

# Vapor–Liquid Equilibria at 413.65 K and Excess Enthalpies at 323.15, 363.15, and 413.15 K for Mixtures of Benzene, Toluene, Phenol, and Benzaldehyde

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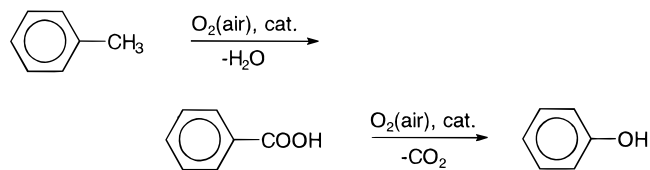
Isothermal  $P, x$  data at 413.65 K, excess enthalpies at 323.15, 363.15, and 413.15 K, and azeotropic data are presented for binary systems containing benzaldehyde, benzene, toluene, and phenol. Reliable information about the real behavior of systems including these components is very important for various chemical processes, e.g., for the production of phenol by toluene oxidation. Furthermore, these data will be used for the revision, extension, and further development of the group contribution method modified UNIFAC (Dortmund). The vapor–liquid equilibrium (VLE) data of four systems were measured using a static apparatus. In the case of the system benzaldehyde + phenol, azeotropic data were determined by distillation. For all systems, the corresponding experimental excess enthalpy ( $H^E$ ) data were determined with the help of an isothermal flow calorimeter. For the simultaneous description of VLE and  $H^E$  data, the NRTL model was used.

## Introduction

At present the application of group contribution methods such as UNIFAC (Fredenslund et al., 1977; Hansen et al., 1991), modified UNIFAC (Dortmund) (Weidlich and Gmehling, 1987; Gmehling et al., 1993), modified UNIFAC (Lyngby) (Larsen et al., 1987), and ASOG (Tochigi et al., 1990) for the prediction of phase equilibria and excess enthalpies in systems containing benzaldehyde can lead to considerable deviations because the interaction parameters for some functional groups such as the aldehyde (CHO) group are used for both aliphatic and aromatic compounds. Since these interaction parameters have predominantly been fitted to data of aliphatic compounds, the prediction of the behavior of aromatic systems can lead to unsatisfactory results. The main reason for this situation is the lack of reliable experimental VLE and  $H^E$  data for aromatic systems (Gmehling et al., 1977; Christensen et al., 1984). To extend the limited database, isothermal  $P, x$  data at 413.65 K and excess enthalpy data at 363.15 and 413.15 K were measured for the following binary mixtures: benzene + benzaldehyde, toluene + benzaldehyde, benzene + phenol, and toluene + phenol. In addition, for the system benzene + benzaldehyde excess enthalpy data were measured at 323.15 K. Owing to chemical reaction, presumably acetal formation (Limbeck, 1997) during the  $P, x$  measurement of the system benzaldehyde + phenol, azeotropic data (from 388 to 448 K) were determined instead of the VLE data together with excess enthalpy data at 363.15 and 413.15 K.

The main objective of the work was to provide an experimental basis for a future extension of the modified UNIFAC (Dortmund) interaction parameter matrix (Gmehling et al., 1998) with aromatic groups, allowing a separate treatment of the above-mentioned aromatic systems.

A further objective was the investigation of the behavior of systems that occur during the manufacture of phenol by toluene oxidation. The toluene oxidation process, which is shown schematically in Figure 1, was originally developed by Dow Chemicals in the United States (The Dow Chemical Company, 1955). It was brought up to industrial standard by Dutch State Mines, presently DSM. The toluene oxidation process is a two step process. In the first stage toluene is oxidized catalytically with atmospheric oxygen to benzoic acid in the liquid phase. In the second stage the benzoic acid is isolated and decarboxylated catalytically in the presence of atmospheric oxygen to produce phenol.



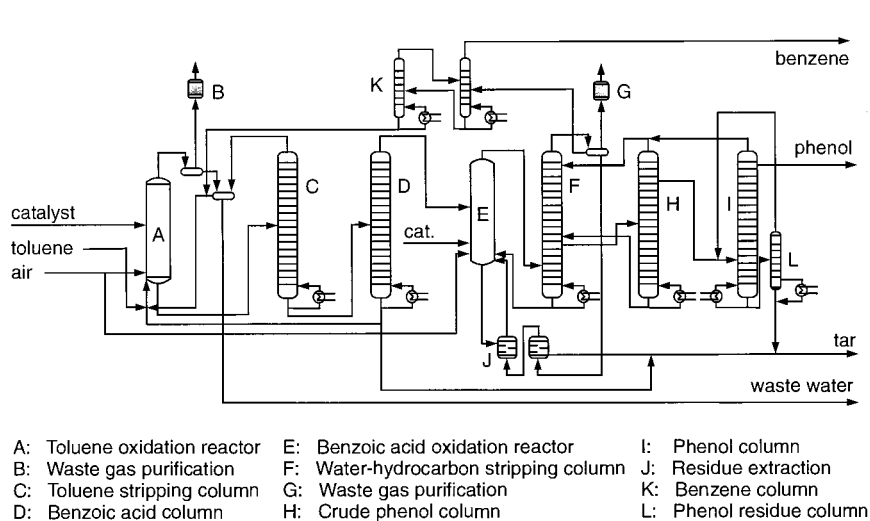
A main problem with this process is the appearance of many byproducts. Owing to the different radicals produced during the oxidation reaction, various recombinations lead to the formation of, e.g., benzene, benzyl benzoate, carboxylic acids, different esters, and various biphenyls. After further purification some of the byproducts, like, e.g., benzaldehyde or benzyl alcohol, are converted to saleable products. Benzoic acid, which is obtained as the main

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**Figure 1.** Scheme of the two-stage toluene oxidation process (The Dow Chemical Company, 1955).

product of the first process step, is also further purified and sold. For a reliable simulation of this process including the large-scale separation steps, thermodynamic data (VLE,  $H^E$ , activity coefficients at infinite dilution ( $\gamma^\infty$ ), azeotropic data, ...) are required, which allow the description of the real behavior of multicomponent mixtures containing the above-mentioned components. The measurement of the data presented here is a first step to overcome the lack of reliable thermodynamic data for the binary systems involved in this process.

