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HEATS OF MIXING OF 2,2-DIMETHOXYPROPANE AND DIETHOXYMETHANE WITH SOME 1-ALKENES

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ABSTRACT

The excess enthalpies of 2,2-dimethoxypropane + 1-hexene, + 1-heptene and + 1-octene, and of diethoxymethane + 1-hexene + 1-octene have been measured at 298.15 K. The values of H^E for all the systems are positive and increase with increasing chain length of the alkene. The results are analysed in term of the quasi-lattice theory of mixtures using the zeroth approximation.

INTRODUCTION

The present work forms part of a program devoted to studies of the thermodynamic properties of mixtures of acetals. Since no thermodynamic measurements exist for binary systems of acetals with alkenes, we have, as a first step, attempted to measure the excess enthalpies of 2,2-dimethoxypropane (D.M.2.2.P.) and diethoxymethane (D.E.M.) with 1-hexene, 1-heptene and 1-octene. We have interpreted the experimental results in terms of molecular surface interactions using the lattice theory in the zeroth approximation.

EXPERIMENTAL

The calorimeter used in this work was an isothermal flow microcalorimeter "Picker" (Setaram, France) which was the same as that described previously by Picker et al.[1]. Details of the procedure have been described earlier[2]. Studies of the test systems[2, 3] indicate that the precision of measurement of H^E is better than one per cent over nearly the entire composition range. All the acetals were obtained from Fluka, the main impurities they contained being alcohol and carbonyl compounds. The acetals were purified by prolonged refluxing over sodium and repeated fractional distillation, the middle fraction being retained at each step. The purity of the components was checked by gas chromatography and by density measurements. The purity

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was estimated to be 99.5 moles per cent or better. The alkenes (supplied by Fluka) were distilled twice, just before their use in calorimetry.

RESULTS AND DISCUSSION

The experimental values of H^E for the five acetal mixtures at 298.15 K are listed in Tables 2–6.

In all cases, x_1 is the mole fraction of the acetal. The results were fitted, using a least-squares computer program, to a smoothing equation:

$$H^E = x_1(1 - x_1)[A + B(1 - 2x_1) + C(1 - 2x_1)^2 + D(1 - 2x_1)^3] \quad (1)$$

TABLE 1

VALUES OF PARAMETERS FOR EQN. (1) DETERMINED BY THE METHOD OF LEAST-SQUARES

System	*A*	$\sigma(A)$	*B*	$\sigma(B)$	*C*	$\sigma(C)$	*D*	$\sigma(D)$	$\sigma(H^E)(J.mol^{-1})$
D.M.2.2.P + 1-hexene	929.5	1.2	25	2.2	76	35	−251	61	0.9
D.M.2.2.P + 1-heptene	1159	1.1	−2.2		−61				0.8
D.M.2.2.P + 1-octene	1320	1.7	−85	3.5	−94	42			1.2
D.E.M. + 1-hexene	1011	1.2	133	2.3	146	33	−455	56	0.9
D.E.M. + 1-octene	1410	1.7	−46	3	365	46	−482	80	1.1

Each point was assigned unit weight. Values of the constants *A*, *B*, *C* and *D*, and their respective standard errors for each representation, are listed in Table 1 with the standard deviations $\sigma(H^E)$ defined by:

$$\sigma(H^E) = [\Sigma(H^E_{expt} - H^E_{calc})^2/m - n]^{1/2} \quad (2)$$

The values of excess enthalpies of 1-alkene with the two acetal isomers are positive and symmetric with composition, and increase in the same way as the molecular volume of olefin. The small values of H^E can be interpreted by assuming a possible n–π interaction between the lone-pair oxygen electrons of the acetal and the π electrons of the 1-alkene.

