

Supplementary Information:

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

S1. Padé-type expressions for surface tension modelling

In this document it is shown that several mixture models, which were originally developed for the description of the surface tension of binary systems, can be recast in forms that have consistent multicomponent extensions. Specifically, these models can be interpreted as special Padé approximations.

S1.1 Eberhard surface tension mixture model

Eberhart (1966) developed an equation for the surface tension of binary liquid mixtures based on the assumption that the surface tension, σ , is a linear function of the surface layer mole fractions:

$$\sigma = \sigma_1 y_1 + \sigma_2 y_2$$

The equilibrium surface compositions (y_i) were linked to the bulk concentrations (x_i) via a distribution coefficient S . For binary mixtures, this resulted in an equation of the form:

$$\sigma = \frac{Sx_1\sigma_1 + x_2\sigma_2}{Sx_1 + x_2}$$

where σ_1 and σ_2 are the surface tensions of the two pure components, x_1 and x_2 are the bulk liquid mole fractions, and S defines the extent of surface layer enrichment in the component of lower surface tension. Setting $S = \beta_1/\beta_2$ yields the $P_1^1(\boldsymbol{\beta}, \mathbf{x}, \boldsymbol{\sigma})$ Padé-type approximant for a binary mixture defined by:

$$\sigma = \frac{\beta_1 x_1 \sigma_1 + \beta_2 x_2 \sigma_2}{\beta_1 x_1 + \beta_2 x_2}$$

The multicomponent version is:

$$\sigma = P_1^1(\boldsymbol{\beta}, \mathbf{x}, \boldsymbol{\sigma}) = \frac{\sum \beta_i x_i \sigma_i}{\sum \beta_i x_i}$$

S1.2 Connors and Wright model

Connors and Wright (1989) considered binary aqueous-organic solutions. Their analysis also starts with the Eberhart (1966) postulate that

$$\sigma = \sigma_1 y_1 + \sigma_2 y_2$$

Their model assumes that, in the surface phase, the organic component (component 2) can exist in two states namely a free and a bound (adsorbed) state. They postulated that the number of binding sites in the surface available to component 2 is proportional to the number of water molecules (component 1) in the surface phase. They adopt a Langmuir adsorption isotherm to develop a link between the surface concentrations (y_i) and the bulk concentrations (x_i). Key expressions in their analysis are:

$$a = \frac{K_2 P_2}{1 + K_2 P_2} \quad \text{and} \quad b = \frac{k K_2 P_1}{1 + K_2 P_2}$$

Where K_2 is the binding site constant for component 2 and the P_i are the partition coefficients linking the surface and bulk concentrations. In this way they derived a semi-theoretical equation for the variation of the surface tension with composition. The final equation for binary mixtures has just two adjustable constants, both of which they claim, carry physical meaning:

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

where σ and σ_i are the surface tensions of mixture and of component i respectively and the parameters a and b carry physical meaning as defined by the equations above. An equivalent, more convenient form of this equation for binary mixtures is:

$$\sigma = \frac{\beta_1 x_1 \sigma_1 [x_1 + \kappa_{12} x_2] + \beta_2 x_2 \sigma_2 [\kappa_{21} x_1 + x_2]}{\beta_1 x_1 + \beta_2 x_2}$$

This shows that the Connors and Wright model is a Padé approximant. It also suggests that a rational extension of the expression to deal with multicomponent mixtures is:

$$\sigma = P_1^2 \left(\left[\kappa_{ij} \right], \boldsymbol{\beta}, \mathbf{x}, \boldsymbol{\sigma} \right) = \sum_i \beta_i x_i \sigma_i \sum_j \kappa_{ij} x_j / \sum_k \beta_k x_k$$

Derivations for the Connors and Wright model:

Start with the following, more general, expression for a binary mixture:

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

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

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

$$\sigma = \frac{\sigma_1 (x_1 + x_2) [(1-a)x_1 + x_2] - [(1-a)x_1 - bx_1 + x_2] x_2 (\sigma_1 - \sigma_2)}{(1-a)x_1 + x_2}$$

$$\sigma = \frac{\sigma_1 x_1 [(1-a)x_1 + x_2] + \sigma_1 x_2 [(1-a)x_1 + x_2]}{(1-a)x_1 + x_2} + \frac{-\sigma_1 x_2 [(1-a)x_1 - bx_1 + x_2] + \sigma_2 x_2 [(1-a)x_1 - bx_1 + x_2]}{(1-a)x_1 + x_2}$$

