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Excess molar enthalpies in binary systems containing aldehydes

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Abstract

Excess enthalpies have been determined at 298.15 K for the binary systems hexanal + *n*-nonane, and + (*n* − 1)-nonene, *trans*-2-butenal + *n*-nonane, +cyclohexane, + (*n* − 1)-nonene, + (*n* − 1)-nonyne, and +1-butanol, and benzaldehyde + *n*-decane, + (*n* − 1)-decene, and +1-hexanol, using a Calvet-type differential microcalorimeter. The results are fitted with a Redlich–Kister-type polynomial and the UNIFAC group-contribution model.

INTRODUCTION

Within the framework of our systematic study of the model systems formed by some aroma compounds, we undertook an investigation of the excess enthalpies in binary systems formed by different kinds of aldehydes with other compounds. The purpose of this work is to evaluate the influence of stucture on the excess enthalpies studied and to supplement the matrix of the UNIFAC group-interaction parameters [1, 2] with those of aldehyde groups.

EXPERIMENTAL

The differential microcalorimeter DAK-1-1 used in this study, together with its operational procedure, has been described previously [3]. The errors of the values determined were less than 2%.

n-Nonane, *n*-decane, cyclohexane, 1-butanol, and 1-hexanol were obtained from Reakhim (Kharkov). They have a purity of 99.9% and were used without further purification. 1-Alkenes and aldehydes were Pure Grade and were further purified by fractional distillation, as was the 1-nonyne synthesized [4] in our laboratory. The aldehydes were distilled in vacuum at temperatures below 323.15 K. The GLC analysis showed the purities of the distilled products to be higher than 99% in all cases.

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RESULTS AND DISCUSSION

Table 1 contains the experimental results for the molar excess enthalpies of ten binary systems formed by mixing hexanal, *trans*-2-butenal and benzaldehyde with other compounds.

The results were fitted with equations of the form

$$H^{\mathrm{E}} = x_1 x_2 \sum_{i=1}^{n} a_i (x_1 - x_2)^{i-1} \tag{1}$$

where x_1 and x_2 represent the molar fraction of the first and second component, respectively. Values of the coefficients a_i, determined by the least-squares method, are summarized in Table 2. The number of coefficients n was varied and in each case the minimum number needed for the best representation of the results was found by examining the standard error of the estimate

$$S(H^{\mathrm{E}}) = \left\{ \sum_{N} (H^{\mathrm{E}}_{\mathrm{exp}} - H^{\mathrm{E}}_{\mathrm{calc}})^2 / (N - n) \right\}^{1/2} \tag{2}$$

where N is the number of experimental points. Values of $S(H^{\mathrm{E}})$ for each of the fits selected are given in the last column of Table 2.

No excess enthalpies were found in the literature for any of the systems studied.

The dependence of endothermic excess enthalpies on composition is nearly parabolic for all the systems containing alkanes and alkenes. The introduction of a double bond into nonane or decane reduces the enthalpy of mixing with an aldehyde. The very much lower H^{E} for *trans*-2-butenal + 1-nonyne is probably due to the strong interaction between aldehyde and alkyne. The behaviour of the H^{E}–x relationship in alcohol systems is more asymmetric, with a maximum occurring in the aldehyde-rich region.

The UNIFAC group-contribution model [5] was fitted to the H^{E} reported here and given in the literature using some group-interaction parameters obtained earlier [1, 2]. The group-interaction parameters were estimated by the simplex method and the Nelder–Mead procedure described by Fredenslund et al. [5]. The results are given in Table 3. The mean relative errors are defined by

$$\delta(H^{\mathrm{E}}) = \frac{1}{N} \sum_{N} \left| \frac{H^{\mathrm{E}}_{\mathrm{calc}} - H^{\mathrm{E}}_{\mathrm{exp}}}{H^{\mathrm{E}}_{\mathrm{exp}}} \right| \times 100\,(\%) \tag{3}$$

where N is the number of experimental points.

TABLE 1

The experimental enthalpy of mixing H^E in J mol^{-1} at 298.15 K for binary systems

