



# Correlating multicomponent surface tension data with Padé approximants. Part I. Surface tension

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## ABSTRACT

Eberhardt (1966), Connors and Wright (1989), Piñeiro et al. (2001), Das and Bhattacharyya (2003) and Belda (2009) all proposed successful mixture models for correlating the surface tension data for binary liquid mixtures. Rational extensions of these semi-theoretical and empirical models are derived in order to cater for multicomponent mixtures. It is shown that a canonical Padé approximant emanates from the Piñeiro et al. (2001) and Das et al. (2003) proposals:

$$\sigma = \frac{\sum_i \beta_{ii} x_i \sigma_i \sum_j \kappa_{ij} x_j}{\sum_i \sum_j \beta_{ij} x_i x_j}$$

Where the  $\sigma_i$ 's are the surface tensions of the pure components as a function of temperature. The  $\beta_{ij}$  and  $\kappa_{ij}$  are adjustable model constants (with  $\kappa_{ii} = 1$ ) and they carry some physical meaning. The other models are special cases that are obtained by the application of different combining rules. For example, when the Extended Langmuir model developed by Piñeiro et al. (2001) holds, one obtains  $\beta_{ij} = \sqrt{\beta_{ii}\beta_{jj}}$ ; on the other hand, it reduces to the Connors and Wright (1989) model if  $\beta_{ij} = (\beta_{ii} + \beta_{jj})/2$ . The theories underpinning these models, suggest that the parameters  $\beta_{ij}$  and  $\kappa_{ij}$  might be temperature dependent. However, Shardt and Elliott (2017) found that, for binary systems they can be assumed constant, i.e. that the temperature dependence is carried solely by the pure component surface tensions. This premise was confirmed for the seven ternary systems which were used to validate the proposed multicomponent canonical Padé approximant.

## 1. Introduction

Surface tension arises due to the cohesive forces between the molecules at the surface of the liquid in contact with a gas. It is a physical property that has important effects on the behaviour of liquids in processes associated with the formation of droplets, the wetting of solid surfaces, and the penetration of liquids by capillary action. These three physical phenomena underpin many practical applications. For example, the surface tension significantly affects the spray atomization of liquid fuels injected into the combustion chambers of high compression engines [1]. This has implications for the efficiency of the combustion performance and consequently also on the nature of the exhaust emissions [1]. Surface tension is also an important parameter that is exploited in industrial applications to improve the efficiency of formulated chemical products such as paints and coatings, detergents, personal care- and pharmaceutical products. It also plays a significant role

in processes such as enhanced oil recovery [2]. Indeed, Fathi Azarbayjani, et al. [3] stated: "In order to meet manufacturing challenges and develop new and better performing products with improved qualities, knowledge of surface tension is of utmost importance." Thus, there is a practical need for knowing how the surface tension of liquid mixtures will vary with composition, temperature and, to a lesser extent, with pressure [4]. Surface tension is one of the physical properties that shows a highly non-linear dependency on composition [1]. Numerous empirical and semi-empirical mixture models have been put forward over the years [1,5–7]. Patiño-Camino et al. [1] recently measured the surface tension of binary blends containing diesel or bio-diesel with either ethanol or butanol. They compared different models to each other in a quest to identify the most suitable one for correlating the experimental data they generated for these blends. Model performance was ranked on the basis of three criteria, i.e. best fit, minimum number of parameters and the existence of a physical basis. Based on this critical analysis, they

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recommended the Connors-Wright model [6] due to its relative simplicity, the fact that the model parameters have physical meaning and its accuracy for such mixtures. Additionally, they observed that a simpler expression, originated by Eberhart [5], also performed well.

More recently, Kleinheins, et al. [8] reviewed the most popular models for surface tension and tested their ability to reproduce experimental data for ten binary aqueous solutions chosen to be representative of different solute types. They also found that the models by Eberhart [5] and Connors and Wright [6] performed very well. Unfortunately, neither Patiño-Camino et al. [1] nor Kleinheins et al. [8] considered the Extended Langmuir (EL) model in their analysis [7]. This model is possibly based on an even more rigorous analysis along the lines initially pioneered by Connors and Wright [6]. Furthermore, several studies showed that the EL model provides superior surface tension data correlation for a wide range of binary mixtures [7,9–11]. In addition, highly nonlinear empirical models for surface tension, put forward by Belda [12], also proved highly effective for correlating data, not only for surface tension, but also for other physical properties such as density, viscosity and refractive index.

