



## $q$ -Quadratic mixing rule for cubic equations of state

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### HIGHLIGHTS

- The  $q$ -Mixing rule is a new nonquadratic mixing rule.
- Correlations between species evaluated by means of the  $q$ -product.
- The proposal is a generalization of van der Waals mixing rules.
- The  $q$ -Mixing rule has been tested by evaluating vapor–liquid equilibrium.

### ARTICLE INFO

#### Article history:

Received 8 January 2015

Received in revised form

7 April 2015

Accepted 11 April 2015

Available online 28 April 2015

#### Keywords:

Mixing rules

Equation of state

Vapor–liquid equilibrium

### ABSTRACT

We introduce a new nonquadratic mixing rule that models correlations between species by means of the  $q$ -product of mole fractions, instead of the ordinary product. The use of the  $q$ -product is a procedure adopted within the nonextensive statistical mechanics formalism in the generalization of the central limit theorem for strongly correlated systems. The proposal is a generalization of the ordinary van der Waals quadratic law that is recovered when the so-called nonquadraticity binary parameter takes the limit  $q_{ij} \rightarrow 1$ . The proposed  $q$ -mixing rule has been tested by evaluating vapor–liquid equilibrium at different temperatures for systems containing alcohol, hydrocarbons and CO<sub>2</sub>, species that yield departures from ideality. Two distinct approaches, the Akaike Information Criterion and the  $F$ -test, were used to compare the  $q$ -mixing rule and the van der Waals mixing rule.

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## 1. Introduction

There have been several proposals of equations of state over more than a century, some based on empirical knowledge and others with a theoretical background (Poling et al., 2001). The first successful approach was the van der Waals equation of state (van der Waals and Rowlinson, 1988). This equation is based on a semi-empirical theory in which pressure is considered as the sum of two contributions, a repulsion term and an attraction term. The equation of state may be represented by

$$P = \frac{RT}{v-b} - \frac{a}{f(v)} \quad (1)$$

where the parameters  $a$  is the attractive parameter and  $b$  is the molar co-volume. They depend on thermodynamic properties of pure substances, and on the composition, for mixtures. Better

accuracy in the predictions of thermodynamic properties, like vapor pressure, liquid density, equilibrium ratios, is achieved by modifications of the original van der Waals equation. Probably the most useful are those of Soave (1972) and Peng and Robinson (1976).

The evaluation of the parameters  $a$  and  $b$  has significant importance for the accurate representation of experimental data. The expressions for the parameters  $a$  and  $b$  used with Peng–Robinson equation of state was proposed in Peng and Robinson (1976) as follows:

$$\begin{aligned} a(T) &= 0.45724 \left( \frac{R^2 T_c^2}{P_c} \right) \left\{ 1 + k \left[ 1 - \left( \frac{T}{T_c} \right)^{0.5} \right] \right\}^2, \\ k &= 0.37464 + 1.5422\omega - 0.26922\omega^2, \\ b &= 0.07780 \frac{RT_c}{P_c}, \end{aligned} \quad (2)$$

where  $\omega$  is the acentric factor,  $T_c$  and  $P_c$  are the critical temperature and pressure, respectively, and  $R$  is the universal gas constant. Mixing rules can be derived from statistical mechanics, or by using

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<http://dx.doi.org/10.1016/j.ces.2015.04.022>

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a phenomenological point of view from classical thermodynamics (Hall et al., 1993). The widely used van der Waals Mixing Rule (vdw-MR) (Vidal, 1978) are:

$$a_M = \sum_i^c \sum_j^c x_i x_j a_{ij}, \quad (3)$$

$$b_M = \sum_i^c \sum_j^c x_i x_j b_{ij}, \quad (4)$$

where  $x_i$  is the molar fraction of species  $i$ ,  $c$  is the number of different species in the mixture,  $a_{ii}$  and  $b_{ii}$  are the pure component parameters ( $a_{ii} \equiv a_i$  and  $b_{ii} \equiv b_i$ ), and  $a_{ij}$  and  $b_{ij}$  ( $i \neq j$ ) are cross parameters (Wei and Sadus, 2000; Peng and Robinson, 1976; Valderrama, 2003) that are represented by the combining rules (Vidal, 1978):

$$a_{ij} = (a_{ii} a_{jj})^{0.5} (1 - k_{ij}), \quad (5)$$

$$b_{ij} = \frac{b_{ii} + b_{jj}}{2} (1 - l_{ij}), \quad (6)$$

where  $k_{ij} = k_{ji}$ ,  $k_{ii} = 0$ ,  $l_{ij} = l_{ji}$ ,  $l_{ii} = 0$ , and consequently  $a_{ij} = a_{ji}$  and  $b_{ij} = b_{ji}$  ( $i \neq j$ ).  $k_{ij}$  and  $l_{ij}$  are binary interaction parameters associated with  $a$  and  $b$  (Poling et al., 2001) that can be adjusted by experimental data.

The vdW-MR have a quadratic dependence on composition ( $b_M$  is reduced to a linear dependence if  $l_{ij} = 0$ ). This functional form is not able to describe all mixtures, and several works have proposed different nonquadratic rules, e.g. Wong and Sandler (1992), Adachi and Sugie (1986), Won (1983), and Higashi et al. (1994). Some proposed models take into account the excess Gibbs energy at infinite pressure calculated from a liquid-phase activity coefficient model (Huron and Vidal, 1979; Michelsen, 1990).

The present work introduces a new nonquadratic mixing rule for cubic equations of state that differs from vdW-MR, once it may consider strong correlations following the lines of nonextensive statistical mechanics (Tsallis, 1988; Borges, 2004; Moyano et al., 2006) through a nonquadraticity parameter  $q_{ij}$ .

The work is organized as follows. Section 2 introduces some basic concepts of nonextensive statistical mechanics, and introduces the semi-empirical model for the  $q$ -Mixing Rule ( $q$ -MR). The methodology, results and discussions appear in Section 3, and finally Section 4 is dedicated to the conclusions.

