Measurement and Calculation of Critical Points for Binary and Ternary Mixtures

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The critical lines (temperatures and pressures) for the three binary mixtures ethane + sulfur hexafluoride (SF_6), SF_6 + propane, and carbon dioxide (CO_2) + SF_6, and the critical surface for the ternary system CO_2 + ethane + SF_6 were determined experimentally by a flow method. The binary data were compared to predictions using the predictive Soave-Redlich-Kwong (PSRK) group contribution equation of state (EoS). For the system CO_2 + SF_6, where no phase equilibrium information is available, the critical points were used to optimize the required PSRK group interaction parameters. Using these binary parameters, the ternary critical plane was predicted reliably.

Introduction

EoS models are suitable approaches to describe the equilibrium behavior of multicomponent mixtures. The (PSRK) Predictive Soave-Redlich-Kwong method (Holderbaum and Gmehling, 1991) merges the advantages of the SRK equation of state and the group contribution model UNIFAC by the PSRK mixing rule. In PSRK, published UNIFAC parameters (Hansen et al., 1991) are used, and the range of application was extended by the introduction of new structural groups (in total 30 gases, such as CO_2, CO, O_2, N_2, H_2, CH_4, SF_6, N_2O, and so on) and by fitting the interaction parameters between these groups and the UNIFAC groups to a large number of experimental data. This work was performed by Fischer and Gmehling (1996), Gmehling et al. (1997), Horstmann et al. (2000a), and Horstmann (2000). In order to improve the results for strongly asymmetric mixtures, that is, mixtures with compounds very different in size, an extension of the PSRK model was proposed by Li et al. (1998). A survey of the current status and different applications of industrial interest of the PSRK group contribution EoS is given at Horstmann et al. (2001a).

In addition to phase equilibrium data or excess properties critical data are also of importance because they reflect the real behavior of mixtures and provide additional information about the location and border of the two-phase region. Especially in the vicinity of the critical locus, often only few phase equilibrium data or data of low quality are available. The relevance of critical points as an additional basis for the fitting of the required interaction parameters was examined previously (Guilbot et al., 2000; Horstmann et al., 2001b). A simultaneous correlation of both critical and phase equilibrium data is recommended most favorably. The use of data of only one type, which often only cover a small temperature range, may cause problems in the correct description of the temperature dependence of the interaction parameters. By performing a simultaneous correlation of all data types, a large temperature and pressure range can be described with one set of temperature-dependent PSRK parameters. For the optimization and calculation of critical points with the PSRK model, the direct algorithm of Heidemann and Khalil (1980), applied by Kolář and Kojima (1996), can be successfully used. This iterative approach is solving a thermodynamic criterion for a critical phase (gas-liquid or also liquid-liquid), and it subsequently requires a stability analysis for the obtained phase to be physically existent. For the correlation of the critical data, the following objective function was used

$$F = \sum_{i=1}^{nd} \left(w_T \left| \frac{T_{c,i}^{\text{exp}} - T_{c,i}^{\text{calc}}}{T_{c,i}^{\text{exp}}} \right| + w_P \left| \frac{P_{c,i}^{\text{exp}} - P_{c,i}^{\text{calc}}}{P_{c,i}^{\text{exp}}} \right| \right) \qquad (1)$$

where nd is the number of data points, and w_T and w_P are weighting factors for the critical temperatures and pressures.

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Table 1. Pure Component Properties of the Chemicals Used

Component	Supplier	(% GC)	Source for Compressed Liquid Density
CO_2	Lübke	99.995	Span and Wagner (1996)
Ethane	Messer Griesheim	99.95	Younglove and Ely (1987)
Propane	Messer Griesheim	99.5	Younglove and Ely (1987)
SF_6	Messer Griesheim	99.9	Ihmels and Gmehling (2002)