The Connors and Wright [6], the Extended Langmuir (EL) [7] and Belda [12] models were all derived for binary liquid mixtures. Extensions to multicomponent mixtures are, by and large, still extant. It is also not yet clear how best to integrate the temperature dependence of surface tension into these model expressions. The present communication is an attempt to make some progress by dealing with these two issues. It is shown that a canonical form of the EL model corresponds to a Padé-like expression which easily extends to multicomponent situations. Moreover, it is shown that the temperature dependence can be incorporated via the pure component properties as first suggested by Shardt and Elliott [13]. Furthermore, it is found that the Connors and Wright [6], Das and Bhattacharyya [14], Belda [12] and Eberhart [5] models are all special cases of the canonical Padé form.

## 2. Theory

Eberhart [5] assumed that the surface tension of a binary mixture is given by a linear blending rule:

$$\sigma = \sigma_1 y_1 + \sigma_2 y_2 \quad (1)$$

where  $\sigma_1$  and  $\sigma_2$  are the surface tensions of the pure components, and  $y_1$  and  $y_2$  are the molar surface concentrations. The implication is that the non-ideal behaviour of the surface tension is fully embodied in the surface concentrations [14]. This assumption served as a cornerstone for the development of other models for binary mixtures [6,14]. Hence, with Eq. (1) as starting point, the objective is to relate the surface compositions to the bulk concentrations. Numerous studies sought to treat the surface layer as a separate phase and used conventional phase equilibrium thermodynamics to determine a link between the surface and bulk concentrations [6]. Eberhart [5] assumed thermodynamic equilibrium between the surface the bulk phases, i.e. that the activity of each component is the same in the two phases. He expressed this as:

$$a_1 = \gamma_1 x_1 = \delta_1 y_1 \quad \text{and} \quad a_2 = \gamma_2 x_2 = \delta_2 y_2 \quad (2)$$

where  $x_i$  and  $y_i$  are the mole fractions of component  $i$  in the bulk and surface phases respectively and  $\gamma_i$  and  $\delta_i$  represent the corresponding activity coefficients. Taking the simplex constraint in each phase into account (i.e. that the mole fractions summate to unity), Eberhart [5] obtained the following equation:

$$\sigma = \frac{\sigma_1 S x_1 + \sigma_2 x_2}{S x_1 + x_2} \quad (3)$$

$$\text{with } S = \frac{\gamma_1 \delta_2}{\gamma_2 \delta_1} \quad (4)$$

However, a symmetric version of this expression is more suitable for the present discussion:

$$\sigma = \frac{\beta_1 x_1 \sigma_1 + \beta_2 x_2 \sigma_2}{\beta_1 x_1 + \beta_2 x_2} \quad (5)$$

$$\beta_i = \gamma_i / \delta_i \quad (6)$$

Aqueous solutions, however, are typically highly nonideal. The observed surface tensions reveal a high surface excess of the organic component. Therefore, Connors and Wright [6] took a different approach. They obtained a useful expression by basing their analysis on two assumptions: (a) The partition between surface and bulk concentrations is defined by a Langmuir absorption isotherm, and (b) that the number of surface sites is proportional to the number of water molecules (component 1) in the surface. On the basis of binding site constants denoted by  $K_i$ , partition functions defined by  $P_i = y_i/x_i$  and a molecular size factor  $k$  for component 2, they finally obtained the following semi-theoretical expression relating the surface tension to bulk mixture composition:

$$\frac{\sigma_1 - \sigma}{\sigma_1 - \sigma_2} = \left( \frac{1 + (b-a)x_1}{1 - ax_1} \right) x_2 \quad (7)$$

$$\text{With } a = \frac{k_2 P_2}{1 + k_2 P_2} \quad \text{and} \quad b = \frac{k K_1 P_1}{1 + K_2 P_2} \quad (8)$$

where, as before,  $x_i$  is the bulk concentration.

Belda [12] took an empirical approach and developed two slightly different equations. However, one of them has a similar functional form as Eq. (7):

$$\frac{\sigma_1 - \sigma}{\sigma_1 - \sigma_2} = \left( \frac{1 + m_1 x_1}{1 + m_2 x_1} \right) x_2 \quad (9)$$

Das and Bhattacharyya [14] proposed the following expression for the surface tension of binary mixtures:

$$\frac{\sigma - \sigma_1}{\sigma_2 - \sigma_1} = \left( \frac{1 + p x_1}{1 + q_1 x_1 + q_2 x_1^2} \right) x_2 \quad (10)$$

Piñero et al. [7] derived the Extended Langmuir (EL) model for the surface tension of liquid mixtures. In their analysis, they consider a binary mixture for which  $\sigma_1 > \sigma_2$ . Their model can be expressed as follows:

$$\frac{\sigma_1 - \sigma}{\sigma_1 - \sigma_2} = \left( \frac{1 + (\alpha/\beta - 1)\varphi_1}{1 + 2(1/\beta - 1)\varphi_1 + (1/\beta^2 - 1)\varphi_1^2} \right) \varphi_2 \quad (11)$$

This form is similar to Eq. (10) except for the composition expressed in terms of volume fractions instead of mole fractions. Note that the parameters  $\alpha$  and  $\beta$  in the EL model have physical meaning.

