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Excess molar enthalpies and excess molar volumes of ternary mixtures of ethers and ketones

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Abstract

The application of the principle of congruence to multicomponent mixtures was tested in a novel way by mixing a symmetrical ether of side chain carbon number m with an equimolar mixture of two symmetrical ethers such that their average side chain carbon number was m. The equimolar mixture was known as a pseudo-ether of carbon number m. Excess molar enthalpies and volumes were measured using these mixtures at atmospheric pressure and at 298.15 K and the results used to test the principle of congruence. The process was repeated for mixtures of ketones and pseudo-ketones. © 1997 Elsevier Science B.V.

Keywords: Excess volumes; Excess enthalpies; Congruency; Ethers; Ketones

1. Introduction

We have recently tested the principle of congruence on a novel set of null mixtures of the type: (i) alkane+a pseudo-alkane [1]; and (ii) cycloalkane+a pseudo-cycloalkane [2]. The experimental H_m^E and V_m^E thermodynamic properties of mixtures of the type (i) showed excellent agreement with the principle of congruence, while mixtures of the type (ii) did not obey the principle. This was assumed to be due to structural implications present in the cycloalkane mixtures [2]. In continuation of these studies, the principle of congruence [3–7] has been applied to a novel set of mixtures involving accurately made up (symmetrical ethers+pseudo-ethers) and (symmetrical ketones+pseudo-ketones). The principle implies that a pseudo-ether or pseudo-ketone, made up of a mixture of the type [0.5 (C_kH_{2k+1} O C_kH_{2k+1}) +0.5 (C_lH_{2l+1} O C_lH_{2l+1})] or [0.5 (C_kH_{2k+1} CO C_kH_{2k+1}) +0.5 (C_lH_{2l+1} CO C_lH_{2l+1})], respectively, will behave like (C_mH_{2m+1} O C_mH_{2m+1}) or (C_mH_{2m+1} CO C_mH_{2m+1}), respectively, where $m=(k+l)/2$. This paper reports the H_m^E and V_m^E for $m=3$, 4 or 5 for the ethers, and $m=2$, 3 or 4 for the ketones over the whole composition range.

2. Experimental

A Thermometric flow microcalorimeter 2277 was used to determine the molar enthalpies of mixing. All the measurements were made at constant temperature (298.15±0.01 K). The calibration and experimental determination have been described elsewhere [8,9].

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Table 1
Experimental excess molar enthalpies, H_m^E for binary mixtures of $\{x[0.5\ C_kH_{2k+1}OC_kH_{2k+1} + 0.5\ C_lH_{2l+1}OC_lH_{2l+1}] + (1-x)\ C_mH_{2m+1}OC_mH_{2m+1}\}$ and $\{x[0.5\ C_kH_{2k+1}COC_kH_{2k+1} + 0.5\ C_lH_{2l+1}COC_lH_{2l+1}] + (1-x)\ C_mH_{2m+1}COC_mH_{2m+1}\}$, where $m=(k+l)/2$ and the deviations δH_m^E at the temperature 298.15 K