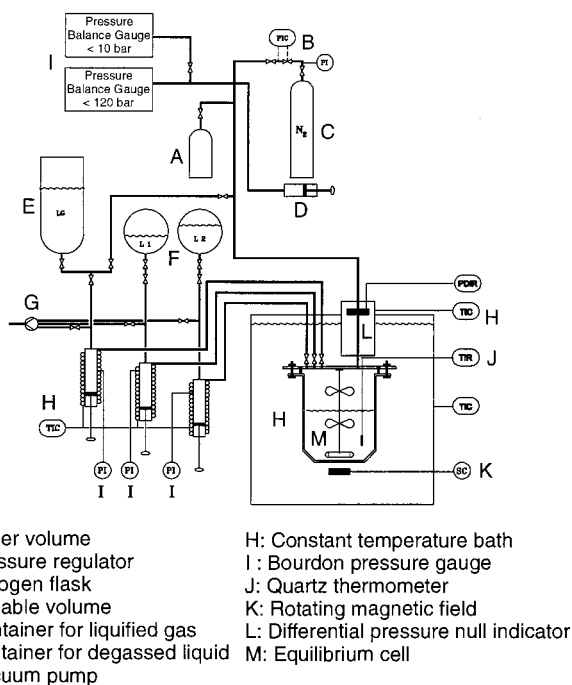
### Experimental Section

For all of the five systems that have been investigated, VLE measurements at 413.65 K had been scheduled. During measurements on the system benzaldehyde + phenol in the static apparatus, the pressure was observed to increase slowly at a constant rate, which led to the conclusion that chemical reaction was involved. As the mixture was expected to show an azeotropic point, azeotropic data were determined using an ordinary distillation apparatus.

**(a) Degassing and Purification.** Benzene and toluene were obtained from commercial sources (Fluka, Merck, Aldrich), and benzaldehyde and phenol were delivered by DSM Research. All components were purified and degassed according to the vacuum rectification method described by Fischer and Gmehling (1994). The purified phenol was additionally degassed by melt-thaw cycles in the equilibrium cell of the static apparatus used, where special care was taken to avoid phenol losses. The final purity of the components determined by gas chromatography and Karl Fischer titration was better than 99.5%.

**(b) VLE Measurements.** Isothermal  $P, x$  data were obtained with a static apparatus, which is described in detail by Fischer and Gmehling (1994) and Kolbe and Gmehling (1985). A schematic diagram of this apparatus is shown in Figure 2.

During a measurement, the system pressure is determined as a function of liquid composition. As the liquid composition is not directly analyzed, it is determined from the volumes of the injected compounds. As described before, these volumes are obtained from precise piston injectors, taking into account the small composition changes caused by evaporation (Fischer and Gmehling, 1994). The piston injectors are thermostated at 303.15 K, in the case of phenol at 333.15 K, in order to keep phenol liquid.



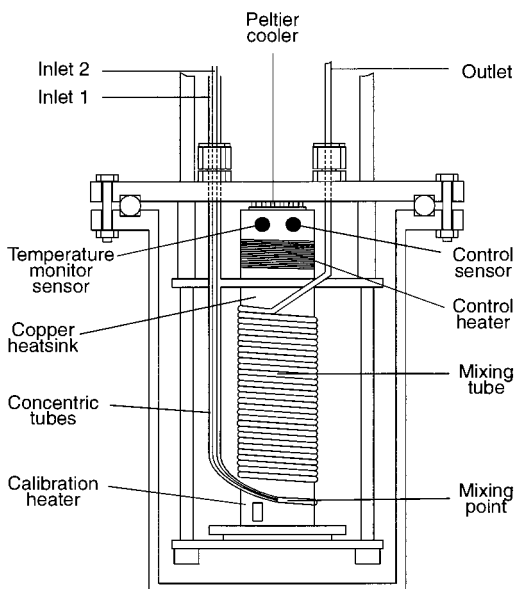
**Figure 2.** Scheme of the static apparatus used for the  $P, x$  measurements (Fischer and Gmehling, 1994).

The pressure for the given composition is determined in a reference system using a differential pressure null indicator manufactured by Ruska and a pressure balance gauge by Desgranges and Huot ( $0.2 \text{ kPa} < P < 1000 \text{ kPa}$ ).

The feed composition error depends on the accuracy of the replacement pumps also manufactured by Ruska, which is given with  $\pm 0.005 \text{ cm}^3$ , but also on the relative molecular weight of both compounds and on the amount of liquid within the equilibrium cell. Therefore, an overall relative accuracy of  $\pm 0.5\%$  concerning the mole fractions is assumed.

The temperature is measured using a platinum resistance thermometer manufactured by Hart Scientific (Model 1506), the resolution of which is smaller than 1 mK. The temperature was kept constant during the measurement of one data set within a fluctuation of  $\pm 10 \text{ mK}$ . The resolution of the pressure balance gauge is 2 Pa.