All the models presented above are for binary mixtures. It is not immediately obvious how to generalise them for multicomponent mixtures. Yet they all have a similar structure (notably Eqs. (10) and (11) are more complicated) with the terms in brackets corresponding to a ratio of a linear term in the composition variable to a quadratic term. In order to assist the derivation of multicomponent forms, it is convenient to first focus on the binary EL model. Straightforward algebraic manipulation leads to an equivalent form that is easier to interpret:

$$\sigma = \frac{\varphi_1^2 \sigma_1 + [(2 - \alpha)\beta \sigma_1 + \alpha \beta \sigma_2] \varphi_1 \varphi_2 + \beta^2 \varphi_2^2 \sigma_2}{\varphi_1^2 + 2\beta \varphi_1 \varphi_2 + \beta^2 \varphi_2^2} \quad (12)$$

In the analysis presented by Piñero et al. [7], the parameter  $\beta$  is defined as the ratio of the absorption ( $k_2$ ) to desorption ( $k_1$ ) rate constants, i.e.

$$\beta = k_2/k_1 \quad (13)$$

Piñero et al. [7] also postulated a Margules interaction term, as a correction for Eq. (1), but used volume fractions instead of mole fractions. The correction term was assumed proportional to  $\lambda = \alpha - 1$ . Recall that volume fractions are nominal mixture descriptors defined by:

$$\varphi_i = \frac{V_i x_i}{V_1 x_1 + V_2 x_2} \quad (14)$$

Substituting Eq. (13) and Eq. (14) into Eq. (12) and simplifying leads to

$$\sigma = \frac{\beta_1 x_1 \sigma_1 (x_1 + \kappa_{12} x_2) + \beta_2 x_2 \sigma_2 (\kappa_{21} x_1 + x_2)}{\beta_1 x_1^2 + 2\sqrt{\beta_1 \beta_2} x_1 x_2 + \beta_2 x_2^2} \quad (15)$$

with  $\beta_i \equiv k_i^2 V_i^2$  (16)

$$\text{and } \kappa_{12} = (1 - \lambda) \frac{k_2 V_2}{k_1 V_1} \quad \text{and} \quad \kappa_{21} = (1 + \lambda) \frac{k_1 V_1}{k_2 V_2} \quad (17)$$

The model formulated by Das and Bhattacharyya [14] corresponds to a slightly more general form which, for binary mixtures, reads as follows (See [Supplementary Information](#)):

$$\sigma = \frac{\beta_{11} x_1 \sigma_1 (x_1 + \kappa_{12} x_2) + \beta_{22} x_2 \sigma_2 (\kappa_{21} x_1 + x_2)}{\beta_{11} x_1^2 + 2\beta_{12} x_1 x_2 + \beta_{22} x_2^2} \quad (18)$$

where  $\beta_{ii} = \beta_i$ .

The straightforward extension of this equation, in order to cater for multicomponent system behaviour, is:

$$\sigma = \frac{\sum_i \beta_{ii} x_i \sigma_i \sum_j \kappa_{ij} x_j}{\sum_i \sum_j \beta_{ij} x_i x_j} \quad (19)$$

With  $\beta_{ii} = \kappa_{ii} = 1$ .

Eq. (19) is denoted the canonical  $P(2,2)$  Padé approximant because it represents a generalisation of several semi-theoretical and empirical mixture models for the surface tension of liquid mixtures. It is defined as the ratio of two quadratic polynomials with mole fractions as the composition variables. It represents a somewhat more general expression than the EL model since the  $\beta_{ij}$  are not defined in terms of a combining rule, i.e. they are free to vary. In the [Supplementary Information](#) it is shown that all of the other models listed above are just special forms of this equation. For instance, the multicomponent EL model is obtained when the  $\beta_{ij}$  are defined by a combining rule corresponding to a geometric mean over the pure component values, i.e.

$$\beta_{ij} = \sqrt{\beta_{ii} \beta_{jj}} = \sqrt{\beta_i \beta_j} \quad (20)$$

which leads to the multicomponent expression:

$$\sigma = \frac{\sum_i \beta_i x_i \sigma_i \sum_j \kappa_{ij} x_j}{\left(\sum_k \sqrt{\beta_k} x_k\right)^2} \quad (21)$$

On the other hand, if the cross parameters ( $\beta_{ij}$ ) are defined by an arithmetic mean over the pure component values, i.e.