We have attempted to interpret our results in terms of molecular surface interactions using the zeroth approximation of the theory formulated by Kehiaian et al.[4]. The experimental excess enthalpy of mixing is defined as:

$$H^E = \frac{x_1x_2}{x_1q_1 + x_2q_2} \cdot q_1q_2A_{12} \quad (3)$$

The molecular interaction parameter A_{12} is given by the relation:

$$A_{12} = -[h^{\bullet}_{a-ac}(\alpha_{1ac} - \alpha_{2ac})(\alpha_{1a} - \alpha_{2a}) + h^{\bullet}_{a-c}(\alpha_{1a} - \alpha_{2a})$$

$$(\alpha_{1c} - \alpha_{2c}) + h^{\bullet}_{ac-c}(\alpha_{1ac} - \alpha_{2ac})(\alpha_{1c} - \alpha_{2c})] \quad (4)$$

TABLE 2

EXCESS ENTHALPY (H^E) OF 2,2-DIMETHOXYPROPANE + 1-HEXENE AT 298.15 K

x_1	$H^E(J.mol^{-1})$	$\delta H^E(J.mol^{-1})^a$	$H^E_{cal}.(J.mol^{-1})^b$
0.2196	157	−1.2	165
0.2376	166.5	−1.5	174
0.2555	176.5	−0.5	182
0.2734	185	−0.4	189
0.2913	193.5	0.4	196
0.3090	200.5	0.6	202
0.3268	207	0.8	207
0.3445	212.5	0.8	212
0.3621	217.5	1	216
0.3798	221	0.4	219.5
0.3973	224	0	222.5
0.4148	227	0	224.5
0.4323	230	0.8	226
0.4497	231	0.2	227.5
0.4671	232	0.1	228
0.4844	232.8	0.4	228
0.5017	232.5	0.1	227
0.5189	232	0.1	226
0.5361	231	0.2	224.5
0.5533	229.6	0.3	222.5
0.5704	227	−0.1	220
0.5874	224	−0.5	216.5
0.6045	220.5	−0.8	213
0.6214	216	−1	209
0.6384	211.5	−1.6	204.5
0.6552	206.5	−1.7	199
0.6721	202	−0.7	194
0.6889	196	−0.6	188
0.7056	190.5	0.4	181.5
0.7223	183.5	0.6	174.5
0.7390	171	1.9	167.5
0.7556	168	1.2	160
0.7722	159	1	152
0.7888	149	0.3	143
0.8053	139	0.1	134.5
0.8217	128	−0.7	125

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[a] $\delta H^E = H^E_{expt} - H^E_{calc}$, H^E_{calc} from eqn. (1).

[b] H^E_{calc} from the lattice theory of mixtures, eqn. (3).

TABLE 3

EXCESS ENTHALPY (H^E) OF 2,2-DIMETHOXYPROPANE + 1-HEPTENE AT 298.15 K

x_1	H^E(J mol^{-1})	δH^E(J mol^{-1})[a]	H^E_{calc}(J mol^{-1})[b]
0.2597	216.5	−1.6	226
0.2786	228	−0.8	236
0.2975	238.5	−0.3	245.5
0.3162	248	0.3	253.5
0.3348	256.5	0.7	261
0.3533	264	1	267.5
0.3899	275	0.3	278
0.4079	279.5	0.3	282
0.4259	283.5	0.6	285.5
0.4438	286.5	0.7	288
0.4615	288	0.1	289.5
0.4791	289.7	0.5	290.5
0.4966	290.5	0.8	291
0.5139	289.5	0	290.5
0.5312	289	0.4	289
0.5483	286.5	−0.4	287.5
0.5654	284	−0.5	285
0.5823	280.5	−1	282
0.5991	276.5	−1.2	278
0.6158	272	−1.3	274
0.6323	267	−1.2	269
0.6652	255.5	−0.6	257
0.6814	249	−0.2	250.5
0.6976	242.5	0.9	243
0.7136	234	0.6	235.5
0.7296	225	0.3	227
0.7454	216	0.5	218
0.7612	207	1.3	209
0.8078	174	0.5	178
0.8231	162.5	0.6	167
0.8384	148.5	−1.4	155

[a] $\delta H^E = H^E_{expt} - H^E_{calc}$, H^E_{calc} from eqn. (1).

[b] H^E_{calc} from the lattice theory of mixtures, eqn. (3).

