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Excess Molar Enthalpies and Excess Molar Volumes of Binary Mixtures Containing 1,3-Dioxolane + Four Pairs of Alkyl Alkanoate Isomers at 298.15 K

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Excess molar enthalpies, H_m^E, and excess molar volumes, V_m^E, have been determined at 298.15 K and at atmospheric pressure for the binary mixtures containing 1,3-dioxolane + four pairs of structural isomers of alkyl alkanoates, namely, propyl ethanoate and ethyl propanoate, butyl ethanoate and ethyl butanoate, pentyl ethanoate and ethyl pentanoate, and hexyl ethanoate and ethyl hexanoate, respectively. H_m^E values are always positive and increase as the chain length of the alkanoate is increased, showing maximum values varying from 153 J·mol^{-1}(propyl ethanoate) to 557 J·mol^{-1}(hexyl ethanoate). In contrast, V_m^E values are positive in mixtures containing ethyl hexanoate, hexyl ethanoate, ethyl pentanoate, and pentyl ethanoate and negative for propyl ethanoate and ethyl propanoate, showing an inversion of sign for ethyl butanoate and butyl ethanoate. V_m^E values vary from −0.07 cm^3·mol^{-1} (propyl ethanoate) up to 0.18 cm^3·mol^{-1} (ethyl hexanoate), increasing as the chain length of the alkanoate is increased. Experimental data have been correlated using the Redlich−Kister equation.

1. Introduction

The present paper continues our latest research studies (Francesconi et al., 1998; Comelli et al., 1998) on excess properties of binary mixtures containing structural isomers of organic compounds and reports the excess molar enthalpies, H_m^E, and the excess molar volumes, V_m^E, of 1,3-dioxolane + four pairs of alkyl alkanoate isomers, namely, propyl ethanoate and ethyl propanoate, butyl ethanoate and ethyl butanoate, pentyl ethanoate and ethyl pentanoate, and hexyl ethanoate and ethyl hexanoate, respectively.

Our aim, as primary interest, is to investigate and give a qualitative interpretation of the interactions between the different types of molecules in binary mixtures, emphasizing the behavior of structural isomers. We are also interested in comparing the excess properties reported in this paper with those obtained previously (Francesconi et al., 1998) on binary mixtures of 2-methoxy-2-methyl propane (MTBE), a noncyclic ether, with the same structural isomers.

Literature data on these mixtures have not been found.

2. Experimental Section

Chemicals. Chemicals were purchased from Aldrich Chemical Co. (Steinheim, Germany). The analyses of the products were performed on a Hewlett-Packard gas chromatograph model 5890 by using an HP (cross-linked 5% ME siloxane) capillary column.

A purity ≥99.4 mol % was obtained for all chemicals, except for ethyl pentanoate and hexyl ethanoate, which were fractionally distilled through a 120 plate laboratory column. Purities of these liquids after distillation were 99.7 mol % and 99.8 mol %, respectively. Other chemicals were used as received.

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

	ρ/g·cm^{-3}		
component (purity/mol %)	this paper	lit.	
1,3-dioxolane (99.8)	1.058 74	1.05865[a]	
ethyl propanoate (99.9)	0.884 32	0.8840[b]	0.883 91[c]
propyl ethanoate (99.5)	0.883 33	0.8826[b]	
ethyl butanoate (99.8)	0.873 60	0.8737[b]	
butyl ethanoate (99.7)	0.876 21	0.8766[b]	0.875 67[d]
ethyl pentanoate (99.8)	0.869 23		
pentyl ethanoate (99.6)	0.872 00	0.8719[b]	0.871 63[d]
ethyl hexanoate (99.4)	0.866 38		
hexyl ethanoate (99.7)	0.868 56	0.8679[b]	0.868 6[e]

[a] Inglese et al. (1983). [b] TRC Thermodynamic Tables (1996). [c] Ortega et al. (1987). [d] Ortega et al. (1995). [e] Arce et al. (1995).