## 2. Nonextensive statistical mechanics

With the advent of the nonextensive statistical mechanics as a generalization of the Boltzmann–Gibbs statistical mechanics, it became clear over the years that the new formalism was able to represent certain classes of systems that were not properly described by Boltzmann–Gibbs statistical mechanics. Indeed, since the original paper (Tsallis, 1988), more than two decades ago, many works have been developed concerning nonlinear systems. The generalized entropy is

$$S_q \equiv k_B \frac{1 - \sum_{i=1}^W p_i^q}{q-1}, \quad (7)$$

with  $p_i$  being the probability of the microscopic state  $i$ ,  $W$  being the number of microscopic states,  $k_B$  being a positive constant (the Boltzmann constant) and  $q$  being the entropic index. If  $q \rightarrow 1$ , Eq. (7) recovers the celebrated Boltzmann–Gibbs entropy:

$$S \equiv -k_B \sum_{i=1}^W p_i \ln p_i. \quad (8)$$

Formal and logical arguments considering an analogy between Eqs. (8) and (7) have lead to the definition of generalized functions

(Tsallis, 1994), particularly the  $q$ -logarithm function

$$\ln_q(x) \equiv \frac{x^{1-q} - 1}{1-q} \quad (x > 0), \quad (9)$$

and its inverse, the  $q$ -exponential function

$$\exp_q(x) \equiv e_q^x \equiv \begin{cases} [1 + (1-q)x]^{1/(1-q)} & \text{if } [1 + (1-q)x] > 0, \\ 0 & \text{if } [1 + (1-q)x] \leq 0. \end{cases} \quad (10)$$

The usual logarithmic and exponential functions are recovered in the limit  $q \rightarrow 1$ .

The maximization of the Tsallis entropy, Eq. (7), with the constraint of constant generalized mean energy, leads to the generalized canonical ensemble distribution (Tsallis, 1988; Tsallis et al., 1998):

$$p(E_i) \propto \exp_q(-\beta_q E_i), \quad (11)$$

where  $\beta_q$  is the Lagrange parameter that is related to the inverse temperature,  $E_i$  is the energy of the  $i$ th state and  $p(E_i)$  is the probability of the state with energy  $E_i$  be occupied. One of the central differences between Tsallis and Boltzmann weights is that the former presents power law tails (long-lasting for  $q > 1$ , and abruptly vanishing for  $q < 1$ ), while the latter has exponential tails.

The difference between Boltzmann and Tsallis weights may be also understood within the following comparison. It is known that the pressure  $P$  of a hypothetical static isothermal ideal gas atmosphere with gradient given by  $dP/dh = -mg\rho$  decreases with height according to an exponential law (Halley's law, see, for instance, Feynman et al., 1963)  $P(h) = P_0 \exp(-mgh/k_B T)$ , where  $P_0$  is the pressure at height  $h=0$ ,  $g$  is the gravitational acceleration. A similar expression holds for the number density  $\rho$  (number of molecules/volume). The numerator of the exponent is the potential energy of a molecule with mass  $m$  and the denominator is its thermal energy. Thermal equilibrium is a very strong simplifying hypothesis that certainly is not valid to our atmosphere. If we consider that the temperature linearly decreases with height, i.e., with a constant temperature gradient instead of a zero temperature gradient, – the second simplest hypothesis possible –, then we find that the pressure decays as  $P(h) = P_0 \exp_q(-mgh/k_B T_0)$ , with  $q = 1 - k_B \gamma / gm$  and  $\gamma = -dT/dh$  is the negative of the atmospheric temperature gradient. Once  $P = \rho k_B T$  and  $T(h) = T_0 - \gamma h$ ,  $\rho(h) = \rho_0 [\exp_q(-mgh/k_B T_0)]^q$ . In both cases we have a ratio between the potential and the thermal energies, but in the former we have an exponential law (Boltzmann weight), while in the latter we have a  $q$ -exponential law (Tsallis weight). The case  $\gamma = 0$  recovers Halley's law.

The introduction of the generalized  $q$ -logarithm and  $q$ -exponential functions has allowed the development of a consistent generalized nondistributive algebra, based on the  $q$ -algebraic operators (Nivanen et al., 2003; Borges, 2004),  $q$ -addition  $x \oplus_q y$ ,  $q$ -difference  $x \ominus_q y$ ,  $q$ -product  $x \otimes_q y$ , and  $q$ -ratio  $x \oslash_q y$  represented as

$$\begin{aligned} x \oplus_q y &= x + y + (1-q)xy, \\ x \ominus_q y &= \frac{x-y}{1+(1-q)y} \quad \left( y \neq \frac{1}{q-1} \right), \\ x \otimes_q y &= [x^{1-q} + y^{1-q} - 1]_+^{1/(1-q)} \quad (x, y > 0), \\ x \oslash_q y &= [x^{1-q} - y^{1-q} + 1]_+^{1/(1-q)} \quad (x, y > 0). \end{aligned} \quad (12)$$

The subscript  $+$  in the  $q$ -product and in the  $q$ -ratio is a short-cut that means  $[A]_+ = \max(A, 0)$ , i.e., whenever the basis is negative or zero,  $(x^{1-q} + y^{1-q} - 1 \leq 0$  for the  $q$ -product, and  $x^{1-q} - y^{1-q} + 1 \leq 0$  for the  $q$ -ratio), the  $q$ -operation ( $q$ -product or  $q$ -ratio) is defined as zero, instead of being calculated by its corresponding mathematical expression. This feature, known as *cut-off*, is essential for the consistency of the formalism, and it is also present in the definition of the  $q$ -exponential, see Eq. (10). The  $q$ -product is commutative

$(x \otimes_q y = y \otimes_q x)$ , but it is not distributive in relation to the ordinary product,  $a(x \otimes_q y) \neq (ax) \otimes_q y \neq x \otimes_q (ay)$ . It is also not distributive in relation to the  $q$ -addition  $(a \oplus_q b) \otimes_q x \neq (a \otimes_q x) \oplus_q (b \otimes_q x)$ ,  $\forall q \neq 1$ . This  $q$ -algebra, particularly the  $q$ -product, has a central role in the generalization of the central limit theorem, and in the generalization of the Fourier transform (Umarov et al., 2008; Jauregui and Tsallis, 2010). It will be clear in the following that the present work is based squarely in the  $q$ -product. Some properties of  $q$ -functions and  $q$ -algebra may be found in Yamano (2002), Naudts (2002), Cardoso et al. (2008), Lobao et al. (2009), and Tsallis (2009).

