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EXCESS MOLAR VOLUMES AND HEAT CAPACITIES OF (1,2,4-TRICHLOROBENZENE + AN *n*-ALKANE) AND (1-CHLORONAPHTHALENE + AN *n*-ALKANE) *

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ABSTRACT

Excesss molar volumes V_m^E at 298.15 K were obtained, as a function of mole fraction x, for several mixtures belonging either to series I: $\{x1,2,4\text{-}C_6H_3Cl_3 + (1-x)n\text{-}C_lH_{2l+2}\}$, or series II: $\{x1\text{-}C_{10}H_7Cl + (1-x)n\text{-}C_lH_{2l+2}\}$, for chain lengths $7 \leqslant l \leqslant 16$. The instrument used was a vibrating-tube densimeter. At the same temperature, a Picker flow calorimeter was used to determine excess molar heat capacities $C_{p,m}^E$ at constant pressure. For both series, the V_m^E values increase with increasing l. In series I, V_m^E for $l = 7$ is negative, for $l = 12$ it is very small and S-shaped, and for $l = 16$ it is positive over the whole composition range. V_m^E is negative for both mixtures ($l = 14$ and 16) of series II. The excess molar heat capacities of the mixtures belonging to series I are all negative, while those of series II are all positive. For both series the plot $C_{p,m}^E(x = 0.5)$ against l shows a maximum (for series I at roughly $l = 10$, and for series II at about $l = 11$).

INTRODUCTION

During the last decade, interest in thermodynamic properties of mixtures of n-alkanes, $n\text{-}C_lH_{2l+2}$, with liquids consisting of rather large and flat "rigid" molecules has increased greatly, with major contributions coming

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from our group [1–10]. Most of the experimental results obtained so far have been tentatively discussed in terms of ordering effects in the mixtures relative to the pure liquid *n*-alkanes [11–13], whence our interest in determining the dependence of various thermodynamic quantities upon the chain length l of the *n*-alkane. We now report excess molar volumes V_m^E and excess molar heat capacities $C_{p,m}^E$ at constant pressure, at 298.15 K and atmospheric pressure, of several mixtures belonging to either series I: (1,2,4-trichlorobenzene + an *n*-alkane), or to series II: (1-chloronaphthalene + an *n*-alkane), thereby augmenting results already published some years ago [1,4,5]. These measurements permit a more detailed description of the dependence on l of V_m^E and $C_{p,m}^E$ in these series.

EXPERIMENTAL

1,2,4-Trichlorobenzene (from Merck, "zur Synthese", with a purity of 98 mol per cent) was purified by repeated fractional crystallization [1,5] and stored in the dark over molecular sieve (Union Carbide Type 4A, beads, from Fluka). 1-Chloronaphthalene (Fluka, puriss., $\geqslant 99$ mol per cent), *n*-heptane (Fluka, puriss., $\geqslant 99.5$ mol per cent), *n*-dodecane (Fluka, purum, $\geqslant 99$ mol per cent), *n*-tetradecane (Fluka, puriss., $\geqslant 99$ mol per cent) and *n*-hexadecane (Merck, "zur Synthese", 99 mol per cent) were carefully dried with molecular sieve, 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 [14].

Densities ρ were measured with a vibrating-tube densimeter from Sodev (model 02D), operated in the flow mode. From the density, V_m^E of any mixture with mole fraction x of the chlorinated aromatic hydrocarbon is obtained from

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

Here, M_i, V_i^* and ρ_i^* denote, respectively, the molar mass, the molar volume and the density of pure component $i = 1$ (either 1,2,4-trichlorobenzene or 1-chloronaphthalene) or $i = 2$ (*n*-alkane), and V_m is the molar volume of the mixture.

Heat capacities per unit volume were measured with a Picker flow calorimeter (from Setaram), using the stepwise procedure. They were converted to molar heat capacities $C_{p,m}$ at constant pressure using our densities. Excess molar heat capacities were then calculated from

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

where $C_{p,i}^*$ is the molar heat capacity of pure component i. Experimental details may be found in previous publications [4,8,15,16].

