Azeotropic Data for Binary and Ternary Systems at Moderate Pressures

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For the synthesis and design of distillation columns the knowledge of azeotropic points is most important. Therefore, a computerized data bank for azeotropic data has been established at the University of Oldenburg to supplement the existing mixture information stored in the Dortmund Data Bank. To check questionable literature data and to extend the contents of the computerized data bank, more than 500 azeotropic and zeotropic data for binary and ternary systems have been measured up to pressures of 3.5 bar with the help of a wire band column. A total of 38 binary azeotropic and zeotropic data for various ethers (MTBE, TAME, TAEE, ETBE, IPTBE) with different alcohols have already been published (Gmehling et al., 1995). A total of 273 binary and 28 ternary azeotropic and zeotropic data are reported in this paper.

Introduction

Azeotropic and zeotropic information are most important for the synthesis of distillation processes (Gmehling and Brehm, 1996). Azeotropic systems cannot be separated by simple distillation. Therefore, for these kinds of systems, besides nondistillation or hybrid processes, more complex distillation processes, such as extractive, azeotropic, salt, or pressure swing distillation, have to be applied. However, the appearance of azeotropic points is not always disadvantageous. For example, heterogeneous azeotropic points are advantageous when small impurities have to removed, as in the case of waste water strippers or the dehydration of solvents.

A data bank with azeotropic data is useful to supplement the already available software tools for the synthesis of rectification processes, since with simple search algorithms suitable solvents for azeotropic distillation (homogeneous, heterogeneous) can be selected. In combination with the data bank for activity coefficients at infinite dilution, simple programs also allow the choice of selective solvents for extractive distillation. Furthermore, from the pressure (temperature) dependence of the azeotropic composition it can be determined if pressure swing distillation can be applied or if the separation problem (azeotropic point) disappears at lower or higher pressures. In contrast to the selection of solvents using well-known group contribution methods such as ASOG (Kojima and Tochigi, 1979), UNIFAC (Fredenslund et al., 1977), modified UNIFAC (Dortmund) (Gmehling et al., 1993), or modified UNIFAC (Lyngby) (Larsen et al., 1987), other solvents, such as sulfolane, *N*-methyl-ϵ-caprolactam, *N*-formylmorpholine, etc. will be discovered for which up to now, because of the missing groups, the required phase equilibria could not be described with the help of the group contribution methods mentioned before.

Data Bank for Azeotropic Data

Because of the importance of azeotropic data for the synthesis and design of distillation processes, a data bank for azeotropic data was added to the Dortmund Data Bank. The data bank for azeotropic data now contains 39 000 pieces of information on azeotropic and zeotropic behavior. All the data (35 000) stored before 1993 have been published after careful evaluation in a unified form as a data compilation (Gmehling et al., 1994).

During the development of the data bank for azeotropic data, different graphical procedures were developed to check the data before storing; e.g., the azeotropic composition for the binary systems published by different authors were plotted as a function of temperature. For ternary systems, the data of different authors were plotted in a triangular diagram. Furthermore, the experimental azeotropic data were compared graphically with the results predicted by different group contribution methods such as UNIFAC (Hansen et al., 1991) and modified UNIFAC (Gmehling et al., 1993). Additionally the temperatures and pressures given for the azeotropes were checked for every binary and ternary system by linear regression analysis of the log P versus $1/T$ values when at least three T/P values were available. The procedure to check the data is described in more detail in the following references: Gmehling et al. (1994, 1995).

Unfortunately in a lot of cases it was impossible to decide about the reliability of the data reported. For example, often the group contribution predicted an azeotropic point, while Lecat in his compilations (Lecat, 1949) reported zeotropic behavior. To be able to decide about the reliability of the data published by Lecat, often measured using chemicals of questionable purity and under difficult conditions (e.g., during the occupation of Belgium by German troops in the first world war), a large number of experimental data up to pressures of 3.5 bar were measured in our laboratory with the help of a wire band column.

Experimental Section

Chemicals with high purity obtained by various suppliers were further purified by different techniques, such as crystallization, extraction, and distillation, and dried with the help of molecular sieves and calcium chloride or by distillation. In the case of tertiary ethers, the last amount of alcohol was removed by shaking (extraction) with water. The purity was checked by gas chromatography and the water content by Karl Fischer titration. In all cases chemicals with a purity greater than 99.8 mass % were used for the experimental investigations.

For the measurements, a commercially available micro spinning band column with an electronically controlled reflux ratio from NORMAG GmbH (Hofheim, FRG) was used. This equipment allows measurements up to pressures of 3.5 bar. The experimental setup is shown sche-