There have been proposed generalizations of equations of state following the lines of nonextensive statistical mechanics. The ideal gas has been revisited in Silva Jr et al. (1998), Plastino and Lima (1999), and the equation of state is written as  $PV = I(q)NRT^*$ , where

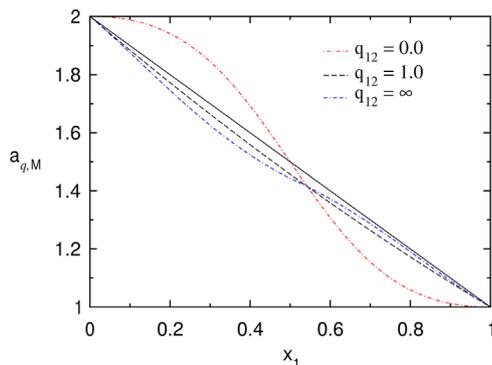
$$I(q) = \frac{1}{\left[1 - (1-q)\beta^* \frac{1}{2}mv^2\right]^{(q/(1-q))d^2v}} \int \left[1 - (1-q)\beta^* \frac{1}{2}mv^2\right]^{1/(1-q)} dv,$$

$\beta^* = 1/(RT^*)$  and  $T^*$  is a function that recovers the temperature  $T$  in the limit  $q \rightarrow 1$ . The van der Waals-EoS has also been revisited along these lines, as Martínez et al. (2001)

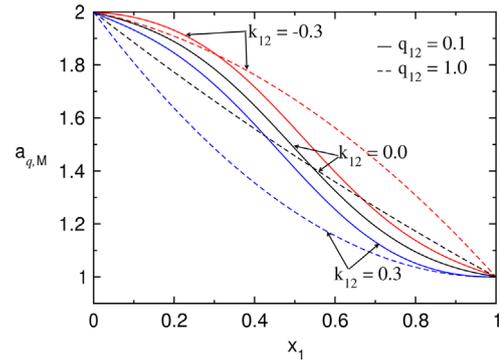
$$\left[P + a_q \left(\frac{1}{V}\right)^2\right] (V - b) = NRT, \quad (13)$$

where  $a_q = a[\beta_q/\beta - (1-q)]$  and  $\beta_q/\beta = [1 + (1-q)\beta]aN^2/\omega$ , with  $\beta = 1/(RT)$ . There are other works dealing with nonextensive classical gas. Negative specific heat and polytrope-type relation are analytically explored in Abe (1999). Equipartition and virial theorems are shown to be valid  $\forall q$  in Martínez et al. (2000). Internal energy and energy correlation are considered in Abe et al. (2001). The kinetic nonextensive generalization of the Maxwellian ideal gas is discussed in Lima and Silva (2005). The Joule, Joule–Thomson, and second virial coefficients are evaluated in Zheng and Du (2007). It was recently shown that the ideal gas in a finite heat reservoir requires the  $q$ -entropy (Biró, 2013). Heat capacities of simple diatomic gases ( $N_2$ ,  $O_2$ ,  $CO$ ) present nonextensive behavior at low temperatures (Guo and Du, 2009). A recent model based on the  $q$ -exponential for evaluating solubility of solids in supercritical solvent was advanced in Taberner et al. (2014).

The present work is confined to mixtures, rather than pure components, and we focus on the mixing rules that are applied to



**Fig. 1.**  $q$ -Mixing rule, Eq. (14) for a binary hypothetical mixture, with arbitrarily chosen values  $a_1 = 1$  and  $a_2 = 2$ , and  $k_{12} = 0$ . The choice was driven by the need to give a good visual representation of the influence of the parameter  $q_{12}$  on the composition. Different values of the parameter  $q_{12}$  are indicated:  $q_{12} = 1$  (dashed line),  $q_{12} = 0$  (dashed–dotted line, red online),  $q_{12} = \infty$  (dashed–dashed–dotted line, blue online). A straight line, that corresponds to  $q_{12} = 1$  and  $k_{12} = 1 - (a_{11} + a_{22}) / (2\sqrt{a_{11}a_{22}})$ , is indicated by a solid line, for comparison. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)



**Fig. 2.** Effect of the parameter  $k_{12}$  in the  $q$ -MR, Eq. (14) for a binary hypothetical mixture with  $a_1 = 1$  and  $a_2 = 2$ .  $q_{12} = 1$  (dashed line),  $q_{12} = 0.1$  (solid line), and  $q_{12} = 0$  (black),  $k_{12} = -0.3$  (red online),  $k_{12} = 0.3$  (blue online). (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

the parameters of cubic equations of state. We have chosen the Peng–Robinson equation of state (Peng and Robinson, 1976), but the expressions for the mixing rules presented below in Section 2.1, may equally be applied to other equations of state, e.g., Soave equation of state (Soave, 1972).

### 2.1. $q$ -mixing rules

Within the pairwise additivity approximation with short-range interactions, the parameter  $a_M$  of the mixture is considered as an average of the interactions between binaries, weighted by the joint probability of finding that particular pair of molecules together, i. e.,  $a_M = \sum_{i,j} p_{ij} a_{ij}$ . If independence between molecules is considered, the joint probability of finding species  $i$  in the neighborhood of species  $j$  is simply the product of finding  $i$  and  $j$  in the bulk solution that is represented by its molar fraction,  $p_{ij} = p_i p_j \sim x_i x_j$ . Thus, the quadratic nature of the mixing rule derives from the hypothesis of independence. Deviation from this scenario is usually considered by the introduction of an additional parameter  $k_{ij}$  according to Eq. (3). This structure preserves the quadratic nature, i.e., the independence hypothesis. The present model follows the procedure used in the generalization of the central limit theorem. It considers the joint probability of strongly correlated systems (that may be a consequence of local inhomogeneities, long-range interactions, or other features that leads to the failure of the independence hypothesis) as the  $q$ -product of the individual probabilities, rather than the ordinary product (Tsallis, 2005; Tsallis et al., 2005). The proposed  $q$ -Mixing Rule is

$$a_{q,M} = \frac{\sum_{i,j} a_{ij} (x_i \otimes_{q_{ij}} x_j)}{\sum_{i,j} (x_i \otimes_{q_{ij}} x_j)}, \quad (14)$$

where  $q_{ji} = q_{ij}$ ,  $q_{ii} = 1$  and  $x_i \otimes_{q_{ij}} x_j$  is the  $q$ -product between the non-negative numbers  $x_i$  and  $x_j$ . The normalizing factor  $\sum_{i,j} (x_i \otimes_{q_{ij}} x_j)$  in the denominator of Eq. (14) is necessary to avoid the Michelsen–Kistenmacher syndrome (Michelsen and Kistenmacher, 1990). The parameter  $q_{ij}$  radically changes the usual mixing rule, it exhibits a nonquadratic dependence on the composition (that is obviously recovered as  $q_{ij} \rightarrow 1$ ), as can be seen below in Figs. 1 and 2. This break with the quadratic dependence on the composition in the mixing rule has led us to call  $q_{ij}$  as *nonquadraticity parameter* within the present context.

