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PSRK group contribution equation of state: revision and extension III

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Abstract

The application range of the predictive Soave–Redlich–Kwong (PSRK) group contribution equation of state (EOS) for the prediction of vapor–liquid equilibria (VLE) and gas solubilities was extended by the introduction of additional structural groups (epoxides, HF, HI, COS) and fitting of 98 pairs of group interaction parameters to experimental phase equilibrium data. These data were systematically measured for the extension of PSRK, or taken from literature and compiled in the Dortmund Data Bank (DDB). Typical results are presented for various systems. Additionally, new experimental VLE data are given for the binary system propylene oxide + benzene at 323.15 K. The new data were required to fit the interaction parameters between the epoxy and the aromatic CH group. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Equation of state; Group contribution; PSRK; UNIFAC; Vapor–liquid equilibrium

1. Introduction

The predictive Soave–Redlich–Kwong (PSRK) group contribution equation of state (EOS) [1] is widely used for the prediction of phase equilibria and further thermophysical mixture properties required for the development, design, and optimization of chemical processes, especially thermal separation processes. The PSRK method allows to use the existing UNIFAC parameters [2] as well as the PSRK parameters for the introduced new structural groups, e.g., 22 different gases (CO_2, N_2, H_2, $CO, \ldots$) [3–5].

The aim of this work is to extend the list of structural groups and interaction parameters of the PSRK model. This was enabled by the growth of the Dortmund Data Bank (DDB), and also by the

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Table 1
Experimental $P-x$ data for the system propylene oxide $(1)+$ benzene (2) at 323.15 K

x	P/kPa	x	P/kPa
0.00000	36.021	0.55787	113.73
0.00507	36.795	0.60177	119.66
0.01001	37.547	0.64666	125.68
0.01521	38.331	0.69132	131.71
0.02029	39.115	0.73501	137.63
0.02532	39.895	0.77703	143.33
0.04229	42.455	0.81686	148.64
0.06130	45.248	0.85322	153.62
0.08322	48.437	0.88610	158.14
0.10878	52.145	0.91210	161.73
0.13883	56.453	0.93421	164.79
0.17298	61.292	0.95228	167.33
0.21048	66.555	0.96637	169.28
0.25513	72.760	0.97730	170.84
0.30152	79.152	0.98432	171.84
0.34956	85.744	0.98903	172.50
0.39780	92.314	0.99294	173.04
0.44537	98.775	0.99587	173.47
0.49183	105.07	0.99779	173.74
0.51498	107.97	0.99931	173.97
0.53640	111.09	1.00000	174.07

systematic experimental determination of new vapor–liquid equilibrium (VLE) and gas solubility data. In this paper, experimental VLE data for the system propylene oxide + benzene are reported. Furthermore, oxygen and nitrogen solubilities in different solvents and VLE of systems containing sulfur compounds were determined in order to achieve the applicability of the PSRK method for specific problems, such as the prediction of air solubilities in organic solvents, and the K-factors of sulfur compounds in liquefied natural gas (LNG).

Table 2
Van der Waals properties for the new subgroups

Subgroup	Main group	R_k	Q_k	Component (example)	Increments
CHSH	29 CH_2SH	1.4250	1.060	*iso*-propyl mercaptan	$1*CHSH, 2*CH_3$
CSH	29 CH_2SH	1.1990	0.752	*tert*-butyl mercaptan	$1*CSH, 3*CH_3$
H_2COCH_2	51 epoxy	1.5926	1.320	ethylene oxide	$1*H_2COCH_2$
H_2COCH	51 epoxy	1.3652	1.008	propylene oxide	$1*H_2COCH, 1*CH_3$
H_2COC	51 epoxy	1.1378	0.780	2-methyl propylene oxide	$1*H_2COC, 2*CH_3$
HCOCH	51 epoxy	1.1378	0.696	2,3-butylene oxide	$1*HCOCH, 2*CH_3$
HCOC	51 epoxy	0.9104	0.468	2-methyl 2,3-butylene oxide	$1*HCOC, 3*CH_3$
COC	51 epoxy	0.6829	0.240	2,3-dimethyl 2,3-butylene oxide	$1*COC, 4*CH_3$
HF	73 HF	1.0160	1.216	hydrogen fluoride	$1*HF$
HI	76 HI	1.3930	1.208	hydrogen iodide	$1*HI$
COS	77 COS	1.6785	1.316	carbonyl sulfide	$1*COS$

Table 3
New group interaction parameters for the PSRK model

i^a	j^a	a_{ij}/K	b_{ij}	c_{ij}/K^{-1}	a_{ji}/K	b_{ji}	c_{ji}/K^{-1}
1[b]	28	−54.433			180.28		
1[b]	29	287.38			−61.863		
1[b]	34	27.139			4518.3		
1[b]	48	298.62			−57.788		
1[c]	51	591.04			−102.09		
1[b]	58	−19.628	1.8192		104.28	−1.2191	
1[c]	70	10.940			102.35		
1[c]	76	−88.341			274.74		
1[c]	77	270.32			−171.06		
2[c]	29	281.67			−74.469		
2[b]	34	74.051			211.88		
2[b]	48	224.31			−62.736		
2[c]	51	282.09			−68.780		
3[c]	34	406.59			−117.14		
3[c]	51	35.973			70.567		
3[b]	58	285.26			−0.6989		
3[c]	76	115.80			−135.70		
4[c]	34	−147.47			774.87		
4[c]	51	4.6162			1475.9		
4[c]	58	130.37	63.323		384.98	−2.1163	
4[c]	76	220.72			−179.19		
5[c]	51	217.22	0.01991		1210.0	−3.8511	
5[c]	55	−252.04			−245.90		
5[c]	58	2018.6			382.59		
5[c]	60	589.20	2.6810		2836.9	−5.2997	
5[c]	69	3222.5			3694.7		
5[c]	72	470.09			559.06		
6[c]	34	−189.07			4040.7		
6[c]	51	9.5251			196.54		
6[c]	58	1061.4	−1.2561		−516.85	1.1696	
6[c]	77	−15.335			609.43		
7[c]	34	752.00			3842.5		
7[c]	51	−159.20			767.82		
7[b]	60	−3123.4	20.683	−0.01956	1459.6	−7.6407	0.009450
7[b]	62	−1531.6	12.396	−0.006931	5564.1	−27.410	0.07115
7[c]	73	−2832.0	9.6630	−0.01247	−1641.0	7.4560	−0.01156
7[c]	74	−2197.8	5.2282		−796.40	−0.2825	
7[c]	75	−1026.7			−954.65		
7[c]	76	696.36			−1270.5		
8[c]	57	824.71	0.06955		2290.5	−2.9588	
9[b]	34	−65.229			−160.70		
9[c]	51	70.160			−72.036		
9[c]	55	0.1619			341.49		
9[c]	57	536.92			−0.8632		
10[c]	51	173.78			−2.6891		
11[c]	34	1184.6			−327.44		
11[c]	51	152.49			−132.47		

