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)-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

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

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

where N is the number of experimental points. Values of $S(H^E)$ 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*-2butenal + 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 aldehyderich 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

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

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

Hexanal(1)-n-nonanc(2)Hexanal(1)-1-noncnc(2)0.3158250.1664090.4498750.1664090.4848830.2645110.5388600.4565480.6328080.5235570.6667780.5405610.6767560.5485570.7906000.5715250.7900.6000.82124110.22011040.9171390.23014040.9171390.338150372212220.40016060.1087320.52016010.13812240.58615670.27512220.59015440.36113670.69514870.51014420.73613630.67212300.69514870.51014420.73598912450.3370.59012450.3372710.59012450.3372710.58114510.6651690.8256280.7661690.83024814681150.42914700.24814480.421145213330.59012450.3372710.56415970.2681150.8339480.2049150.26710151460.59012450.337271	<i>x</i> ₁	$H^{\rm E}$	<i>x</i> ₁	H ^E
0.315 825 0.103 300 0.409 875 0.166 409 0.484 883 0.241 485 0.498 898 0.264 511 0.538 860 0.456 548 0.632 808 0.523 557 0.666 778 0.540 561 0.676 756 0.548 557 0.660 484 17an-2-Butenal(1)-n-nonanc(2) 0.821 241 0.220 1104 0.917 139 0.280 1430 0.280 1430 0.280 100 0.440 1606 0.108 732 0.440 1606 0.108 732 0.440 1606 0.108 823 0.550 1547 0.275 1222 0.590 1544 0.361 1367 0.667 0.275 1222 0.590 1544 0.361 1367 0.667 0.275 1222 0.590 1548 0.412 1424 0.695 1487 0.510 1442 0.375 989 17an-2-Butenal(1)-1-nonync(2) 0.586 1363 0.672 1230 0.590 1544 0.361 1367 0.477 164 0.590 1548 0.412 1424 0.695 1487 0.510 1442 0.735 989 17an-2-Butenal(1)-1-nonync(2) 0.580 1231 0.230 230 0.669 1231 0.230 230 0.669 1231 0.230 230 0.454 1161 0.659 236 0.459 1231 0.230 230 0.468 1239 0.337 271 0.590 1245 0.497 262 0.580 1205 0.639 236 0.454 1161 0.659 236 0.459 1231 0.230 240 0.459 1245 0.497 262 0.580 1205 0.639 242 0.454 1161 0.659 236 0.454 1161 0.459 236 0.459 130 0.459 1303 0.290 1182 0.454 1161 0.459 130 0.459 130 0.465 1453 0.470 148 0.428 1468 0.005 64 115 0.459 130 0.268 1115 0.459 130 0.268 1115 0.459 130 0.454 883 0.440 150 0.454 883 0.440 110 0.455 883 0.440 1182 0.454 883 0.454 833 0.454 833 0.455 83 0.454 833 0.454 833 0.454 833 0.454 833 0.454 833 0	Hexanal(1)-n-non	ane(2)	Hexanal(1)-1-nd	onene(2)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.315	825	0.103	300
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.409	875	0.166	409
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.484	883	0.241	485
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.498	898	0.264	511
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.538	860	0.456	548
$\begin{array}{ccccc} & 0.540 & 561 \\ 0.676 & 778 & 0.540 & 561 \\ 0.676 & 736 & 0.548 & 557 \\ 0.680 & 444 \\ trans-2-Butenal(1)-ronnanc(2) & 0.821 & 241 \\ 0.20 & 1104 & 0.917 & 139 \\ 0.280 & 1430 & & & & & & & & & & & & & & & & & & &$	0.632	808	0.523	557
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.666	778	0.540	561
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.676	756	0 548	557