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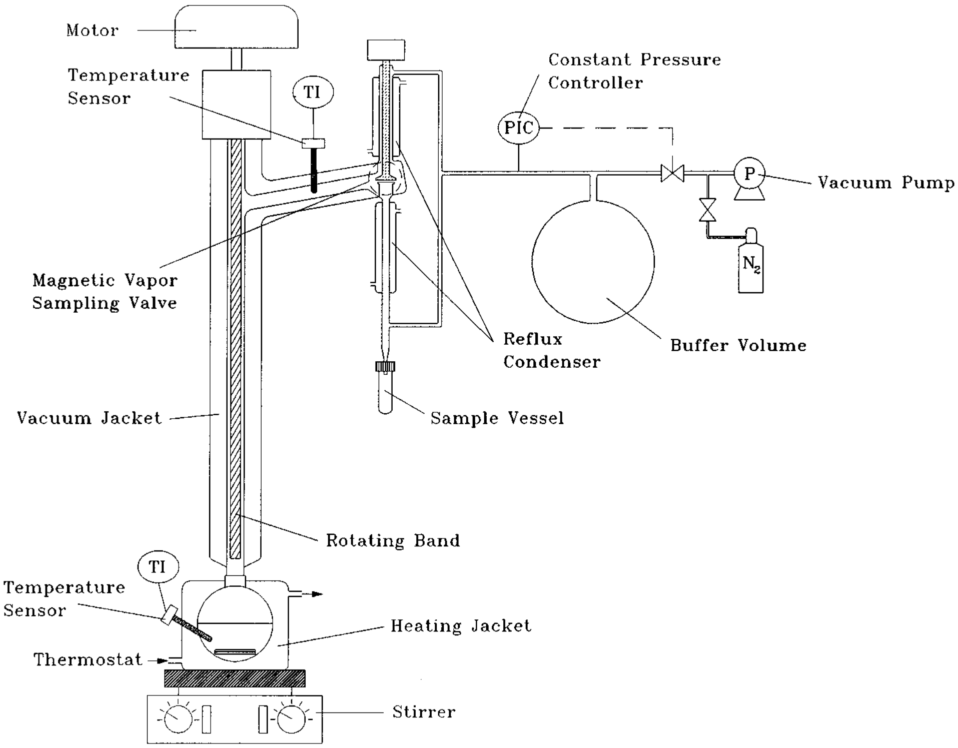

Figure 1. Scheme of the experimental setup for the measurement of homogeneous and heterogeneous azeotropes with the help of a wire band column.

matically in Figure 1. Depending on the liquid load and the number of revolutions of the spinning band (optimum speed 2000 rpm), up to 50 theoretical stages at a low pressure drop can be realized. Since the reflux is realized on the basis of a vapor dividing principle, not only homogeneous but also heterogeneous pressure maximum azeotropes can be determined. With the help of a vacuum pump for pressures below atmospheric and a nitrogen reservoir with a pressure of ~5 bar for higher pressures in connection with the manostat (Kobold type DCM1 (0.2−1.6 bar) or type DGM6 (0.7−6 bar)) the desired pressure is kept constant. The temperature was determined with the help of a resistance thermometer with an accuracy of ±0.1 °C and the pressure by means of a sensor (Druck Limited, type PDCR) with an accuracy of ±0.05 kPa.

For the analytical determination of the azeotropic composition, gas−liquid chromatography was used. In the case of heterogeneous azeotropes a suitable solvent (e.g., acetone, 1-propanol, 1-butanol) was used as the homogenizer. The required factors to determine the compositions from the recorded peak areas were obtained using prepared test mixtures of exactly known composition. The accuracy of the azeotropic composition determined is approximately 0.25 mol % in the case of homogeneous and approximately 0.5 mol % in the case of heterogeneous azeotropes.

Usually homogeneous or heterogeneous pressure maximum azeotropes were obtained. This means the samples were taken from the top of the column. In the case of a pressure minimum azeotrope, e.g., 2-propanol + 2-methyl-2-propanol, the samples were taken from the bottom of the column after a great part of the mixture had been distilled off. To check that the system shows azeotropic (separation factor $\alpha_{12} = 1$) and not quasiazeotropic ($\alpha_{12} \approx 1$) behavior, the investigations were repeated starting with a different feed composition. In the case of homogeneous azeotropes the distillate at the given pressure was used as the feed to check again for azeotropy.

Results

The results for the binary systems are given in Table 1. Besides the system, the composition $y_{1,\mathrm{az}}$ and the type of azeotrope for the given temperature *t* (°C) (pressure *P*, kPa) are listed. Furthermore, in most cases, it is also mentioned why these systems were investigated. The experimental data were compared with the results of different group contribution methods, such as UNIFAC (Fredenslund et al., 1977; Hansen et al., 1991), ASOG (Kojima and Tochigi, 1979; Tochigi et al., 1990), modified UNIFAC (Dortmund) (Weidlich and Gmehling, 1987; Gmehling et al., 1993), and modified UNIFAC (Lyngby) (Larsen et al., 1987), whereby the required pure component data (Antoine constants, structural information) were directly taken from the Dortmund Data Bank. A summary with the number of calculated data and the resulting mean deviations in vapor phase composition and pressure for the different models are given in Table 3. Original UNIFAC and modified UNIFAC because of the large parameter matrix available allowed most of the azeotropic systems to be calculated. More detailed information about the distribution of the deviations in the vapor phase mole fraction (Δy_{az}) at the azeotropic point is shown in Figure 2 for all four group contribution methods. From Table 3 and Figure 2 it can be concluded that the modified UNIFAC version developed in Dortmund (Weidlich and Gmehling, 1987; Gmehling et al., 1993) provides the best results. While original UNIFAC shows an absolute mean deviation of 4.32 mol % in the vapor phase composition with modified UNIFAC (Dortmund), a mean deviation of 2.3 mol % is observed. Similar improvements are achieved for the predicted pressure. While a mean deviation of 2.44 kPa is predicted with the original UNIFAC method, approximately half of the deviation (1.28 kPa) results from modified UNIFAC. For other systems the mean deviation may still be lower, since the reason for the experimental investigation of azeotropic data for the systems given in Tables 2 and 3 was often that disagreement between prediction and experiment was observed during buildup of the data bank for azeotropic data.