Fig. 1 illustrates the dependence of  $a_{q,M}$  with the molar fraction, for different values of  $q_{12}$  in a hypothetical binary mixture, with  $k_{12} = 0$ .  $a_{q,M}$  is limited by  $q_{12} = 0$  with

$$a_{0,M} = \frac{x_1^2 a_{11} + x_2^2 a_{22}}{x_1^2 + x_2^2}, \quad (15)$$

that does not depend on the cross parameter  $a_{12}$ , and  $q_{12} = \infty$ , with

$$a_{\infty, M} = \frac{x_1^2 a_{11} + x_2^2 a_{22} + 2a_{12}[x_1 H(x_2 - x_1) + x_2 H(x_1 - x_2)]}{x_1^2 + x_2^2 + 2[x_1 H(x_2 - x_1) + x_2 H(x_1 - x_2)]}, \quad (16)$$

and  $H(u)$  is the Heaviside step function. The parameter  $q_{12} \neq 1$  introduces two distinct regions, with positive and negative concavities (the concavity of the usual vdW-MR is fixed, given by  $a_{11} + a_{22} - 2a_{12}$ ). Proper fitting of the parameter  $k_{12}$  leads to a shift of the inflection point, as shown in Fig. 2, and thus allowing better description of experimental data. It is worth noting that this shift may be such that the inflection point can be located outside the physical region  $0 \leq x_1 \leq 1$ , so the model, with  $q_{12} \neq 1$ , is able to represent data without the inflection point, but in a nonquadratic form.

Derivatives of Eq. (14) are necessary for the calculation of various thermodynamic properties of mixtures, e.g., fugacities, and they are given by

$$\frac{\partial a_{q, M}}{\partial N_i} = \frac{1}{\sum_{ij} (x_i \otimes_{q_{ij}} x_j)} \left\{ \sum_{ij} \left( \frac{\partial a_{ij} (x_i \otimes_{q_{ij}} x_j)}{\partial N_i} \right) - a_{q, M} \sum_{ij} \left( \frac{\partial (x_i \otimes_{q_{ij}} x_j)}{\partial N_i} \right) \right\}, \quad (17)$$

with

$$\sum_{ij} \frac{\partial (x_i \otimes_{q_{ij}} x_j)}{\partial N_i} = \frac{2}{N_T} \left\{ \sum_i (x_i \otimes_{q_{ij}} x_j) x_j (x_i^{q_{ij}} - x_j^{q_{ij}} (1 - \delta_{ij})) \right\}$$

$$\begin{aligned} & - \frac{2}{N_T} (x_j \otimes_{q_{ij}} x_j)^{q_{ij}} x_j^{1-q_{ij}}, \\ \sum_{ij} \frac{\partial a_{ij} (x_i \otimes_{q_{ij}} x_j)}{\partial N_i} & = \frac{2}{N_T} \left\{ \sum_i a_{ij} (x_i \otimes_{q_{ij}} x_j) x_j (x_i^{q_{ij}} - x_j^{q_{ij}} (1 - \delta_{ij})) \right\} \\ & - \frac{2a_{ij}}{N_T} (x_j \otimes_{q_{ij}} x_j)^{q_{ij}} x_j^{1-q_{ij}}, \end{aligned} \quad (18)$$

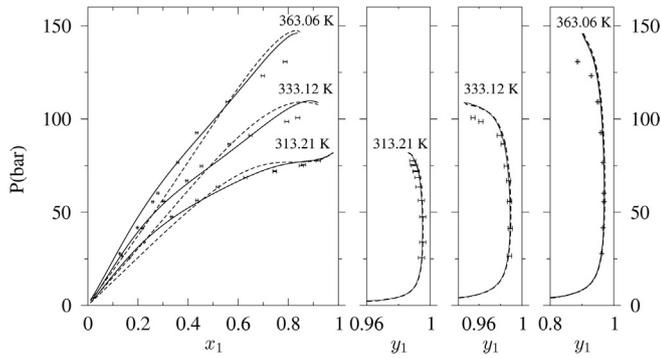
where  $N_T$  is the total number of moles and  $\delta_{ij}$  is the Dirac delta. As it happens in this generalized formalism, all equations are reduced to the ordinary ones in the limit  $q_{ij} \rightarrow 1$ .

### 3. Parameter estimation, results and discussions

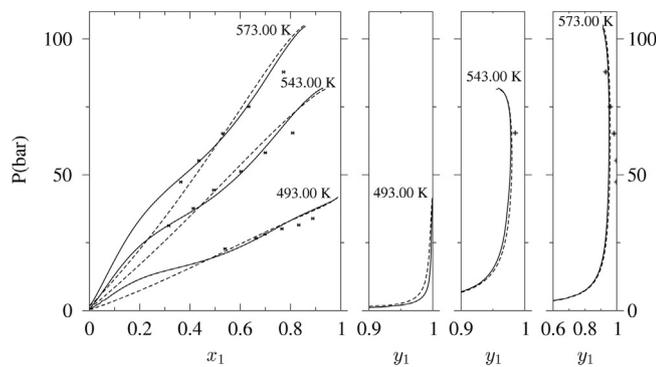
In this section, a comparative analysis between the performance of  $q$ -MR and vdW-MR for the prediction of vapor–liquid equilibrium (VLE) of systems at different temperatures is shown. The Peng–Robinson equation of state (Peng and Robinson, 1976) together with vdW-MR and  $q$ -MR were used for calculating the vapor–liquid equilibrium for the following binary systems at different temperatures: CO<sub>2</sub>+2-butanol (Elizalde-Solis and Galicia-Luna, 2010), ethanol+glycerol (Shimoyama et al., 2009), ethane+decane (Gardeler et al., 2002), CO<sub>2</sub>+ethanol (Galicia-Luna et al., 2000), CO<sub>2</sub>+styrene (Tenório Neto et al., 2013), CO<sub>2</sub>+acetic acid (Bamberger et al., 2000), CO<sub>2</sub>+H<sub>2</sub>S (Chapoy et al., 2013) and ethylene+1-decanol (Gardeler et al., 2002). The fitting parameters of the model are  $k_{12}$  and  $q_{12}$  (we remind the reader that the vdW-MR uses fixed  $q_{12} = 1$ , so it is not a fitting parameter for this case, but only for  $q$ -MR). The

**Table 1**  
Relative errors between experimental and calculated values of pressure (in bar), and vapor mole fraction of species 1.

