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

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ABSTRACT

Volumetric heat capacities were measured for binary mixtures of *n*-heptane with *n*-hexane, 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 latter is discussed.

INTRODUCTION

Recently we have been investigating the changes in the thermodynamic properties of a binary mixture, which result from isomeric variations in the molecular configuration of one of its components. Several sets of mixtures are being studied from this point of view. One of these is the set formed by mixing *n*-heptane with each of 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 the excess enthalpies [1], excess volumes [2], and ultrasonic speeds and isentropic compressibilities [3] of these mixtures. The present paper describes determinations of their excess isobaric heat capacities.

EXPERIMENTAL

The component liquids were obtained from the Phillips Petroleum Co. The *n*-heptane was Pure Grade with a purity of at least 99 mol%, and the

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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})
	Obs.	Lit.	
n-Heptane	679.66	679.46 [a]	(224.764) [b]
n-C6	654.90	654.84 [a]	195.80
2-MP	648.62	648.52 [c]	193.92
3-MP	659.80	659.76 [c]	190.86
2,2-DMB	644.47	644.46 [c]	189.16
2,3-DMB	657.26	657.02 [c]	188.67

[a] Ref. 4, see table 23-2-(1.101)-a, dated October 31, 1977.
[b] Adopted from ref. 8.
[c] Ref. 4, see table 23-2-(1.201)-a, dated October 31, 1952.

hexane isomers were Research Grade with purities of at least 99.88 mol%. Prior to use, the liquids were stored over molecular sieves (BDH Type 4A). Densities characterizing the samples used in the calorimetric measurements were determined at 298.15 K in an Anton Paar densimeter. The results are listed in Table 1, where values compiled by the TRC [4] are given for comparison.

Heat capacities per unit volume were obtained from a series of comparisons between pairs of liquids flowing in the test and reference cells of a Picker microcalorimeter. This apparatus and its operational procedure have been described previously [5–7]. A temperature increment of about 1.5 K centred on 298.15 K was adopted. In most of the work the stepwise procedure [6] was followed, but single reference measurements were carried out in a few cases. The initial reference liquid was *n*-heptane, and a value of 224.764 J K^{-1} mol^{-1} [8] was used for its molar isobaric heat capacity.

Mixtures were prepared by weighing, and an allowance for the effect of buoyancy was included in calculating their mole fractions. The error of the latter is estimated to be less than 5×10^{-5}. 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 V_m^E [2]. Excess molar isobaric heat capacities were obtained from the relation

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

where x is the mole fraction of *n*-heptane, and $C_{p,1}^*$ and $C_{p,2}^*$ are the molar isobaric heat capacities of the pure component liquids, *n*-heptane and the hexane isomer, respectively. For the present mixtures, the error of $C_{p,m}^E$ is believed to be less than 0.02 J K^{-1} mol^{-1}.

RESULTS AND DISCUSSION

The molar isobaric heat capacities determined for the hexane isomers at 298.15 K are listed in Table 1. Each value is the average of the results from several stepwise runs and/or direct comparisons with *n*-heptane. These averages agree to within 0.1 J K^{-1} mol^{-1} with those obtained in our study of binary mixtures of 1-hexanol with samples of the hexane isomers having slightly different densities [7].

The results for the mixtures are summarized in Table 2, where $C^{E}_{p,m}$ is given for various mole fractions, x, of *n*-heptane. The Redlich–Kister equation

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

was fitted to each set of results. Values of the coefficients c_j, determined by the method of unweighted least-squares, are listed in Table 3 along with the standard deviations s of the representations.

The experimental results and their representations by eqn. (2) are plotted in Fig. 1. We are not aware of any comparable previous studies of the present mixtures. In all cases, $C^{E}_{p,m}$ is negative and nearly symmetric about $x = 0.5$. The latter observation is not unexpected in view of the similar sizes of the component molecules. At a fixed x the magnitude of $C^{E}_{p,m}(x)$ decreases in the order 2,2-DMB > 2,3-DMB > 3-MP > 2-MP > *n*-C6 which differs from that found for the excess molar enthalpies [1]. However, for both properties the largest and smallest effects are observed for 2,2-DMB and *n*-C6, respectively.

