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CALORIMETRIC EFFECTS OF SHORT-RANGE ORIENTATIONAL ORDER IN SOLUTIONS OF BENZENE OR *n*-ALKYLBENZENES IN *n*-ALKANES *

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ABSTRACT

A Picker flow microcalorimeter was used to determine molar excess heat capacities, C_p^E, at 298.15 K, as function of concentration, for the eleven liquid mixtures: benzene+*n*-tetradecane; toluene+*n*-heptane, and +*n*-tetradecane; ethylbenzene+*n*-heptane, +*n*-decane, +*n*-dodecane; and +*n*-tetradecane; *n*-propylbenzene+*n*-heptane, and +*n*-tetradecane; *n*-butylbenzene+*n*-heptane, and +*n*-tetradecane. In addition, molar excess volumes, V^E, at 298.15 K, were obtained for each of these systems (except benzene+*n*-tetradecane) and for toluene+*n*-hexane. The excess volumes which are generally negative with a short alkane, increase and become positive with increasing chain length of the alkane. The excess heat capacities are negative in all cases. The absolute $|C_p^E|$ increased with increasing chain length of the *n*-alkane. A formal interchange parameter, C_{p12}, is calculated and its dependence on *n*-alkane chain length is discussed in terms of molecular orientations.

INTRODUCTION

As pointed out recently [1] a systematic study of liquid systems in which one component is an *n*-alkane and the other a simple organic substance is important for a better understanding of the thermodynamic behavior of non-electrolyte mixtures. One aspect of this study is related to the interpretation of the thermodynamic functions in terms of group contributions [2,3]. Another aspect is the question as to the "structure" of pure liquid *n*-alkanes and the influence exerted upon it when various second components are added. Short-range orientational order (or correlation of segmental orientations [4]) in pure liquid *n*-alkanes and its destruction by mixing with more or less globular molecules has been recently observed using such molecular probes as CCl_4 [1] or cyclohexane [5].

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Decrease in order during mixing manifests itself in a positive contribution to the molar excess enthalpy, H^E, which contribution increases with (a) increasing chain length m of the n-alkane (b) decreasing temperature, T.

The scarce experimental results available to date prove that the temperature derivative of H^E, i.e. the molar excess heat capacity, C_p^E, is a much more sensitive function than H^E with respect to orientational effects. This is corroborated by a quantitative interpretation of H^E and C_p^E data of mixtures containing n-alkanes in terms of group contribution theory.

In the simplest zeroth approximation version, the interactional excess enthalpy term of a binary mixture is given by

$$H^E = q_1 q_2 \frac{x_1 x_2}{q_1 x_1 + q_2 x_2} h_{12} \tag{1}$$

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 interchange enthalpy. 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 or a heterogeneous molecule. In fact, it has been observed with CCl_4 [1] and cyclohexane [6,7] which are homogeneous molecules that h_{12} increases with increasing m, 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 $H_{int}^E \simeq H^E$, and h_{12} is calculated from eqn. (1) in a conventional way [3].

Differentiation of H_{int}^E with respect to T, assuming q_i constant, yields an equation for $C_{p\,int}^E$ similar to eqn. (1)

$$C_{p\,int}^E = q_1 q_2 \frac{x_1 x_2}{q_1 x_1 + q_2 x_2} C_{p12} \tag{2}$$

where C_{p12} represents a formal excess heat capacity of interchange.

The values of C_{p12} calculated from eqn. (2) for CCl_4 [1] were found to depend on m much more than h_{12}. The same conclusion is reached when examining the H^E and C_p^E of cyclohexane + n-alkane mixtures.

As a consequence, the study of C_p^E is of interest in assessing the relative importance of the different contributions to the excess functions. Furthermore precise C_p^E data are needed for extrapolation of other excess quantities, such as H^E or the molar excess Gibbs energy, G^E, over an extended temperature range, and calculation of liquid–vapor and solid–liquid phase equilibrium diagrams [8].

The purpose of the present work was to investigate another homogeneous molecule, benzene, and the first four members of the series of n-alkylbenzenes. The latter are heterogeneous molecules consisting of a phenyl group, C_6H_5-, and aliphatic groups, $-CH_2-$ or $-CH_3$. We measured the molar heat capacities, C_p, at constant pressure and 298.15 K of the following eleven systems: benzene (1) + n-tetradecane (2); toluene (1) + n-heptane (2), and + n-tetradecane; ethylbenzene (1) + n-heptane (2), + n-decane (2) + n-dodecane (2), and + n-tetradecane (2); n-propylbenzene (1) + n-heptane (2), and + n-tetradecane (2); n-butylbenzene (1) + n-

heptane (2) and *n*-tetradecane (2) and calculated

$$C_p^E = C_p - (x_1 C_{p1} + x_2 C_{p2}) \qquad (3)$$

The subscripts 1 and 2 denote, respectively, pure component 1 and pure component 2.