x	H_m^E J mol^{-1}	δH_m^E J mol^{-1}	x	H_m^E J mol^{-1}	δH_m^E J mol^{-1}	x	H_m^E J mol^{-1}	δH_m^E J mol^{-1}
$x[0.5C_2H_5OC_2H_5 + 0.5C_4H_9OC_4H_9] + (1-x)C_3H_7OC_3H_7$								
0.0833	0.9	−0.2	0.5099	4.1	0.0	0.7641	2.7	−0.1
0.1552	1.9	−0.0	0.6061	3.9	−0.0	0.8711	1.7	0.1
0.1937	2.5	0.1	0.7001	3.4	−0.0	0.9066	1.3	0.1
0.2835	3.2	−0.0	0.7551	2.9	−0.0	0.9197	1.1	0.0
0.4297	4.0	0.0						
$x[0.5C_3H_7OC_3H_7 + 0.5C_5H_{11}OC_5H_{11}] + (1-x)C_4H_9OC_4H_9$								
0.0632	0.6	−0.2	0.5034	3.7−0.0	0.6739	3.2	−0.0	
0.1326	1.5	−0.0	0.5067	3.7	−0.0	0.7441	2.8	0.0
0.2105	2.4	0.1	0.5274	3.7	0.0	0.7980	2.4	0.1
0.2982	3.1	0.1	0.6005	3.5	−0.1	0.8650	1.7	0.1
0.4057	3.5	0.0	0.6495	3.3	−0.0	0.9055	1.1	−0.0
$x[0.5C_2H_5OC_2H_5+0.5C_8H_{17}OC_8H_{170}]+(1-x)C_5H_{11}OC_5H_{11}$								
0.0780	8.8	0.3	0.3319	27.8	1.2	0.7499	19.8	0.5
0.1215	12.0	−0.8	0.4119	29.4	0.7	0.8098	15.5	0.3
0.1563	15.4	−0.4	0.4121	29.0	0.3	0.8974	8.4	0.0
0.1750	16.8	−0.5	0.5176	28.2	−0.6	0.9335	5.9	0.4
0.2562	23.0	0.1	0.6110	24.9	−1.6			
$x[0.5CH_3COCH_3+0.5C_3H_7COC_3H_7]+(1-x)C_2H_5COC_2H_5$								
0.0505	1.8	0.2	0.4108	5.9	0.0	0.7755	3.5	−0.1
0.1276	3.3	−0.1	0.4443	5.9	0.0	0.8172	3.2	0.1
0.1762	4.2	−0.1	0.4974	5.6	−0.1	0.8931	2.0	0.0
0.2104	4.9	0.1	0.6066	5.1	−0.0	0.9211	1.8	0.2
0.2800	5.5	−0.0	0.6435	5.0	0.1	0.9432	1.0	−0.1
0.3329	5.90	0.15	0.7131	4.3	−0.0			
$x[0.5C_2H_5COC_2H_5+0.5C_4H_9COC_4H_9]+(1-x)C_3H_7COC_3H_7$								
0.1254	1.6	0.2	0.4118	4.6	0.2	0.7853	2.0	0.0
0.1841	2.4	−0.2	0.4432	4.6	0.1	0.8294	1.6	0.1
0.2245	3.1	0.0	0.5422	4.2	−0.1	0.9042	1.0	0.3
0.2900	3.8	0.0	0.6265	3.6	−0.2	0.9730	0.3	0.1
0.359	4.4	0.2	0.7014	2.9	−0.2			
$x[0.5C_3H_7COC_3H_7+0.5C_5H_{11}COC_5H_{11}]+(1-x)C_4H_9COC_4H_9$								
0.0895	−0.2	0.4061	−0.1	0.8305	−0.1			
0.0997	−0.1	0.5100	0.1	0.8689	0.2			
0.2143	0.1	0.6152	−0.1	0.8916	0.1			
0.2588	−0.0	0.7483	0.9					
$x[0.5CH_3COCH_3+0.5C_5H_{11}COC_5H_{11}]+(1-x)C_3H_7COC_3H_7$								
0.0288	−0.34	−0.89	0.2209	5.9	0.2	0.5507	10.8	0.20
0.0708	1.09	−0.43	0.3257	8.3	−0.1	0.6246	10.1	−0.46
0.0938	1.64	−0.46	0.3446	9.0	0.2	0.6739	9.5	−0.4
0.1236	3.04	0.13	0.4215	10.2	0.1	0.7997	6.6	−0.3
0.1732	4.75	0.43	0.5089	11.2	0.2	0.8356	5.9	0.1
0.1975	4.96	−0.06	0.5110	11.14	0.20	0.9111	4.1	0.9

