Excess molar enthalpies of binary mixtures containing acetic or propionic acid+eight ethyl alkanoates at 298.15 K

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Abstract

Excess molar enthalpies, H_m^E of binary mixtures containing acetic or propionic acid+eight ethyl alkanoates have been determined at 298.15 K using a flow microcalorimeter. H_m^E values have been found to be positive with the exception of the acetic acid+ethyl acetate mixtures where an inversion of sign from positive to negative values occurs at the mole fraction of acetic acid $x_1 \approx 0.62$ J mol^{-1}. H_m^E values vary in the range from -30 to 440 J mol^{-1}. The experimental results have been correlated using the Redlich–Kister equation. © 1998 Elsevier Science B.V.

Keywords: Calorimeter; Enthalpy; Data correlation

1. Introduction

In this paper, excess molar enthalpies, H_m^E, for acetic or propionic acid+eight ethyl alkanoates are reported at 298.15 K as a prosecution of our research project on thermodynamic properties of binary mixtures containing acids, ethers and esters with aliphatic alkanoates [1,2].

Previous measurements of the excess enthalpies on these mixtures have not been found in the literature.

2. Experimental

2.1. Materials

All compounds used were of analytical grade and purchased from commercial sources. Table 1

reports origins and stated purities of the pure compounds which were used without further purification.

The purities of the samples were also checked by comparing the measured densities, ρ, of the pure compounds with those reported in the literature [3–7], as shown in Table 2.

Before measurements, the chemicals were kept in dark bottles and degassed by ultrasound (Ultrasonic bath, Hellma, type 460, Milan, Italy). Ethyl alkanoates have also been dried over molecular sieves (Union Carbide, type 4A, 1/16 inches pellets).

Densities, ρ, have been determined at 293.15 or 298.15 K using a digital density meter (Anton Paar, model DMA 60, Graz, Austria) equipped with a measuring cell type 602 which offers an accuracy of the oscillation period τ of $\pm 1.10^{-6}$ s^{-1}, leading to density values with an estimated error of $\pm 1.10^{-5}$ g cm^{-3}.

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Table 1
Origins and stated purities of the pure compounds

Compound	Origin	Stated purity (mol%)
Acetic acid	Merck AG (D)	99.8
Propionic acid	Fluka AG (CH)	≥99.5
Ethyl acetate	Aldrich (D)	≥99.5
Ethyl propionate	Aldrich (D)	99
Ethyl butyrate	Aldrich (D)	99
Ethyl pentanoate	Aldrich (D)	99
Ethyl hexanoate	Aldrich (D)	99+
Ethyl heptanoate	Aldrich (D)	99
Ethyl octanoate	Aldrich (D)	99+
Ethyl decanoate	Aldrich (D)	99+

Table 2
Comparison between measured densities, ρ, and literature values for pure compounds

Compound	T (K)	ρ (g cm^{-3})	
		This work	Literature
Acetic acid	298.15	1.04372	1.04392 [3]
			1.0437 [4]
Propionic acid	298.15	0.98791	0.98808 [3]
			0.9879 [5]
Ethyl acetate	298.15	0.89438	0.89455 [3]
Ethyl propionate	298.15	0.88333	0.8831 [3]
Ethyl butyrate	298.15	0.87356	0.87394 [3]
Ethyl pentanoate	298.15	0.86938	0.8690 [6]
Ethyl hexanoate	293.15	0.87301	0.8730 [7]
Ethyl heptanoate	293.15	0.88151	0.8815 [7]
Ethyl octanoate	298.15	0.86232	0.8624 [6]
Ethyl decanoate	293.15	0.86501	0.8650 [7]

2.2. Apparatus

The flow microcalorimeter (LKB, model 2107, produkter AB, Bromma, Sweden) used for the H_m^E measurements and the experimental procedure have been described elsewhere [8,9].

Two automatic burets (ABU, Radiometer, Copenhagen, Denmark) were used to pump pure liquids into the mixing cell of the calorimeter, thermostated at 298.15±0.01 K and controlled by calibrated thermoresistors inside the apparatus.

Mole fractions x_1 (acetic or propionic acids are component 1) were determined from flow rates which were selected to cover the whole mole fraction range.

Accuracy on mole fraction and on H_m^E was estimated to be 2.10^{-4} and 1%, respectively.