EXPERIMENTAL

Materials

The hydrocarbons were commercial products (Fluka) and stated purities ≥ 99 mole per cent. They were carefully dried with a molecular sieve (Union Carbide Type 4A), and used without further purification. Phillips research grade *n*-heptane (lot 1405) of stated purity > 99.92 mole per cent was used as an ultimate reference liquid. For its molar heat capacity we adopted the value [9] $C_p = 224.781$ J K^{-1} mole^{-1} at 298.15 K and the corresponding density $d = 679.43$ kg m^{-3}.

Apparatus and procedure

Volumetric heat capacities C_p/V (V being the molar volume) were determined with a Picker flow microcalorimeter [10,11] from Setaram, using the stepwise procedure. Details as to experimental technique and accuracy attainable with non-electrolyte mixtures may be found in the literature [12–15]. The molar volumes, V, and the molar excess volumes, V^E, of all the investigated mixtures (except benzene + *n*-tetradecane) were calculated from densities, d, measured with a vibrating tube densimeter from Sodev (model 01D). The molar volumes of benzene + *n*-tetradecane mixtures were calculated from pure component densities, as measured by us, and V^E taken from the literature [16].

The imprecision of the V^E and C_p^E values is estimated to be less than, respectively, 0.005×10^{-6} m^3 mole^{-1} and 0.05 J K^{-1} mole^{-1}.

Results

In general the experimental results for the pure substances, C_p and d, agree satisfactorily with the most reliable literature data [17–19]. Larger differences were noted only for the heat capacities, C_p (298.15 K)/J K^{-1} mole^{-1}, of *n*-tetradecane (433.86, this work; 438.4, ref. 18), *n*-propylbenzene (214.30, this work; 219.7, ref. 20), and *n*-butylbenzene (242.76, this work; 243.3, ref. 20).

Since two reliable sets of direct calorimetric C_p^E data exist for mixtures of toluene + *n*-heptane [12,21], we just carried out a few check measurements. Our results [22] are in very good agreement with these two sets of data (see ref. 12). No other data were available for comparison.

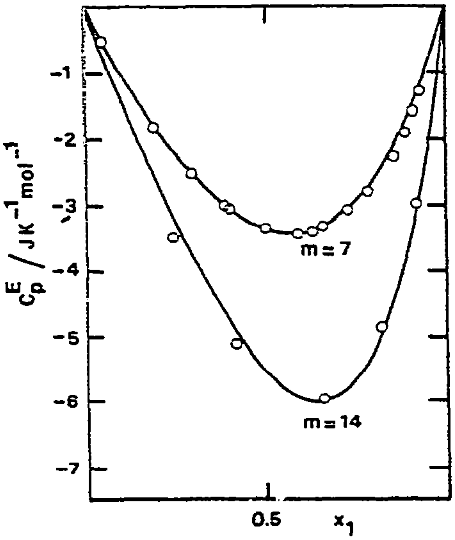
The direct experimental $C_{p,exp}^E$ values, (usually, but not less than, 5 points in the

TABLE 1

Coefficients a_i, eqn. (3), for excess molar heat capacities of $C_6H_5(CH_2)_nH(1)+CH_3(CH_2)_{m-2}CH_3(2)$ systems at 298.15 K.

n	m	a_0	a_1	a_2	a_3	a_4
0	7[a]	−13.35	−3.54	−3.60	−1.93	
	14	−22.02	−10.95	−11.50		
	7[b]	−5.4601	−1.1728	−1.0771	−0.5539	0.3292
	14	−14.95	−4.90	−4.8		
2	7	−6.498	−1.13	−2.34	−1.08	
	10	−9.921	−3.414	−1.31		
	12	−12.10	−2.90	−0.93		
	14	−17.44	−4.14	−1.76		
3	7	−5.703	−0.462	0.41		
	14	−15.808	−2.79			
4	7	−5.560	−0.746	−1.23		
	14	−17.72	−3.39	−4.77		

[a] Ref. 24; [b] ref. 12.



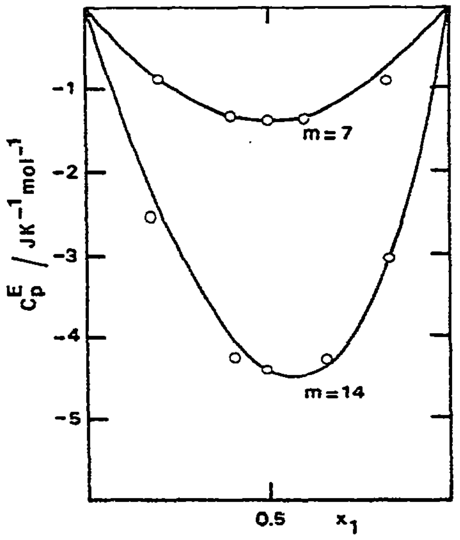


Fig. 1. Molar excess heat capacities at constant pressure, C_p^E, at 298.15 K, of benzene+n-heptane ($m=7$) or +n-tetradecane ($m=14$) versus x_1, the mole fraction of benzene. Full lines, calculated by means of eqn. (2) with $q_1=2.0724$, $q_2=3.7897$ ($m=7$) or $q_2=7.0483$ ($m=14$) and C_{p12} of Table 2. Circles denote individual experimental results.