Table 2
Experimental excess molar volumes, V_m^E for binary mixtures of $x[0.5\ C_kH_{2k+1}OC_kH_{2k+1} + 0.5\ C_lH_{2l+1}OC_lH_{2l+1}] + (1-x)\ C_mH_{2m+1}OC_mH_{2m+1}\}$ and $\{x[0.5\ C_kH_{2k+1}COC_kH_{2k+1} + 0.5\ C_lH_{2l+1}COC_lH_{2l+1}] + (1-x)\ C_mH_{2m+1}COC_mH_{2m+1}\}$, where $m=(k+l)/2$ at 298.15 K

x	V_m^E / cm^3 mol^{-1}	x	V_m^E / cm^3 mol^{-1}	x	V_m^E / cm^3 mol^{-1}
$x[0.5C_4H_9OC_4H_9+0.5C_2H_5OC_2H_5]+(1-x)C_3H_7OC_3H_7$					
0.0080	0.0037	0.4140	0.0038	0.8621	−0.0014
0.1069	−0.0012	0.4668	0.0033	0.9321	−0.0110
0.1535	−0.0029	0.5180	0.0041	0.9557	−0.0147
0.2264	−0.0048	0.6497	0.0034	0.9864	−0.0136
0.3360	−0.0017	0.7739	0.0007	0.9924	−0.0151
$x[0.5C_3H_7OC_3H_7+0.5C_5H_{11}OC_5H_{11}]+(1-x)C_4H_9OC_4H_9$					
0.0134	−0.0060	0.2352	−0.0017	0.5940	0.0091
0.0146	−0.0056	0.2746	0.0079	0.6393	−0.0067
0.1055	−0.0011	0.2889	0.0027	0.6624	0.0091
0.1160	−0.0042	0.4005	0.0065	0.7492	−0.0080
0.1744	−0.0052	0.4549	0.0110	0.9092	−0.0040
0.2194	−0.0016	0.5489	0.0013		
$x[0.5C_2H_5OC_2H_5+0.5C_8H_{17}OC_8H_{17}]+(1-x)C_5H_{11}OC_5H_{11}$					
0.0096	−0.0036	0.3783	−0.0035	0.7115	−0.0022
0.1645	−0.0025	0.5006	−0.0046	0.7503	−0.0012
0.2508	−0.0031	0.5313	−0.0030	0.8285	−0.0021
0.3246	−0.0038	0.5972	−0.0011	0.9013	−0.0076
$x[0.5CH_3COCH_3+0.5C_3H_7COC_3H_7]+(1-x)C_2H_5COC_2H_5$					
0.0058	−0.0013	0.2450	−0.0090	0.6975	−0.0097
0.0126	−0.0026	0.3297	−0.0106	0.6979	−0.0097
0.0226	−0.0023	0.4194	−0.0114	0.7929	−0.0074
0.0468	−0.0039	0.4955	−0.0115	0.7973	−0.0071
0.0682	−0.0056	0.5214	−0.0115	0.8027	−0.0065
0.0882	−0.0060	0.5609	−0.0114	0.8711	−0.0041
0.2107	−0.0085	0.6227	−0.0108		
$x[0.5C_2H_5COC_2H_5+0.5C_4H_9COC_4H_9]+(1-x)C_3H_7COC_3H_7$					
0.0113	−0.0016	0.4005	−0.0030	0.8219	−0.0024
0.0592	−0.0009	0.4691	−0.0020	0.8587	0.0006
0.1187	−0.0010	0.5231	−0.0003	0.8738	−0.0013
0.2229	−0.0001	0.5929	0.0005	0.9354	0.0036
0.2720	0.0038	0.6357	0.0024	0.9940	0.0037
0.2981	−0.0036	0.7188	0.0007		
0.3626	−0.0034	0.7791	0.0005		
$x[0.5C_3H_7COC_3H_7+0.5C_5H_{11}COC_5H_{11}]+(1-x)C_4H_9COC_4H_9$					
0.0051	−0.0014	0.4710	−0.0010	0.7203	−0.0000
0.1049	−0.0020	0.5015	−0.0003	0.7973	−0.0008
0.2804	−0.0003	0.5320	−0.0017	0.8372	−0.0009
0.3008	−0.0006	0.6201	−0.0007	0.9546	−0.0005
0.4132	−0.0002	0.6438	−0.0007	0.9909	−0.0024
$x[0.5CH_3COCH_3+0.5C_5H_{11}COC_5H_{11}]+(1-x)CH_3COCH_3$					
0.0054	−0.0152	0.2524	−0.0085	0.5151	−0.0060
0.0588	−0.0115	0.3027	−0.0108	0.5977	−0.0077
0.1323	−0.0057	0.4007	−0.0070	0.7065	−0.0107
0.1669	−0.0091	0.4449	−0.0014	0.8950	−0.0096
0.2143	−0.0109	0.5046	−0.0044	0.9881	−0.0067

