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Excess molar volumes and isentropic compressibilities of binary mixtures containing methyl methacrylate–n-alcohols at 303.15 and 313.15 K

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Abstract

Excess molar volumes and isentropic compressibilities were measured at 303.15 and 313.15 K over the whole range of composition for methyl methacrylate (MMA)–n-alcohol mixtures from density and sound velocities, respectively. Excess volumes for MMA–methanol and MMA–propanol were found to be negative for the entire range except at higher MMA concentrations. Positive excess volumes were, however, noted for MMA–butanol, MMA–pentanol and MMA–hexanol systems. The temperature coefficients of expansion at an ester mole fraction of 0.5 were estimated and observed to decrease with increase in the carbon chain-length of the alcohols. The excess isentropic compressibilities show a similar trend. The results are explained in terms of specific packing and non-specific dispersing interactions.

Keywords: Alcohol; Binary mixtures; Excess molar volumes; Isentropic compressibilities

1. Introduction

The thermodynamic properties of binary mixtures involving non-electrolytes have received extensive theoretical and experimental considerations [1]. Acrylic esters, despite their wide industrial use and importance, have rarely been evaluated for their binary mixtures with other components, which are often used either as the medium or reactants for ester interchange reactions. A knowledge of the various properties of mixtures involving acrylic esters and polar self-associating liquids, such as alcohols and non-polar hydrocarbons, helps in designing an efficient industrial process and also in understanding their separation processes.

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Von Rätzch and coworkers [2,3] and Benson and coworkers [4,5] have reported excess enthalpies and volumes for binary mixtures of methyl methacrylate with several hydrocarbons. Hull and Lu [6] and Lu et al. [7] have also investigated the isothermal vapour–liquid equilibria in mixtures of methyl methacrylates and hydrocarbons. Recently the same group carried out measurements of excess enthalpies and molar volumes of methyl methacrylate–methanol/ethanol systems at 298.15 K [8].

In order to measure systematically the various excess thermodynamic functions of binary mixtures involving acrylic esters and self-associating alcohols or non-polar hydrocarbons for a comprehensive understanding of these systems, this paper presents the experimentally measured excess volumes and isentropic compressibilities for binary mixtures containing methyl methacrylate and several normal alcohols at 303.15 and 313.15 K.

2. Experimental

The MMA was Merck product with > 99% purity, used without further purification. Methanol was of BDH AnalaR grade and further purified by warming it with iodine over magnesium foils until the first disappearance of I_2 colour. More I_2 was then dissolved and the contents were refluxed for 30 min. The product was then distilled with the exclusion of moisture and redistilled once more over tribromo-benzoic acid to remove basic impurities. *n*-Propanol was of technical grade, purified by refluxing for 5 h and distilled through a 1-m column in a stream of hydrogen at 40–50 mm pressure. *n*-Butanol of technical grade was kept over unslaked lime overnight and distilled. The central portion was further digested over barium oxide, then treated with sodium and finally fractionally distilled. *n*-Pentanol and *n*-hexanol were Fluka purum grade chemicals and were used as such without any treatment. The purity of all the chemicals was checked by measuring various physical properties and comparing them with the literature values (Table 1).

Table 1
Physical properties of pure components

	303.15 K				313.15 K			
	Denisty/g cm^{-3}		Viscosity/cP		Density/gcm^{-3}		Viscosity/cP	
	This work	Lit.[a]	This work	Lit.[a]	This work	Lit.	This work	Lit.
MMA	0.9323	–	0.529	–	0.9230	–	0.453	–
Methanol	0.7818	0.7816	0.495	–	0.7770	–	0.445	–
n-Propanol	0.7953	0.7955	1.917	–	0.7880	–	1.432	–
n-Butanol	0.8023	0.8021	2.300	2.271	0.7945	–	1.900	–
n-Pentanol	0.8075	0.8076	3.345	3.347	0.7993	–	2.460	–
n-Hexanol	0.8121	0.8120	3.762	3.765	0.8034	–	3.110	–

[a] From Ref. [9].

