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Optimum reparameterization of power function models

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ABSTRACT

Power function models are frequently used to describe rates of adsorption (as in the common Freundlich model) and chemical reaction (for estimation of reaction orders). When power function models are used to fit available experimental data, correlations among obtained parameter estimates are normally very high, which may cause significant numerical problems during the estimation of the model parameters and lead to misinterpretation of the statistical significance of final results. In this work, a reparameterization technique is presented to allow for reduction of parameter correlations in power function models. Afterwards, the two-step parameter estimation procedure [Schwaab, M., Pinto, J.C., 2007. Optimum reference temperature for reparameterization of the Arrhenius equation. Part 1: problems involving one kinetic constant. Chemical Engineering Science 62, 2750–2764; Schwaab, M., Lemos, L.P., Pinto, J.C., 2008b. Optimum reference temperature for reparameterization of the Arrhenius equation. Part 2: problems involving multiple reparameterizations. Chemical Engineering Science 63, 2895–2906.] is used for optimum reparameterization and estimation of uncorrelated model parameters in power function models.

1. Introduction

Existence of high correlations among the parameter estimates of a mathematical model can cause significant numerical problems during the estimation of model parameters, as the minimization of the objective function may become inefficient (Espie and Macchietto, 1988) and the statistical characterization of the final parameter estimates may lack significance (Watts, 1994). Some of these difficulties can be observed during the estimation of parameters of power function models because of the usually very high correlations among the obtained parameter estimates. Power function models are commonly used in the chemical engineering field to describe rate expressions and equilibrium conditions. Some examples are the Freundlich equation, used to describe adsorption of gases and liquids onto solid surfaces (Guo et al., 2006), and the well-known *n*th-order reaction rate models.

Schwaab and Pinto (2007) and Schwaab et al. (2008b) have recently proposed an algorithm for optimum reparameterization of the Arrhenius equation (frequently used in kinetic models) and reduction of parameter correlations in parameter estimation problems. It was shown that the explicit introduction of a reference temperature into the standard Arrhenius equation and the proper selection of reference temperature values can allow for minimization (and sometimes elimination) of correlations among parameter estimates and simultaneous minimization of the relative standard errors of the parameter estimates.

In this work, a reparameterization technique is proposed in order to allow for minimization of correlations among parameter estimates during estimation of the parameters of power function models. The proposed reparameterization technique is based on the definition of a reference value, which is used to renormalize the original model equation. First, the proposed technique is applied in a simple problem, where it is possible to derive an analytical solution for the reference value that leads to null parameter correlations (and minimum relative error content of final parameter estimates). Then, the numerical optimization procedures proposed by Schwaab and Pinto (2007) and Schwaab et al. (2008a,b) are used to provide the optimum reference values (and, consequently, uncorrelated parameter estimates) in a more complex numerical parameter estimation problem, where an analytical solution cannot be derived.

2. Theoretical framework

A simple power function model can be defined as

$$y = kx^n \tag{1}$$

where x and y are the independent and the dependent measured variables and k and n are two model parameters. The correlation between the parameter estimates for k and n are usually very high. In order to minimize the correlation between the two parameter

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estimates, Eq. (1) can be rewritten in reparameterized forms as

$$y = k_{\mathrm{ref}}(x/x_{\mathrm{ref}})^n \tag{2a}$$

$$y = \exp[A_{\mathrm{ref}} + n\ln(x/x_{\mathrm{ref}})] \tag{2b}$$

where x_{ref} is the reference variable. (The second reparameterization form is particularly interesting when the Arrhenius equation is also used in the model, as it will be shown in Example 2). One must observe that model responses are not affected by the reparameterization, since the inclusion of the reference variable leads to redefinition of the model parameters, k_{ref} and A_{ref}, as