The performance of the calorimeter was checked by measuring H_m^E of the test mixture (benzene+cyclohexane). Agreement with the literature results was always within 1% [10]. The V_m^E values were calculated from molar masses and densities of pure liquids and mixtures using an Anton Paar DMA 601 vibrating tube density meter, thermostatted at the temperature (298.15±0.01 K) as previously reported [11]. Diethyl ether was obtained from Acros (>99 mol %), di-*n*-propyl ether from Aldrich (>99 mol %), di-*n*-butyl ether from Fluka (99.5 mol %), di-isoamyl ether from Riedel de Haen (97 mol %) and di-*n*-octyl ether from Aldrich (99 mol %). All of the ethers were used without further purification except di-isoamyl ether. Distillation [12,13] of the di-isoamyl ether improved the purity to 98 mol %, at best. The cost of purchasing purer di-isoamyl ether was prohibitive. The ketones were distilled before use [12,13], dried using 0.4 nm molecular sieves. Acetone was obtained from Baxter,

Table 3
Coefficients A_r(J mol^{-1}) for H_m^E $\{x[0.5\ C_kH_{2k+1}OC_kH_{2k+1}+0.5\ C_lH_{2l+1}OC_lH_{2l+1}]+(1-x)\ C_mH_{2m+1}OC_mH_{2m+1}\}$ and $\{x[0.5\ C_kH_{2k+1}COC_kH_{2k+1}+0.5\ C_lH_{2l+1}COC_lH_{2l+1}]+(1-x)\ C_mH_{2m+1}COC_mH_{2m+1}\}$, where $m=(k+l)/2$ at the temperature 298.15 K by Eq.(1)

Mixture	A_0	A_1	A_2
$x[0.5C_2H_5OC_2H_5+0.5C_4H_9OC_4H_9]+(1-x)C_3H_7OC_3H_7$	16.46	0.15	−3.48
$x[0.5C_3H_7OC_3H_7+0.5C_5H_{11}OC_5H_{11}]+(1-x)C_4H_9OC_4H_9$	14.82	0.45	−1.97
$x[0.5C_2H_5OC_2H_5+0.5C_8H_{17}OC_8H_{17}]+(1-x)C_4H_9OC_4H_9$	116.05	−17.25	−17.60
$x[0.5CH_3COCH_3+0.5C_3H_7COC_3H_7]+(1-x)C_2H_5COC_2H_5$	22.90	−7.02	5.70
$x[0.5C_2H_5COC_2H_5+0.5C_4H_9COC_4H_9]+(1-x)C_3H_7COC_3H_7$	17.86	−4.65	−8.87
$x[0.5CH_3COCH_3+0.5C_5H_{11}COC_5H_{11}]+(1-x)C_3H_7COC_3H_7$	43.59	9.42	−16.96