x_1	H^E
Hexanal(1)–*n*-nonane(2)	
0.315	825
0.409	875
0.484	883
0.498	898
0.538	860
0.632	808
0.666	778
0.676	756
0.790	600
trans-2-Butenal(1)–*n*-nonane(2)	
0.220	1104
0.280	1430
0.338	1503
0.407	1567
0.440	1606
0.520	1601
0.586	1567
0.590	1544
0.607	1538
0.695	1487
0.736	1363
0.928	457
trans-2-Butenal(1)–1-nonene(2)	
0.155	667
0.267	1015
0.369	1231
0.408	1239
0.509	1245
0.580	1205
0.634	1161
0.825	628
0.863	486
trans-2-Butenal(1)–1-butanol(2)	
0.183	948
0.290	1271
0.373	1393
0.429	1470
0.490	1476
0.608	1471
0.622	1464
0.759	1167
0.862	683
1-Decene(1)–benzaldehyde(2)	
0.161	705
0.267	1036
0.439	1300
0.459	1307
0.523	1323
0.558	1341
0.741	1112
0.808	910
Hexanal(1)–1-nonene(2)	
0.103	300
0.166	409
0.241	485
0.264	511
0.456	548
0.523	557
0.540	561
0.548	557
0.571	525
0.680	484
0.821	241
0.893	218
0.917	139
trans-2-Butenal(1)–cyclohexane(2)	
0.108	732
0.138	824
0.275	1222
0.361	1367
0.412	1424
0.510	1442
0.672	1230
0.697	1142
0.735	989
0.870	564
trans-2-Butenal(1)–1-nonyne(2)	
0.085	101
0.230	230
0.337	271
0.497	262
0.630	242
0.659	236
0.766	169
0.905	64
n-Decane(1)–benzaldehyde(2)	
0.204	915
0.268	1115
0.290	1182
0.428	1468
0.510	1509
0.685	1433
0.710	1394
0.854	883
1-Hexanol(1)–benzaldehyde(2)	
0.132	816
0.227	1270
0.358	1615
0.397	1623
0.481	1682
0.530	1667
0.629	1546
0.714	1374
0.860	794

TABLE 2

Coefficients a_i of eqn. (1) and standard deviations $S(H^E)$ in J mol^{-1} for binary systems

System	a_1	a_2	a_3	a_4	a_5	$S(H^E)$
Hexanal(1)–*n*-nonane(2)	3522.0	−448.0	1013.5	–	–	8.8
Hexanal(1)–1-nonene(2)	2231.6	−502.4	553.8	−446.9	–	25.3
trans-2-Butenal(1)–*n*-nonane(2)	6361.8	−636.4	4947.5	4363.5	−9959.8	28.6
trans-2-Butenal(1)–cyclohexane(2)	5854.0	−521.9	−1811.4	−1753.1	4025.9	23.4
trans-2-Butenal(1)–1-nonene(2)	5051.4	−441.9	296.6	−353.7	−2351.5	18.2
trans-2-Butenal(1)–1-nonyne(2)	1088.0	−323.3	–	–	–	9.5
trans-2-Butenal(1)–1-butanol(2)	5955.7	584.2	2733.4	−1824.1	−5009.9	10.8
n-Decane(1)–benzaldehyde(2)	6071.9	1209.2	1287.7	−127.1	−1761.6	14.4
1-Decene(1)–benzaldehyde(2)	5311.4	590.2	1570.5	−287.0	−2367.0	8.2
1-Hexanol(1)–benzaldehyde(2)	6686.6	−561.0	1865.9	337.2	−2904.8	14.5

The H^E values used in the calculations are given in Table 4 together with the literature references.

The interaction parameters of the groups $CH_2/CH_2{=}CH$, $CH_2/CH{\equiv}C$, CH_2/OH and $CH_2{=}CH/OH$ also used in these calculations were taken from our earlier work [2]. It was shown in this paper that in order to improve the H^E representation in some systems, including the alkane–ester and alkane–ketone systems, the group surface-area parameters of the original UNIFAC, Q_s, has to be enhanced by a factor of about 3. To test this conclusion, trebled values of Q_s were applied to the systems formed by aldehydes. Therefore Table 3 contains the calculation results corresponding to the original Q_s and to their trebled values.

It is evident from Table 3 that the trebled values of Q_s have an advantage over those of the original UNIFAC for aldehyde mixtures with *n*-alkane, cycloalkane and alcohol. It can be seen from Fig. 1 that the prediction of H^E for the *trans*-2-butenal–cyclohexane system formed by acyclic CH_2, cyclic $CH_2(cCH_2)$, CH=CH and CHO groups also gives much better results using the UNIFAC group-interaction parameters corresponding to the trebled values of Q_s.

Because the group interaction parameters of aliphatic aldehydes have been found to be unsuitable for benzaldehyde, the latter is regarded as a special C_6H_5CHO group or as containing a new group, AC–CHO. The very close H^E reproduction obtained for both these approaches can be seen in Table 3. The agreement between the calculated and experimental results is quite satisfactory although the use of trebled Q_s values is not advantageous. It is significant that the largest deviations occur for benzaldehyde mixtures with alkanes. Data on H^E are scarce for mixtures formed by aldehydes. New experimental data are needed to confirm the suitability of group parameters obtained from limited information.