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

Purities of liquids were also checked by measuring their densities, which were in good agreement with the available literature. Purities, density values, and comparisons with literature data are reported in Table 1.

Apparatus and Procedure. Excess molar enthalpies, H_m^E, were determined using a flow microcalorimeter (LBK Produkter, model 2107, Bromma, Sweden) at the temperature (298.15 ± 0.01) K controlled by calibrated thermistors inside the apparatus and under ambient pressure. Two automatic burets (ABU, Radiometer, Copenhagen, Denmark) were used to pump pure liquids into the mixing cell of the calorimeter.

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

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Table 2. Mole Fraction, x_1, and Excess Molar Enthalpies, $H_{\mathrm{m}}^{\mathrm{E}}$, of 1,3-Dioxolane + Alkyl Alkanoates at 298.15 K

x_1	$H_{\mathrm{m}}^{\mathrm{E}}/\mathrm{J\cdot mol^{-1}}$	x_1	$H_{\mathrm{m}}^{\mathrm{E}}/\mathrm{J\cdot mol^{-1}}$
1,3-Dioxolane (1) + Ethyl Propanoate (2)			
0.0644	39	0.6231	196
0.1211	71	0.7126	179
0.1713	98	0.7678	159
0.2160	118	0.8322	127
0.2924	147	0.9084	76
0.3553	170	0.9297	59
0.4526	197	0.9520	43
0.5243	200	0.9754	24
1,3-Dioxolane (1) + Propyl Ethanoate (2)			
0.0645	27	0.6234	151
0.1212	50	0.7129	140
0.1714	70	0.7680	125
0.2162	87	0.8324	101
0.2927	111	0.9085	64
0.3555	128	0.9298	49
0.4528	145	0.9521	35
0.5246	151	0.9754	18
1,3-Dioxolane (1) + Ethyl Butanoate (2)			
0.0735	70	0.6557	319
0.1369	129	0.7407	289
0.1922	170	0.7920	251
0.2408	206	0.8510	196
0.3224	261	0.9195	118
0.3882	293	0.9384	93
0.4876	326	0.9581	66
0.5593	334	0.9789	34
1,3-Dioxolane (1) + Butyl Ethanoate (2)			
0.0733	53	0.6549	261
0.1365	96	0.7400	232
0.1917	131	0.7914	208
0.2402	162	0.8390	169
0.3217	208	0.9193	98
0.3874	231	0.9382	78
0.4868	259	0.9579	55
0.5585	269	0.9785	28
1,3-Dioxolane (1) + Ethyl Pentanoate (2)			
0.0820	99	0.6819	420
0.1515	179	0.7628	364
0.2113	245	0.8109	321
0.2632	293	0.8654	250
0.3489	361	0.9279	148
0.4167	400	0.9449	107
0.5173	441	0.9626	80
0.5883	444	0.9809	42
1,3-Dioxolane (1) + Pentyl Ethanoate (2)			
0.0817	85	0.6811	360
0.1511	150	0.7621	330
0.2107	200	0.8103	286
0.2625	239	0.8650	227
0.3481	293	0.9276	134
0.4158	328	0.9447	107
0.5164	367	0.9625	75
0.5874	377	0.9809	39
1,3-Dioxolane (1) + Ethyl Hexanoate (2)			
0.0903	134	0.7044	521
0.1656	239	0.7814	471
0.2295	312	0.8265	403
0.2842	372	0.8773	320
0.3733	452	0.9346	187
0.4426	507	0.9502	144
0.5437	551	0.9662	104
0.6137	556	0.9828	54
1,3-Dioxolane (1) + Hexyl Ethanoate (2)			
0.0901	110	0.7039	469
0.1653	194	0.7810	415
0.2290	262	0.8262	362
0.2837	325	0.8770	283
0.3727	396	0.9345	172
0.4420	446	0.9500	131
0.5430	487	0.9661	93
0.6104	496	0.9831	47