Mixtures were prepared in stoppered pyrex glass vials by accurate weighings. The densities of pure liquids and their binary mixtures were measured by a Lypkin-type bicapillary Pyknometer [10]. The pyknometer was suspended vertically in a thermostat maintained at a constant measuring temperature of ± 0.01 K. The pyknometer was calibrated with triple-distilled water and double-distilled benzene in the temperature range of 28–50°C. The accuracy in the density measurement was within 0.0001 units.

The isentropic compressibilities K_S were evaluated from the following relation

$$K_S = 1/v^2 d \tag{1}$$

where v is the velocity of sound in m s^{-1}, and d the density in kg m^{-3}. The sound velocities in pure liquids and their binary solutions were measured with an Ultrasonic Interferometer (Mittal Enterprises, New Delhi, India). The apparatus was built to operate at a single frequency of 2 MHz. The temperature of the double-jacketed

Table 2
Excess molar volumes V_m^E for $\{x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{OH}\}$ at 303.15 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	V_m^E/ cm^{3}mol^{-1}
$x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{CH_3OH}$							
0.0410	−0.0564	0.1959	−0.3689	0.4707	−0.5163	0.8785	0.0712
0.0865	−0.1117	0.2702	−0.5447	0.6040	−0.4032	0.9348	0.091
0.1400	−0.2179	0.3613	−0.5616	0.7744	−0.2381		
$x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{C_3H_7OH}$							
0.0710	−0.0132	0.3199	−0.0732	0.6199	−0.1191	0.9278	0.1032
0.1480	−0.0260	0.4146	−0.1120	0.7343	−0.0563	0.9639	0.0755
0.2323	−0.0432	0.5093	−0.1523	0.8721	0.0563		
$x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{C_4H_9OH}$							
0.0881	0.1164	0.3634	0.3821	0.6653	0.3912	0.9391	0.1762
0.1778	0.2142	0.4629	0.4134	0.7741	0.3036	0.9715	0.1088
0.2689	0.2840	0.5599	0.4096	0.8866	0.2219		
$x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{C_5H_{11}OH}$							
0.1003	0.2077	0.4038	0.6140	0.6997	0.6574	0.9491	0.2284
0.2009	0.3725	0.5067	0.6628	0.8036	0.5178	0.9883	0.1484
0.3036	0.5105	0.6015	0.6849	0.9002	0.3328		
$x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{C_6H_{13}OH}$							
0.1136	0.3089	0.4351	0.7780	0.7275	0.8203	0.9537	0.3605
0.2237	0.5254	0.5420	0.9025	0.8200	0.6271	0.9786	0.2145
0.3312	0.6754	0.6322	0.8707	0.9134	0.4656		

interferometer cell was maintained by circulating water from a constant temperature bath. The measured sound velocities have an error of ± 0.02%.

3. Results and discussion

3.1. Excess molar volumes

The densities measured over the entire composition range of binary mixtures at 303.15 and 313.15 K were used for calculating the excess molar volumes V_m^E using the relation

$$V_m^E = \frac{x_1 M_1 + x_2 M_2}{d_{12}} - [x_1 M_1/d_1 + x_2 M_2/d_2] \tag{2}$$

Table 3
Excess molar volumes V_m^E for $\{xCH_2{:}C(CH_3)CO_2CH_3 + (1-x)C_nH_{2n+1}OH\}$ at 313.15 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	V_m^E/ cm^{3}mol^{-1}
$xCH_2{:}C(CH_3)CO_2CH_3 + (1-x)CH_3OH$							
0.0410	−0.0580	0.1959	−0.4220	0.4707	−0.4420	0.8785	0.0820
0.0865	−0.1200	0.2702	−0.5880	0.6040	0.0615	0.9348	0.0450
0.1400	−0.2310	0.3613	−0.5760	0.7744	0.1121		
$xCH_2{:}C(CH_3)CO_2CH_3 + (1-x)C_3H_7OH$							
0.0710	−0.0526	0.3199	−0.1746	0.6199	−0.1688	0.9278	−0.0460
0.1480	−0.0820	0.4146	−0.2100	0.7343	−0.1443	0.9639	−0.0245
0.2323	−0.1402	0.5093	−0.1820	0.8721	−0.0720		
$xCH_2{:}C(CH_3)CO_2CH_3 + (1-x)C_4H_9OH$							
0.0881	0.1243	0.3634	0.2605	0.6653	0.3622	0.9391	0.1865
0.1778	0.1809	0.4629	0.3101	0.7741	0.3035	0.9715	0.1176
0.2689	0.2200	0.5599	0.3401	0.8866	0.2050		
$xCH_2{:}C(CH_3)CO_2CH_3 + (1-x)C_5H_{11}OH$							
0.1003	0.1935	0.4038	0.6177	0.6997	0.7050	0.9491	0.4215
0.2009	0.3842	0.5067	0.6728	0.8030	0.6835	0.9883	0.2839
0.3036	0.5112	0.6015	0.7146	0.9002	0.6025		
$xCH_2{:}C(CH_3)CO_2CH_3 + (1-x)C_6H_{13}OH$							
0.1136	0.3245	0.4351	0.6992	0.7275	0.8048	0.9537	0.6068
0.2237	0.5275	0.5420	0.7651	0.8200	0.7159	0.9786	0.3250
0.3312	0.6183	0.6322	0.7972	0.9134	0.6975		

