Excess Properties of Binary Mixtures Containing 2-Methoxy-2-methylpropane (MTBE) and Alkyl Alkanoates at 298.15 K

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Excess molar enthalpies, H_m^E, and excess molar volumes, V_m^E, of 2-methoxy-2-methylpropane (MTBE) and four pairs of structural isomers of alkyl alkanoates (ethyl propanoate, propyl ethanoate, ethyl butanoate, butyl ethanoate, ethyl pentanoate, pentyl ethanoate, ethyl hexanoate, and hexyl ethanoate) have been determined at 298.15 K and at atmospheric pressure using a flow microcalorimeter and an Anton Paar density meter. H_m^E and V_m^E values decrease as the chain length of the alkanoates is increased, showing marked negative values for V_m^E. In contrast the H_m^E values are small for all mixtures and vary from ≈ 95 J·mol^{-1} (ethyl propanoate) up to ≈ -70 J·mol^{-1} (ethyl hexanoate); they are positive only for mixtures with ethyl propanoate, propyl ethanoate, ethyl butanoate, and butyl ethanoate and negative for the other mixtures. Results have been correlated using the Redlich−Kister equation.

Introduction

The industrial use of 2-methoxy-2-methylpropane (MTBE) as a solvent has increased in the past years. Particularly, there is a currently considerable interest in MTBE, as an oxygenated antiknock agent for gasoline, which is added because of its octane-enhancing and expected pollution-reducing capabilities.

This paper reports the results of the measurements of excess molar enthalpies, H_m^E, and excess molar volumes, V_m^E, of the binary mixtures containing MTBE and one of the following structural isomers of alkyl alkanoates: $CH_3(CH_2)_mCOOC_2H_5$ or $CH_3COO(CH_2)_mC_2H_5$, with $m = 1$, 2, 3, 4, corresponding respectively to ethyl propanoate or propyl ethanoate ($m = 1$), ethyl butanoate or butyl ethanoate ($m = 2$), ethyl pentanoate or pentyl ethanoate ($m = 3$), ethyl hexanoate or hexyl ethanoate ($m = 4$).

The aim of the present paper is to give a qualitative interpretation of the relative influence of the ether group on the molecular interactions of these mixtures and to explain the behavior of the chemicals having the same molecular weight but a different molecular structure.

A literature survey showed that no measurements have been previously reported for the mixtures studied in this paper.

Experimental Section

Chemicals. All chemicals were Aldrich products and were used without further purification since gas chromatography failed to show any significant peak's from impurities. The purities were also checked by comparing the densities, ρ, of pure compounds at (293.15 or 298.15) K with those reported in the literature and are listed in Table 1.

Table 1. Mole Percent Purities, Temperature, and Densities, ρ, and Comparison with Literature Values of Pure Components at 298.15 K

component (purity/mol %)	ρ/g·cm^{-3} this work	ρ/g·cm^{-3} lit.
MTBE (99.8)	0.735 41	0.7356[a]
ethyl propanoate (99.9)	0.884 34	0.8840[b]
propyl ethanoate (99.5)	0.883 33	0.8826[b]
ethyl butanoate (99.8)	0.873 60	0.8739[b]
butyl ethanoate (99.7)	0.876 19	0.87634[b]
ethyl pentanoate (98.7)	0.869 39	
pentyl acetate (99.6)	0.872 58	0.8719[c]
ethyl hexanoate (99.4)	0.866 44	
hexyl ethanoate (98.9)	0.868 55	0.8679[b]

[a] Arce et al., 1996. [b] TRC Thermodynamic Tables, 1997. [c] Riddick et al., 1986.

Before measurements, liquids were kept in dark bottles, dried over molecular sieves (Union Carbide, type 4A, $^1/_{16}$ in. pellets), and degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy).

Calorimetric Measurements. Measurements of H_m^E were carried out by an LKB flow microcalorimeter (LKB produkter, model 2107, Bromma, Sweden) working in the absence of vapor phase and equipped with two automatic burets (ABU, Radiomater, Copenhagen, Denmark), necessary to pump pure liquids into the mixing cell of the calorimeter. Temperature was kept constant at (298.15 ± 0.01) K and controlled by calibrated transistors inside the apparatus.