RESULTS

Experimental densities and molar heat capacities of the pure liquids are given in Table 1. In general, the densities are in good agreement with

TABLE 1

Density ρ^* and molar heat capacity $C_{p,m}^*$ of the pure liquids at 298.15 K

	ρ^* (g cm^{-3})			$C_{p,m}^*$ (J K^{-1} mol^{-1})		
	This work	Literature		This work	Literature	
n-C_7H_{16}	0.67952	0.67949 [a]	0.67945 [b]		224.78 [g]	
n-$C_{12}H_{26}$	0.74540	0.74514 [a]	0.74510 [b]	373.30	374.93 [b]	375.97 [h]
n-$C_{14}H_{30}$	0.75935	0.75928 [a]	0.75912 [b]	433.98	436.91 [b]	438.48 [h]
n-$C_{16}H_{34}$	0.77046	0.76994 [a]	0.77018 [b]	495.73	499.97 [e]	501.45 [h]
1,2,4-$C_6H_3Cl_3$	1.44820	1.44804 [c]	1.44815 [d]	194.90	194.55 [d]	
1-$C_{10}H_7Cl$	1.18784	1.18811 [e]	1.1893 [f]	211.28	211.37 [e]	

[a] Ref. 17. [b] Ref. 8. [c] Ref. 18. [d] Ref. 5. [e] Ref. 4. [f] Ref. 19, interpolated. [g] This value (from Fortier et al. [20]) was adopted for the n-heptane sample used in this work; it served as reference liquid in all our heat-capacity measurements. [h] Ref. 21.

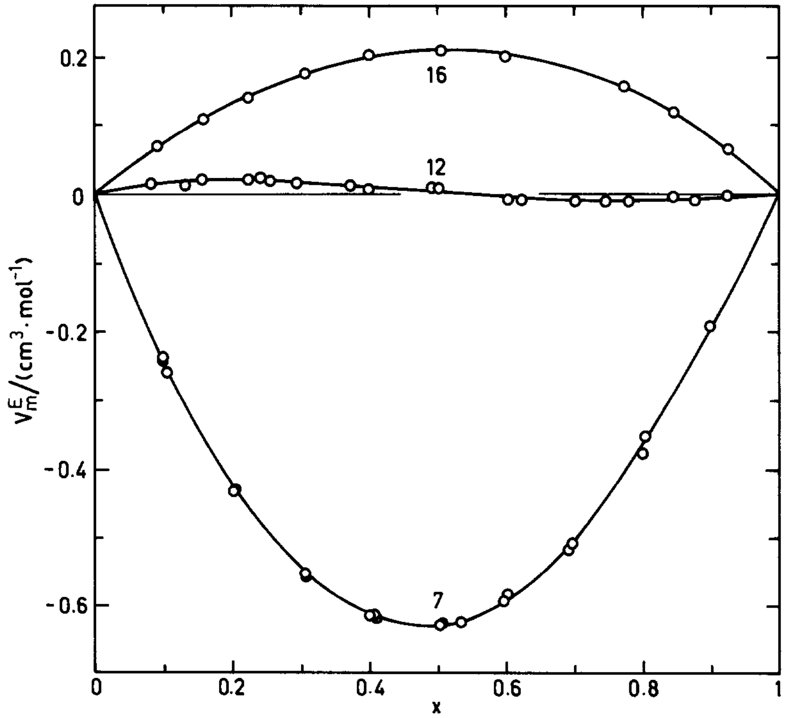

Fig. 1. Excess molar volumes V_m^E of $\{x1,2,4\text{-}C_6H_3Cl_3 + (1-x)n\text{-}C_lH_{2l+2}\}$ at 298.15 K. (O) Experimental points; (———) calculated from eqn. (3) with coefficients from Table 3. The numbers are values of l.