Typical results are shown in Figures 3 and 4. In Figure 3 the experimental data for the system methyl *tert*-butyl ether + ethanol are shown in the form of a $T{-}y_{\mathrm{az}}$ diagram together with the results obtained by modified

Table 1. Azeotropic Information for Selected Binary Systems

component 1 + component 2	t/°C	P/kPa	y_1	type[f]
acetonitrile + 2-propanol[a]	33.30	19.66	0.7175	homPmax
	57.30	53.25	0.6148	homPmax
	75.00	100.82	0.5287	homPmax
acetone + diisopropyl ether[b]	29.30	40.31	0.7316	homPmax
	42.10	66.41	0.7363	homPmax
	53.95	100.17	0.7424	homPmax
acetone + 1-hexene[a]	28.90	46.42	0.5817	homPmax
	38.45	66.65	0.5876	homPmax
	50.20	101.40	0.5973	homPmax
acetone + methanol	54.70	99.28	0.7863	homPmax
acetone + tetrachloromethane[c]	21.90	26.53	0.9763	homPmax
	30.90	39.54	0.9696	homPmax
	38.20	52.96	0.9627	homPmax
	49.20	79.94	0.9587	homPmax
	56.00	101.80	0.9555	homPmax
	56.10	101.23	0.9602	homPmax
	62.30	125.07	0.9628	homPmax
	68.10	149.93	0.9663	homPmax
	74.50	188.86	0.9657	homPmax
	84.40	251.18	0.9712	homPmax
	90.90	301.17	0.9752	homPmax
	96.30	349.21	0.9831	homPmax
acetone + tetrahydrofuran[b]	31.20	40.09	0.9870	homPmax
	44.40	66.61	0.9729	homPmax
	55.70	100.35	0.9603	homPmax
acetone + propyl bromide[b]	33.80	32.74	0.9888	homPmax
	44.00	66.59	0.9895	homPmax
	55.60	99.75	0.9915	homPmax
ethanol + acetonitrile	48.00	39.33	0.4353	homPmax
ethanol + benzene	67.80	100.42	0.4403	homPmax
ethanol + 2-pentanone	32.40	13.21	0.8001	homPmax
	56.30	40.43	0.8944	homPmax
	78.00	100.50	0.9779	homPmax
ethanol + fluorobenzene[b]	31.50	19.89	0.3421	homPmax
	53.90	53.47	0.4148	homPmax
	70.70	101.54	0.4752	homPmax
ethyl acetate + benzene[a]	24.90	13.11	0.4524	homPmax
	50.95	40.03	0.7804	homPmax
	77.40	102.45	0.9453	homPmax
ethyl acetate + 2-butanone[a]	33.75	20.05	0.7198	homPmax
	50.65	40.03	0.7908	homPmax
	76.80	101.00	0.8343	homPmax
ethyl acetate + cyclohexene[a]	31.30	20.07	0.5236	homPmax
	55.80	53.64	0.5741	homPmax
	74.30	100.87	0.6183	homPmax
ethyl acetate + methylcyclohexane[d]	33.90	20.15	0.8215	homPmax
	57.80	53.06	0.8645	homPmax
	76.75	101.83	0.9000	homPmax
ethyl acetate + 2-methyl-2-propanol[b]		13.25		none
	40.70	26.33	0.9569	homPmax
	50.75	39.79	0.9095	homPmax
	76.60	101.28	0.7778	homPmax
2-butanol + ethylbenzene[a]	30.40	3.82	0.7202	homPmax
	52.00	12.62	0.8203	homPmax
	66.50	26.04	0.8832	homPmax
		101.47		none
2-butanol + 1,4-dioxane[a]	30.00	6.36	0.1023	homPmax
	44.40	13.11	0.1696	homPmax
	79.80	53.47	0.3841	homPmax
	98.60	100.77	0.5268	homPmax
2-butanol + 3-pentanone	38.60	9.38	0.1611	homPmax
	61.70	26.46	0.3416	homPmax
	97.35	99.98	0.6075	homPmax
2-butanol + ethyl *tert*-amyl ether	27.50	6.44	0.1746	homPmax
	58.00	26.72	0.3072	homPmax
	94.60	102.89	0.4931	homPmax
benzene + heptane[c]	24.80	12.89	0.9706	homPmax
	34.20	19.81	0.9842	homPmax
	41.20	26.20	0.9898	homPmax
	47.20	32.83	0.9930	homPmax
		53.39		none
		66.49		none
2-butanone + acetonitrile	25.65	12.92	0.5082	homPmax
	47.55	33.15	0.5843	homPmax
	60.10	53.10	0.6344	homPmax
	71.80	80.05	0.6686	homPmax
	79.00	101.15	0.6805	homPmax
2-butanone + methylcyclohexane[a]	34.15	20.20	0.7557	homPmax
	51.25	40.15	0.7726	homPmax
	77.35	98.93	0.7983	homPmax
2-butanone + dipropyl ether[d]	34.80	19.77	0.7518	homPmax
	50.80	39.79	0.7602	homPmax
	78.25	100.88	0.7785	homPmax