where M, x, d correspond to molecular weight, mole fraction and densities respectively for the pure ester (2) and alcohol (1) and their mixtures (12). The results thus obtained are presented in Tables 2 and 3. The excess molar volumes are further fitted to a Redlich–Kister-type smoothing equation

$$X^E = x(1-x)\sum_{i=0}^{i=7}(2x-1)^i \tag{3}$$

where X^E is the excess volume or compressibility and x the mole fraction of the ester component. The polynomial coefficients i are calculated by a multiple regression analysis based on a least-squares method using the program STATGRAPHICS Version 5 on a PC 80386. The degree of the polynomial was raised successively until a value close to 1 was obtained for the regression coefficient. The values of the coefficients together with the standard deviations in V_m^E in cm^3 mol^{-1} are presented in Table 4. The fitted values together with the experimental points for the various MMA–alcohol mixtures are shown in the Figs. 1 and 2 at 303.15 and 313.15 K respectively.

The excess volumes for MMA–methanol and MMA–propanol mixtures were found to be negative in the whole range of mole fractions except at higher proportions

Table 4
Coefficients a_i and standard deviation s for the least-squares fittings of V_m^E (cm^{3}mol^{-1}) for $\{x\text{CH}_2\text{:C(CH}_3\text{)CO}_2\text{CH}_3 + (1-x)\text{C}_n\text{H}_{2n+1}\text{OH}\}$ at 303.15 and 313.15 K by Eq. (3)

T/K	a_0	a_1	a_2	a_3	a_4	a_5	a_6	a_7	s
$x\text{CH}_2\text{:C(CH}_3\text{)CO}_2\text{CH}_3 + (1-x)\text{CH}_3\text{OH}$									
303.15	−1.825	1.677	−6.709	−5.629	27.125	15.811	−19.994	−11.364	0.0004
313.15	−1.115	6.672	−1.363	−15.450	7.269	14.290	−5.558	−4.482	0.001
$x\text{CH}_2\text{:C(CH}_3\text{)CO}_2\text{CH}_3 + (1-x)\text{C}_3\text{H}_7\text{OH}$									
303.15	−0.562	−0.018	−1.545	−1.789	−1.975	7.662	2.843	−4.624	0.0001
313.15	−0.759	0.323	−0.495	−1.383	2.691	1.372	−2.671	0.071	0.0001
$x\text{CH}_2\text{:C(CH}_3\text{)CO}_2\text{CH}_3 + (1-x)\text{C}_4\text{H}_9\text{OH}$									
303.15	1.689	0.179	−0.505	0.553	0.241	−1.900	1.708	3.153	0.0003
313.15	1.284	1.053	1.224	−2.912	−4.317	3.113	6.086	0.277	0.002
$x\text{CH}_2\text{:C(CH}_3\text{)CO}_2\text{CH}_3 + (1-x)\text{C}_5\text{H}_{11}\text{OH}$									
303.15	2.715	−1.830	−1.634	35.846	12.575	−113.25	−16.079	98.005	0.0005
313.15	2.852	−4.414	−5.605	71.967	38.659	−219.69	−44.060	191.41	0.0004
$x\text{CH}_2\text{:C(CH}_3\text{)CO}_2\text{CH}_3 + (1-x)\text{C}_6\text{H}_{13}\text{OH}$									
303.15	3.396	1.650	1.315	−2.407	−4.580	−1.535	7.223	7.768	0.004
313.15	2.857	2.636	6.609	−18.411	−24.837	55.255	34.756	−40.394	0.001