For critical data of mixtures, not much more than 1,000 data sets can be found in literature, where less than 10% are for ternary or higher mixtures. Reviews are given by Hicks and Young (1975) or Sadus (1992). In this work, the critical lines for the binary mixtures ethane + SF_6, SF_6 + propane, and CO_2 + SF_6 were determined by means of a flow method (Horstmann et al., 1999). By adding a third syringe pump to the apparatus, the critical points for the ternary system CO_2 + ethane + SF_6 were also determined experimentally. The behavior (phase equilibrium behavior, excess properties like enthalpies and volumes, and critical data) of the binary subsystem CO_2 + ethane was discussed in detail by Horstmann et al. (2000b). Herein, the critical points of this system are given again for sake of completeness. The experimental data from this work are used to test the applicability of PSRK for the prediction of critical data of mixtures. The experimental data are compared with published data, predictions using PSRK parameters obtained from phase equilibrium information, and the calculations using new parameters, which were fitted to the critical data of this work. Special attention is paid to the prediction of the behavior of multicomponent mixtures using the interaction parameters fitted only to the binary subsystems. Naturally, simple EoS models like Soave-Redlich-Kwong or Peng-Robinson using the classical van der Waals mixing rules are able to describe the behavior of these systems containing small and simple molecules. Also, the prediction of the multicomponent mixtures is expected to be possible. However, the choice of the PSRK model was made in the frame of the group contribution concept describing systems belonging to the same structural groups with the same set of interaction parameters.

Experimental Studies

Chemicals

All chemicals were purchased from commercial sources. With the exception of ethane, which was dried in an autoclave over phosphorous pentoxide before loading the pump, they were used without any further purification. Also, for these liquefied gases, no degassing was necessary because they did not contain volatile inert components. The suppliers and the purities of the compounds are listed in Table 1. For the measurements, the compressed liquid densities of the pure components at injection temperature are required. They were obtained from the literature for CO_2, ethane, and propane, or were determined experimentally using an automated vibrating tube densimeter for SF_6 (see also Table 1). With this device (Ihmels et al., 2000), liquid and supercritical density data can be measured in a wide temperature (270 to 600 K) and pressure range (up to 40 MPa).

Apparatus and Procedure

The flow apparatus used in this work (Figure 1) can be applied to determine the critical temperatures and pressures of both, pure substances and mixtures. The principle of the flow method was first introduced by Rosenthal and Teja (1989) for high boiling pure substances, which show thermal decomposition at elevated temperatures. Currently, our apparatus can be operated at temperatures between 280 and

