

Binary Azeotropic Data at Different Pressures for Systems with 2-Ethoxyethanol, 2-Methyl-1-butanol, and Dimethyl Carbonate. 2

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Binary azeotropic data for 2-ethoxyethanol + ethylbenzene, 2-ethoxyethanol + *o*-xylene, 2-ethoxyethanol + *m*-xylene, 2-ethoxyethanol + *p*-xylene, 2-methyl-1-butanol + ethylbenzene, 2-methyl-1-butanol + *o*-xylene, 2-methyl-1-butanol + *m*-xylene, 2-methyl-1-butanol + *p*-xylene, dimethyl carbonate + cyclohexane, dimethyl carbonate + methylcyclopentane, dimethyl carbonate + hexane, and dimethyl carbonate + heptane have been measured at different pressures. The experimental azeotropic data were compared with the results predicted using the group contribution methods ASOG, UNIFAC, modified UNIFAC (Dortmund), and modified UNIFAC (Lyngby).

Introduction

Systems that show homogeneous azeotropic points cannot be separated by ordinary distillation. When the azeotrope does not disappear at lower or higher pressures, more complex distillation processes, such as extractive, azeotropic, salt, pressure swing distillation, or hybrid separation processes, have to be applied. The knowledge of azeotropic points as a function of pressure (temperature) is of particular importance for the synthesis and design of distillation processes (Gmehling and Brehm, 1996). Experimental azeotropic information can directly be used, for example, to select suitable solvents for azeotropic distillation by access to a factual data bank with azeotropic data. This possibility is one of the reasons that a data bank for azeotropic data was added to the Dortmund Data Bank. The data (35 000) stored before 1993 have been published in the form of a data compilation (Gmehling et al., 1994).

Continuously this data bank will be updated using new published data and data measured in our laboratory (Gmehling and Boelts, 1996). Today this data bank contains more than 41 000 pieces of information on azeotropic or nonazeotropic behavior.

In this paper new experimental binary azeotropic data are presented for 2-ethoxyethanol and 2-methyl-1-butanol + ethylbenzene + *o*-xylene + *m*-xylene + *p*-xylene and dimethyl carbonate + cyclohexane + methylcyclopentane + hexane + heptane at different pressures.

It has been shown that group contribution methods such as ASOG (Kojima and Tochigi, 1979), UNIFAC (Fredenslund et al., 1977), modified UNIFAC (Dortmund) (Weidlich and Gmehling, 1987; Gmehling et al., 1993), and modified UNIFAC (Lyngby) (Larsen et al., 1987) are effective methods for the prediction of phase equilibria and other thermodynamic properties. In this paper these group contribution methods have been used to predict and to compare with the experimental azeotropic points for the systems mentioned above.

Experimental Section

2-Ethoxyethanol, 2-methyl-1-butanol, dimethyl carbonate, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, cyclohex-

Table 1. Supplier and Purity of the Chemicals

compound	supplier	purity
2-ethoxyethanol	Aldrich	>99%
2-methyl-1-butanol	Merck	>97%
dimethyl carbonate	Aldrich	>99%
ethylbenzene	Merck	>99%
<i>o</i> -xylene	Janssen	>99%
<i>m</i> -xylene	Aldrich	>99%
<i>p</i> -xylene	Aldrich	>99%
cyclohexane	Scharlau	>99.5%
methylcyclopentane	Janssen	>99%
hexane	Riedel de Haen	>97%
heptane	Merck	>99%

ane, methylcyclopentane, hexane, and heptane used in this work were obtained from different suppliers. 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. The suppliers of the chemicals are listed in Table 1. All chemicals used were dried prior to measurements with the help of molecular sieve 4A.

The experiments were performed using a commercially available micro-spinning band column with an electronically controlled reflux ratio from NORMAG GmbH (Hofheim, Germany). This apparatus allows measurements at both low pressures and pressures up to 3.5 bar with the help of a vacuum pump for pressures below atmospheric and a nitrogen reservoir with a pressure of ~5 bar for higher pressures. 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. During the experiments the temperature was measured 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. A more detailed description of the apparatus and the experimental procedure are given by Gmehling and Boelts (1996).