Table 3
Mole fractions, x_1, and excess molar enthalpies, H_m^E, of acetic or propionic acid+ethyl alkanoates at 298.15 K

x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})
Acetic acid (1)+*ethyl acetate* (2)			
0.6666	54	0.6313	1
0.1248	75	0.7198	−18
0.1763	81	0.7740	−26
0.2220	81	0.8370	−30
0.2997	74	0.9113	−26
0.3633	64	0.9320	−22
0.4612	43	0.9536	−16
0.5330	25	0.9762	−9
Acetic acid (1)+*ethyl propionate* (2)			
0.0772	87	0.6675	120
0.1433	134	0.7507	90
0.2006	162	0.8006	72
0.2507	174	0.8576	50
0.3342	183	0.9233	24
0.4009	178	0.9414	16
0.5009	163	0.9601	12
0.5727	145	0.9797	6
Acetic acid (1)+*ethyl butyrate* (2)			
0.0878	116	0.7762	125
0.1615	175	0.8221	102
0.2241	206	0.8740	74
0.2780	220	0.9024	56
0.3662	230	0.9327	38
0.4351	225	0.9487	28
0.5361	212	0.9652	19
0.6064	193	0.9823	10
0.6981	161		
Acetic acid (1)+*ethyl pentanoate* (2)			
0.0978	104	0.7224	174
0.2031	179	0.7961	138
0.2455	198	0.8388	118
0.3025	218	0.8865	87
0.3942	233	0.9398	49
0.4645	233	0.9542	35
0.5655	220	0.9690	26
0.6344	204	0.9842	14
Acetic acid (1)+*ethyl hexanoate* (2)			
0.1076	134	0.7432	208
0.1942	202	0.8128	167
0.2656	236	0.8526	144
0.3253	257	0.8968	109
0.4197	271	0.9455	62
0.4909	272	0.9586	48
0.5912	259	0.9720	35
0.6585	240	0.9858	18

Table 3 (continued)

Acetic acid (1)+*ethyl heptanoate* (2)

0.1170	161	0.7609	249
0.2096	239	0.8268	205
0.2846	280	0.8642	176
0.3465	297	0.9052	134
0.4431	312	0.9502	78
0.5147	314	0.9622	60
0.6141	307	0.9745	41
0.6796	287	0.9871	21

Acetic acid (1)+*ethyl octanoate* (2)

0.1264	163	0.7765	292
0.2244	245	0.8390	241
0.3027	293	0.8741	206
0.3665	322	0.9124	157
0.4647	353	0.9542	89
0.5365	358	0.9653	70
0.6345	352	0.9766	47
0.6983	330	0.9881	24

Acetic acid (1)+*ethyl decanoate* (2)

0.1443	190	0.8019	358
0.2523	316	0.8586	302
0.3360	383	0.8901	255
0.4029	412	0.9239	200
0.5030	435	0.9605	120
0.5744	443	0.9701	95
0.6694	427	0.9798	63
0.7297	402	0.9898	34

Propionic acid (1)+*ethyl acetate* (2)

0.0519	61	0.6634	185
0.0987	104	0.7243	166
0.1411	135	0.7976	131
0.1796	156	0.8401	111
0.2472	185	0.8874	80
0.3045	198	0.9131	65
0.3964	212	0.9404	45
0.4669	214	0.9693	24
0.5678	206		

Propionic acid (1)+*ethyl propionate* (2)

0.0603	81	0.6063	210
0.1137	134	0.6979	182
0.1614	168	0.7549	159
0.2042	186	0.8221	125
0.2780	214	0.9024	73
0.3392	226	0.9249	55
0.4351	231	0.9487	39
0.5066	227	0.9737	20

Table 3 (continued)

Propionic acid (1)+*ethyl butyrate* (2)

0.0739	95	0.6395	191
0.1278	145	0.7296	160
0.1814	180	0.7801	137
0.2281	200	0.8418	105
0.3072	216	0.9141	60
0.3715	228	0.9342	47
0.4700	225	0.9551	33
0.5418	213	0.9770	18

Propionic acid (1)+*ethyl pentanoate* (2)

0.0768	82	0.6664	161
0.1427	131	0.7497	134
0.1998	158	0.7998	116
0.2497	178	0.8570	89
0.3333	191	0.9230	52
0.3996	195	0.9411	39
0.4996	191	0.9599	28
0.5711	181	0.9796	14

Propionic acid (1)+*ethyl hexanoate* (2)