Electrical calibration and operating procedure have been described previously (Monk and Wadso, 1968; Francesconi and Comelli, 1986).

Mole fractions x_1 of MTBE (component 1) have been determined from calibrated flow rates with a precison of $\pm 1 \times 10^{-4}$, which leads to an error in H_m^E of 0.5−1 J·mol^{-1}.

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Table 2. Mole Fractions, x_1, and Excess Molar Enthalpies, H_m^E, of MTBE + Alkyl Alkanoates at 298.15 K

x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}
MTBE (1) + Ethyl Propanoate (2)					
0.0386	9	0.3251	78	0.7940	62
0.0743	17	0.3911	89	0.8525	46
0.1075	26	0.4907	98	0.8851	36
0.1383	33	0.5910	98	0.9204	23
0.1941	51	0.6583	87	0.9585	12
0.2431	62	0.7429	75		
MTBE (1) + Propyl Ethanoate (2)					
0.0386	2	0.3253	64	0.7941	55
0.0744	8	0.3913	73	0.8527	43
0.1076	15	0.4910	78	0.8853	32
0.1385	24	0.5913	80	0.9205	22
0.1943	39	0.6586	76	0.95865	11
0.2433	47	0.7432	65		
MTBE (1) + Ethyl Butanoate (2)					
0.0442	1	0.3567	19	0.8161	13
0.0846	2	0.4251	22	0.8694	9
0.1218	4	0.5260	23	0.8987	7
0.1560	8	0.6247	22	0.9301	4
0.2171	11	0.6893	20	0.9638	3
0.2699	14	0.7689	16		
MTBE (1) + Butyl Ethanoate (2)					
0.0440	1	0.3560	23	0.8156	17
0.0844	2	0.4243	26	0.8690	11
0.1214	6	0.5251	27	0.8984	8
0.1556	9	0.6239	26	0.9299	5
0.2166	14	0.6886	24	0.9637	2
0.2693	19	0.7523	20		
MTBE (1) + Ethyl Pentanoate (2)					
0.0495	−3	0.3845	−26	0.8332	−23
0.0943	−7	0.4544	−29	0.8823	−19
0.1351	−10	0.5554	−29	0.9090	−16
0.1723	−13	0.6520	−28	0.9375	−12
0.2380	−18	0.7141	−27	0.9677	−7
0.2940	−23	0.7894	−26		
MTBE (1) + Pentyl Ethanoate (2)					
0.0493	−2	0.3836	−22	0.8327	−18
0.0939	−4	0.4534	−23	0.8819	−14
0.1346	−8	0.5545	−24	0.9087	−11
0.1718	−10	0.6512	−23	0.9372	−9
0.2373	−15	0.7131	−22	0.9676	−5
0.2932	−18	0.7888	−20		
MTBE (1) + Ethyl Hexanoate (2)					
0.0547	−7	0.4097	−65	0.8474	−43
0.1037	−16	0.4807	−68	0.8928	−34
0.1479	−25	0.5814	−68	0.9174	−27
0.1879	−33	0.6757	−65	0.9434	−20
0.2577	−46	0.7352	−60	0.9709	−11
0.3162	−55	0.8064	−51		
MTBE (1) + Hexyl Ethanoate (2)					
0.0546	−4	0.4092	−30	0.8471	−27
0.1035	−8	0.4801	−34	0.8926	−22
0.1476	−11	0.5807	−36	0.9172	−18
0.1875	−15	0.6751	−36	0.9433	−14
0.2572	−21	0.7347	−35	0.9708	−7
0.3158	−25	0.8060	−31		

Two replicate measurements of H_m^E were made for each point.

Before measurements, the apparatus was checked using the test mixture cyclohexane + hexane for which literature values are well-known (Gmehling, 1993), and the agreement between our and literature data was ±0.5% over the central range of mole fraction of cyclohexane.