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.070	600	0.540	525
$\begin{tabular}{ c c c c c } & 0.000 & 1430 & 0.017 & 139 & 0.038 & 1218 & 0.280 & 1430 & 0.917 & 139 & 0.338 & 1503 & trans-2-Butenal(1)-cyclohexane(2) & 0.400 & 1606 & 0.108 & 824 & 0.586 & 1567 & 0.275 & 1222 & 0.520 & 1601 & 0.138 & 824 & 0.586 & 1567 & 0.361 & 1367 & 0.590 & 1544 & 0.361 & 1367 & 0.607 & 1538 & 0.412 & 1424 & 0.695 & 1487 & 0.510 & 1442 & 0.736 & 0.500 & 1442 & 0.735 & 989 & 0.510 & 1442 & 0.735 & 989 & 0.735 & 0.825 & 0.634 & 0.497 & 262 & 0.634 & 0.161 & 0.659 & 2336 & 0.825 & 0.632 & 0.766 & 169 & 0.863 & 0.905 & 64 & 0.905 & 64 & 0.905 & 64 & 0.905 & 0.408 & 0.905 & 0.415 & 0.226 & 0.825 & 0.628 & 0.766 & 169 & 0.863 & 0.905 & 0.415 & 0.204 & 915 & 0.236 & 0.825 & 0.284 & 0.766 & 169 & 0.865 & 0.4143 & 0.685 & 0.4143 & 0.685 & 0.4143 & 0.685 & 0.4143 & 0.685 & 0.4143 & 0.685 & 0.4143 & 0.685 & 0.4143 & 0.685 & 0.4143 & 0.685 & 0.4143 & 0.685 & 0.4143 & 0.685 & 0.4143 & 0.685 & 0.377 & 0.714 & $	0.790	600	0.571	JZJ 191
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$			0.000	404
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	trans-2-Butenal(1)	-n-nonane(2)	0.821	241
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.220	1104	0.893	218
$\begin{array}{llllllllllllllllllllllllllllllllllll$	0.280	1430	0.917	139
1567 $ram-2$ -Butenal(1)-cyclohexane(2) 0.440 1606 0.108 732 0.520 1601 0.138 824 0.586 1567 0.275 1222 0.590 1544 0.361 1367 0.607 1538 0.412 1424 0.695 1487 0.510 1442 0.736 1363 0.672 1230 0.928 457 0.697 1142 0.735 989 0.735 989 0.735 0.697 1142 0.735 0.928 457 0.697 1142 0.369 1231 0.230 230 0.490 1245 0.497 262 0.580 1005 0.639 236 0.863 486 0.905 64 trans-2-Butenal(1)-1-butanol(2) n -Decane(1)-benzaldehyde(2) 0.182 0.863 486	0.338	1503		
$\begin{array}{c cccc} 0.108 & 732 \\ 0.520 & 1601 & 0.138 & 824 \\ 0.586 & 1567 & 0.275 & 1222 \\ 0.590 & 1544 & 0.361 & 1367 \\ 0.607 & 1538 & 0.412 & 1424 \\ 0.736 & 1363 & 0.672 & 1230 \\ 0.695 & 1487 & 0.510 & 1442 \\ 0.736 & 1363 & 0.6697 & 1142 \\ 0.735 & 989 \\ \hline rans-2-Butenal(1)-1-nonene(2) & 0.870 & 564 \\ \hline rans-2-Butenal(1)-1-nonene(2) & 0.870 & 564 \\ \hline 0.267 & 1015 & 0.085 & 101 \\ 0.369 & 1231 & 0.230 & 230 \\ 0.408 & 1239 & 0.337 & 271 \\ 0.500 & 1245 & 0.497 & 262 \\ 0.509 & 1245 & 0.497 & 262 \\ 0.634 & 1161 & 0.659 & 236 \\ 0.863 & 486 & 0.766 & 169 \\ 0.905 & 64 \\ \hline rans-2-Butenal(1)-1-butanol(2) & n-Decane(1)-benzaldehyde(2) \\ 0.183 & 0.905 & 64 \\ \hline rans-2-Butenal(1)-1-butanol(2) & n-Decane(1)-benzaldehyde(2) \\ 0.183 & 0.200 & 1182 \\ 0.490 & 1476 & 0.510 & 1509 \\ 0.608 & 1471 & 0.685 & 1433 \\ 0.622 & 1470 & 0.428 & 1468 \\ 0.490 & 1476 & 0.510 & 1509 \\ 0.608 & 1471 & 0.685 & 1433 \\ 0.622 & 1464 & 0.710 & 1394 \\ 0.759 & 1167 & 0.854 & 883 \\ 0.862 & 683 \\ \hline \end{array}$	0.407	1567	trans-2-Butenal(1)-cyclohexane(2)
0.750 1.050 0.138 824 0.520 1601 0.275 1222 0.590 1544 0.361 1367 0.607 1538 0.412 1424 0.695 1487 0.510 1442 0.735 1363 0.672 1230 0.928 457 0.697 1142 0.735 989 0.735 989 trans-2-Butenal(1)-1-nonene(2) 0.870 564 0.267 1015 0.085 101 0.369 1231 0.288 101 0.580 1205 0.497 262 0.534 1161 0.659 236 0.863 486 0.905 64 trans-2-Butenal(1)-1-butanol(2) n-Decane(1)-benzaldehyde(2) 0.183 0.863 486 0.905 64 trans-2-Butenal(1)-1-butanol(2) n-Decane(1)-benzaldehyde(2) 0.182 0.183 948 0.204 915 0.209 0.290 1271 0.268 1115 0.373 1393 </td <td>0.440</td> <td>1606</td> <td>0.108</td> <td>732</td>	0.440	1606	0.108	732