$$\beta_{ij} = (\beta_i + \beta_j)/2 \quad (22)$$

the multicomponent [6] model is obtained:

$$\sigma = \frac{\sum_i \beta_i x_i \sigma_i \sum_j \kappa_{ij} x_j}{\sum_k \beta_k x_k} \quad (23)$$

Eq. (23) is the canonical  $P(2,1)$  Padé approximant for the surface tension corresponding to the Connors and Wright model. It also embodies some of the models proposed by Belda [12]. See the [Supplementary Information](#) for details. Finally, if in addition it holds that  $\kappa_{ij} = 1 \forall i, j$ , the multicomponent form of the Eberhart [5] is obtained:

$$\sigma = \frac{\sum_i \beta_i x_i \sigma_i}{\sum_j \beta_j x_j} \quad (24)$$

Eq. (24) is the canonical  $P(1,1)$  Padé approximant form. By analogy, the  $P(1,2)$  canonical Padé form is defined by:

$$\sigma = \frac{\sum_i \beta_i x_i \sigma_i}{\sum_i \sum_j \beta_{ij} x_i x_j} \quad (25)$$

The nonlinear composition behaviour of some systems is such that it requires implementation of a  $P(3,2)$  Padé approximant which is defined as follows:

$$\sigma = \frac{\sum_i \beta_{ii} x_i \sigma_i \left(\sum_j \kappa_{ij} x_j\right) \left(\sum_j \lambda_{ij} x_j\right)}{\sum_i \sum_j \beta_{ij} x_i x_j} \quad (26)$$

with  $\kappa_{ii} = \lambda_{ii} = 1$ .

The expressions defined by Eq. (25) and Eq. (26) have not yet been tested for use in the correlation of surface tension data.

The theory-based derivations [5–7], on which the canonical Padé approximants are based, suggest that the parameters  $\beta_{ij}$  and  $\kappa_{ij}$  might well be temperature-dependent. However, Shardt and Elliott [13] showed that the Connors model, including an extension they proposed [4], applies to a wide range of temperatures even if the model parameters are assumed constant, i.e. independent of the solution temperature. The implication is that the pure-component temperature dependence is the controlling factor for binary mixtures. This communication focused on testing this important idea using actual surface tension data for ternary mixtures that were obtained over a range of temperatures.

Eqs. (18), (23) to (26) are the most general canonical Padé approximant forms proposed for surface tension. Noteworthy is the fact that all the adjustable parameters either characterise pure component behaviour or binary interactions. Therefore, pure component information together with data obtained for binary mixtures should suffice to predict multicomponent behaviour under isothermal conditions. If, in addition, the postulate posited by Shardt and Elliott [13] holds, this would presumably even be true for data collected over some limited temperature range. The original derivations of these models featured fewer adjustable parameters that differ from those present in Eqs. (18), (23) and (24). The assumptions (or empirical conjectures) made in the original development of these equations define links between the parameters found in the extended canonical versions. See the [Supplementary Information](#) for details.

Note also that the canonical Padé approximants defined above are based on mole fractions as the mixture composition descriptors. Any other rational choice can be used including volume or mass fractions. While that would change the  $\beta$ - and  $\kappa$ -values in the model expressions, the predicted data trends will be identical. A proof of this assertion is provided in the [Supplementary Information](#) for binary mixtures.

### 3. Data analysis

The capacity of the various canonical Padé models for accurately representing real experimental information was tested using experimental data gleaned from the literature. The seven ternary systems shown in [Table 1](#) were used. They were selected because they included binary and ternary data that was generated over a range of temperatures. This made it possible to test the hypothesis, made by Shardt and

**Table 1**  
Ternary systems used in the data reduction exercise.

#	Components	T-range, °C	References
I	monoethanolamine (1) – 2-amino-2-methyl-1-propanol (2) – water (3)	25–50	[16]
II	water (1) – acetone (2) – toluene (3)	15–55	[17]
III	2-propanol (1) – 1,2-propanediol (2) – water (3)	25–55	[18,19]
IV	tetrahydrofuran (1) 2-propanol (2) – 2,2,4-trimethylpentane (3)	15–35	[20]
V	2-propanol (1) – tetrahydropyran (2) – 2,2,4-trimethylpentane (3)	20–50	[21]
VI	ethanol (1) – benzyl acetate (2) – benzyl alcohol (3)	15–35	[22]
VII	2-propanol (1) – benzyl alcohol (2) – phenylethanol (3)	25–45	[23,24]

Elliott [13], that the temperature dependence of the surface tension of a mixture is adequately accounted for by the pure component surface tension behaviour.