$$\sigma = \frac{\sigma_1 x_1 [(1-a)x_1 + x_2] + \sigma_1 b x_1 x_2 + \sigma_2 x_2 [(1-a)x_1 - bx_1 + x_2]}{(1-a)x_1 + x_2}$$

$$\sigma = \frac{(1-a)x_1^2 \sigma_1 + (\sigma_1 + \sigma_1 b + (1-a)\sigma_2 - b\sigma_2) x_1 x_2 + \sigma_2 x_2^2}{(1-a)x_1 + x_2}$$

$$\sigma = \frac{(1-a)x_1^2 \sigma_1 + (1+b)x_1 x_2 \sigma_1 + (1-a-b)x_1 x_2 \sigma_2 + \sigma_2 x_2^2}{(1-a)x_1 + x_2}$$

$$\sigma = \frac{[(1-a)x_1 + (1+b)x_2] x_1 \sigma_1 + [(1-a-b)x_1 + x_2] x_2 \sigma_2}{(1-a)x_1 + x_2}$$

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

Let $1-a = \beta_1/\beta_2$

$$\sigma = \frac{\beta_1 x_1 \sigma_1 \left[x_1 + \left(\frac{1+b}{1-a} \right) x_2 \right] + \beta_2 x_2 \sigma_2 [(1-a-b)x_1 + x_2]}{\beta_1 x_1 + \beta_2 x_2}$$

$$\sigma = \frac{\beta_1 x_1 \sigma_1 [x_1 + \kappa_{12} x_2] + \beta_2 x_2 \sigma_2 [\kappa_{21} x_1 + x_2]}{\beta_1 x_1 + \beta_2 x_2}$$

Where the following definitions were used:

$$\kappa_{12} \equiv \left(\frac{1+b}{1-a} \right) \quad \text{and} \quad \kappa_{21} \equiv (1-a-b)$$

Link to the model parameters $a = \frac{K_2 P_2}{1 + K_2 P_2}$ and $b = \frac{k K_2 P_1}{1 + K_2 P_2}$:

$$1-a = \frac{1}{1 + K_2 P_2} \quad \text{and} \quad 1+b = \frac{1 + K_2 P_2 + k K_2 P_1}{1 + K_2 P_2}$$

$$\kappa_{12} \equiv 1 + K_2 P_2 + k K_2 P_1$$

$$\kappa_{21} \equiv (1-a-b) = 1 - \frac{K_2 P_2}{1 + K_2 P_2} - \frac{k K_2 P_1}{1 + K_2 P_2}$$

$$\kappa_{21} = \frac{1 - k K_2 P_1}{1 + K_2 P_2}$$

$$\frac{\beta_1}{\beta_2} = \frac{1}{1 + K_2 P_2}$$

Links between the three parameters:

$$K_2 P_2 = \frac{\beta_2}{\beta_1} - 1$$

$$\kappa_{12} = 1 + K_2 P_2 + k K_2 P_1 = \frac{\beta_2}{\beta_1} + k K_2 P_1$$

$$\kappa_{21} = \frac{1 - k K_2 P_1}{1 + K_2 P_2} = \frac{1 - \kappa_{12} + \frac{\beta_2}{\beta_1}}{\frac{\beta_2}{\beta_1}} = 1 + \frac{\beta_1}{\beta_2} (1 - \kappa_{12})$$

$$\frac{\beta_1}{\beta_2} = \frac{\kappa_{21} - 1}{1 - \kappa_{12}}$$

$$\beta_2 \kappa_{21} + \beta_1 \kappa_{12} = \beta_1 + \beta_2$$

$$\beta_2 \kappa_{21} + \beta_1 \kappa_{12} = \beta_1 + \beta_2$$

The implication is that, for binary systems, the original Connors and Wright (1989) model has only two freely adjustable parameters.

S1.3 Belda's mixture rule proposals

Belda (2009) introduced a nonlinear expression to fit binary experimental data for the physical property of a mixture. Here it will be denoted by the symbol c . It will be shown that it also leads to Padé-type expressions. Belda (2009) started from the linear blending rule:

$$c = c_1x_1 + c_2x_2$$

Where c_i and x_i respectively represent the property value for pure component i and x_i is the mole fraction of the component in the binary mixture.