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.520	1600	0.138	824
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.520	1567	0.275	1222
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.580	1507	0.361	1367
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.590	1544	0.412	1424
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.607	1538	0.412	1442
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.695	1487	0.510	1442
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.736	1363	0.072	1250
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.928	457	0.697	1142
$\begin{array}{c cccccc} 0.870 & 564 \\ \hline 0.155 & 667 & trans-2-Butenal(1)-1-nonyne(2) \\ 0.267 & 1015 & 0.085 & 101 \\ 0.369 & 1231 & 0.230 & 230 \\ 0.408 & 1239 & 0.337 & 271 \\ 0.509 & 1245 & 0.497 & 262 \\ 0.580 & 1205 & 0.630 & 242 \\ 0.634 & 1161 & 0.659 & 236 \\ 0.825 & 628 & 0.766 & 169 \\ 0.863 & 486 & 0.905 & 64 \\ \hline trans-2-Butenal(1)-1-butanol(2) & n-Decane(1)-benzaldehyde(2) \\ 0.183 & 948 & 0.204 & 915 \\ 0.290 & 1271 & 0.268 & 1115 \\ 0.373 & 1393 & 0.290 & 1182 \\ 0.429 & 1470 & 0.428 & 1468 \\ 0.490 & 1476 & 0.510 & 1509 \\ 0.608 & 1471 & 0.685 & 1433 \\ 0.622 & 1464 & 0.710 & 1394 \\ 0.759 & 1167 & 0.854 & 883 \\ 0.862 & 63 \\ \hline t - Deccne(1)-benzaldehyde(2) & 0.132 & 816 \\ 0.161 & 705 & 0.227 & 1270 \\ 0.267 & 1036 & 0.397 & 1623 \\ 0.439 & 1300 & 0.397 & 1623 \\ 0.439 & 1300 & 0.397 & 1623 \\ 0.459 & 1307 & 0.481 & 1682 \\ 0.523 & 1323 & 0.530 & 1667 \\ 0.558 & 1341 & 0.629 & 1546 \\ 0.523 & 1323 & 0.530 & 1667 \\ 0.558 & 1341 & 0.629 & 1546 \\ 0.714 & 1112 & 0.714 & 1374 \\ 0.808 & 910 & 0.860 & 794 \\ \hline \end{array}$			0.735	989
Indise-bluchal(1)=1-nonyne(2) 0.155 667 trans-2-Butenal(1)=1-nonyne(2) 0.267 1015 0.085 101 0.369 1231 0.230 230 0.408 1239 0.337 271 0.509 1245 0.497 262 0.580 1205 0.630 242 0.634 1161 0.659 236 0.825 628 0.766 169 0.863 486 0.905 64 trans-2-Butenal(1)=1-butanol(2) n -Decane(1)=benzaldehyde(2) 0.183 948 0.204 915 0.290 1271 0.268 1115 0.373 1393 0.290 1182 0.429 1470 0.428 1468 0.490 1476 0.510 1509 0.608 1471 0.685 1433 0.622 1464 0.710 1394 0.759 1167 0.854 883 0.862 683 615 0.439 1300 0.397 1623 0.4439 1300 0.397 1623 0.459 1307 0.481 1682 0.523 1323 0.530 1667 0.558 1341 0.629 1346 0.741 1112 0.714 1374 0.808 910 0.860 794	trans_2-Butenal(1)	-1-nonene(2)	0.870	564
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0 155	-1-nonene(2) 667		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.155	1015	trans-2-Butenal((1)-1-nonyne(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.267	1015	0.085	101
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.369	1231	0.230	230
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.408	1239	0.337	271
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.509	1245	0.497	262
