

## EXCESS MOLAR HEAT CAPACITY AND EXCESS MOLAR VOLUME OF 1,6-DICHLOROHEXANE + *n*-OCTANE

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### ABSTRACT

Excess molar volumes,  $V^E$ , at 298.15 K were determined, as a function of mole fraction,  $x$ , for  $\{x1,6\text{-C}_6\text{H}_{12}\text{Cl}_2 + (1-x)n\text{-C}_8\text{H}_{18}\}$ .  $V^E$  is small and shows S-shaped composition dependence. For the same mixture at the same temperature, a Picker flow calorimeter was used to determine excess molar heat capacities,  $C_p^E$ , at constant pressure.  $C_p^E$  is negative with a minimum at, roughly  $x = 0.2$ , and a pronounced, rather flat, shoulder around  $x = 0.6$ . This behavior is similar to that found previously with (1,2-dichloroethane + an *n*-alkane) and (1,4-dichlorobutane + an *n*-alkane).

### INTRODUCTION

The concept of rotational isomerism, say around a carbon–carbon single bond, has had a long and varied history, with roots going back to the latter part of the nineteenth century. The general situation up to the 1950s has been summarized in Mizushima's classic text on molecular structure and internal rotation [1]. Since then, application of modern physical methods has produced a plethora of data on conformational equilibria in pure substances. However, solvent-induced changes of such equilibria have received less attention, although, of course, it has long been realized that dissolution of a flexible molecule in a dense fluid may considerably alter the population of

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its various conformational states [2–4]. The effect of the environment is reasonably well documented for mixtures of simple, torsionally flexible molecules, say 1,2-dihaloethanes, with more or less “rigid” molecules (see, for instance, refs. 5–8). However, when both components exhibit conformational equilibria, surprisingly few systematic determinations of thermodynamic (and other physico-chemical) properties of such mixtures have been reported, despite their importance in a variety of areas, including polymer solutions and model systems of biophysical interest.

Recent measurements of excess molar heat capacities,  $C_P^E$ , of {an  $\alpha$ ,  $\omega$ -dichloroalkane  $\{\text{Cl}(\text{CH}_2)_k\text{Cl}\}$  + an  $n$ -alkane ( $n\text{-C}_l\text{H}_{2l+2}$ )} for  $k = 2$  and 4, and  $7 \leq l \leq 16$ , have revealed an unusual composition dependence of this excess quantity [9,10]. For example, for  $k = 2$  and  $l = 7$  a minimum is observed at rather small mole fraction of 1,2-dichloroethane (abbreviated 1,2-DCE),  $x_{1,2\text{-DCE}} \approx 0.3$ , and a pronounced rather flat shoulder, almost a second minimum, around  $x_{1,2\text{-DCE}} \approx 0.7$ . Two minima are indeed found for  $k = 4$  and  $l = 7$ , though the second one at mole fraction  $x_{1,4\text{-DCBu}} = 0.703$  of 1,4-dichlorobutane (1,4-DCBu) is exceedingly shallow. The main purpose of this work is to augment these data by extending the range to  $k = 6$ , and to provide thereby some information as to the influence of proximity of the two chloro-substituents upon  $C_P^E$ . We note that  $n$ -octane is homomorphic to 1,6-dichlorohexane.

## EXPERIMENTAL

1,6-Dichlorohexane (abbreviated 1,6-DCHe;  $1,6\text{-C}_6\text{H}_{12}\text{Cl}_2$ ) and  $n$ -octane ( $n\text{-C}_8\text{H}_{18}$ ) were of the best quality obtainable from Fluka. The liquids were dried with molecular sieve (Union Carbide type 4A, beads, from Fluka), stored in the dark, and used without further purification. Mixtures were prepared by mass. All molar quantities are based on the relative atomic mass table of IUPAC, 1983 [11].

Densities,  $\rho$ , were measured with a vibrating-tube densimeter from Sodev (model O2D), which was used in the flow mode. From the density, the excess molar volume,  $V^E$ , of a mixture with mole fraction  $x$  of 1,6-DCHe is obtained according to

$$\begin{aligned} V^E &= V - [xV_1^* + (1-x)V_2^*] \\ &= xM_1(1/\rho - 1/\rho_1^*) + (1-x)M_2(1/\rho - 1/\rho_2^*) \end{aligned} \quad (1)$$

Here,  $M_i$ ,  $V_i^*$  and  $\rho_i^*$  are, respectively, the molar mass, the molar volume and the density of pure component  $i = 1$  (1,6-DCHe) or  $i = 2$  ( $n$ -octane), and  $V = [xM_1 + (1-x)M_2]/\rho$  is the molar volume of the mixture.

Heat capacities per unit volume,  $C_p/V$ , were measured with a Picker flow calorimeter (from Setaram), using the stepwise procedure. They were con-

verted to molar heat capacities,  $C_p$ , at constant pressure through use of our density data. Excess molar heat capacities were then calculated from

$$C_p^E = C_p - [xC_{p,1}^* + (1-x)C_{p,2}^*] \quad (2)$$

where  $C_{p,i}^*$  is the molar heat capacity of pure component  $i$  ( $= 1$  or  $2$ ). Details of the experimental techniques may be found in previous publications or our group, say in refs. 8, 12–14.

