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Excess enthalpies of cyclohexane + (benzene or toluene) + cyclohexanone ternary mixtures at 298.15 K

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Abstract

Excess molar enthalpies, measured at 298.15 K in a flow microcalorimeter, are reported for the ternary mixtures (cyclohexane + benzene + cyclohexanone) and (cyclohexane + toluene + cyclohexanone), and also for the binary mixtures (cyclohexane + cyclohexanone) and (benzene + cyclohexanone). Smooth representations of the data are presented, and are used to calculate constant excess enthalpy contours for the ternary systems.

INTRODUCTION

In view of the industrial importance of information about the thermodynamic properties of multicomponent systems, we recently initiated an investigation of the excess molar enthalpies, H^E, of some ternary mixtures and reported results for mixtures of the type (*n*-alkane + tetrachloromethane + benzene) [1]. As an extension of that work, we have made similar measurements for (cyclohexane + benzene + cyclohexanone) and (cyclohexane + toluene + cyclohexanone). These systems are of interest since, in contrast to those studied previously, the sign of H^E may change as the ternary composition is varied. In addition, the excess enthalpies of (cyclohexane + benzene + cyclohexanone) are of practical use in the recovery of cyclohexane and benzene during the manufacture of cyclohexanone.

EXPERIMENTAL

Materials

High quality cyclohexanone (from Merck) was dried over anhydrous sodium sulfate, and fractionated in a 1 m glass column filled with McMahon

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packing. Cyclohexane, benzene and toluene (from Merck) were purified and dried by standard procedures [2]. The purities of the samples were checked by density and refractive index measurements using an Anton Paar densimeter (Model DMA 55) and a five-digit precision refractometer. The observed values of the density ρ (kg m^{-3}) and the refractive index n_D, both at 293.15 K, were respectively 778.60 and 1.42645 for cyclohexane, 877.75 and 1.50115 for benzene, 866.92 and 1.49645 for toluene, and 947.05 and 1.45075 for cyclohexanone. These results are in reasonable agreement with the literature values [2].

In the present work, the compositions of the mixtures are stated in terms of the mole fraction x_i of the components. The subscripts 1, 2, and 3 are used to designate cyclohexane, benzene (or toluene) and cyclohexanone, respectively.

Equipment and technique

Excess molar enthalpies were measured in an LKB flow microcalorimeter (Model 2107-121) at 298.15 ± 0.05 K. The auxiliary equipment and operating procedure have been described previously [1,3,4]. The uncertainty in the determination of H^E is estimated to be less than 1%.

In studying the ternary mixtures $(x_1C_6H_{12} + x_2C_6H_6 + x_3C_6H_{10}O)$ and $(x_1C_6H_{12} + x_2C_7H_8 + x_3C_6H_{10}O)$, the excess molar enthalpy H^E_{1-23} was measured for several pseudobinary systems, in which component 1 (cyclohexane) was added to a binary mixture of components 2 and 3 having a fixed composition. These binaries were prepared by weighing, and errors in the ratio x_2/x_3 were negligible. The excess molar enthalpy H^E_{123} was then obtained from the relation

$$H^E_{123} = H^E_{1-23} + (1 - x_1) H^E_{23} \quad (1)$$

where H^E_{23} is the excess molar enthalpy of the particular binary mixture.

RESULTS AND DISCUSSION

Binary mixtures

Although the excess enthalpies of the five binary mixtures derived from the present ternary systems have been studied previously, we redetermined H^E for all of them. In several instances our results agree to within 3% with those of earlier investigations [5–7] and are not reported here. However, there are significant differences between the results obtained in previous investigations of $(x_1C_6H_{12} + x_3C_6H_{10}O)$ [8–10] and of $(x_2C_6H_6 + x_3C_6H_{10}O)$ [7,11]. Our new results for these systems are summarized in Table 1. Representations of the data by the Redlich–Kister form

$$H^E_{ij} = x_i x_j \sum_{k=1}^{n} h_k (x_j - x_i)^{k-1} \quad (j > i) \quad (2)$$