Next, Belda (2009) considered deviations from the LBR:

$$\Delta c = c - c_1x_1 - c_2x_2$$

The deviations can be expressed in two different ways:

$$c = c_2 + (c_1 - c_2)x_1 \quad \text{or} \quad c = c_1 + (c_2 - c_1)x_2$$

From these, Belda (2009) proposed two alternative corrections for the two separate expressions:

$$c = c_2 + (c_1 - c_2)x_1 \left[\frac{1 + m_1(1 - x_1)}{1 + m_2(1 - x_1)} \right] \quad \text{and} \quad c = c_1 + (c_2 - c_1)x_2 \left[\frac{1 + m_1(1 - x_2)}{1 + m_2(1 - x_2)} \right]$$

These corrections are not identical. However, irrespective of which one is selected, ultimately a Padé-like expression is obtained:

$$c = \frac{\beta_1 x_1 c_1 [x_1 + \kappa_{12} x_2] + \beta_2 x_2 c_2 [\kappa_{21} x_1 + x_2]}{\beta_1 x_1 + \beta_2 x_2}$$

The multicomponent extension is:

$$y = \frac{\sum_i \sum_j \beta_{ij} c_{ij} x_i x_j}{\sum_k \beta_k x_k}$$

If, however, both of his proposals are forced to hold simultaneously, the governing mixing rule reduces to the model proposed by Eberhart (1966):

$$c = \frac{\beta_1 x_1 c_1 + \beta_2 x_2 c_2}{\beta_1 x_1 + \beta_2 x_2}$$

Derivations related to Belda's models:

(i) Consider one of the Belda model equations in isolation:

$$c = c_2 + (c_1 - c_2)x_1 \left[\frac{1 + m_1(1 - x_1)}{1 + m_2(1 - x_1)} \right]$$

$$c = \frac{c_2(x_1 + x_2)[1 + m_2x_2] + (c_1 - c_2)x_1[1 + m_1x_2]}{1 + m_2x_2}$$

$$c = \frac{c_2x_2[1 + m_2x_2] + c_2x_1[1 + m_2x_2] + c_1x_1[1 + m_1x_2] - c_2x_1[1 + m_1x_2]}{1 + m_2x_2}$$

$$c = \frac{c_2x_2 + c_2m_2x_2x_2 + c_2m_2x_1x_2 + c_1x_1 + c_1m_1x_1x_2 - c_2m_1x_1x_2}{1 + m_2x_2}$$

$$c = \frac{c_2x_2(x_1 + x_2) + c_2m_2x_2x_2 + c_2m_2x_1x_2 + c_1x_1(x_1 + x_2) + c_1m_1x_1x_2 - c_2m_1x_1x_2}{1 + m_2x_2}$$

$$c = \frac{c_1x_1^2 + c_1(1 + m_1)x_1x_2 + c_2(1 + m_2 - m_1)x_1x_2 + c_2(1 + m_2)x_2^2}{x_1 + (1 + m_2)x_2}$$

$$c = \frac{c_1x_1[x_1 + (1 + m_1)x_2] + (1 + m_2)c_2x_2 \left[\left(\frac{1 + m_2 - m_1}{1 + m_2} \right) x_1 + x_2 \right]}{x_1 + (1 + m_2)x_2}$$

Let $1 + m_2 = \beta_2/\beta_1$, substitute and simplify:

$$c = \frac{\beta_1x_1c_1[x_1 + (1 + m_1)x_2] + \beta_2x_2c_2 \left[\left(\frac{1 + m_2 - m_1}{1 + m_2} \right) x_1 + x_2 \right]}{\beta_1x_1 + \beta_2x_2}$$

Let $\kappa_{12} = 1 + m_1$ and $\kappa_{21} = 1 - m_1/(1 + m_2)$

$$c = \frac{\beta_1x_1c_1[x_1 + \kappa_{12}x_2] + \beta_2x_2c_2[\kappa_{21}x_1 + x_2]}{\beta_1x_1 + \beta_2x_2}$$

This expression is identical to the Connors and Wright (1989) expressions for $c = \sigma$.

Note however, that Belda (2009) claimed that it is useful for other physical properties too.

(ii) Consider the second Belda equation:

$$c = c_1 + (c_2 - c_1)x_2 \left[\frac{1 + m_1x_1}{1 + m_2x_1} \right]$$

$$c = \frac{c_1(x_1 + x_2)((1 + m_2)x_1 + x_2) + (c_2 - c_1)x_2[(1 + m_1)x_1 + x_2]}{(1 + m_2)x_1 + x_2}$$

$$c = \frac{(1 + m_2)c_1x_1^2 + c_1x_1x_2 + (1 + m_2)c_1x_1x_2 + (1 + m_1)c_2x_1x_2 - (1 + m_1)c_1x_1x_2 + c_2x_2^2 + c_1x_2^2 - c_1x_2^2}{(1 + m_2)x_1 + x_2}$$

$$c = \frac{(1 + m_2)c_1x_1^2 + (1 + m_2 - m_1)c_1x_1x_2 + (1 + m_1)c_2x_1x_2 + c_2x_2^2}{(1 + m_2)x_1 + x_2}$$

$$c = \frac{(1 + m_2)c_1x_1 \left[x_1 + \left(\frac{1 + m_2 - m_1}{1 + m_2} \right) x_2 \right] + c_2x_2[(1 + m_1)x_1 + x_2]}{(1 + m_2)x_1 + x_2}$$

