

EXCESS HEAT CAPACITIES OF BINARY MIXTURES OF CARBON TETRACHLORIDE WITH *n*-ALKANES AT 298.15 K

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(Received 27 June 1978)

ABSTRACT

A Picker flow microcalorimeter was used to determine molar excess heat capacities C_p^E at 298.15 K for mixtures of carbon tetrachloride + *n*-heptane, *n*-nonane, and *n*-decane. The excess heat capacities are negative in all cases. The absolute value $|C_p^E|$ increases with increasing chain length of the alkane. A formal interchange parameter, c_{p12} , is calculated and its dependence on *n*-alkane chain length is discussed briefly in terms of molecular orientations.

INTRODUCTION

Considerable effort has been directed towards the investigation of binary liquid mixtures of *n*-alkanes¹. Several years ago², we stressed the importance of a systematic study of mixtures in which one component is a *n*-alkane and the other a simple organic substance, but until recently only few experimental data were available¹.

One aspect for this study is related to the interpretation of thermodynamic functions in terms of group contribution, i.e. the determination of the interaction (interchange) parameters within the frame of an appropriate theoretical model. Simple theories, based essentially on the rigid quasi-lattice model^{3, 4} as well as more elaborate theories have been used for the purpose of correlating or predicting molar excess Gibbs energies G^E , and molar excess enthalpies⁴ H^E .

Another interesting aspect of this topic is related to the question as to the "structure" of pure liquid *n*-alkanes, and the influence exerted upon it when various second components are added. Recently, Patterson et al.⁵⁻⁸ have accumulated evidence in favor of the existence of short range orientational order (or correlation

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of molecular orientation) in pure liquid n -alkanes, and its destruction by mixing with more or less globular molecules.

Intuitively, one would expect that decrease in order during mixing should manifest itself in a positive contribution to H^E , which should increase with (a) increasing chain length, n , of the n -alkane and (b) decreasing temperature⁵. In fact, such a behavior has been observed with systems containing isomeric (normal or branched-chain) alkanes^{5, 8}.

The interpretation of H^E data of mixtures containing n -alkanes in terms of group contribution theories corroborates the above conclusions. In the simplest zeroth approximation version, the interactional excess enthalpy term of a binary mixture is given by

$$H_{\text{int}}^E = q_1 q_2 \frac{x_1 x_2}{q_1 x_1 + q_2 x_2} h_{12} \quad (1)$$

where q_1 and q_2 denote suitably reduced surfaces of the molecular species 1 and 2, x is the mole fraction, and h_{12} is the interaction parameter (corresponding to the parameter $v^* s^{-1} X_{12}$ in the Flory theory⁹). Provided the equation of state (or free volume) contribution is properly eliminated and the n -alkane (component 2) is regarded as a homogeneous species, the parameter h_{12} should be a constant, irrespective whether component 1 is a homogeneous molecule, like CCl_4 , or a heterogeneous molecule¹⁰. However, it is often observed (e.g. with cyclohexane as second component^{6, 11}) that h_{12} increases with increasing n , thus revealing the orientational contribution. The same conclusion is reached even if the free volume contribution is neglected, i.e. if the assumption is made that $H_{\text{int}}^E \approx H^E$, and h_{12} is calculated from eqn. (1) in a conventional way³.

For many solutes, the dependence of H^E on n is fairly well represented by eqn. (1), with $H_{\text{int}}^E \approx H^E$. This may be observed if the free volume contribution is relatively small, compared with H_{int}^E , or where it is compensated, at a certain temperature, by the orientational contribution.

As pointed out by Croucher and Patterson⁸, the study of the temperature dependence of H_E , i.e. of the excess molar heat capacity C_P^E , should be of interest in assessing the relative importance of the different contributions.

