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High-Pressure Vapor−Liquid Equilibria of Two Binary Systems: Carbon Dioxide + Cyclohexanol and Carbon Dioxide + Cyclohexanone

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Vapor−liquid equilibria for carbon dioxide + cyclohexanol and carbon dioxide + cyclohexanone were measured using an apparatus based on a static-analytic method with in situ samplings. *P*, *T*, *x*, *y* measurements were made at pressures up to 22 MPa. The carbon dioxide + cyclohexanol system was studied at 433 and 473 K, and carbon dioxide + cyclohexanone, at 433 and 473 K. The results are correlated by the Redlich−Kwong−Soave and Peng and Robinson equations and several mixing rules. The best fittings are obtained with the Peng−Robinson equation of state and a two-parameter mixing rule, i.e. within 1.1% for both pressures and vapor mole fractions on the carbon dioxide + cyclohexanone system and within 1.9% for pressures and 2.9% for vapor mole fractions on the carbon dioxide + cyclohexanol system. More recent equations by Patel and Teja and Salim and Trebble show no significant advantages.

Introduction

The use of carbon dioxide for supercritical fluid extraction has been extensively studied. Studies on mixtures of carbon dioxide + cyclohexanol and carbon dioxide + cyclohexanone are important, as these mixtures have industrial applications, for example the crystallization of cyclotrimethylenetrinitramine in cyclohexanone under supercritical conditions.

For the carbon dioxide + cyclohexanone system, results have been published by Chang (1992) and Chang et al. (1995). For the carbon dioxide + cyclohexanol system, there are results by Chen and Lee (1996). The *P*, *T*, *x*, *y* data by Chang was at 298 K while Chang et al. (*P*, *T*, *x*, *y* data) made measurements at 290.8, 300.9, and 310.1 K. These temperatures are much lower than ours and allow a measurement representation over a large temperature range. Chen and Lee have reported solubility (*P*, *T*, *x*) data at 333.15, 393.15, and 453.15 K.

Table 1. Vapor−Liquid Equilibrium for Carbon Dioxide (1) + Cyclohexanol (2)

T/K	P/MPa	x_1	$10^3\sigma(x_1)$	y_1	$10^3\sigma(y_1)$	$P_{\mathrm{cal}}{}^a$/MPa	$y_{1,\mathrm{cal}}{}^a$
433.2	3.55	0.089	3	0.943	3	3.67	0.958
433.2	7.06	0.180	4	0.947	4	7.20	0.966
433.2	10.45	0.271	5	0.946	4	10.60	0.963
433.2	14.05	0.368	6	0.932	5	14.10	0.955
433.2	17.77	0.469	8	0.922	5	17.60	0.940
433.2	19.87	0.542	8	0.904	4	19.98	0.924
433.2	21.50	0.602	7	0.889	4	21.80	0.906
433.2	22.48	0.650	7			23.10	0.887
473.2	7.60	0.180	4	0.888	6	7.51	0.919
473.2	11.00	0.265	5	0.893	6	10.77	0.920
473.2	14.11	0.348	7	0.885	6	13.84	0.913
473.2	17.58	0.438	8	0.865	7	17.00	0.898
473.2	19.82	0.520	8	0.840	6	19.66	0.877
473.2	21.20	0.573	6			21.21	0.859

[a] Calculated values with the PR equation of state and mixing rule R2.

Experimental Section

Apparatus. The apparatus is fully described by Figuière et al. (1980). The reliability of measurements with this apparatus was successfully checked against literature data. It was used without any modification, except the position of the pressure transducer. The pressure transducer, Sedeme type MD500, has a 0−50 MPa range. It was used at 333 K at the end of a capillary connected to the equilibrium cell. Pressure transducer calibrations were performed to an accuracy of ±0.003 MPa against a dead weight balance from Desgranges and Huot (model 5202). Thermocouples were calibrated within ±0.1 K by a 25 Ω platinum probe, Lyon-Alemand-Louyot (model STHP-B) using a four-lead multimeter (Enertec, Schlumberger 7081, 2×10^7 points). Because of temperature instabilities in the air thermostat and small temperature gradients at the bottom of the equilibrium cell, equilibrium temperatures are only accurate to within ±0.25 K at 473 K and ±0.15 K at the lower temperatures. A Girdel gas chromatograph, model 3000, fitted with a thermal conductivity detector (TCD) was used for the analyses. The TCD was repeatedly calibrated by introducing pure components through a syringe. Uncertainties in the mole fractions (both vapor and liquid) were obtained from GC calibration curves, and the dispersion was observed on at the least five samples successively withdrawn from the cell. Each sample withdrawn is very small in order not to disturb the equilibrium, less than 1 mg compared to the volume of the cell which is 50 cm^3. Uncertainties in the mole fractions are given, for each measured point, in the tables of experimental results.