Now set $\frac{\beta_1}{\beta_2} = 1 + m_2$, substitute and simplify:

$$c = \frac{\beta_1x_1c_1[x_1 + (1 + m_2 - m_1)x_2] + \beta_2x_2c_2[(1 + m_1)x_1 + x_2]}{\beta_1x_1 + \beta_2x_2}$$

Define $\kappa_{12} = 1 - m_1/(1 + m_2)$ and $\kappa_{21} = 1 + m_1$

This yields the same composition dependence as the expression above:

$$c = \frac{\beta_1x_1c_1[x_1 + \kappa_{12}x_2] + \beta_2x_2c_2[\kappa_{21}x_1 + x_2]}{\beta_1x_1 + \beta_2x_2}$$

(iii) The result when both equations are forced to hold simultaneously:

$$c = c_2 + (c_1 - c_2)x_1 \left[\frac{1 + m_1(1 - x_1)}{1 + m_2(1 - x_1)} \right]$$

$$c = c_1 + (c_2 - c_1)x_2 \left[\frac{1 + m_1(1 - x_2)}{1 + m_2(1 - x_2)} \right]$$

$$c(1 + m_2x_2) = c_2(1 + m_2x_2) + (c_1 - c_2)x_1(1 + m_1x_2)$$

$$c(1 + m_2x_1) = c_1(1 + m_2x_1) + (c_2 - c_1)x_2(1 + m_1x_1)$$

$$c(1 + m_2x_2) = c_1x_1(1 + m_1x_2) + c_2[1 + m_2x_2 - x_1(1 + m_1x_2)]$$

$$c(1 + m_2x_1) = c_1[1 + m_2x_1 - x_2(1 + m_1x_1)] + c_2x_2(1 + m_1x_1)$$

Make use of the fact that $x_1 + x_2 = 1$:

$$c(x_1 + x_2 + m_2x_2) = c_1x_1(1 + m_1x_2) + c_2[x_1 + x_2 + m_2x_2 - x_1 - m_1x_1x_2]$$

$$c(x_1 + x_2 + m_2x_1) = c_1[x_1 + x_2 + m_2x_1 - x_2 - m_1x_1x_2] + c_2x_2(1 + m_1x_1)$$

$$c[x_1 + (1 + m_2)x_2] = c_1x_1(1 + m_1x_2) + c_2[x_2 + m_2x_2 - m_1x_1x_2]$$

$$c[(1 + m_2)x_1 + x_2] = c_1[x_1 + m_2x_1 - m_1x_1x_2] + c_2x_2(1 + m_1x_1)$$

Add the two equations:

$$c[x_1 + (1 + m_2)x_2 + (1 + m_2)x_1 + x_2] = c_1x_1(1 + m_1x_2) + c_2[x_2 + m_2x_2 - m_1x_1x_2] \\ + c_1[x_1 + m_2x_1 - m_1x_1x_2] + c_2x_2(1 + m_1x_1)$$

$$c[(2 + m_2)x_2 + (2 + m_2)x_1] = c_1[x_1 + m_1x_1x_2 + x_1 + m_2x_1 - m_1x_1x_2] \\ + c_2[x_2 + m_2x_2 - m_1x_1x_2 + x_2 + m_1x_1x_2]$$

$$c[(2 + m_2)x_1 + (2 + m_2)x_2] = (2 + m_2)x_1c_1 + (2 + m_2)x_2c_2$$

$$c = \frac{(2 + m_2)x_1c_1 + (2 + m_2)x_2c_2}{(2 + m_2)x_1 + (2 + m_2)x_2}$$

Let $\beta_i = 2 + m_i$:

$$c = \frac{\beta_1x_1c_1 + \beta_2x_2c_2}{\beta_1x_1 + \beta_2x_2}$$

This recovers the model proposed by Eberhart (1966) for $c = \sigma$.