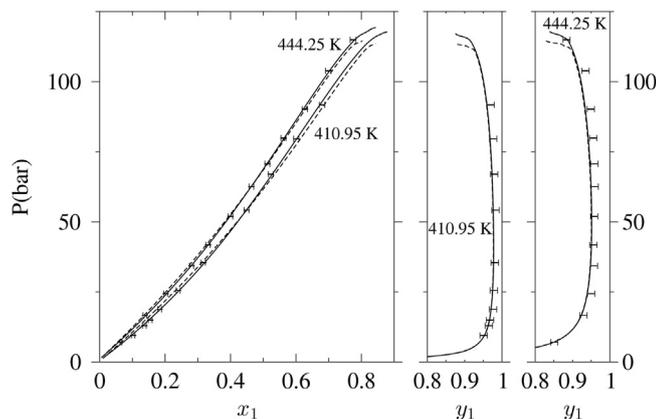
System	Temperature (K)	Classical mixing rule			$q$ -mixing rule			
		$k_{12}$	$\Delta p(\%)$	$\Delta y$	$k_{12}$	$q_{12}$	$\Delta p(\%)$	$\Delta y$
CO <sub>2</sub> +2-butanol	313.21	0.1144	6.2	0.0005	0.1238	1.0506	2.4	0.0005
	333.12	0.1052	10.8	0.003	0.1220	1.0695	4.0	0.001
	363.06	0.0917	9.9	0.007	0.1069	1.0683	5.0	0.008
	All temperatures	0.1012	9.2	0.002	0.1162	1.0656	4.6	0.003
Ethanol+glycerol	493.00	-0.1047	5.1	0.002	-0.0487	1.1698	5.4	0.003
	543.00	-0.0789	7.2	0.02	-0.0477	1.1662	3.7	0.02
	573.00	-0.0926	6.2	0.02	-0.0502	1.1877	3.2	0.03
	All temperatures	-0.0848	6.8	0.01	-0.0487	1.1699	4.7	0.01
Ethane+decane	410.95	0.0166	5.7	0.005	0.0118	0.9754	2.1	0.005
	444.25	-0.0015	2.8	0.01	-0.0064	0.9831	1.7	0.01
	All temperatures	0.0071	4.5	0.008	0.0024	0.9817	3.0	0.008
CO <sub>2</sub> +ethanol	312.82	0.0931	1.2	0.006	0.0928	0.9966	1.0	0.006
	348.40	0.0889	6.3	0.006	0.1004	1.0411	1.1	0.01
	373.00	0.0852	8.3	0.01	0.1013	1.0620	1.8	0.01
	All temperatures	0.0881	6.1	0.006	0.0963	1.0352	3.4	0.008
CO <sub>2</sub> +styrene	303.00	0.0550	5.3	-	-0.0383	0.7982	2.6	-
	313.00	0.0781	4.9	-	-0.0213	0.8151	2.3	-
	323.00	0.0735	5.2	-	-0.0392	0.7890	2.5	-
	All temperatures	0.0755	5.1	-	-0.0328	0.7984	2.5	-
CO <sub>2</sub> +acetic acid	313.20	0.0492	3.0	0.0009	0.0512	1.0178	0.9	0.0008
	333.20	0.0586	3.0	0.002	0.0623	1.0284	0.7	0.002
	353.20	0.0697	4.8	0.005	0.0681	1.0300	1.7	0.006
	All temperatures	0.0623	4.3	0.003	0.0636	1.0320	3.5	0.003
Ethylene+1-decanol	308.15	0.0314	4.5	0.0003	0.0238	0.9859	3.8	0.0004
	318.15	0.0323	4.2	0.004	0.0260	0.9881	2.3	0.004
	All temperatures	0.0319	4.3	0.002	0.0251	0.9875	2.9	0.002
CO <sub>2</sub> +H <sub>2</sub> S	258.41	0.0977	1.1	0.01	0.1044	0.8488	0.9	0.01
	273.15	0.0980	1.2	0.01	0.0959	1.0884	0.2	0.01
	293.47	0.1019	0.9	0.01	0.1053	0.8729	0.5	0.01
	All temperatures	0.1004	1.1	0.01	0.1031	0.9043	0.9	0.01



**Fig. 3.** Pressure–composition diagram for the CO<sub>2</sub> (1)+2-butanol (2) system. Experimental data with error bars, and calculated values with *q*-MR (solid line) and vdW-MR (dashed line) are displayed. The main panel (graph at the left) shows the mole fraction of species 1 ( $x_1$ ) of the liquid phase, and the three thin panels at the right show the mole fraction of species 1 ( $y_1$ ) of the vapor phase.



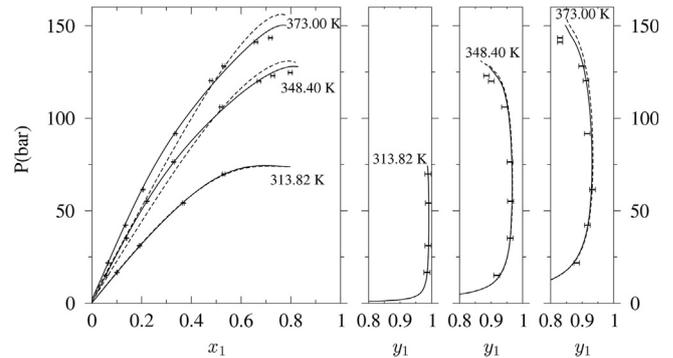
**Fig. 4.** Pressure–composition diagram for the ethanol (1)+glycerol (2) system. Experimental data with error bars, and calculated values with *q*-MR (solid line) and vdW-MR (dashed line) are displayed. The main panel (graph at the left) shows the mole fraction of species 1 ( $x_1$ ) of the liquid phase, and the three thin panels at the right show the mole fraction of species 1 ( $y_1$ ) of the vapor phase.