$\begin{array}{cccccccc} 0.634 & 1161 & 0.659 & 2.36 \\ 0.825 & 6.28 & 0.766 & 169 \\ 0.863 & 486 & 0.905 & 64 \\ \hline trans-2-Butenal(1)-1-butanol(2) & n-Decane(1)-benzaldehyde(2) \\ 0.183 & 948 & 0.204 & 915 \\ 0.290 & 1271 & 0.268 & 1115 \\ 0.373 & 1393 & 0.290 & 1182 \\ 0.429 & 1470 & 0.428 & 1468 \\ 0.490 & 1476 & 0.510 & 1509 \\ 0.608 & 1471 & 0.685 & 1433 \\ 0.622 & 1464 & 0.710 & 1394 \\ 0.759 & 1167 & 0.854 & 883 \\ 0.862 & 683 & & & \\ \hline 1-Deccne(1)-benzaldehyde(2) & 0.132 & 816 \\ 0.161 & 705 & 0.227 & 1270 \\ 0.267 & 1036 & 0.358 & 1615 \\ 0.439 & 1300 & 0.397 & 1623 \\ 0.439 & 1300 & 0.397 & 1623 \\ 0.439 & 1307 & 0.481 & 1682 \\ 0.523 & 1323 & 0.530 & 1667 \\ 0.558 & 1341 & 0.629 & 1546 \\ 0.741 & 1112 & 0.714 & 1374 \\ 0.808 & 910 & 0.860 & 794 \\ \hline \end{array}$	0.580	1205	0.630	242
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.634	1161	0.659	236
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.825	628	0.055	160
trans-2-Butenal(1)-1-butanol(2) n -Decane(1)-benzaldehyde(2)0.1839480.2049150.29012710.26811150.37313930.29011820.42914700.42814680.49014760.51015090.60814710.68514330.62214640.71013940.75911670.8548830.862683	0.863	486	0.700	64
$\begin{array}{ccccccc} trans-2-Butenal(1)-1-butanol(2) & n-Decane(1)-benzaldehyde(2) \\ 0.183 & 948 & 0.204 & 915 \\ 0.290 & 1271 & 0.268 & 1115 \\ 0.373 & 1393 & 0.290 & 1182 \\ 0.429 & 1470 & 0.428 & 1468 \\ 0.490 & 1476 & 0.510 & 1509 \\ 0.608 & 1471 & 0.685 & 1433 \\ 0.622 & 1464 & 0.710 & 1394 \\ 0.759 & 1167 & 0.854 & 883 \\ 0.862 & 683 & & & & \\ \hline & & & & & & \\ \hline & & & & & &$			0.905	84
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	trans-2-Butenal(1)	-1-butanol(2)	n-Decane(1)-be	enzaldehyde(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.183	948	0 204	915
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.290	1271	0.204	1115
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.373	1393	0.200	1182
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.429	1470	0.290	1469
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.490	1476	0.428	1406
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.608	1470	0.510	1509
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.000	1464	0.685	1433
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.022	1167	0.710	1394
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.759	£92	0.854	883
1-Decene(1)-benzaldehyde(2)0.1328160.1617050.22712700.26710360.35816150.43913000.39716230.45913070.48116820.52313230.53016670.55813410.62915460.74111120.71413740.8089100.860794	0.862	085	1 Heneral(1) h	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1 Decenc(1) h	aldahuda(2)	1-riexanoi(1)-D	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1-Decene(1)-benz		0.132	810
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.101	/05	0.227	1270
0.43913000.39716230.45913070.48116820.52313230.53016670.55813410.62915460.74111120.71413740.8089100.860794	0.267	1036	0.358	1615
0.45913070.48116820.52313230.53016670.55813410.62915460.74111120.71413740.8089100.860794	0.439	1300	0.397	1623
0.523 1323 0.530 1667 0.558 1341 0.629 1546 0.741 1112 0.714 1374 0.808 910 0.860 794	0.459	1307	0.481	1682
0.55813410.62915460.74111120.71413740.8089100.860794	0.523	1323	0.530	1667
0.741 1112 0.714 1374 0.808 910 0.860 794	0.558	1341	0.629	1546
0.808 910 0.860 794	0.741	1112	0.714	1374
	0.808	910	0.860	794