TABLE 1

Experimental results for excess molar enthalpies, H_{ij}^E, of some binary mixtures at 298.15 K

x_3	H_{ij}^E (J mol^{-1})	x_3	H_{ij}^E (J mol^{-1})	x_3	H_{ij}^E (J mol^{-1})	x_3	H_{ij}^E (J mol^{-1})
$x_1C_6H_{12} + x_3C_6H_{10}O$ [a]							
0.0685	350.2	0.2623	858.1	0.4404	946.7	0.7096	718.9
0.1119	523.8	0.3212	911.5	0.4901	935.4	0.7963	542.7
0.1637	678.2	0.3587	930.7	0.5645	897.9	0.8304	463.7
0.2227	802.2	0.4222	945.4	0.6320	833.1	0.9319	197.6
$x_2C_6H_6 + x_3C_6H_{10}O$ [b]							
0.0920	−110.7	0.3879	−285.3	0.5997	−272.5	0.7677	−196.7
0.1535	−170.6	0.4405	−292.5	0.6333	−261.0	0.8095	−169.8
0.2072	−206.7	0.5179	−290.5	0.6887	−240.5	0.8668	−123.3
0.2537	−232.8	0.5635	−282.6	0.7221	−223.4	0.9252	−70.3
0.3032	−260.8						

[a] H_{13}^E (J mol^{-1}) $= x_1x_3[3732.9 - 723.1(x_3 - x_1) + 983.7(x_3 - x_1)^2 - 1611.8(x_3 - x_1)^3 - 288.5(x_3 - x_1)^4 + 980.7(x_3 - x_1)^5]$; $s = 0.8$.

[b] H_{23}^E (J mol^{-1}) $= x_2x_3[-1166.7 + 147.9(x_3 - x_2) - 37.0(x_3 - x_2)^2]$; $s = 1.9$.

and the standard deviations, s, of these representations are given in the footnotes to the table. Deviations of the experimental H_{ij}^E from these representations are plotted in Fig. 1. Also shown, for comparison, are the results of the earlier investigations [7–11].

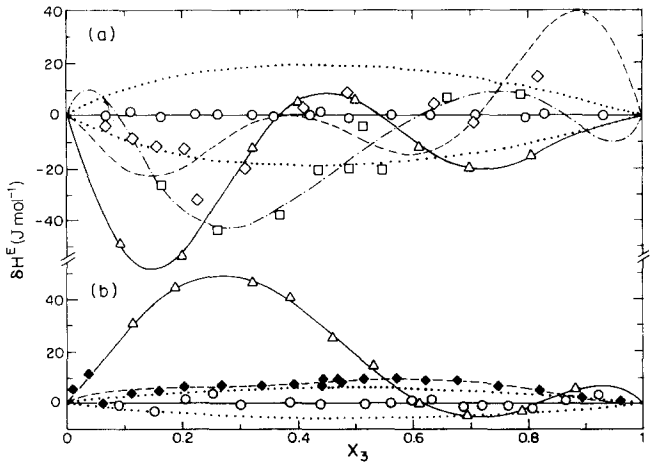

Fig. 1. Deviations $\delta H^E = H^E(\text{expt.}) - H^E(\text{eqn. (2)})$ of the excess molar enthalpy at 298.15 K for two binary mixtures. (a) Experimental results for $(x_1C_6H_{12} + x_3C_6H_{10}O)$: ○, present results; □, –·–·, Polo et al. [8]; ◇, ---, Herrero et al. [9]; △, ———, Marongiu [10]. (b) Experimental results for $(x_2C_6H_6 + x_3C_6H_{10}O)$: ○, present results; ◆, ---, Tamura et al. [7]; △, ———, Marongiu [11]. ···, ±2% deviations from eqn. (2).

