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THERMODYNAMICS OF MIXTURES CONTAINING TRIETHOXYMETHANE*

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ABSTRACT

Excess molar volumes V^E at 298.15 K were obtained, as a function of mole fraction, for the three binary liquid mixtures triethoxymethane $\{CH(OC_2H_5)_3$, TEOM$\}$ + n-heptane, + n-decane and + cyclohexane. The instrument used was a vibrating-tube densimeter. A Picker flow calorimeter was used to determine excess molar heat capacities C_p^E at constant pressure for these mixtures at the same temperature. All excess volumes are positive with $V^E(x_1= 0.5)$ = 0.743 $cm^3.mol^{-1}$ for the mixture (TEOM + n-heptane), 0.974 $cm^3.mol^{-1}$ for (TEOM + n-decane), and 0.972 $cm^3.mol^{-1}$ for (TEOM + cyclohexane). The corresponding values for $C_p^E(x_1= 0.5)/(J.K^{-1}.mol^{-1})$ are, in the same sequence, -0.58, -1.38 and -1.40. The curves $C_p^E(x_1)$, where x_1 is the mole fraction of TEOM, are all rather broad.

INTRODUCTION

During the last several years we have investigated systematically selected thermodynamic properties of binary liquid mixtures containing either an ether

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or an ester as one component, and a hydrocarbon as the other.[1-11] Some of these mono- and polyoxaalkanes (monoethers or polyethers) and alkylalkanoates (esters) are solvents of technical importance, and the mixtures are particularly convenient for testing group contribution models.[12-15] Perhaps the most interesting aspect is, however, connected with the appearance, in some of these mixtures, of W-shaped curves C_p^E vs. x, i.e. of curves with *two* minima. Such a composition dependence - first found for (1,4-dioxane + n-heptane)[7] - is now recognized as being of wide occurrence.[8-10,16-25] Against this background it seemed desirable to inquire as to the thermodynamics of mixtures containing a 1,1,1-trialkoxyalkane (orthoester) as one component and an alkane as the other. Thus we present here results on excess molar volumes V^E and excess molar heat capacities C_p^E at constant pressure of binary liquid mixtures containing triethoxymethane (triethyl orthoformate, $CH(OC_2H_5)_3$, TEOM), that is of $\{x_1CH(OC_2H_5)_3 + x_2n\text{-}C_\ell H_{2\ell+2}\}$ with $\ell = 7$ and $\ell = 10$, and of $\{x_1CH(OC_2H_5)_3 + x_2c\text{-}C_6H_{12}\}$, all at 298.15 K and atmospheric pressure. Together with previously published data on mixtures of n-alkanes and cyclohexane with ethers and esters, and with as yet unpublished material on mixtures of alkylalkanoates with branched alkanes,[26] these results will be instrumental in assessing the influence of polarity as well as of molecular size and shape upon thermodynamic mixing quantities.

EXPERIMENTAL

The pure liquids, that is triethoxymethane, n-heptane, n-decane and cyclohexane, were all of the best quality available from Fluka (puriss. or purum quality). They were carefully dried with molecular sieve (Union Carbide Type 4A, beads, from Fluka) and used without further purification. Binary mixtures for both V^E and C_p^E determinations were prepared by mass with a possible error in the mole fractions estimated to be less than 10^{-4}. All molar quantities are based on the relative atomic mass table of IUPAC, 1986.[27]

Densities ρ were measured with a vibrating-tube densimeter from Sodev (model 02D), which was operated under flow conditions.[28] Before each series of measurements the instrument was calibrated with vacuum and doubly distilled and degassed water using $\rho_{H_2O}(298.15\ K) = 997.047\ kg.m^{-3}$ as reported by Kell.[29] From the measured density, the excess molar volume of any mixture is obtained according to

$$V^E = x_1M_1(1/\rho - 1/\rho_1^*) + x_2M_2(1/\rho - 1/\rho_2^*) \qquad (1)$$

where M_i, ρ_i^* and x_i denote, respectively, the molar mass, the density and the mole fraction of triethoxymethane (i = 1) or hydrocarbon (i = 2).

