Excess Enthalpy Data for Seven Binary Systems at Temperatures between 50 and 140 ˚C

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Experimental excess enthalpies for the following seven systems have been determined with the help of isothermal flow calorimetry: benzene + cyclohexane at 50, 90, and 140 °C, heptane + diethyl carbonate at 100 and 140 °C, hexane + dimethyl carbonate at 90 °C, dimethyl carbonate + heptane at 90 and 140 °C, perfluoro-2-methylpentane + benzene at 50, 90, and 140 °C, 1,2-epoxybutane + methanol at 90 and 140 °C, and 1,2-expoxybutane + 2-ethyl-1-hexanol at 90 and 140 °C. The experimental H^E values have been used for the revision and extension of the group contribution method Modified UNIFAC (Dortmund). The predicted results are in good agreement with the experimental data.

Introduction

Excess enthalpies (H^E) measured at different temperatures are most valuable for the revision and extension of group contribution methods such as Modified UNIFAC (Dortmund) or for fitting temperature-dependent G^E model parameters. On one hand, H^E data sets at high temperatures (up to 140 °C) are used as supporting data at high temperatures for fitting temperature-dependent group interaction parameters.[1] On the other hand, these data (measured at various temperatures) deliver the correct temperature dependence of the activity coefficient, which is described quantitatively by the Gibbs−Helmholtz equation:[2]

$$\left(\frac{\partial \ln \gamma_i}{\partial (1/T)}\right)_{P,x} = \frac{H_i^E}{R} \qquad (1)$$

Following this equation, a direct relationship between the temperature dependence of the activity coefficient (γ_i) and the partial molar excess enthalpy (H_i^E) is given. Unfortunately, most of the published H^E data were determined around ambient temperature.[1,3] To overcome the lack of data at higher temperatures, systematic measurements are carried out in our laboratory using isothermal flow calorimetry, which allows a fast and reliable determination of this property.[3,4]

Experimental Section

The 15 experimental H^E data sets were determined with the help of a commercially available isothermal flow calorimeter (Hart Scientific, model 7501), which allows us to detect endothermic and exothermic effects. The temperatures are measured correctly within ±0.005 K; the uncertainty in H^E is estimated to be less than ±1%.[3] A back-pressure regulator ensures keeping the pressure at a level at which evaporation effects can be neglected.

The chemicals were received from different commercial suppliers or kindly placed at our disposal by the former Hoechst AG (Table 1), carefully degassed, and distilled

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Table 1. CAS Numbers and Suppliers of the Applied Chemicals in Alphabetical Order[a]

compound	supplier	CAS number
benzene	Scharlau	[71-43-2]
benzonitrile	Acros	[100-47-0]
2-butanol	Aldrich	[78-92-2]
cyclohexane	Scharlau	[110-82-7]
diethyl carbonate	Aldrich	[616-38-6]
dimethyl carbonate	Acros	[105-58-8]
1,2-epoxybutane	Aldrich	[106-88-7]
2-ethyl-1-hexanol	Fluka	[104-76-7]
heptane	Merck	[142-82-5]
hexane	Fluka	[110-54-3]
methanol	Scharlau	[67-56-1]
perfluoro-2-methylpentane	Hoechst AG	[355-04-4]

[a] The purities were found to be at least 99.9% by gas chromatography.

using a 1.5 m Vigreux column.[5] The resulting purities were determined by gas chromatography, and the water content was determined by Karl Fischer titration. The purities of the applied chemicals were found to be at least 99.9%.

The systems presented in this paper were chosen to extend the H^E database at higher temperatures, which is required for the systematic further development of Modified UNIFAC (Dortmund). In particular, it was the idea to reduce the lack of data for the main group *carbonates* ($CH_xOCOOCH_x$), *perfluorinated compounds* (CF_x), and *epoxides*.

Diethyl carbonate and dimethyl carbonate are predominantly used as intermediates for the production of urethanes and ureas or applied as solvents for organic compounds as well as inorganic salts.[6]

Binary systems with perfluorinated compounds often show a strong temperature-dependent miscibility gap. This special behavior can be applied for example for the recovery of the catalysts used for the reaction in the fluorous phase.[7]

Epoxides are among the most important basic chemicals of all. Because of the wide range of applicability of all mentioned compounds, there is a great industrial interest and a strong demand for reliable predictions of the corresponding mixture behavior.