Volumetric Measurements. Densities, ρ, of pure liquids and their mixtures were measured using a digital density meter (Anton Paar, model DMA 60, Graz, Austria) equipped with a measuring cell (Anton Paar, type 602) whose operating procedure has been described elsewere (Fermeglia and Lapasin, 1988).

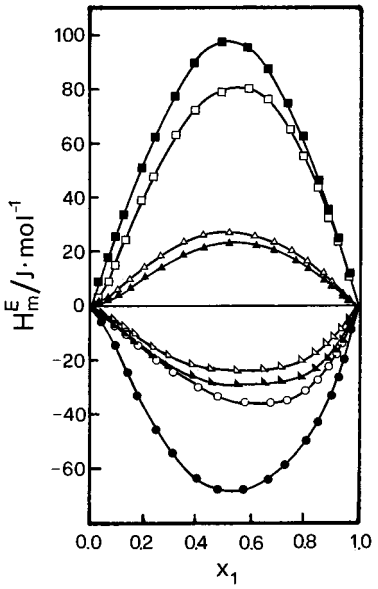

Figure 1. Excess molar enthalpies, H_m^E, at 298.15 K of MTBE + alkyl alkanoates. Isomers: open and corresponding closed symbols. (■), (□), ethyl propanoate and propyl ethanoate; (▲), (△), ethyl butanoate and butyl ethanoate; (♦), (◊), ethyl pentanoate and pentyl ethanoate; (●), (○), ethyl hexanoate and hexyl ethanoate. Solid lines, calculated with eq 2.

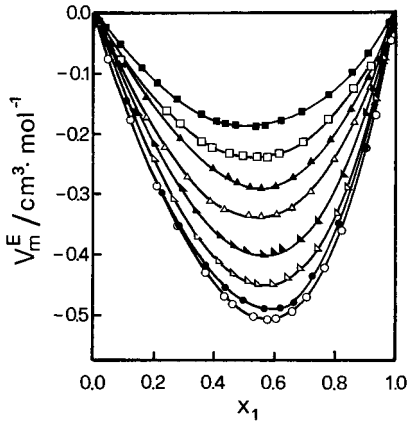

Figure 2. Excess molar volumes, V_m^E, at 298.15 K of MTBE + alkyl alkanoates. Isomers: open and corresponding close symbols. (■), (□), ethyl propanoate and propyl ethanoate; (▲), (△), ethyl butanoate and butyl ethanoate; (♦), (◊), ethyl pentanoate and pentyl ethanoate; (●), (○), ethyl hexanoate and hexyl ethanoate. Solid lines, calculated with eq 2.

Densities were determined from measurements of the vibrational period τ of the density meter (precision 1×10^{-6} s) with an accuracy of 1×10^{-5} g·cm^{-3}.

The measuring cell of the apparatus was thermostated at the temperature (298.15 ± 0.01) K using an ultrathermostat bath circulator (Heto, type 01 DBT 623, Birkerød, Denmark).

Mole fractions x_1 of MTBE were prepared by mass using an electronic balance (Mettler, model AE 160) that had a resolution of ±0.1 mg and a maximum capacity of 150 g.

The sample cell volume was approximately 15 cm^3, and to minimize the error in composition, the heavier component was charged first. The procedure used in preparing solutions is the same as that described by Fermeglia and Lapasin (1988).

Values of V_m^E were obtained from densities using the

Table 3. Mole Fractions, x_1, and Excess Molar Volumes, V_m^E, of MTBE + Alkyl Alkanoates at 298.15 K