Table 3 (*continued*)

i[a]	j[a]	a_{ij}/K	b_{ij}	c_{ij}/K^{-1}	a_{ji}/K	b_{ji}	c_{ji}/K^{-1}
12[c]	51	333.00			−189.89		
13[c]	34	−117.71			−198.49		
13[c]	51	109.27			−28.097		
13[c]	58	147.51			1986.8		
13[c]	60	3191.3			266.63		
13[c]	63	382.82			881.01		
15[c]	65	−628.26			−497.83		
16[c]	65	−935.40			−730.22		
18[c]	56	43.717			−109.83		
18[c]	57	208.55	−0.1098		226.85	−0.6121	
18[c]	60	337.77	15.524		132.98	−1.1326	
18[c]	62	634.45			−68.653		
20[c]	63	301.76	2.6956		−263.27	1.1376	
20[c]	76	2051.6			−549.40		
21[c]	51	31.401			−66.608		
23[c]	76	92.002			−17.588		
24[c]	34	222.38			195.84		
24[c]	51	259.39			−43.834		
24[c]	76	−80.976			323.47		
25[c]	62	477.45			17.600		
25[c]	76	537.50			−105.78		
28[c]	45	130.13	−0.05848		446.14	−0.8047	
29[c]	61	−194.98			23.324		
33[c]	56	100.31			39.267		
34[c]	44	−404.41			16.285		
34[c]	55	32.648			−173.86		
34[c]	56	−10.699			−9.775		
37[b]	48	−32.104			83.451		
37[c]	55	713.90			−547.63		
39[c]	65	−1013.7	2.6354		165.65	−1.6026	
40[c]	73	1204.0			86.243		
41[c]	56	183.65			−5.8025		
44[c]	65	−233.85			−382.92		
50[c]	62	200.48	19.011		−361.75	−0.1675	
51[c]	56	−1329.9	3.2325		531.64	−0.8032	
51[c]	57	276.13			2.8372		
51[c]	60	43.461			−3.2734		
51[c]	72	208.66			234.81		
55[c]	57	1080.3	−1.9075		4278.7	3.1197	
55[c]	70	1369.3	−2.5805		−144.22	5.0788	
57[c]	67	−27.596			211.01		
57[c]	77	271.31			−103.94		
58[c]	67	535.78	−2.9826		−1101.9	6.9864	
59[c]	62	190.87			4196.2		
59[c]	69	217.20			4536.0		
61[c]	77	75.680	0.003298		229.32	−0.5352	
62[c]	69	62.017			372.00		

Table 3 (*continued*)

i^{a}	j^{a}	a_{ij}/K	b_{ij}	c_{ij}/K^{-1}	a_{ji}/K	b_{ji}	c_{ji}/K^{-1}
67[c]	74	−27.216			76.955		
69[c]	70	44.729	4.6709		109.55	−1.4647	
70[c]	72	1731.3	−5.7368		366.81	−1.3366	
73[c]	74	169.99			613.10		

[a]Indices correspond to numbering in Fig. 1 (consistent to former articles [1–4]).
[b]Revised parameters.
[c]New parameters.

For the dimer-forming substances such as carboxylic acids, or the hexamer-forming HF it is known that chemical equilibria have to be taken into account to represent the real behavior of the pure components and mixtures. In this work, these dimerization or hexamerization reactions are not considered and the components are treated in the same simplified way as all the other substances. It can be shown that a reliable estimation of phase equilibria, e.g., the bubble point curve of the $HF + H_2O$, is still possible. The drawback of this approach, however, becomes apparent when for example the heat of vaporization or other thermophysical properties of systems containing these substances are calculated with the help of PSRK. Nevertheless, the advantage to allow a consideration of these compounds in the application range of PSRK for gas solubility and VLE calculations predominates in the praxis of chemical engineering.

Encouraging results of the PSRK method were also recently reported for the calculation of critical data [6]. Furthermore, a detailed examination of the unusual behavior of the system CO_2 + ethane was carried out [7], where the calculated results for different thermodynamic properties were found to be in very good agreement with the experimental data.

2. Experimental

Isothermal VLE measurements for the binary system propylene oxide + benzene at 323.15 K were carried out by means of the static synthetic method.

2.1. Chemicals, apparatus, and procedure

The chemicals were dried over molecular sieve, degassed, and distilled as described by Fischer and Gmehling [8]. The final purities for both components (> 99.99% GC) were determined by gas chromatography. The water contents as determined by Karl Fischer titration were 25 ppm weight for propylene oxide and 20 ppm weight for benzene.

