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High-Pressure Vapor–Liquid Equilibria for CO_2 + Benzonitrile, CO_2 + Benzyl Alcohol, CO_2 + 2-*tert*-Butylphenol, CO_2 + Methoxybenzene, and CO_2 + 1,2,3,4-Tetrahydronaphthalene at Temperatures between 313 and 393 K and Pressures up to 20 MPa

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High-pressure vapor–liquid equilibria are reported for CO_2 + benzonitrile, CO_2 + benzyl alcohol, CO_2 + 2-*tert*-butylphenol, CO_2 + methoxybenzene, and CO_2 + 1,2,3,4-tetrahydronaphthalene at three temperatures from 313 to 393 K and pressures up to 20 MPa. The investigations were made by using a flow-type apparatus. The results for CO_2 + methoxybenzene are compared to literature values. On the other systems no literature values are available.

Introduction

High-pressure vapor–liquid equilibria of CO_2 in mixtures with substituted benzenes are of increased interest to develop and simulate separation processes, especially with relation to supercritical extraction in pharmaceutical and biotechnological industries. To reduce costly and expensive experimental investigations, new methods for correlating and predicting high-pressure phase equilibria are needed. Developing such methods requires more experimental data.

The present investigation is primarily aimed at providing more information on the phase behavior in mixtures of CO_2 and aromatic hydrocarbons.

The measurements were done using a flow-technique apparatus described elsewhere (*1–3*). Experimental results are reported for five binary mixtures of CO_2 and benzonitrile, benzyl alcohol, 2-*tert*-butylphenol, methoxybenzene, and 1,2,3,4-tetrahydronaphthalene at temperatures between 313 and 393 K and pressures up to 20 MPa. For CO_2 + methoxybenzene the new experimental data are compared to literature values of Park et al. (*4*).

Experimental Section

The flow apparatus used in this work was designed for temperatures from 300 to 420 K and pressures up to 30 MPa. The apparatus and the procedures were identical with those described elsewhere (*1–3*).

The pure liquids were compressed, mixed, and equilibrated. The vapor and the liquid were separated and collected in different cooling traps, where the aromatic compound was retained while the carbon dioxide escaped through wet test meters.

During an experiment, which typically lasted for about 3–15 min, pressure and temperature fluctuated by less than ±0.1 MPa and ±0.1 K, respectively. These fluctuations correspond to the uncertainties of the measurement of pressure and temperature. Pressure was measured by a calibrated high-precision gauge, and temperature by a calibrated platinum resistance thermometer placed in the bath used for thermostating the coexisting phases. The volume of gaseous carbon dioxide passing the wet test meters was typically about 60 dm^3 (vapor phase) and about 3 dm^3 (liquid phase). It was determined by an uncertainty of less than ±0.6%. The amount of the aromatic component collected in the cooling traps was typically about 14 g (liquid phase) and 2 g (gaseous phase). It was determined with an uncertainty of about ±0.002 g.

Table I. Vapor–Liquid Equilibria for the System Carbon Dioxide (1) + Benzonitrile (2)

T/K	p/MPa	x_1	y_2	T/K	p/MPa	x_1	y_2
313.2	6.09	0.5666	0.0008	353.2	16.08	0.7789	0.0370
	6.59	0.6225	0.0008		16.08	0.7775	0.0356
	6.59	0.6178	0.0007	393.2	6.49	0.2491	0.0062
	7.09	0.6766	0.0013		8.09	0.3040	0.0066
	7.09	0.6830	0.0012		10.09	0.3716	0.0077
	7.59	0.7723	0.0014		10.09	0.3733	0.0076
	8.09	0.9267	0.0028		12.09	0.4411	0.0094
	8.09	0.9379	0.0030		12.09	0.4416	0.0094
353.2	6.09	0.3320	0.0019		14.09	0.5027	0.0122
	8.09	0.4335	0.0023		14.09	0.5052	0.0120
	8.09	0.4281	0.0022		14.09	0.5020	0.0116
	10.09	0.5232	0.0035		16.09	0.5589	0.0163
	10.09	0.5221	0.0037		16.09	0.5614	0.0165
	12.09	0.6007	0.0069		16.09	0.5609	0.0158
	12.09	0.6019	0.0072		18.09	0.6263	0.0224
	14.09	0.6882	0.0139		18.09	0.6217	0.0236

