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Solubility of Ethene in Water and in a Medium for the Cultivation of a Bacterial Strain

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ABSTRACT: The solubility of ethene in water and in the fermentation medium of *Xanthobacter* Py2 was determined with a Ben-Naim−Baer type apparatus. The solubility measurements were carried out in the temperature range of (293.15 to 323.15) K and at atmospheric pressure with a precision of about ± 0.3 %. The Ostwald coefficients, the mole fractions of the dissolved ethene, at the gas partial pressure of 101.325 kPa, and the Henry coefficients, at the water vapor pressure, were calculated using accurate thermodynamic relations. A comparison between the solubility of ethene in water and in the cultivation medium has shown that this gas is about 2.4 % more soluble in pure water. On the other hand, from the solubility temperature dependence, the Gibbs energy, enthalpy, and entropy changes for the process of transferring the solute from the gaseous phase to the liquid solutions were also determined. Moreover, the perturbed-chain statistical associating fluid theory equation of state (PC-SAFT EOS) model was used for the prediction of the solubility of ethene in water. New parameters, k_{ij}, are proposed for this system, and it was found that using a k_{ij} temperature-dependent PC-SAFT EOS describes more accurately the behavior solubilities of ethene in water at 101.325 kPa, improving the deviations to 1 %.

INTRODUCTION

The solubility of gases in liquids is important in many application areas, such as in chemical engineering (gas absorption and striping process design), in biotechnology and environmental sciences.[1,2] This research area also has a special theoretical interest. For instance, studies on model systems, like simple hydrocarbons in water, are important to test liquid theories and provide information on aqueous solutions' structure and hydrophobic interactions.[1,3] The difficulties involved in modeling gas−liquid equilibrium (GLE) especially at low pressures are known. Correlation and predictive methods are necessary for applications of phase equilibria if a few information are available for the systems under study. One of the main problems is the lack of accurate data to verify the performance of the models. However, several theoretical, semiempirical, and empirical methods have been proposed to correlate and predict solubilities of gases in liquids which depend on the nature of the system. In particular, semiempirical versions of scale particle theory (SPT) have been used to describe the GLE, working remarkably well even for aqueous solutions, as pointed out by Rettich et al.[4]

In recent years, many efforts were done for applying equations of state (EOS) to solve this problem. The success of an EOS is determined by the type of compounds and also by the working conditions. For associating fluids, a method based in EOS has been proposed: the statistical associating fluid theory (SAFT) model. The SAFT equation of state developed by Chapman et al.[5,6] is a molecular-based equation, which was designed to take into account the effects of molecular association.

An improvement of the SAFT model, the perturbed-chain SAFT (PC-SAFT),[7] has been proposed as a result of the application of the perturbation theory, suggested by Barker Henderson, to the hard-chain reference fluid. This model has been already successfully used with a huge number of systems containing gases, solvents, polymers, and copolymers, as well as to associating systems.[7,8] In 2004, a theoretical study was carried out by García et al. using SAFT and PC-SAFT equations to model the solubilities (at 1 atm) of CO_2 in halohydrocarbons.[9] Since then, high pressure solubility of gases in many solvents, such us perfluoroalkanes,[10] polymers,[11] and ionic liquids[12,13] also have been modeled using SAFT based theories.

On the other hand, the solubility measurements of ethene in the aqueous growth medium of *Xanthobacter* Py2 will be important for the quantification of the fermentation processes. These microorganisms are able to oxidize ethene and to resolve racemic mixtures of 2,3-epoxyalkanes to optically pure compounds,[14] which may be interesting for the pharmaceutical industry. Furthermore, as the growth medium is an aqueous solution of different salts, a comparison with the ethene solubility in pure water will provide information for the discussion of the salting-out effect. To the best of our knowledge, there are no studies on the solubilities of ethene in the medium for cultivation of bacterial strain, *Xanthobacter* Py2. On the other hand, for the solubility of ethene in pure water the only measurements were carried out by Morrison and Billet[15] with the precision of ± 0.5 %. This work on ethene belongs to a program developed in CQE

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involving solubility measurements of simple gases in liquids, such as argon in micellar aqueous solutions,[16] and propene,[17] butene,[18] and methane[19] in pure water and in fermentation media, which also includes the application of theorical models.[20]

The aim of this work was to measure the solubility of ethene in water and in the medium for cultivation of a bacterial strain, *Xanthobacter* Py2, in the temperature range of (293.15 to 333.15) K and at atmospheric pressure. Furthermore, the PC-SAFT EOS model was tested for the prediction of the solubility of ethene in water.