$$k_{\mathrm{ref}} = kx_{\mathrm{ref}}^n \tag{3a}$$

$$A_{\mathrm{ref}} = \ln(kx_{\mathrm{ref}}^n) \tag{3b}$$

Following Schwaab and Pinto (2007), when the usual least-square minimization problem is used to provide the parameter estimates, the correlation (ρ) between the two model parameters can be defined as

$$\rho \propto \sum_{i=1}^{NE} -\frac{\partial y_i}{\partial k_{\mathrm{ref}}}\frac{\partial y_i}{\partial n} = 0 \tag{4}$$

where y_i represents the output response at experiment i. The reference value, x_{ref}, that solves Eq. (4) leads to null parameter correlation. Differentiating Eq. (2a) in respect to the model parameters:

$$\frac{\partial y_i}{\partial k_{\mathrm{ref}}} = (x_i/x_{\mathrm{ref}})^n = \frac{y_i}{k_{\mathrm{ref}}} \tag{5a}$$

$$\frac{\partial y_i}{\partial n} = k_{\mathrm{ref}}(x_i/x_{\mathrm{ref}})^n \ln(x_i/x_{\mathrm{ref}}) = y_i \ln(x_i/x_{\mathrm{ref}}) \tag{5b}$$

Eq. (4) can be rewritten as

$$\sum_{i=1}^{NE} \frac{y_i}{k_{\mathrm{ref}}} y_i \ln(x_i/x_{\mathrm{ref}}) = 0 \tag{6}$$

The solution of Eq. (6) gives

$$x_{\mathrm{ref}} = \exp\left[\sum_{i=1}^{NE} y_i^2 \ln(x_i) \Big/ \sum_{i=1}^{NE} y_i^2\right] \tag{7}$$

which is the reference value that allows for estimation of uncorrelated model parameters. It is important to emphasize that Eq. (7) depends only on the available experimental data and can be computed before the estimation of the model parameters. Although the analytical solution presented in Eq. (7) is a particular solution for the model form defined in Eq. (2a), it clearly shows that the proper definition of x_{ref} can lead to the estimation of uncorrelated model parameters.

Following Schwaab and Pinto (2007), the relative standard error of the final parameter estimates can be defined as

$$e_\theta = \frac{t_{NE-NP}^{(1+\alpha)/2}\sqrt{s_\theta}}{\theta} \tag{8}$$

where e_θ is the relative error of parameter θ, s_θ is the variance of parameter uncertainties, $t_{NE-NP}^{(1+\alpha)/2}$ is the t-Student distribution value with a confidence level equal to α (always assumed to be equal to 0.95 in this work) and NE –NP represents the degree of freedom. As presented by Schwaab and Pinto (2007), it can be easily shown that x_{ref} also leads to minimum e_θ.

Eqs. (1–8) can be immediately extended to describe multivariable power function models. In this case, however, the number of parameter correlations becomes larger than the number of reference values, as discussed by Schwaab et al. (2008b). Besides, it becomes very difficult to obtain closed solutions for Eq. (7) in this case. In more complex models, where an analytical solution cannot be obtained, a numerical procedure must be used to minimize the correlations among the possibly many parameter estimates. In these cases, a two-step parameter estimation procedure can be devised, as discussed by Schwaab and Pinto (2007) and Schwaab et al. (2008b). According to this numerical procedure, estimation of model parameters is carried out first, using a set of initial guesses for the reference values. Then, the optimization of the reference values is performed during the second step. The procedure may be repeated to overcome numerical problems associated with the estimation of model parameters, when the initial guesses of the reference values are poor.

3. Examples

In the following examples the parameter estimation procedure is performed with a hybrid estimation method. The particle swarm optimization method (Kennedy and Eberhart, 1995) is used first to provide a set of initial guesses, which is used for fine tuning of model parameters with the help of a Gauss–Newton procedure (Noronha et al., 1993), as described by Schwaab and Pinto (2007) and Schwaab et al. (2008a,b). The optimization of the reference variables was also performed with the particle swarm optimization method, due its inherent capabilities to solve complex minimization problems (Schwaab et al., 2008a,b).