Aside from the intrinsic molecular thermodynamical merit of determining C_P^E , precise C_P^E data are needed for extrapolation of other excess quantities, such as H^E or G^E , over an extended temperature range, and calculation of liquid-vapor and solid-liquid phase equilibrium diagrams¹². The Picker flow calorimeter, with its excellent precision, is particularly well suited for this task. With these objectives in view, we have started, within the frame of the "TOM Project"⁴, a rather extensive experimental program on high precision measurements of C_P^E , paralleling our efforts on H^E and molar excess volumes V^E for such binaries. In this communication, we report molar excess heat capacities at constant pressure

$$C_P^E = C_{Pm} - (x_1 C_{P1} + x_2 C_{P2}) \quad (2)$$

for the three systems $\text{CCl}_4(1) + n\text{-heptane}(2)$, $\text{CCl}_4(1) + n\text{-nonane}(2)$, and $\text{CCl}_4(1) + n\text{-decane}(2)$ at 298.15 K. The subscripts m , 1, and 2 denote, respectively, mixture, pure component 1, and pure component 2; C_p is the molar heat capacity at constant pressure.

EXPERIMENTAL

Molar heat capacities C_p were determined with a Picker-type flow microcalorimeter^{13, 14}. The calorimeter was used in the stepwise mode, that is the volumetric heat capacity, C_p/V (V being the molar volume), of the liquid under investigation is related to that of the reference liquid, $(C_p/V)_0$, by

$$C_p/V = (C_p/V)_0[1 + (\Delta W/W)] \quad (3)$$

Here, W is the initial heating power (ca. 20 mW) applied to both measuring and reference cells, and ΔW is the change in power to keep the temperature gradients equal in both cells. A temperature increment of about 1 K, centered on 298.15 K, was used for all measurements. Results refer to a mean temperature of $T/\text{K} = 298.15 \pm 0.10$. The imprecision of the molar excess heat capacities is believed to be less than $\pm 0.03 \text{ JK}^{-1}\text{mole}^{-1}$.

Densities of the pure liquids were measured with a vibrating tube densimeter^{14, 15} (from Sodev, Inc., Sherbrooke, Canada) operating under flow conditions. Binary mixtures were prepared by mass. The possible error of the mole fractions is estimated to be less than 0.0001. All molar quantities are based on the relative atomic mass table of IUPAC, 1975. Specifically, 1.0079(H), 12.011(C), and 35.453(Cl).

Source and purity of the solvents have been given elsewhere¹⁶. They were carefully dried with molecular sieve, and partially degassed. Phillips Research Grade n -heptane (lot 1405) of stated purity > 99.92 moles per cent was used as ultimate reference liquid. For its molar heat capacity, we adopted the value¹³ $C_p = 224.781 \text{ JK}^{-1}\text{mole}^{-1}$.

RESULTS

Experimental results pertaining to the pure liquids are summarized in Table 1. In order to convert C_p/V of the mixtures to C_p , we utilized literature data¹⁷⁻¹⁹ for V_E . Table 2 gives C_p^E at 298.15 K for each system. These data were fitted by the method of least squares with a smoothing polynomial

$$C_p^E/\text{JK}^{-1}\text{mole}^{-1} = x_1x_2 \sum_{i=0}^{m-1} A_i(x_1 - x_2)^i \quad (4)$$

The coefficients A_i and the standard deviation

$$\sigma = \left\{ \sum [C_p^E(\text{expt.}) - C_p^E(\text{calc.})]^2 / (N - m) \right\}^{1/2} \quad (5)$$

are given in Table 3. All C_p^E vs. x_1 curves are noticeably skewed towards higher mole fractions (x_1) of CCl_4 , the minimum being near $x_1 \approx 0.6$ (Fig. 1).

TABLE 1

MOLAR HEAT CAPACITY C_P AND DENSITY d OF THE PURE LIQUIDS AT 298.15 K AND ATMOSPHERIC PRESSURE

Substance	$C_P/\text{JK}^{-1} \text{ mole}^{-1}$		$d/10^3 \text{ kg m}^{-3}$	
	This work ^a	Literature	This work	Literature
<i>n</i> -Heptane	224.57	224.781 ^b	0.67933	0.67951 ^c
<i>n</i> -Nonane	284.04	284.4 ^c	0.71398	0.71381 ^c
<i>n</i> -Decane	313.30	314.5 ^c	0.72656	0.72625 ^c
Carbon tetrachloride	131.57	131.36 ^b	1.58473	1.58439 ^c

^a Molar heat capacities measured relative to *n*-heptane, Phillips Petroleum Co. Research Grade (lot 1405), using $C_P = 224.781 \text{ JK}^{-1} \text{ mole}^{-1}$ as determined by Fortier et al.¹³.