Gas-liquid chromatography was used for the analytical determination of the azeotropic composition. The required

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Table 2. Experimental Azeotropic Data for the Binary Systems with 2-Ethoxyethanol (1)

component 2	$t/^\circ\text{C}$	P/kPa	y_1
ethylbenzene	51.70	5.85	0.2924
	67.90	12.45	0.3254
	86.20	26.02	0.3645
	106.10	52.06	0.4147
	127.90	100.94	0.4632
<i>o</i> -xylene	43.90	3.31	0.3940
	45.20	3.51	0.4028
	60.70	7.52	0.4366
	76.50	15.38	0.4773
	95.60	32.73	0.5271
	114.20	59.17	0.5682
	123.60	79.69	0.5876
	131.80	101.36	0.5965
<i>m</i> -xylene	40.20	3.32	0.3161
	68.00	13.11	0.3810
	86.40	27.21	0.4196
	107.80	55.22	0.4726
	119.90	79.14	0.5008
<i>p</i> -xylene	129.20	100.73	0.5245
	38.00	2.80	0.2995
	88.90	27.29	0.4061
	109.20	55.41	0.4634
	120.70	79.17	0.4894
	129.40	102.19	0.5042

factors to determine the compositions from the recorded peak area ratios were obtained using prepared test mixtures of accurately known composition. The accuracy of the azeotropic composition measured is approximately 0.25 mol %. To check that the system shows azeotropic (separation factor $\alpha_{12} = 1$) and not quasiazeotropic ($\alpha_{12} \approx 1$) behavior, the experiments were always repeated starting with a different feed composition. In addition, the distillate at the given pressure was used as the feed to check again for azeotropy in the case of homogeneous azeotropes.

Results

The results for the eight binary systems with 2-ethoxyethanol and 2-methyl-1-butanol at different pressures are listed in Tables 2 and 3. All systems investigated show a homogeneous pressure maximum azeotrope in the temperature range covered, whereby the concentration of the polar compound (2-ethoxyethanol, 2-methyl-1-butanol) strongly increases with pressure (temperature) because of the stronger temperature dependence of the vapor pressure for these compounds.

The experimental data were compared with published data (Garber and Bovkun, 1965; Lecat, 1993–94) and the results obtained by different group contribution methods, such as ASOG (Kojima and Tochigi, 1979), UNIFAC (Fredenslund et al., 1977), 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 and in all cases ideal behavior in the vapor phase, respectively, $\varphi_i^s = \varphi_i^v$ was assumed. This means that the following simplified equation was used for predicting the azeotropic composition:

$$x_i \gamma_i P_i^s = y_i P$$

A summary of the comparison (mean absolute deviation in vapor-phase composition) for the different group contribution models is given in Table 4. It can be seen that the two modified UNIFAC versions perform a little better than the original UNIFAC and the ASOG method.

Table 3. Binary Azeotropic Data for the Systems with 2-Methyl-1-butanol (1)

component 2	$t/^\circ\text{C}$	P/kPa	y_1
ethylbenzene	36.30	2.61	0.2107
	87.50	27.13	0.3989
	106.90	55.06	0.4834
	118.20	78.94	0.5468
	125.60	99.46	0.5657
<i>o</i> -xylene	41.00	2.62	0.3321
	91.10	26.99	0.5548
	109.20	54.93	0.6500
	120.30	78.83	0.6942
	128.90	101.87	0.7417
	<i>m</i> -xylene	37.20	2.80
87.20		27.20	0.4549
106.70		55.14	0.5407
<i>p</i> -xylene	118.20	79.05	0.5946
	127.50	101.85	0.6316
	36.70	2.65	0.2424
	85.00	27.08	0.4412
	103.30	55.00	0.5103
115.30	78.77	0.5734	
127.00	101.07	0.6273	

Table 4. Mean Absolute and Maximum Deviation between Experimental and Predicted Azeotropic Compositions