Heat capacities per unit volume were measured with a Picker flow calorimeter (from Setaram), using the stepwise procedure.[28,30,31] For all measurements we used a temperature increment of approximately 1 K centered on 298.15 K. The heat capacities per unit volume were converted to molar heat capacities C_P with use of our measured densities. Excess molar heat capacities were then calculated from

$$C_P^E = C_P - (x_1 C_{P,1}^* + x_2 C_{P,2}^*) \tag{2}$$

where $C_{P,1}^*$ is the molar heat capacity of pure triethoxymethane, and $C_{P,2}^*$ is the molar heat capacity of pure alkane.

For both densimeter and flow calorimeter, temperature control was better than ± 0.002 K as checked by a quartz thermometer (Hewlett Packard, model 2801 A).

RESULTS AND DISCUSSION

Experimental results for density and molar heat capacity at constant pressure of the pure liquids are given in Table 1 along with selected values from the literature. In general, agreement with the literature data is excellent. No published value for $C_{P,1}^*$ of triethoxymethane could be found for comparison.

Results for the excess molar volumes and the excess molar heat capacities of the mixtures at 298.15 K are given in Table 2, while graphical representations are provided by Figs.1 and 2. For each mixture, the excess quantities were fitted with a smoothing function of Redlich-Kister type, that is

$$Q^E = x_1 x_2 \sum_{i=0}^{k} A_i (x_1 - x_2)^i \tag{3}$$

where either $Q^E = V^E/(\mathrm{cm^3.mol^{-1}})$ or $Q^E = C_P^E/(\mathrm{J.K^{-1}.mol^{-1}})$, x_1 is the mole fraction of TEOM and x_2 is the mole fraction of hydrocarbon. The coefficients A_i and the corresponding standard deviations $s(Q^E)$ are shown in Table 3. These coefficients were used to obtain the calculated curves in the figures. No literature results could be found for comparison.

For the mixtures (TEOM + an n-alkane) the dependence of V^E on the chain length ℓ of the n-alkane n-$C_\ell H_{2\ell+2}$ is as expected, that is V^E increases with increasing ℓ. The magnitude of the excess molar volumes is similar to that found for corresponding mixtures of n-alkanes with alkylalkanoates of comparable

TABLE 1

Density ρ^* and molar heat capacity C_p^* at constant pressure of the pure liquids at 298.15 K

	$\rho^*/(g.cm^{-3})$		$C_p^*/(J.K^{-1}.mol^{-1})$	
	This work	Literature	This work	Literature
n-C_7H_{16}	0.6795	0.67949[a)]	224.78[d)]	
n-$C_{10}H_{22}$	0.7261	0.72623[a)]	313.30	314.47[e)]
c-C_6H_{12}	0.7737	0.77384[b)]	157.07	157.35[f)]
$CH(OC_2H_5)_3$	0.8876	0.88757[c)]	290.84	—

[a)] American Petroleum Institute.[32] [b)] Tanaka.[33] [c)] Timmermans,[34] interpolated. [d)] This value (from Fortier et al.[35]) was adopted for the n-heptane sample used as ultimate reference liquid in all our heat capacity measurements. [e)] Messerly et al.[36] [f)] Grolier et al.[28]

size.[10,26] For (TEOM + cyclohexane) V^E_{max} = 1.004 $cm^3.mol^{-1}$ at $x_{1,max}$ = 0.4096, which is similar to the V^Es measured previously[9] for mixtures of cyclohexane with alkylalkanoates.

As concerns the excess molar heat capacities, the curves $C_p^E(x_1)$ are quite broad, which shape is reminiscent of that observed for mixtures of cyclohexane (or n-alkane) with higher members of the alkylalkanoates, such as for (n-propylpropanoate + cyclohexane).[9] We note that TEOM has a smaller reduced electric dipole moment than propylmethanoate,[37-39] whose mixtures with n-heptane, n-decane and cyclohexane[9,10] all show a W-shaped composition dependence[24,40-43] of C_p^E at 298.15 K. The relative dielectric permittivity (at about 293 K) of TEOM [34] is 4.8, that of propylmethanoate[44] is 7.7.