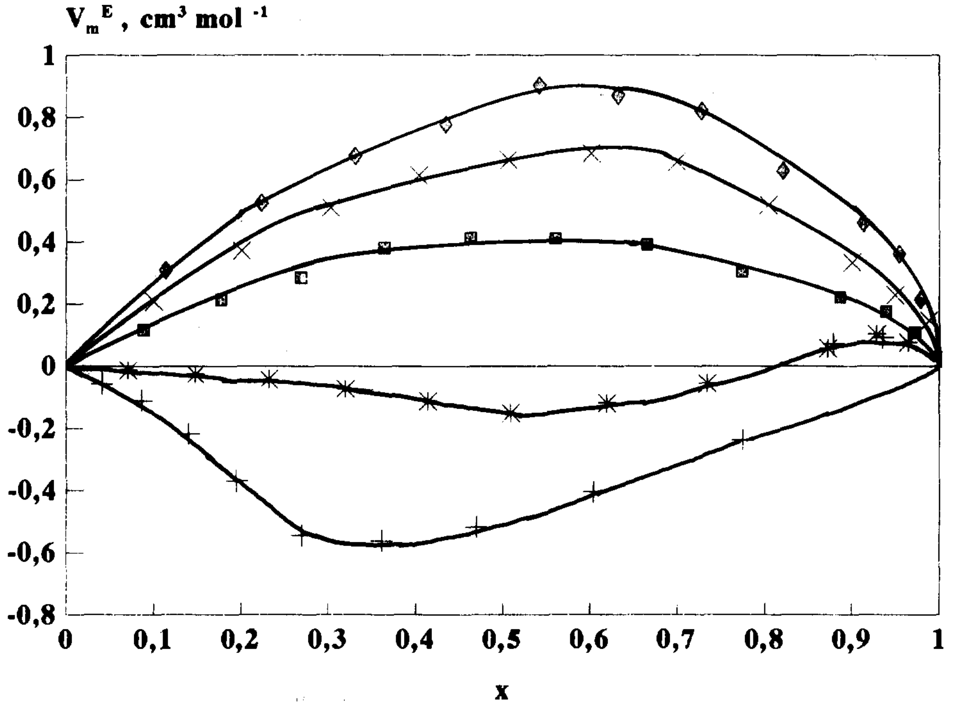

Fig. 1. Excess molar volumes V_M^E for $\{xCH_2{:}C(CH_3)CO_2CH_3 + (1-x)C_nH_{2n+1}OH\}$ at 303.15 K: +, CH_3OH; ✱, C_3H_7OH; □, C_4H_9OH; ×, $C_5H_{11}OH$; ◇, $C_6H_{13}OH$; ———, calculated from Eq. (3) with coefficients from Table 4.

of ester, where a slight positive trend was observed both at 303.15 and 313.15 K. However for the higher homologous alcohols, positive excess volumes were found over the entire range of ester proportions. The excess volumes in general were found to increase in the following order: $CH_3OH < C_3H_7OH < C_4H_9OH < C_5H_{11}OH < C_6H_{13}OH$.

As far as we are aware, there are no V_m^E data for these systems in the literature for comparison at 303.15 and 313.15 K. However Zhang et al. (8) have also reported negative excess molar volumes for MMA–methanol and positive excess volumes for MMA–ethanol mixtures at 298.15 K.

It has been suggested that two possible opposing effects, namely specific interactions between the ester and the –OH group of the alcohol, and non-specific dispersing intractions, i.e. the breaking of intramolecular hydrogen bondings in the alcohol molecules by unlike ester components for the alkyl formate–[11, 12] and alkyl alkanoate–[13, 14] alcohol mixtures. The relative sizes of both the ester and alcohol molecules are thus expected to play a role in the net total interactions.