In contrast to normal static VLE measurements, which are performed in two half-isotherms and which are there-



**Figure 3.** Scheme of the flow cell of the isothermal flow calorimeter used for the measurements of excess enthalpy data (Gmehling, 1993).

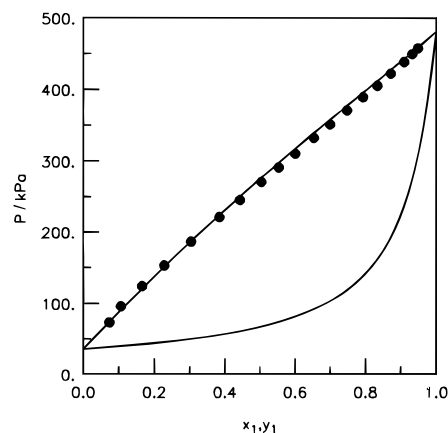
fore very time-consuming, only a single isotherm was recorded. Since for the measurements a comparably small amount of the first component was chosen (about 30–50 cm<sup>3</sup>, compared to the total volume of the equilibrium cell which was 195.79 cm<sup>3</sup>), it was finally possible to cover nearly the complete concentration range. Therefore only one pure component vapor pressure of this first component could be measured. The vapor pressures for the corresponding components were calculated using the Antoine equation. The uncertainty in pressure was estimated to be about 0.1–0.2 kPa throughout the measurements.

**(c) Excess Enthalpy Measurements.** For the measurement of the excess enthalpies an isothermal flow calorimeter (Hart Scientific, model 7501) was used. A scheme of the flow cell of the apparatus is given in Figure 3. The experimental setup has been described previously (Gmehling, 1993). With this type of calorimeter, the heat effects that occur during the mixing process are compensated for with a pulsed heater. With the help of a Peltier cooler, the frequency of the heater is controlled and the baseline is set. Therefore, also exothermic effects can be measured. To prevent evaporation, the pressure is kept at a constant level (above the vapor pressure) using a back-pressure regulator.

The use of a flow-calorimetric equipment requires working with fluids. In this work, three systems containing phenol were investigated. For these measurements, the complete equipment was thermostated at 323.15 K to avoid phenol crystallization.

**(d) Measurement of Azeotropic Data.** As mentioned above, for the system benzaldehyde + phenol the measurement of isothermal VLE data with the static apparatus at 413.5 K was not successful because of chemical reaction. From the attempts made and from already existing azeotropic data (Gmehling et al., 1994), it was clear that this system shows an azeotropic point with a pressure minimum. To obtain reliable information about the VLE behavior of this system in the temperature range of interest, the pressure dependence of the azeotropic point was determined using a distillation setup with a 1.5 m Vigreux column.

Within the equipment, constant pressure was established using an online pressure controller connected with



**Figure 4.** Experimental  $P, x$  data (●) and  $P-x-y$  behavior calculated by NRTL (—) for the system benzene (1) + benzaldehyde (2) at 413.68 K.

a valve. To avoid pressure fluctuation, the distillate was collected in a big flask, which also functioned as a buffer volume. By this means, deviations in pressure could be reduced to  $\pm 0.2$  kPa. To be able to take samples during the distillation process, the distillation flask was sealed with a septum.

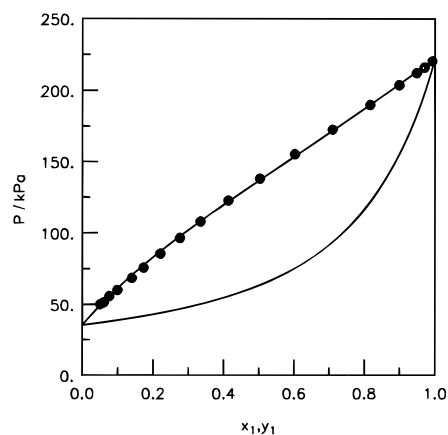
To obtain the azeotropic composition as a function of pressure and temperature, the composition in the distillation flask was repeatedly determined during the distillation until the mole fractions at the top and the bottom of the column were observed to be constant. The composition was finally determined with an accuracy of  $\pm 0.5$  mol % using a gas chromatograph HP 5890 with an integrator HP 3396A, both manufactured by Hewlett-Packard equipped with a Permabond column (CW-20M) and flame ionization detection (FID).

## Results

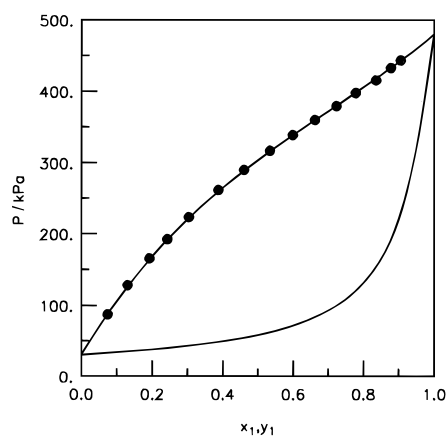
Tables 1–4 present the results of the isothermal  $P, x$  measurements of the systems benzene + benzaldehyde, toluene + benzaldehyde, benzene + phenol, and toluene + phenol. The experimentally obtained pressures  $P$  are given as a function of liquid composition  $x_1$  at 413.62 or 413.68 K. In addition, the Antoine constants for the calculation of the pure component vapor pressures are given. The corresponding graphical representations are shown in Figures 4–7. From the  $P, x$  data it can be seen that all systems show a behavior not far away from ideality, with only a slightly positive deviation from Raoult's law over the complete concentration range. As all of the systems investigated are more or less low-pressure systems, the vapor phase can be expected to show ideal behavior. This assumption turns out to be correct, as the application of the virial equation for the calculation of the real behavior of the vapor phase does not show a significant change for the calculation of the  $P, x$  data.