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TABLE 2

Excess molar volumes V^E and excess molar heat capacities C_p^E as functions of mole fraction x_1 for $\{x_1CH(OC_2H_5)_3 + x_2n\text{-}C_\ell H_{2\ell+2}\}$, ℓ = 7 and 10, and for $\{x_1CH(OC_2H_5)_3 + x_2c\text{-}C_6H_{12}\}$ at 298.15 K

x_1	$\frac{V^E}{cm^3 \cdot mol^{-1}}$	$\frac{C_p^E}{J \cdot K^{-1} \cdot mol^{-1}}$	x_1	$\frac{V^E}{cm^3 \cdot mol^{-1}}$	$\frac{C_p^E}{J \cdot K^{-1} \cdot mol^{-1}}$	x_1	$\frac{V^E}{cm^3 \cdot mol^{-1}}$	$\frac{C_p^E}{J \cdot K^{-1} \cdot mol^{-1}}$
$\{x_1CH(OC_2H_5)_3 + x_2C_7H_{16}\}$								
0.0675	0.2314	-	0.4571	0.7523	-0.568	0.7471	0.5243	-0.496
0.1075	0.3470	-	0.5006	0.7452	-0.585	0.8397	0.3670	-0.410
0.1582	0.4663	-0.293	0.5615	0.7093	-0.564	0.8812	0.2824	-0.349
0.2554	0.6300	-0.414	0.6522	0.6462	-0.551	0.9412	0.1471	-0.236
0.3487	0.7175	-0.529						
$\{x_1CH(OC_2H_5)_3 + x_2C_{10}H_{22}\}$								
0.0657	0.2487	-0.485	0.3997	-	-1.417	0.7295	0.7946	-
0.0681	0.3077	-	0.4435	0.9532	-1.371	0.7371	0.7733	-1.078
0.1134	0.4052	-0.683	0.4790	0.9770	-	0.8383	0.5500	-
0.1156	0.4210	-	0.4921	0.9801	-1.349	0.8391	0.5522	-0.818
0.1627	0.5350	-0.972	0.5016	0.9743	-	0.8821	0.4256	-
0.1680	0.5515	-	0.5441	0.9682	-1.370	0.8834	0.4265	-0.660
0.2552	0.7485	-1.242	0.5503	0.9652	-	0.9334	0.2182	-
0.2562	0.7438	-	0.6395	0.9100	-	0.9337	0.2620	-0.480
0.3530	0.8899	-	0.6436	0.9028	-1.265			
$\{x_1CH(OC_2H_5)_3 + x_2c\text{-}C_6H_{12}\}$								
0.0564	0.3175	-0.649	0.4649	0.9808	-1.395	0.7361	0.6574	-0.952
0.0735	0.3965	-0.755	0.4752	-	-1.456	0.7448	0.6317	-0.949
0.1124	0.5464	-1.022	0.5204	0.9459	-1.345	0.8371	0.4533	-0.604
0.1141	0.5526	-1.069	0.5229	0.9578	-1.391	0.8382	0.4361	-0.671
0.1619	0.6839	-1.300	0.5621	0.9171	-1.302	0.8974	0.2897	-0.478
0.1695	0.7191	-1.239	0.5709	0.9179	-1.319	0.8997	0.2945	-
0.2649	0.9044	-1.507	0.6450	0.8130	-1.162	0.9325	0.2024	-0.313
0.2738	0.9134	-1.456	0.6669	0.7901	-1.120	0.9351	0.1899	-0.367
0.3569	0.9876	-1.549						