The VLE measurement (isothermal P–x data) was performed using a computer-operated static apparatus following the principle proposed by Gibbs and Van Ness [9]. With this technique, the total pressure at different overall compositions is measured at constant temperature. The apparatus, and the experimental procedure were described previously [10,11]. The total compositions are determined from known volumes of the liquids (at given temperature and pressure) injected into the equilibrium cell using stepping motor-driven injection pumps and valves. The liquid phase compositions are derived from the injected quantities by solving the mass and volume balance taking into account VLE.

At the low pressures of this investigation the calculated liquid phase compositions are identical to the feed compositions within $x_i = \pm 0.001$. The apparatus can be used in the temperature range between 278 and 368 K and at pressures between 0 and 0.3 MPa. The experimental uncertainties are as follows: $\sigma(T) = 0.03$ K, $\sigma(P) = 20$ Pa $+ 0.0001$ (P/Pa), $\sigma(x_i) = 0.0001$.

2.2. Results

The experimental P–x data of the system propylene oxide (1) + benzene (2) at 323.15 K are listed in Table 1. From these data, the PSRK interaction parameters between the epoxy and the aromatic CH group were established.
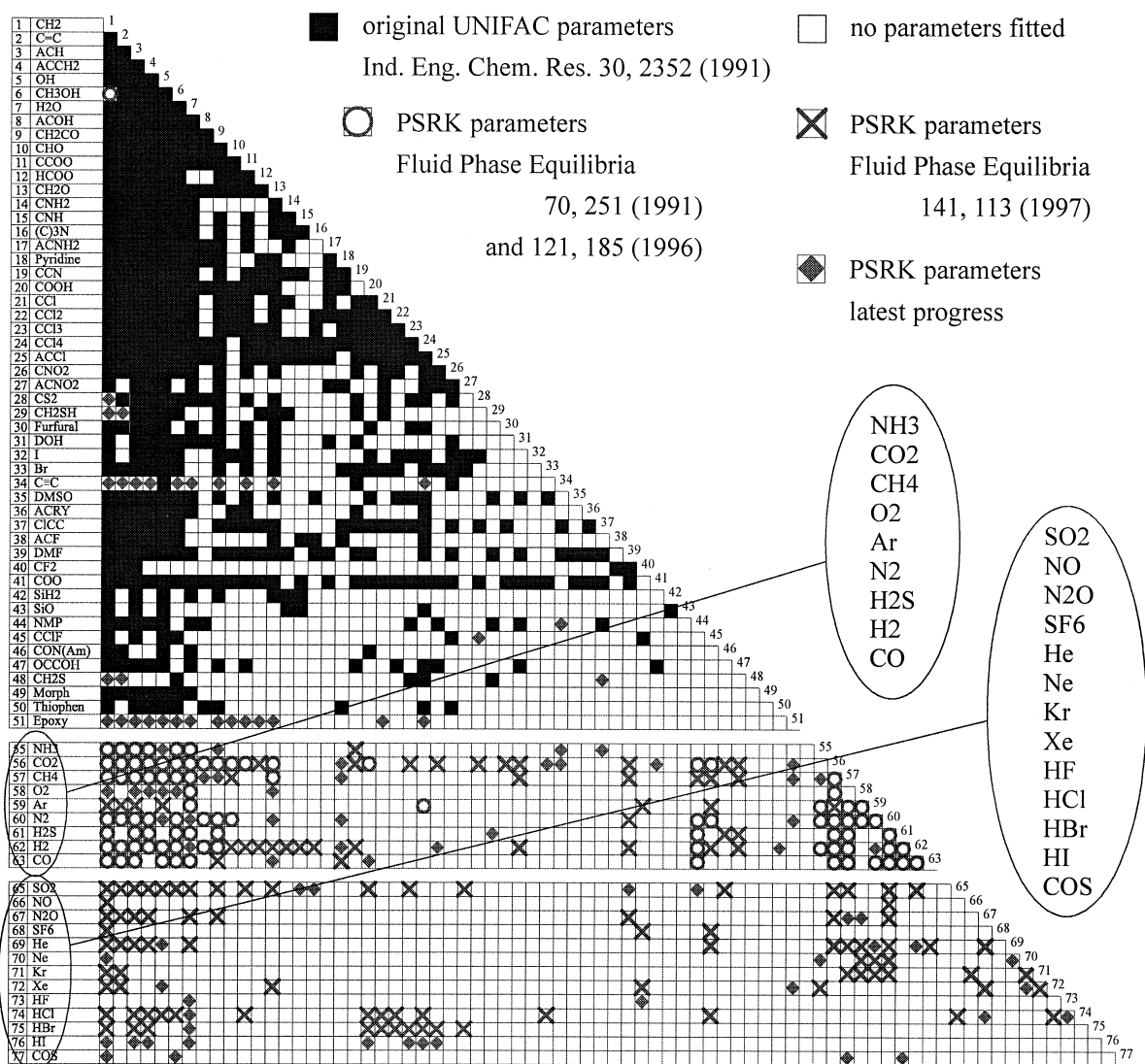
Fig. 1. Current status of the PSRK group interaction parameter matrix.

3. Introduction of new groups and fitting of new PSRK interaction parameters

Four new structural groups (epoxides, HF, HI, COS), which are of great importance for chemical industry, were introduced into the PSRK model. For this purpose and also for the revision of existing group interaction parameters new subgroups had to be defined. The required van der Waals properties for the new sub- and main groups are listed in Table 2. They were fitted simultaneously with the group interaction parameters to experimental VLE and gas solubility data in the case of, e.g., HF, HI or calculated using the Bondi method [12], for example, for sulfides, mercaptans, and epoxides.

Details about the parameter fitting procedure were described previously [1,3]. The temperature dependence of the interaction parameters is described by the following expression:

$$\text{par}_{ij} = a_{ij} + b_{ij}T + c_{ij}T^2 \tag{1}$$

where T and par_{ij} have the unit Kelvin (K). In most cases, only two interaction parameters (a_{ij}, a_{ji}) were fitted. In a few cases, linear (b_{ij}, b_{ji}) or even a quadratic (c_{ij}, c_{ji}) temperature-dependent parameters were required to describe the correct temperature dependence of the phase equilibrium behavior, for example for the systems $H_2 + H_2O$ or $N_2 + H_2O$. The obtained parameters for 98 group pairs are given in Table 3. The current status of the PSRK/UNIFAC parameter matrix is shown in Fig. 1.