S1.4 Extended Langmuir model (EL model)

Piñeiro et al. (2001) derived the Extended Langmuir model for the surface tension of liquid mixtures. In their analysis, they consider a binary mixture for which $\sigma_1 > \sigma_2$. In the analysis presented by Piñeiro et al. (2001), the parameter β was defined as the ratio of the absorption (k_2) to desorption (k_1) rate constants, i.e.

$$\beta = k_2/k_1$$

In their analysis they also postulated a Margules interaction term as a correction for equation 2 albeit using volume fractions instead of mole fraction. The correction term was assumed proportional to

$$\lambda = \alpha - 1.$$

This means that the two adjustable parameters, i.e. α and β have physical meaning.

Their model for binary mixtures can be expressed into the following way:

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

Expressed in canonical form using mole fractions instead of volume fractions, this equation reads:

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

or

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

Note the similarity of this equation to the one due to Connors and Wright (1989). Both are Padé-type expressions. However, whereas the latter used mole fractions, the original EL model used volume fractions to define the mixture composition. While the Connors and Wright (1989) model features a first order polynomial as the denominator polynomial, a quadratic K-polynomial is used in the EL model (Piñeiro et al., 2001). The most general extension to multicomponent mixtures is given by:

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

However, the original derivation also pointed to a geometric combining rule as follows:

$$\beta_{ij} = \sqrt{\beta_i \beta_j}$$

With this combining rule the original EL model expression for multicomponent systems is actually:

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

Reformulation of the EL model:

Piñeiro et al. (2001) defined:

$$\pi^o = \sigma_1 - \sigma_2, \quad \pi = \sigma_1 - \sigma \quad \text{and} \quad \pi^* = \pi / \pi^o$$

The final model form for binary mixtures is stated as follows:

$$\pi^* = \frac{\beta[\beta + \alpha(\varphi_1/\varphi_2)]}{[\beta + (\varphi_1/\varphi_2)]^2}$$

The following manipulations are executed in order to obtain the Padé-type expression:

$$\pi^* = \frac{\sigma_1 - \sigma}{\sigma_1 - \sigma_2}$$

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

Expand the square and multiply numerator and denominator with φ^2 .

$$\frac{\sigma_1 - \sigma}{\sigma_1 - \sigma_2} = \frac{\beta^2 \varphi_2^2 + \alpha \beta \varphi_1 \varphi_2}{\varphi_1^2 + 2\beta \varphi_1 \varphi_2 + \beta^2 \varphi_2^2}$$

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

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

Recall that $\varphi_i = \frac{V_i x_i}{V_1 x_1 + V_2 x_2}$. Substitute and simplify

$$\sigma = \frac{V_1 x_1 \sigma_1 (V_1 x_1 + 2\beta V_2 x_2 - \alpha \beta V_2 x_2) + \beta^2 V_2 x_2 \sigma_2 \left(V_2 x_2 + \frac{\alpha}{\beta} V_1 x_1 \right)}{V_1^2 x_1^2 + 2\beta V_1 V_2 x_1 x_2 + \beta^2 V_2^2 x_2^2}$$

$$\sigma = \frac{V_1^2 x_1 \sigma_1 \left(x_1 + (2 - \alpha) \beta \frac{V_2}{V_1} x_2 \right) + \beta^2 V_2^2 x_2 \sigma_2 \left(\frac{\alpha V_1}{\beta V_2} x_1 + x_2 \right)}{V_1^2 x_1^2 + 2\beta V_1 V_2 x_1 x_2 + \beta^2 V_2^2 x_2^2}$$

$$\sigma = \frac{x_1 \sigma_1 \left(x_1 + (2 - \alpha) \beta \frac{V_2}{V_1} x_2 \right) + \beta^2 \frac{V_2^2}{V_1^2} x_2 \sigma_2 \left(\frac{\alpha V_1}{\beta V_2} x_1 + x_2 \right)}{x_1^2 + 2\beta \frac{V_2}{V_1} x_1 x_2 + \beta^2 \frac{V_2^2}{V_1^2} x_2^2}$$