x_1	ρ/g·cm^{-3}	V_m^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	V_m^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	V_m^E/cm^3·mol^{-1}
				MTBE (1) + Ethyl Propanoate (2)				
0.0373	0.878 76	−0.024	0.4099	0.823 18	−0.178	0.6893	0.781 56	−0.165
0.0853	0.871 60	−0.052	0.4416	0.818 46	−0.182	0.7779	0.768 39	−0.136
0.1581	0.860 71	−0.090	0.4822	0.812 41	−0.186	0.8561	0.756 76	−0.100
0.2073	0.853 38	−0.115	0.5384	0.804 03	−0.187	0.9101	0.748 74	−0.067
0.2828	0.842 12	−0.144	0.5690	0.799 48	−0.186	0.9819	0.738 06	−0.015
0.3620	0.830 31	−0.168	0.6275	0.790 76	−0.178			
				MTBE (1) + Propyl Ethanoate (1)				
0.0168	0.880 87	−0.014	0.4526	0.816 69	−0.235	0.6938	0.780 99	−0.216
0.1005	0.868 57	−0.078	0.4987	0.809 85	−0.236	0.7719	0.769 36	−0.176
0.2384	0.848 28	−0.164	0.5352	0.804 47	−0.238	0.8578	0.756 60	−0.126
0.2890	0.840 83	−0.188	0.5768	0.798 34	−0.241	0.9191	0.747 48	−0.079
0.3560	0.830 97	−0.215	0.6180	0.792 23	−0.233	0.9796	0.738 46	−0.021
0.3960	0.825 05	−0.225						
				MTBE (1) + Ethyl Butanoate (2)				
0.0551	0.867 00	−0.047	0.4809	0.812 47	−0.278	0.7261	0.777 67	−0.241
0.1063	0.860 76	−0.084	0.5243	0.806 49	−0.278	0.7909	0.768 02	−0.209
0.1751	0.852 30	−0.138	0.5639	0.801 00	−0.282	0.8574	0.757 89	−0.158
0.2871	0.838 18	−0.210	0.6062	0.795 06	−0.282	0.9157	0.748 82	−0.102
0.3939	0.824 20	−0.258	0.6617	0.787 09	−0.267	0.9389	0.745 16	−0.077
0.4445	0.817 40	−0.269						
				MTBE (1) + Butyl Ethanoate (2)				
0.0794	0.866 56	−0.085	0.4331	0.820 73	−0.321	0.6568	0.788 97	−0.322
0.1766	0.854 42	−0.169	0.4835	0.813 74	−0.330	0.7168	0.780 05	−0.298
0.2386	0.846 52	−0.219	0.5208	0.808 53	−0.334	0.7991	0.767 51	−0.244
0.3110	0.837 12	−0.269	0.5653	0.802 22	−0.336	0.8675	0.756 83	−0.181
0.3920	0.826 32	−0.309	0.6089	0.795 95	−0.331	0.9163	0.749 01	−0.121
				MTBE (1) + Ethyl Pentanoate (2)				
0.0666	0.862 60	−0.075	0.4622	0.817 07	−0.379	0.6830	0.786 88	−0.375
0.1508	0.853 68	−0.163	0.5037	0.811 71	−0.393	0.7386	0.778 57	−0.340
0.2027	0.848 01	−0.216	0.5619	0.803 94	−0.399	0.8287	0.764 56	−0.267
0.2939	0.837 65	−0.292	0.5942	0.799 48	−0.392	0.9026	0.752 38	−0.167
0.3405	0.832 15	−0.324	0.6265	0.794 99	−0.390	0.9296	0.747 78	−0.126
0.4209	0.822 34	−0.371						
				MTBE (1) + Pentyl Ethanoate (2)				
0.0130	0.871 24	−0.016	0.4655	0.818 68	−0.431	0.7453	0.778 65	−0.388
0.1263	0.859 28	−0.165	0.5173	0.811 79	−0.448	0.8080	0.768 68	−0.332
0.1937	0.851 80	−0.239	0.5461	0.807 84	−0.449	0.8421	0.763 04	−0.286
0.2649	0.843 60	−0.307	0.5935	0.801 21	−0.448	0.9360	0.746 95	−0.141
0.3460	0.833 85	−0.368	0.6433	0.794 03	−0.437	0.9666	0.741 46	−0.077
0.4167	0.824 99	−0.409	0.6868	0.787 59	−0.423			
				MTBE (1) + Ethyl Hexanoate (2)				
0.0324	0.863 61	−0.047	0.4972	0.814 64	−0.478	0.7719	0.775 87	−0.400
0.1065	0.856 86	−0.146	0.5683	0.805 46	−0.487	0.8164	0.768 66	−0.352
0.2301	0.844 86	−0.300	0.6215	0.798 22	−0.483	0.9050	0.753 36	−0.220
0.2849	0.839 14	−0.350	0.6617	0.792 53	−0.472	0.9365	0.747 58	−0.156
0.3769	0.829 01	−0.420	0.7265	0.782 93	−0.435	0.9834	0.738 68	−0.053
0.4333	0.822 46	−0.456						
				MTBE (1) + Hexyl Ethanoate (2)				
0.0474	0.864 33	−0.075	0.4609	0.820 46	−0.484	0.7701	0.776 85	−0.423
0.1179	0.857 76	−0.174	0.5316	0.811 47	−0.504	0.8250	0.767 80	−0.363
0.2103	0.848 63	−0.286	0.5791	0.805 13	−0.507	0.9063	0.753 42	−0.224
0.2801	0.841 32	−0.358	0.6181	0.799 74	−0.506	0.9334	0.748 41	−0.174
0.3714	0.831 13	−0.431	0.6620	0.793 44	−0.493	0.9848	0.738 47	−0.048
0.4374	0.823 34	−0.473	0.7129	0.785 86	−0.473			