Table 1. (continued)

component 1 + component 2	t/°C	P/kPa	y_1	type[f]
chloroform + methanol	54.00	103.55	0.6420	homPmax
cyclohexane + 2-butanol[a]	33.50	20.24	0.9059	homPmax
	58.15	53.39	0.8571	homPmax
	76.75	101.02	0.8108	homPmax
cyclohexane + 2-methyl-1-propanol[a]	33.20	19.84	0.9499	homPmax
	50.80	39.82	0.9233	homPmax
	78.20	101.44	0.8675	homPmax
cyclohexane + trichloroethylene[b]	34.50	19.81	0.9310	homPmax
	52.20	39.81	0.9202	homPmax
	80.25	101.32	0.9025	homPmax
cyclohexane + propyl acetate[d]	34.50	19.76	0.9658	homPmax
	52.20	39.78	0.9558	homPmax
	80.00	100.43	0.9402	homPmax
cyclohexene + 2-butanol	26.15	13.03	0.9214	homPmax
	52.95	40.05	0.8678	homPmax
	79.60	101.25	0.7954	homPmax
cyclohexene + 1,4-dioxane[a]	27.10	13.18	0.9303	homPmax
	54.50	39.94	0.9121	homPmax
	82.60	101.44	0.8935	homPmax
cyclohexene + 2-methyl-1-propanol	26.30	12.94	0.9531	homPmax
	53.20	40.13	0.9144	homPmax
	80.60	100.31	0.8637	homPmax
methylcyclohexane + 3-pentanone	30.65	9.52	0.6629	homPmax
	65.55	39.77	0.5866	homPmax
	93.80	99.82	0.5559	homPmax
methylcyclohexane + 2-methyl-2-butanol	34.45	10.66	0.8470	homPmax
	74.05	53.27	0.6877	homPmax
	93.45	99.87	0.6035	homPmax
methylcyclopentane + 1,4-dioxane[b]	29.30	26.41	0.9566	homPmax
	47.90	53.13	0.9546	homPmax
	70.70	99.79	0.9462	homPmax
methylcyclopentane + 2-propanol	30.20	26.65	0.8180	homPmax
	46.80	53.14	0.7628	homPmax
	63.30	98.14	0.7100	homPmax
methylcyclopentane + 2-methyl-1-propanol	33.20	26.57	0.9708	homPmax
	51.20	53.08	0.9676	homPmax
	70.00	100.35	0.9433	homPmax
methylcyclopentane + 1-propanol[a]	41.90	39.70	0.9358	homPmax
	49.50	53.13	0.8731	homPmax
	67.70	101.18	0.8271	homPmax
methylcyclopentane + 2-methyl-2-propanol	26.20	26.51	0.8606	homPmax
	45.05	53.12	0.8077	homPmax
	66.20	99.93	0.7441	homPmax
methylcyclopentane + tetrachloromethane[d]		26.46		none
		100.10		none
methylcyclopentane + 2-methyl-2-butanol	30.80	26.43	0.9793	homPmax
	49.90	52.96	0.9645	homPmax
	71.60	101.80	0.9449	homPmax
2,3-butanedione + 1-propanol[b]	36.10	12.86	0.7652	homPmax
	61.30	39.77	0.7114	homPmax
	86.15	100.67	0.6400	homPmax
2,3-butanedione + toluene[b]	37.50	12.92	0.8870	homPmax
	63.20	39.65	0.9326	homPmax
	89.55	101.34	0.9513	homPmax
1,1-dichloroethane [R150A] + hexane[d]	30.80	40.30	0.7784	homPmax
	56.15	101.21	0.8025	homPmax
	88.35	264.50	0.8590	homPmax
1,1-dichloroethane [R150A] + 2-propanol[a]	31.10	39.77	0.9286	homPmax
	56.40	101.60	0.8928	homPmax
1,2-dichloroethane + methylcyclohexane[d]	27.30	13.11	0.7394	homPmax
	54.10	39.81	0.7704	homPmax
	81.50	101.21	0.8036	homPmax
1,2-dichloroethane + 2-methyl-1-propanol[b]	28.95	13.02	0.9811	homPmax
	55.90	39.77	0.9641	homPmax
	82.90	101.25	0.9173	homPmax
1,2-dichloroethane + trichloroethylene[b]	27.20	12.76	0.6530	homPmax
	55.00	40.10	0.6506	homPmax
	82.20	101.36	0.6676	homPmax
dichloromethane + ethanol[a]	27.20	66.50	0.9774	homPmax
	39.90	101.07	0.9689	homPmax
1,4-dioxane + toluene[a]		6.48		none
		26.22		none
		99.79		none
1,4-dioxane + propyl acetate[b]	30.60	6.40	0.7368	homPmax
	61.95	26.46	0.6837	homPmax
	100.20	101.13	0.6334	homPmax
1,4-dioxane + 2-methyl-2-butanol[b,c]		6.57		none
	61.80	26.36	0.9654	homPmax
	100.60	99.62	0.8119	homPmax
methyl acetate + cyclohexene[d]	32.10	40.03	0.8782	homPmax
	45.20	67.03	0.8957	homPmax
	57.20	102.87	0.9121	homPmax