In Table 5 the azeotropic data of the system benzaldehyde + phenol are given. The azeotropic compositions  $x_{1,az}$  are plotted together with the azeotropic pressure as a function of temperature (388 K–447 K). The azeotropic composition as a function of temperature is also shown graphically in Figure 8, together with azeotropic data determined by other authors (Gmehling et al., 1994).

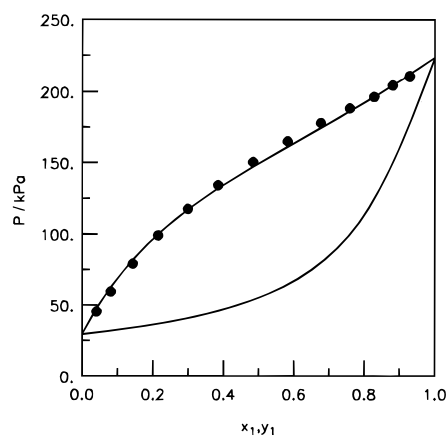
In Tables 6–16 the experimental excess enthalpy ( $H^E$ ) data at 323.15, 363.15, and 413.15 K are given as a function of liquid composition  $x_1$  for the systems benzene + benzaldehyde, toluene + benzaldehyde, benzene + phenol, toluene + phenol, and benzaldehyde + phenol. The corresponding



**Figure 5.** Experimental  $P, x$  data (●) and  $P$ - $x$ - $y$  behavior calculated by NRTL (—) for the system toluene (1) + benzaldehyde (2) at 413.62 K.



**Figure 6.** Experimental  $P, x$  data (●) and  $P$ - $x$ - $y$  behavior calculated by NRTL (—) for the system benzene (1) + phenol (2) at 413.62 K.



**Figure 7.** Experimental  $P, x$  data (●) and  $P$ - $x$ - $y$  behavior calculated by NRTL (—) for the system toluene (1) + phenol (2) at 413.68 K.

plots of these data are given in Figures 9–13. In Figure 11, for the system benzene + phenol, one additional excess enthalpy data set taken from literature (313.15 K, Kohler et al., 1975) is shown together with our experimental data.

Using the  $P, x$ , and  $H^E$  data measured within this work, temperature-dependent parameters for the NRTL model (Renon and Prausnitz, 1968) have been fitted. As for the system benzaldehyde + phenol no complete VLE data at 413.5 K were available owing to chemical reaction, the NRTL parameters were fitted to VLE data at lower

**Table 1.** Experimental  $P, x$  Data for the System Benzene (1) + Benzaldehyde (2) at 413.68 K

$x_1$	$P/\text{kPa}$	$x_1$	$P/\text{kPa}$
0.0000	35.54	0.6531	332.13
0.0733	73.26	0.6994	350.86
0.1060	95.75	0.7478	370.62
0.1655	123.94	0.7931	388.91
0.2282	152.87	0.8338	405.14
0.3049	186.19	0.8717	422.09
0.3846	220.88	0.9097	438.10
0.4430	245.10	0.9321	449.13
0.5042	270.48	0.9486	457.50
0.5534	291.01	1.0000	480.92 <sup>a</sup>
0.6003	310.22		

<sup>a</sup> Pure component vapor pressure for benzene calculated with the help of the Antoine equation:  $\log P = A - B/(C + T)$ ; ( $P/\text{kPa}$ ,  $T/\text{K}$ ). Antoine constants used:  $A = 6.325\ 80$ ,  $B = 1415.80$ ,  $C = -25.122$ .

**Table 2.** Experimental  $P, x$  Data for the System Toluene (1) + Benzaldehyde (2) at 413.62 K

$x_1$	$P/\text{kPa}$	$x_1$	$P/\text{kPa}$
0.0000	35.22 <sup>a</sup>	0.4133	122.61
0.0509	49.97	0.5030	138.04
0.0605	51.28	0.6027	155.24
0.0763	55.87	0.7097	172.52
0.0989	60.06	0.8166	189.84
0.1399	68.54	0.8990	203.54
0.1733	75.76	0.9484	212.12
0.2208	85.55	0.9702	215.93
0.2759	96.46	0.9924	220.31
0.3342	107.95	1.0000	221.98

<sup>a</sup> Pure component vapor pressure for benzaldehyde calculated with the help of the Antoine equation:  $\log P = A - B/(C + T)$ ; ( $P/\text{kPa}$ ,  $T/\text{K}$ ). Antoine constants used:  $A = 5.568\ 23$ ,  $B = 1197.54$ ,  $C = -115.829$ .

**Table 3.** Experimental  $P, x$  Data for the System Benzene (1) + Phenol (2) at 413.62 K

$x_1$	$P/\text{kPa}$	$x_1$	$P/\text{kPa}$
0.0000	30.16	0.5986	338.84
0.0741	87.16	0.6616	360.02
0.1306	128.05	0.7226	379.34
0.1921	165.46	0.7776	397.67
0.2424	192.27	0.8354	415.61
0.3034	223.49	0.8774	432.51
0.3870	261.79	0.9051	443.43
0.4598	290.03	1.0000	480.30 <sup>a</sup>
0.5336	317.03		

<sup>a</sup> Pure component vapor pressure for benzene calculated with the help of the Antoine equation:  $\log P = A - B/(C + T)$ ; ( $P/\text{kPa}$ ,  $T/\text{K}$ ). Antoine constants used:  $A = 6.325\ 80$ ,  $B = 1415.80$ ,  $C = -25.122$ .