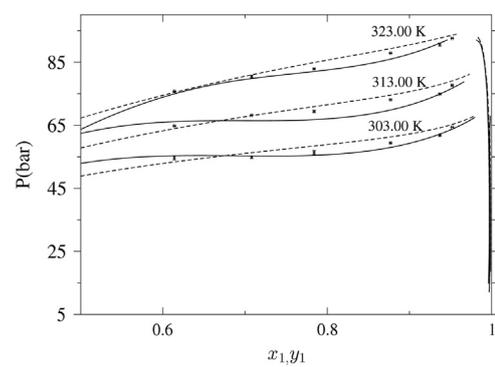
**Fig. 5.** Pressure–composition diagram for the ethane (1)+1-decane (2) system. Experimental data with error bars, and calculated values with *q*-MR (solid line) and vdW-MR (dashed line) are displayed. The main panel (graph at the left) shows the mole fraction of species 1 ( $x_1$ ) of the liquid phase, and the two thin panels at the right show the mole fraction of species 1 ( $y_1$ ) of the vapor phase.

parameters were estimated using the boiling point calculation programmed in FORTRAN language, and the particle swarm optimization algorithms from ESTIMA packages (Schwaab et al., 2008; Alberton et al., 2013) was used to minimize the objective function, given by Eq. (19).

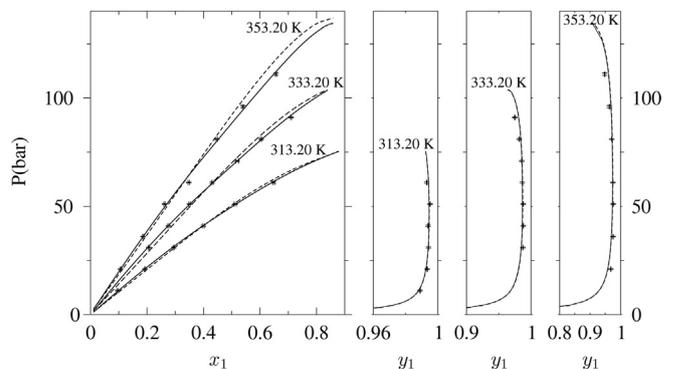
Considering that the dependent variables  $y^{\text{exp}}$  and  $P^{\text{exp}}$  are uncorrelated ( $y^{\text{exp}}$  is the mole fraction of the vapor phase), and



**Fig. 6.** Pressure–composition diagram for the CO<sub>2</sub> (1)+ethanol (2) system. Experimental data with error bars, and calculated values with *q*-MR (solid line) and vdW-MR (dashed line) are displayed. The main panel (graph at the left) shows the mole fraction of species 1 ( $x_1$ ) of the liquid phase, and the three thin panels at the right show the mole fraction of species 1 ( $y_1$ ) of the vapor phase.



**Fig. 7.** Pressure–composition diagram for the CO<sub>2</sub> (1)+styrene (2) system at 303 K, 313 K and 323 K. Experimental data with error bars, and calculated values with *q*-MR (solid line) and vdW-MR (dashed line) are displayed. The graph shows the mole fraction of species 1 ( $x_1$ ) of the liquid phase and the mole fraction of species 1 ( $y_1$ ) of the vapor phase.

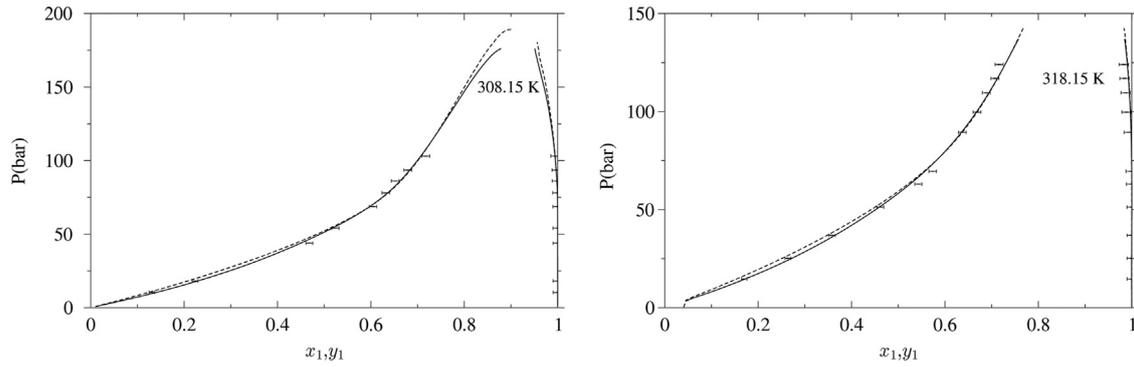


**Fig. 8.** Pressure–composition diagram for the CO<sub>2</sub> (1)+acetic acid (2) system. Experimental data with error bars, and calculated values with *q*-MR (solid line) and vdW-MR (dashed line) are displayed. The main panel (graph at the left) shows the mole fraction of species 1 ( $x_1$ ) of the liquid phase, and the three thin panels at the right show the mole fraction of species 1 ( $y_1$ ) of the vapor phase.

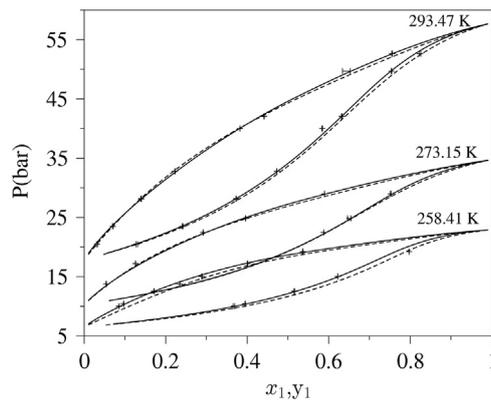
assuming that the residuals are independent and normally distributed with zero mean, the parameters can be evaluated by minimizing the objective function:

$$F_{\text{ob}}(\theta) = \sum_n \frac{(y_n^{\text{calc}}(x, T, \theta) - y_n^{\text{exp}})^2}{\sigma_{y^{\text{exp},n}}^2} + \frac{(P_n^{\text{calc}}(x, T, \theta) - P_n^{\text{exp}})^2}{\sigma_{P^{\text{exp},n}}^2}, \quad (19)$$