Table II. Vapor–Liquid Equilibria for the System Carbon Dioxide (1) + Benzyl Alcohol (2)

T/K	p/MPa	x_1	y_2	T/K	p/MPa	x_1	y_2
313.2	6.09	0.2760	0.0003	353.2	12.09	0.3397	0.0026
	6.09	0.2768	0.0003		14.09	0.3805	0.0052
	8.09	0.3568	0.0006		14.09	0.3852	0.0050
	8.09	0.3581	0.0005		16.08	0.4121	0.0087
	8.09	0.3605	0.0007		16.08	0.4114	0.0090
	8.09	0.3624	0.0006	393.1	6.09	0.1622	0.0025
	8.09	0.3642	0.0007		6.09	0.1614	0.0024
	9.09	0.3739	0.0027		8.09	0.2013	0.0032
	9.09	0.3777	0.0028		8.09	0.2012	0.0029
	10.09	0.3879	0.0076		10.09	0.2438	0.0037
	10.09	0.3908	0.0083		10.09	0.2415	0.0038
	12.09	0.3986	0.0110		12.09	0.2830	0.0046
	12.09	0.3987	0.0113		12.09	0.2858	0.0045
	12.09	0.4008	0.0115		14.09	0.3225	0.0061
	12.09	0.3970	0.0116		14.09	0.3248	0.0055
	14.09	0.4035	0.0136		16.08	0.3604	0.0079
	14.09	0.4115	0.0135		18.08	0.3966	0.0114
353.2	6.09	0.1933	0.0009		18.08	0.3995	0.0114
	8.09	0.2423	0.0009		20.08	0.4293	0.0159
	8.09	0.2468	0.0008		20.08	0.4268	0.0160
	10.09	0.2980	0.0012				

The repeatability of the measurements at constant temperature and pressure was in general within ±1.5% of the mole fraction of carbon dioxide in the liquid phase and within

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Table III. Vapor–Liquid Equilibria for the System Carbon Dioxide (1) + 2-*tert*-Butylphenol (2)

T/K	p/MPa	x_1	y_2	T/K	p/MPa	x_1	y_2
353.2	6.09	0.3099	0.0006	373.2	14.09	0.5374	0.0046
	6.09	0.3085	0.0008		16.08	0.5932	0.0101
	8.09	0.3982	0.0006		16.08	0.6038	0.0099
	8.09	0.3851	0.0006		18.08	0.6648	0.0155
	8.09	0.3948	0.0008		18.08	0.6646	0.0157
	8.09	0.3928	0.0006		18.08	0.6657	0.0162
	10.09	0.4817	0.0014		20.09	0.6954	0.0285
	10.09	0.4706	0.0012		20.09	0.7224	0.0275
	10.09	0.4766	0.0013		20.09	0.7371	0.0281
	12.09	0.5553	0.0033	393.1	6.09	0.2367	0.0022
	12.09	0.5502	0.0034		6.09	0.2435	0.0021
	14.08	0.6204	0.0070		8.09	0.3041	0.0022
	14.08	0.6277	0.0070		8.09	0.3167	0.0023
	16.08	0.6798	0.0161		10.09	0.3733	0.0028
	16.08	0.6968	0.0165		10.09	0.3775	0.0027
	18.08	0.7515	0.0348		10.09	0.3748	0.0030
	18.08	0.7436	0.0340		10.09	0.3789	0.0030
373.2	6.09	0.2678	0.0011		12.09	0.4324	0.0043
	6.09	0.2688	0.0009		12.09	0.4270	0.0043
	8.09	0.3456	0.0012		14.09	0.4978	0.0059
	8.09	0.3484	0.0013		16.08	0.5408	0.0089
	8.09	0.3426	0.0014		16.08	0.5464	0.0088
	10.09	0.4162	0.0020		18.08	0.6003	0.0130
	10.09	0.4076	0.0020		18.08	0.6042	0.0128
	12.09	0.4861	0.0024		20.08	0.6411	0.0204
	12.09	0.4881	0.0022		20.08	0.6484	0.0198
	12.09	0.4897	0.0027		20.08	0.6494	0.0200
	14.09	0.5511	0.0046				