Table 1. (continued)

component 1 + component 2	t/°C	P/kPa	y_1	type[f]
methyl acetate + methylcyclopentane	28.60	40.40	0.6621	homPmax
	52.70	99.50	0.6917	homPmax
methyl acetate + methanol	36.70	52.87	0.6986	homPmax
	53.50	101.32	0.6618	homPmax
hexane + 1,4-dioxane[a]		26.56		none
		101.74		none
heptane + 1-butanol	55.30	25.63	0.8693	homPmax
	74.00	52.68	0.8290	homPmax
	93.40	101.38	0.7728	homPmax
heptane + 1,4-dioxane	29.05	9.98	0.5489	homPmax
	52.00	26.53	0.5347	homPmax
	91.15	101.05	0.5132	homPmax
heptane + propyl acetate	31.75	9.62	0.6523	homPmax
	54.65	26.33	0.6215	homPmax
	93.60	101.38	0.5785	homPmax
2-propanol + cyclohexene	31.45	20.04	0.2770	homPmax
	47.15	40.27	0.3357	homPmax
	71.50	101.40	0.4271	homPmax
2-propanol + 2,3-butanedione	30.85	12.80	0.4545	homPmax
	54.35	39.61	0.5267	homPmax
	77.70	100.95	0.6454	homPmax
2-propanol + 1,2-dichloroethane	34.03	19.68	0.3268	homPmax
	57.10	53.15	0.4088	homPmax
	74.10	100.32	0.4742	homPmax
2-propanol + 2-methyl-2-propanol[d]	40.25	13.08	0.4242	homPmin
	55.20	30.36	0.4843	homPmin
	69.90	60.27	0.5551	homPmin
		251.78		none
2-propanol + fluorobenzene	34.20	19.67	0.2959	homPmax
	57.20	52.90	0.3907	homPmax
	74.60	101.25	0.4666	homPmax
2-propanol + 3-pentanone[c]	31.40	9.53	0.6437	homPmax
	60.20	39.95	0.8663	homPmax
		101.64		none
diisopropyl ether + 2-butanone[b]	24.95	20.31	0.8506	homPmax
	48.70	53.39	0.8315	homPmax
	67.40	101.56	0.8062	homPmax
diisopropyl ether + 2-propanol	30.60	25.84	0.9154	homPmax
	48.30	52.85	0.8543	homPmax
	66.60	103.05	0.7801	homPmax
diisopropyl ether + isopropyl *tert*-butyl ether		26.09		none
		103.20		none
1-hexene + 2-butanone	35.75	40.15	0.8412	homPmax
	61.60	100.58	0.8240	homPmax
	93.40	264.87	0.7635	homPmax
methanol + 2,3-butanedione[d]		26.64		none
		101.63		none
methanol + fluorobenzene[a]	28.80	26.55	0.5996	homPmax
	44.10	52.74	0.6314	homPmax
	60.20	101.62	0.6625	homPmax
methanol + ethyl *tert*-butyl ether[e]	26.60	26.30	0.4933	homPmax
	52.20	80.26	0.5811	homPmax
	57.80	101.54	0.6002	homPmax
octane + acetic anhydride[e]	32.50	3.71	0.7497	hetPmax LL2
	47.50	7.94	0.7068	hetPmax LL2
	63.00	16.06	0.6750	hetPmax LL2
	78.30	29.88	0.6548	hetPmax LL2
	93.60	51.50	0.6466	hetPmax LL2
pentane + methanol	24.40	79.91	0.8045	homPmax
pentane + methyl *tert*-amyl ether[e]		79.83		none
		102.30		none
2-methyl-2-propanol + ethylbenzene[c]	28.87	7.16	0.9669	homPmax
		27.19		none
		101.18		none
2-methyl-2-propanol + cyclohexene	33.20	20.03	0.2328	homPmax
	49.20	39.95	0.3049	homPmax
	72.85	99.61	0.4172	homPmax
2-methyl-2-propanol + 1,2-dichloroethane	26.30	13.08	0.2730	homPmax
	50.55	39.81	0.3553	homPmax
	76.30	101.43	0.4664	homPmax
tetrahydrofuran + acetonitrile[b]	29.10	26.31	0.9616	homPmax
	46.85	53.22	0.9467	homPmax
	65.80	101.12	0.9216	homPmax
tetrahydrofuran + ethanol[b]	46.70	53.31	0.9869	homPmax
	53.05	66.13	0.9612	homPmax
	65.50	100.53	0.9048	homPmax
tetrahydrofuran + water	63.25	100.93	0.8122	homPmax
	75.20	150.69	0.7709	homPmax LL2
	91.30	250.15	0.7194	homPmax LL2
	102.75	349.96	0.6975	homPmax LL2
tetrachloroethylene + octane[a,b]	30.40	3.36	0.8665	homPmax
	60.10	12.96	0.8343	homPmax
	98.75	53.44	0.8781	homPmax