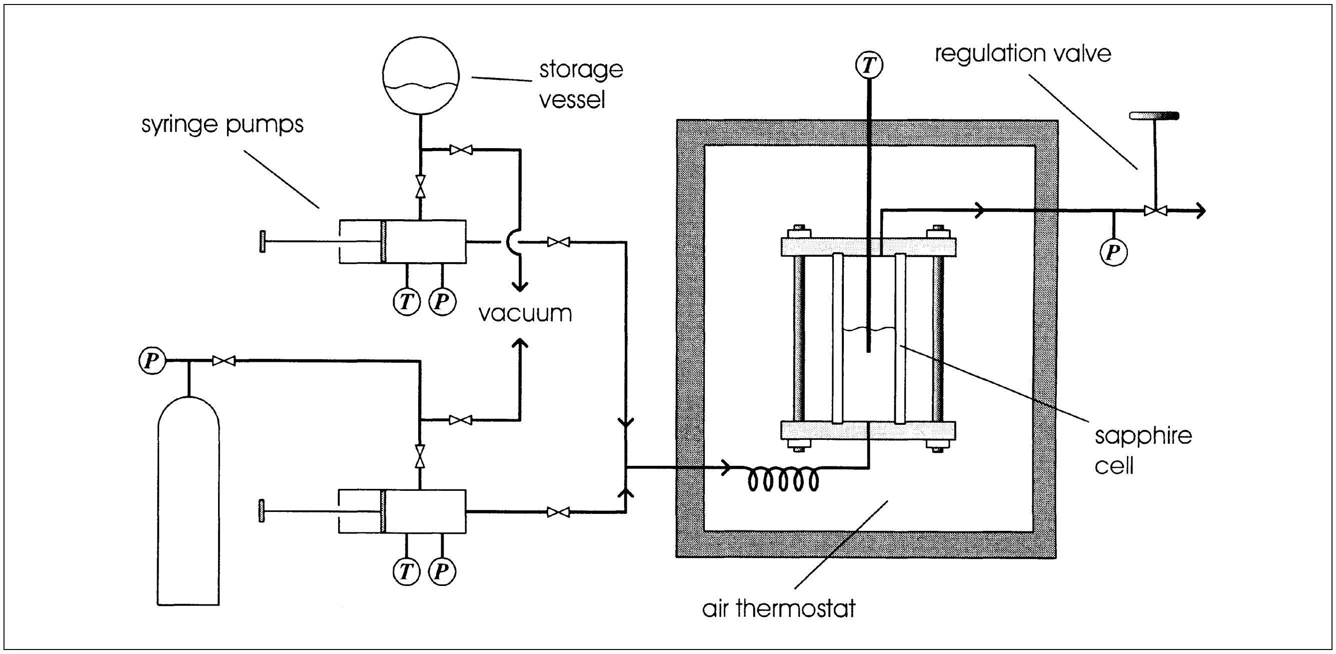

Figure 1. Flow apparatus.

670 K and pressures up to 35 MPa. Some results for binary systems have been already published (Horstmann et al., 1999, 2000b, 2001b; Guilbot et al., 2000).

In this device, up to three thermoregulated chromatographic syringe pumps (Model 260D, ISCO), which contain the pure substances (such as liquefied gases), provide a flow of defined constant composition. After a short heating section, the mixture enters a transparent sapphire cell from the bottom. The cell is placed in an air thermostat. A regulation valve (Whitey) allows to control the substance flow out of the cell. This valve can be operated manually in a way that the system can be kept in the two-phase state. The cell is made of a sapphire tube, which is mounted between two stainless steel flanges, and sealed with glass-loaded PTFE or gold seals. The volume of the cell is about 10 cm^3. For the temperature measurements, a Pt100 probe connected to an electronic display is placed in the center of the cell. For the pressure measurements, a sensor (Model PDCR 910, Druck) between the outlet of the cell and the regulation valve is used.

The measurement is started with a constant flow and closed regulation valve until half of the equilibrium cell is filled with liquid. Then, the regulation valve is adjusted, so that the position of the liquid-vapor phase boundary is kept at a constant level. While increasing the temperature, the position of the phase border will move. This effect can be compensated with the help of the regulation valve. A little below the critical temperature, the phases become cloudy and the disappearance of the meniscus can be visually observed. When the critical temperature is exceeded, only the transparent supercritical phase is left. Subsequently, the reappearance of the meniscus can be observed by a slight opening of the regulation valve and the corresponding temperature and pressure drop. Measurements with this visual method performed by different people and a comparison with literature data led to estimate the experimental errors for pure compounds to be within ± 0.1 K and within ± 10 kPa. In Figure 2, a picture is given of the different states occurring slightly below, at, and slightly beyond the critical temperature.

When applying this method for binary or higher systems, additional effects occur. The low boiling component disappears faster from the equilibrium cell than the high boiling component, so that a high flow rate has to be used to compensate this effect at a given heating rate (about 0.05 K per min). Typical flow rates are about 3 cm^3 per min. However, approaching the critical point, the composition and density of both phases become identical, that is, the composition in the cell is equal to that given by the flow rates of the pumps. The whole procedure is carried out several times for each data point in order to check for repeatability. Generally, we estimate uncertainties of the critical temperature, of the critical pressure, and of the composition to be about ± 0.5 K, ± 0.05 MPa, and ± 0.005, respectively.

Experimental Results and Calculations Using PSRK

The experimental critical points for the system SF$_6$ + propane are listed in Table 2. For the ternary system CO$_2$ + ethane + SF$_6$ and the corresponding subsystems, the experimental data from this work are given in Table 3 together with PSRK calculations using the group interaction parameters given in Table 4. In Figures 3–7 the experimental data of this work are compared graphically with the data of other authors and the PSRK calculations.