Table 2. Experimental H^E Data for the System Benzene (1) + Cyclohexane (2)

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
50 °C and 9.63 bar					
0.0604	157.3	0.4490	710.6	0.7857	505.7
0.1196	295.0	0.5000	720.7	0.8302	429.0
0.1774	413.3	0.5500	720.5	0.8738	337.4
0.2340	508.9	0.5990	701.9	0.9167	234.4
0.2895	585.6	0.6471	672.6	0.9587	122.7
0.3438	642.1	0.6942	628.6		
0.3969	684.2	0.7404	575.2		
90 °C and 17.54 bar					
0.0304	72.8	0.3969	599.6	0.7404	503.5
0.0604	139.5	0.4490	623.0	0.7857	443.4
0.1196	259.7	0.5000	631.4	0.8302	375.3
0.1774	362.0	0.5500	633.4	0.8738	295.5
0.2341	445.5	0.5990	616.0	0.9167	205.4
0.2895	511.6	0.6471	589.9	0.9587	108.4
0.3438	563.0	0.6942	551.8	0.9795	56.0
140 °C and 14.10 bar					
0.0604	111.8	0.4490	527.1	0.8521	288.2
0.1196	217.0	0.5500	538.3	0.9167	174.4
0.2059	342.2	0.6470	504.4	0.9587	92.6
0.2895	431.0	0.7174	449.1		
0.3704	493.0	0.7857	378.7		

Table 3. Experimental H^E Data for the System Heptane (1) + Diethyl Carbonate (2)

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
100 °C and 14.10 bar					
0.0209	96.5	0.3091	1054.6	0.6598	1181.4
0.0419	190.6	0.3565	1136.7	0.7137	1087.7
0.0845	379.5	0.4047	1199.7	0.7687	964.8
0.1279	548.0	0.4539	1248.7	0.8248	798.1
0.1720	702.5	0.5039	1265.7	0.8821	584.7
0.2169	835.4	0.5549	1262.1	0.9404	316.8
0.2626	956.1	0.6068	1232.4	0.9701	159.9
140 °C and 14.79 bar					
0.0207	111.0	0.3070	1052.8	0.6575	1145.0
0.0415	201.4	0.3542	1131.4	0.7117	1052.8
0.0838	379.1	0.4023	1192.8	0.7670	930.6
0.1268	545.7	0.4514	1236.1	0.8234	708.2
0.1706	690.7	0.5014	1245.0	0.8810	550.1
0.2152	836.3	0.5524	1240.0	0.9399	291.7
0.2607	950.1	0.6044	1203.4	0.9698	137.9

Table 4. Experimental H^E Data for the System Hexane (1) + Dimethyl Carbonate (2)

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
90 °C and 16.17 bar					
0.0162	127.0	0.2570	1452.6	0.5998	1826.3
0.0327	264.2	0.2998	1587.3	0.6583	1728.8
0.0666	489.5	0.3445	1700.8	0.7198	1576.4
0.1018	715.1	0.3911	1793.9	0.7845	1345.4
0.1384	927.7	0.4398	1842.0	0.8525	1022.2
0.1763	1119.0	0.4907	1873.8	0.9243	585.5
0.2158	1295.0	0.5440	1869.3	0.9616	310.2

Table 5. Experimental H^E Data for the System Dimethyl Carbonate (1) + n-Heptane (2)

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
90 °C and 15.48 bar					
0.0428	340.5	0.5376	1961.5	0.8395	1137.4
0.0841	637.1	0.5879	1920.5	0.8746	943.1
0.1623	1113.8	0.6355	1857.3	0.9081	730.2
0.2353	1450.1	0.6806	1754.3	0.9401	499.6
0.3036	1687.4	0.7234	1630.7	0.9707	256.7
0.3676	1842.5	0.7641	1485.7	0.9855	127.8
0.4843	1969.1	0.8027	1358.6		
140 °C and 16.86 bar					
0.0428	288.5	0.4844	1978.3	0.8028	1326.9
0.0841	574.8	0.5377	1975.6	0.8396	1139.8
0.1624	1074.0	0.5880	1930.7	0.8747	943.5
0.2354	1423.6	0.6356	1869.7	0.9081	729.4
0.3037	1672.3	0.6807	1769.7	0.9401	500.4
0.3677	1838.4	0.7235	1645.6	0.9707	265.0
0.4278	1936.8	0.7641	1494.6		