Materials. Cyclohexanone and cyclohexanol are from Prolabo (Grade: chemical for analysis), and their certified

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Table 2. Vapor−Liquid Equilibrium for Carbon Dioxide (1) + Cyclohexanone (2)

T/K	P/MPa	x_1	$10^3\sigma(x_1)$	y_1	$10^3\sigma(y_1)$	$P_{cal}{}^a$/MPa	$y_{1,cal}{}^a$
433.5	3.03	0.103	4	0.946	5	3.12	0.945
433.5	5.83	0.195	6	0.962	3	5.86	0.958
433.5	9.55	0.315	7	0.961	3	9.51	0.959
433.5	13.05	0.428	8	0.943	3	13.03	0.951
433.5	16.49	0.528	8	0.927	4	16.17	0.938
433.5	19.40	0.638	8	0.902	4	19.48	0.913
433.5	21.30	0.736	6	0.865	4	21.87	0.872
453.2	4.43	0.137	4	0.928	4	4.43	0.928
453.2	8.93	0.276	6	0.943	3	8.85	0.940
453.2	13.48	0.409	8	0.920	4	13.16	0.932
453.2	17.46	0.531	8	0.904	6	17.09	0.914
453.2	20.86	0.660	7	0.854	5	20.83	0.874
453.2	21.52	0.714	7	0.843	5	22.02	0.847

[a] Calculated values with the PR equation of state and mixing rule R2.

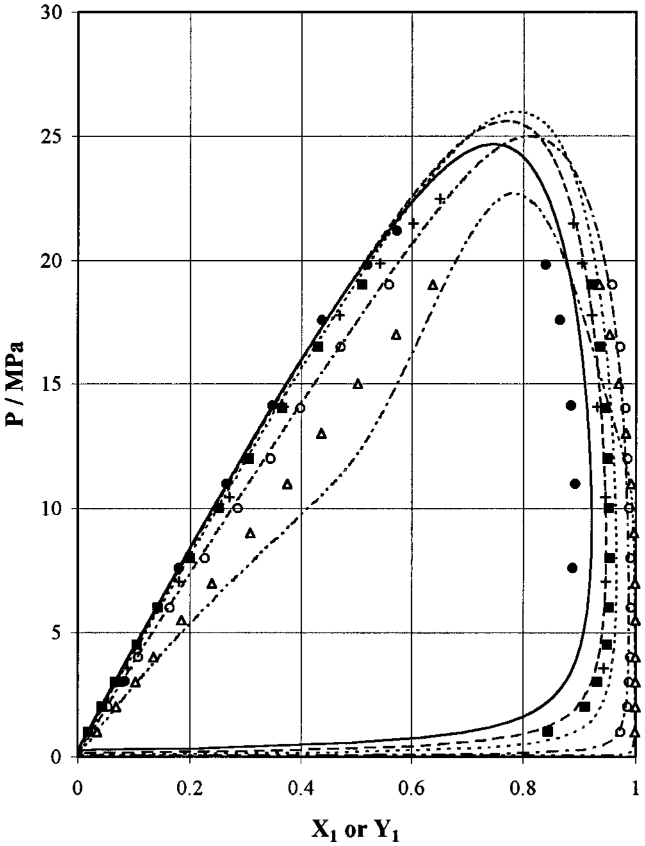

Figure 1. Pressure as a function of carbon dioxide mole fraction in the carbon dioxide(1) + cyclohexanol (2) system at different temperatures: 333 K (△), 393 K (○), and 453 K (+), from Chang et al. (1995); 433 K (■) and 473 K (●), this work. Lines were calculated with the PR EoS and the mixing rule R2: (−••−) at 333 K; (−•−) at 393 K; (•••) at 433 K; (- - -) at 453 K; (—) at 473 K.

