)_p$ is assumed to be zero, the curves calculated for the five systems fall above the experimental curve for (n-dodecane + n-C$_6$) and the estimates of $C_{p,m}^{E}$ ($x = 0.5$) are limited to the narrow range from -0.47 to -0.60 J K^{-1} mol^{-1}. Thus the calculations again show that the contribution of the last term in eqn. (4) is very important.

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