For the cyclohexane system, there is agreement between our results and those of the three prior investigations [8–10] within ±2% over most of the mole fraction range. The data of Marongiu [10] show much larger deviations for $x_3 < 0.3$. For the benzene system, the results of Tamura et al. [7] are systematically higher than ours by about 3%. The data of Marongiu [11] for

TABLE 2

Experimental excess molar enthalpies, H^E_{1-23}, at 298.15 K for the addition of cyclohexane to a binary mixture of benzene and cyclohexanone to form ($x_1C_6H_{12} + x_2C_6H_6 + x_3C_6H_{10}O$), and values of H^E_{123} calculated from eqn. (1) using H^E_{23} from Table 1

x_1	H^E_{1-23} (J mol^{-1})	H^E_{123} (J mol^{-1})	x_1	H^E_{1-23} (J mol^{-1})	H^E_{123} (J mol^{-1})	x_1	H^E_{1-23} (J mol^{-1})	H^E_{123} (J mol^{-1})
$x_2/x_3 = 0.3333$, H^E_{23} (J mol^{-1}) = −206.6								
0.0185	63.5	−139.3	0.3120	830.3	688.1	0.6559	973.5	902.4
0.0341	118.6	−81.0	0.3463	880.5	745.4	0.6746	959.9	892.7
0.0769	254.9	64.1	0.3949	935.2	810.2	0.7244	906.1	849.1
0.0904	297.6	109.7	0.4294	964.1	846.2	0.7546	855.4	804.7
0.1138	371.4	188.2	0.4674	996.1	886.1	0.7808	798.2	752.9
0.1628	503.4	330.4	0.5044	1009.3	906.9	0.8077	742.2	702.5
0.1971	593.0	427.1	0.5185	1016.2	916.7	0.8259	690.5	654.6
0.2144	632.0	469.7	0.5350	1015.8	919.7	0.8463	642.1	610.3
0.2466	707.1	551.5	0.5544	1012.4	920.3	0.8991	468.7	447.8
0.2687	753.7	602.6	0.5822	1007.3	921.0	0.9250	365.1	349.6
0.2913	794.8	648.4	0.6332	985.6	909.8	0.9551	224.8	215.6
$x_2/x_3 = 1.0004$, H^E_{23} (J mol^{-1}) = −291.7								
0.0225	92.7	−192.4	0.3376	884.3	691.1	0.6456	963.0	859.6
0.0462	172.6	−105.6	0.3638	920.6	735.0	0.6709	943.3	847.3
0.0882	308.5	42.5	0.3878	947.5	769.0	0.6988	910.5	822.7
0.1064	369.2	108.6	0.4132	975.0	803.8	0.7466	831.6	757.7
0.1350	460.4	208.1	0.4442	992.5	830.4	0.7985	722.1	663.3
0.1845	597.3	359.4	0.4722	1007.6	853.6	0.8174	674.0	620.7
0.2080	648.8	417.8	0.4907	1008.8	860.2	0.8339	629.6	581.2
0.2397	707.9	486.2	0.5172	1016.4	875.5	0.8632	542.6	502.7
0.2607	761.0	545.3	0.5414	1013.1	879.4	0.8915	452.7	421.1
0.2846	797.5	588.8	0.5717	1008.0	883.1	0.9160	369.0	344.5
0.3018	840.5	636.9	0.5954	997.6	879.6	0.9462	249.2	233.5
$x_2/x_3 = 3.0032$, H^E_{23} (J mol^{-1}) = −234.2								
0.0212	94.1	−135.2	0.3772	889.1	743.2	0.6342	898.6	812.9
0.0402	160.1	−64.8	0.4082	911.9	773.3	0.6692	873.6	796.1
0.1885	580.2	390.1	0.4270	928.2	794.0	0.6875	849.2	776.0
0.2089	624.5	439.2	0.4530	944.0	815.9	0.7172	806.5	740.3
0.2364	672.9	494.1	0.4793	951.1	829.2	0.7381	768.3	707.0
0.2618	719.8	546.8	0.5021	949.8	833.1	0.7624	724.3	668.7
0.2849	760.0	592.5	0.5376	945.0	836.7	0.8285	575.5	535.3
0.3082	799.7	637.7	0.5566	941.3	837.5	0.8600	487.5	454.7
0.3336	833.5	677.4	0.5850	926.8	829.6	0.8877	405.2	378.9
0.3567	861.1	710.4	0.6080	918.8	827.0	0.9641	150.1	141.7