Previously [2,3], it was found that the excess molar enthalpies, excess molar volumes and excess isentropic compressibilities of (*n*-heptane + hexane isomer) mixtures could be correlated fairly satisfactorily by means of the Flory theory [9,10]. This treatment used the molar volume, isobaric thermal expansivity, and isothermal compressibility of each component liquid to calculate its characteristic pressure, p^*, molar volume, V^*, and temperature, T^*. For a mixture, the ratio s_{12} of molecular surface areas of contact was estimated from the characteristic volumes of the components, assuming the molecules to be approximately spherical. The interchange energy parameter X_{12} was determined to give a least-squares fit between the experimental and theoretical excess molar enthalpy curves.

Differentiating the Flory expression for the excess molar enthalpy [9] with respect to the temperature, T, leads to the following equation for the excess molar isobaric heat capacity

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

TABLE 2

Excess molar isobaric heat capacities for $x\mathrm{C_7H_{16}} + (1-x)\mathrm{C_6H_{14}}$ mixtures at 298.15 K

x	$C^{E}_{p,m}$ ($J\ K^{-1}\ mol^{-1}$)	x	$C^{E}_{p,m}$ ($J\ K^{-1}\ mol^{-1}$)	x	$C^{E}_{p,m}$ ($J\ K^{-1}\ mol^{-1}$)	x	$C^{E}_{p,m}$ ($J\ K^{-1}\ mol^{-1}$)
n-Heptane + *n*-C6							
0.20309	−0.058	0.40016	−0.098	0.60829	−0.087	0.75000	−0.065
0.25000	−0.047	0.47178	−0.098	0.74786	−0.050	0.79560	−0.076
0.25230	−0.064	0.50000	−0.077				
n-Heptane + 2-MP							
0.05331	−0.055	0.27670	−0.208	0.52376	−0.255	0.77540	−0.167
0.07837	−0.075	0.30579	−0.233	0.55045	−0.244	0.81093	−0.170
0.11860	−0.113	0.34862	−0.235	0.56789	−0.263	0.84868	−0.120
0.14738	−0.133	0.41964	−0.247	0.64318	−0.237	0.90190	−0.094
0.17806	−0.148	0.45007	−0.251	0.66916	−0.231	0.93132	−0.067
0.22089	−0.189	0.47354	−0.269	0.70816	−0.215	0.94637	−0.058
0.24898	−0.191	0.49945	−0.275	0.71629	−0.216	0.96983	−0.038
n-Heptane + 3-MP							
0.04967	−0.055	0.30417	−0.289	0.55631	−0.315	0.74928	−0.232
0.10445	−0.132	0.31776	−0.276	0.56580	−0.312	0.86189	−0.151
0.14745	−0.146	0.36948	−0.313	0.64817	−0.298	0.89918	−0.106
0.17443	−0.182	0.45130	−0.319	0.70118	−0.265	0.94101	−0.084
0.24575	−0.242	0.49185	−0.319	0.74373	−0.242	0.96777	−0.048

