

MOLAR HEAT CAPACITY OF BINARY LIQUID MIXTURES: 1,2-DICHLOROETHANE + CYCLOHEXANE AND 1,2-DICHLOROETHANE + METHYLCYCLOHEXANE

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ABSTRACT

The molar heat capacity at constant pressure, C_p , of the two binary liquid mixtures 1,2-dichloroethane + cyclohexane and 1,2-dichloroethane + methylcyclohexane were determined at 298.15 K from measurements of the volumetric heat capacity, C_p/V , in a Picker flow microcalorimeter (V is the molar volume). For the molar excess heat capacity, C_p^E , the imprecision of the adopted stepwise procedure is characterized by a standard deviation of about $\pm 0.05 \text{ J K}^{-1} \text{ mole}^{-1}$, which amounts to ca. 3% of C_p^E . Literature data on ultrasonic velocities, on molar volumes, and on coefficients of thermal expansion were used to calculate the molar heat capacity at constant volume, C_v , and the isothermal compressibility, β_T , of the pure substances, as well as the corresponding excess quantities C_v^E and $(V\beta_T)^E$ of the binary mixture 1,2-dichloroethane + cyclohexane. A preliminary discussion of our results in terms of external and internal rotational behavior (*trans-gauche* equilibrium of 1,2-dichloroethane) is presented.

INTRODUCTION

The molar heat capacity at constant volume of pure liquids consisting of polyatomic, nonassociating molecules may be separated¹⁻¹² according to

$$C_v = C_{tr} + C_r + C_i + C_{or} \quad (1)$$

that is, the discussion of C_v is performed in terms of contributions of various external⁹ and internal degrees of freedom of the molecules. C_{tr} denotes the translational (or configurational) contribution resulting from the translational movements of the particles within their free volumes; it is of the order $(3R/2) + R$, where R is (approximately) the excess over the translational heat capacity of the ideal gas. C_r is due to rotation or libration of the molecules as a whole. The contribution from internal

modes, C_i , can be further subdivided into a part resulting from vibrations, which is *not* appreciably influenced by changes of phase, and another part C_{conf} which results from conformational equilibria^{13, 14} (internal rotations etc.). This latter quantity may often depend rather strongly on changes in the surroundings of the molecule and thus may change appreciably when going from the gaseous to the liquid phase. Lastly, for polar substances, a further contribution, C_{or} , must be considered which results from the change of the dipole-dipole orientational energy with variation of temperature¹⁵. Preferably, all these contributions are discussed in terms of residual quantities^{8, 10}, indicated by a superscript asterisk:

$$\begin{aligned} C_v^* &= C_v(\text{liquid}) - C_v(\text{ideal gas}) \\ &= C_{\text{ir}}^* + C_r^* + C_i^* + C_{\text{or}}^* \end{aligned} \quad (2)$$

where $C_{\text{ir}}^* = C_{\text{ir}}(\text{liquid}) - C_{\text{ir}}(\text{ideal gas})$ etc., all heat capacities referring to the same temperature.

In binary mixtures, the quantity of interest is the molar excess heat capacity at constant volume

$$C_v^E = C_{v\text{m}} - (x_1 C_{v1} + x_2 C_{v2}) \quad (3)$$

with $C_{v\text{m}}$ and C_{vi} denoting the molar heat capacity of the mixture and of component $i = 1$ or 2 at mole fraction x_i , respectively. Since detailed information on the variation of the free volume of each of the components with variation of concentration is not available, we will assume, as a first approximation, that the translational heat capacity of relatively simple mixtures is additive. The rotational behavior may change with concentration; yet, in contrast to systems composed of more or less rigid molecules⁸ (e.g. CCl_4) where $C_v^E \approx C_r^E = C_r^{*E}$, a semiquantitative estimate of C_r^E for 1,2-dichloroethane (DCE) systems requires reliable estimates of C_i^E and C_{or}^E . For the system DCE + cyclohexane, the former quantity is taken to result entirely from the dependence of the conformational (*trans-gauche*) equilibrium of DCE on concentration; the latter quantity is estimated via Kohler's formalism¹⁵ of pseudoternary mixtures.