0.0846	90	0.6895	150
0.1561	136	0.7691	126
0.2172	162	0.8161	107
0.2700	176	0.8694	82
0.3569	188	0.9302	48
0.4252	190	0.9467	36
0.5260	182	0.9638	25
0.5967	172	0.9816	13

Propionic acid (1)+*ethyl heptanoate* (2)

0.0923	110	0.7095	164
0.1690	161	0.7855	134
0.2338	184	0.8300	116
0.2892	197	0.8799	89
0.3790	207	0.9361	50
0.4487	207	0.9513	38
0.5497	201	0.9670	26
0.6195	190	0.9832	15

Propionic acid (1)+*ethyl octanoate* (2)

0.0999	106	0.7272	181
0.1817	164	0.7999	147
0.2498	194	0.8420	126
0.3075	213	0.8888	98
0.3998	221	0.9411	55
0.4703	225	0.9552	44
0.5712	220	0.9697	29
0.6398	205	0.9846	15

Table 3 (continued)

Propionic acid (1)+*ethyl decanoate* (2)

0.1146	123	0.8233	180
0.2056	187	0.8549	158
0.2797	226	0.9031	116
0.3411	246	0.9255	95
0.4371	264	0.9491	68
0.5087	272	0.9613	53
0.6084	265	0.9739	37
0.6744	251	0.9868	18
0.7565	220		

Two replicate measurements were made for each point.

The performance and reliability of the apparatus were checked using the test mixture cyclohexane+hexane [10]. Our H_m^E values agreed with those of literature to within 0.5%, over the central range of mole fraction of cyclohexane.

3. Results and discussion

The experimental H_m^E, at 298.15 K are summarized in Table 3. Each set of data was fitted to the Redlich–Kister equation

$$Q_m^E = x_1 x_2 \sum_{k \geq 0} a_k (x_1 - x_2)^k \qquad (1)$$

where a_k are the adjustable parameters obtained by the method of least-squares with all points weighed equally and x_1, x_2 are the mole fractions of acid and ethyl alkanoate, respectively.

The results of this analysis are reported in Table 4.

Plots of the representation by Eq. (1) are shown in Figs. 1 and 2. Owing to the overlapping of the experimental points for mixtures containing propionic acid, Figs. 1 and 2 show only soothed curves obtained from Eq. (1) and parameters of Table 4.

Fig. 3 represents $H_m^E(x_1 = 0.5)$, the equimolar excess enthalpy of H_m^E, plotted against the number of carbon atoms n_c in the ethyl alkanoate molecule.

The excess molar enthalpies, H_m^E, are always positive with the exception of acetic acid+ethyl acetate mixtures where a inversion of sign from positive to negative values occurs at the mole fraction $x_1 = 0.62$ J mol^{-1}.

Positive values of H_m^E are consistent with breakage of the hydrogen bonds of pure organic acids during mixing, keeping in mind that these acids form cyclic

Table 4

Adjustable parameters, a_k, Eq. (1), and standard deviations, σ (H_m^E), for excess molar enthalpies, H_m^E, of acetic and propionic aid+ethyl alkanotes at 298.15 K