n-Heptane + 2,2-DMB							
0.02869	−0.085	0.32886	−0.608	0.55197	−0.605	0.82207	−0.372
0.05025	−0.132	0.35474	−0.645	0.59725	−0.613	0.82207	−0.353
0.10300	−0.285	0.35474	−0.594	0.59824	−0.634	0.84687	−0.289
0.12729	−0.359	0.39894	−0.674	0.65087	−0.571	0.84789	−0.300
0.15615	−0.391	0.40073	−0.625	0.65087	−0.575	0.84789	−0.284
0.18218	−0.445	0.45024	−0.674	0.70245	−0.521	0.87097	−0.288
0.20002	−0.447	0.49243	−0.683	0.70245	−0.511	0.90047	−0.218
0.20170	−0.462	0.49243	−0.629	0.70482	−0.477	0.90047	−0.227
0.22993	−0.537	0.49974	−0.660	0.75166	−0.448	0.90095	−0.182
0.25360	−0.536	0.51940	−0.661	0.76881	−0.411	0.94931	−0.115
0.30566	−0.574	0.55197	−0.621	0.79541	−0.393	0.97365	−0.050
0.30566	−0.582						
n-Heptane + 2,3-DMB							
0.02380	−0.039	0.24875	−0.368	0.49282	−0.468	0.74997	−0.331
0.04811	−0.061	0.27528	−0.390	0.49772	−0.492	0.78292	−0.301
0.07666	−0.141	0.30147	−0.415	0.52273	−0.439	0.79402	−0.274
0.10368	−0.190	0.32454	−0.434	0.55006	−0.489	0.82065	−0.232
0.11901	−0.172	0.34540	−0.420	0.57364	−0.445	0.85084	−0.255
0.14469	−0.252	0.37621	−0.467	0.59610	−0.429	0.87361	−0.176
0.14559	−0.260	0.38205	−0.468	0.62645	−0.447	0.89952	−0.174
0.17965	−0.299	0.41849	−0.457	0.66916	−0.404	0.93080	−0.117
0.20024	−0.286	0.44575	−0.466	0.70586	−0.394	0.94708	−0.095
0.21991	−0.310	0.47988	−0.483	0.71979	−0.363	0.96889	−0.047

TABLE 3

Coefficients, c_j, and standard deviation, s, for least-squares representation of $C_{p,m}^{E}$ for $xC_7H_{16}+(1-x)C_6H_{14}$ mixtures at 298.15 K by eqn. (2)

	n-Heptane +				
	n-C6	2-MP	3-MP	2,2-DMB	2,3-DMB
c_1	−0.3514	−1.0432	−1.2869	−2.6245	−1.8780
c_2				−0.4292	−0.1354
s	0.013	0.008	0.009	0.018	0.017

where $\tilde{v}$ denotes the reduced volume, θ is the site fraction, and the derivatives $(\partial\tilde{v}/\partial T)_p$ can be evaluated from Flory's equation of state. In the present application, the subscripts 1 and 2 refer to *n*-heptane and the hexane isomer, respectively. Insertion in eqn. (3) of the values of p^*, V^*, T^*, s_{12} and X_{12} from ref. 2, leads to small negative values of $C_{p,m}^{E}$ which are significantly

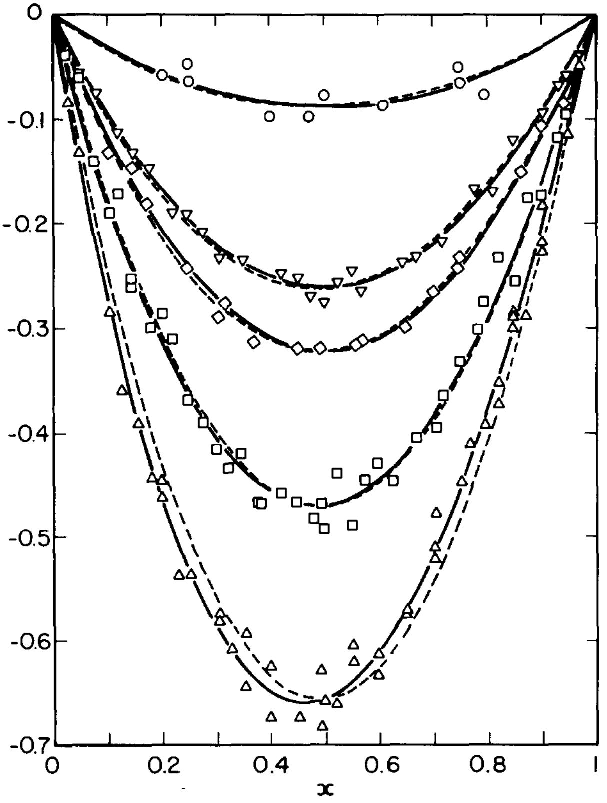

Fig. 1. Excess molar isobaric heat capacities $C_{p,m}^{E}$ of x-$C_7H_{16}+(1-x)C_6H_{14}$ mixtures at 298.15 K. Experimental results: (○) *n*-C6; (▽) 2-MP; (◇) 3-MP; (△) 2,2-DMB; (□) 2,3-DMB. (———) calculated from eqn. (2) with coefficients from Table 3; (— — —) calculated from eqn. (5) with $(\partial X_{12}/\partial T)_p$ from Table 4.