The main purpose of this paper is to provide reliable, high-precision heat capacity data. With accumulating experimental results¹¹, a more detailed treatment is envisaged.

EXPERIMENTAL

Molar heat capacities at constant pressure, C_p , of the pure liquids cyclohexane, methylcyclohexane and 1,2-dichloroethane, and of the two binary mixtures 1,2-dichloroethane (x_1) + cyclohexane (x_2), and + methylcyclohexane (x_2) were determined with a Picker-type flow microcalorimeter¹⁶⁻¹⁹ (see also ref. 10). This instrument measures directly the change of *volumetric* heat capacity, C_p/V (V being the molar volume), of a liquid relative to a reference liquid to $\pm 7 \times 10^{-8} \text{ J K}^{-1} \text{ mm}^{-3}$. Before entering the actual calorimeter, the substances are thermostatted to $\pm 0.5 \text{ mK}$. The absolute temperature is determined by a calibrated quartz thermo-

meter (Hewlett-Packard, model 2801 A). The calorimeter is essentially a thermal balance using a heating power, W , of approximately 20 mW, which at a flow rate of ca. $10 \text{ mm}^3 \text{ s}^{-1}$, corresponds to a temperature rise of about 1 K. The volumetric heat capacity of the liquid under investigation is given by

$$C_P/V = (C_P/V)_0 (1 + \Delta W/W), \quad (4)$$

where subscript 0 denotes the reference liquid and ΔW is the power added by the thermal feedback circuit to the initial power to maintain equal temperature gradients in both measuring and reference cell. Since we adopted a stepwise procedure in which the mixtures are studied in order of increasing concentration of one component, and each mixture is used as reference for the subsequent one in the series, the volumetric heat capacity of the n th mixture is given by

$$(C_P/V)_n = (C_P/V)_0 \prod_{i=1}^n (1 + \Delta W_i/W) \quad (5)$$

We note that any error in the assigned molar heat capacity of the reference liquid will be reflected by an equivalent error for the pure second component. However, for the *excess quantity*, its influence will generally be negligibly small and will rarely exceed $\pm 0.02 \text{ J K}^{-1} \text{ mole}^{-1}$ at equimolar concentration.

All substances were of Fluka puriss. quality (purity > 99.5 mole %). They were carefully dried by molecular sieve, partially degassed, and used directly without further purification. Phillips Research Grade *n*-heptane with purity > 99.92 mole % was used as ultimate reference liquid. For its molar heat capacity, we adopted the value of Fortier et al.¹⁸, i.e. $224.781 \text{ J K}^{-1} \text{ mole}^{-1}$ at 298.15 K. All molar quantities are based on the relative atomic mass table of IUPAC, 1975 (ref. 20). Specifically, $A_r(\text{H}) = 1.0079$, $A_r(\text{C}) = 12.011$, and $A_r(\text{Cl}) = 35.453$.

RESULTS

In order to convert experimental volumetric heat capacities to C_P , we utilized the volumetric data of Wilhelm et al.²¹. Results for the pure components at 298.15 K are given in Table 1. They agree satisfactorily with the most reliable literature data.

TABLE 1

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

Substance	C_P ($\text{J K}^{-1} \text{ mole}^{-1}$)	
	Expt.	Literature
Cyclohexane	156.41	156.75 (ref. 8), 156.07 (ref. 18)
Methylcyclohexane	184.75	184.54 (ref. 22), 185.14 (ref. 23)
1,2-Dichloroethane	128.95	129.54 (ref. 24), 129.35 (ref. 25), 128.60 (ref. 6), 128.99 (ref. 10)

TABLE 2

EXPERIMENTAL RESULTS OF THE MOLAR EXCESS HEAT CAPACITY C_P^E AT 298.15 K FOR THE SYSTEMS 1,2-DICHLOROETHANE(x_1) + CYCLOHEXANE AND 1,2-DICHLOROETHANE(x_1) + METHYLCYCLOHEXANE

<i>DCE(x₁) + cyclohexane</i>		<i>DCE(x₁) + methylcyclohexane</i>	
x_1	C_P^E ($J K^{-1} mole^{-1}$)	x_1	C_P^E ($J K^{-1} mole^{-1}$)
0.1633	-2.110	0.1709	-0.950
0.2645	-2.512	0.2427	-1.267
0.3877	-2.293	0.3719	-1.168
0.4931	-2.142	0.4674	-1.107
0.5776	-1.876	0.5605	-0.918
0.6996	-1.648	0.6634	-0.861
0.7859	-1.411	0.8567	-0.584
0.8922	-0.907	0.8818	-0.577