^b Ref. 14.

^c Ref. 24.

TABLE 2

MOLAR EXCESS HEAT CAPACITIES AT CONSTANT PRESSURE C_P^E AT 298.15 K OF $\text{CCl}_4(1) + n\text{-ALKANE}(2)$ MIXTURES

$\text{CCl}_4(1) + n\text{-heptane}(2)$		$\text{CCl}_4(1) + n\text{-nonane}(2)$		$\text{CCl}_4(1) + n\text{-decane}(2)$	
x_1	$C_P^E/\text{JK}^{-1} \text{ mole}^{-1}$	x_1	$C_P^E/\text{JK}^{-1} \text{ mole}^{-1}$	x_1	$C_P^E/\text{JK}^{-1} \text{ mole}^{-1}$
0.1026	-0.490	0.1037	-0.605	0.4044	-2.090
0.1753	-0.758	0.1422	-0.820	0.4153	-2.125
0.2678	-1.074	0.2927	-1.530	0.5872	-2.414
0.2748	-1.124	0.3729	-1.804	0.6565	-2.357
0.3809	-1.383	0.4765	-2.056	0.7246	-2.266
0.4879	-1.555	0.5528	-2.143	0.7786	-2.052
0.5301	-1.546	0.6246	-2.156	0.7890	-2.025
0.6434	-1.530	0.7233	-1.996	0.8421	-1.709
0.7238	-1.393	0.7935	-1.744	0.8916	-1.321
0.7733	-1.255	0.8715	-1.304	0.9410	-0.820
0.8308	-1.050	0.9340	-0.800		
0.8821	-0.819				
0.9322	-0.507				

TABLE 3

VALUES OF COEFFICIENTS A_i IN EQN. (4) DETERMINED BY LEAST SQUARES ANALYSIS, AND STANDARD DEVIATION σ , EQN. (5) (298.15 K)

System	A_0	A_1	A_2	$\sigma/\text{JK}^{-1} \text{ mole}^{-1}$
$\text{CCl}_4(1) + n\text{-heptane}(2)$	-6.178	-1.601	-0.527	0.014
$\text{CCl}_4(1) + n\text{-nonane}(2)$	-8.354	-3.176	-1.479	0.024
$\text{CCl}_4(1) + n\text{-decane}(2)$	-9.214	-3.271	-3.071	0.014