TABLE 4

EXCESS ENTHALPY (H^E) OF 2,2-DIMETHOXYPROPANE + 1-OCTENE AT 298.15 K

x_1	$H^E(J\,mol^{-1})$	$\delta H^E(J\,mol^{-1})$[a]	$H^E_{calc}(J\,mol^{-1})$[b]
0.2405	226.5	−3	248
0.2609	242	−1.5	263
0.2810	256.5	0.2	276
0.3009	269	0.9	287
0.3206	280	1.2	298
0.3401	289.5	1.1	308
0.3594	298	1	316
0.3973	313	1.8	330
0.4159	317	0.3	336
0.4343	321	−0.3	339
0.4526	324.5	−0.5	343
0.4706	328	0.3	345
0.4885	329.3	−0.1	347
0.5061	330	−0.3	348
0.5236	330	−0.4	347
0.5409	329.3	−0.2	346
0.5580	328.5	0.6	344
0.5750	326.5	0.1	342
0.5917	322	−0.1	338
0.6083	318	−0.1	334
0.6248	312.5	−0.8	329
0.6410	306.5	−1.4	324
0.6571	299.5	−2.3	317
0.6888	286	−1.6	303
0.7045	278.5	−1	294
0.7199	271	0.1	286
0.7352	262	0.3	276
0.7504	253	1.1	266
0.7654	243	1.4	255
0.7803	232.5	1.7	244
0.8096	209.5	1.9	220
0.8240	196	0.6	207
0.8383	182	−0.7	194
0.8525	168	−1.5	180

[a] $\delta H^E = H^E_{calc} - H^E_{expt}$, H^E_{calc} from eqn. (1).

[b] H^E_{calc} from the lattice theory of mixtures, eqn. (3).

TABLE 5

EXCESS ENTHALPY (H^E) OF DIETHOXYMETHANE + 1-OCTENE AT 298.15 K

x_1	$H^E (J.mol^{-1})$	$\delta H^E (J.mol^{-1})$[a]	$H^E_{calc} (J.mol^{-1})$[b]
0.2157	237	−2	229.5
0.2562	269.5	−0.7	259.5
0.2761	282	−1.6	272.5
0.2958	296	0.4	284.5
0.3153	306	−0.2	295.5
0.3347	317.5	1.9	305
0.3538	324.5	0.8	314
0.3727	331.5	0.9	321.5
0.3915	338	1.6	328
0.4284	347	1.8	338.5
0.4466	348.5	0.5	342
0.4646	350	−0.3	345
0.4824	351.5	−0.3	346
0.5001	352	−0.5	347.5
0.5349	351.5	−0.5	347
0.5520	350	−0.7	345.5
0.5690	348	−0.7	343
0.5859	345.5	−0.5	340
0.6025	343	0.3	336
0.6191	338.5	0	331.5
0.6354	333	−0.5	326
0.6516	326	−1.8	320
0.6677	321	−0.4	313
0.6836	313	−1.1	305
0.6994	305	−1.1	297.5
0.7150	298	0.7	289
0.7305	289	1.2	279.5
0.7458	279	1.5	269.5
0.8058	230	0.8	223.5
0.8205	216	0.6	211

[a] $\delta H^E = H^E_{expt} - H^E_{calc}$, H^E_{calc} from eqn. (1).

[b] H^E_{calc} from the lattice theory of mixtures, eqn. (3).