For several systems surprisingly good results were obtained at temperatures even far from the conditions of the experimental data considered for fitting the interaction parameters. This is especially true for Henry coefficients, which are not included in the database for parameter regression. This is shown in the present and former articles for different systems, e.g., $H_2 + H_2O$, $CO + H_2O$, and $CO_2 + H_2O$ [13].

4. Results and discussion

In Figs. 2–9 various results based on new PSRK parameters are presented. To improve the results for systems containing alkynes and sulfur compounds all the parameters for the groups CS_2, CH_2SH,
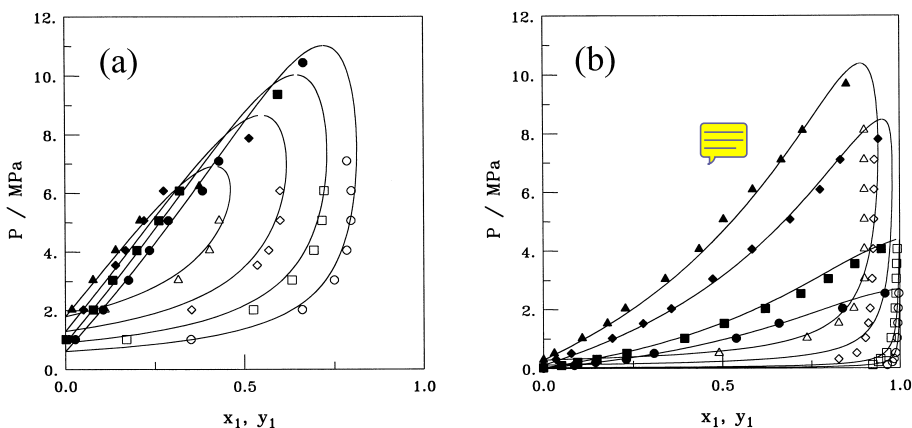

Fig. 2. Experimental and predicted VLE for systems with acetylene: (a) acetylene (1) + *n*-hexane (2): experimental data [14] at (●,○) 413.15 K, (■,□) 433.15 K, (♦,◇) 453.15 K, (▲,△) 473.15 K; (b) acetylene (1) + acetone (2): experimental data [15] at (●,○) 273.15 K, (■,□) 293.15 K, (♦,◇) 333.15 K, (▲,△) 363.15 K; (—) PSRK.
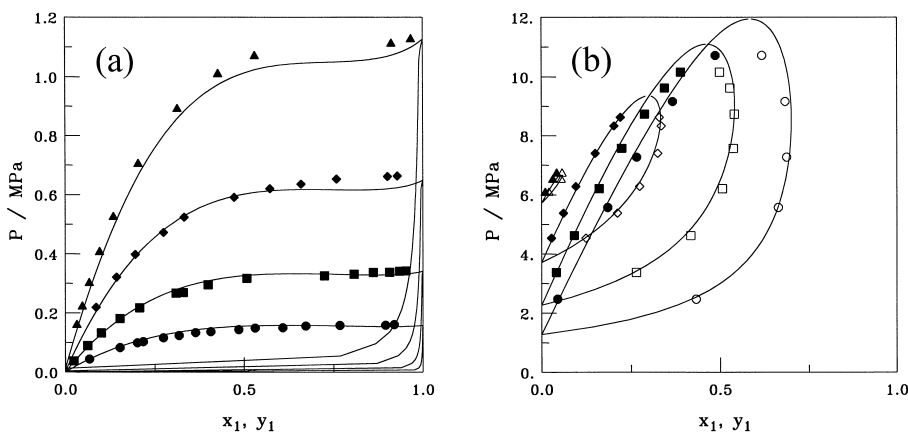
Fig. 3. Experimental and predicted VLE for systems with carbonyl sulfide: (a) carbonyl sulfide (1) + methanol (2): experimental data [17] at (●) 233.2 K, (■) 253.2 K, (♦) 273.2 K, (▲) 293.2 K; (b) methane (1) + carbonyl sulfide (2): experimental data [18] at (●,○) 298.15 K, (■,□) 323.15 K, (♦,◇) 348.15 K, (▲,△) 373.15 K; (—) PSRK.

CH_2S and alkyne (28, 29, 48, and 34) were verified, revised, or fitted using published or new experimental VLE data. In most cases, temperature-independent parameters were sufficient to provide reliable results. In Fig. 2, results for the alkyne group (acetylene (1) + *n*-hexane (2) and acetylene (1) + acetone (2)) are given. With the new parameters also systems containing acetylene, which were not included in the UNIFAC method, can be predicted satisfactory. This fact allowed, furthermore, to fit several alkyne main group parameters, for which only acetylene solubility data are available and no UNIFAC parameters could be fitted before. This means that the PSRK parameters can be used to extend the range of applicability of the UNIFAC method.

In a recent Gas Processors Association (GPA) project (GPA project 986), the PSRK model was extended for the prediction of *K*-factors (distribution coefficients between the vapor and the liquid phase) of sulfur components (H_2S, CS_2, COS, sulfides (CH_2S), and mercaptans (CH_2SH)) in LNG. For this reason, the main groups, CS_2, CH_2SH and CH_2S, had to be revised and the new subgroups, CHSH and CSH, were linked to the CH_2SH main group. The interactions between the above main groups and CH_4, H_2S, and also the new COS group are important, because for these systems the deviation from ideality is considerable. Additionally, VLE and critical data for the system H_2S + COS were measured [16] to extend the database for fitting the required interaction parameters. In Fig. 3, a few PSRK results are compared with experimental data for the systems carbonyl sulfide (1) + methanol (2) and methane (1) + carbonyl sulfide (2). Further measurements are in progress in GPA project 986, so that in the near future additional PSRK parameters can be determined for the group combinations of CH_4 with CH_2SH, CH_2S and H_2S with CH_2S.