Table 2 contains the molar excess heat capacity

$$C_P^E = C_{Pm} - (x_1 C_{P1} + x_2 C_{P2}) \quad (6)$$

where C_{Pm} and C_{Pi} are the molar heat capacity of the mixture and of component i , respectively. Least squares analysis was used to fit the results for each excess function Q^E (see also below) with a polynomial of the form

$$Q^E = x_1 x_2 \sum_{i=0}^{n-1} A_i (x_1 - x_2)^i \quad (7)$$

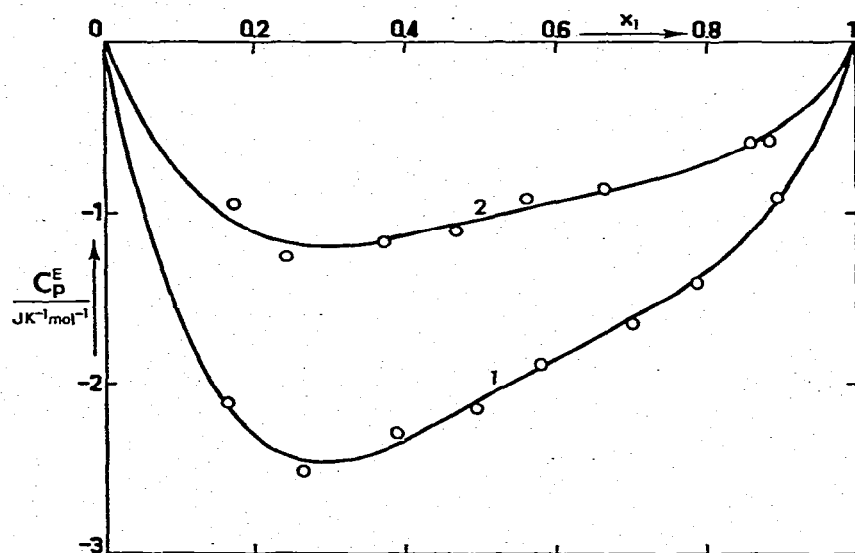


Fig. 1. Experimental molar excess heat capacities at constant pressure C_P^E at 298.15 K. Circles denote individual experimental results and the full curves correspond to the least squares representation by eqn. (7) (for the constants see Table 3). Curve 1, 1,2-dichloroethane (x_1) + cyclohexane; curve 2, 1,2-dichloroethane (x_1) + methylcyclohexane.

with n adjustable coefficients A_i (see Table 3) and with a standard deviation σ defined by

$$\sigma^2 = \frac{\sum_N [Q^E(\text{expt}) - Q^E(\text{eqn. (7)})]^2}{(N - n)} \quad (8)$$

Here, N denotes the number of experimental points.

For brevity and convenience, experimental excess molar heat capacities and their least squares representations are compared graphically in Fig. 1. At 298.15 K, C_p^E is negative for both DCE systems and considerably skewed toward the hydrocarbon side, the minimum being, in both cases, around $x_1 = 0.3$. For DCE + cyclohexane, its absolute value is about twice as large as for DCE + methylcyclohexane. A particularly interesting (and rather unusual) feature is the practically zero curvature within the (approximate) concentration range $0.4 < x_1 < 0.8$. Our results for DCE + cyclohexane agree with those of ref. 6 (interpolated) within the limits of error quoted there. No literature data are available for comparison on DCE + methylcyclohexane.

The imprecision (σ) of molar excess heat capacities for nonelectrolyte mixtures determined by this flow technique is generally of the order of $\pm 0.05 \text{ J K}^{-1} \text{ mole}^{-1}$ or less, making this method distinctly superior when compared with methods using classical absolute measurements of C_p . As already discussed^{10, 17, 19}, the stepwise procedure is to be preferred over the method using a single reference liquid, since in this way full advantage can be taken of the increased sensitivity of the apparatus.