**Table 4.** Experimental  $P, x$  Data for the System Toluene (1) + Phenol (2) at 413.68 K

$x_1$	$P/\text{kPa}$	$x_1$	$P/\text{kPa}$
0.0000	29.31	0.5820	165.04
0.0409	45.38	0.6768	177.96
0.0808	59.47	0.7591	188.35
0.1431	79.17	0.8283	196.45
0.2144	98.98	0.8809	204.49
0.2986	117.50	0.9289	210.58
0.3848	134.19	1.0000	223.53 <sup>a</sup>
0.4837	150.44		

<sup>a</sup> Pure component vapor pressure for toluene calculated with the help of the Antoine equation:  $\log P = A - B/(C + T)$ ; ( $P/\text{kPa}$ ,  $T/\text{K}$ ). Antoine constants used:  $A = 6.115\ 39$ ,  $B = 1346.86$ ,  $C = -56.049$ .

temperatures and at low pressures available from literature (Vostrikova et al., 1978) as well as to the experimental  $H^E$  data. During the fitting procedure, ideal behavior of the vapor phase was assumed and the following objective

**Table 5. Azeotropic Data for the System Benzaldehyde (1) + Phenol (2) from 388 K to 447 K (10 kPa–73 kPa)**

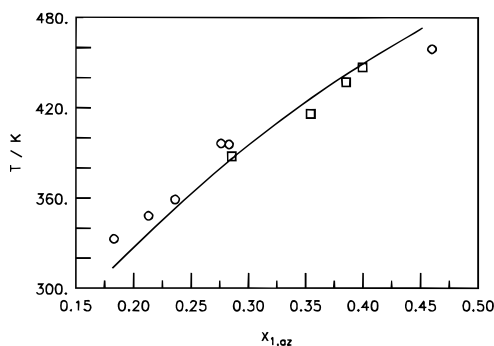
$x_1$	$P/\text{kPa}$	$T/\text{K}$
0.2852	10.0	388
0.3542	27.5	416
0.3852	53.0	437
0.3999	73.0	447

**Table 6. Experimental Excess Enthalpies for the System Benzene (1) + Benzaldehyde (2) at 323.15 K and 1617 kPa**

$x_1$	$H^E/\text{J mol}^{-1}$	$x_1$	$H^E/\text{J mol}^{-1}$
0.0285	13.49	0.5832	119.10
0.0568	25.90	0.6320	112.71
0.1129	48.58	0.6801	102.28
0.1681	68.32	0.7276	90.14
0.2225	84.50	0.7745	75.87
0.2762	97.54	0.8208	60.14
0.3292	108.37	0.8664	39.84
0.3814	117.32	0.9115	17.48
0.4329	122.07	0.9560	-8.38
0.4837	125.11	0.9781	-20.91
0.5338	124.58		

**Table 7. Experimental Excess Enthalpies for the System Benzene (1) + Benzaldehyde (2) at 363.15 K and 1445 kPa**

$x_1$	$H^E/\text{J mol}^{-1}$	$x_1$	$H^E/\text{J mol}^{-1}$
0.0285	9.71	0.5832	102.29
0.0568	20.50	0.6320	96.68
0.1129	41.51	0.6801	87.43
0.1681	59.09	0.7276	77.40
0.2225	73.96	0.7745	63.61
0.2762	86.14	0.8208	46.88
0.3292	93.76	0.8665	27.10
0.3814	100.59	0.9115	2.91
0.4329	104.56	0.9561	-25.33
0.4837	106.03	0.9781	-38.91
0.5338	105.75	0.9891	-39.14

**Figure 8.** Experimental azeotropic data for the system benzaldehyde (1) + phenol (2) measured by different authors (O) (Gmehling et al., 1994) and in this work (□) together with the temperature dependence of the azeotropic point calculated by NRTL (—).

function  $F$  has been chosen

$$F = w_1 \sum_{i=1}^{n_1} \left| \frac{P_{i,\text{exp}} - P_{i,\text{cal}}}{P_{i,\text{exp}}} \right| + w_2 \sum_{i=1}^{n_2} \left| \frac{H_{i,\text{exp}}^E - H_{i,\text{cal}}^E}{|H_{i,\text{max}}^E|} \right| \quad (1)$$

where  $w_1$  and  $w_2$  are variable weighting factors,  $n_1$  and  $n_2$  are the number of experimental data sets,  $P_{i,\text{exp}} - P_{i,\text{cal}}$  is the difference between experimental and calculated pressures,  $H_{i,\text{exp}}^E - H_{i,\text{cal}}^E$  is the difference between experimental and calculated excess enthalpies, and  $H_{i,\text{max}}^E$  is the maximum excess enthalpy value of the corresponding data set. The NRTL parameters were fitted simultaneously with emphasis on the accurate description of the VLE data.