Table 2 shows the canonical Padé expression as they relate to ternary mixtures. As mentioned, the original derivations of these expressions included constraints on the model parameters. See the Supplementary Information for details. However, these were ignored during the least-squares data regression performed presently. All the parameters in the canonical forms were allowed to vary freely and they were determined using least-squares regression.

Data for the monoethanolamine (1) – 2-amino-2-methyl-1-propanol (2) binary was not available for System I in Table 1. Therefore, when regressing the binary data, the following parameter settings were imposed:  $\kappa_{12} = \kappa_{21} = 1$ , and  $\beta_{12} = (\beta_1 + \beta_2)/2$ . This is equivalent to assuming that the behaviour of this particular binary is adequately described by the  $P(1,1)$  Padé approximant. A similar strategy was implemented for system II for which data for the water (1) - toluene (3) binary was not available.

The Akaike information criterion (AIC) [15] was used to rank the relative performance of the models. The governing equation is

$$AIC = n \ln(SSE) + 2df \tag{27}$$

where  $n$  is the number of data points,  $SSE$  is the sum of the square errors, and  $df$  is the degrees of freedom, i.e. the number of parameters that are fitted. To compare models, it is only the difference between the AIC values that matters. On taking differences, the units cancel out and the result is unitless:

$$\Delta AIC = n \ln(SSE_{ref}/SSE_{model}) + 2\Delta df \tag{28}$$

Eq. (28) makes intuitive sense as it balances the change in goodness of fit, as assessed by the sum-of-squares, with the change in the degrees of freedom (due to differences in the number of parameters in the models being compared). In each case, the multicomponent version of the Eberhart [5] model, i.e. the  $P(1,1)$  Padé expression, served as the reference model. In a first step, the full data sets were regressed. However, in a second round, only the binary data were used to fix the model parameters. This provided an indication as to whether ternary data can be predicted from knowledge of binary data. In both cases, the SSE values for the full data sets were used to calculate the  $\Delta AIC$  values. Comprehensive details, including the numerical values assumed by the model parameters, are provided in the Supplementary Information.

### 4. Results

Fig. 1 shows the average absolute deviations (AAD) between predicted and experimental values for the different systems and the models that were tested. Fig. 1(a) shows the results for the case where the model parameters were obtained using both the binary and ternary data.

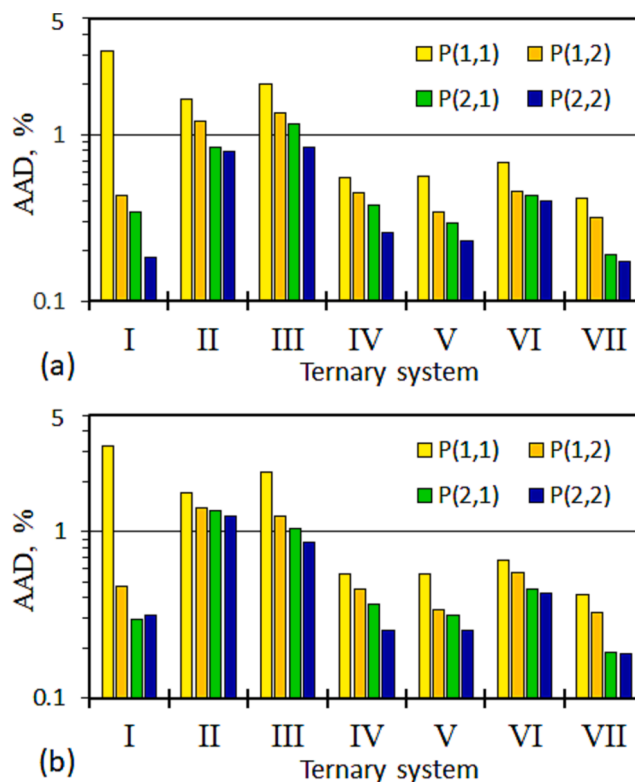


Fig. 1. Absolute average deviations (AAD) between all predicted and experimental surface tension values. Results obtained when (a) regressing the full data set, and (b) using only the binary data.

Interestingly, the  $P(2,1)$  Padé approximant always performed better than the  $P(1,2)$  expression. Evidently, the prediction errors decrease as the model order is increased. This was to be expected since more adjustable parameters were available. Fig. 1(b) shows the AAD values for the full data sets when, instead, the model parameters are fixed using just the binary data. As anticipated (but not shown here), better fits of the binary data were obtained. However, the predictions for ternary composition became slightly worse and this is reflected in the larger overall AAD values. As before, the  $P(2,1)$  model consistently outperformed the  $P(1,2)$  Padé approximant. Otherwise, increasing the model order again led to a reduction of the AADs.