The observed negative excess molar volumes for MMA–methanol and MMA–propanol are thus indicative of net specific interactions between the ester and –OH groups through hydrogen bondings and of further packing effects induced by additional interactions between the Π-electrons of the ester and –OH groups of the

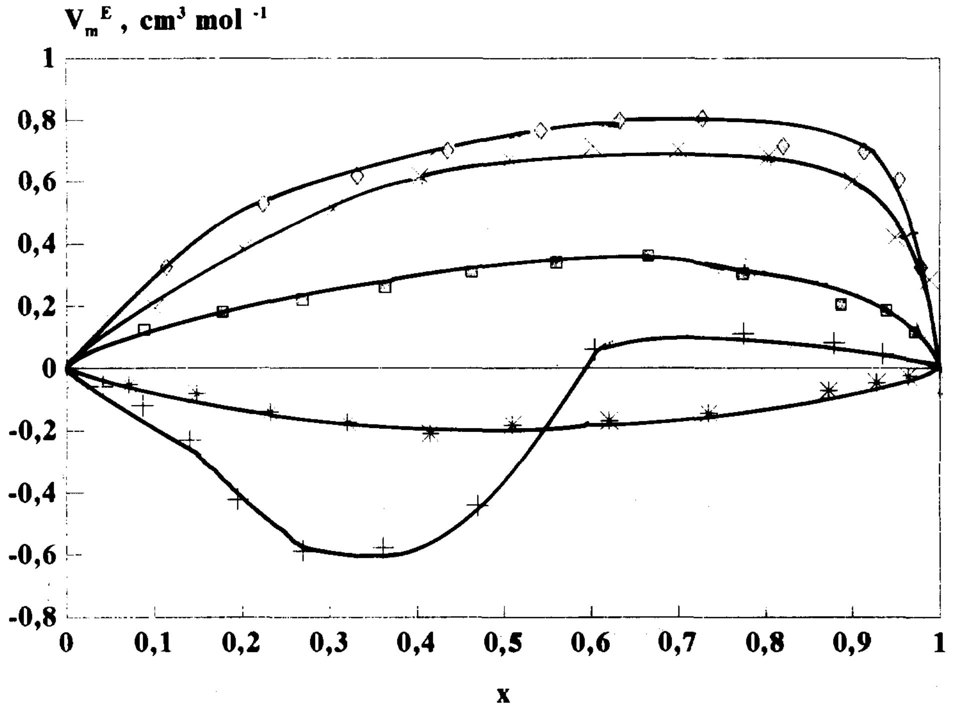

Fig. 2. Excess molar volumes V_m^E for $\{xCH_2{:}C(CH_3)CO_2CH_3+(1-x)C_nH_{2n+1}OH\}$ at 313.15 K: +, CH_3OH; ✱, C_3H_7OH; □, C_4H_9OH; ×, $C_5H_{11}OH$; ◇, $C_6H_{13}OH$; ———, calculated from Eq. (3) with coefficients from Table 4.

alcohols. Letcher et al. [15] have also discussed the role of double bonds in 1-alkenes –methanol or –ethanol interactions. However, with the increase in the carbon chain length in the alcohols, such interstitial accomdation becomes poorer because of steric factors and thus dispersing interactions predominate, resulting in overall positive excess volumes as observed in our case from *n*-butanol to *n*-hexanol. The temperature coefficients of expansion at an ester mole fraction of 0.5 are given in Table 5.

Table 5
Excess molar volume (V_m^E) and temperature coefficeint $(\partial V^E/\partial T)_p$ at $x = 0.5$

Mixture	V_m^E/cm^3mol^{-1}		$(\partial V_m^E/\partial T)/$ $cm^3mol^{-1}K^{-1}$
	303.15 K	313.13 K	
$xCH_2{:}C(CH_3)CO_2CH_3+(1-x)CH_3OH$	−0.492	−0.365	0.0127
$xCH_2{:}C(CH_3)CO_2CH_3+(1-x)C_3H_7OH$	−0.150	−0.185	−0.0035
$xCH_2{:}C(CH_3)CO_2CH_3+(1-x)C_4H_9OH$	0.414	0.320	−0.0094
$xCH_2{:}C(CH_3)CO_2CH_3+(1-x)C_5H_{11}OH$	0.652	0.651	−0.0010
$xCH_2{:}C(CH_3)CO_2CH_3+(1-x)C_6H_{13}OH$	0.8622	0.720	−0.0142