**Table 8. Experimental Excess Enthalpies for the System Benzene (1) + Benzaldehyde (2) at 413.15 K and 1617 kPa**

$x_1$	$H^E/\text{J mol}^{-1}$	$x_1$	$H^E/\text{J mol}^{-1}$
0.0285	10.76	0.5832	97.25
0.0568	20.73	0.6320	91.62
0.1129	37.07	0.6801	84.94
0.1681	54.51	0.7276	73.71
0.2225	69.51	0.7745	63.56
0.2762	80.14	0.8208	45.77
0.3292	87.91	0.8664	25.13
0.3814	92.85	0.9115	0.13
0.4329	96.58	0.9560	-30.31
0.4837	99.16	0.9781	-47.32
0.5338	100.92		

**Table 9. Experimental Excess Enthalpies for the System Toluene (1) + Benzaldehyde (2) at 363.15 K and 1617 kPa**

$x_1$	$H^E/\text{J mol}^{-1}$	$x_1$	$H^E/\text{J mol}^{-1}$
0.0240	14.20	0.7419	128.06
0.1204	66.57	0.9739	23.25
0.2420	116.63	0.9804	20.84
0.3650	148.63	0.9870	14.78
0.4893	165.26	0.9935	8.81
0.6149	158.24		

**Table 10. Experimental Excess Enthalpies for the System Toluene (1) + Benzaldehyde (2) at 413.15 K and 1824 kPa**

$x_1$	$H^E/\text{J mol}^{-1}$	$x_1$	$H^E/\text{J mol}^{-1}$
0.0237	13.34	0.5366	184.96
0.0475	27.90	0.5870	181.66
0.0952	57.40	0.6376	172.41
0.1433	86.76	0.6886	157.89
0.1915	111.09	0.7398	136.40
0.2400	127.87	0.7912	112.13
0.2888	148.87	0.8430	76.47
0.3378	160.66	0.8950	34.56
0.3871	172.18	0.9474	-15.76
0.4367	180.83	0.9737	-45.32
0.4865	185.57	0.9737	-27.27

**Table 11. Experimental Excess Enthalpies for the System Benzene (1) + Phenol (2) at 363.15 K and 1858 kPa**

$x_1$	$H^E/\text{J mol}^{-1}$	$x_1$	$H^E/\text{J mol}^{-1}$
0.0489	95.11	0.5443	843.82
0.0979	194.03	0.5944	870.04
0.1717	337.40	0.6699	876.61
0.2457	470.32	0.7456	830.73
0.3200	594.73	0.8216	717.57
0.3945	701.22	0.8979	495.79
0.4443	759.51	0.9489	272.78
0.4942	811.13		

**Table 12. Experimental Excess Enthalpies for the System Benzene (1) + Phenol (2) at 413.15 K and 1755 kPa**

$x_1$	$H^E/\text{J mol}^{-1}$	$x_1$	$H^E/\text{J mol}^{-1}$
0.0489	109.36	0.5443	827.60
0.0979	220.05	0.5945	844.59
0.1717	368.75	0.6699	827.31
0.2457	507.00	0.7457	769.71
0.3200	621.90	0.8217	649.98
0.3945	720.54	0.8979	433.15
0.4443	769.18	0.9489	238.61
0.4943	812.82		

The obtained binary parameters for the NRTL model  $\Delta g_{ij}$  as well as the nonrandomness parameters  $\alpha_{ij}$  are given in Table 17. The nonresponding expression for the temperature dependence is given by the following equation

$$\Delta g_{ij} = \Delta g_{ij}^0 + \Delta g_{ij}^1 T + \Delta g_{ij}^2 T^2 \quad (2)$$

**Table 13. Experimental Excess Enthalpies for the System Toluene (1) + Phenol (2) at 363.15 K and 1824 kPa**

$x_1$	$H^E/\text{J mol}^{-1}$	$x_1$	$H^E/\text{J mol}^{-1}$
0.0414	94.38	0.5008	912.23
0.0836	193.71	0.5519	944.19
0.1483	340.50	0.6303	962.01
0.2149	477.07	0.7112	928.67
0.2833	607.39	0.7947	820.39
0.3537	730.03	0.8808	582.16
0.4018	803.66	0.9398	345.23
0.4508	868.75		

**Table 14. Experimental Excess Enthalpies for the System Toluene (1) + Phenol (2) at 413.15 K and 1824 kPa**

$x_1$	$H^E/\text{J mol}^{-1}$	$x_1$	$H^E/\text{J mol}^{-1}$
0.0414	115.72	0.5008	921.00
0.0836	228.17	0.5519	962.08
0.1483	377.82	0.6303	958.08
0.2149	538.14	0.7112	893.54
0.2833	658.69	0.7947	760.85
0.3537	776.84	0.8808	538.47
0.4018	830.52	0.9398	294.09
0.4508	888.00		

**Table 15. Experimental Excess Enthalpies for the System Benzaldehyde (1) + Phenol (2) at 363.15 K and 1824 kPa**

$x_1$	$H^E/\text{J mol}^{-1}$	$x_1$	$H^E/\text{J mol}^{-1}$
0.0435	-237.42	0.5647	-1340.20
0.0877	-459.97	0.4144	-1399.84
0.1550	-755.57	0.6424	-1197.56
0.2238	-1034.50	0.7218	-995.55
0.2940	-1234.26	0.8030	-739.77
0.3657	-1357.61	0.8862	-442.11
0.4638	-1421.85	0.9426	-215.55
0.5139	-1393.76		