Table 3. Mole Fractions, x_1, and Excess Molar Volumes, $V_{\mathrm{m}}^{\mathrm{E}}$, of 1,3-Dioxolane + Alkyl Alkanoates at 298.15 K

x_1	$\rho/\mathrm{g\cdot cm^{-3}}$	$V_{\mathrm{m}}^{\mathrm{E}}/\mathrm{cm^3\cdot mol^{-1}}$	x_1	$\rho/\mathrm{g\cdot cm^{-3}}$	$V_{\mathrm{m}}^{\mathrm{E}}/\mathrm{cm^3\cdot mol^{-1}}$
1,3-Dioxolane (1) + Ethyl Propanoate (2)					
0.0819	0.893 37	−0.012	0.6947	0.986 22	−0.069
0.1604	0.902 63	−0.026	0.7810	1.004 32	−0.060
0.2266	0.910 93	−0.036	0.8655	1.023 73	−0.044
0.4303	0.939 70	−0.029	0.9070	1.033 96	−0.033
0.5416	0.957 82	−0.070	0.9272	1.039 13	−0.027
0.6482	0.977 14	−0.071	0.9624	1.048 39	−0.014
1,3-Dioxolane (1) + Propyl Ethanoate (2)					
0.0613	0.890 09	−0.011	0.5559	0.959 74	−0.073
0.1706	0.903 01	−0.031	0.6227	0.971 82	−0.073
0.2160	0.908 75	−0.040	0.6788	0.982 63	−0.072
0.2899	0.918 54	−0.050	0.7468	0.996 57	−0.065
0.3269	0.923 70	−0.056	0.8436	1.018 26	−0.048
0.4062	0.935 33	−0.065	0.9134	1.035 43	−0.030
0.4803	0.946 97	−0.071	0.9626	1.048 38	−0.014
1,3-Dioxolane (1) + Ethyl Butanoate (2)					
0.0487	0.878 41	0.006	0.5885	0.952 99	0.012
0.1426	0.888 38	0.017	0.6784	0.970 95	0.005
0.2579	0.902 03	0.025	0.7513	0.987 27	0.001
0.2780	0.904 60	0.025	0.8013	0.999 50	−0.004
0.3731	0.917 57	0.023	0.8495	1.017 75	−0.006
0.4715	0.932 58	0.020	0.9312	1.036 06	−0.006
0.5238	0.941 32	0.017	0.9638	1.046 47	−0.003
1,3-Dioxolane (1) + Butyl Ethanoate (2)					
0.0476	0.880 86	0.006	0.6324	0.962 93	0.015
0.1580	0.892 55	0.016	0.7004	0.976 92	0.011
0.2901	0.908 43	0.022	0.7514	0.988 33	0.007
0.3237	0.912 85	0.023	0.8095	1.002 43	0.003
0.4122	0.925 32	0.024	0.8734	1.019 44	0.001
0.4877	0.937 06	0.022	0.9386	1.033 86	−0.001
0.5672	0.950 67	0.019	0.9633	1.046 50	−0.001
1,3-Dioxolane (1) + Ethyl Pentanoate (2)					
0.0351	0.872 31	0.015	0.6062	0.947 63	0.094
0.1540	0.883 72	0.057	0.7097	0.969 48	0.077
0.2836	0.898 21	0.087	0.7736	0.985 03	0.066
0.3461	0.906 09	0.097	0.8243	0.998 75	0.054
0.4511	0.921 00	0.101	0.86857	1.011 88	0.042
0.5009	0.928 87	0.101	0.92181	1.029 30	0.024
0.5622	0.939 40	0.101	0.9663	1.045 57	0.011
1,3-Dioxolane (1) + Pentyl Ethanoate (2)					
0.0625	0.878 10	0.023	0.6577	0.959 88	0.098
0.1471	0.886 20	0.051	0.7353	0.977 01	0.086
0.2668	0.899 15	0.083	0.7881	0.990 10	0.073
0.3300	0.906 85	0.093	0.8531	1.008 06	0.057
0.4255	0.919 76	0.105	0.9034	1.023 71	0.039
0.4843	0.928 63	0.107	0.9359	1.034 73	0.025
0.5466	0.938 89	0.106	0.9588	1.042 95	0.016
0.5984	0.948 21	0.104			
1,3-Dioxolane (1) + Ethyl Hexanoate (2)					
0.0535	0.870 64	0.036	0.6274	0.944 54	0.176
0.1863	0.882 63	0.107	0.6898	0.957 75	0.162
0.3396	0.899 48	0.162	0.7327	0.967 86	0.148
0.4238	0.910 50	0.181	0.7904	0.982 94	0.128
0.5126	0.923 89	0.185	0.8491	1.000 41	0.099
0.5352	0.927 63	0.185	0.9367	1.031 49	0.045
0.5951	0.938 28	0.181	0.9643	1.042 80	0.027
1,3-Dioxolane (1) + Hexyl Ethanoate (2)					
0.0910	0.875 97	0.051	0.7014	0.911 59	0.163
0.1856	0.884 64	0.098	0.7381	0.970 24	0.154
0.3314	0.900 41	0.150	0.7671	0.977 60	0.144
0.3925	0.908 08	0.167	0.8468	1.000 36	0.108
0.5036	0.924 09	0.182	0.8996	1.017 96	0.077
0.5663	0.934 55	0.183	0.9373	1.032 04	0.050
0.6277	0.945 98	0.179	0.9692	1.045 05	0.026
0.6620	0.952 97	0.171			