Table IV. Vapor–Liquid Equilibria for the System Carbon Dioxide (1) + Methoxybenzene (2)

T/K	p/MPa	x_1	y_2	T/K	p/MPa	x_1	y_2
313.2	5.69	0.5210	0.0018	353.1	13.54	0.7621	0.0341
	5.69	0.5251	0.0018		13.54	0.7600	0.0334
	6.16	0.5945	0.0018		13.54	0.7673	0.0340
	6.16	0.6002	0.0018	393.2	6.16	0.2355	0.0157
	6.66	0.6562	0.0026		6.16	0.2344	0.0163
	6.66	0.6533	0.0025		7.63	0.2973	0.0160
	7.16	0.7867	0.0028		7.63	0.2923	0.0165
	7.16	0.7801	0.0030		7.63	0.2938	0.0161
	7.16	0.7817	0.0029		9.59	0.3630	0.0181
	7.16	0.7864	0.0026		9.59	0.3590	0.0179
	7.63	0.9145	0.0042		11.56	0.4377	0.0216
	7.63	0.9186	0.0051		11.56	0.4441	0.0206
353.1	5.69	0.3022	0.0053		13.54	0.5217	0.0276
	5.69	0.3010	0.0053		13.54	0.5221	0.0279
	7.63	0.4088	0.0067		15.49	0.5914	0.0377
	7.63	0.4070	0.0067		15.49	0.6016	0.0385
	9.59	0.5094	0.0091		16.47	0.6271	0.0466
	11.56	0.6240	0.0147		16.47	0.6359	0.0466
	11.56	0.6232	0.0149		16.47	0.6217	0.0465

±5% for the mole fraction of the aromatic compound in the vapor phase, only increasing to ±20% at vapor phase concentrations of the aromatic compound of less than 0.5 mol%.

The total relative uncertainty for the mole fraction of CO_2 in the liquid phase was less than ±2.5%. The corresponding value for the vapor phase concentration of the substituted benzene was ±5%, increasing to about ±20% when the concentration of the aromatic compound decreased to less than 0.5 mol %. A detailed discussion of the experimental uncertainties were given elsewhere (*3*).

Carbon dioxide was supplied by TV Kohlensäure, Ludwigshafen, Germany, with a purity of better than 99.95 mol %. The aromatic compounds were purchased from Riedel de Haen, Seelze, Germany (methoxybenzene, 99.0 mass %), and Merck, Darmstadt, Germany (benzyl alcohol, 99.0; benzonitrile, 99.0; 2-*tert*-butylphenol, 98.0; and 1,2,3,4-tetrahydronaphthalene, 98.0 mass %), and used without further purification.