3.2. Excess isentropic compressibilities

The excess isentropic compressibilities of binary mixtures are calculated using the relation

$$K_S^E = K_{S12} - (\phi_1 K_{S1} + \phi_2 K_{S2}) \tag{4}$$

where ϕ and K_S represent the volume fraction and isentropic compressibility for pure ester (2) and alcohol (1) and their mixture (12) components, respectively. The experimental K_S^E values at 303.15 and 313.15 K are given in Tables 6 and 7. The K_S^E values were fitted using Eq. (3), as described earlier, and the estimated polynomial coefficients together with the standard deviations (in Tpa^{-1}) are given in Table 8. The smoothed curves along with the experimental points for K_S^E at 303.15 and 313.15 K are presented in Figs. 3 and 4.

Table 6
Excess isoentropic compressibilities K_S^E for $\{x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{C_nH_{2n+1}OH}\}$ at 303.15 K

x	K_S^E/ TPa^{-1}	x	K_S^E/ TPa^{-1}	x	K_S^E/ TPa^{-1}	x	K_S^E/ TPa^{-1}
			$x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{CH_3OH}$				
0.0410	−2.080	0.1959	−6.725	0.4707	−9.739	0.8785	1.629
0.0865	−3.565	0.2702	−8.693	0.6040	−8.056	0.9348	1.357
0.1400	−4.456	0.3613	−9.249	0.7744	−3.792		
			$x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{C_3H_7OH}$				
0.0710	−1.477	0.3199	2.020	0.6199	3.791	0.9278	1.967
0.1480	−2.397	0.4146	2.555	0.7343	2.916	0.9639	1.550
0.2323	1.630	0.5093	3.486	0.8721	2.537		
			$x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{C_4H_9OH}$				
0.0881	3.582	0.3634	10.616	0.6653	9.172	0.9391	1.041
0.1778	8.099	0.4629	10.916	0.7741	6.056	0.9715	0.214
0.2689	9.551	0.5599	10.207	0.8866	1.425		
			$x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{C_5H_{11}OH}$				
0.1003	11.425	0.4038	21.584	0.6997	12.044	0.9491	1.561
0.2009	16.932	0.5067	19.158	0.8036	7.953	0.9883	1.013
0.3036	22.816	0.6015	16.444	0.9002	4.514		
			$x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{C_6H_{13}OH}$				
0.1136	19.654	0.4351	33.499	0.7275	25.149	0.9537	5.039
0.2237	26.534	0.5420	31.671	0.8200	18.602	0.9786	2.884
0.3312	33.924	0.6322	29.801	0.9134	9.179		

Table 7
Excess isoentropic compressibilities K_S^E for $\{x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{OH}\}$ at 313.15 K

x	K_S^E/ TPa^{-1}	x	K_S^E/ TPa^{-1}	x	K_S^E/ TPa^{-1}	x	K_S^E/ TPa^{-1}
			$x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{CH_3OH}$				
0.0410	−12.696	0.1959	−21.296	0.4707	−22.540	0.8785	−5.845
0.0865	−16.050	0.2702	−23.103	0.6040	−18.546	0.9348	−2.135
0.1400	−18.950	0.3613	−23.000	0.7744	−11.390		
			$x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{C_3H_7OH}$				
0.0710	−6.740	0.3199	−20.520	0.6199	−16.250	0.9278	−1.500
0.1480	−12.856	0.4146	−22.255	0.7343	−11.545	0.9639	−0.424
0.2323	−16.434	0.5093	−20.200	0.8721	−5.360		
			$x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{C_4H_9OH}$				
0.0881	2.370	0.3634	3.711	0.6653	2.817	0.9391	0.935
0.1778	2.909	0.4629	4..496	0.7741	2.456	0.9715	0.348
0.2689	3.214	0.5599	3.556	0.8866	1.074		
			$x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{C_5H_{11}OH}$				
0.1003	2.492	0.4038	5.047	0.6997	3.902	0.9491	1.985
0.2009	3.771	0.5067	5.432	0.8036	2.435	0.9883	0.468
0.3036	4.445	0.6015	4.371	0.9002	2.176		
			$x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{C_6H_{13}OH}$				
0.1136	3.724	0.4351	7.745	0.7275	7.055	0.9537	2.457
0.2237	5.343	0.5420	8.441	0.8200	5.256	0.9786	1.820
0.3312	6.924	0.6322	8.260	0.9134	3.120		