**Table 16. Experimental Excess Enthalpies for the System Benzaldehyde (1) + Phenol (2) at 413.15 K and 1824 kPa**

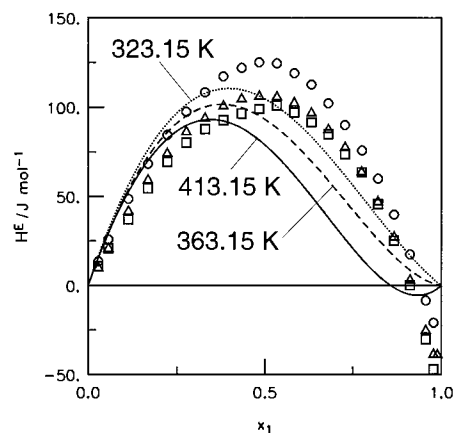
$x_1$	$H^E/\text{J mol}^{-1}$	$x_1$	$H^E/\text{J mol}^{-1}$
0.0435	-248.05	0.5139	-1362.24
0.0877	-424.67	0.5647	-1340.80
0.1550	-717.41	0.6424	-1201.53
0.2238	-979.15	0.7218	-971.52
0.2940	-1187.49	0.8030	-761.99
0.3657	-1296.41	0.8862	-439.17
0.4144	-1333.52	0.9426	-242.59
0.4638	-1371.90		

for binary systems containing the components  $i$  and  $j$ .

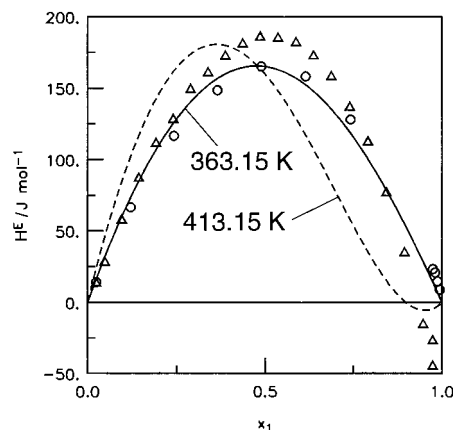
In Figures 4–13, the experimental VLE and  $H^E$  data are compared with the behavior calculated with the help of the NRTL model using the simultaneously fitted parameters. In any case, it was not possible to obtain smaller deviations between experimental and calculated data.

The isothermal  $P, x$  data are well described by the NRTL equation, which is true for all of the four systems investigated. Regarding the azeotropic data of the system benzaldehyde + phenol, which are shown in Figure 8, a satisfactory description of the temperature dependence of the azeotropic point is obtained, even though these data have not been included into the fitting procedure for the NRTL parameters. One reason for the successful description of these data is that temperature-dependent  $H^E$  data have been taken into account simultaneously.

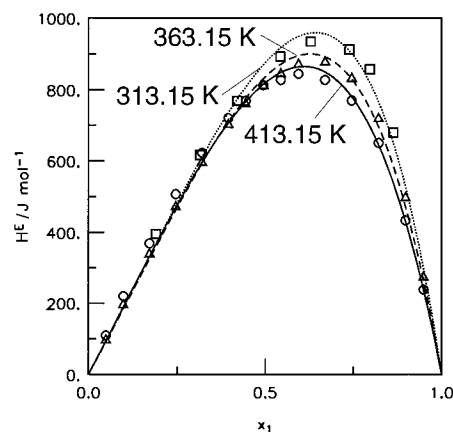
Regarding the  $H^E$  data, all systems show mainly endothermal mixing behavior except for the system benzaldehyde + phenol, which shows exothermal excess enthalpies over the whole concentration range. A special phenomenon



**Figure 9.** Experimental  $H^E$  data at 323.15 K (o), 363.15 K ( $\Delta$ ), and at 413.15 K ( $\square$ ) for the system benzene (1) + benzaldehyde (2) together with the results of the NRTL model.



**Figure 10.** Experimental  $H^E$  data at 363.15 K (o) and at 413.15 K ( $\Delta$ ) for the system toluene (1) + benzaldehyde (2) together with the results of the NRTL model.

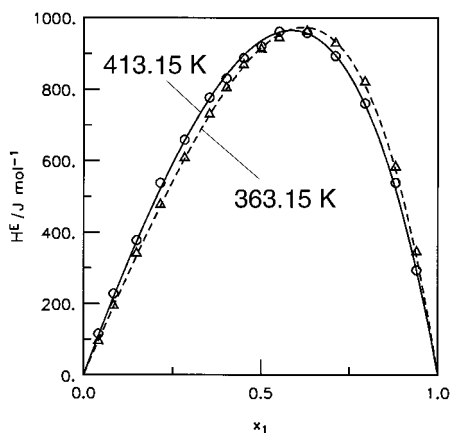
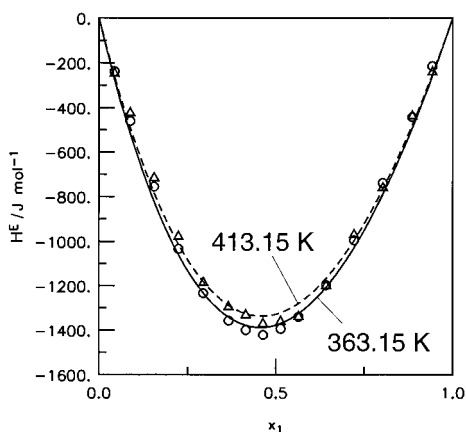


**Figure 11.** Experimental  $H^E$  data from literature (Kohler et al., 1975) at 313.15 K ( $\square$ ) and from this work at 363.15 K ( $\Delta$ ) and 413.15 K (o) for the system benzene (1) + phenol (2) together with the results of the NRTL model.