3.1. Example 1—the Freundlich equation

The Freundlich equation relates the volume of fluid that is adsorbed onto a solid surface as a function of pressure, in the form

$$V = kP^n \tag{9}$$

where k and n are the Freundlich equation parameters. This equation can be written in a reparametrized form after definition of a reference pressure:

$$V = k_{\mathrm{ref}}(P/P_{\mathrm{ref}})^n \tag{10}$$

where

$$k_{\mathrm{ref}} = kP_{\mathrm{ref}}^n \tag{11}$$

Eq. (10) is similar to Eq. (2a). According to Eq. (7), the optimum value for P_{ref} is

$$P_{\mathrm{ref}} = \exp\left[\sum_{i=1}^{NE} V_i^2 \ln(P_i) \Big/ \sum_{i=1}^{NE} V_i^2\right] \tag{12}$$

Experimental data was obtained from Guo et al. (2006) for the adsorption of carbon dioxide on activated carbon. (The data used here correspond to Sample C at 333 K.) As observed by Guo et al. (2006) and shown in Fig. 1, the obtained fit is very good. It must be noted that the quality of the model fit does not depend on the reparameterized form of the model equation. Consequently, Fig. 1 represents the model fit for all possible reparameterizations that are based on Eqs. (9)–(10).

In order to observe the effect of the reference pressure on the parameter correlation and relative error of parameter estimates, the reference pressure was allowed to vary, as shown in Figs. 2 and 3. Fig. 2 shows that parameter correlation varies from −1.0 to +1.0 as P_{ref} increases and shows very clearly that the proper definition of the reference pressure can lead to the estimation of uncorrelated parameters. Fig. 3 shows that the relative error of parameter n is independent of the reference pressure and that the relative error of parameter k_{ref} presents a minimum value at the same reference

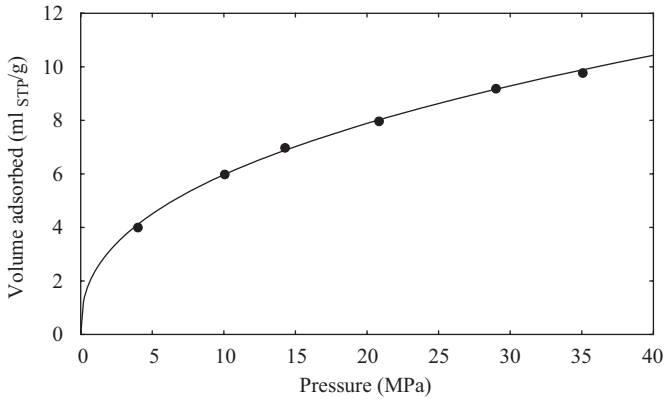

Fig. 1. Model fit in Example 1.

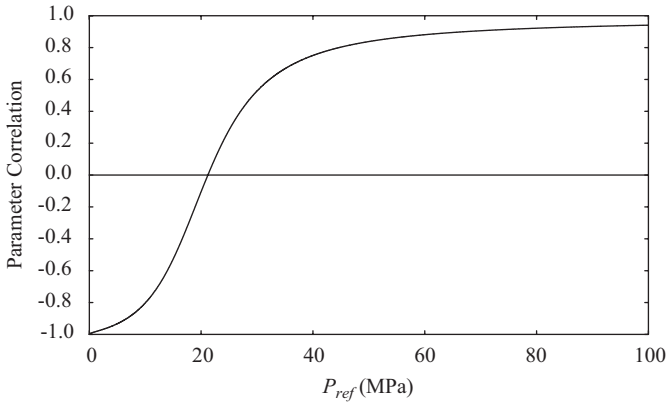

Fig. 2. Parameter correlation as a function of P_{ref} in Example 1.