## RESULTS

For the pure liquids, at 298.15 K, we measured the following: for 1,6-dichlorohexane,  $\rho_1^* = 1064.39 \text{ kg mol}^{-1}$  and  $C_{p,1}^* = 239.57 \text{ J K}^{-1} \text{ mol}^{-1}$ ; for *n*-octane,  $\rho_2^* = 698.62 \text{ kg mol}^{-1}$  and  $C_{p,2}^* = 254.18 \text{ J K}^{-1} \text{ mol}^{-1}$ . For *n*-octane, agreement with reliable values from the literature [14–16] is excellent. For 1,6-DCHe, Müller and Vanc [17] report  $\rho_1^* = 1067.7 \text{ kg mol}^{-1}$  at 293.15 K, which is in reasonable accord with our result. We are unaware of any other literature values for the density of 1,6-DCHe, and no heat capacity data could be found for comparison.

Experimental results for  $V^E$  and  $C_p^E$  at 298.15 K of the mixture  $\{x1,6\text{-C}_6\text{H}_{12}\text{Cl}_2 + (1-x)n\text{-C}_8\text{H}_{18}\}$  are presented in Table 1, and in graphical form by Figs. 1 and 2. Adequate analytical representations of our data (least-squares fits) are provided by

$$V^E(\text{cm}^3 \text{ mol}^{-1}) = x(1-x) \left[ -0.6136 - 0.6136(2x-1) + 0.3075(2x-1)^2 - 0.1254(2x-1)^3 \right] \quad (3)$$

with a standard deviation  $\sigma = 0.001_5 \text{ cm}^3 \text{ mol}^{-1}$ , and by

$$C_p^E(\text{J K}^{-1} \text{ mol}^{-1}) = x(1-x) \left[ -1.770 + 0.294(2x-1) - 3.099(2x-1)^2 + 3.236(2x-1)^3 \right] \quad (4)$$

with  $\sigma = 0.01_1 \text{ J K}^{-1} \text{ mol}^{-1}$ . The full curves were obtained through use of

TABLE 1

Excess molar volumes,  $V^E$ , and excess molar heat capacities,  $C_p^E$ , as functions of mole fraction,  $x$ , for  $\{x1,6\text{-C}_6\text{H}_{12}\text{Cl}_2 + (1-x)n\text{-C}_8\text{H}_{18}\}$  at 298.15 K

$x$	$V^E$ ( $\text{cm}^3 \text{ mol}^{-1}$ )	$C_p^E$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$x$	$V^E$ ( $\text{cm}^3 \text{ mol}^{-1}$ )	$C_p^E$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )
0.0834	0.0140	-0.465	0.6034	-0.1746	-0.425
0.1571	-0.0006	-0.591	0.7017	-0.1730	-0.402
0.2183	-0.0260	-0.581	0.7688	-0.1572	-0.348
0.2956	-0.0630	-0.547	0.8494	-0.1167	-0.255
0.4029	-0.1158	-0.485	0.9244	-0.0698	-0.125
0.5181	-0.1571	-0.461			