Mole fractions of 1,3-dioxolane (component 1) were determined from fluxes with an accuracy of $\pm 2 \times 10^{-4}$, and flow rates were selected to cover the whole mole fraction range.

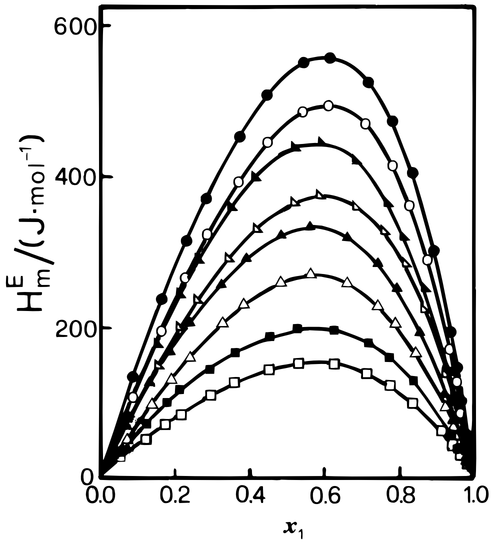

Figure 1. Excess molar enthalpies, H_m^E, at 298.15 K of 1,3-dioxolane + alkyl alkanoates. Isomers: open and corresponding closed symbols. (■, □), ethyl propanoate and propyl ethanoate; (▲, △), ethyl butanoate and butyl ethanoate; (♦, ◊), ethyl pentanoate and pentyl ethanoate; (●, ○), ethyl hexanoate and hexyl ethanoate. Solid lines, calculated with eq 2.