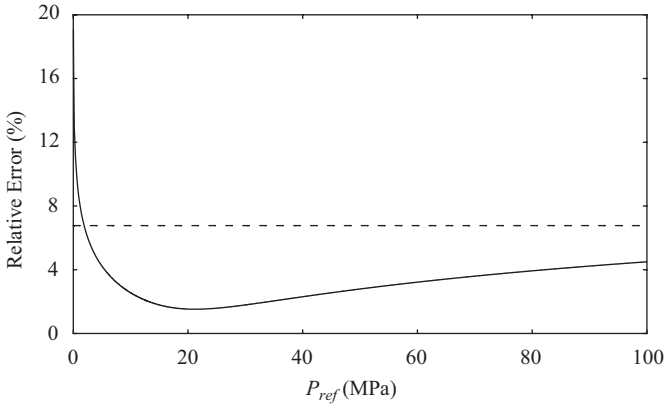

Fig. 3. Relative error of parameters k_{ref} (line) and n (dashed line) as a function of P_{ref} in Example 1.

pressure where the correlation between the parameter estimates is null, as it might be already expected. It must be observed that the parameter correlation approaches the value -1.0 and that the relative error of parameter k_{ref} increases sharply when the pressure reference tends to 1 Pa, corresponding to the non-reparameterized model.

The optimum reference pressure calculated by Eq. (12) is equal to 21.21 MPa, leading to uncorrelated parameters and with minimum relative error. Using this optimum reference pressure value, the

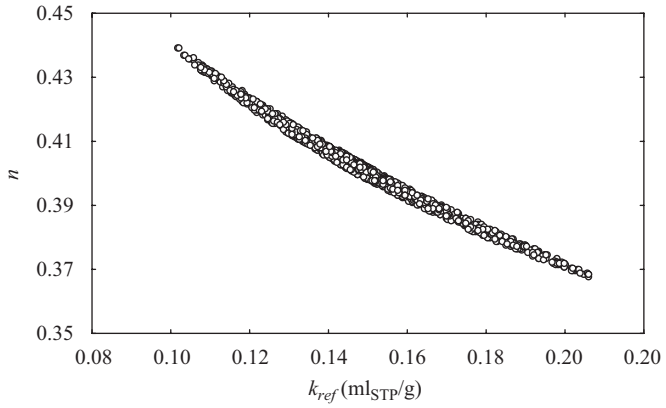

Fig. 4. Confidence region of parameter estimates with non-reparameterized model in Example 1.

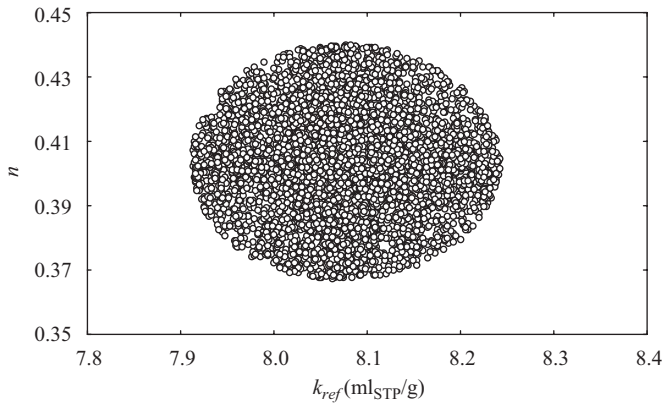

Fig. 5. Confidence region of parameter estimates with optimum reparametrization of model in Example 1.

obtained parameter estimates for k_{ref} and n are equal to 8.08 ml$_{\text{STP}}$/g and 0.403 for k_{ref} and n. The relative errors are equal to 1.52% for k_{ref} and 6.77% for n. For comparison, the parameter estimates for the non-reparameterized model (corresponding to P_{ref} equal to 1 Pa) are 0.145 ml$_{\text{STP}}$/g and 0.403 for k_{ref} and n. (These values are very close to the ones obtained by Guo et al., 2006). The correlation between k_{ref} and n is equal to -0.998 in this case, while the relative errors are equal to 27.2% for k_{ref} and 6.77% for n. The significant reduction of the correlation between the parameter estimates can be clearly seen in Figs. 4 and 5, where the parameter confidence regions are shown (with a confidence level of 95%).