TABLE 2

Excess molar volumes V_m^E and excess molar heat capacities $C_{p,m}^E$ as functions of mole fraction x for $\{x1,2,4\text{-}C_6H_3Cl_3+(1-x)n\text{-}C_lH_{2l+2}\}$ and for $\{x1\text{-}C_{10}H_7Cl+(1-x)n\text{-}C_lH_{2l+2}\}$ at 298.15 K

x	V_m^E (cm^3 mol^{-1})	$C_{p,m}^E$ (J K^{-1} mol^{-1})	x	V_m^E (cm^3 mol^{-1})	$C_{p,m}^E$ (J K^{-1} mol^{-1})	x	V_m^E (cm^3 mol^{-1})	$C_{p,m}^E$ (J K^{-1} mol^{-1})
$x1,2,4\text{-}C_6H_3Cl_3+(1-x)n\text{-}C_7H_{16}$								
0.1012	−0.2376	–	0.3089	−0.5445	–	0.6021	−0.5805	–
0.1017	−0.2412	–	0.4018	−0.6152	–	0.6941	−0.5177	−0.852
0.1043	−0.2574	−0.369	0.4097	−0.6152	−0.853	0.6979	−0.5066	–
0.2014	−0.4317	–	0.4105	−0.6189	–	0.7998	−0.3766	−0.695
0.2053	−0.4309	−0.589	0.5033	−0.6299	−0.915	0.8027	−0.3521	–
0.2062	−0.4290	–	0.5088	−0.6253	–	0.8976	−0.1920	−0.400
0.3056	−0.5531	–	0.5342	−0.6246	–			
0.3072	−0.5556	−0.771	0.5965	−0.5933	−0.891			
$x1,2,4\text{-}C_6H_3Cl_3+(1-x)n\text{-}C_{12}H_{26}$								
0.0830	0.0156	–	0.2958	0.0169	–	0.7028	−0.0085	–
0.1343	0.0133	−0.248	0.3745	0.0129	−0.599	0.7493	−0.0089	−0.719
0.1355	0.0127	−0.254	0.4005	0.0066	–	0.7820	−0.0081	–
0.1567	0.0214	–	0.4921	0.0098	−0.682	0.8453	−0.0029	–
0.2254	0.0221	–	0.5011	0.0076	–	0.8778	−0.0073	−0.549
0.2449	0.0244	–	0.6043	−0.0067	–	0.9247	−0.0018	–
0.2565	0.0194	−0.455	0.6242	−0.0071	−0.745			

x1,2,4-$C_6H_3Cl_3$ + $(1-x)$$n$-$C_{14}H_{30}$								
0.3204	[a]	−1.056	0.4787	[a]	−1.310	0.6369	[a]	−1.329
x1,2,4-$C_6H_3Cl_3$ + $(1-x)$$n$-$C_{16}H_{34}$								
0.0931	0.0706	−0.555	0.4011	0.2036	−1.799	0.8476	0.1190	−1.320
0.1592	0.1102	−0.894	0.5063	0.2089	−1.914	0.9258	0.0643	−0.830
0.2258	0.1412	−1.222	0.6000	0.2008	−1.915			
0.3088	0.1763	−1.555	0.7718	0.1564	−1.614			
x1-$C_{10}H_7Cl$ + $(1-x)$$n$-$C_{14}H_{30}$								
0.0905	−0.1378	0.443	0.4012	−0.4562	1.292	0.8477	−0.3392	0.638
0.1573	−0.2219	0.703	0.4995	−0.5003	1.332	0.9221	−0.2100	0.332
0.2576	−0.3357	1.050	0.5947	−0.5128	1.261			
0.2879	−0.3655	1.117	0.6968	−0.4829	1.084			
x1-$C_{10}H_7Cl$ + $(1-x)$$n$-$C_{16}H_{34}$								
0.0823	−0.0918	–	0.3905	−0.3598	–	0.6984	−0.4091	–
0.1558	−0.1713	–	0.4889	–	0.990	0.7732	−0.3680	–
0.2240	−0.2340	–	0.4940	−0.4102	–	0.8484	−0.2876	–
0.2956	−0.2934	–	0.5931	−0.4271	–	0.9215	−0.1898	–

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[a] For V_m^E of $\{x1,2,4\text{-}C_6H_3Cl_3 + (1-x)n\text{-}C_{14}H_{30}\}$ see ref. 5.