relation

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

where M_i and ρ_i are the molar mass and density of component i.

The estimated uncertainty in V_m^E is less than 3×10^{-3} cm^3 × mol^{-1}.

Corrections for buoyancy and evaporation of the components were made.

Before measurements, the density meter was checked with the test mixture benzene + cyclohexane (Wilhelm, 1985), and our V_m^E results are in agreement with literature data showing a discrepancy of ±0.5% in the central range of mole fraction of benzene.

Results and Discussion

The experimental values of H_m^E and V_m^E are reported in Tables 2 and 3, respectively.

The Redlich−Kister polynomial

$$Q_m^E = x_1x_2 \sum_{k\geq 0} a_k(x_1 - x_2)^k \qquad (2)$$

where $Q_m^E = H_m^E/(\text{J·mol}^{-1})$ or $V_m^E/(\text{cm}^3\text{·mol}^{-1})$, x_1, x_2 are the mole fractions of components 1 and 2, and a_k are the

Table 4. Least-Squares Parameters, a_k, Eq 2, and Standard Deviations, $\sigma(Q_m^E)$, Eq 3, of MTBE + Alkyl Alkanoates at 298.15 K

mixture	function	a_0	a_1	a_2	a_3	a_4	$\sigma(Q_m^E)$
MTBE							
+ ethyl propanoate	H_m^E/J·mol^{-1}	391.5	47.6	−130.2			1.1
	V_m^E/cm^3·mol^{-1}	−0.7463	−0.0797				0.0009
+ propyl ethanoate	H_m^E/J·mol^{-1}	317.2	61.3	0	58.3	−199.3	0.8
	V_m^E/cm^3·mol^{-1}	−0.9584	−0.1093				0.0021
+ ethyl butanoate	H_m^E/J·mol^{-1}	94.4	16.4	−56.3	14.2		0.4
	V_m^E/cm^3·mol^{-1}	−1.1184	−0.2401				0.0023
+ butyl ethanoate	H_m^E/J·mol^{-1}	107.3	13.8	0	22.2	−106.0	0.3
	V_m^E/cm^3·mol^{-1}	−1.3425	−0.2683				0.0026
+ ethyl pentanoate	H_m^E/J·mol^{-1}	−115.2	−22.1	−34.5	−72.9		0.4
	V_m^E/cm^3·mol^{-1}	−1.5709	−0.4130				0.0028
+ pentyl ethanoate	H_m^E/J·mol^{-1}	−97.6	−16.7	0	−53.3		0.3
	V_m^E/cm^3·mol^{-1}	−1.7637	−0.4834	−0.1686			0.0019
+ ethyl hexanoate	H_m^E/J·mol^{-1}	−267.7	−36.5	0	−126.9	43.6	0.4
	V_m^E/cm^3·mol^{-1}	−1.9117	−0.5565	−0.2221			0.0041
+ hexyl ethanoate	H_m^E/J·mol^{-1}	−135.6	−63.8	−35.2	−44.7		0.4
	V_m^E/cm^3·mol^{-1}	−1.9852	−0.6144	−0.2887			0.0026