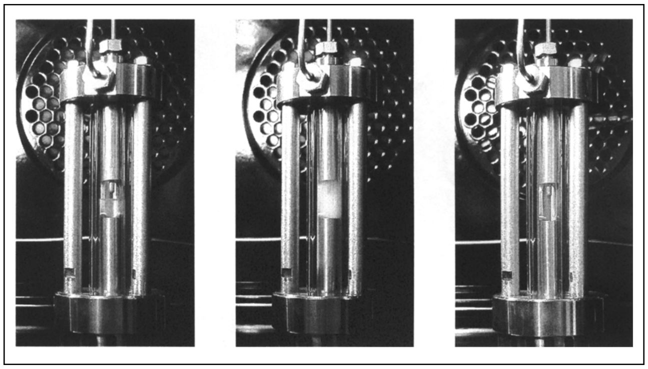

Figure 2. Different states during the measurement of the critical point for ethane.

Lefthand side: two subcritical phases (liquid and vapor) at $T_c - 0.5$ K; center: critical point (cloud point), $T_c = 305.41$ K; righthand side: one supercritical phase at $T_c + 0.5$ K.

For all binary systems, a behavior of the critical temperature is observed which is typical for systems with components of similar volatility and similar pure component critical temperatures. In such systems, a minimum in the temperature of the critical line is leading to the occurrence of a maximum pressure azeotrope. An azeotropic mixture may become supercritical when both pure components are still in the subcritical state. For CO$_2$ + ethane, this phenomenon was discussed in detail before (Horstmann et al., 2000b). As can be seen in Figure 3, the agreement between our experimental data and the data of three other authors for this system is very good. For the well-known systems CO$_2$ + alkane, much experimental information is available in literature, so that the prediction of the critical line for the system CO$_2$ + ethane is possible using PSRK interaction parameters fitted to the phase equilibrium data for the CO$_2$ + alkane systems. Also, the S-shape of the critical pressure curve, which is observed in all investigated binary systems, can be described.

The same behavior can be observed for the system ethane + SF$_6$ (Figure 4), but no published data are available to compare the experimental results. For the system SF$_6$ + propane (Figure 5), a minimum in the critical temperature is again obtained, while a slightly different behavior is observed for

Table 2. Experimental Critical Points of the Binary System SF$_6$ (1) + Propane (2)

x_1	T_c/K	P_c/MPa
0.0000	369.70	4.250
0.0820	362.34	4.290
0.1605	355.58	4.295
0.2497	347.42	4.235
0.3705	338.19	4.102
0.5003	328.81	3.915
0.6206	322.36	3.772
0.7307	318.49	3.695
0.8209	317.26	3.684
0.9197	317.50	3.716
1.0000	318.66	3.749

Table 3. Experimental and Predicted (PSRK) Critical Points of Ternary System CO_2 (1) + Ethane (2) + SF_6 (3) and Binary Subsystems