EXPERIMENTAL SECTION

The solubility measurements of ethene in water and in the cultivation medium of *Xanthobacter* Py2 were carried out using an apparatus similar to that design by Ben-Naim and Baer,[3] which has been detailed described in a previous paper.[16] The solubility of ethene was measured at 13 temperatures in the range (293.15 to 323.15) K. The gas solubility in the fermentation medium was determined at five temperatures in the range (298.15 to 308.15) K which includes the optimal growth temperature of that strain (303.15 K).[21,22] All of the solubility measurements were performed at the atmospheric pressure with a precision of about ± 0.3 %.

Ethene was purchased from Air Liquide with a minimum purity of 0.9995. The water was distilled and deionized in a Millipore apparatus. The growth medium of *Xanthobacter* Py2 is a very dilute aqueous solution of different salts which composition is reported by Wiegant and de Bont,[21] Vishniac and Santer,[22] and Serra et al.[17]

RESULTS AND DISCUSSION

From the measurements of the temperature, pressure, volume of solvent and the corresponding volume of absorbed gas it is possible to calculate:

- The Ostwald coefficients at the experimental conditions, $L_{2,1}(T,P)$ and at infinite dilution, $L_{2,1}^{\infty}(T,P_{s,1})$;
- The mole fractions of dissolved gas, at the gas partial pressure of 101.325 kPa, x_2^N;
- The Henry coefficients, at the water vapor pressure, $H_{2,1}(T,P_{s,1})$.

In these calculations the nonideality corrections for the vapor and liquid phases were carried out using an iterative method similar to that proposed by Vosmansky and Dohnal,[23] which was described in a previous paper.[18]

Assuming that the indexes 1 and 2 represent the solvent and the solute, respectively, and the superscripts V and L indicate the vapor and the liquid phases, the Ostwald coefficient, $L_{2,1}(T,P)$, at the experimental conditions T and P,[1] may be obtained by the relation:

$$L_{2,1}(T,P) = (c_2^{\mathrm{L}}/c_2^{\mathrm{V}})_{\mathrm{eq}} \tag{1}$$

where c_2^{L} and c_2^{V} are the molar concentrations of the gas in the liquid and vapor phases, respectively. For a very dilute solution it is possible to define the Ostwald coefficient at infinite dilution, $L_{2,1}^{\infty}(T, P_{s,1})$, by the limiting value of $L_{2,1}(T,P)$:[1]

$$L_{2,1}^{\infty}(T,P_{s,1}) = \lim_{\substack{c_2^{\mathrm{L}} \to 0 \\ P \to P_{s,1}}} L_{2,1}(T,P) = \lim_{\substack{c_2^{\mathrm{L}} \to 0 \\ P \to P_{s,1}}} (c_2^{\mathrm{L}}/c_2^{\mathrm{V}})_{\mathrm{eq}} \tag{2}$$

In this equation, $P_{s,1}$ is the vapor pressure of the pure solvent, which was obtained by a Wagner equation.[24]

On the other hand, the Ostwald coefficient at infinite dilution is related with the Henry coefficient at the water vapor pressure[1] through the equation:

$$L_{2,1}^{\infty}(T,P_{s,1}) = RTZ_1^{*}(T,P_{s,1})\phi_2^{\infty\mathrm{V}}(T,P_{s,1})/H_{2,1}(T,P_{s,1})V_1^{*\mathrm{L}}(T,P_{s,1}) \tag{3}$$

$Z_1^{*}(T, P_{s,1})$ is a compressibility factor calculated[25] from the relation:

$$Z_1^{*}(T,P_{s,1}) = 1 + (B_{11}P_{s,1}/RT) \tag{4}$$

and $\phi_2^{\infty\mathrm{V}}(T, P_{s,1})$ represents the fugacity coefficient of the gas at infinite dilution in the vapor phase, which was obtained[25] by the equation:

$$\phi_2^{\infty\mathrm{V}}(T,P_{s,1}) = \exp[P_{s,1}(2B_{12} - B_{11})/RT] \tag{5}$$