The parameter confidence region for the non-reparameterized model (Fig. 4) consists in a very narrow and slightly curved surface, indicating that parameter estimates are highly correlated. When the optimum reference pressure is used, the parameter confidence region becomes almost spherical, indicating that uncorrelated parameters were estimated.

3.2. Example 2—the TPR model

This example consists in the modeling of a temperature programmed reduction experiment, generally used for catalysts characterization. In this experiment the catalyst (generally, a metal oxide supported onto an inert porous solid) is exposed to a reducible atmosphere (usually containing H_2). As the temperature is increased, the metal oxide is reduced into the metal state. As different oxide species can be present in the catalyst, the rates of catalyst reduction

can be very different at different temperatures. Modeling of this type of experiment can allow for the proper catalyst characterization.

The model equations that describe the experimental system include a mass balance of the solid oxide species i, defined as

$$\frac{dN_i}{dt} = r_i, \quad N_i(0) = N_{i0} \tag{13}$$

and a hydrogen balance, defined as

$$v_0(C^{in}_{H_2} - C_{H_2}) - \sum_{i=1}^{NS} r_i = 0 \tag{14}$$

where N_i is the molar quantity of reducible species i (mol), v_0 is the volumetric flow (m^3/s), $C^{in}_{H_2}$ and C_{H_2} are the inlet and outlet concentration of hydrogen (mol/m^3), NS is the number of reducible species and r_i is the rate of reduction of species i, defined as

$$r_i = \exp(A_i - E_i/RT_i)N_i^n C_{H_2} \tag{15}$$

where n is the reaction order and the Arrhenius equation is used to describe the temperature dependence of reaction rates. Using the proposed reparameterizations, the reaction rate expression can be written as

$$r_i = \exp\left[A_i^{ref} - \frac{E_i}{R}\left(\frac{1}{T_i} - \frac{1}{T_i^{ref}}\right) + n\ln\left(\frac{N_i}{N_i^{ref}}\right)\right] C_{H_2} \tag{16}$$

where A_i^{ref} is related to the original parameters as

$$A_i^{ref} = A_i - \frac{E_i}{RT_i^{ref}} + n\ln(N_i^{ref}) \tag{17}$$

In this example, the reduction of Ni/SiO_2 catalyst in H_2/Ar atmosphere is considered. The experimental conditions were defined as volumetric flow of 20 cm^3/min; linear heating rate of 5 K/min; and H_2 inlet fraction equal to 1.64% (V/V). Additional details about catalyst preparation, experimental setup procedures can be found in Nele et al. (1999) and Bhering et al. (2002).

Based on previous experience, three different reducible species were assumed to exist; consequently, the number of model parameters to be estimated from the TPR data was equal to 10: A_i^{ref}, E_i, N_{i0}, $(i = 1, \ldots, 3)$ and n. Besides, it was necessary to define six distinct reference variables: three T_i^{ref} values and three N_i^{ref}values. Fig. 6 shows that the model adjustment to the experimental TPR data can be regarded as very good.

The two-step parameter estimation procedure (Schwaab and Pinto, 2007, Schwaab et al., 2008a,b) was used for optimization of the six reference variables through minimization of the norm of the

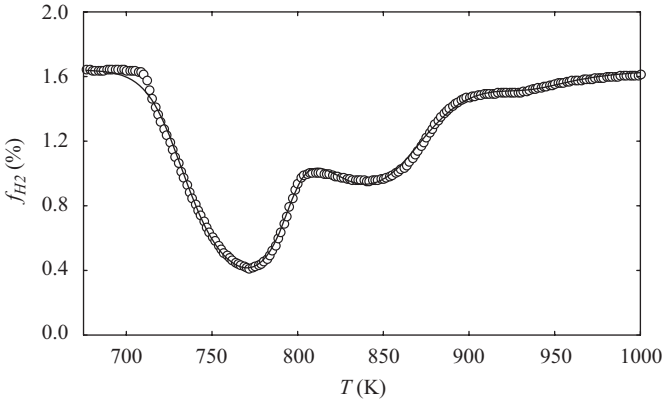

Fig. 6. Model fit in Example 2.