CPG purities are respectively 99 and 98.5%. Their densities, measured with an Anton Paar DMA 55 vibrating tube densimeter are respectively 0.942 38 g·cm^{-3} and 0.944 65 g·cm^{-3} at 298.15 K and 0.937 95 g·cm^{-3} and 0.940 77 g·cm^{-3} at 303.15 K. Corresponding literature data are 0.942 21 g·cm^{-3} (Dernini et al., 1989) and 0.945 11 g·cm^{-3} (Rajagopal and Subrahmanyam, 1980) at 298.15 K and 0.9374 g·cm^{-3} (Durov and Arkymov, 1986) and 0.9412 g·cm^{-3} (Shinomiya, 1990) at 303.15 K. These two compounds were used without further purification except for careful degassing before loading into the equilibrium cell. Carbon dioxide was from l'Air Liquide with a certified minimum purity of 99.995 volume %.

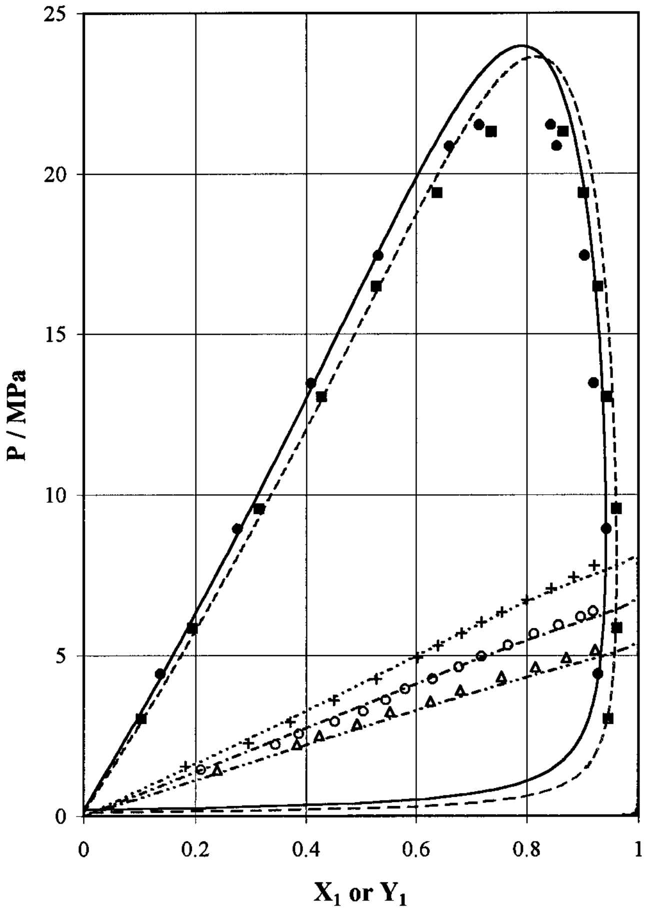

Figure 2. Pressure as a function of carbon dioxide mole fraction in the carbon dioxide (1) + cyclohexanone (2) system at different temperatures: 290 K (△), 300 K (○), and 310 K (+), from Chen and Lee (1996); 433 K (■) and 453 K (●), this work. Lines were calculated with the PR EoS and the mixing rule R3: (−••−) at 290 K; (−•−) at 300K; (•••) at 310 K; (- - -) at 433 K; (—) at 453 K.

Experimental Results

P, T, x, y results for carbon dioxide + cyclohexanol are given in Table 1 and carbon dioxide + cyclohexanone in Table 2. The first, second, third, and fifth columns give respectively temperatures, pressures, liquid mole fractions, and vapor mole fractions. The fourth and sixth columns give uncertainties on liquid $\sigma(x_1)$ and vapor $\sigma(y_1)$ mole fractions, while the seventh and eighth columns give the calculated pressures and calculated vapor mole fractions using the Peng−Robinson equation of state and the mixing rule R2 (see Appendix).

The results are plotted in Figures 1 and 2, and the corresponding K values are plotted in Figures 3 and 4.

Measurements on the carbon dioxide + cyclohexanone system were limited to 453 K, because of the observed decomposition of cyclohexanone in the equilibrium cell. The chromatograms of the samples withdrawn from the cell showed two new peaks which increased with time; the area of these new peaks being about 8% of the cyclohexanone peak after 8 h at 473 K. At 453 K, degradation after 8 h was negligible.