Also epoxides were introduced as a new main group. Several interaction parameters for this group were fitted to published VLE data and the VLE data measured in this work. In Fig. 4, typical PSRK results for systems containing epoxides are given. The results for the propylene oxide (1) + benzene (2) system from this work are included in this diagram. In Fig. 5, the results of the two azeotropic systems, 1,2-epoxybutane (1) + *n*-hexane (2) and 1,2-epoxybutane (1) + methanol (2), are shown. It can be seen that the predicted azeotropic compositions are in good agreement with the experimental data. The reliable knowledge of the azeotropic compositions as function of temperature and pressure is of particular importance for process synthesis.
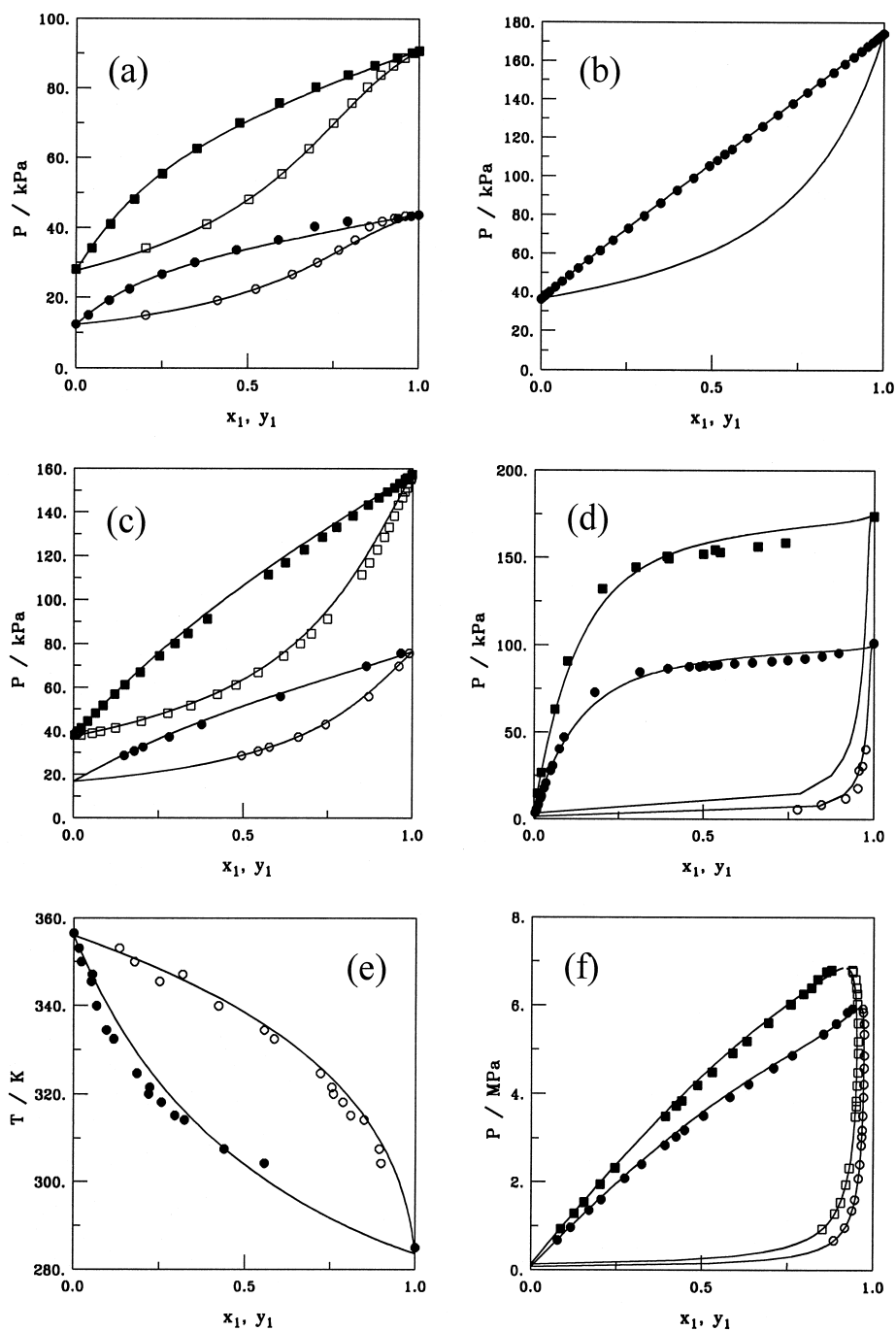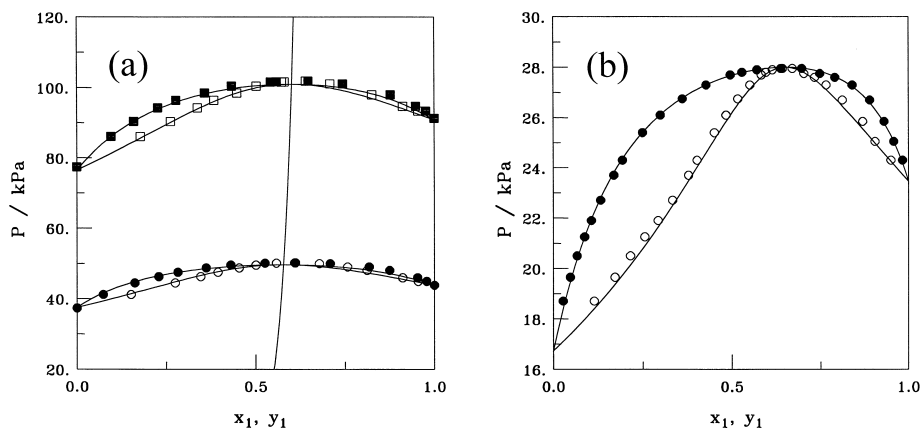
Fig. 4. Experimental and predicted VLE for epoxide systems: (a) 1,2-epoxybutane (1) + *n*-heptane (2): experimental data [19] at (●,○) 313.15 K, (■,□) 333.15 K; (b) propylene oxide (1) + benzene (2): experimental data this work at (●) 323.15 K; (c) propylene oxide (1) + tetrachloromethane (2): experimental data [20] at (●,○) 300.00 K, (■,□) 320.00 K; (d) ethylene oxide (1) + water (2): experimental data [21,22] at (●,○) 283.15 K, [22] at (■) 298.15 K; (e) ethylene oxide (1) + 1,2-dichloroethane (2): experimental data [23] at (●,○) 101.325 kPa; (f) ethylene (1) + propylene oxide (2): experimental data [24] at (●,○) 298.15 K, (■,□) 313.15 K; (—) PSRK.