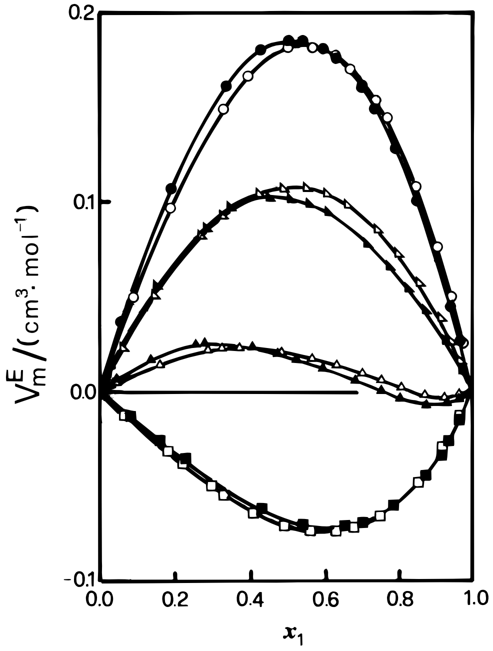

Figure 2. Excess molar volumes, V_m^E, at 298.15 K of 1,3-dioxolane + alkyl alkanoates. Isomers: open and corresponding closed symbols. (■, □), ethyl propanoate and propyl ethanoate; (▲, △), ethyl butanoate and butyl ethanoate; (♦, ◊), ethyl pentanoate and pentyl ethanoate; (●, ○), ethyl hexanoate and hexyl ethanoate. Solid lines, calculated with eq 2.

Before measurements, calibration of the apparatus was carried out by measuring the excess molar enthalpies of the standard mixture cyclohexane + hexane at 298.15 K (Gmehling, 1993). The difference between our values of the excess molar enthalpies and the literature values was found to be less than 0.5% over most of the mole fraction range of cyclohexane.

Excess molar volumes, V_m^E, were determined using a digital density meter (Anton Paar, model DMA 60, Graz, Austria) equipped with a measuring cell (Anton Paar, type 602) as described previously (Fermeglia and Lapasin, 1988).

Table 4. Adjustable Parameters, a_k, Eq 2, and Standard Deviations, $\sigma(Q_m^E)$, Eq 2, of Binary Mixtures Containing 1,3-Dioxolane + Alkyl Alkanoate Structural Isomers at 298.15 K

	a_0	a_1	a_2	a_3	$\sigma(Q_m^E)$
1,3-Dioxolane (1) + Ethyl Propanoate (2)					
$H_m^E/J \cdot mol^{-1}$	793.3	171.9			1.3
$V_m^E/cm^3 \cdot mol^{-1}$	−0.2727	−0.1273	−0.0160	−0.0091	0.0003
1,3-Dioxolane (1) + Propyl Ethanoate (2)					
$H_m^E/J \cdot mol^{-1}$	606.1	175.2			1.0
$V_m^E/cm^3 \cdot mol^{-1}$	−0.2890	−0.1041			0.0006
1,3-Dioxolane (1) + Ethyl Butanoate (2)					
$H_m^E/J \cdot mol^{-1}$	1314.9	347.8			1.9
$V_m^E/cm^3 \cdot mol^{-1}$	0.0754	−0.1295	−0.0531		0.0006
1,3-Dioxolane (1) + Butyl Ethanoate (2)					
$H_m^E/J \cdot mol^{-1}$	1053.8	321.6			1.8
$V_m^E/cm^3 \cdot mol^{-1}$	0.0865	−0.0749	−0.0455		0.0003
1,3-Dioxolane (1) + Ethyl Pentanoate (2)					
$H_m^E/J \cdot mol^{-1}$	1743.3	514.5			3.0
$V_m^E/cm^3 \cdot mol^{-1}$	0.4063	−0.0540			0.0010
1,3-Dioxolane (1) + Pentyl Ethanoate (2)					
$H_m^E/J \cdot mol^{-1}$	1447.2	546.8			2.8
$V_m^E/cm^3 \cdot mol^{-1}$	0.4294	0.0019			0.0010
1,3-Dioxolane (1) + Ethyl Hexanoate (2)					
$H_m^E/J \cdot mol^{-1}$	2139.6	846.7	299.8		3.6
$V_m^E/cm^3 \cdot mol^{-1}$	0.7410	0.0461			0.0008
1.3-Dioxolane (1) + Hexyl Ethanoate (2)					
$H_m^E/J \cdot mol^{-1}$	1895.6	826.7	187.8		2.4
$V_m^E/cm^3 \cdot mol^{-1}$	0.7278	0.1382			0.0010

Mole fractions of dioxolane were prepared by mass, using an electronic balance (Mettler, model AE 160) that had a resolution of ±0.0001 g and a maximum capacity of 150 g. The accuracy in the mole fraction determination was $\pm 1 \times 10^{-4}$.