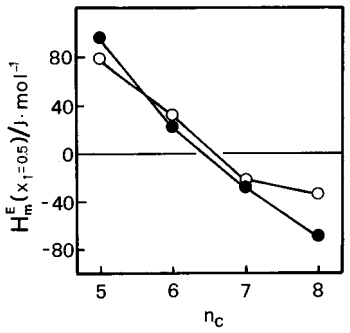

Figure 3. Values of equimolar $H_m^E(x_1 = 0.5)$ at 298.15 K as a function of the number n_C of C atoms in the alkanoate molecules. Open and closed circles refer to isomers $CH_3(CH_2)_mCOOC_2H_5$ and $CH_3COO(CH_2)_mC_2H_5$, respectively, with $m = 1, 2, 3, 4$ and $n_C = 5, 6, 7, 8$.

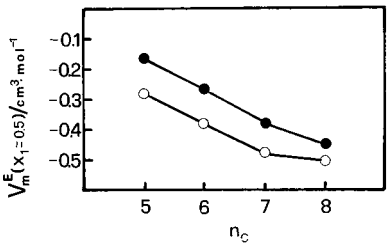

Figure 4. Values of equimolar $V_m^E(x_1 = 0.5)$ at 298.15 K as a function of the number n_C of C atoms in the alkanoate molecules. Open and closed circles refer to isomers $CH_3(CH_2)_mCOOC_2H_5$ and $CH_3COO(CH_2)_mC_2H_5$, respectively, with $m = 1, 2, 3, 4$ and $n_C = 5, 6, 7, 8$.

adjustable parameters, was fitted to each set of data by an unweighted least-squares regression.

Parameters a_k are listed in Table 4, together with the standard deviation $\sigma(Q_m^E)$ defined as

$$\sigma(Q_m^E) = |\Phi/(N - n)|^{0.5} \quad (3)$$

with N = number of experimental points and n = number of the adjustable parameters. Φ is the objective function defined as

$$\Phi = \sum_{k\geq 0}^{N} \eta_k^2 \quad (4)$$

where $\eta = Q_{m,calcd}^E - Q_m^E$, $Q_{m,calcd}^E$ being determined from the right-hand side of eq 2. Figures 1 and 2 show the graphical representations of H_m^E anf V_m^E vs x_1, the mole fraction of MTBE.

Figures 3 and 4 report $H_m^E(x_1=0.5)$ and $V_m^E(x_1 = 0.5)$, the equimolar excess enthalpy H_m^E and the equimolar excess volume V_m^E, plotted against the number n_C of carbon atoms in the isomer alkanoate molecules.

Values of V_m^E are always negative and relatively large and decrease with increase in molecular size.

Also values of H_m^E decrease with increase in isomer size, but they pass regularly from positive to negative values.

The differences in $V_m^E(x_1 = 0.5)$ between each pair of the isomers are nearly the same with increase in molecular size and have the same sign for all isomers, whereas the corresponding differences for H_m^E have no regular trend.

Mixtures of MTBE with isomers of the type CH_3-$(CH_2)_mC_2H_5$ have values of V_m^E less negative than the corresponding mixtures with isomers $CH_3COO(CH_2)_mC_2H_5$.

Values of H_m^E show the opposite, with the exception of the larger-sized molecule isomers ($m = 4$).

The results show values of V_m^E decreasing about 3-fold and values of H_m^E changing from positive to negative values with the increase of the C atoms of esters, a result that would be difficult to predict for isomers and make it hard to be explained in terms of molecular features.

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