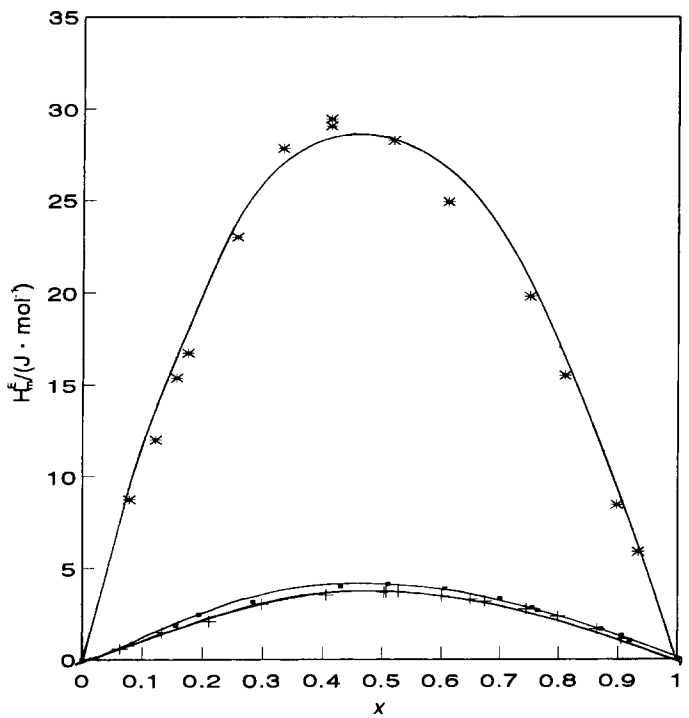

Fig. 1. Excess molar enthalpy H_m^E for: ■ $\{x[0.5C_2H_5OC_2H_5+0.5C_4H_9OC_4H_9]+(1-x)C_3H_7OC_3H_7\}$;+$\{x[0.5C_3H_7OC_3H_7\ 0.5C_5H_{11}OC_5H_{11}]+(1-x)C_4H_9OC_4H_{11}\}$ and * $\{x[0.5C_2H_5OC_2H_5+0.5C_8H_{17}OC_8H_{17}]+(1-x)C_5H_{11}OC_5H_{11}\}$ at 298.15 K.

Burdick and Jackson (>99 mol %), pentan-3-one from Riedel de Haen (99 mol %), heptan-4-one (98 mol %), nonan-5-one (98 mol %) and undecan-6-one (97 mol %) from Acros. Distillation of the solvents improved the purity by at least 1 mol %. The mole fraction of H_2O in each of the liquids was determined by Karl Fischer titration to be <0.0002. All of the solvents used in this work were kept in a dry box before use. The pseudo-mixtures were made up as previously described [1]. The mole fractions of the pseudo-ether and pseudo-ketone are calculated by using their respective mean molar mass, and regarding the pseudo-compound as a single pure substance.

3. Results

The H_m^E results are given in Table 1, together with the deviations δ, where

$$\delta = H_m^E/\mathrm{J\,mol^{-1}} - x(1-x)\sum_{r=0}^{n} A_r(1-2x)^r.$$

The V_m^E results are given in Table 2. The Redlich–Kister polynomial was not applied to V_m^E for most of the systems as the V_m^E results showed a large scatter in V_m^E. The experimental error in H_m^E is of the order of 1 J mol^{-1} or 1%; in V_m^E it is of the order 0.004 cm^3 mol^{-1}, and in x it is estimated to be less than 1×10^{-3}. The coefficients A_r are given in Table 3.

4. Discussion

The results show a small positive excess enthalpy, 4.2 J mol^{-1} < $H^E_{m(max)}$<29 J mol^{-1} for all the mixtures investigated here except the x[0.5 ($C_5H_{11}OC_5H_{11}$)+ 0.5 ($C_3H_7OC_3H_7$)]+(1−x) $C_4H_9OC_4H_9$ ether system and the x[0.5 ($C_5H_{11}COC_5H_{11}$)+0.5 ($C_3H_7COC_3H_7$)] +(1−x) $C_4H_9COC_4H_9$ ketone system. The enthalpic behaviour of the latter two mixtures over the whole composition range were small (0.9 J mol^{-1} <$H^E_{m(max)}$<3.7 J mol^{-1}) and suggest confirmation of the congruency principle for pseudo mixtures containing constituent liquids which do not differ from one another by more than one –CH_2– group. The H_m^E data