x_1	x_2	T_c (Exp.) K	P_c (Exp.) MPa	T_c (Calc.) K	P_c (Calc.) MPa	ΔT_c (Exp.-Calc.) K	ΔP_c (Exp.-Calc.) MPa
0.0000	1.0000	305.41	4.881	305.40	4.884	0.01	−0.003
1.0000	0.0000	304.16	7.395	304.20	7.376	−0.04	0.019
0.0000	0.0000	318.66	3.749	318.70	3.760	−0.04	−0.011
0.1223	0.8777	300.70	5.162	301.29	5.143	−0.59	0.019
0.2403	0.7597	296.82	5.352	297.48	5.342	−0.66	0.010
0.3548	0.6452	293.66	5.485	294.27	5.499	−0.61	−0.014
0.4607	0.5393	291.80	5.644	292.11	5.641	−0.31	0.003
0.5605	0.4395	291.04	5.787	291.15	5.802	−0.11	−0.015
0.6601	0.3399	291.48	6.026	291.55	6.025	−0.06	0.001
0.7657	0.2343	293.71	6.358	293.65	6.353	0.06	0.005
0.8805	0.1195	298.16	6.831	297.90	6.820	0.26	0.011
0.0000	0.1403	312.13	3.918	312.95	3.966	−0.82	−0.048
0.0000	0.2792	305.99	4.002	307.19	4.090	−1.20	−0.088
0.0000	0.4207	300.77	4.047	301.80	4.150	−1.03	−0.103
0.0000	0.5395	297.55	4.097	298.27	4.185	−0.71	−0.088
0.0000	0.6400	296.09	4.174	296.52	4.238	−0.43	−0.064
0.0000	0.7306	296.17	4.271	296.34	4.330	−0.17	−0.059
0.0000	0.8213	297.85	4.435	297.77	4.479	0.08	−0.044
0.0000	0.9109	300.89	4.631	300.85	4.676	0.04	−0.045
0.2496	0.0000	309.94	4.502	310.08	4.503	−0.14	−0.001
0.3825	0.0000	305.12	4.877	305.30	4.830	−0.18	0.047
0.5111	0.0000	300.73	5.181	301.11	5.119	−0.38	0.062
0.6302	0.0000	297.66	5.500	298.23	5.409	−0.57	0.091
0.7302	0.0000	296.67	5.792	297.13	5.723	−0.46	0.069
0.8207	0.0000	297.25	6.182	297.62	6.113	−0.37	0.069
0.9103	0.0000	299.75	6.684	299.88	6.649	−0.13	0.035
0.1009	0.7997	297.47	4.772	297.24	4.830	0.23	−0.058
0.1997	0.7004	294.43	4.913	294.35	4.977	0.08	−0.064
0.2995	0.6009	291.67	5.073	291.91	5.110	−0.24	−0.037
0.3993	0.5005	289.75	5.220	290.17	5.242	−0.42	−0.022
0.5000	0.4001	289.06	5.393	289.44	5.403	−0.38	−0.010
0.5998	0.3007	289.57	5.601	289.96	5.611	−0.39	−0.010
0.7001	0.2001	291.66	5.884	291.85	5.882	−0.19	0.002
0.8001	0.1003	294.92	6.226	295.09	6.214	−0.17	0.012
0.0997	0.6992	294.57	4.523	294.64	4.604	−0.07	−0.081
0.1988	0.6002	292.32	4.661	292.43	4.755	−0.11	−0.094
0.2998	0.5006	290.52	4.834	290.76	4.905	−0.24	−0.071
0.3994	0.4008	289.48	5.021	289.92	5.063	−0.44	−0.042
0.4990	0.3004	289.58	5.206	290.10	5.246	−0.52	−0.040
0.6008	0.1991	290.92	5.467	291.42	5.473	−0.50	−0.006
0.7003	0.1003	293.45	5.742	293.85	5.733	−0.40	0.009
0.2008	0.4991	292.18	4.578	292.81	4.641	−0.63	−0.063
0.3010	0.3993	291.39	4.757	291.98	4.812	−0.59	−0.055
0.4004	0.3001	291.33	4.960	291.94	4.990	−0.61	−0.030
0.5009	0.1999	292.43	5.155	292.79	5.188	−0.36	−0.033
0.6000	0.1000	294.45	5.373	294.60	5.398	−0.15	−0.025
0.1997	0.4005	294.34	4.522	295.06	4.591	−0.72	−0.069
0.2998	0.3006	294.19	4.727	294.91	4.777	−0.72	−0.050
0.2000	0.4005	294.89	4.957	295.47	4.964	−0.57	−0.007
0.4999	0.1004	296.44	5.155	296.77	5.149	−0.33	0.006
0.1998	0.2996	297.72	4.474	298.56	4.572	−0.84	−0.098
0.3001	0.2005	298.23	4.712	298.89	4.760	−0.66	−0.048
0.3998	0.1005	299.65	4.943	299.86	4.935	−0.21	0.008
0.2327	0.1336	304.19	4.500	304.47	4.584	−0.28	−0.084