Molar heat capacity at constant volume

The relevant equations for calculating the adiabatic compressibility $\beta_S = -V^{-1} (\partial V / \partial P)_S$, the isothermal compressibility $\beta_T = -V^{-1} (\partial V / \partial P)_T$, and the molar heat capacity at constant volume are

$$\beta_S = \frac{V}{Mu^2}$$

$$\kappa = \frac{C_p}{C_v} = \frac{\beta_T}{\beta_S} = 1 + \frac{TM\alpha^2 u^2}{C_p} \quad (9)$$

Here, $\alpha = V^{-1} (\partial V / \partial T)_P$ is the thermal expansivity, u is the ultrasonic velocity, and M is the molar mass. For the pure liquid components, the auxiliary quantities V , α and u^* were obtained from refs. 5, 8, 10, and 27 and are included in Table 4, together with C_v , β_T , and β_S .

Only for the system 1,2-dichloroethane (x_1) + cyclohexane (x_2) are all necessary data for evaluating C_v^E and the excess quantity (with appropriate subscript S or T)

$$(V\beta)^E = V_m\beta_m - [x_1V_1\beta_1 + x_2V_2\beta_2] \quad (10)$$

* There is a considerable discrepancy between the ultrasonic velocity of methylcyclohexane (at 20°C) as reported by Dexter and Matheson⁵ ($u = 1158 \text{ ms}^{-1}$) and by Schaaffs²⁸ ($u = 1247 \text{ ms}^{-1}$).

TABLE 3

VALUES OF COEFFICIENTS A_i IN EQN. (7) DETERMINED BY LEAST SQUARES ANALYSIS, AND STANDARD DEVIATION σ ($T = 298.15$ K)

System	Function Q^E	A_0	A_1	A_2	A_3	σ
DCE(x_1) + cyclohexane	C_P^E (J K ⁻¹ mole ⁻¹)	-8.363	4.992	-8.57		0.04
	$10^9 (V\alpha)^E$ (m ³ K ⁻¹ mole ⁻¹)	13.646	-0.512	-1.48	-0.67	
	$10^{15} (V\beta_S)^E$ (m ³ Pa ⁻¹ mole ⁻¹)	17.116	-7.455	1.13	-0.92	
	$10^{15} (V\beta_T)^E$ (m ³ Pa ⁻¹ mole ⁻¹)	24.662	-9.475	1.84	-1.31	
	C_V^E (J K ⁻¹ mole ⁻¹)	-4.496	3.937	-6.64		
DCE(x_1) + methylcyclohexane	C_P^E (J K ⁻¹ mole ⁻¹)	-4.143	2.117	-4.37		0.06

available^{6, 21}. The corresponding constants of the smoothing functions are also contained in Table 3, a graphical representation is given in Figs. 2-4. Considering the rather involved, conventional experimental technique of ref. 6, agreement with the results obtained there is quite satisfactory.

The inaccuracy of C_V , C_V^E , β_T and $(V\beta_T)^E$ can only be assessed roughly, since the inaccuracy of the various contributions, in particular of the thermal expansivity, is rather difficult to estimate⁸. We believe that the possible absolute error of C_V and β_T