Table 1. (continued)

component 1 + component 2	t/°C	P/kPa	y_1	type[f]
tert-butyl chloride + acetone[a]	31.25	53.23	0.8277	homPmax
	48.90	102.11	0.8056	homPmax
1,1,2-trichloro-1,2,2-trifluoroethane [R113] + ethanol[e]	27.45	53.16	0.8825	homPmax
	44.60	101.42	0.8456	homPmax
1,1,2-trichloro-1,2,2-trifluoroethane [R113] + 2-propanol[e]	28.60	53.10	0.9467	homPmax
	46.20	100.95	0.9159	homPmax
1,1,2-trichloro-1,2,2-trifluoroethane [R113] + 2-methyl-2-propanol[e]	29.00	52.97	0.9601	homPmax
	46.80	101.08	0.9426	homPmax
propyl acetate + methylcyclohexane	38.50	12.99	0.3337	homPmax
	66.75	39.83	0.3896	homPmax
	95.25	100.90	0.4746	homPmax
1-pentene + methanol	26.90	102.47	0.8531	homPmax
methyl *tert*-butyl ether + ethanol[a]		39.30		none
	42.40	66.29	0.9827	homPmax
	55.10	101.15	0.9417	homPmax
	70.90	170.00	0.8868	homPmax
	85.55	259.34	0.8228	homPmax
	93.10	318.49	0.7987	homPmax
methyl *tert*-butyl ether + acetone[a]	29.50	46.85	0.5539	homPmax
	39.10	67.02	0.5363	homPmax
	51.20	102.19	0.5176	homPmax
methyl *tert*-amyl ether + 2-butanol[c]		12.90		none
	58.15	39.96	0.9766	homPmax
	78.05	80.09	0.9356	homPmax
	86.00	102.12	0.9009	homPmax

[a] Contradictory published azeotropic data. [b] Greater deviations between experimental and predicted azeotropic data. [c] Interesting azeotropic behavior. [d] Different (zeotropic or azeotropic) behavior reported by Lecat (1949). [e] No azeotropic behavior published in the literature. [f] See Table 2 for the definition of the abbreviations used for the type of azeotrope.

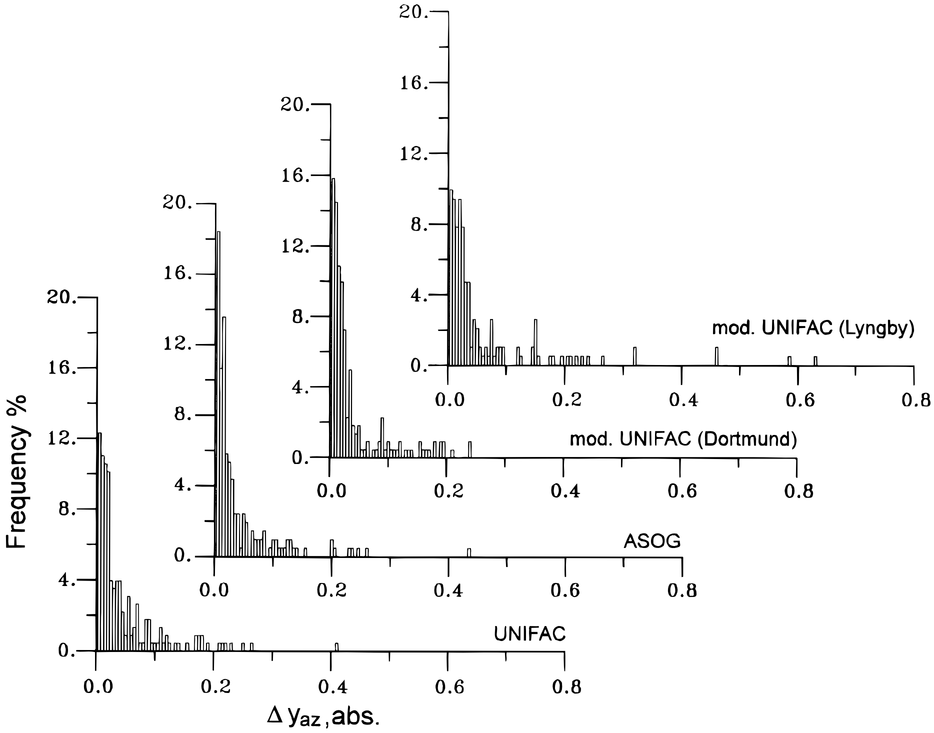

Figure 2. Distribution of deviations between experimental and predicted binary azeotropic composition for the different group contribution methods.

UNIFAC (Gmehling et al., 1993). There is good agreement between experiment and prediction. Also the correct temperature dependence is obtained, which in most cases mainly depends on the slope of the vapor pressure data (enthalpy of vaporization) and only to a smaller extent on the temperature dependence of the activity coefficients and the partial molar excess enthalpies. Figure 3 also shows that the experimental (predicted) azeotropic behavior of the system methyl *tert*-butyl ether + ethanol disappears below 40 °C (~36 °C).

Figure 4 shows the interesting azeotropic behavior of the system acetone (1) + carbon tetrachloride (2). Because of the change of the sign of the partial molar excess enthalpies with temperature, which is connected with a maximum value of the activity coefficient at infinite dilution γ_2^∞ as a function of temperature, this system shows azeotropic behavior only in a narrow temperature range to fulfill the well-known condition for pressure maximum azeotropes (Gmehling et al., 1994):

$$\ln \gamma_2^\infty > \ln(P_1^s/P_2^s) > -[\ln \gamma_1^\infty] \qquad (1)$$

γ_i^∞ is the activity coefficient of component i at infinite dilution, and P_i^s is the vapor pressure of component i.