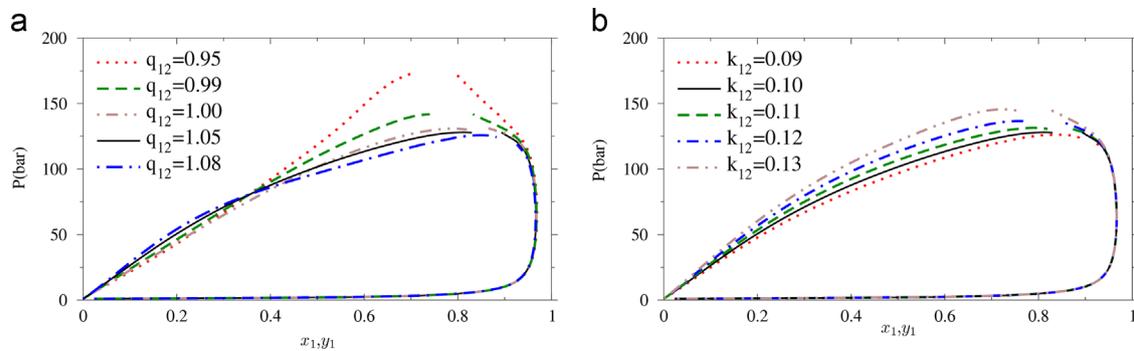
where  $\theta$  represents the set of fitting parameters,  $N_{\text{exp}}$  is the number of experiments and  $P_n^{\text{exp}}$  and  $P_n^{\text{calc}}$  are respectively the experimental



**Fig. 9.** Pressure–composition diagram for the ethylene (1)+1-decanol (2) system. Experimental data with error bars, and calculated values with  $q$ -MR (solid line) and vdW-MR (dashed line) are displayed. Both graphs show the mole fraction of species 1 ( $x_1$ ) of the liquid phase and the mole fraction of species 1 ( $y_1$ ) of the vapor phase.



**Fig. 10.** Pressure–composition diagram for the CO<sub>2</sub> (1)+H<sub>2</sub>S (2) system. Experimental data with error bars, and calculated values with  $q$ -MR (solid line) and vdW-MR (dashed line) are displayed. The graph shows the mole fraction of species 1 ( $x_1$ ) of the liquid phase and the mole fraction of species 1 ( $y_1$ ) of the vapor phase.



**Fig. 11.** Influence of the parameters  $q_{12}$  and  $k_{12}$  on the pressure composition diagram. The curve for the system CO<sub>2</sub> (1)+ethanol (2) at 348.40 K is taken as a baseline for comparison (solid black line), as it is in Fig. 6. Left panel displays different values of  $q_{12}$  for fixed  $k_{12}=0.1004$ . Right panel displays different values of  $k_{12}$  for fixed  $q_{12}=1.0411$ .

and calculated pressure of system, for the  $n$ th data set, and  $\sigma$  is the estimated standard deviation for each experimental point. Uncertainty of experimental data for each considered system was provided by the corresponding references, according to two cases: they were explicitly given for the following systems: CO<sub>2</sub>+acetic acid, CO<sub>2</sub>+H<sub>2</sub>S and CO<sub>2</sub>+styrene. Estimated uncertainties were provided for the systems CO<sub>2</sub>+2-butanol, ethanol+glycerol, ethane+1-dodecane, CO<sub>2</sub>+ethanol and ethylene+1-decanol systems.

Table 1 shows the fitted parameters  $k_{12}$  and  $q_{12}$ , and deviations between experimental data and predicted results, according to

$$\Delta P = \frac{100}{N_{\text{exp}}} \sum_{i=1}^{N_{\text{exp}}} \frac{|P_i^{\text{exp}} - P_i^{\text{calc}}|}{P_i^{\text{exp}}} \quad (20)$$

and

$$\Delta y = \frac{1}{N_{\text{exp}}} \sum_{i=1}^{N_{\text{exp}}} |y_i^{\text{exp}} - y_i^{\text{calc}}| \quad (21)$$

It can be seen that the Peng–Robinson equation of state with  $q$ -MR presents a good prediction of the phase behavior for all systems, with smaller deviations in the pressure than those using vdW-MR.

Deviations in the vapor phase concentration using Peng–Robinson equation of state were small for both mixing rules. Ref. Tenório Neto et al. (2013) does not bring data for the vapor phase of the system CO<sub>2</sub>+styrene. At low pressures, the results calculated with  $q$ -MR for the system CO<sub>2</sub>+2-butanol are better than those

**Table 2**  
AIC values (all temperatures have been considered).

System	Number of data points	$F_{ob}^{q-MR}(\theta_{opt})$	$F_{ob}^{vdW-MR}(\theta_{opt})$	$AIC^{q-MR}$	$AIC^{vdW-MR}$	$\frac{AIC^{q-MR}}{AIC^{vdW-MR}}$
CO <sub>2</sub> +2-butanol	29	80 339.28	208 483.45	80 343.28	208 485.45	0.38
Ethanol+glycerol	22	5113.12	8419.57	5117.12	8421.57	0.61
Ethane+decane	22	6686.10	10 317.19	6690.10	10 319.19	0.65
CO <sub>2</sub> +ethanol	43	6870.52	18 739.05	6874.52	18 741.05	0.34
CO <sub>2</sub> +styrene	18	2154.63	13 187.47	2158.63	13 189.47	0.16
CO <sub>2</sub> +acetic acid	20	17 866.15	24 490.74	17 870.15	24 492.74	0.73
Ethylene+1-decanol	20	13 126.17	19 343.19	13 130.17	19 345.19	0.68
CO <sub>2</sub> +H <sub>2</sub> S	18	4024.09	64 537.57	4028.09	64 539.57	0.06

**Table 3**  
 $F$ -ratio (all temperatures considered) and significance levels of  $\alpha = 0.01$ ,  $\alpha = 0.05$  and  $\alpha = 0.1$ .