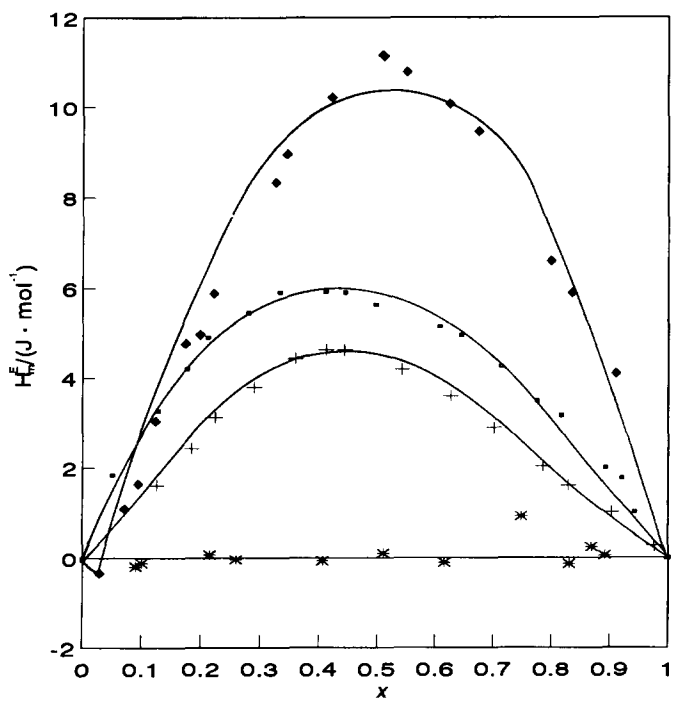

Fig. 2. Excess molar enthalpy H_m^E for: ■ {x[0.5CH_3COCH_3 + 0.5$C_3H_7COC_3H_7$] +(1−x) $C_2H_5COC_2H_5$}; +{x[0.5$C_2H_5COC_2H_5$+0.5$C_4H_9COC_4H_9$]+ (1−x)$C_3H_7COC_3H_7$ }; * {x[0.5$C_3H_7COC_3H_7$+0.5$C_5H_{11}COC_5H_{11}$]+(1−x)$C_4H_9COC_4H_9$} and ◆ {x[0.5CH_3COCH_3+0.5$C_5H_{11}COC_5H_{11}$]+(1−x)$C_3H_7COC_3H_7$} at 298.15 K.

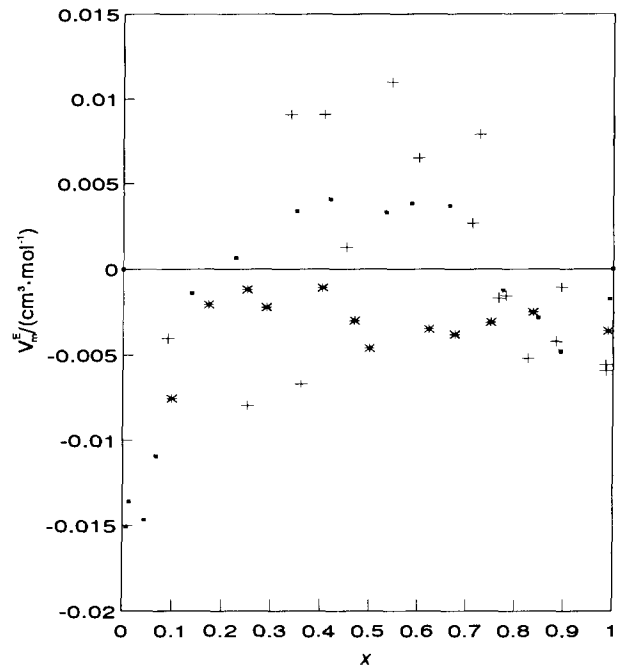

Fig. 3. Excess molar volume V_m^E for: ■ $\{x[0.5C_2H_5OC_2H_5\ 0.5C_4H_9OC_4H_9]+(1-x)C_3H_7OC_3H_7\}$;+$\{x[0.5C_3H_7OC_3H_7+0.5C_5H_{11}OC_5H_{11}]+(1-x)C_4H_9OC_4H_{11}\}$ and * $\{x[0.5C_2H_5OC_2H_5+0.5C_8H_{17}OC_8H_{17}]+(1-x)C_5H_{11}OC_5H_{11}\}$ at 298.15 K.