Table 6. Experimental H^E Data for the System Perfluoro-2-methylpentane (1) + Benzene (2)

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
50 °C and 12.04 bar					
0.0539	617.8	0.5449	1123.7	0.8384	575.4
0.1048	1124.1	0.5971	1020.8	0.8696	515.2
0.1981	1775.4	0.6453	929.8	0.8989	458.9
0.2818	1617.9	0.6898	854.7	0.9265	407.9
0.3573	1475.6	0.7310	775.7	0.9524	358.4
0.4257	1347.3	0.7693	703.2	0.9769	312.4
0.4879	1230.4	0.8050	637.3	0.9886	219.9
90 °C and 17.20 bar					
0.0271	341.8	0.2797	2505.7	0.9258	1043.3
0.0534	609.5	0.3549	2854.7	0.9519	797.0
0.1038	1132.0	0.4232	2935.3	0.9766	396.5
0.1514	1565.3	0.8685	1259.8	0.9885	186.5
0.1965	1946.8	0.8980	1149.7		
140 °C and 16.86 bar					
0.0534	677.7	0.3549	3074.0	0.8370	2103.7
0.1038	1229.7	0.4854	3394.4	0.8980	1512.1
0.1514	1691.0	0.5947	3319.8	0.9519	806.0
0.1965	2090.0	0.6876	3034.6	0.9766	401.4
0.2797	2691.7	0.7675	2606.6	0.9885	185.1

**Table 7. Experimental H^E Data for the System 1,2-Epoxybutane (1) + Methanol (2)**

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
90 °C and 16.31 bar					
0.0118	35.9	0.2012	635.7	0.5839	1153.0
0.0240	78.6	0.2377	752.0	0.6517	1125.1
0.0494	162.9	0.2767	842.2	0.7260	1031.3
0.0762	249.6	0.3187	972.3	0.8080	842.3
0.1047	341.2	0.4123	1087.3	0.8988	522.0
0.1349	433.5	0.4648	1125.5	0.9480	276.9
0.1670	523.6	0.5218	1156.0		
140 °C and 17.55 bar					
0.0119	41.6	0.2012	781.9	0.5219	1568.8
0.0240	87.4	0.2377	915.4	0.5839	1576.6
0.0494	186.3	0.2768	1065.7	0.6517	1504.7
0.0763	287.8	0.3187	1186.1	0.7261	1337.2
0.1047	406.4	0.3638	1325.3	0.8081	1062.3
0.1349	529.8	0.4123	1412.4	0.8989	627.2
0.1670	656.1	0.4649	1486.0	0.9480	326.9

Results

In Tables 2−8 the experimental excess enthalpy data sets for the seven investigated systems are given. Besides the temperatures of the measurements, the pressures regulated by the back-pressure regulator are given. The corresponding diagrams are presented in Figures 1−7. The symbols represent the experimental data; the lines (dashed and solid) are the results of predictions carried out with Modified UNIFAC (Dortmund).[8−12]

All diagrams show that Modified UNIFAC (Dortmund) is able to predict thermophysical mixture data at temperatures up to 140 °C. This confirms investigations which have been published previously.[13] Especially the accurate description of the temperature dependence of the H^E data sets has to be pointed out. For the system perfluoro-2-methylpentane + benzene (Figure 5) also the miscibility gap at lower temperatures is described accurately.
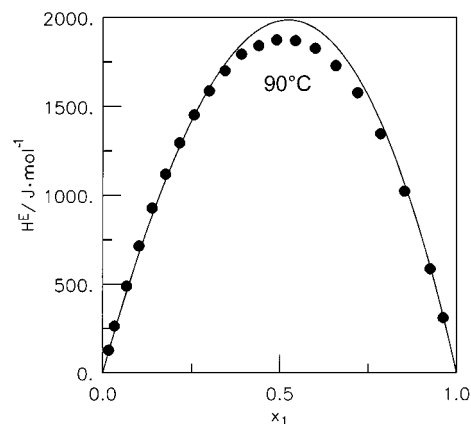
All systems were investigated within the research work of the UNIFAC consortium to extend the necessary database at higher temperatures, where H^E data are used as supporting data. SLE data cover the range at lower (<0 °C) temperatures.[1,14] Together with vapor−liquid equilibria