System	$F$ -ratio	$F$ -ratio $_{\alpha=0.01}$	$F$ -ratio $_{\alpha=0.05}$	$F$ -ratio $_{\alpha=0.1}$
CO <sub>2</sub> +2-butanol	43.1	7.7	4.2	2.9
Ethanol+glycerol	12.9	8.1	4.3	3.0
Ethane+decane	10.9	8.1	4.3	3.0
CO <sub>2</sub> +ethanol	70.8	7.3	4.1	2.8
CO <sub>2</sub> +styrene	81.983	8.5	4.5	3.0
CO <sub>2</sub> +acetic acid	6.7	8.2	4.4	3.0
Ethylene+1-decanol	8.5	8.3	4.4	3.0
CO <sub>2</sub> +H <sub>2</sub> S	240.6	8.5	4.5	3.0

calculated with vdW-MR, however the predicted values by these models for higher pressures are similar. The results obtained for the systems CO<sub>2</sub>+acetic acid and CO<sub>2</sub>+styrene with  $q$ -MR are significantly better than with the conventional mixing rule, by providing qualitatively correct predictions of pressure and vapor concentration. However both mixing rules show similar results for the CO<sub>2</sub>+H<sub>2</sub>S system. The  $q$ -MR is able to present a smooth inflection for the system CO<sub>2</sub>+styrene, which is in agreement with the data. Figs. 3–10 show pressure–composition diagrams with comparison between experimental data and calculated results for the considered examples.

Some pressure–composition diagrams, particularly Figs. 3, 4 and 7, display an inflection point. This change in the concavity is due to the stronger influence of interactions between molecules under high pressures, and the ability of the  $q$ -MR model to represent this behavior is a consequence of the inflection point of the curves of the interaction parameter of the mixture  $a_{q,M}$  versus composition, see Fig. 1 and 2. Fig. 11 shows the effect of the parameters  $q_{12}$  and  $k_{12}$  on the inflection point. It can be seen that as the parameter  $q_{12}$  departs from unit the difference in concavities becomes more pronounced, whereas the parameter  $k_{12}$  is related to a shift of the curves.

The  $q$ -MR model has two binary parameters, while the original vdW-MR has only one. In order to make a unbiased comparison, we have implemented the Akaike Information Criterion (AIC) (Akaike, 1974) that is a suitable tool for these situations. It is defined as

$$AIC_i = -2\log(\text{maximum likelihood}) + 2k_i. \quad (22)$$

If the standard deviations  $\sigma_i$  are known and the residuals are normally distributed, the AIC is written as

$$AIC_i = F_{ob}^{opt}(\theta) + 2k_i + \frac{2k_i(k_i + 1)}{n - k_i - 1} \quad (23)$$

where  $k_i$  is the number of parameters of the model  $i$ ,  $N_{exp}$  is the number of experiments and  $\theta_{opt}$  is the set of optimal parameters (in our case, parameters estimated for all temperatures, as showed in Table 1). According to the Akaike procedure the more appropriate model among those that are being compared is that one which results in the lower AIC value. The results are shown in Table 2. It is also useful to compare the relative AIC values, and this is shown in the last column of the Table. Values less than 1 indicate that the  $q$ -MR is better than vdW-MR. All considered systems present relative AIC index smaller than 1, indicating that the improvement achieved by the  $q$ -MR is not simply due to the existence of an additional parameter.

We have also considered the  $F$ -test as an additional criterium for discrimination between models with different numbers of parameters (Ludden et al., 1994; Motulsky and Christopoulos, 2004). The  $F$ -ratio is defined as

$$F_{ratio} = \frac{F_{ob}^{vdW-MR}(\theta_{opt}) - F_{ob}^{q-MR}(\theta_{opt})}{F_{ob}^{q-MR}(\theta_{opt})} \frac{df^{q-MR}}{df^{vdW-MR} - df^{q-MR}} \quad (24)$$

where  $df^{q-MR}$  and  $df^{vdW-MR}$  are the degrees of freedom ( $df^i = N - k_i$ ) of the equation of state with  $q$ -MR and the equation of state with vdW-MR, respectively. The calculated  $F$ -ratios are showed in Table 3 and they are compared to the critical  $F$ -ratios taken from the  $F$ -Distribution Table (with the same number of degrees of freedom) for three different values of significance level,  $\alpha = 0.01$ , 0.05 and 0.1.

The greater the value of the  $F$ -ratio, the greater the statistical significance of the  $q$ -MR model compared to the vdW-MR model. Only one system considered in the present work presented  $F$ -ratio smaller than the critical  $F$ -ratio: the calculated  $F$ -ratio for the system CO<sub>2</sub>+acetic acid is slightly smaller than  $F$ -ratio $_{\alpha=0.01}$ .

#### 4. Conclusions

This work introduces a new nonquadratic mixing rule that is a generalization of the usual quadratic mixing rule, which is recovered in a special limit  $q_{ij} \rightarrow 1$ . The  $q$ -mixing rule here introduced, generalized through the nonquadraticity parameter  $q_{ij}$ , is free from the Michelsen–Kistenmacher syndrome. It is based on the  $q$ -product that is able to reflect correlations. Departures from the quadratic nature of the mixing rule, as described by the  $q$ -mixing rule, may be so strong as to present an inflection point in the graph of the parameter of the mixture  $a_{q,M}$  as a function of composition. This is distinctive from the original parabolic mixing rule, which has constant concavity. This feature is also responsible for the change in concavity in the pressure–composition diagram, specially at high pressures, when interaction between molecules becomes more significant. It is a common practise to use the binary parameter  $k_{ij}$  with quadratic mixing rules to increase the fitting power of the models, though this parameter preserves the quadratic nature of the rule. We also use the parameter  $k_{12}$  in our proposal. Indeed it is essential in the present model once it allows proper adjustment of the inflection point of the mixing rule.

We have used the Peng–Robinson equation of state in the presented examples, but the procedure can readily be applied to virtually any cubic equation of state that uses mixing rules *à la* van der Waals.

We have exemplified the usefulness of the proposed  $q$ -mixing rule with vapor–liquid equilibrium calculations for binary systems containing carbon dioxide (CO<sub>2</sub>+2-butanol, CO<sub>2</sub>+ethanol, CO<sub>2</sub>+styrene, CO<sub>2</sub>+acetic acid, CO<sub>2</sub>+H<sub>2</sub>S), and also for the mixtures ethanol+glycerol, ethane+decane, and ethylene+1-decanol. We have used two procedures to compare the proposed model with the usual one, the Akaike Information Criterion and the  $F$ -test, and the  $q$ -MR has succeeded in all instances considered.

#### Acknowledgements

Leonardo S. Souza and Fernando L.P. Pessoa thank ANP (Brazilian agent) for financial support. Ernesto P. Borges acknowledges National Institute of Science and Technology for Complex Systems, and FAPESB (Brazilian agencies).

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