Table 8
Coefficients a_i and standard deviation s for the least-squares fittings of K_S^E in TPa^{-1} for $\{x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{OH}\}$ at 303.15 and 313.15 K by Eq. (3)

T/K	a_0	a_1	a_2	a_3	a_4	a_5	a_6	a_7	s
				$x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{CH_3OH}$					
303.15	−34.900	10.304	−92.111	5.534	469.211	115.748	−418.856	−87.657	0.001
313.15	−84.968	20.729	−69.928	332.015	180.139	−937.977	−242.483	902.941	0.310
				$x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{C_3H_7OH}$					
303.15	11.447	17.995	66.521	−147.170	−342.483	521.136	325.950	−400.76	0.0001
313.15	−83.148	72.070	62.614	−315.577	−199.036	723.455	204.208	−467.86	0.003

Table 8 *(continued)*

T/K	a_0	a_1	a_2	a_3	a_4	a_5	a_6	a_7	s
				$x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{C_4H_9OH}$					
303.15	43.097	2.275	5.530	−103.148	−10.089	111.471	−39.874	−1.399	0.002
313.15	15.365	0.3849	−7.124	−15.252	22.458	–	–	–	0.576
				$x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{C_5H_{11}OH}$					
303.15	77.901	−92.929	42.254	370.152	−137.47	−852.22	127.220	571.398	1.165
313.15	20.577	5.760	2.657	−129.15	−86.18	390.20	154.71	−317.47	0.175
				$x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{C_6H_{13}OH}$					
303.15	132.328	−65.21	96.98	316.240	−348.72	−643.90	−418.806	254.23	1.013
313.15	33.323	−78.22	−8.303	129.457	−50.522	−504.02	−51.891	474.944	0.243

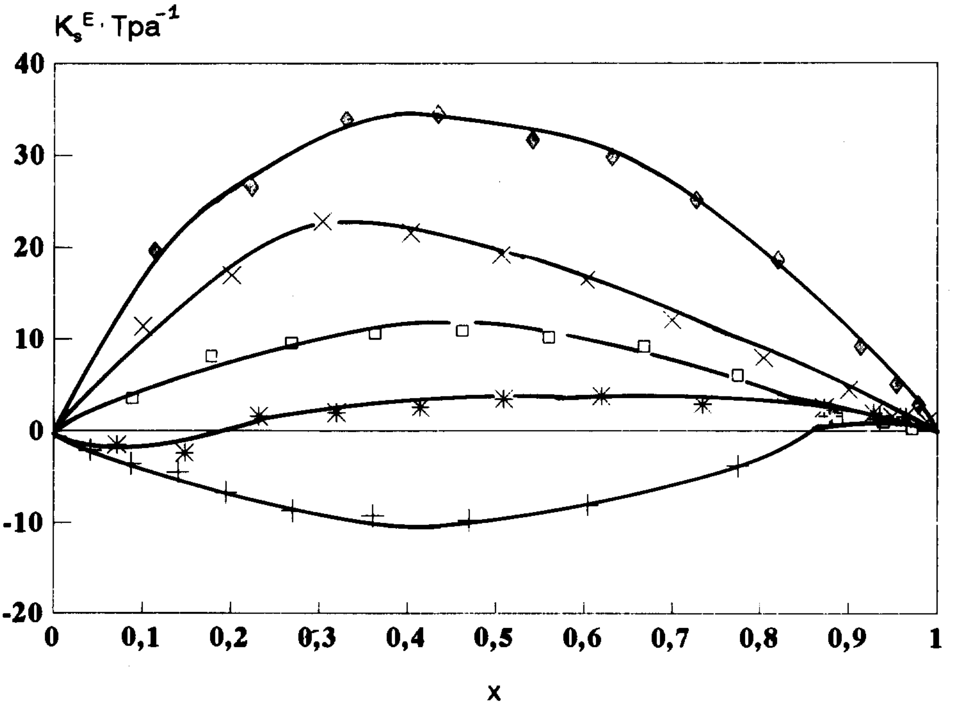

Fig. 3. Excess isentropic compressibilities K_S^E for $\{x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{OH}\}$ at 303.15 K: +, $\mathrm{CH_3OH}$; ✱, $\mathrm{C_3H_7OH}$; □, $\mathrm{C_4H_9OH}$; ×, $\mathrm{C_5H_{11}OH}$; ◇, $\mathrm{C_6H_{13}OH}$; ———, calculated from Eq. (3) and coefficients from Table 8.