Composition uncertainties resulting from an error calculation take into account the uncertainty in the detector calibration, $\sigma(R_i)$, and the repeatibility of chromatographic areas, $\sigma(A_i)$, corresponding to component i. The number of moles, N_i, of each component is computed from the chromatograph peak areas, A_i:

$$N_i = A_i R_i \tag{1}$$

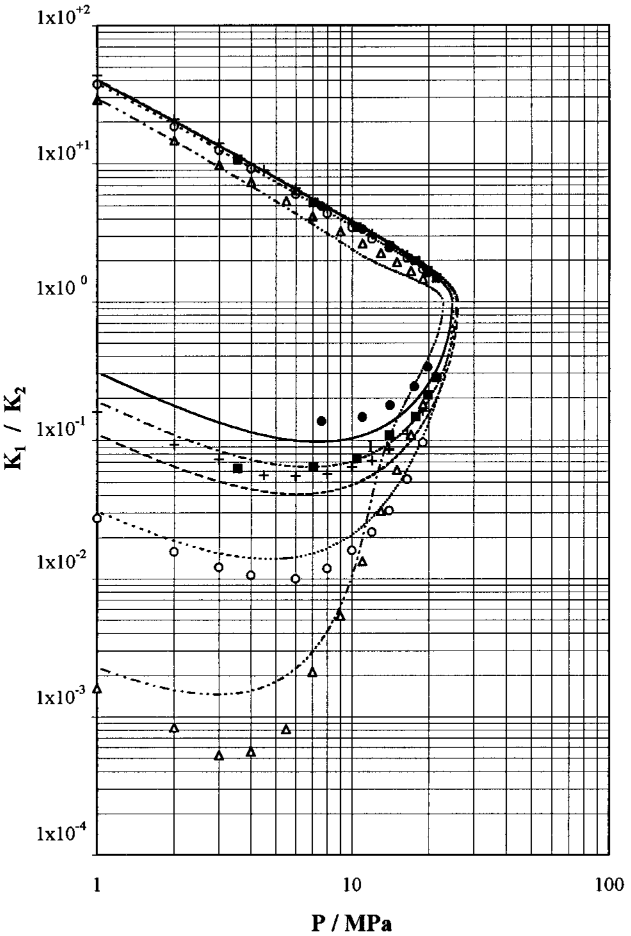

Figure 3. *K* values as a function of pressure in the carbon dioxide (1) + cyclohexanol (2) system at different temperatures: 333 K (△), 393 K (○), and 453 K (+), from Chang et al. (1995); 433 K (■) and 473 K (●), this work. Lines were calculated with the PR EoS and the mixing rule R2: (—••—) at 333 K; (—•—) at 393 K; (•••) at 433 K; (- - -) at 453 K; (—) at 473 K.

where R_i is the response coefficient of the detector for component *i*. Thus for a binary system, the uncertainty on mole fractions, $\sigma(z_1)$, where $z = x$(liquid) or $z = y$(vapor), is

$$\sigma(z_1)/z_1 = A_2R_2/(A_1R_1 + A_2R_2)[\sigma(A_1)/A_1 + \sigma(R_1)/R_1 + \sigma(A_2)/A_2 + \sigma(R_2)/R_2] \quad (2)$$

The data results were correlated by the equations of state: Redlich−Kwong−Soave (RKS) (Soave, 1972), Peng and Robinson (PR) (1976), Patel and Teja (PT) (1982), and Salim and Trebble (ST) (1991). The combining rules used in combination with these EoS are given in the Appendix. The binary interaction parameters were adjusted using the two following objective functions:

−for *P*, *T*, *x*, *y* data

$$Q = \sum_{j=1}^{n}[((P_{j,\exp} - P_{j,\mathrm{cal}})/P_{j,\exp})^2 + ((y_{1,\exp} - y_{1,\mathrm{cal}})/y_{1,\exp})^2] \quad (3)$$

−for *P*, *T*, *x* data

$$Q = \sum_{j=1}^{n}[(P_{j,\exp} - P_{j,\mathrm{cal}})/P_{j,\exp}]^2 \quad (4)$$

with *n* being the total number of experimental values.