TABLE 3

UNIFAC group-interaction parameters based on the H^E data, and the correlation standard $S(H^E)$ and mean $\delta(H^E)$ errors

Groups		Original UNIFAC Q_s values [a]				Trebled Q_s values [b]			
s	t	a_{st}	a_{ts}	$S(H^E)$/ J mol^{-1}	$\delta(H^E)$/ %	a_{st}	a_{ts}	$S(H^E)$/ J mol^{-1}	$\delta(H^E)$/ %
CHO	CH_2	179.26	712.06	418.2	35.9	−31.91	354.44	96.5	8.0
	cCH_2	304.54	597.71	274.5	31.1	−70.07	420.67	23.7	2.5
	CH_2=CH	−5.85	426.29	25.4	5.4	−171.10	630.71	27.4	6.0
	HC≡C	−145.61	388.60	20.9	9.9	217.89	−124.22	31.5	12.6
	OH	478.77	586.48	318.7	19.4	−29.29	374.54	42.5	2.8
CH_2	cCH_2	−30.26	71.94	22.7	8.8	−35.15	52.31	22.7	8.9
CH_2=CH	cCH_2	23.89	49.27	15.8	6.7	11.93	13.52	19.3	9.1
	CH≡C	95.90	192.40	5.6	2.1	91.42	−13.22	5.9	2.0
C_6H_5CHO	CH_2	4.57	299.07	82.7	6.4	−60.48	168.74	91.5	6.6
	CH_2=CH	50.14	98.13	33.1	1.9	−7.75	62.02	38.7	2.5
	OH	570.67	129.50	33.6	2.0	60.47	80.52	29.4	1.6
	ACH	−49.69	103.51	67.9	4.6	−49.88	73.81	6.5	4.4
AC–CHO	CH_2	20.16	784.07	86.5	6.3	−117.94	377.45	86.9	6.4
	CH_2=C	14.87	443.84	34.3	1.6	−31.30	185.62	86.4	2.3
	OH	405.91	357.34	44.4	2.9	90.73	113.89	21.8	1.3
	ACH	−86.18	299.39	7.2	4.9	−109.07	213.14	6.6	4.5
ACH	CH_2	[1]				13.35	36.47	50.6	4.6
	CH_2=C	52.19	−12.10	41.6	6.8	−15.61	28.05	38.7	5.9
	OH	[1]				484.09	−149.85	96.3	7.0

[a] Group surface-area parameters Q [5]. [b] See text

TABLE 4

H^E data used to calculate the group interaction parameters given in Table 3

Groups	Systems	Number of points	Reference
CH_2/CHO	*n*-Heptane + propanal	9	[6]
	n-Nonane + hexanal (T = 298.15 K)	9	This work
cCH_2/CHO	Cyclohexane + butanal, +pentanal (T = 298.15 K)	18	[7]
CH_2=CH/CHO	1-Nonene + hexanal (T = 298.15 K)	13	This work
CH≡C/CHO	1-Nonyne + *trans*-2-butenal (T = 298.15 K)	8	This work
OH/CHO	1-Butanol + *trans*-2-butenal (T = 298.15 K)	9	This work
CH_2/cCH_2	Cyclohexane + *n*-hexane, +*n*-decane; cycloheptane + *n*-heptane, +*n*-nonane (T = 298.15 K)	83	[7]
CH_2=CH/CH≡C	1-Octene + 1-octyne; 1-nonene + 1-nonyne (T = 298.15 K)	17	[1]
CH_2=CH/cCH_2	1-Heptene + cyclohexane	9	[7]
	1-Octene + cyclohexane (T = 298.15–313.15 K)	18	Our data (unpubl.)
CH_2/C_6H_5CHO/AC–CHO	*n*-Heptane + benzaldehyde	8	[8]
	n-Decane + benzaldehyde (T = 298.15 K)	8	This work
CH_2=CH/C_6H_5CHO/AC–CHO	1-Decene + benzaldehyde (T = 298.15 K)	8	This work
OH/C_6H_5CHO/AC–CHO	1-Hexanol + benzaldehyde (T = 298.15 K)	9	This work
ACH/C_6H_5CHO/AC–CHO	Benzene + benzaldehyde (T = 298.15 K)	7	[9]
ACH/CH_2	Benzene + *n*-hexane, +*n*-heptane, +*n*-hexadecane (T = 298.15–323.15 K)	96	[10]
ACH/OH	Benzene + 1-propanol, +1-butanol, +2-methyl-1-pentanol (T = 293.15–303.15 K)	154	[7]
ACH/CH_2=CH	Benzene + 1-hexene, +1-heptene, +1-octene (T = 298.15 K)	42	[6]

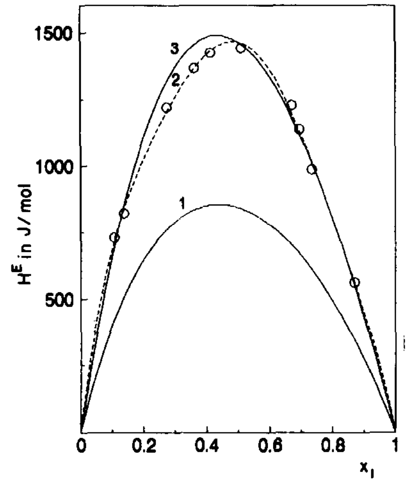

Fig. 1. Experimental (○) and calculated (curves) excess enthalpies of *trans*-2-butenal(1)–cyclohexane(2) at 298.15 K. Curves 1 and 3 are predicted by UNIFAC using the group surface-area parameters Q_s calculated by Bondi [11] and their trebled values, respectively. Curve 2 is calculated from eqn. (1) with the coefficients from Table 2.

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