In this latter relation B_{11} is the second virial coefficient for water, which was calculated by the equation proposed by Keyes,[26] and B_{22} represents this coefficient for ethene given by Dymond.[27] In the same equation, B_{12} represents the second cross virial coefficient which was estimated using the Tsonopoulos correlation.[28]

Furthermore, the molar volume of the pure water, represented by $V_1^{*\mathrm{L}}(T,P_{s,1})$ in eq 3, was taken from Kell.[29]

In this work, the Henry coefficients at the water vapor pressure, $H_{2,1}$ $(T, P_{s,1})$, and the mole fractions of the dissolved ethene, x_2, were obtained from the solubility measurements, applying the thermodynamic equilibrium relation

$$\phi_2^{\mathrm{V}}y_2P = \gamma_2'x_2H_{2,1}(T,P_{s,1})\boldsymbol{P}_2 \tag{6}$$

and using an iterative calculation method.[18]

In eq 6, x_2 and y_2 represent the gas mole fraction in the liquid and vapor phases at the temperature, T, and pressure, P, respectively; γ_2' is liquid phase activity of the gas, ϕ_2^{V} its vapor phase fugacity coefficient, and $\boldsymbol{P}_2$ represents the Poynting term, which can be calculated by the approximate relation:

$$\boldsymbol{P}_2 \approx \exp[V_2^{\infty\mathrm{L}}(P - P_{s,1})/RT] \tag{7}$$

For the determination of this term it is necessary the knowledge of the partial molar volume of the ethene at infinite dilution, $V_2^{\infty\mathrm{L}}$, which may be obtained[23,23,30] by the equation:

$$V_2^{\infty\mathrm{L}} = [0.092 + (2.674TP_{c,2}/T_{c,2}\Pi_{s,1}^{*\mathrm{L}})]RT_{c,2}/P_{c,2} \tag{8}$$

where $\Pi_{s,1}^{*\mathrm{L}}$, represents the internal pressure of water, which is equal to 41 atm,[31] and $T_{c,2}$ (= 282.4 K) and $P_{c,2}$ (= 49.7 atm) are the critical temperature and pressure of ethene,[24] respectively.

The activity coefficients in the liquid phase were determined applying the Margules equations,[1,18] and for this system their values are approximately equal to unity.

In the eq 6, the vapor phase fugacity coefficients of the compound it may be obtained[23] by the relation:

$$\ln \phi_i^{v} = (2/v)\sum_{j=1}^{2} y_jB_{ij} - \ln(1 + B/v) \qquad i = 1,2 \tag{9}$$

in which v is the molar volume of the vapor phase, calculated[23] using the expression:

$$v = (RT/P)[0.5 + \sqrt{0.25 + BP/(RT)}] \tag{10}$$

Table 1. Solubility of Ethene in Water, Expressed in Ostwald Coefficients at Experimental Conditions, $L_{2,1}(T,P)$, and at Infinite Dilution $L_{2,1}^{\infty}(T,P_{s,1})$, in Mole Fractions at the Gas Partial Pressure of 101.325 kPa, $x_2{}^N\cdot 10^5$ and in Henry Coefficients at the Water Vapor Pressure, $H_{2,1}(T,P_{s,1})$

T/K	$L_{2,1}(T,P)$	$L_{2,1}^{\infty}(T,P_{s,1})$	$x_2{}^N\cdot 10^5$	$H_{2,1}(T,P_{s,1})\cdot 10^{-9}$/Pa
293.15	0.1318	0.1334	9.946	1.012
295.15	0.1255	0.1270	9.410	1.070
298.15	0.1184	0.1198	8.786	1.145
300.15	0.1140	0.1153	8.411	1.197
303.15	0.1083	0.1096	7.921	1.271
305.15	0.1046	0.1059	7.611	1.323
308.15	0.1004	0.1014	7.228	1.393
310.15	0.09734	0.09835	6.969	1.445
313.15	0.09219	0.09250	6.543	1.539
315.15	0.09045	0.09133	6.382	1.578
318.15	0.08695	0.08777	6.084	1.656
320.15	0.08427	0.08504	5.864	1.718
323.15	0.08063	0.08133	5.565	1.811