Table 4. PSRK Interaction Parameters: $par_{ij} = a_{ij} + b_{ij}\,(T/K) + c_{ij}\,(T/K)^2$

Main Group i	Main Group j	i	j	a_{ij} (K)	a_{ji} (K)	b_{ij}	b_{ji}	c_{ij} (K^{-1})	c_{ji} (K^{-1})
CH_2*	CO_2	1	56	919.80	−38.672	−3.9132	0.86149	0.0046309	−0.0017906
CH_2*	SF_6	1	68	172.90	27.870	—	—	—	—
CO_2†	SF_6	56	68	38.274	198.92	—	—	—	—

*Fitted to vapor-liquid equilibrium data.
†Fitted to the critical data of this work.

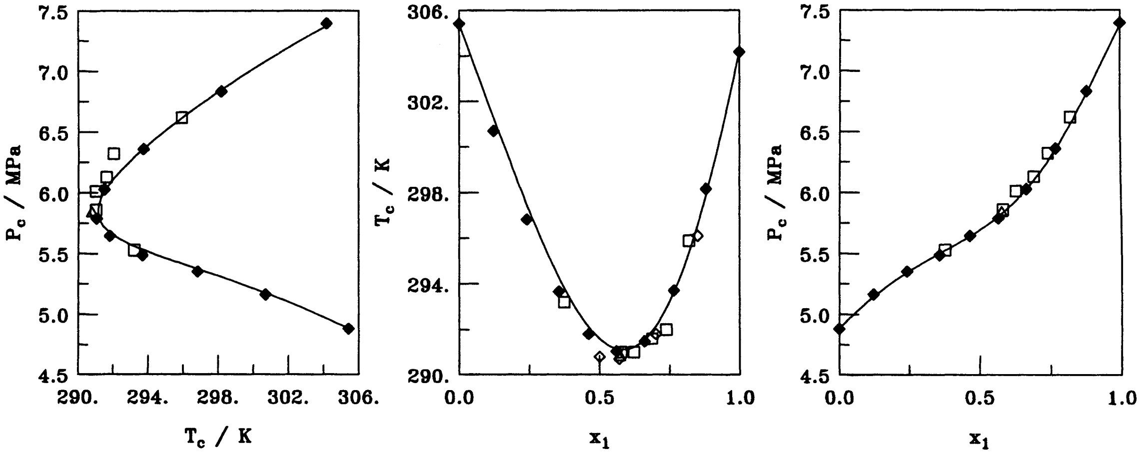

Figure 3. Experimental and predicted critical points for binary system CO_2 (1) + ethane (2).

Experimental data: (♦) This work; (◇) Kuenen (1897); (□) Ohgaki and Katayama (1977); (△) Khazanova et al. (1966); (—) PSRK: parameters fitted to phase equilibrium data.