Define $\frac{\beta_2}{\beta_1} = \beta^2 \frac{V_2^2}{V_1^2} = \left(\frac{k_2 V_2}{k_1 V_1}\right)^2$. Substitute and simplify

$$\sigma = \frac{x_1 \sigma_1 \left(x_1 + (2 - \alpha) \sqrt{\frac{\beta_2}{\beta_1}} x_2 \right) + \frac{\beta_2}{\beta_1} x_2 \sigma_2 \left(\alpha \sqrt{\frac{\beta_1}{\beta_2}} x_1 + x_2 \right)}{x_1^2 + 2 \sqrt{\frac{\beta_2}{\beta_1}} x_1 x_2 + \frac{\beta_2}{\beta_1} x_2^2}$$

$$\sigma = \frac{\beta_1 x_1 \sigma_1 \left(x_1 + (2 - \alpha) \sqrt{\frac{\beta_2}{\beta_1}} x_2 \right) + \beta_2 x_2 \sigma_2 \left(\alpha \sqrt{\frac{\beta_1}{\beta_2}} x_1 + x_2 \right)}{\beta_1 x_1^2 + 2 \sqrt{\beta_1 \beta_2} x_1 x_2 + \beta_2 x_2^2}$$

Define $\kappa_{12} = (2 - \alpha) \sqrt{\beta_2 / \beta_1} = (1 - \lambda) \frac{k_2 V_2}{k_1 V_1}$ and $\kappa_{21} = \alpha \sqrt{\beta_1 / \beta_2} = (1 + \lambda) \frac{k_1 V_1}{k_2 V_2}$

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

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

Connection between the parameters in the original model expression:

$$\frac{\kappa_{12}}{\sqrt{\beta_2 / \beta_1}} + \frac{\kappa_{21}}{\sqrt{\beta_1 / \beta_2}} = 2$$

Link between the “old” and the new parameters:

$$\alpha = \frac{\kappa_{21}}{\sqrt{\beta_1 / \beta_2}} \quad \text{and} \quad \beta = \frac{V_1}{V_2} \sqrt{\frac{\beta_2}{\beta_1}}$$

S1.5 Das and Bhattacharyya model

Das and Bhattacharyya (2003) proposed the following expression for the surface tension of binary mixtures:

$$\frac{\sigma - \sigma_1}{\sigma_2 - \sigma_1} = \frac{x_2 + px_1x_2}{1 + q_1x_1 + q_2x_1^2}$$

In this equation, σ , σ_1 and σ_2 are the surface tensions of the mixture and those of the two pure components respectively. This equation has three adjustable parameters p , q_1 and q_2 . It can be shown that their proposal is in fact equivalent to the following Padé P_2^2 form:

$$\sigma = \frac{\beta_1x_1\sigma_1[x_1 + \kappa_{12}x_2] + \beta_2x_2\sigma_2[\kappa_{21}x_1 + x_2]}{\beta_1x_1^2 + 2\beta_{12}x_1x_2 + \beta_2x_2^2}$$

The multicomponent version is:

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

with $\kappa_{ii} = 1$ and $\beta_{ij} = \beta_{ji}$.

When $2\beta_{ij} = \beta_i + \beta_j$, the Das and Bhattacharyya (2003) expression reduces to the Connors and Wright (1989) model. Furthermore, it is mathematically equivalent to the EL model. This is because, for Padé-type models, changing from mole fractions to volume fractions, mass fractions and even q -fractions does change the values assumed by the adjustable parameters but it does not affect the outcome predicted by the model itself.

Derivation (Das and Bhattacharyya, 2003):

Note: the original paper used the symbol “ S ” for the surface tension. Here “ σ ” is used instead.

$$\frac{\sigma - \sigma_1}{\sigma_2 - \sigma_1} = \frac{x_2 + px_1x_2}{1 + q_1x_1 + q_2x_1^2}$$

$$\sigma = \frac{(x_2 + px_1x_2)(\sigma_2 - \sigma_1) + \sigma_1(1 + q_1x_1 + q_2x_1^2)}{1 + q_1x_1 + q_2x_1^2}$$

$$\sigma = \frac{\sigma_1(1 + q_1x_1 + q_2x_1^2 - x_2 - px_1x_2) + \sigma_2(x_2 + px_1x_2)}{1 + q_1x_1 + q_2x_1^2}$$

Invoke $x_1 + x_2 = 1$

$$\sigma = \frac{\sigma_1(x_1 + x_2 + q_1x_1 + q_2x_1^2 - x_2 - px_1x_2) + \sigma_2(x_2 + px_1x_2)}{(x_1 + x_2)^2 + q_1x_1(x_1 + x_2) + q_2x_1^2}$$

$$\sigma = \frac{x_1\sigma_1[(1 + q_1 + q_2)x_1 + (1 + q_1 - p)x_2] + x_2\sigma_2[(1 + p)x_1 + x_2]}{(1 + q_1 + q_2)x_1^2 + (2 + q_1)x_1x_2 + x_2^2}$$