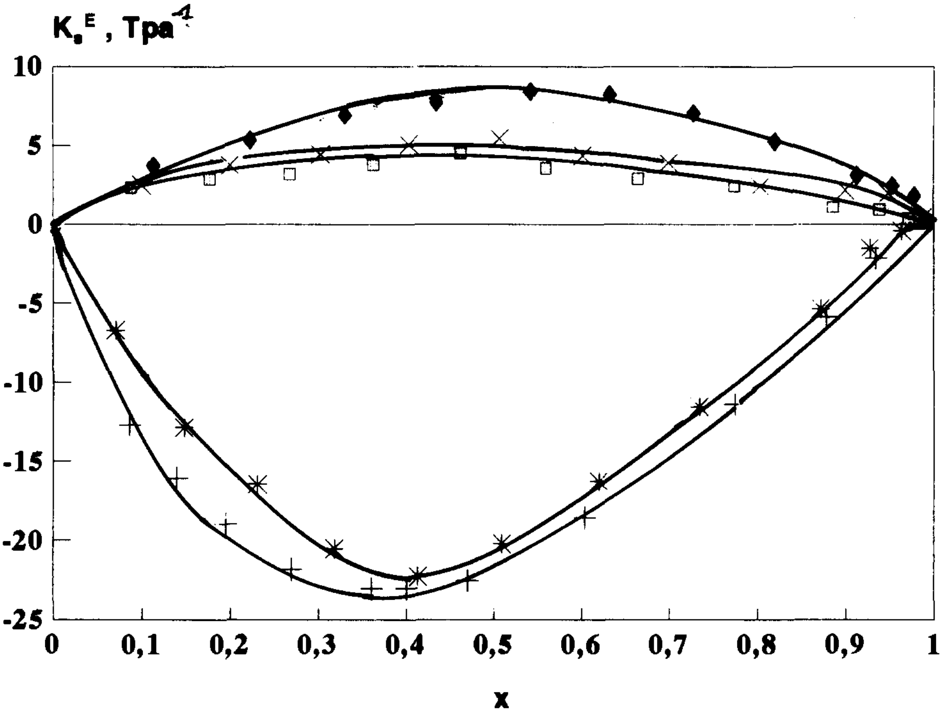

Fig. 4. Excess isentropic compressibilities K_S^E for $\{x\mathrm{CH_2{:}C(CH_3)CO_2CH_3} + (1-x)\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{OH}\}$ at 313.15 K: +, CH_3OH; ✱, C_3H_7OH; □, C_4H_9OH; ×, $C_5H_{11}OH$; ◇, $C_6H_{13}OH$; ———, calculated from Eq. (3) and coefficients from Table 8.

The observed results can be explained in the following manner. As can be seen from Figs. 3 and 4, the K_S^E values for MMA–alcohol systems showed two different trends, one for MMA–methanol/propanol and another for MMA–higher alcohol mixtures. In both the MMA–methanol and –propanol systems, K_S^E values were negative for the entire concentration range (except slight positive values for MMA–propanol systems in ester-rich regions) at 303.15 and 313.15 K. With the rise in temperature, less negative K_S^E values are observed. The negative K_S^E values confirm the specific interactions in these systems through a better interstitial accomodatioin of smaller alcohol molecules among the ester molecules, leaving less free volume. In the case of higher chain alcohols, namely C_4H_9OH, $C_5H_{11}OH$ and $C_6H_{13}OH$, the K_S^E values both at 303.15 and 313.15 K were found to be positive, with a general decrease at 313.15 K, over the entire concentration range. The positive K_S^E values suggest the dominance of non-specific structure-breaking dispersing interactions, as discussed earlier.

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