The improved performance offered by the higher order Padé approximants is to be expected. However, the substantial increase in the number of adjustable model parameters poses a risk of overfitting the data. Fig. 2 shows the Akaike information results. The plotted  $\Delta AIC$

Table 2  
Canonical Padé approximants for correlating the surface tension of ternary mixtures.

Form	Padé approximant	Eq.	References
P(2,2)	$\sigma = \frac{\beta_1 x_1 \sigma_1 (x_1 + \kappa_{12} x_2 + \kappa_{13} x_3) + \beta_2 x_2 \sigma_2 (\kappa_{21} x_1 + x_2 + \kappa_{23} x_3) + \beta_3 x_3 \sigma_3 (\kappa_{31} x_1 + \kappa_{32} x_2 + x_3)}{\beta_1 x_1^2 + \beta_2 x_2^2 + \beta_3 x_3^2 + 2\beta_{12} x_1 x_2 + 2\beta_{13} x_1 x_3 + 2\beta_{23} x_2 x_3}$	19	[14]
	$\sigma = \frac{\beta_1 x_1 \sigma_1 (x_1 + \kappa_{12} x_2 + \kappa_{13} x_3) + \beta_2 x_2 \sigma_2 (\kappa_{21} x_1 + x_2 + \kappa_{23} x_3) + \beta_3 x_3 \sigma_3 (\kappa_{31} x_1 + \kappa_{32} x_2 + x_3)}{(\sqrt{\beta_1} x_1 + \sqrt{\beta_2} x_2 + \sqrt{\beta_3} x_3)^2}$	20	[7]
P(2,1)	$\sigma = \frac{\beta_1 x_1 \sigma_1 (x_1 + \kappa_{12} x_2 + \kappa_{13} x_3) + \beta_2 x_2 \sigma_2 (\kappa_{21} x_1 + x_2 + \kappa_{23} x_3) + \beta_3 x_3 \sigma_3 (\kappa_{31} x_1 + \kappa_{32} x_2 + x_3)}{\beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3}$	23	[612]
P(1,2)	$\sigma = \frac{\beta_1 x_1 \sigma_1 + \beta_2 x_2 \sigma_2 + \beta_3 x_3 \sigma_3}{\beta_1 x_1^2 + \beta_2 x_2^2 + \beta_3 x_3^2 + 2\beta_{12} x_1 x_2 + 2\beta_{13} x_1 x_3 + 2\beta_{23} x_2 x_3}$	25	
P(1,1)	$\sigma = \frac{\beta_1 x_1 \sigma_1 + \beta_2 x_2 \sigma_2 + \beta_3 x_3 \sigma_3}{\beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3}$	24	[5]

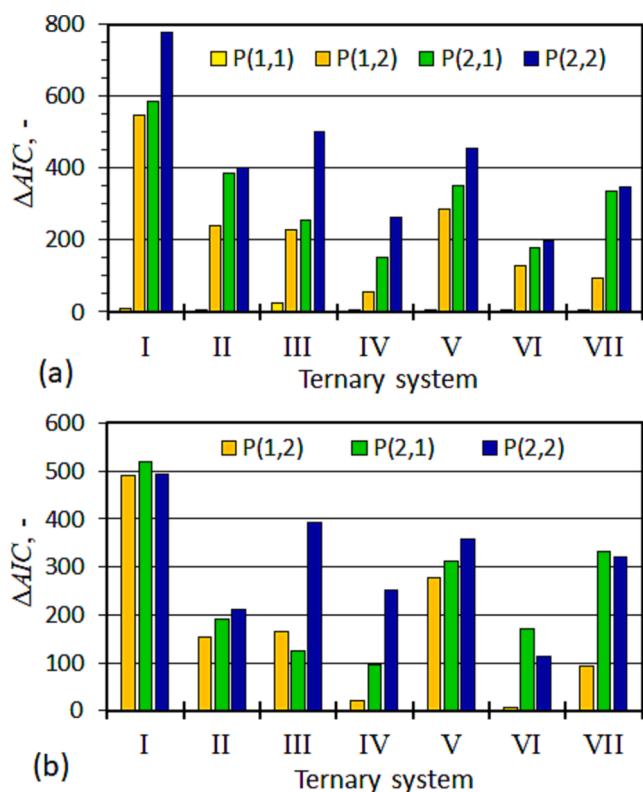


Fig. 2. Akaike information results for (a) regression of the full data sets, and (b) data regression performed on the binary data alone.

values provide a relative measure of model performance which considers that better performance is to be expected for models with a greater number of adjustable parameters. Models with fewer parameters are preferred as this lowers the risk of overfitting. The  $P(1,1)$  model, applied to the binary data of each system, was used as the reference for calculating the  $\Delta AIC$  values. Large  $\Delta AIC$  values indicate improved data fits compared to the reference model. Fig. 2(a) shows that the use of higher order models was particularly beneficial when the data regression considered the full data sets. With one exception (the  $P(2,2)$  model applied to ternary system I), this was also true when the regression exercise considered only the binary data.