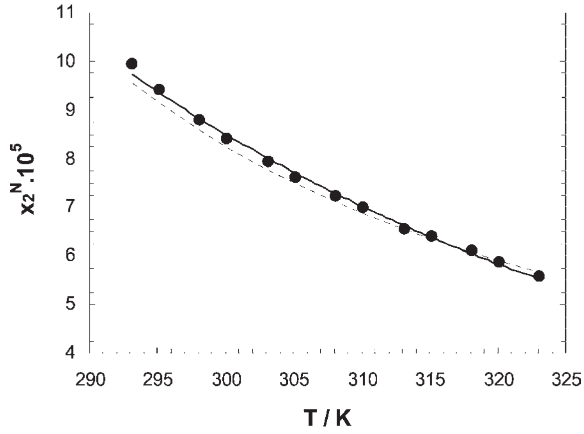

Figure 1. Mole fractions of ethene in water in the temperature range of (293.15 to 323.15) K and at the gas partial pressure of 101.325 kPa, $x_2{}^N\cdot 10^5$: ●, experimental data and calculated values from eq 12; (—), in comparison with the results carried out by Wilhelm et al.[32] correlation (- - -).

Table 2. Thermodynamic Properties, Gibbs Energy, $\Delta G°$, Enthalpy, $\Delta H°$, and Entropy, $\Delta S°$, for the Dissolution of Ethene in Water

T	$\Delta G°$	$\Delta H°$	$\Delta S°$
K	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}\cdot.\text{K}^{-1}$
293.15	22.48	−16.8	−134
295.15	22.74	−16.5	−133
298.15	23.14	−16.1	−132
300.15	23.40	−15.9	−131
303.15	23.80	−15.5	−130
305.15	24.05	−15.2	−129
308.15	24.44	−14.8	−128
310.15	24.69	−14.6	−127
313.15	25.07	−14.2	−125
315.15	25.32	−13.9	−124
318.15	25.69	−13.5	−123
320.15	25.94	−13.3	−122
323.15	26.30	−12.9	−121

Table 3. Solubility of Ethene in the Growth Medium of *Xanthobacter* Py2, Expressed in Ostwald Coefficients at Experimental Conditions, $L_{2,1}(T,P)$, and at Infinite Dilution $L_{2,1}^{\infty}(T,P_{s,1})$, in Mole Fractions at the Gas Partial Pressure of 101.325 kPa, $x_2{}^N\cdot 10^5$ and in Henry Coefficients at the Water Vapour Pressure, $H_{2,1}(T,P_{s,1})$

T/K	$L_{2,1}(T,P)$	$L_{2,1}^{\infty}(T,P_{s,1})$	$x_2{}^N\cdot 10^5$	$H_{2,1}(T,P_{s,1})\cdot 10^{-9}$/Pa
298.15	0.1158	0.1172	8.602	1.170
300.15	0.1116	0.1129	8.239	1.222
303.15	0.1050	0.1062	7.678	1.311
305.15	0.1025	0.1036	7.448	1.352
308.15	0.09790	0.09893	7.050	1.428

In this late relation, B represents the second virial coefficient of the vapor phase, determined by:

$$B = y_1^2 B_{11} + y_2^2 B_{22} + 2y_1 y_2 B_{12} \qquad (11)$$

It should be noted that for the calculation of the solubility of ethene in the growth medium of the bacterial strain it was necessary to assume that the properties of this solution were similar to those in pure water. However, this approximation will be acceptable, since the fermentation medium is a very dilute aqueous solution.

The solubility data of ethene in water at the experimental temperature range are presented in Table 1. A comparison of our results with those obtained by the correlation of Wilhelm et al.[32] based on the solubility measurements reported by Morrison and Billet[15] are shown in Figure 1. The differences are more significant at the lowest temperatures, and the average deviation between both data sets is about 1.3 %.

To account for the temperature effect on the gas solubility in water, the equation recommended by Clarke and Glew[33] and Weiss[34] with three parameters was used:

$$\ln x_2^N = A_0 + A_1(T/100)^{-1} + A_2 \ln(T/100) \qquad (12)$$

Using this equation $A_0 = -48.4219$, $A_1 = 65.8275$ K, and $A_2 = 15.5683$ for this system. The standard deviation in $\ln x_2^N$ is 0.0045.