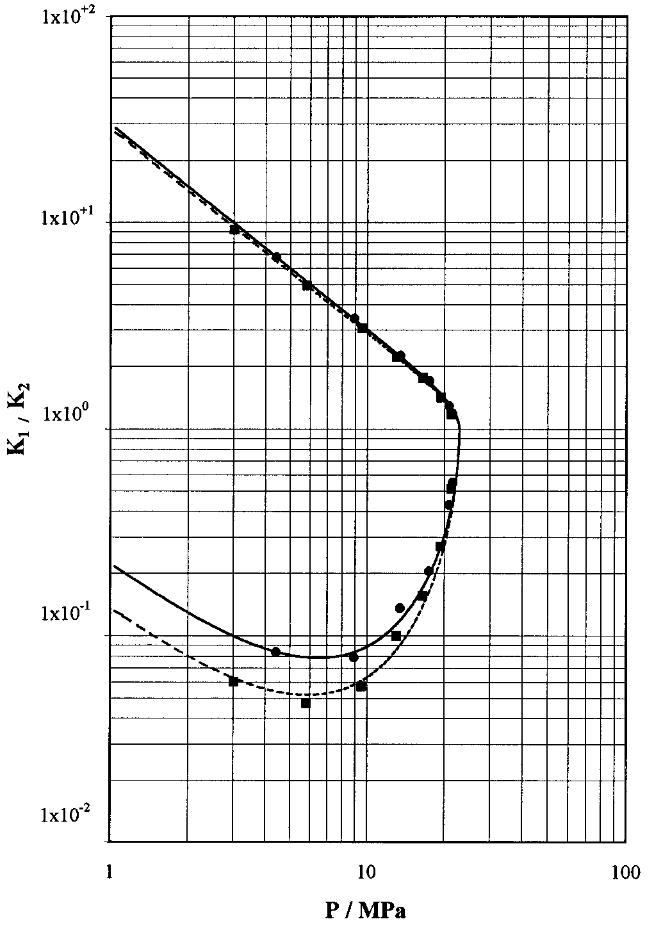

Figure 4. *K* values as a function of pressure in the carbon dioxide (1) + cyclohexanone (2) system at different temperatures: 433 K (■) and 453 K (●), this work. Lines were calculated with the PR EoS and the mixing rule R3: (- - -) at 433 K; (—) at 453 K.

Table 3. Critical Parameters and Acentric Factors, ω, Used in the Cubic Equations of State

compound	ref	P_c/MPa	T_c/K	ω
carbon dioxide	Reid et al. (1977)	7.38	304.2	0.225
cyclohexanol	DIPPR (1987)	3.75	625.0	0.550
cyclohexanone	DIPPR (1987)	3.85	629.0	0.443

The critical values and acentric factors are reported in Table 3. Binary interaction parameters are given in Table 4. The quality of the corresponding representations is given in Table 5. For carbon dioxide + cyclohexanol, rules R0 and R1 give poor results. Rule R2 gives a marked improvement, especially with the PR EoS, which gives a relative mean square deviations of 1.9% on pressure and 2.9% on the vapor mole fraction. The same conclusion results from treating simultaneously all the data (our data with the two highest isotherms of Chen and Lee, 1996), and it is concluded that all the data are consistent. The results of Chen and Lee (1996) at 333.15 K are not well represented, probably because the cubic EoS exhibits a tendency to show liquid−liquid phase separation (see Figure 1). Our carbon dioxide + cyclohexanone results are badly represented with both R0 and R1 rules. The rule R2 is the best, with a relative mean square deviation of 1.1%, in both the pressure and vapor mole fraction (PR EoS). Simultaneous representation of our data with those of Chang et al. (1995) requires the rule R3 (three parameters, one for temperature dependence of the binary interaction parameter on the *a* term). With the rule R3 (parameter adjustment done with an objective function

Table 4. Binary Interaction Parameter Values Associated with the Redlich−Kwong−Soave (RKS) and Peng−Robinson (PR) Equation of State

mixture	EoS and combining rule	ka_{ij}	kb_{ij}	ka^{t}_{ij}
carbon dioxide + cyclohexanol	RKS-R1[a]	0.133		
	RKS-R2[a]	0.089	−0.065	
	PR-R1[a]	0.125		
	PR-R2[a]	0.082	−0.064	
	RKS-R1[b]	0.150		
	RKS-R2[b]	0.090	−0.063	
	PR-R1[b]	0.141		
	PR-R2[b]	0.082	−0.064	
carbon dioxide + cyclohexanone	RKS-R1[c]	0.077		
	RKS-R2[c]	0.056	−0.031	
	PR-R1[c]	0.072		
	PR-R2[c]	0.052	−0.026	
	RKS-R2[d]	0.020	−0.013	
	PR-R2[d]	0.024	−0.012	
	RKS-R3[d]	−0.102	−0.012	0.391
	PR-R3[d]	−0.077	−0.011	0.322

[a] 14 data, this work. [b] 36 data; 14 data from this work + 22 data from Chen and Lee (1996) (isotherms at 393.15 and 453.15 K). [c] 13 data, this work. [d] 53 data; 13 data from this work + 40 data from Chang et al. (1995).