	UNIFAC (Dortmund)	modified UNIFAC (Lyngby)	modified UNIFAC (Lyngby)	ASOG
Systems with 2-Methyl-1-butanol				
mean Δy deviation	0.0130	0.0130	0.0094	0.0170
maximum Δy deviation	0.0298	0.0368	0.0266	0.0654
Systems with 2-Ethoxyethanol				
mean Δy deviation	0.0192	0.0138	0.0150	0.0225
maximum Δy deviation	0.0438	0.0430	0.0325	0.0513

Table 5. Binary Azeotropic Data for Hydrocarbon Systems with Dimethyl Carbonate (1)

hydrocarbon (2)	$t/^\circ\text{C}$	P/kPa	y_1	$y_{1,\text{calcd}}$	Δy_1^a
cyclohexane	39.60	30.13	0.342	0.3495	0.0075
	58.10	59.97	0.362	0.3641	0.0021
	73.80	101.49	0.378	0.3761	-0.0019
methylcyclopentane	34.20	29.96	0.238	0.2403	0.0023
	52.70	60.36	0.255	0.2531	-0.0019
	69.20	103.46	0.268	0.2635	-0.0045
hexane	32.40	30.10	0.216	0.2388	0.0228
	50.60	60.23	0.234	0.2540	0.0200
	65.00	98.46	0.254	0.2649	0.0109
heptane	48.40	29.89	0.565	0.5810	0.0160
	66.80	60.15	0.577	0.5982	0.0212
	82.00	99.67	0.593	0.6127	0.0197
mean absolute deviation					0.0109
maximum absolute deviation					0.0228

$$^a \Delta y_1 = y_{1,\text{calcd}} - y_1.$$

The experimental results for the binary systems with dimethyl carbonate are given in Table 5 together with the predicted results. Since systems with dimethyl carbonate can only be described with new parameters of the modified UNIFAC (Dortmund) method, no results are given for the other group contribution methods. As can be seen nearly perfect agreement (mean deviation $\Delta y = 0.0034$) is obtained for the systems with cyclic alkanes (naphthenes). For *n*-alkanes (hexane, heptane) a larger mean deviation is obtained (mean deviation $\Delta y = 0.0184$).

Figure 1 shows a comparison between the experimental and the predicted results for all systems with dimethyl carbonate. At the same time the values reported by Lecat (1949) and Cocero et al. (1991) are given. It can be seen

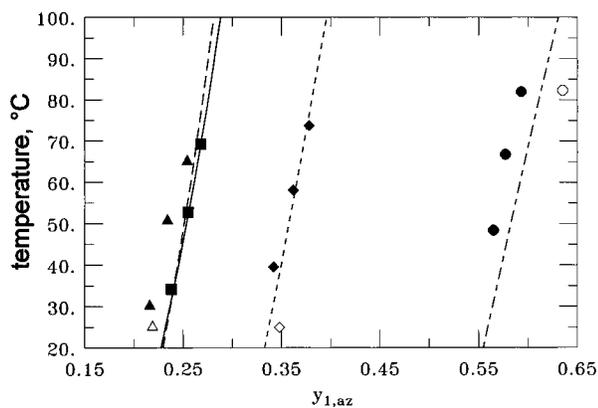


Figure 1. Experimental and predicted (modified UNIFAC (Dortmund)) azeotropic data for different systems with dimethyl carbonate (1): (◆) ---, cyclohexane, (◇) Cocero et al. (1991); (■) —, methylcyclopentane; (▲) — —, hexane, (△) Cocero et al. (1991); (●) — — —, heptane, (○) Lecat (1946).

that our data are in good agreement with the predicted results and with the data reported by other authors.

Conclusion

Binary azeotropic data for systems with 2-ethoxyethanol, 2-methyl-1-butanol, and dimethyl carbonate with different hydrocarbons have been measured. The data will be used for the further development of group contribution methods and to extend the applicability of factual data banks for the selection of entrainers for azeotropic distillation (Möllmann and Gmehling, 1997).

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