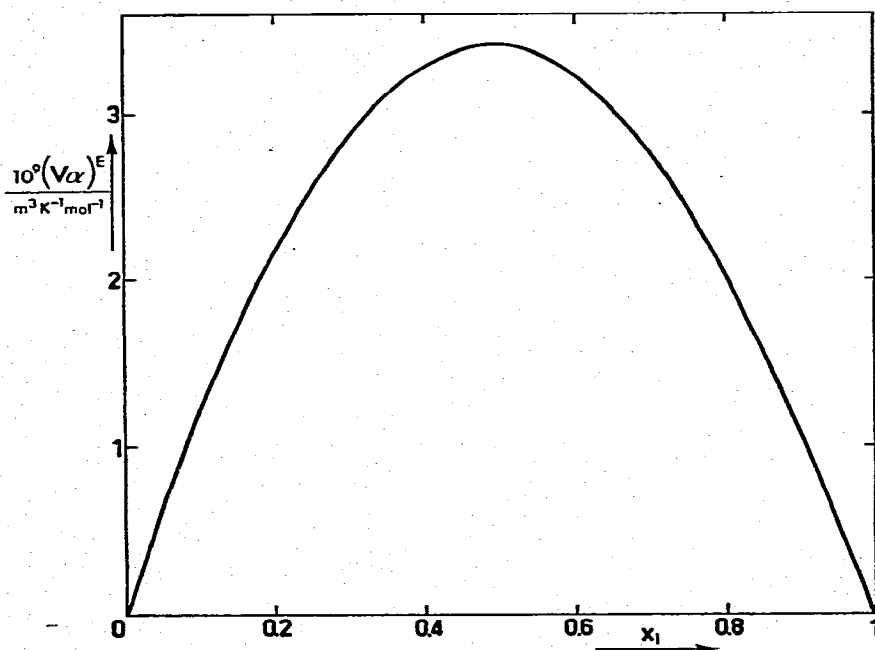


Fig. 2. "Excess thermal expansivity" $(V\alpha)^E = V_m\alpha_m - [x_1V_1\alpha_1 + x_2V_2\alpha_2]$ at 298.15 K for the system 1,2-dichloroethane (x_1) + cyclohexane (x_2) (m denotes mixture). Interpolated⁶ and smoothed results according to eqn. (7) and Table 3.

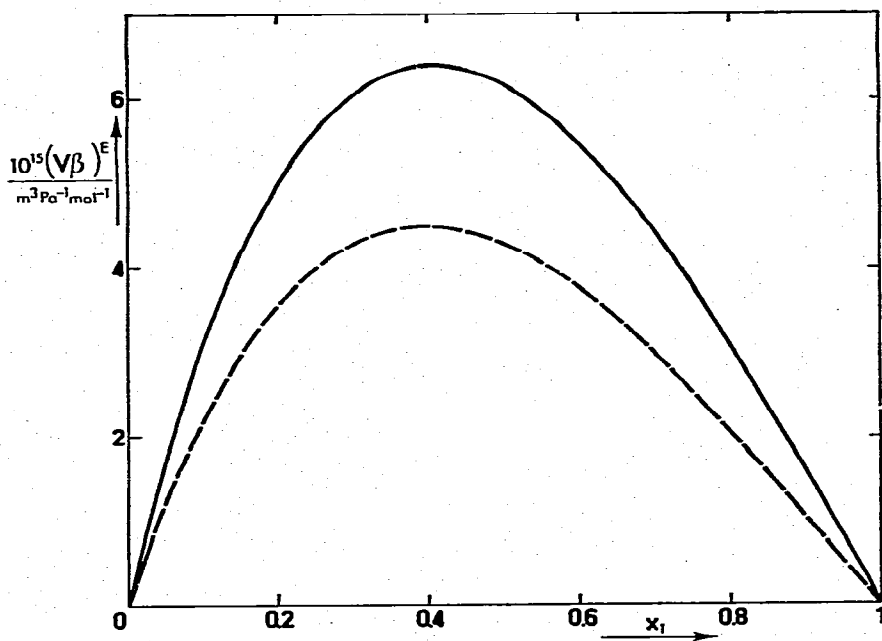


Fig. 3. "Excess isothermal compressibility" $(V\beta_T)^E$ (full curve) and "excess adiabatic compressibility" $(V\beta_S)^E$ (broken curve) at 298.15 K for the system 1,2-dichloroethane (x_1) + cyclohexane (x_2). Smoothed results according to eqn. (7) and Table 3.