Fig. 5. Experimental and predicted VLE and azeotropic behavior of epoxide systems: (a) 1,2-epoxybutane (1) + *n*-hexane (2): experimental data [19] at (●,○) 313.15 K, (■,□) 333.15 K; (b) 1,2-epoxybutane (1) + methanol (2): experimental data [25] at (●,○) 298.15 K; (—) PSRK.

In addition to the COS and the epoxy group, the groups HF and HI were introduced into the PSRK matrix, whereby the hexamer-forming hydrogen fluoride was pragmatically treated as a non-associating component. As can be seen in Fig. 6, the phase equilibrium behavior of HF can be still predicted very well for the systems hydrogen fluoride (1) + water (2) and hydrogen chloride (1) + hydrogen fluoride (2).

Because of the continuously growing VLE and gas solubility database also a large number of new parameters were fitted for the already existing main groups. Fig. 7 shows examples for systems containing different sub- or supercritical components (difluorochloromethane (1) + carbon disulfide
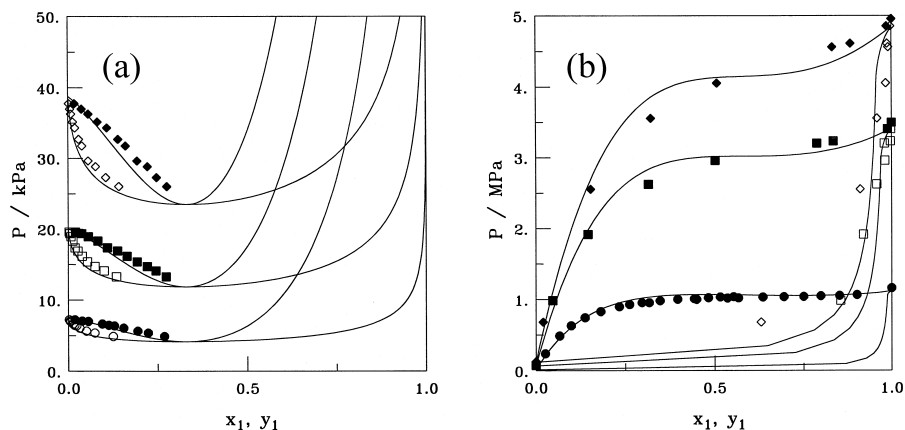
Fig. 6. Experimental and predicted VLE for systems with hydrogen fluoride: (a) hydrogen fluoride (1) + water (2): experimental data [26] at (●,○) 313.15 K, (■,□) 333.15 K, (♦,◇) 348.15 K; (b) hydrogen chloride (1) + hydrogen fluoride (2): experimental data [27] at (●) 244.15 K, [28] at (■,□) 283.15 K, (♦,◇) 298.15 K; (—) PSRK.
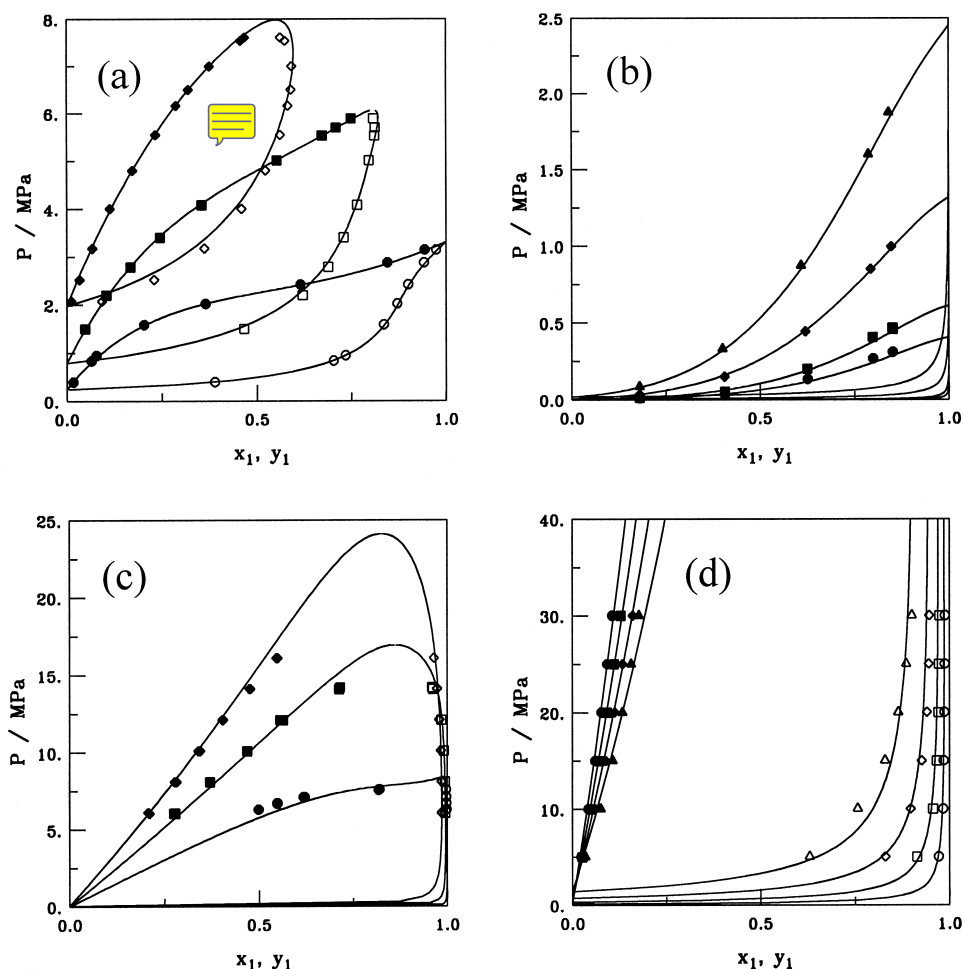
Fig. 7. Experimental and predicted VLE for different systems: (a) difluorochloromethane (1) + carbon disulfide (2): experimental data [29] at (●,○) 348.15 K, (■,□) 398.15 K, (♦,◇) 448.15 K; (b) sulfur dioxide (1) + *N,N*-dimethylformamide (2): experimental [30] at (●) 298.15 K, (■) 310.93 K, (♦) 338.71 K, (▲) 366.48 K; (c) carbon dioxide (1) + bromobenzene (2): experimental data [31] at (●,○) 313.2 K, (■,□) 353.1 K, (♦,◇) 393.2 K; (d) hydrogen (1) + pyridine (2): experimental data [32] at (●,○) 393.2 K, (■,□) 433.2 K, (♦,◇) 473.2 K, (▲,△) 513.2 K; (—) PSRK.