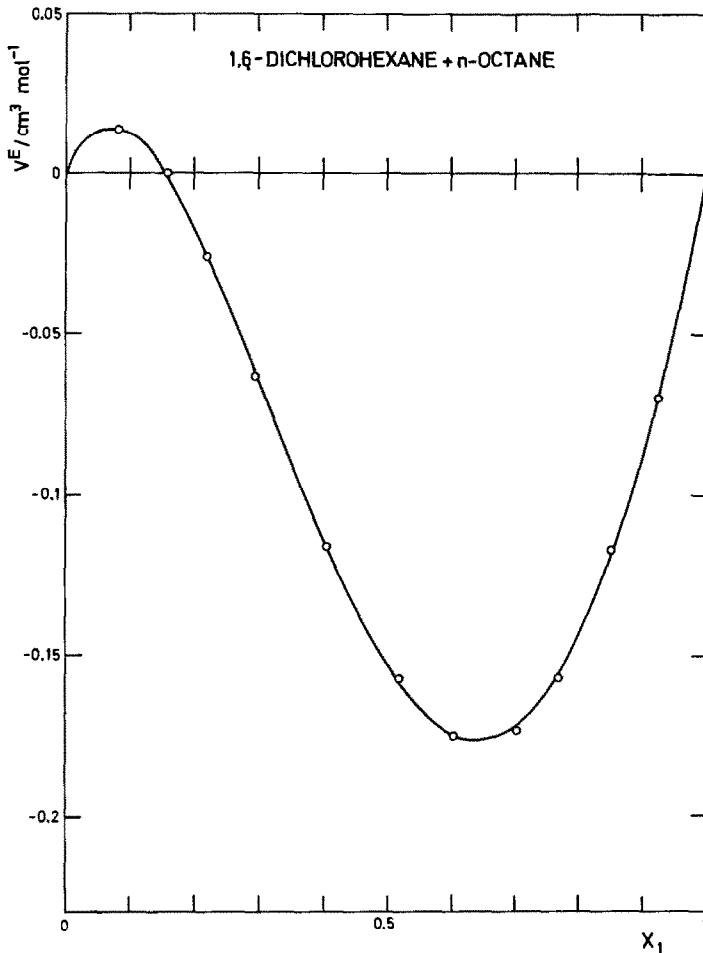


Fig. 1. Excess molar volumes,  $V^E$ , of  $\{x1,6\text{-C}_6\text{H}_{12}\text{Cl}_2 + (1-x)n\text{-C}_8\text{H}_{18}\}$  at 298.15 K. Circles denote experimental points, the curve has been calculated from eqn. (3).

eqns. (3) and (4), respectively. No literature results could be found for comparison.

#### DISCUSSION

The magnitude of the excess molar volume and its S-shaped composition dependence are similar to the results obtained with 1,4-DCBu + *n*-heptane [10], but quite different from those with 1,2-DCE + *n*-heptane [9]. For the latter mixture,  $V^E$  is positive over the whole composition range and much larger:  $V^E(x_{1,2\text{-DCE}} = 0.5) = 0.918 \text{ cm}^3 \text{ mol}^{-1}$  at 298.15 K.

Definitely the most interesting aspect of this work concerns the variation of the excess molar heat capacity with composition. The shape of the curve  $C_P^E$  vs.  $x$  is strikingly similar to that found previously within the series

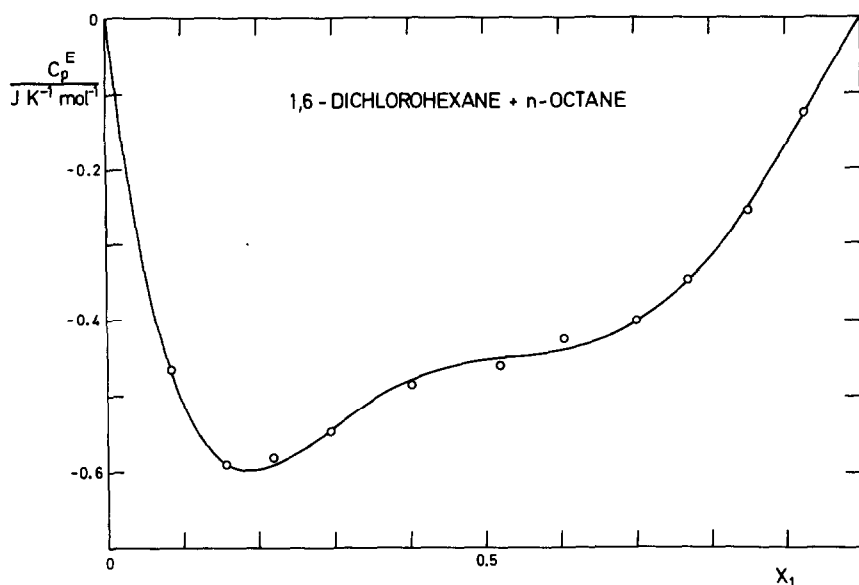


Fig. 2. Excess molar heat capacities,  $C_p^E$ , at constant pressure of  $\{x_{1,6}\text{-C}_6\text{H}_{12}\text{Cl}_2 + (1-x)n\text{-C}_8\text{H}_{18}\}$  at 298.15 K. Circles denote experimental points, the curve has been calculated from eqn. (4).

(1,2-DCE + an *n*-alkane) [9], i.e.,  $k = 2$ , and (1,4-DCBu + an *n*-alkane) [10], i.e.,  $k = 4$ . The minimum is situated around  $x_{1,6\text{-DCHe}} = 0.2$ , and a very broad shoulder extends, roughly, over the range  $0.5 < x_{1,6\text{-DCHe}} < 0.7$ . As concerns the magnitude of the excess heat capacity, comparison is possible only with mixtures of *n*-heptane with 1,4-DCBu or 1,2-DCE. While  $C_p^E$  of the former is about the same as for 1,6-DCHe + *n*-octane,  $C_p^E$  of 1,2-DCE + *n*-heptane is much more negative, thus paralleling the trend observed with  $V^E$ .

In summary, the present results support the contention [9,10] that the unusual composition dependence of  $C_p^E$  in mixtures of  $\alpha,\omega$ -dichloroalkanes with *n*-alkanes (and in similar systems) is linked (a) to the existence of conformers with distinctly different polarity (for instance, *trans* and *gauche* rotamers in 1,2-DCE), and (b) to the quite different interaction of these conformers with the flexible molecules of the *n*-alkane. In general, the population of the various conformational states of  $\text{Cl}(\text{CH}_2)_k\text{Cl}$  will change through addition of the *n*-alkane, whose rotamer population itself will be influenced by the changing environment. Systematic investigations along these lines are in progress [18,19].

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