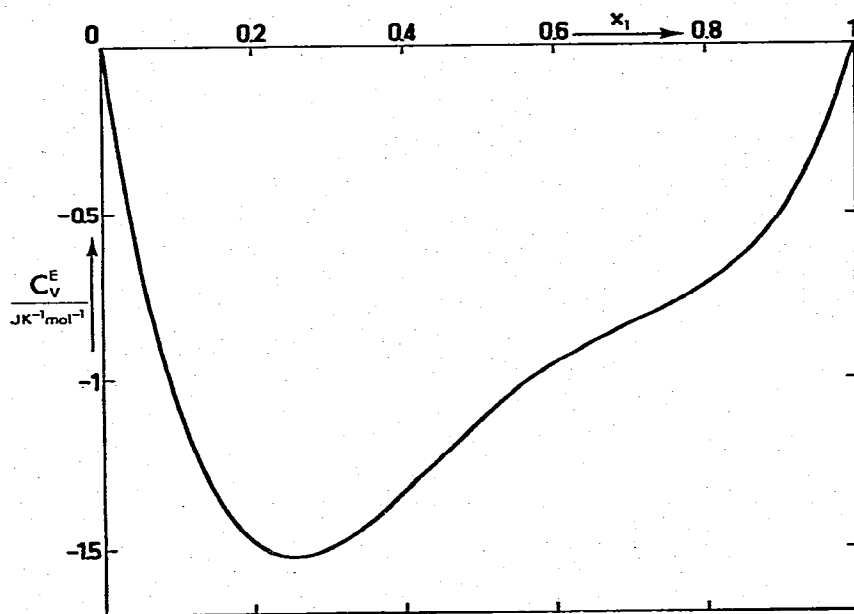


Fig. 4. Molar excess heat capacity at constant volume C_V^E at 298.15 K for the system 1,2-dichloroethane (x_1) + cyclohexane (x_2). Smoothed results according to eqn. (7) and Table 3. Note the unusual, highly asymmetric concentration dependence of this function.

TABLE 4

MOLAR VOLUME, V , COEFFICIENT OF THERMAL EXPANSION, α , ULTRASONIC VELOCITY, u , $\kappa = C_p/C_v$, MOLAR HEAT CAPACITY AT CONSTANT VOLUME, C_v , ADIABATIC COMPRESSIBILITY, β_s , AND ISOTHERMAL COMPRESSIBILITY, β_T , ALL AT 298.15 K

Substance	$10^6 V$ ($m^3 \text{ mole}^{-1}$)	$10^3 \alpha$ (K^{-1})	u (ms^{-1})	κ	C_v ($J K^{-1} \text{ mole}^{-1}$)	$10^{12} \beta_s$ (Pa^{-1})	$10^{12} \beta_T$ (Pa^{-1})
Cyclohexane	108.753	1.220	1255.9	1.3766	113.62	819.3	1127.8
Methylcyclohexane	128.345	1.136	1133.2	1.2626	146.33	1017.9	1285.2
1,2-Dichloroethane	79.444	1.172	1194.0	1.4481	89.05	563.1	815.4

TABLE 5

RESIDUAL MOLAR HEAT CAPACITY, C_v^* , TEMPERATURE DEPENDENCE OF C_v AND C_v^* AT ORTHOBARIC AND ISOCHORIC CONDITIONS, AND $\alpha V(\partial C_v/\partial V)_T$

All quantities refer to 298.15 K and the corresponding orthobaric volume.

	C_v^* ($J K^{-1} \text{ mole}^{-1}$)	$(\partial C_v/\partial T)_p$ ($J K^{-2} \text{ mole}^{-1}$)	$(\partial C_v^*/\partial T)_p$ ($J K^{-2} \text{ mole}^{-1}$)	$(\partial C_v/\partial T)_v$ ($J K^{-2} \text{ mole}^{-1}$)	$(\partial C_v^*/\partial T)_v$ ($J K^{-2} \text{ mole}^{-1}$)	$\alpha V(\partial C_v/\partial V)_T$ ($J K^{-2} \text{ mole}^{-1}$)
Cyclohexane	15.7	0.339	-0.090	0.42	-0.01	-0.076
Methylcyclohexane	19.6	0.493	-0.024	0.58	0.06	-0.087 ^a
1,2-Dichloroethane	20.1	0.113	-0.042	0.17	0.01	-0.056

^a In calculating $(\partial C_v/\partial V)_T$ according to ref. 28, the contribution involving the second derivative of the effective hard core diameter with respect to temperature was neglected, since no information is available on this quantity. Thus, the figure given above represents, in fact, a lower limit.

of cyclohexane and 1,2-dichloroethane is less than $\pm 0.5\%$. Because of the uncertainty associated with the literature values of u for methylcyclohexane (see footnote p.63), the error of C_V and β_T might be substantially greater for this compound. The error of C_V^E for DCE + cyclohexane should not exceed $\pm 0.2 \text{ J K}^{-1} \text{ mole}^{-1}$.