(2), sulfur dioxide (1) + *N,N*-dimethylformamide (2), carbon dioxide (1) + bromobenzene (2), and hydrogen (1) + pyridine (2)). Also, for these systems, a good agreement between the experimental and predicted results is obtained.

One interesting example for the revision of already existing parameters is given for the system hydrogen (1) + water (2). With the new interaction parameters, it is now possible to represent the minimum of the hydrogen solubility in water as a function of temperature (maximum of the Henry coefficient, Fig. 8). To enable the calculation of oxygen and nitrogen (or air) solubilities in different solvents (alkanes, alkenes, aromatics, alcohols, ketones and water) [13] several gas solubility measurements were performed up to pressures of 10 MPa [33]. In Fig. 9, our experimental Henry
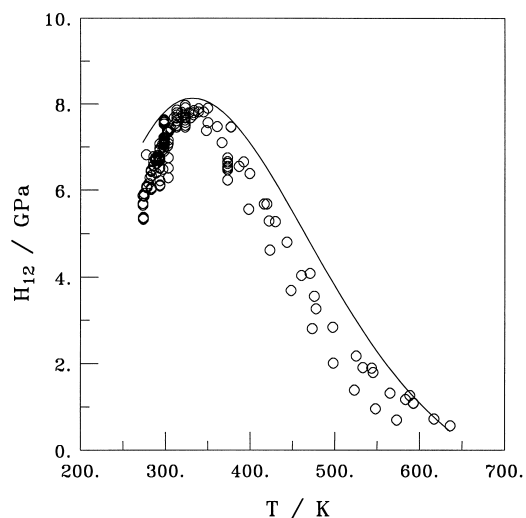
Fig. 8. Experimental and predicted Henry coefficients for the systems hydrogen (1)+water (2); experimental data of different authors taken from the DDB ($\bigcirc$); (—) PSRK.

coefficients for oxygen and nitrogen in 1-propanol are shown together with those of other authors and the PSRK predictions. This means, that now, the prediction of air solubilities, which is very important, e.g., for transport or storage of organic mixtures, is also possible with PSRK. We believe that PSRK is the first reliable existing method for the prediction air (oxygen and nitrogen) solubilities.
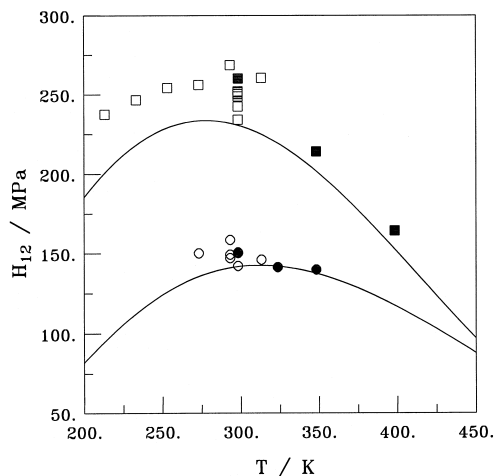

Fig. 9. Experimental and predicted Henry coefficients of oxygen and nitrogen in 1-propanol; experimental data for the system oxygen (1)+1-propanol (2) ($\bullet$) [33], ($\bigcirc$) different authors (taken from the DDB); experimental data for the system nitrogen (1)+1-propanol (2) ($\blacksquare$) [33], ($\square$) different authors (taken from the DDB); (—) PSRK.

5. Conclusions

With the systematic experimental determination of precise VLE or gas solubility data the application range of PSRK was extended to different specific classes of substances, such as air, sulfur compounds, and epoxides. Additional structural groups (epoxides, HF, HI, COS) were introduced into the PSRK group contribution EOS, and in total 98 pairs of group interaction parameters for the new and the existing main groups were fitted to experimental phase equilibrium data measured for the extension of PSRK or taken from literature. This leads to a remarkable extension of the application range of PSRK, which can be employed for the prediction of VLE and gas solubilities of a large number of different substances, regardless whether they are non-polar or polar, sub- or supercritical, large or small molecules. As it was demonstrated in this and other papers, the agreement between experimental and predicted values proves the reliability of PSRK.