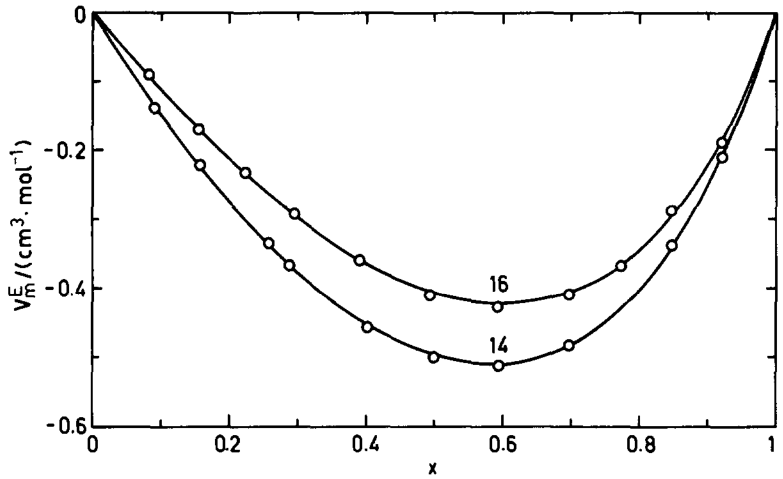

Fig. 2. Excess molar volumes V_m^E of $\{x\text{1-}C_{10}H_7Cl+(1-x)n\text{-}C_lH_{2l+2}\}$ at 298.15 K. (O) Experimental points; (———) calculated from eqn. (3) with coefficients from Table 3. The numbers are values of l.

reliable literature values. As regards heat capacity, our results for *n*-dodecane, *n*-tetradecane and *n*-hexadecane are somewhat lower than those reported by Messerly et al. [21]. The heat capacities of 1,2,4-trichlorobenzene and 1-chloronaphthalene are in accord with previously published values [4,5].

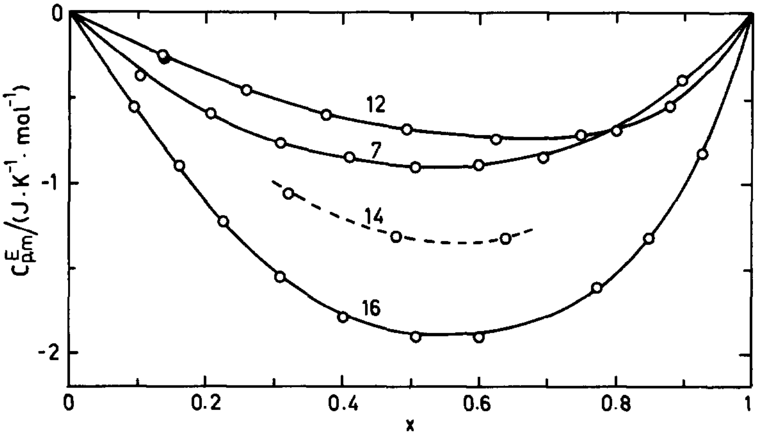

Fig. 3. Excess molar heat capacities $C_{p,m}^E$ at constant pressure of $\{x1,2,4\text{-}C_6H_3Cl_3+(1-x)n\text{-}C_lH_{2l+2}\}$ at 298.15 K. (O) Experimental points; (———) calculated from eqn. (3) with coefficients from Table 3. The broken curve for $l=14$ was obtained by graphical smoothing. The numbers are values of l.