Fig. 2. Molar excess heat capacities at constant pressure, C_p^E, at 298.15 K, of n-butylbenzene+n-heptane ($m=7$) or n-tetradecane ($m=14$) versus x_1, the mole fraction of the n-alkylbenzene. Full lines, calculated by means of eqn. (2) with $q_1=3.9655$, $q_2=3.7897$ ($m=7$) or $q_2=7.0483$ ($m=14$) and C_{p12} of Table 2. Circles denote individual experimental results.

range $0.2 < x_1 < 0.8$) were fitted by least squares to the equation

$$C^{E}_{p,calc}/\text{J K}^{-1}\text{ mole}^{-1} = x_1 x_2 \sum_{i=0}^{n-1} a_0(x_1 - x_2)^i \qquad (3)$$

The coefficients a_i are given in Table 1. In view of the small number of points, eqn. (3) should be used only for calculating the integral value of C_p^E (not the partial molar) in the specified concentration range.

For toluene + n-heptane we have reported the a_i coefficients calculated by Fortier and Benson [12] from their own measurements: 9 points in the range $0.09 < x_1 < 0.9$. The coefficients a_i of benzene + n-heptane have been determined prevoiusly [24].

All our direct experimental C_p^E and V^E data are published elsewhere [22,23]. The C_p^E data are represented in part in Figs. 1 and 2.

DISCUSSION

The H^E of all the mixtures investigated are positive and are due essentially to the interchange of the alkane–alkane and the relatively stronger Π–Π (benzene or phenyl) interactions with the relatively weaker alkane–Π interactions [25].

The anisotropic Π–Π interactions decrease with increasing temperature, which explains the negative C_p^E. Both H^E and $|C_p^E|$ increase with increasing chain lentgh m of the n-alkane.

The interchange parameters h_{12} and C_{p12}, eqns. (1) and (2), calculated from the equimolar experimental H^E and C_p^E (neglecting free-volume effects), are given in Table 2. It follows quite clearly that h_{12} is almost constant for a given aromatic solute in the range $m = 7$ to $m = 16$, whereas C_{p12} decreases rapidly with m in the range $m = 7$ to $m = 14$. We attribute this effect to orientational order changes in n-alkanes, the same as is claimed to occur in the n-alkane + CCl_4 or + cyclohexane systems.

The variation of C_{p12} is less accentuated for benzene, probably due to a better mutual correlation of the molecular orientations of benzene with n-alkanes [26].

TABLE 2

Interchange parameters h_{12} and C_{p12} eqns. (1) and (2), for C_6H_5R + n-heptane ($m = 7$), n-tetradecane ($m = 14$), or n-hexadecane ($m = 16$) at $T = 298.15$ K. (R = H, Me, Et, n-Pr, n-Bu)

R	h_{12}/J mole^{-1}		C_{p12}/J K^{-1} mole^{-1}	
	$m = 7$	$m = 16$	$m = 7$	$m = 14$
H	1393 [a]	1478 [a]	−5.04	−6.88
Me	721 [a]	750 [a]	−1.78	−3.97
Et	657 [b]	667 [b]	−1.93	−4.11
n-Pr	489 [c]	493 [d]	−1.57	−3.38
n-Bu	382 [b]	377 [b]	−1.43	−3.49

H^E data taken from following sources: [a] ref. 27; [b] ref. 28; [c] ref. 29; [d] interpolated from data reported in ref. 27.

Equation (1), which represents reasonably well H^E for n-alkylbenzenes + n-alkanes [3], using a parameter h_{12} independent of m, cannot be applied, as eqn. (2) to correlate C_p^E by means of a constant parameter C_{p12}. However, with an adjusted C_{p12}, the composition dependence of C_p^E is represented satisfactorily by eqn. (2), as shown for example in Figs. 1 and 2.

It is noteworthy that the composition dependence of C_p^E of CCl_4 + n-alkanes is also well described by eqn. (2), using the corresponding q_i values. A more careful comparison reveals however that the symmetry of the curves, predicted by eqns. (1) and (2), is poorer the larger the orientational order effect. A detailed discussion, considering other solutes, will be given in a later paper.

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