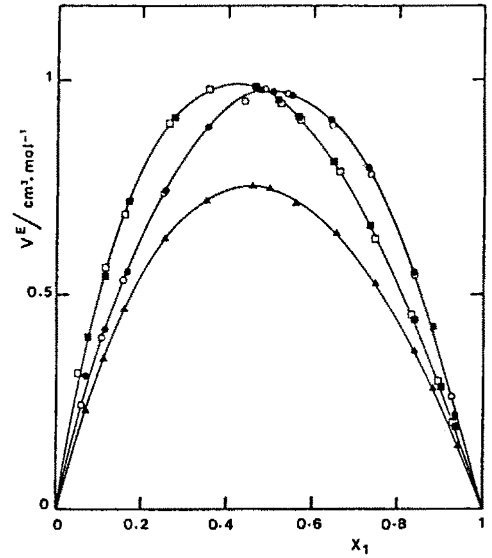

Fig. 1. Excess molar volumes V^E at 298.15 K. Experimental results: ▲, $\{x_1CH(OC_2H_5)_3 + x_2n\text{-}C_7H_{16}\}$; ● (run 1) and ○ (run 2), $\{x_1CH(OC_2H_5)_3 + x_2n\text{-}C_{10}H_{22}\}$; ■ (run 1) and □ (run 2), $\{x_1CH(OC_2H_5)_3 + x_2c\text{-}C_6H_{12}\}$. The curves have been calculated from eqn.(3) with coefficients from Table 3.

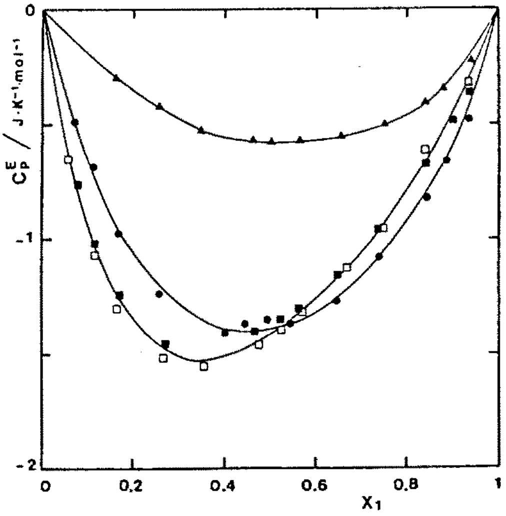

Fig. 2. Excess molar heat capacities C_p^E at 298.15 K. Experimental results: ▲, $\{x_1CH(OC_2H_5)_3 + x_2n\text{-}C_7H_{16}\}$; ●, $\{x_1CH(OC_2H_5)_3 + x_2\text{-}C_{10}H_{22}\}$; ■ (run 1) and □ (run 2), $\{x_1CH(OC_2H_5)_3 + x_2c\text{-}C_6H_{12}\}$. The curves have been calculated from eqn.(3) with coefficients from Table 3.

TABLE 3

Coefficients A_i and standard deviations $s(Q^E)$ for least-squares representation by eqn.(3) of $Q^E = V^E/(\text{cm}^3.\text{mol}^{-1})$ and $Q^E = C_p^E/(\text{J.K}^{-1}.\text{mol}^{-1})$ for $\{x_1CH(OC_2H_5)_3 + x_2n\text{-}C_\ell H_{2\ell+2}\}$, $\ell = 7$ and 10, and for $\{x_1CH(OC_2H_5)_3 + x_2c\text{-}C_6H_{12}\}$ at 298.15 K

Mixture	Q^E	A_0	A_1	A_2	A_3	A_4	A_5	$s(Q^E)$
$x_1CH(OC_2H_5)_3$								
+ $n\text{-}C_7H_{16}$	$V^E/(\text{cm}^3.\text{mol}^{-1})$	2.9727	-0.5628	0.2941	-	-	-	0.003
	$C_p^E/(\text{J.K}^{-1}.\text{mol}^{-1})$	-2.324	-0.085	0	-1.227	-1.418	-	0.010
+ $n\text{-}C_{10}H_{22}$	$V^E/(\text{cm}^3.\text{mol}^{-1})$	3.8965	0	0.3036	1.0463	0	-1.8613	0.012
	$C_p^E/(\text{J.K}^{-1}.\text{mol}^{-1})$	-5.505	1.167	-2.370	-1.260	-	-	0.032
+ $c\text{-}C_6H_{12}$	$V^E/(\text{cm}^3.\text{mol}^{-1})$	3.8875	-1.3786	0.4514	0	0.4882	-	0.009
	$C_p^E/(\text{J.K}^{-1}.\text{mol}^{-1})$	-5.619	2.565	-2.423	1.471	-1.764	-	0.033

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