Table V. Vapor–Liquid Equilibria for the System Carbon Dioxide (1) + 1,2,3,4-Tetrahydronaphthalene (2)

T/K	p/MPa	x_1	y_2	T/K	p/MPa	x_1	y_2
313.2	6.09	0.4153	0.0005	353.2	14.09	0.5577	0.0091
	6.09	0.4125	0.0004		16.08	0.6229	0.0233
	6.59	0.4479	0.0004		16.09	0.6198	0.0229
	6.59	0.4499	0.0004	393.1	6.09	0.2183	0.0040
	7.09	0.4777	0.0007		6.09	0.2178	0.0041
	7.09	0.4757	0.0009		8.09	0.2766	0.0045
	7.59	0.5360	0.0011		8.09	0.2755	0.0045
	7.59	0.5328	0.0010		10.09	0.3363	0.0056
	8.09	0.6010	0.0024		10.09	0.3370	0.0057
	8.09	0.5991	0.0023		12.09	0.3925	0.0062
353.2	6.09	0.2787	0.0010		14.09	0.4447	0.0093
	6.09	0.2671	0.0011		14.09	0.4437	0.0092
	8.08	0.3470	0.0012		16.09	0.4851	0.0128
	8.08	0.3442	0.0011		16.09	0.4850	0.0127
	10.08	0.4298	0.0021		18.08	0.5434	0.0177
	10.08	0.4228	0.0023		18.08	0.5448	0.0183
	12.09	0.5002	0.0052		18.08	0.5435	0.0183
	12.09	0.5033	0.0051		20.08	0.5886	0.0267
	14.09	0.5576	0.0111		20.08	0.5964	0.0274
	14.09	0.5607	0.0114		20.08	0.5854	0.0275

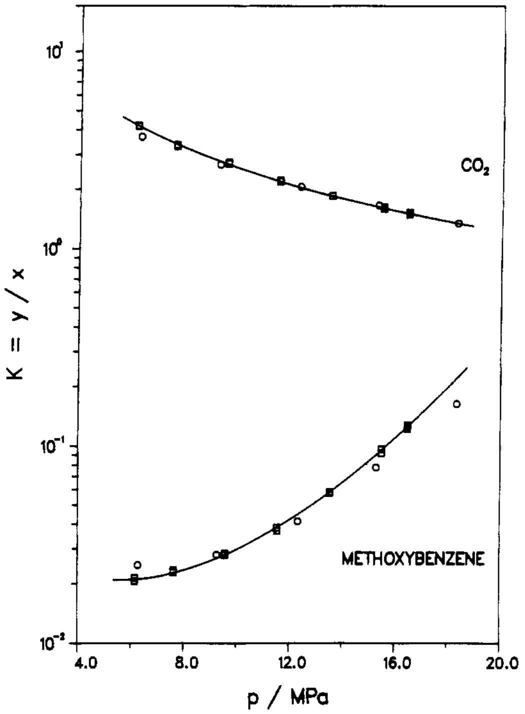

Figure 1. Comparison of the new experimental data (□) for carbon dioxide + methoxybenzene with literature values of Park et al. (○) for 393.2 K.

Results and Discussion

The vapor–liquid equilibria of the five binary systems CO_2 (1) + benzonitrile (2), CO_2 (1) + benzyl alcohol (2), CO_2 (1) + 2-*tert*-butylphenol (2), CO_2 (1) + methoxybenzene (2), and CO_2 (1) + 1,2,3,4-tetrahydronaphthalene (2) were determined for three temperatures (313, 353, and 393 K) and at pressures from about 5.7 to 20.1 MPa. The maximum pressure was limited by problems in separating the liquid and the vapor phases near the mixture critical point. The liquid mole fraction of carbon dioxide x_1 ranged from about 0.16 to 0.94. The vapor-phase mole fraction of the aromatic compound y_2 ranged from less than 0.0005 to about 0.047. The experimental results for all five binary systems are given in Tables I–V.

The experimental results for the binary system carbon dioxide + methoxybenzene can be compared with those of Park et al. (*4*), who reported data for 393 K, measured by a circulation method. For this system K factors are plotted in

Figure 1. As shown in Figure 1 the new data compare well with those of Park et al. especially at higher pressures. By interpolating our data to the liquid-phase compositions of the literature data, the resulting average relative deviations of pressure and vapor-phase composition of methoxybenzene are about 3.6% and 13.7%, respectively.

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