Table 5. Representation of Vapor−Liquid Equilibria of Mixtures Using Cubic Equations of State

mixture	combining rule	$100\sigma_P^{R}$ [e]		$100\sigma_{y_1}^{R}$ [e]	
		RKS	PR	RKS	PR
carbon dioxide (1) + cyclohexanol (2)	R0[a]	36	36	4.6	5.1
	R1[a]	11.	10	4.9	4.2
	R2[a]	2.4	1.9	3.8	2.9
	R1[b]	12.9	13.1	3.2	2.8
	R2[b]	2.1	1.8	2.4	2.0
carbon dioxide (1) + cyclohexanone (2)	R0[c]	19	19	3.7	3.0
	R1[c]	5.6	5.3	2.4	1.6
	R2[c]	1.8	1.1	2.0	1.1
	R2[d]	6.9	6.4		
	R3[d]	3.6	3.6		

[a] 14 data, this work. [b] 36 data; 14 data from this work + 22 data from Chen and Lee (1996) (isotherms at 393.15 and 453.15 K). [c] 13 data, this work. [d] 53 data; 13 data from this work + 40 data from Chang et al. (1995). [e] $\sigma_u^{R} = 100\sqrt{\sum_{j=1}^{n}((\boldsymbol{u}_{j,\mathrm{exp}} - u_{j,\mathrm{cal}})/\boldsymbol{u}_{j,\mathrm{exp}})^2/(n-k)}$, with u = either P or y and k = number of model parameters.

appearing in eq 4), the relativemean square deviations in pressures are 3.6% either for PR EoS or RKS EoS. The relative mean square deviations in pressures of 3.6% is satisfactory because the correlation includes all the results from Chang et al. (1995) at low pressures where the relative deviations are significant. The results of Chang (1992) were found to be inconsistent with the results of Chang et al. (1995) and with our values. Chang et al. (1995) made no comparison with their earlier results, Chang (1992). As the Patel and Teja EoS (1982) and the Salim and Trebble EoS (1991) were found to give results similar to those with PR EoS and RKS EoS, the corresponding results are not reported in this paper, but on request, they are available from the authors.

Acknowledgment

We are to Albert Chareton who took part in the VLE measurements.

Appendix

The generalized form of cubic equations of state is

$$P = RT/(v - b) - a/(v^2 + uv + wb)$$

For the PR EoS, we have $u = 2b$ and $w = -b$ while for RKS EoS, we have $u = b$ and $w = 0$.

Mixing rules are

$$a_{\mathrm{m}} = \sum_{i=1}^{n_{\mathrm{c}}}\sum_{j=1}^{n_{\mathrm{c}}} a_{ij}x_i x_j$$

$$b_{\mathrm{m}} = \sum_{i=1}^{n_{\mathrm{c}}} b_i x_i$$

except for rule R3 where

$$b_{\mathrm{m}} = \sum_{i=1}^{n_{\mathrm{c}}}\sum_{j=1}^{n_{\mathrm{c}}} b_{ij}x_i x_j$$

Combining rules are

R0: no adjustable parameter

$$a_{ij} = (a_i a_j)^{1/2}$$

R1: one adjustable parameter

$$a_{ij} = (1 - ka_{ij})(a_i a_j)^{1/2}$$

R2: two adjustable parameters

$$a_{ij} = (1 - ka_{ij})(a_i a_j)^{1/2}$$

$$b_{ij} = (1 - kb_{ij})(b_i b_j)^{1/2}$$

R3: three adjustable parameters

$$a_{ij} = (1 - ka_{ij} - ka^{\mathrm{t}}_{ij}\, T)(a_i a_j)^{1/2}$$

$$b_{ij} = (1 - kb_{ij})(b_i b_j)^{1/2}$$

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