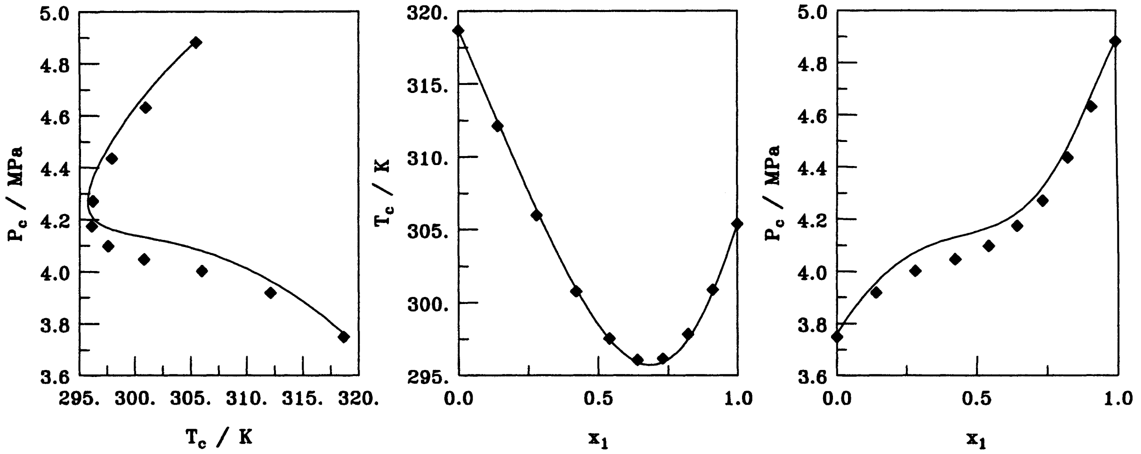

Figure 4. Experimental and predicted critical points for binary system ethane (1) + SF_6 (2).

Experimental data: (♦) this work; (—) PSRK: parameters fitted to phase equilibrium data.

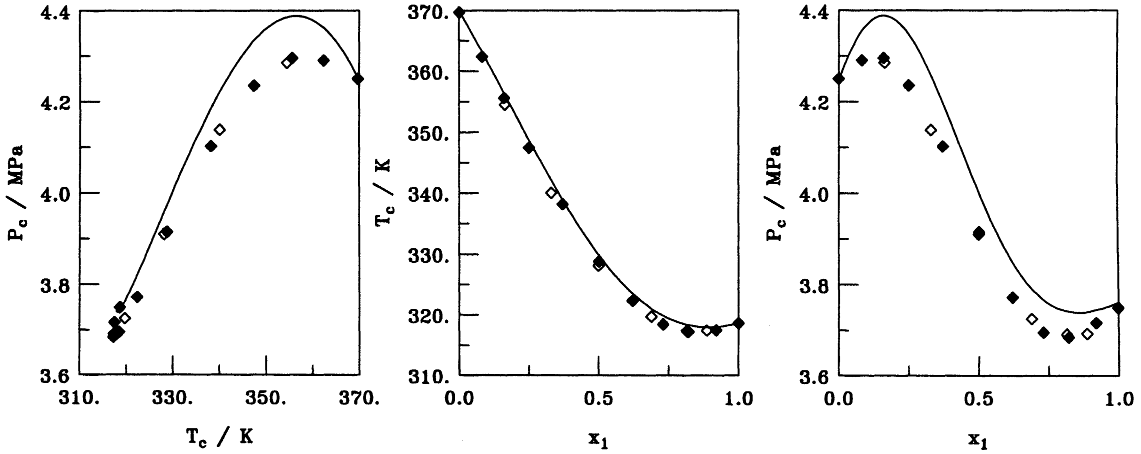

Figure 5. Experimental and predicted critical points for binary system SF_6 (1) + propane (2).

Experimental data: (♦) this work; (◇) Clegg and Rowlinson (1955); (—) PSRK: parameters fitted to phase equilibrium data.

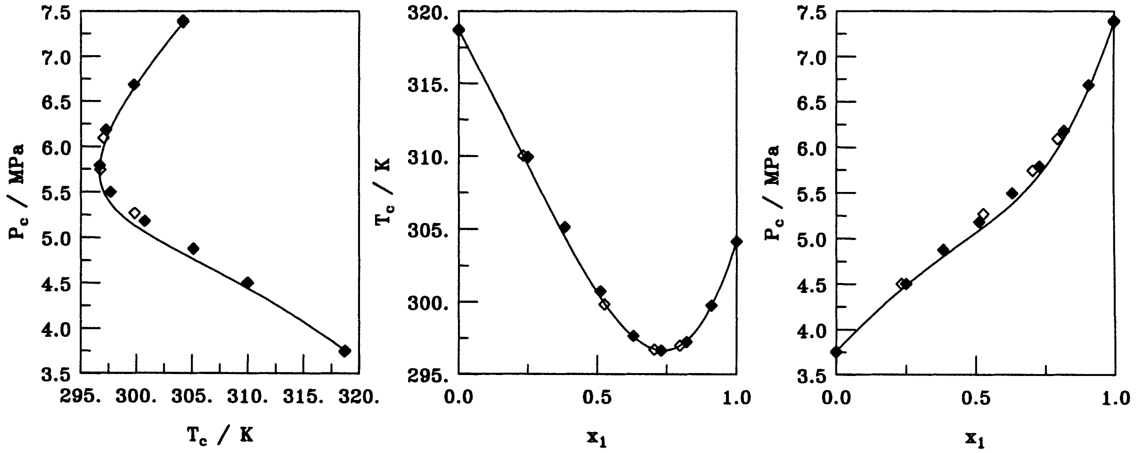

Figure 6. Experimental and predicted critical points for binary system CO_2 (1) + SF_6 (2).