$$\sigma = \frac{(1 + q_1 + q_2)x_1\sigma_1\left[x_1 + \frac{(1 + q_1 - p)}{1 + q_1 + q_2}x_2\right] + x_2\sigma_2[(1 + p)x_1 + x_2]}{(1 + q_1 + q_2)x_1^2 + (2 + q_1)x_1x_2 + x_2^2}$$

$$\text{Define } \frac{\beta_1}{\beta_2} = 1 + q_1 + q_2 \text{ then } \sigma = \frac{\beta_1x_1\sigma_1\left[x_1 + (1 + q_1 - p)\frac{\beta_2}{\beta_1}x_2\right] + \beta_2x_2\sigma_2[(1 + p)x_1 + x_2]}{\beta_1x_1^2 + (2 + q_1)\beta_2x_1x_2 + \beta_2x_2^2}$$

$$\text{Define } 2\beta_{12} = 2 + q_1, \quad \kappa_{12} = (1 + q_1 - p)\frac{\beta_2}{\beta_1} \quad \text{and} \quad \kappa_{21} = 1 + p$$

$$\sigma = \frac{\beta_1x_1\sigma_1[x_1 + \kappa_{12}x_2] + \beta_2x_2\sigma_2[\kappa_{21}x_1 + x_2]}{\beta_1x_1^2 + 2\beta_{12}x_1x_2 + \beta_2x_2^2}$$

Connection between the “new” model parameters:

$$\kappa_{12} = (2\beta_{12} - \kappa_{21})\frac{\beta_2}{\beta_1} \quad \beta_1\kappa_{12} + \beta_2\kappa_{21} = 2\beta_{12}\beta_2 \quad 2\beta_{12} = \frac{\beta_1}{\beta_2}\kappa_{12} + \beta_2\kappa_{21}$$

The link between the new and “old” parameters:

$$p = \kappa_{21} - 1$$

$$q_1 = 2(\beta_{12} - 1)$$

$$q_2 = \frac{\beta_1}{\beta_2} - 1 - q_1 = \frac{\beta_1}{\beta_2} + 1 - 2\beta_{12}$$

S1.6 FLW model (Fu et al., 1986)

Fu et al. (1986) applied Wilson's local composition concept to the Hildebrandt-Scott equation and obtained the following expression for binary mixtures:

$$\sigma = \frac{\sigma_1 x_1}{x_1 + f_{12} x_2} + \frac{\sigma_2 x_2}{f_{21} x_1 + x_2} + \frac{|\sigma_1 - \sigma_2| x_1 x_2}{(x_1 + f_{12} x_2)(f_{21} x_1 + x_2)}$$

For a binary mixture, this expression can also be rewritten in the format of a Padé form:

$$\sigma = \frac{f_{21} \sigma_1 x_1^2 + (\sigma_1 + \sigma_2 + |\sigma_1 - \sigma_2|) x_1 x_2 + f_{12} \sigma_2 x_2^2}{f_{21} x_1^2 + (1 + f_{12} f_{21}) x_1 x_2 + f_{12} x_2^2}$$

S1.7 Alternative model forms for isothermal data

The general expression $P(2,2)$ Padé form for an isothermal mixture is:

$$\sigma = \left(\sum_i \beta_i \sigma_i x_i^2 + 2 \sum_i \sum_{j < i} \beta_{ij} \sigma_{ij} x_i x_j \right) / \left(\sum_i \beta_i x_i^2 + 2 \sum_i \sum_{j < i} \beta_{ij} x_i x_j \right)$$

with $2\beta_{ij}\sigma_{ij} = \beta_i\kappa_{ij}\sigma_i + \beta_j\kappa_{ji}\sigma_j$

For example, for a binary system the expression is

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

An alternative form is:

$$\sigma = P_2^2([\sigma_{ij}], [\beta_{ij}], \mathbf{x}) = \sum \beta_{ij} \sigma_{ij} x_i x_j / \sum \beta_{ij} x_i x_j$$

with $\beta_{ii} = \beta_i$, and $\beta_{ij} = \beta_{ji}$, and $\sigma_{ij} = \sigma_{ji}$

S1.8 Invariance of Padé-type models with respect to the composition descriptors

It is possible to write the equations detailed above in slightly more compact forms:

$$\sigma = P_1^1(\boldsymbol{\sigma}, \boldsymbol{\beta}, \mathbf{x}) = \sum \beta_i \sigma_i x_i / \sum \beta_i x_i$$

$$\sigma = P_1^2([\sigma_{ij}], \boldsymbol{\beta}, \mathbf{x}) = \sum \beta_i \sigma_{ij} x_i x_j / \sum \beta_i x_i$$

$$\sigma = P_2^2([\sigma_{ij}], [\beta_{ij}], \mathbf{x}) = \sum \beta_{ij} \sigma_{ij} x_i x_j / \sum \beta_{ij} x_{ij}$$

The reason for this suggestion is that changing the mole fractions to mass, volume or even q -fractions does not change the value of the property predicted by the model. The only effect is to change the values of the adjustable parameters.