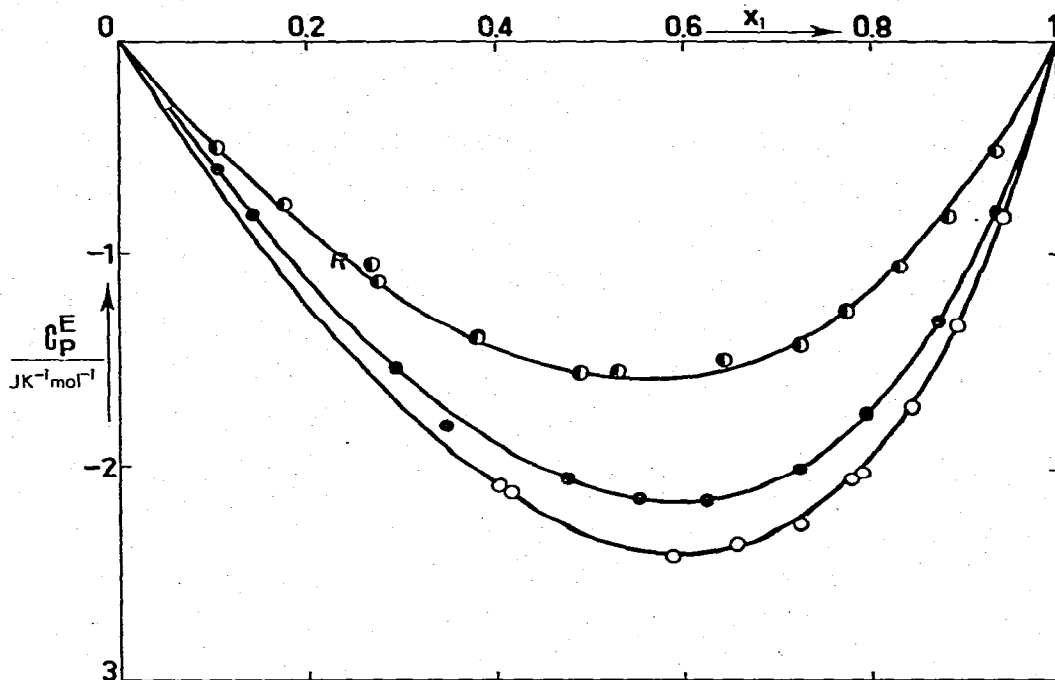


Fig. 1. Molar excess heat capacities at constant pressure C_p^E at 298.15 K. Circles denote individual experimental results; the full curves correspond to the least squares representation by eqn. (3) with constants given in Table 3; \circ , $\text{CCl}_4(1) + n\text{-heptane}(2)$; \bullet , $\text{CCl}_4(1) + n\text{-nonane}(2)$; \circ , $\text{CCl}_4(1) + n\text{-decane}(2)$.

Only two direct determinations of C_p^E could be found in the literature for mixtures of CCl_4 with n -alkane. The first²⁰, for $\text{CCl}_4(1) + n\text{-heptane}(2)$ yields $C_p^E = -2.03 \text{ JK}^{-1} \text{ mole}^{-1}$ at $x_1 \approx 0.7$, and is considerably more negative than ours ($-1.45 \text{ JK}^{-1} \text{ mole}^{-1}$). The second²¹, for $\text{CCl}_4(1) + n\text{-hexadecane}(2)$, $C_p^E = -(2.5 \pm 1.5) \text{ JK}^{-1} \text{ mole}^{-1}$ at $x_1 \approx 0.5$, provides merely a plausible estimate. The C_p^E value of $\text{CCl}_4(1) + n\text{-heptane}(2)$ derived from published²² excess enthalpies at 293.15, 303.15 and 313.15 K, averaged over the entire temperature range, is $-1.47 \text{ JK}^{-1} \text{ mole}^{-1}$ at $x_1 = 0.5$, in good agreement with our result ($-1.545 \text{ JK}^{-1} \text{ mole}^{-1}$).

DISCUSSION

Positive values of H^E and very small values of C_p^E are to be expected for mixtures of simple nonpolar molecules of similar free volume which interact primarily through dispersion forces. Weak orientation-dependent interactions in either one of the pure components gives $C_p^E < 0$. We note that for the three systems investigated, $H^E > 0$ (ref. 16) and $C_p^E < 0$. Both H^E and $|C_p^E|$ increase with increasing chain length of the n -alkane. This behavior is quite similar to that observed, say, with cyclohexane + n -alkanes¹¹.

We used eqn. (1) to calculate tentatively h_{12} and a parameter c_{p12} , defined formally as $c_{p12} = dh_{12}/dT$, using the equimolar experimental H^E (ref. 16) and C_p^E

data (neglecting free volume effects). With $q_1 = 2.4966$ and $q_2(n)$ given below³, we obtained the following results at 298.15 K.

n	q_2	$h_{12}/\text{J mole}^{-1}$	$c_{p12}/\text{JK}^{-1}\text{mole}^{-1}$
7	3.7897	462	-2.05
9	4.7207	488	-2.56
10	5.1862	492	-2.73

It is worthwhile to note that c_{p12} changes considerably more rapidly with n (33% in the range $7 \leq n \leq 10$) compared with h_{12} (6%), thus illustrating the necessity of precise C_p^E measurements. Moreover, it is interesting to observe that differences between the h_{12} parameters will become increasingly larger at lower temperatures, as expected from an increase of order. At higher temperatures, the h_{12} values will become almost constant. The behavior of cyclohexane + n -alkane¹¹ and of benzene or n -alkylbenzene + n -alkane mixtures is quite similar^{2,3}. Evidently, any detailed discussion must also consider the free volume contribution. Such a treatment, including our recent results on excess enthalpies¹⁶, is deferred to a later paper pending the availability of accurate ultrasonic velocities (isothermal compressibilities) and thermal expansivities.

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