PSRK is a general method for a large number of applications. In the future, it will be possible to extend PSRK to numerous problems by introducing the missing groups and fitting the required interaction parameters. To reach this goal, at least a limited number of systematic measurements have to be performed. Furthermore, it is planned to apply the PSRK method also to electrolyte and polymer containing systems. For the latter systems, the function for correcting the r and q values [5] was recently modified in order to achieve a reasonable extrapolation to polymers. A method for a suitable prediction of the pure component EOS parameters a and b is under development.

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References

[1] T. Holderbaum, J. Gmehling, Fluid Phase Equilib. 70 (1991) 251–265.
[2] H.K. Hansen, P. Rasmussen, Aa. Fredenslund, M. Schiller, J. Gmehling, Ind. Eng. Chem. Res. 30 (1991) 2352–2355.
[3] K. Fischer, J. Gmehling, Fluid Phase Equilib. 121 (1996) 185–206.
[4] J. Gmehling, J. Li, K. Fischer, Fluid Phase Equilib. 141 (1997) 113–127.
[5] J. Li, K. Fischer, J. Gmehling, Fluid Phase Equilib. 143 (1998) 71–82.
[6] S. Horstmann, K. Fischer, J. Gmehling, Experimental determination of critical points of pure components and binary mixtures using a flow apparatus, Chem. Eng. Technol. 22 (1999) 839–842.
[7] S. Horstmann, K. Fischer, P. Kolář, J. Gmehling, Experimental determination of the critical line for the CO_2 + ethane system and calculation of various thermodynamic properties for CO_2 n-alkane systems using the PSRK model, J. Chem. Thermodyn. (2000) in press.
[8] K. Fischer, J. Gmehling, J. Chem. Eng. Data 39 (1994) 309–315.
[9] R.E. Gibbs, H.C. Van Ness, Ind. Eng. Chem. Fundam. 11 (1972) 410–413.
[10] J. Rarey, J. Gmehling, Fluid Phase Equilib. 83 (1993) 279–287.
[11] J. Rarey, S. Horstmann, J. Gmehling, J. Chem. Eng. Data 44 (1999) 532–538.
[12] A. Bondi, Physical Properties of Molecular Crystals, Liquids and Glasses, Wiley, New York, 1968.

[13] K. Fischer, M. Wilken, J. Gmehling, Proceedings of the International Meeting of the GVC-Fachausschuss ''Hochdruckverfahrenstechnik'' on High Pressure Chemical Engineering, March 3-5, 1999, Forschungszent. Karlsruhe (1999) 167–172.

[14] V.S. Mislavskaya, S.M. Khodeeva, Zh. Fiz. Khim. 43 (1969) 1887–1888.

[15] A.P. Voronkov, V.S. Mislavskaya, R.Y. Mushii, S.M. Khodeeva, Zh. Fiz. Khim. 49 (1975) 3128–3130.

[16] P. Guilbot, P. Theveneau, A. Baba-Ahmed, S. Horstmann, K. Fischer, D. Richon, Vapor–liquid equilibrium data and critical points for the system $H_2S + COS$. Extension of the PSRK group contribution equation of state, Fluid Phase Equilib., submitted for publication.

[17] J.L. Ocarson, S.O. Lundell, J.R. Cunningham, AIChE Symp. Ser. 256 (1987) 1–17.

[18] N.H. Senturk, H. Kalra, D.B. Robinson, J. Chem. Eng. Data 24 (1979) 311–313.

[19] A. Jonasson, M. Savoia, O. Persson, Aa. Fredenslund, J. Chem. Eng. Data 39 (1994) 134–139.

[20] B. Gutsche, H. Knapp, Pol. J. Chem. 54 (1980) 2261–2267.

[21] K.E. MacCormack, J.H.B. Chenier, Ind. Eng. Chem. 47 (1955) 1454–1458.

[22] P.C. Gillespie, J.R. Cunningham, G.M. Wilson, AIChE Symp. Ser. 244 (1985) 26–40.

[23] S.I. Kaplan, N.A. Grishin, A.A. Skvotsova, Zh. Obshch. Khim. 7 (1937) 538–544.

[24] K. Ohgaki, T. Nakatani, T. Saito, T. Katayama, J. Chem. Eng. Jpn. 15 (1982) 91–97.

[25] F. Comelli, R. Francesconi, J. Chem. Eng. Data 41 (1996) 1392–1396.

[26] J.C. Brosheer, F.A. Lenfesty, K.L. Elmore, Ind. Eng. Chem. 39 (1947) 423–427.

[27] P.C. Gillespie, J.R. Cunningham, G.M. Wilson, AIChE Symp. Ser. 244 (1985) 41–48.

[28] M.A. Zapolskaya, T.V. Emelina, E.G. Komarova, V.B. Kogan, Sb. Teor. Osn. Khim. Tekhnol. (Leningrad) (1975) 3–11.

[29] H. Roth, P. Peters-Gerth, K. Lucas, Fluid Phase Equilib. 73 (1992) 147–166.

[30] L.F. Albright, P.T. Shannon, S.-N. Yu, P.L. Chueh, Chem. Eng. Prog., Symp. Ser. 59 (1963) 66–74.

[31] D. Walther, G. Maurer, Ber. Bunsen-Ges. Phys. Chem. 96 (1992) 981–988.

[32] I.I. Vasil'eva, A.A. Naumova, A.A. Polyakov, T.N. Tyvina, V.V. Fokina, Zh. Prikl. Khim. 60 (1987) 559–562.

[33] K. Fischer, M. Wilken, J. Gmehling, Experimental determination of oxygen and nitrogen solubilities in organic solvents up to 10 MPa, J. Chem. Thermodyn. (1999) submitted for publication.