Experimental data: (◆) this work; (◇) Diefenbacher and Türk (1999); (—) PSRK: parameters fitted to the critical data.

the critical pressure. The distinct S-shape causes extreme values in the critical pressure curve. Experimental data of Clegg and Rowlinson (1955) validate our results. For SF_6 + alkane systems, a few experimental phase equilibrium data were available to optimize the PSRK group interaction parameters. Both systems, ethane + SF_6 and SF_6 + propane, can be qualitatively described with these parameters. While the agreement between experiments and predictions is very good for the critical temperatures, small deviations up to about 0.1 MPa are obtained for the critical pressures. However, the critical data were not considered in the parameter regression, because even the correlation of both separate data sets gives only marginal improvements for the prediction of the critical pressures, while the critical temperatures are described worse.

For the system CO_2 + SF_6 (Figure 6), no PSRK predictions are possible on the basis of phase equilibrium information. Anyway, the experimental critical data of Diefenbacher and Türk (1999) verify our results again showing a similar azeotropic behavior as for the systems CO_2 + ethane. With the PSRK parameters fitted to the experimental critical data, a reliable description of this system is enabled.

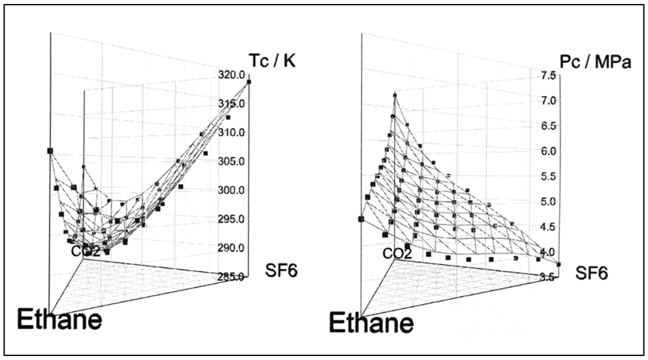

Figure 7. Experimental and predicted critical points for ternary system CO_2 (1) + ethane (2) + SF_6 (3).

Experimental data: (■) this work; (—) PSRK: lines connected between every 10 mol%.

The critical points for the ternary system CO_2 + ethane + SF_6 (Figure 7) were measured in order to examine the reliability of the PSRK method for the prediction of the behavior of multicomponent systems. In this ternary system composed of binary azeotropic subsystems, a minimum in the critical temperature is observed, which is located at a lower temperature than the binary minima. As can be seen in the figure and also in Table 3, the critical locus of this ternary system and the discussed phenomena can be reliably predicted with the PSRK model. In spite of the ternary minimum in the critical temperature, no ternary azeotrope is predicted with the model.

Conclusions

An experimental flow method for the determination of critical points (pressure and temperature) of binary and higher mixtures is presented in this article. The experimental results for the binary systems CO_2 + ethane, ethane + SF_6, SF_6 + propane, and CO_2 + SF_6 are compared to the predictions using PSRK parameters obtained from phase equilibrium information, or, if no such data are available, the critical data were used for the regression of the desired parameters. With these parameters, the experimental critical points for the ternary system CO_2 + ethane + SF_6 were also predicted, and reliable results were obtained. The measurement of the critical line in combination with VLE measurements at moderate conditions (low pressures) for a binary system is recommended due to the significance of critical data for the phase equilibrium behavior. With this approach, the experimental difficulties of determining high pressure VLE data can be avoided.

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