Table 8. Experimental H^E Data for the System 1,2-Epoxybutane (1) + 2-Ethyl-1-hexanol (2)

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
		90 °C and 13.42 bar			
0.0442	150.9	0.4927	1173.3	0.8080	814.3
0.0867	298.9	0.5460	1192.6	0.8440	694.9
0.1670	556.9	0.5961	1176.4	0.8783	572.7
0.2415	766.1	0.6433	1146.6	0.9109	437.5
0.3108	932.1	0.6880	1094.7	0.9420	299.0
0.3755	1048.1	0.7301	1011.4	0.9716	153.6
0.4360	1128.3	0.7701	920.2	0.9860	74.5
		140 °C and 17.55 bar			
0.0442	74.6	0.4928	540.0	0.8081	352.8
0.0867	144.1	0.5461	543.2	0.8441	301.7
0.1670	267.2	0.5962	529.6	0.8783	248.1
0.2415	368.0	0.6434	510.8	0.9109	189.2
0.3109	438.8	0.6880	478.8	0.9420	128.2
0.3756	489.8	0.7302	442.0	0.9717	66.8
0.4361	530.5	0.7702	403.4	0.9860	31.7
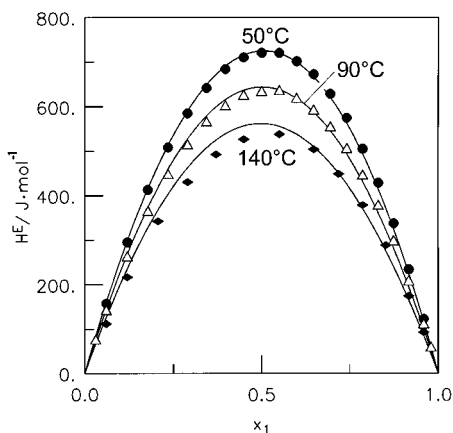
Figure 1. Excess enthalpies for the system benzene (1) + cyclohexane (2): ●, △, ◆, experimental data; —, Modified UNIFAC (Dortmund).
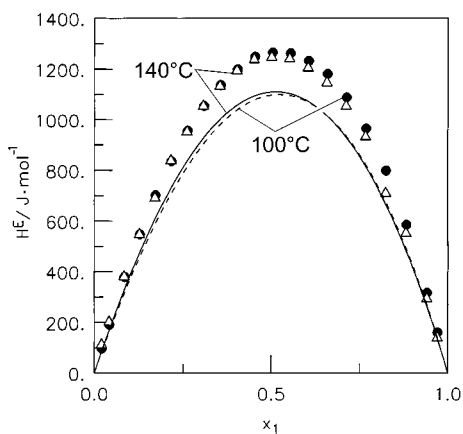
Figure 2. Excess enthalpies for the system heptane (1) + diethyl carbonate (2): ●, △, experimental data; —, - - -, Modified UNIFAC (Dortmund).