Table 1
Optimum values for the reference variables in Example 2

Reference	Value
T_1^{ref} (K)	716.2
T_2^{ref} (K)	806.0
T_3^{ref} (K)	908.7
N_1^{ref} (mol)	2.0×10^{-4}
N_2^{ref} (mol)	1.1×10^{-4}
N_3^{ref} (mol)	6.8×10^{-6}

Table 2
Parameter estimates with the reparameterized model with optimized values for T_i^{ref} and N_i^{ref} in Example 2

Parameter	Value	Relative error
N_{10} (mol)	0.1384	3.47
N_{20} (mol)	0.0842	4.98
N_{30} (mol)	0.0078	25.4
A_1^{ref}	−14.87	0.26
A_2^{ref}	−14.23	0.36
A_3^{ref}	−17.88	2.26
E_1 (kJ/mol)	445.8	3.87
E_2 (kJ/mol)	369.5	11.2
E_3 (kJ/mol)	563.5	28.8
n	2.82	12.0

Table 3
Correlation matrix of parameter estimates with the reparameterized model with optimized values for T_i^{ref} and N_i^{ref} in Example 2

	N_{10}	N_{20}	N_{30}	A_1^{ref}	A_2^{ref}	A_3^{ref}	E_1	E_2	E_3	n
N_{10}	1	−0.91	−0.43	0.07	−0.07	−0.02	0.76	0.95	0.44	0.94
N_{20}	−0.91	1	0.19	0.01	0.01	−0.01	−0.64	−0.94	−0.24	−0.84
N_{30}	−0.43	0.19	1	−0.10	0.04	−0.17	−0.56	−0.34	−0.82	−0.54
A_1^{ref}	0.07	0.01	−0.10	1	0.11	0.00	−0.18	−0.02	0.07	0.04
A_2^{ref}	−0.07	0.01	0.04	0.11	1	0.10	0.16	−0.05	−0.09	0.06
A_3^{ref}	−0.02	−0.01	−0.17	0.00	0.10	1	−0.01	−0.01	−0.12	−0.02
E_1	0.76	−0.64	−0.56	−0.18	0.16	−0.01	1	0.80	0.52	0.91
E_2	0.95	−0.94	−0.34	−0.02	−0.05	−0.01	0.80	1	0.37	0.94
E_3	0.44	−0.24	−0.82	0.07	−0.09	−0.12	0.52	0.37	1	0.52
n	0.94	−0.84	−0.54	0.04	0.06	−0.02	0.91	0.94	0.52	1

correlation matrix of parameter estimates defined in Eq. (18), as recommended by Schwaab et al. (2008b).

$$F = \sum_{i=1}^{NP-1} \sum_{j=i+1}^{NP} \rho_{ij}^2 \tag{18}$$

The optimum values obtained for the reference variables are shown in Table 1. The minimum value for the norm (Eq. (18)) was equal to 10.28. The parameter estimates and the relative errors are shown in Table 2 and the correlation matrix of parameter estimates is shown in Table 3.

It must be noted that the parameter estimates and the relative errors of parameters N_{i0}, E_i $(i = 1, \ldots, 3)$ and n are independent of the reference variable values. Besides, the correlations among the final estimates of these model parameters are also independent of the reference variable values. Table 2 shows that the relative errors of parameters A_i^{ref} $(i = 1, \ldots, 3)$ are very small and that correlations involving these parameters are always very small. This shows very clearly the improved quality of the parameter estimates obtained after reparameterization of the power function model and of the Arrhenius equation models.