TABLE 6

EXCESS ENTHALPY (H^E) OF DIETHOXYMETHANE + 1-HEXENE AT 298.15 K

x_1	$H^E(J.mol^{-1})$	$\delta H^E(J.mol^{-1})^a$	$H^E_{calc}(J.mol^{-1})^b$
0.1620	140	0.5	132.5
0.1799	153	0	143.5
0.2155	178.5	0.8	163
0.2332	189	0.3	172
0.2509	199.5	0.7	180
0.2686	208.5	0.4	187.5
0.2863	216.5	0	194
0.3039	224.5	0.5	200
0.3215	230	−0.6	206
0.3390	235.5	−0.7	210.5
0.3566	240.5	−0.6	215
0.3740	245	−0.1	218.5
0.3915	248	−0.4	221.5
0.4089	250	−0.8	224
0.4263	252	−0.6	226
0.4437	253	−0.7	227
0.4610	253.3	−0.8	228
0.4784	253	−0.9	228
0.4956	252.9	−0.2	227.5
0.5129	251.5	−0.4	226.5
0.5301	250	0	225
0.5473	248	0.3	223
0.5644	246	1.2	221
0.5815	243	1.6	218
0.5989	239	1.8	214
0.6157	234	1.4	210.5
0.6667	215.5	0.7	195.5
0.6837	207.5	0	190
0.7006	200.5	0.7	183.5
0.7175	190	−1.3	176.5
0.7511	171	−1.7	162
0.7679	162	−0.5	154
0.7847	151.5	−0.4	145.5

[a] $\delta H^E = H^E_{expt} - H^E_{calc}$, H^E_{calc} from eqn. (1).
[b] H^E_{calc} from the lattice theory of mixtures, eqn. (3).

where h^* is the molar interchange enthalpy per conventional unit area for contact between surfaces of the types considered. Three kinds of surfaces will be considered for the molecules studied in this work, namely,

aliphatic (CH_3, CH_2) = a
ethylenic ($CH_2 = CH$) = e
acetal oxygen (O) = ac

The aliphatic–acetal interchange enthalpy h^*_{a-ac} has been determined previously[3] from the heats of mixing of acetal + heptane mixtures ($A_{12} = h^*_{a-ac}\ \alpha^2_{i-ac}$) The value adopted for aliphatic–ethylenic interchange enthalpy h^*_{a-e} has been deduced recently by H. K. Ghassemi et al.[5] from the H^E values of 1-alkene + n alkanes. The only unknown quantity is the acetal–ethylenic interchange enthalpy h^*_{ac-e}: this was calculated from eqn. (4). The total contact area q_i and the fraction of surface α_i are estimated using a lattice coordination number of $Z = 8$, according to the convention adopted by some authors[4-8].

The values of molecular parameters are summarized in Table 7. The agreement between the H^E values calculated from the quasi-lattice theory and the experimental points for the five binary mixtures seem very satisfactory (see Tables 2–7) if one takes into account that all the data are correlated using only one adjusted parameter, namely, $h^*_{ac-e} = 2800$ J.mol^{-1}. We have also studied the mixture of two isomers, D.M.2.2.P + D.E.M (see Table 8): the excess enthalpies approach zeroth as predicted by the theory ($\alpha_{1ac} = \alpha_{2ac}$ and $A_{12} \simeq 0$).

TABLE 7

MOLECULAR PARAMETERS OF COMPOUNDS STUDIED

	q_i	α_{ia}	α_{i-ac}	α_{ie}
D.M.2.2.P	5.5	0.7273	0.2727	0
D.E.M.	5.5	0.7273	0.2727	0
1-Hexene	4.5	0.6944	0	0.3056
1-Heptene	5.25	0.7381	0	0.2619
1-Octene	6	0.7708	0	0.2292
h^*_{a-ac}($J.mol^{-1}$)[a]	h^*_{a-e}($J.mol^{-1}$)[b]		h^*_{ac-e}($J.mol^{-1}$)[c]	
6100	510		2800	

[a] Ref. 3, [b] Ref. 5. [c] This work.

TABLE 8

EXCESS ENTHALPY (H^E) OF THE MIXTURE: D.M.2.2.P$_1$ + D.E.M$_2$ AT 298.15 K

x_1	H^E($J.mol^{-1}$)	x_1	H^E($J.mol^{-1}$)
0.1484	3.2	0.4216	7.7
0.1669	3.7	0.4575	8
0.1852	4.1	0.4934	8
0.2036	4.5	0.5290	8.1
0.2219	4.8	0.5469	8.1
0.2402	5.2	0.5646	8.1
0.2585	5.5	0.6000	8
0.2767	5.8	0.6355	7.7
0.3131	6.4	0.7058	7.3
0.3494	6.9	0.8452	4.2
0.3856	7.4	0.9143	2.6

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