DISCUSSION

In this paper, the discussion will be rather brief, since most of the basis of the arguments has already been presented^{6, 8, 10, 15}.

For the pure liquids, the quantity of interest (as indicated in the introduction) is the residual molar heat capacity, C_V^* , and its variation with temperature and volume, that is

$$(\partial C_V^*/\partial T)_\sigma = (\partial C_V^*/\partial T)_V + \alpha V(\partial C_V/\partial V)_T \quad (11)$$

where the subscript σ denotes orthobaric conditions. Estimation of $(\partial C_V/\partial V)_T$ constitutes a somewhat delicate problem: for cyclohexane and DCE we adopted the values of Wilhelm et al.^{8, 10}, for methylcyclohexane we chose to use the appropriate relation of a modified van der Waals equation of state²⁸ in conjunction with parameters given elsewhere^{29, 30}. All pertinent results are summarized in Table 5.

$(\partial C_V^*/\partial T)_\sigma$ is negative in all cases, with a large part of the overall decrease being due to volume expansion. As regards the residual rotational heat capacity, let it suffice to reiterate^{6, 10, 15} that the data indicate (because of the considerable dipole-dipole orientational energy) strong hindrance of rotation, or even torsional vibration, of DCE molecules as a whole in liquid 1,2-dichloroethane. For cyclohexane, on the other hand, it appears that, again in terms of a model of hindered external rotation^{8, 12}, this compound is already well past the maximum of the curve C_r^* vs. T (which is somewhat higher than $3R/2$), that is on the high temperature decline. In the case of methylcyclohexane, in principle one has to consider the contribution, C_i^* , due to the conformational equilibrium between conformers with the methyl group in either the axial or equatorial position*. However, since methylcyclohexane is essentially a nonpolar molecule, and since there is no indication that the potential energy difference between the two conformers will change drastically with a change of phase¹³, C_i^* is assumed to be small. If C_V^* of argon³¹ at the same reduced temperature is taken as an approximation to C_{tr}^* , we obtain at 298.15 K for $C_r^* = C_V^* - C_V^*(Ar) \approx 9.5 \text{ J K}^{-1} \text{ mole}^{-1}$. Qualitatively, this result indicates that methylcyclohexane is not quite as near to the maximum of the curve C_r^* vs. T than, say its aromatic counterpart toluene. The

* When the methyl group is axial (a), one of its hydrogens approaches the syn-axial ring hydrogens to within ca. 0.18 nm. Therefore, the axial methyl group encounters van der Waals repulsion which is absent for the equatorial (e) methyl group. This repulsion may be estimated with the aid of the same type of interaction in *gauche*-butane: the enthalpy difference between the a and e forms of methylcyclohexane should be twice the butane value, that is ca. 7 kJ mole⁻¹, in good agreement with experiment¹³. From this result, we infer that at 298.15 K roughly 95% of all methylcyclohexane molecules are in the equatorial form.

uncertainty associated with calculated $(\partial C_V^*/\partial T)_V$ is always considerable. In addition, no information is available on the quantities $(\partial C_i^*/\partial T)_V$ and $(\partial C_i^*/\partial V)_T$. Thus, further conclusions are rendered somewhat speculative: the rather large positive value of $(\partial C_V^*/\partial T)_V$ suggests that this compound is still on the low temperature rise of the hindered-rotor curve.

For the binary mixture 1,2-dichloroethane + cyclohexane, Kohler and co-workers^{6, 15} have presented a treatment which is based on a cell theory of pseudo-ternary mixtures. In the present context, the important point is that the (calculated) quantity

$$C_V^E - C_{\text{conf}}^E - C_{\text{or}}^E \approx C_r^E \quad (12)$$

is rather large (ca. $16 \text{ J K}^{-1} \text{ mole}^{-1}$ at equimolar concentration). Although this result has to be considered as being a tentative first approximation, it shows qualitatively that external rotation of 1,2-dichloroethane is less hindered and/or external rotation of cyclohexane is more hindered in the mixture than in the pure liquids. Almost certainly, the former effect will give the more important contribution. As compared with our results for DCE + benzene¹⁰, the somewhat larger value of C_r^E seems reasonable.

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