Figure 3. Excess enthalpy for the system hexane (1) + dimethyl carbonate (2): ●, experimental data; —, Modified UNIFAC (Dortmund).
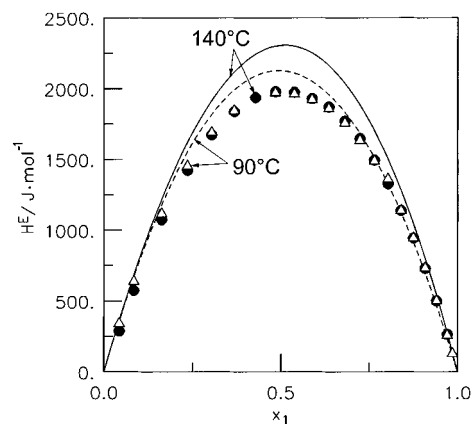
Figure 4. Excess enthalpies for the system dimethyl carbonate (1) + heptane (2): ●, △, experimental data; —, - - -, Modified UNIFAC (Dortmund).
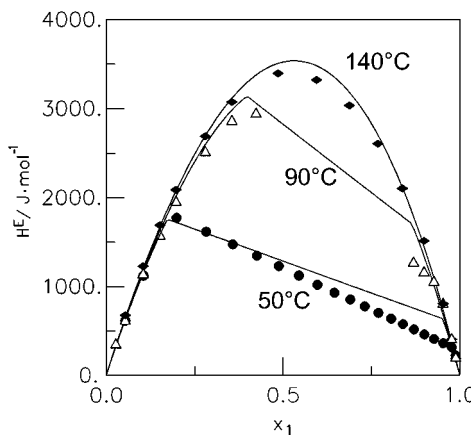
Figure 5. Excess enthalpies for the system perfluoro-2-methyl-pentane (1) + benzene (2): ●, △, ◆, experimental data; —, Modified UNIFAC (Dortmund).

and activity at infinite dilution, a sufficient database is available to fit reliable temperature-dependent parameters for Modified UNIFAC (Dortmund) covering a large temperature range from (−80 to +140) °C. This ensures the reliable usage of this group contribution method for a large number of applications of industrial interest. In particular, it can be applied for different aspects during the synthesis and optimization of thermal separation processes.[11] In this reference also the new or revised parameters for epoxides and perfluorinated compounds are given. The parameters for carbonates will be published elsewhere.[12]

Summary

The experimental and predicted excess enthalpies of seven systems (in total 15 data sets between (50 and 140) °C) are given.

The agreement between experimental and predicted data shows that Modified UNIFAC (Dortmund) allows a reliable description of the temperature dependence of the activity coefficients. The continuously growing number of experimental data sets (not only H^E data but also vapor−liquid equilibria, solid−liquid equilibria, activity coefficients at
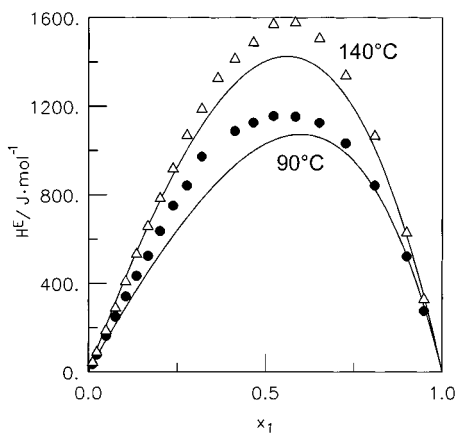
Figure 6. Excess enthalpies for the system 1,2-epoxybutane (1) + methanol (2): ●, △, experimental data; —, Modified UNIFAC (Dortmund).
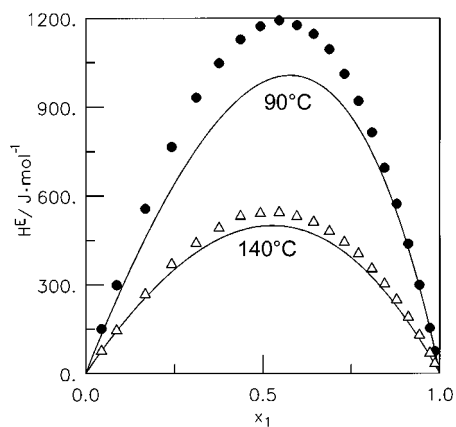

Figure 7. Excess enthalpies for the system 1,2-epoxybutane (1) + 2-ethyl-1-hexanol (2): ●, △, experimental data; —, Modified UNIFAC (Dortmund).

infinite dilution, ...) allows a systematic revision and extension of Modified UNIFAC (Dortmund). The present status of the research work on this group contribution method is available via http://www.uni-oldenburg.de/tchemie/consortium/.

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