In the temperature range covered by these measurements, the solubility of ethene decreases with increase of temperature. A similar behavior was found in the dissolution of propene[17] and 1-butene[18] in water, propene being the most soluble alkene followed, respectively, by ethene and 1-butene.

From the eq 12 it is possible to calculate the thermodynamic quantities for the process of transferring the ethene molecules from the vapor to the water phase. In this way, the standard molar Gibbs energy, entropy, and enthalpy changes, ΔG^0, ΔS^0, and ΔH^0, respectively, were determined by the relations:

$$\Delta G^0 = -RT \ln x_2^N \qquad (13)$$

$$\begin{aligned}\Delta S^0 &= -(\partial \Delta G^0/\partial T) \\ &= R\{A_0 + A_2[1 + \ln(T/100)]\} \qquad (14)\end{aligned}$$

$$\Delta H^0 = \Delta G^0 + T\Delta S^0 = R(-100A_1 + A_2 T) \qquad (15)$$

The values of these thermodynamic quantities, in the temperature range (293.15 to 323.15) K, are presented in Table 2. A positive solvating Gibbs energy that increases with temperature is observed. Furthermore, the solvating enthalpy and entropy for ethene in water are both negative and also increase with the temperature. This behavior was also observed in the dissolution of propene[17] and 1-butene[18] in water, which has been interpreted by several authors[35−37] in terms of changes induced by the gas dissolution on the structure of water.

The solubility of ethene in the growth medium of *Xanthobacter* Py2 was also measured at five different temperatures in the range of (298.15 to 308.15) K and at atmospheric pressure. The results are presented in Table 3 and in Figure 2. As expected, the solubility of ethene in the fermentation medium also decreases with temperature. The comparison between the mole fractions of ethene in the cultivation medium and those obtained in pure water (Figure 2) shows that ethene is about 2.4 % more soluble in water. This behavior is also observed with the solubility of propene[16] and 1-butene[17] in the same solution. Since the cultivation medium of the *Xanthobacter* Py2 is an electrolytic solution, this behavior may be a consequence of possible water structural changes by the ions in solution, resulting in a lower gas solubility (salting-out effect).

The Clarke−Glew−Weiss[33,34] equation was also used to describe the temperature dependence of the mole fractions of ethene in the cultivation medium:

$$\ln x_2^N = A_0 + A_1(T/100)^{-1} \tag{16}$$

where A_0 = −15.5202 and A_1 = 18.3543 K. The standard deviation in $\ln x_2^N$ was 0.0052.

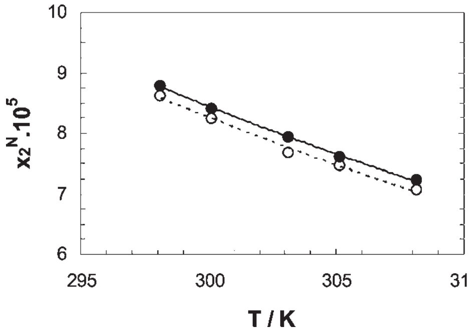

Figure 2. Comparison between the experimental molar fractions of ethene in ●, water and in the ○, fermentation medium at the gas partial pressure of 101.325 kPa, $x_2{}^N \cdot 10^5$, in the temperature range of (298.15 to 308.15) K.

Table 4. Gibbs Energy Changes, $\Delta G°$, for the Dissolution of Ethene in the Cultivation Medium

T/K	298.15	300.15	303.15	305.15	308.15
$\Delta G°/\text{kJ}\cdot\text{mol}^{-1}$	23.21	23.47	23.86	24.12	24.50

The thermodynamic quantities for the dissolution of ethene in the fermentation medium were determined using the eq 13 to 15 considering A_2 = 0. The values of the Gibbs energy are listed in Table 4, and the enthalpy and entropy changes for dissolution process are −15.3 $\text{kJ}\cdot\text{mol}^{-1}$ and −129 $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, respectively. As can be observed, there is no significant change in these thermodynamic properties from those calculated for pure water. Since the medium is a very dilute aqueous solution, this behavior was predictable.