TABLE 3

Experimental excess molar enthalpies, H^E_{1-23}, at 298.15 K for the addition of cyclohexane to a binary mixture of toluene and cyclohexanone to form ($x_1C_6H_{12} + x_2C_7H_8 + x_3C_6H_{10}O$), and values of H^E_{123} calculated from eqn. (1) using H^E_{23} from ref. 7

x_1	H^E_{1-23} (J mol^{-1})	H^E_{123} (J mol^{-1})	x_1	H^E_{1-23} (J mol^{-1})	H^E_{123} (J mol^{-1})	x_1	H^E_{1-23} (J mol^{-1})	H^E_{123} (J mol^{-1})
$x_2/x_3 = 0.3326$, H^E_{23} (J mol^{-1}) = −112.4								
0.0640	180.6	75.4	0.4397	903.1	840.1	0.7394	813.9	784.6
0.1180	327.2	228.1	0.4869	937.5	879.8	0.7933	731.4	708.2
0.1714	476.7	383.5	0.5412	952.5	901.0	0.8237	657.3	637.5
0.2316	611.8	525.4	0.5939	937.1	891.5	0.8845	485.0	472.0
0.2823	706.1	625.4	0.6385	913.4	872.7	0.9120	386.6	376.7
0.3388	801.8	727.5	0.6918	874.3	839.7	0.9575	212.1	207.3
0.3844	850.4	781.2						
$x_2/x_3 = 0.9992$, H^E_{23} (J mol^{-1}) = −164.6								
0.0747	218.4	66.1	0.3469	781.2	673.8	0.6081	886.0	821.5
0.1276	361.0	217.4	0.4040	848.5	750.4	0.6675	842.4	787.7
0.1851	510.3	376.2	0.4573	883.6	794.3	0.7047	800.7	752.1
0.2421	635.0	510.3	0.5064	911.1	829.9	0.7542	735.0	694.6
0.2947	718.4	602.3	0.5608	907.4	835.2	0.7996	660.3	627.4
$x_2/x_3 = 2.9984$, H^E_{23} (J mol^{-1}) = −127.7								
0.0731	204.3	85.9	0.4106	764.3	689.0	0.7068	700.9	663.5
0.1304	346.4	235.4	0.4640	792.6	724.1	0.7569	631.7	600.6
0.1869	462.8	358.9	0.5161	807.3	745.5	0.8005	558.8	533.4
0.2414	564.9	468.0	0.5651	804.4	748.9	0.8933	345.8	332.2
0.2946	646.4	556.3	0.6183	781.8	733.0	0.9350	223.6	215.2
0.3449	703.6	619.9	0.6603	741.9	698.5			

this system show much larger deviations, particularly for $x_3 > 0.5$. In the following analyses of the ternary data, we have adopted the smooth representations of our results for both of the binary systems in Table 1.

Ternary mixtures

The experimental results for H^E_{1-23} and the corresponding H^E_{123} for the two ternary systems are listed in Tables 2 and 3. For both systems, at a fixed ratio of x_2/x_3, the maximum values of H^E_{1-23} and H^E_{123} occur near $x_1 = 0.5$, and at a constant value of x_1, the enthalpies increase as x_2/x_3 decreases. For comparable values of x_2/x_3, the maxima for the benzene system are greater than those for the toluene system.