is observed for the excess enthalpy data of the systems benzene + benzaldehyde (Figure 9) and toluene + benzaldehyde (Figure 10), which is a change of sign. In the benzene-rich region, or the toluene-rich region, respectively, negative values for the excess enthalpy are obtained, so that a minimum of  $H^E$  must be assumed in the strongly diluted region. For the system benzene + benzaldehyde this behavior is observed over the whole temperature range investigated. The main tendency is reproduced by the temperature-dependent description with the help of the

**Table 17. NRTL Interaction Parameters Fitted Simultaneously to VLE and  $H^E$  Data**

system comp (1) + comp (2)	$\Delta g_{12}^0 /$ J mol <sup>-1</sup>	$\Delta g_{12}^1 /$ J mol <sup>-1</sup> K <sup>-1</sup>	$\Delta g_{12}^2 /$ J mol <sup>-1</sup> K <sup>-2</sup>	$\Delta g_{21}^0 /$ J mol <sup>-1</sup>	$\Delta g_{21}^1 /$ J mol <sup>-1</sup> K <sup>-1</sup>	$\Delta g_{21}^2 /$ J mol <sup>-1</sup> K <sup>-2</sup>	$\alpha_{12}$
benzene (1) + benzaldehyde (2)	$-5.3639 \times 10^2$	$1.6185 \times 10^{-2}$	$1.5188 \times 10^{-2}$	$1.6824 \times 10^3$	$-5.1057 \times 10^0$	$-3.3968 \times 10^{-3}$	0.4700
toluene (1) + benzaldehyde (2)	$9.9264 \times 10^3$	$-5.1454 \times 10^1$	$8.1404 \times 10^{-2}$	$-4.7981 \times 10^3$	$2.7677 \times 10^1$	$-4.4811 \times 10^{-2}$	0.4695
benzene (1) + phenol (2)	$5.7745 \times 10^3$	$5.1345 \times 10^0$	$-3.0302 \times 10^{-2}$	$3.3030 \times 10^3$	$-3.0272 \times 10^1$	$5.2340 \times 10^{-2}$	0.2244
toluene (1) + phenol (2)	$9.1696 \times 10^3$	$-2.5540 \times 10^1$	$2.1637 \times 10^{-2}$	$-3.6036 \times 10^1$	$1.5397 \times 10^0$	$-2.5183 \times 10^{-5}$	0.4712
benzaldehyde (1) + phenol (2)	$-3.2030 \times 10^3$	$2.0995 \times 10^0$	$-3.3886 \times 10^{-3}$	$-1.6708 \times 10^3$	$4.1203 \times 10^0$	$2.7012 \times 10^{-3}$	0.2940

**Figure 12.** Experimental  $H^E$  data at 363.15 K ( $\Delta$ ) and at 413.15 K ( $\circ$ ) for the system toluene (1) + phenol (2) together with the results of the NRTL model.**Figure 13.** Experimental  $H^E$  data at 363.15 K ( $\circ$ ) and at 413.15 K ( $\Delta$ ) for the system benzaldehyde (1) + phenol (2) together with the results of the NRTL model.

NRTL model, but not the negative excess enthalpy values in the dilute region for 363.15 K and 323.15 K. The measurements for the system toluene + benzaldehyde show negative values at 413.15 K, which disappear at lower temperatures (363.15 K). This behavior is also described, not in quantity but in quality, by the temperature-dependent NRTL parameters. In addition, for both of these systems it has to be noted that the total excess enthalpy values are very small compared to the other systems investigated ( $H_{\max}^E \approx 100\text{--}200 \text{ J mol}^{-1}$  vs  $H_{\max}^E \approx 1000\text{--}1500 \text{ J mol}^{-1}$ ). While for the system benzene + benzaldehyde the excess enthalpy decreases with temperature, the opposite behavior is observed for the system toluene + benzaldehyde.

The temperature dependence of the remaining  $H^E$  data is in any case well described by the temperature dependent parameters, as to be seen in Figures 11–13. Regarding the system benzene + phenol (Figure 11), the excess enthalpy slightly decreases with temperature. For the system toluene + phenol (Figure 12), not the maximum in  $H^E$  but only the shape of the  $H^E$  curve is slightly temper-

ature dependent. A tendency of the negative  $H^E$  values to increase moderately with temperature is finally observed for the system benzaldehyde + phenol (Figure 13).

## Conclusion

Using reliable VLE,  $H^E$  and azeotropic data, the behavior of binary mixtures of benzene, toluene, phenol, and benzaldehyde at high temperatures has been investigated. The experimental data have been fitted using temperature-dependent NRTL parameters, which allow the description of the vapor–liquid equilibrium and excess enthalpy behavior for all of the mixtures as well as the temperature dependence of the azeotropic point for the system benzaldehyde + phenol, in a reliable manner over a large temperature range.

The measurement of the required reliable experimental data for the introduction of the aromatic aldehyde group (AC-CHO) into the modified UNIFAC (Dortmund) model has therefore been completed with this work. In addition, the parameters for the phenol group (AC-OH) can be revised, since new supporting data at higher temperatures are available now. Generally, isothermal data are more valuable for the extension and further development of group contribution methods such as UNIFAC or modified UNIFAC (Dortmund) because isobaric data do not allow to distinguish between composition and temperature effects (Van Ness, 1995).

During the following parts of this project, further phase equilibrium and excess enthalpy data of aromatic systems, also with high-boiling components, will be measured. It is scheduled to define some more aromatic structural groups, e.g. aromatic acids (AC-COOH), aromatic esters (AC-COO-) or ethers (AC-O-) for the group contribution method modified UNIFAC (Dortmund) on the basis of the continuously growing database. The extension of the model with these functional groups will be addressed in a future paper.

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