The evidence presented in Fig. 1, and Fig. 2, confirms that the canonical Padé approximants have merit for correlating surface tension data as a function of both composition and temperature. This was

confirmed for data available over a limited range of temperature near ambient, i.e. 15 °C–50 °C. This implies that the effect of temperature was adequately accounted for ternary mixtures by the temperature dependence of the pure components alone, a premise first posited by Shardt and Elliott [13].

Apart from the various linear blending rules, mixture models generally require data for all binary subsystems in order to predict multicomponent behaviour. The  $P(1,1)$  model is an interesting exception. If the model provides an adequate representation of the composition dependence of an  $n$ -component system, the multicomponent behaviour is fixed even when no data is available for one of the constituent binaries. Unfortunately, Figs. 1 and 2 both indicate that the  $P(1,1)$  model was inadequate for representing the full data sets of the systems considered presently. Nevertheless, when the  $P(1,1)$  model was applied to cater for the missing binaries of ternary system I and II, excellent ternary data prediction was achieved on the basis of data for just two of the binaries in the mixture. See Figs. 1(b) and 2(b).

The Supplementary Information includes Figures that visualize the fits for the binary data and the ternary data of each system. In each case, the  $P(2,2)$  model with the parameters obtained by regressing the full data, are shown. This model proved adequate for all systems in that the AAD values were very low, less than 0.84 % and even as low as 0.17 %. However, the benzyl acetate – benzyl alcohol binary showed an unusual composition dependence as shown in Fig. 3. Only in this case, was the application of Eq. (26) required in order to fit the isothermal surface tension vs. composition curves.

## 5. Conclusion

The canonical  $P(2,2)$  Padé approximant for the surface tension, with the multicomponent version defined by Eq. (19), was obtained on the basis of a rational extension of the proposals initially made by Eberhardt (1966), Connors and Wright (1989), Piñeiro et al. (2001), Das et al. (2003) and Belda (2009) for binary mixtures. This general model includes the other multicomponent forms as those are obtained via various combining rules. The data correlation prowess of these models was tested using seven ternary systems for which data was available over a significant temperature range. The model performance was ranked using the Akaike Information criterion (AIC). It was found that, irrespective of whether the data regression was done over the binary data alone, or the full data set, that the  $P(2,2)$  model performed best when considered in terms of the AIC criterion. Furthermore, the postulate that the temperature dependence of the surface tension is determined by that of the pure component surface tensions [13] was confirmed for the present data sets. Lastly, it holds that the canonical Padé approximations are invariant with respect to the composition descriptor used, e.g. mole, volume or mass fraction.

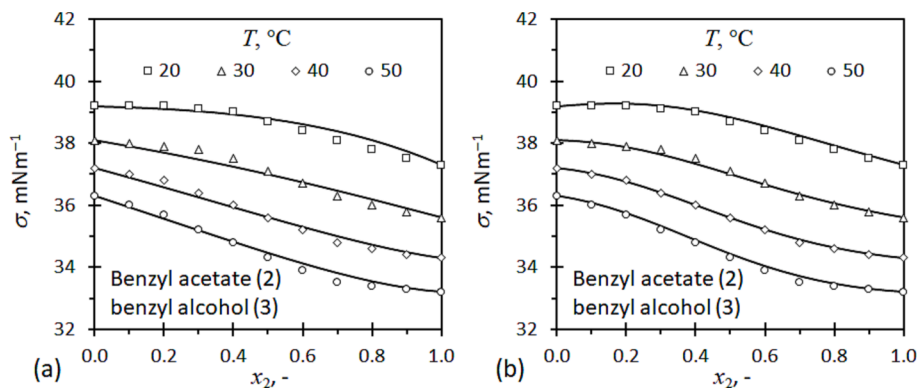


Fig. 3. Data fits for the benzyl acetate – benzyl alcohol binary on regressing the full data set for System VI. (a) Result obtained for the  $P(2,2)$  Padé approximant defined by Eq. (19). (b) Adjusting the result for (a) by implementing Eq. (26) for the benzyl acetate – benzyl alcohol binary.

**Consent to participate**

Consent to participate was not necessary as human subjects were not involved in any experiments.

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**CRediT authorship contribution statement**

**Pethile Dzingai:** . Franco Pretorius: Validation, Writing – review & editing, Visualization, Software. **Walter W. Focke:** .

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Data availability**

Data will be made available on request.