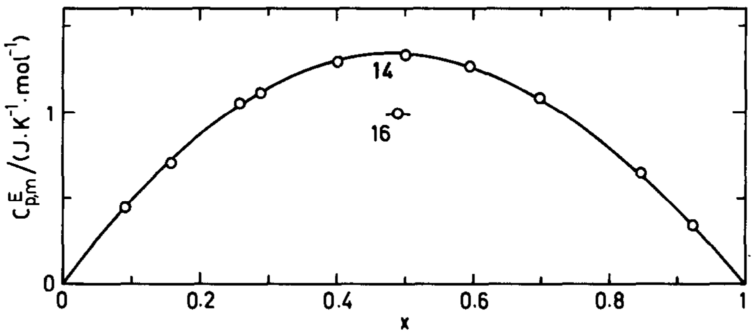

Fig. 4. Excess molar heat capacities $C^E_{p,m}$ at constant pressure of $\{x1\text{-}C_{10}H_7Cl+(1-x)n\text{-}C_lH_{2l+2}\}$ at 298.15 K. (○) Experimental points; (———) calculated from eqn. (3) with coefficients from Table 3. For $l=16$, only 1 point is available. The numbers are values of l.

Experimental results for the excess molar volumes and excess molar heat capacities at 298.15 K of mixtures belonging to either series I or series II are contained in Table 2, while graphical representations are provided by Figs. 1

TABLE 3

Coefficients A_i and standard deviations $s(Q^E_m)$ for least-squares representation by eqn. (3) of V^E_m (cm^3 mol^{-1}) and $C^E_{p,m}$ (J K^{-1} mol^{-1}) for $\{x1,2,4\text{-}C_6H_3Cl_3+(1-x)n\text{-}C_lH_{2l+2}\}$ and for $\{x1\text{-}C_{10}H_7Cl+(1-x)n\text{-}C_lH_{2l+2}\}$ at 298.15 K

	Q^E_m	A_0	A_1	A_2	A_3	$s(Q^E_m)$
$x1,2,4\text{-}C_6H_3Cl_3$ $+(1-x)n\text{-}C_7H_{16}$	$\frac{V^E_m}{(\text{cm}^3\ \text{mol}^{-1})}$	−2.5170	0.2184	0.1548	0.2039	0.0063
	$\frac{C^E_{p,m}}{(\text{J K}^{-1}\ \text{mol}^{-1})}$	−3.642	−0.396	−0.848	-	0.017
$+(1-x)n\text{-}C_{12}H_{26}$	$\frac{V^E_m}{(\text{cm}^3\ \text{mol}^{-1})}$	0.0131	−0.1364	0.0763	-	0.0035
	$\frac{C^E_{p,m}}{(\text{J K}^{-1}\ \text{mol}^{-1})}$	−2.755	−1.087	−1.496	−1.570	0.005
$+(1-x)n\text{-}C_{16}H_{34}$	$\frac{V^E_m}{(\text{cm}^3\ \text{mol}^{-1})}$	0.8361	0.0620	0.0687	-	0.0024
	$\frac{C^E_{p,m}}{(\text{J K}^{-1}\ \text{mol}^{-1})}$	−7.566	−1.056	−2.114	−3.142	0.021
$x1\text{-}C_{10}H_7Cl$ $+(1-x)n\text{-}C_{14}H_{30}$	$\frac{V^E_m}{(\text{cm}^3\ \text{mol}^{-1})}$	−1.9872	−0.5933	−0.3966	−0.2118	0.0035
	$\frac{C^E_{p,m}}{(\text{J K}^{-1}\ \text{mol}^{-1})}$	5.347	−0.385	−0.471	-	0.009
$+(1-x)n\text{-}C_{16}H_{34}$	$\frac{V^E_m}{(\text{cm}^3\ \text{mol}^{-1})}$	−1.6252	−0.5691	−0.3677	−0.3448	0.0053