■ PC-SAFT EQUATION OF STATE

The PC-SAFT equation of state was derived by Gross and Sadowski.[7] This equation is given in terms of the compressibility factor, Z, by the relation:

$$Z = 1 + Z^{\text{hc}} + Z^{\text{disp}} + Z^{\text{assoc}} \tag{17}$$

where Z^{id} (= 1), Z^{hc}, Z^{disp}, and Z^{assoc} are the ideal gas, the hard-chain,[5,38−40] the dispersive, and the association contributions, respectively (details given in refs 6 and 41). Apart from the three pure-component parameters of the PC-SAFT for nonassociating compounds (segment number m, segment diameter σ, and segment energy parameter ε/k), two pure-component parameters determine the associating interactions between the association site A_i and B_i of water (component i): the association energy $\varepsilon^{A_iB_i}/k$ and the effective association volume $\kappa^{A_iB_i}$. In this report, the modified Berthelot-Lorentz mixing rule is used

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \tag{18}$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\cdot\varepsilon_{jj}}(1 - k_{ij}) \tag{19}$$

where k_{ij} is introduced to correct the dispersive interaction.

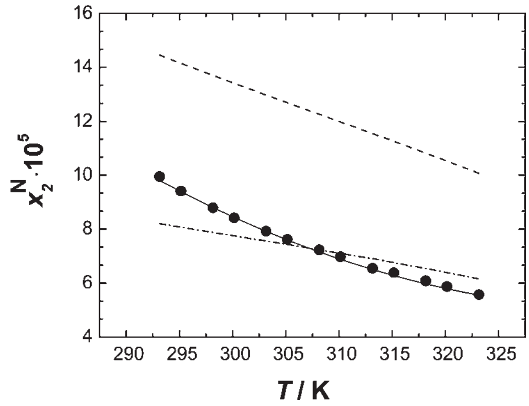

Figure 3. Comparison between ●, experimental results and calculated values given by the PC-SAFT EOS (- - - -, k_{ij} = 0; — · — · —, k_{ij} = 0.043 and ——, $k_{ij} = f(T)$ eq 20) for the solubility of ethene in water in the temperature range of (293.15 to 323.15) K and at the gas partial pressure of 101.325 kPa, $x_2{}^N \cdot 10^5$.

Table 5. Pure-Component Parameters of the PC-SAFT EOS for Water and Ethene Used in This Work and Absolute Average Percentage Deviation, AAD,[a] for the Correlation of Saturation Properties

component	m_i	σ_i	ε_i/k/K	$\kappa^{A_iB_i}$	$\varepsilon^{A_iB_i}/k$/K	AAD %		T range/K
						P_{sat}	ρ^{sat}	
ethene[42]	1.5518	3.4393	179.84	-	-	0.17	0.75	154−275
water[43]	0.925310	2.7322	142.42	0.049988	3298.4	0.24	1.0	280−370

[a] AAD= $100/N\cdot\Sigma|\rho_{i,\text{EOS}} - \rho_{i,\text{exp}}|/\rho_{i,\text{exp}}$ where N = number of points.

Pure Compounds. For ethene (m_i, σ_i, and ε_i/k) and water (m_i, σ_i, and ε_i/k; $\kappa^{A_iB_i}$ and $\varepsilon^{A_iB_i}/k$), new pure-component parameters of the PC-SAFT EOS were calculated fitting the vapor pressure and density in the temperature range under study. A two-site model was used for the water molecule. The values obtained are gathered in Table 5 together with the relative mean deviation of vapor pressures and liquid densities, along with the temperature range covered.

Ethene–Water System. The PC-SAFT predictions for the ethene–water system are presented in Figure 3. As can be seen, from this figure, the model is unable to reproduce the experimental results, unless $k_{ij} = 0.043$ is introduced. In this case, an overall agreement of 8.1 % is achieved. This agreement can be improved introducing a temperature dependence in k_{ij}.

New calculations of k_{ij} in the range (293.15 to 323.15) K were then performed. The obtained values ranging from 0.028 to 0.052 were fitted by a second-order polynomial in temperature

$$k_{ij} = -1.450 + 9.81 \cdot 10^{-3} T(T/\mathrm{K}) - 1.32 \cdot 10^{-5} T^2 (T/\mathrm{K}) \tag{20}$$

Using eq 20 the model is able to predict the experimental solubilities of the ethene–water system better than 1 %.

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