For comparison purposes, the non-reparameterized model (Eq. (15)) was used for parameter estimation. It must be noted that the minimization of the objective function was very difficult and failed several times, due the existence of very high parameter

Table 4
Parameter estimates with the non-reparameterized model in Example 2

Parameter	Value	Relative error (%)
N_{10} (mol)	0.1384	3.47
N_{20} (mol)	0.0842	4.98
N_{30} (mol)	0.0078	25.4
A_1^{ref}	84.03	6.73
A_2^{ref}	66.57	13.8
A_3^{ref}	90.17	26.4
E_1 (kJ/mol)	445.8	3.87
E_2 (kJ/mol)	369.5	11.2
E_3 (kJ/mol)	563.5	28.8
n	2.82	12.0

Table 5
Correlation matrix of parameter estimates with the unreparameterized model in Example 2

	N_{10}	N_{20}	N_{30}	A_1^{ref}	A_2^{ref}	A_3^{ref}	E_1	E_2	E_3	n
N_{10}	1	−0.91	−0.43	0.87	0.96	0.56	0.76	0.95	0.44	0.94
N_{20}	−0.91	1	0.19	−0.75	−0.92	−0.36	−0.64	−0.94	−0.24	−0.84
N_{30}	−0.43	0.19	1	−0.57	−0.41	−0.84	−0.56	−0.34	−0.82	−0.54
A_1^{ref}	0.87	−0.75	−0.57	1	0.93	0.65	0.98	0.89	0.53	0.98
A_2^{ref}	0.96	−0.92	−0.41	0.93	1	0.55	0.85	0.99	0.42	0.97
A_3^{ref}	0.56	−0.36	−0.84	0.65	0.55	1	0.62	0.49	0.99	0.64
E_1	0.76	−0.64	−0.56	0.98	0.85	0.62	1	0.80	0.52	0.91
E_2	0.95	−0.94	−0.34	0.89	0.99	0.49	0.80	1	0.37	0.94
E_3	0.44	−0.24	−0.82	0.53	0.42	0.99	0.52	0.37	1	0.52
n	0.94	−0.84	−0.54	0.98	0.97	0.64	0.91	0.94	0.52	1

correlations. The parameter estimates and respective relative errors are shown in Table 4, while Table 5 shows the correlation matrix of final parameter estimates.

The relative errors of the parameters A_i^{ref} $(i = 1, \ldots, 3)$ presented in Table 4 are much higher than the values obtained after optimization of the reference variables. Also the absolute parameter correlation values are very close to 1.0 for several pairs of parameters. If the norm defined in Eq. (18) is calculated based on the correlation matrix presented in Table 5, a value equal to 24.25 is found. This high correlation explains the difficulties found during minimization of the objective function used for parameter estimation. If only the correlations involving the parameters A_i^{ref} $(i=1, \ldots, 3)$ are considered (which are the parameter correlations that can be modified through the proposed reparameterization), the average correlation among the parameters A_i^{ref} is equal to 0.74 when the non-reparameterized model form is used, while the average correlation among the parameters A_i^{ref} is equal to 0.06 when the reparameterized model form is used. This shows that correlations among parameters A_i^{ref} can almost be eliminated after proper reparameterization of the model equations.

4. Conclusions

In this work a reparameterization technique was proposed for power function models, through introduction of a set of reference concentration (pressure) values. In the first example it was shown that there is an optimum value for the reference pressure that leads to estimation of uncorrelated model parameters for the Freundlich isotherm. In the second example, it was shown that the two-step parameter estimation procedure (Schwaab and Pinto, 2007; Schwaab et al., 2008b) can be readily extended for complex problems that involve several reference variables (reference temperatures and concentrations) and contain different types of reparameterizations (reparameterized Arrhenius and power function equations), allowing for almost complete elimination of model parameter correlations. Besides the significant reduction of the parameter correlation, the simultaneous decrease of the relative error of the parameter estimates can also be obtained.

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