Besides the current data, values reported by other authors (Gmehling et al., 1994) are shown together with

Table 2. Azeotropic Information for Selected Ternary Systems

component 1 + component 2 + component 3	t/°C	P/kPa	y_1	y_2	type[f]
acetone + methanol + ethanol[e]		99.28			none
acetone + methanol + benzene[e]		99.04			none
acetone + methanol + cyclohexane	51.90	103.35	0.4270	0.3071	homPmax
acetone + methanol + hexane[d]	30.80	53.09	0.4076	0.2164	homPmax
	41.20	80.03	0.3635	0.2668	homPmax
	47.30	100.82	0.3280	0.2951	homPmax
ethanol + acetonitrile + water[c]		39.33			none
	55.30	52.57	0.4608	0.5315	homPmax
	73.00	101.98	0.5206	0.4518	homPmax
acetone + ethanol + benzene[e]		100.42			none
ethanol + 2-butanone + cyclohexane[d]	30.90	26.17	0.2508	0.1940	homPmax
	47.40	52.65	0.3277	0.1314	homPmax
	65.00	102.05	0.4182	0.0536	homPmax
ethanol + 2-butanone + water	39.20	26.03	0.0324	0.7365	homPmax
	56.10	52.99	0.0461	0.6839	homPmax
	73.10	101.10	0.1140	0.6108	homPmax
ethanol + 1,2-dichloroethane + trichloroethylene[a]	31.40	20.37	0.3548	0.4463	homPmax
	53.60	53.59	0.4317	0.3551	homPmax
	70.50	101.86	0.4824	0.2818	homPmax
ethanol + water + ethylbenzene[a]	35.50	14.54	0.6221	0.2561	homPmax LL2
	77.43	100.64	0.6474	0.2624	homPmax LL2
benzene + cyclohexane + 1-butanol[a]	31.60	19.91	0.4720	0.5153	homPmax
	57.50	53.52	0.4784	0.4992	homPmax
	76.90	100.51	0.4770	0.4889	homPmax
benzene + cyclohexane + 2-methyl-2-propanol[a]	29.60	19.74	0.3446	0.4888	homPmax
	53.30	53.19	0.2906	0.4534	homPmax
	71.70	101.99	0.2331	0.4335	homPmax
chloroform + methanol + ethanol[e]		103.55			none

[a] Contradictory published azeotropic data. [b] Greater deviations between experimental and predicted azeotropic data. [c] Interesting azeotropic behavior. [d] Different (zeotropic or azeotropic) behavior reported by Lecat (1949). [e] No azeotropic behavior published in the literature. [f] Abbreviations used for the type of azeotrope: homPmax, homogeneous pressure maximum azeotrope; homPmin, homogeneous pressure minimum azeotrope; hetPmax, heterogeneous pressure maximum azeotrope; none, zeotrope; LL2, heterogeneous system (two liquid phases).

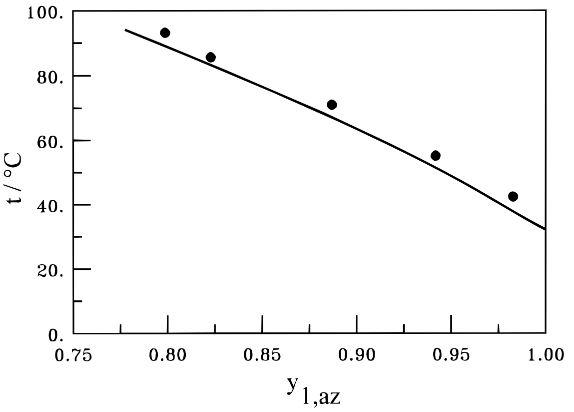

Figure 3. Experimental azeotropic data for the binary system MTBE + ethanol in the temperature range 0−100 °C: (—) modified UNIFAC.

Table 3. Mean Deviation between Experimental and Predicted Binary Azeotropic Data for Different Group Contribution Methods

group contribution model	number of azeotropic data	ΔP_{abs}/kPa	$\Delta y_{az,abs}$
UNIFAC	227	2.44	0.0432
ASOG	206	1.77	0.0374
modified UNIFAC (Lyngby)	191	1.91	0.0384
modified UNIFAC (Dortmund)	221	1.28	0.0230

the results predicted with the help of modified UNIFAC (Gmehling et al., 1993). For the modified UNIFAC besides the parameters published, revised parameters have been used, which were fitted simultaneously to vapor−liquid equilibria (VLE), heat of mixing data (H^E), activity coefficients at infinite dilution (γ^∞), and solid−liquid equilibrium data.

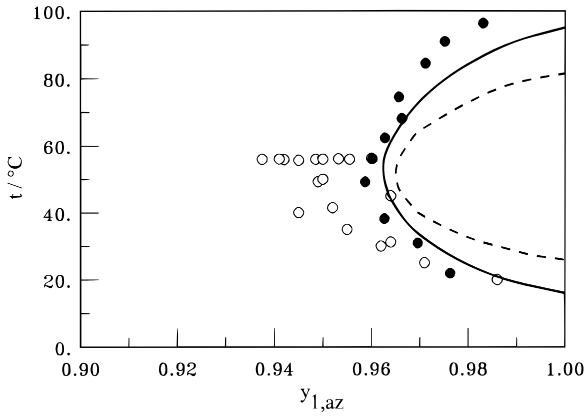

Figure 4. Experimental and calculated azeotropic data for the system acetone (1) + carbon tetrachloride (2) as a function of temperature: (●) own data, (○) data from the literature, (—) modified UNIFAC (new), (- - -) modified UNIFAC (old).