The volumes of the flasks in which mixtures were prepared were ≈15 cm^3, and the heavier component was charged first to minimize the composition error due to vaporization. The procedure used in preparing solutions is the same indicated by Fermeglia and Lapasin (1988).

The density measurements were reproducible to $\pm 1 \times 10^{-5} g \cdot cm^{-3}$, leading to an accuracy in excess molar volumes less than $\pm 0.003\ cm^3 \cdot mol^{-1}$.

A thermostatically well-stirred bath circulator (Heto, type 01 DBT 623, Birkerød, Denmark) whose temperature was controlled to ±0.005 K was used as external bath, while inside the apparatus a calibrated thermistor (Anton Paar DT 100−25) maintained the test temperature at (298.15 ± 0.001) K.

Corrections were made for buoyancy and evaporation of the components.

For each experimental set of measurements, the apparatus was calibrated with doubly distilled water and dry air and was also checked against literature data of the mixture benzene + cyclohexane (Wilhelm, 1985). An agreement of our data better than 0.5% in the central range of mole fraction of benzene was found.

3. Results and Discussion

The excess molar volumes were calculated with the following equation

$$V_m^E/(cm^3 \cdot mol^{-1}) = V - \sum x_i V_i \tag{1}$$

where V is the molar volume of the mixture and x_i and V_i

are the mole fractions and molar volumes of the pure components, respectively.

The experimental values of H_m^E and V_m^E are listed in Tables 2 and 3 and graphically represented in Figures 1 and 2. All experimental data were fitted by a least-squares method to the Redlich−Kister equation

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

where $Q_m^E = H_m^E/(J \cdot mol^{-1})$ or $V_m^E/(cm^3 \cdot mol^{-1})$ with all points weighted equally. a_k are the adjustable parameters, and, in each case, their number was ascertained from variance analysis of the standard deviation $\sigma(Q_m^E)$.

The adjustable parameters a_k and the standard deviation σ, as computed from eqs 2 and 3, are presented in Table 4.

Figures 1 and 2 show an interesting different behavior of mixtures when calorimetric and volumetric data are considered.

In fact, both ethyl alkanoates and the corresponding structural isomers propyl alkanoates in mixtures with 1,3-dioxolane (a cyclic diether) show a regular increase of H_m^E and V_m^E with chain length. However, calorimetric data show a marked and constant difference of H_m^E between the corresponding isomers, while in the V_m^E plots such differences are negligible.

Moreover, it must pointed out that the same isomers of this paper, in mixtures with 2-methoxy-2-methyl propane (MTBE) (a linear ether), exhibit quite a different behavior (Francesconi et al., 1998). Values of both H_m^E and V_m^E decrease as the chain length of alkanoates is increased. V_m^E have markedly negative values and relatively small values of H_m^E were obtained, whereas mixtures reported in this paper show smaller values of V_m^E and larger values of H_m^E.

This contrasting results for the binary mixtures of alkanoates containing 1,3-dioxolane or MTBE may be ascribed to the peculiarity of 1,3-dioxolane, having a positively charged carbon atom closed to the two ethereal oxygen atoms, which implies a relatively strong interaction with the negatively charged oxygen in the C═O groups of alkanoates.

This interaction leads to large negative values of V_m^E and takes part in lowering H_m^E, as can be seen if the approximate expression $H_m^E \approx E_{11} + E_{22} - 2E_{12}$ is considered, where E_{12} is the interaction energy between dissimilar molecules of the mixture.

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