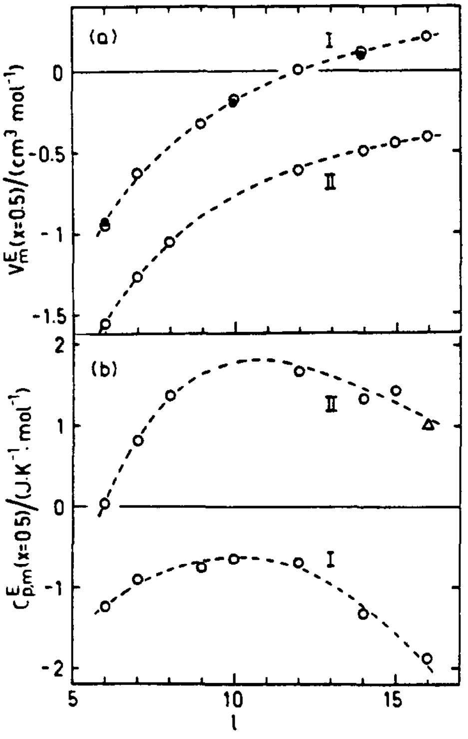

Fig. 5. Plot of (a) excess molar volume at $x = 0.5$, $V^E_m(x = 0.5)$, against chain length l of the n-alkane, and (b) excess molar heat capacity at $x = 0.5$, $C^E_{p,m}(x = 0.5)$, against l, at 298.15 K. Series I: $\{x1,2,4\text{-}C_6H_3Cl_3 + (1-x)n\text{-}C_lH_{2l+2}\}$; series II: $\{x1\text{-}C_7H_{10}Cl + (1-x)n\text{-}C_lH_{2l+2}\}$. (○) Experimental results either from this work or from refs. 4 and 5; (●) experimental results either from ref. 18 ($l = 6$) or 22 ($l = 10$ and $l = 14$), interpolated between 293.15 K and 313.15 K; (△) $C^E_{p,m}$ for a mixture of series II with $l = 16$ and $x = 0.4889$.

to 4. With the exception of $\{x1,2,4\text{-}C_6H_3Cl_3 + (1-x)n\text{-}C_{14}H_{30}\}$ and $\{x1\text{-}C_{10}H_7Cl + (1\text{-}x)n\text{-}C_{16}H_{34}\}$, where $C^E_{p,m}$ was determined only for a few mixtures in the central composition range, the excess quantities were fitted for each mixture with a smoothing function of the form

$$Q^E_m = x(1-x)\sum_{i=0}^{k} A_i(2x-1)^i \qquad (3)$$

by the method of unweighted least squares, where either $Q^E_m = V^E_m/(cm^3\ mol^{-1})$, or $Q^E_m = C^E_{p,m}/(J\ K^{-1}\ mol^{-1})$. The coefficients A_i and the corresponding standard deviations $s(Q^E_m)$ are given in Table 3. These coefficients were used to obtain the calculated curves in the Figures.

We have already reported a few excess molar volumes for $\{x1\text{-}C_{10}H_7Cl + (1-x)n\text{-}C_{16}H_{34}\}$ at 298.15 K for $x > 0.48$: they are in good agreement with the present values [4]. No other literature results could be found for comparison.

DISCUSSION

In Fig. 5(a), excess molar volumes at $x = 0.5$ and 298.15 K for both series I and II are plotted against the chain length of the *n*-alkane. Results obtained in this work as well as published (interpolated) values [4,5,18,22] have been incorporated: they show the familiar dependence on l [8,23]. However, the corresponding plots of $C_{p,m}^{E}(x = 0.5)$ against l in Fig. 5(b) are remarkably different from those observed for mixtures of *n*-alkanes with liquids consisting of more or less spherical molecules [11–13,24–26]. We note the initial increase of $C_{p,m}^{E}$ with increasing l, its passing through a maximum at $l \approx 10$ (series I) or $l \approx 11$ (series II), and its decrease for larger values of l [11,13]. Again, results obtained in this work have been combined with already published values [4,5]. To further elucidate the dependence of $C_{p,m}^{E}$ on l, experimental results on other selected mixtures of *n*-alkanes with liquids consisting of sufficiently anisotropic plate-like molecules will be communicated in forthcoming articles.

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