Another typical example is shown in Figure 5. It shows the results of the different group contribution methods for acetonitrile with 2-propanol. The improvement achieved by modified UNIFAC (Dortmund) compared to original UNIFAC comes from the distinctive better description of the temperature dependence of the activity coefficients (excess enthalpies). This is also demonstrated in Figure 6, where besides the experimental the predicted heats of mixing, results for this system at 25 °C using UNIFAC and modified UNIFAC (Dortmund) are shown.

As can be seen from Figure 2 also for modified UNIFAC (Dortmund), poor results are obtained for a limited number of systems. All models show great deviations for the nearly ideal system 2-propanol + 2-methyl-2-propanol because the ratio of the vapor pressures is nearly unity and the azeotropic composition responds very sensitively to the small deviations from Raoult's law predicted by the different group contribution methods. Furthermore, all models have difficulty describing the behavior of systems with butane-2,3-dione and *tert*-butyl chloride, since up to now proximity effects were not described properly with the

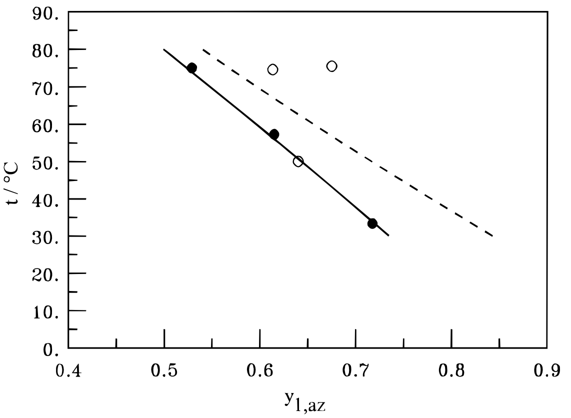

Figure 5. Experimental and predicted azeotropic data for binary systems with acetonitrile as a function of temperature: (●) own data, (○) data from the literature, (—) modified UNIFAC, (- - -) UNIFAC.

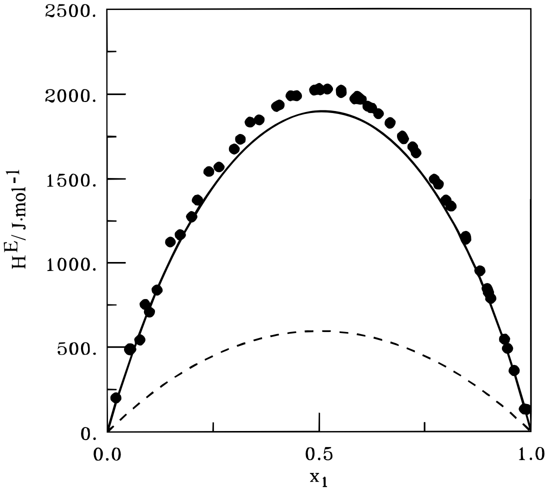

Figure 6. Experimental and predicted H^E data for the binary system acetonitrile (1) + 2-propanol (2) at 25 °C: (—) modified UNIFAC, (- - -) UNIFAC.

limited number of group interaction parameters. With the exception of modified UNIFAC (Dortmund) all other group contribution methods show great problems for systems with 1,4-dioxane. With modified UNIFAC (Lyngby), further poor results are obtained for systems with esters.

The experimental data for the ternary systems are listed in Table 2. All experimental ternary data were compared with the results of the group contribution methods UNIFAC and modified UNIFAC (Dortmund). Both methods were able to confirm the observed (zeotropic and azeotropic, respectively) behavior of the systems investigated. The mean deviations between experimental and predicted results for the two group contribution methods are listed in Table 4. Again it can be seen that better results are achieved by modified UNIFAC (Dortmund). The larger deviations of the mole fraction at the azeotropic point ($\Delta y_{az,abs} = 0.0324$) of modified UNIFAC (Dortmund) compared to those of binary systems ($\Delta y_{az} = 0.0230$) are mainly caused by the poor results obtained for the system ethanol + 2-butanone + water. Neglecting this system, a mean deviation of 1.74 mol % in the vapor phase mole fraction is obtained for modified UNIFAC (Dortmund). The larger deviations obtained for original UNIFAC are caused by the fact that for original UNIFAC poor results are obtained not only for the system ethanol + 2-butanone + water but also for the systems ethanol + acetonitrile + water and ethanol + 1,2-dichloroethane + trichloroethylene.

Table 4. Mean Deviation between Experimental and Predicted Ternary Azeotropic Data for the UNIFAC and Modified UNIFAC (Dortmund) Methods

group contribution model	number of azeotropic data	ΔP_{abs}/kPa	$\Delta y_{az,abs}$
UNIFAC	21	1.53	0.0767
modified UNIFAC (Dortmund)	21	1.33	0.0324

Conclusions

A total of 273 binary and 28 ternary azeotropic and zeotropic data at moderate pressures have been measured with the help of a wire band column. These data were measured primarily to judge the reliability of published azeotropic and zeotropic data. Furthermore, data have been measured to complete the data bank on azeotropic data which will be used as an additional software tool for the synthesis of distillation processes and in addition with other data banks (e.g., for VLE, h^E, γ^∞, ...) for the further development of group contribution methods and the determination of reliable temperature dependent excess Gibbs energy (g^E) model parameters by a simultaneous fit to the various thermodynamic properties. Besides VLE, h^E, and γ^∞ in particular, reliable ternary azeotropic data are ideal to check the reliability of the parameters before starting the process simulation.

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