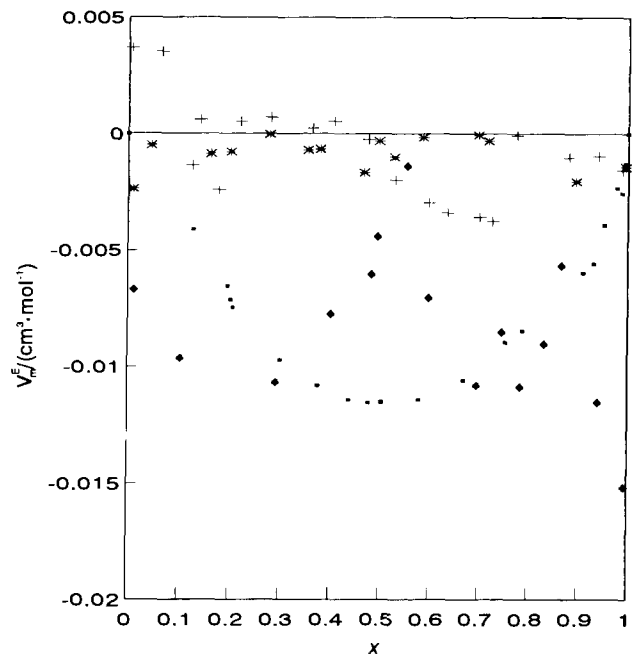

Fig. 4. Excess molar volume V_m^E for: ■ $\{x[0.5CH_3COCH_3\ 0.5C_3H_7COC_3H_7]+(1-x)C_2H_5COC_2H_5\}$;+$\{x[0.5C_2H_5COC_2H_5+0.5C_4H_9COC_4H_9]+(1-x)C_3H_7COC_3H_7\}$; * $\{x[0.5C_3H_7COC_3H_7+0.5C_5H_{11}COC_5H_{11}]+(1-x)C_4H_9COC_4H_9\}$ and ◆ $\{x[0.5CH_3COCH_3+0.5C_5H_{11}COC_5H_{11}]+(1-x)C_3H_7COC_3H_7\}$ at 298.15 K.

for the remainder of the mixtures, in general, seems to indicate that the greater disparity in the carbon number for the pseudo mixture, the greater the divergence from the principle of congruency, for example $H^E_{m(max)}$ for x[0.5 (CH_3COCH_3)+0.5 ($C_5H_{11}COC_5H_{11}$)]+ (1−x) $C_3H_7COC_3H_7$ is 11.2 J mol^{-1} while $H^E_{m(max)}$ for x[0.5 (CH_3COCH_3) +0.5 ($C_3H_7COC_3H_7$)]+(1−x) $C_2H_5COC_2H_5$ is 5.9 J mol^{-1} (see Figs. 1 and 2).

The V^E_m data for all the systems investigated here show no regular pattern and the data are scattered around ±0.01 cm^3 mol^{-1}, except for the x[0.5 ($C_3H_7COC_3H_7$) +0.5 (CH_3COCH_3)] + (1−x) $C_2H_5COC_2H_5$ system. In the latter system the V^E_m curves are symmetrical around x=0.7 with $V^E_{m(max)}$=−0.012 cm^3 mol^{-1} (see Figs. 1–2).

The results for (an alkane of carbon number m+a pseudo-alkane of the same carbon number) reported by Letcher et al. [1] show H^E_m and V^E_m within a limit of 0±1.1 J mol^{-1} and 0±0.005 cm^{3}mol^{-1}, respectively, while the results presented here are within 0.3–29 J mol^{-1} and 0±0.01 cm^{3}mol^{-1}, respectively. In general, the V^E_m and H^E_m data presented here for most of the systems, as well as the data for the n-alkanes have been shown to do [1] (see Figs. 3 and 4), do not satisfy the congruency principle.

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