smaller in magnitude than the experimental results. For equimolar mixtures the estimates of $C_{p,m}^{E}$ from eqn. (3) amount to only 40 and 10% of the experimental results for *n*-C6 and 2,2-DMB, respectively. Similar discrepancies have been reported recently for binary *n*-alkane mixtures by Rodriguez and Patterson [11] who also noted that the temperature dependence of $C_{p,m}^{E}$ predicted by the theory differs in sign from that found experimentally for those mixtures. They suggested [12] that in addition to the exchange interaction and equation of state terms considered by the Flory theory, changes in orientational order may also contribute to the excess thermodynamic functions of mixtures.

According to Flory's formulation X_{12} is independent of T, however, in applying the theory to cyclohexane + *n*-alkane mixtures, Heintz and Lichtenthaler [13] found that a temperature-dependent X_{12} was needed to fit the excess enthalpies at different temperatures. They assumed that the variation of X_{12} could be represented by the equation

$$X_{12}(T) = X_{12}^{\infty} T/(T - T_u) \tag{4}$$

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

If the Flory theory is extended empirically by considering X_{12} to depend on T, a term in $(\partial X_{12}/\partial T)_p$ must be added to the expression for $C_{p,m}^{E}$

$$C_{p,m}^{E} = C_{p,m}^{E}[\text{eqn. (9)}] - \frac{x_1 V_1^* \theta_2}{\tilde{v}^2}\left(\frac{\partial X_{12}}{\partial T}\right)_p \tag{5}$$

Values of $(\partial X_{12}/\partial T)_p$ at 298.15 K, determined by a least-squares fitting of eqn. (5) to our smoothed results, are listed in Table 4 along with the corresponding values of X_{12}^{∞} and T_u obtained by assuming that eqn. (4) is valid. The broken curves in Fig. 1 were calculated from eqn. (5) using the values of $(\partial X_{12}/\partial T)_p$ from Table 4. For the most part these agree with our experimental results within the experimental uncertainty of the latter. A reconsideration of the excess isentropic compressibilities κ_S^E of (*n*-heptane +

TABLE 4

Exchange interaction 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*-heptane + hexane isomer) mixtures

Hexane isomer	X_{12} [a] (J cm^{-3})	$(\partial X_{12}/\partial T)_p$ ($\text{J cm}^{-3}\,\text{K}^{-1}$)	X_{12}^{∞} (J cm^{-3})	T_u (K)
n-C6	0.1097	−0.00239	0.01465	258
2-MP	0.6041	−0.00997	0.10204	248
3-MP	0.4880	−0.01381	0.05170	267
2,2-DMB	1.0346	−0.02794	0.11430	265
2,3-DMB	0.4435	−0.02107	0.02924	278

[a] Ref. 2.

hexane isomer) mixtures [3] also tends to support the present treatment. Our previous estimates of κ_S^E from the Flory theory assumed $(\partial X_{12}/\partial T)_p = 0$. Correcting those estimates on the basis of the values of $(\partial X_{12}/\partial T)_p$ in Table 4 decreases the discrepancies between theory and experiment for equimolar mixtures in all cases except for *n*-C6. Thus, for 2,2-DMB the discrepancy is decreased by about 1.0 TPa^{-1} but for *n*-C6 it is increased by only 0.1 TPa^{-1}. However, this support of the present approach is rather indirect and it is clear that further comparisons with the results of excess enthalpy and excess isobaric heat capacities at other temperatures are needed to assess its usefulness more directly.

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