As in our previous work [1], H^E_{123} was represented as a sum of binary terms with an added ternary contribution:

$$H^E_{123} = H^E_{12} + H^E_{13} + H^E_{23} + x_1x_2x_3\left(c_0 + c_1x_1 + c_2x_2 + c_3x_1^2 + c_4x_1x_2 + c_5x_2^2\right) \quad (3)$$

TABLE 4

Coefficients, c_i, in the representations of the excess molar enthalpies, H^E_{123} (J mol^{-1}), for system I ($x_1C_6H_{12} + x_2C_6H_6 + x_3C_6H_{10}O$) and system II ($x_1C_6H_{12} + x_2C_7H_8 + x_3C_6H_{10}O$) calculated using eqn. (3); standard deviations, s, of the representations, and references for the representations of the excess molar enthalpies, H^E_{ij}, for the binary mixtures calculated using eqn. (2)

System	c_0	c_1	c_2	c_3	c_4	c_5	s	Binary refs.		
								H^E_{12}	H^E_{13}	H^E_{23}
I	−155.4	3172.5	4445.2	760.7	−7534.9	−3994.0	5.5	5	pw [a]	pw [a]
II	−3239.5	13468.0	8554.3	−11311.1	−10337.3	−5066.1	5.7	6	pw [a]	7

[a] Present work; see Table 1.

The values of H^E_{ij} were calculated from eqn. (2) with coefficients from the literature [5–7] and from the present work. Values of the parameters, c_i, were determined by least-squares analyses in which eqn. (3) was fitted to the values of H^E_{123} for each mixture. The results of these calculations are given in Table 4, where the standard deviations, s, of the representations are also listed.

Some constant H^E_{123} contours, calculated from eqn. (3) for ($x_1C_6H_{12} + x_2C_7H_8 + x_3C_6H_{10}O$), are shown in Fig. 2. The plot for the benzene system (not shown here) is similar, but the region of negative values is larger.

If the ternary term in eqn. (3) is omitted, estimates of H^E_{123} can be obtained solely from the excess molar enthalpies of the constituent binaries,

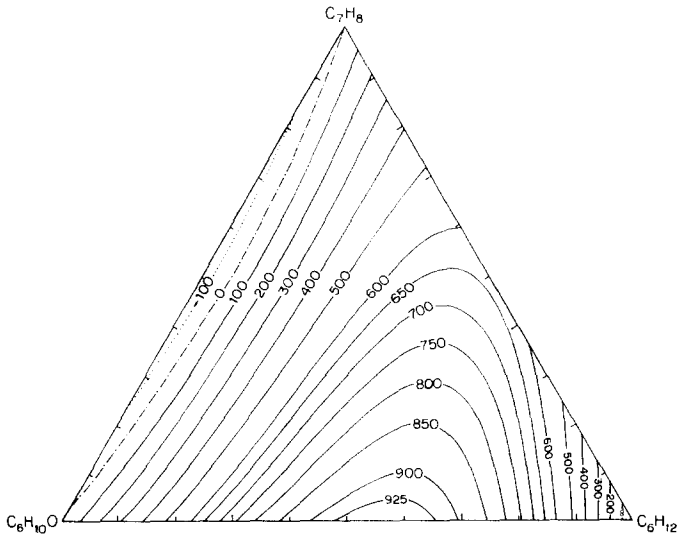

Fig. 2. Contours for constant values of the excess molar enthalpy, H^E_{123} (J mol^{-1}), of ($x_1C_6H_{12} + x_2C_7H_8 + x_3C_6H_{10}O$) at 298.15 K, calculated from the representation of the experimental results using eqn. (3) with coefficients from Table 4.

as represented by their Redlich–Kister forms. The root-mean square deviations between the predicted and experimental values are 25.2 J mol^{-1} and 22.2 J mol^{-1} for the benzene and toluene systems, respectively.

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