| Mixture	a_0	a_1	a_2	a_3	a_4	σ (H_m^E (J mol^{-1})
Acetic acid (1)						
+ethyl acetate(2)	133.1	−480.4	33.2	−278.1	173.8	0.6
+ethyl propionate (2)	655.1	−405.9	196.2	−171.5		1.1
+ethyl butyrate (2)	873.0	−340.9	257.1	−242.5		1.0
+ethyl pentanoate (2)	922.9	−205.1	162.0			1.1
+ethyl hexanoate (2)	1082.8	−140.8	310.4			1.1
+ethyl heptanoate (2)	1263.8	−29.0	474.8			1.4
+ethyl octanoate (2)	1418.3	247.9	442.9			2.2
+ethyl decanoate (2)	1752.7	216.8	512.5	866.5		2.7
Propionic acid (1)						
+ethyl acetate (2)	851.1	−115.3	217.4	−175.3		1.1
+ethyl propionate (2)	910.6	−186.4	275.0	−220.5		1.1
+ethyl butyrate (2)	882.0	−253.5	285.6	−168.0		1.5
+ethyl pentanoate (2)	764.2	−201.5	256.7	−80.1		0.9
+ethyl hexanoate (2)	738.9	−186.6	290.3	−100.2		0.8
+ethyl heptanoate (2)	818.8	−151.0	367.4	−212.7		1.5
+ethyl octanoate (2)	899.8	−125.0	288.2			1.7
+ethyl decanoate (2)	1082.5	63.7	304.9			1.2
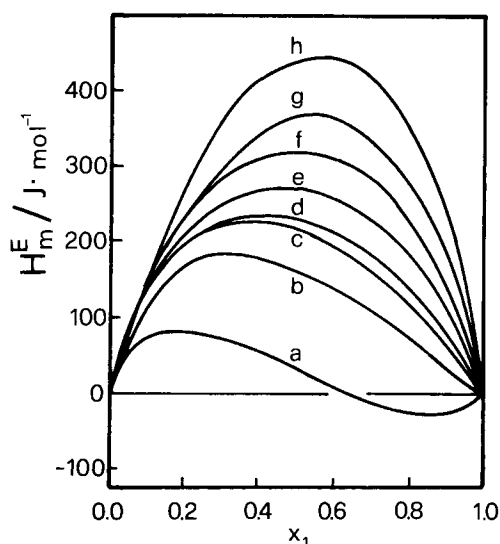
Fig. 1. Excess molar enthalpies, H_m^E, for binary mixtures of acetic acid+ethyl alkanoates at 298.15 K. Solid curves, Redlich–Kister equation, Eq. (1): (a) ethyl acetate (b) ethyl propionate (c) ethyl butyrate (d) ethyl pentanoate (e) ethyl hexanoate (f) ethyl heptanoate (g) ethyl octanoate (h) ethyl decanoate.
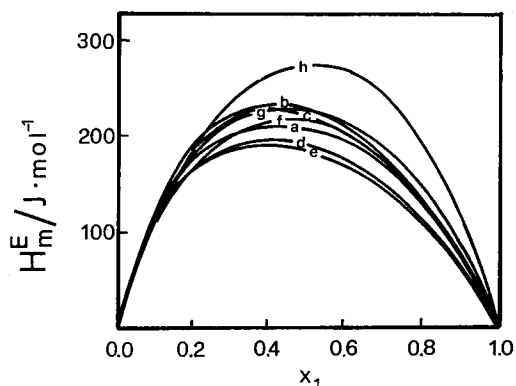

Fig. 3. Values of equimolar excess molar enthalpies, $H_m^E(x_1=0.5)$ at 298.15 K as a function of the number of carbon atoms, n_c, of ethyl alkanoate for the binary mixtures with (a) acetic acid or (b) propionic acid.

Fig. 2. Excess molar enthalpies, H_m^E, for binary mixtures of propionic acid+ethyl alkanoates at 298.15 K. Solid curves, Redlich–Kister equation, Eq. (1): (a) ethyl acetate (b) ethyl propionate (c) ethyl butyrate (d) ethyl pentanoate (e) ethyl hexanoate (f) ethyl heptanoate (g) ethyl octanoate (h) ethyl decanoate.

dimers involving two hydrogen bonds whereas interaction of acid OH group with C=O group of ester implies only one hydrogen bond.

The inversion sign shown by the mixture acetic acid+ethyl acetate is observed frequently when a
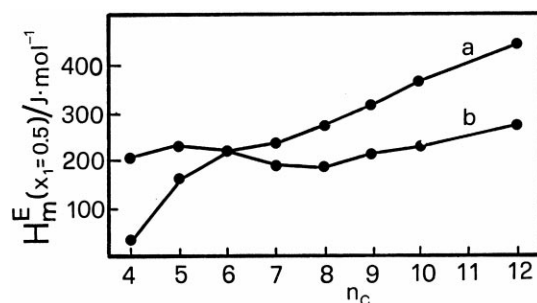
strong interaction occurs both between molecules of one component and between molecules of the two different species. Typical examples are the mixtures 1,4-dioxane+water [11] and 1,3-dioxolane+water [12].

In the series of mixtures containing acetic acid (Fig. 1), the experimental H_m^E increase as the aliphatic chain length of the ethyl alkanoate increases, but we do not observe the same results for propanoic acid.

In fact, if we exclude the mixture containing propionic acid+ethyl decanoate, which shows the highest H_m^E values of all mixtures $H_{m,max}^E=270$ J mol^{-1}), we note that all curves overlap in a close range of H_m^E, whose maxima vary from 190 to 230 J mol^{-1}, with no regular increase as the chain length of alkanoate increases. This trend is due to most probably, the different contributions to H_m^E of hydrogen bonding between acid and esters and of steric effects acting as the chain length of esters increases.

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