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**Appendix A. Supplementary material**

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2024.124003>.

**References**

- [1] R. Patiño-Camino, A. Cova-Bonillo, M. Lapuerta, J. Rodríguez-Fernández, L. Segade, Fluid Phase Equilib. 555 (2022) 113363, <https://doi.org/10.1016/j.fluid.2021.113363>.
- [2] A. Samanta, A. Bera, K. Ojha, A. Mandal, J. Pet. Explor. Prod. Technol. 2 (2012) 67, <https://doi.org/10.1007/s13202-012-0021-2>.
- [3] A. Fathi Azarbayjani, A. Jouyban, S.Y. Chan, J. Pharm. Pharmaceut. Sci. 12 (2009) 218 10.18433/J32P40.
- [4] N. Shardt, Y. Wang, Z. Jin, J.A.W. Elliott, Chem. Eng. Sci. 230 (2021), <https://doi.org/10.1016/j.ces.2020.116095>.
- [5] J.G. Eberhart, J. Phys. Chem. 70 (1966) 1183, <https://doi.org/10.1021/j100876a035>.
- [6] K.A. Connors, J.L. Wright, Anal. Chem. 61 (1989) 194, <https://doi.org/10.1021/ac00178a001>.
- [7] Á. Piñero, P. Brocos, A. Amigo, J. Gracia-Fadrique, M.G. Lemus, Langmuir 17 (2001) 4261, <https://doi.org/10.1021/la001210s>.
- [8] J. Kleinheins, N. Shardt, M. El Haber, C. Ferronato, B. Nozière, T. Peter, C. Marcolli, PCCP 25 (2023) 11055, <https://doi.org/10.1039/d3cp00322a>.
- [9] P. Brocos, J. Gracia-Fadrique, A. Amigo, A. Piñero, Fluid Phase Equilib. 237 (2005) 140, <https://doi.org/10.1016/j.fluid.2005.08.020>.
- [10] K. Granados, J. Gracia-Fadrique, A. Amigo, R. Bravo, J. Chem. Eng. Data 51 (2006) 1356, <https://doi.org/10.1021/je060084c>.
- [11] A. Bagheri, K. Alizadeh, Colloids Surf A Physicochem Eng Asp 467 (2015) 78, <https://doi.org/10.1016/j.colsurfa.2014.11.037>.
- [12] R. Belda, Fluid Phase Equilib. 282 (2009) 88, <https://doi.org/10.1016/j.fluid.2009.04.023>.
- [13] N. Shardt, J.A.W. Elliott, Langmuir 33 (2017) 11077, <https://doi.org/10.1021/acs.langmuir.7b02587>.
- [14] S. Das, K. Bhattacharyya, Chem. Phys. Lett. 374 (2003) 676, [https://doi.org/10.1016/S0009-2614\(03\)00813-3](https://doi.org/10.1016/S0009-2614(03)00813-3).
- [15] H. Akaike, Bulletin of the International Statistical Institute 50 (1983) 277.
- [16] G. Vázquez, E. Alvarez, J.M. Navaza, R. Rendo, E. Romero, J. Chem. Eng. Data 42 (1997) 57, <https://doi.org/10.1021/je960238w>.
- [17] S. Enders, H. Kahl, J. Winkelmann, J. Chem. Eng. Data 52 (2007) 1072, <https://doi.org/10.1021/je7000182>.
- [18] C.-W. Chang, T.-L. Hsiung, C.-P. Lui, C.-H. Tu, Fluid Phase Equilib. 389 (2015) 28, <https://doi.org/10.1016/j.fluid.2014.12.040>.
- [19] Y.-F. Lin, C.-H. Tu, J. Taiwan Inst. Chem. Eng. 45 (2014) 2194, <https://doi.org/10.1016/j.jtice.2014.04.010>.
- [20] H.-C. Ku, C.-C. Wang, C.-H. Tu, J. Chem. Eng. Data 53 (2008) 566, <https://doi.org/10.1021/je700626v>.
- [21] Y.-C. Kao, C.-H. Tu, J. Chem. Thermodyn. 43 (2011) 216, <https://doi.org/10.1016/j.jct.2010.08.019>.
- [22] K.-D. Chen, Y.-F. Lin, C.-H. Tu, J. Chem. Eng. Data 57 (2012) 1118, <https://doi.org/10.1021/je201009c>.
- [23] C.-T. Yeh, C.-H. Tu, J. Chem. Eng. Data 52 (2007) 1760, <https://doi.org/10.1021/je700140j>.
- [24] T.T. Huang, C.T. Yeh, C.H. Tu, J. Chem. Eng. Data 53 (2008) 1203, <https://doi.org/10.1021/je7007445>.