TABLE 2

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System	<i>a</i> ₁	<i>a</i> ₂	<i>a</i> ₃	<i>a</i> ₄	a ₅	$S(H^{\rm E})$
Hexanal(1)- <i>n</i> -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

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

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

The interaction parameters of the groups $CH_2/CH_2=CH$, $CH_2/CH=C$, 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 CH₂, cyclic CH₂(cCH₂), 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 C₆H₅CHO 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.

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 $\delta(H^{\rm E})/$ 8.0 6.0 2.0 4.6 5.9 7.0 2.6 2.8 8.9 9.1 6.6 2.5 1.6 6.4 2.3 1.3 4.5 % J mol⁻¹ $S(H^{\rm E})/$ 96.5 23.7 27.4 31.5 42.5 5.9 38.7 29.4 6.5 86.4 21.8 6.6 50.6 38.7 96.3 22.7 19.3 86.9 91.5 UNIFAC group-interaction parameters based on the $H^{\rm E}$ data, and the correlation standard $S(H^{\rm E})$ and mean $\delta(H^{\rm E})$ errors 62.02 80.52 73.81 36.47 28.05 -149.85 354.44 420.67 -124.22 374.54 -13.22 168.74 377.45 185.62 113.89 213.14 13.52 52.31 630.71 Frebled Q_{s} values ^b aus -31.91-70.07217.89 -29.29 -35.15-60.48 -7.75 60.47 13.35 -15.61 484.09 -171.1091.42 11.93 -49.88 -117.94-31.3090.73 -109.07 $a_{\rm sl}$ $\delta(H^{\rm E})/$ 35.9 31.1 5.4 9.9 9.4 8.8 1.9 2.0 4.6 1.6 2.9 4.9 6.8 6.7 2.1 6.4 6.3 % $S(H^{\rm E})/$ J mol⁻¹ 418.2 274.5 25.4 20.9 22.7 15.8 5.6 82.7 33.1 33.6 67.9 86.5 34.3 44.4 7.2 41.6 318.7 Original UNIFAC Q_s values^a 299.07 98.13 129.50 103.51 71.94 49.27 192.40 784.07 443.84 357.34 299.39 712.06 597.71 426.29 388.60 586.48 -12.10 $a_{\rm ts}$ Ξ 4.57 50.14 570.67 -49.69 179.26304.54 -145.61 478.77 -30.26 23.89 95.90 20.16 14.87 405.91 -86.18 52.19 -5.85 $a_{\rm st}$ CH2 cCH2 CH2=CH CH₂ CH₂=CH OH ACH CH₂=C CH₂=C HC≣C 6CH₂ CH≡C CH₂ CH₂=C OH ACH cCH_2 HO C₆H₅CHO AC-CHO CH₂=CH Groups CHO ACH CH_2 Ś

81

^a Arniin siirfare-area narametere A [5] ^b Caa taut

Ξ

НО

Groups	Systems	Number of points	Reference
CH ₂ /CHO	n-Heptane + propanal n-Nonane + hexanal ($T = 298.15$ K)	6	[6] This work
¢CH ₂ /CHO	Cyclohexane + butanal, + pentanal $(T = 298.15 \text{ K})$ 1-Nonene + hexanal $(T = 298.15 \text{ K})$	18 13	[7] This work
CHEC/CHO	1-Nonyne + trans-2-butenal $(T = 298.15 \text{ K})$	~ ~	This work
0H/CH0 CH ₂ /cCH ₂	Cyclohexane + <i>trans-z-o</i> utenar $(T = 290.15 \text{ A})$ Cyclohexane + <i>n</i> -hexane, + <i>n</i> -decane; cycloheptane + <i>n</i> -heptane, + <i>n</i> -nonane $(T = 298.15 \text{ K})$	83	TION STIT
CH ₂ =CH/CH≡C CH ₂ =CH/6CH2	1-Octene + 1-octyne; 1-nonene + 1-nonyne ($T = 298.15$ K) 1-Hentene + cyclohexane	17 9	[1] [7]
	1-Octene + cyclohexane $(T = 298.15-313.15 \text{ K})$	18	Our data (unpubl.)
CH ₂ /C ₆ H ₅ CHO/AC-CHO	n-Heptane + benzaldehyde	× 0	(1997) [8] This most
CH ₃ =CH/C,H,CHO/AC-CHO	<i>n</i> -Decane + benzaldenyde ($T = 298.15$ K) 1-Decene + benzaldehyde ($T = 298.15$ K)	0 00	This work
OH/C,H,CHO/AC-CHO	1-Hexanol + benzaldehyde $(T = 298.15 \text{ K})$	6	This work
ACH/C,H,CHO/AC-CHO	Benzene + benzaldehyde $(T = 298.15 \text{ K})$	7	[6]
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 $(T = 293, 15-303, 15 \text{ K})$	154	[2]
ACH/CH ₂ =CH	Benzene + 1-hexene, +1-heptene, +1-octene ($T = 298.15$ K)	42	[6]

TABLE 4 $H^{\rm E}$ data used to calculate the group interaction parameters given in Table 3



Fig. 1. Experimental (\bigcirc) 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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