Proof for Padé-type $P(2,2)$ models:

The canonical Padé form (Type I) is defined as follows for a binary mixture:

$$\sigma = P_2^2([\sigma_{ij}], [\beta_{ij}], \mathbf{x}) = \frac{\beta_{11} \sigma_{11} x_1^2 + 2\beta_{12} \sigma_{12} x_1 x_2 + \beta_{22} \sigma_{22} x_2^2}{\beta_{11} x_1^2 + 2\beta_{12} x_1 x_2 + \beta_{22} x_2^2}$$

This form employs mole fractions as the composition descriptors.

Padé Type II form:

This form employs generalised q -fractions as the composition variables. For a binary mixture the expression is:

$$\sigma = \frac{\gamma_{11} \sigma_{11} q_1^2 + 2\gamma_{12} \sigma_{12} q_1 q_2 + \gamma_{22} \sigma_{22} q_2^2}{\gamma_{11} q_1^2 + 2\gamma_{12} q_1 q_2 + \gamma_{22} q_2^2}$$

Where the q -fractions are definition as follows: $q_i = Q_i / (Q_1 x_1 + Q_2 x_2)$

Multiplying numerator and denominator with $(Q_1 x_1 + Q_2 x_2)^2$ and simplifying results in:

$$\sigma = \frac{\gamma_{11} Q_{11}^2 \sigma_{11} x_1^2 + 2\gamma_{12} Q_{11} Q_{22} \sigma_{12} x_1 x_2 + \gamma_{22} Q_{22}^2 \sigma_{22} x_2^2}{\gamma_{11} Q_{11}^2 x_1^2 + 2\gamma_{12} Q_{11} Q_{22} x_1 x_2 + \gamma_{22} Q_{22}^2 x_2^2}$$

The canonical Padé form is recovered by defining: $\beta_{ii} = \gamma_{ii} Q_{ii}^2$ and $2\beta_{ij} = \gamma_{ij} Q_i Q_j$

The same result is obtained when using M_i or V_i instead of Q_i . The implication is that changing the composition descriptor from mole fractions to mass- or volume fractions will not affect the predictions obtained when using canonical Padé approximants. This holds even when the denominator or numerator polynomials in the equation are linear as either of them is readily transformed into a quadratic polynomial by multiplying with $q_1 + q_2 = 1$.

This shows that the two equations are mathematically identical irrespective of whether we use volume-, mass- or mole fractions as the composition descriptors.

Consider the full quadratic canonical form

$$\sigma = \frac{\beta_{11}\sigma_{11}x_1^2 + 2\beta_{12}\sigma_{12}x_1x_2 + \beta_{22}\sigma_{22}x_2^2}{\beta_{11}x_1^2 + 2\beta_{12}x_1x_2 + \beta_{22}x_2^2}$$

This form readily reduces to the simpler forms under certain conditions. Furthermore, this model is fully defined by binary interactions.

Shardt and Elliott (2017) and Shardt et al. (2021) considered extensions to the Connors and Wright (1989) model. Interestingly, they suggested that the temperature dependence of the surface tension might be fully accounted for by the temperature dependence of the pure components present in the mixture. The implication of this assumption is that all the other model parameters in the canonical Padé approximant should be temperature independent. Their role is to define an interpolation procedure that accounts for the temperature dependence of a mixture of fixed composition on the basis of the limiting values defined by the pure components. This interesting idea can be incorporated in the canonical Padé model. Since the model only considers binary interactions, it is sufficient to show the development for binary mixtures. First, we modify equation a as follows:

$$\sigma = \frac{\beta_{11}\sigma_{11}x_1^2 + (\beta_{11}\sigma_{12} + \beta_{22}\sigma_{21})x_1x_2 + \beta_{22}\sigma_{22}x_2^2}{\beta_{11}x_1^2 + 2\beta_{12}x_1x_2 + \beta_{22}x_2^2}$$

$$\sigma = \frac{\beta_{11}\sigma_{11}x_1 \left(x_1 + \frac{\sigma_{12}}{\sigma_{11}}x_2 \right) + \beta_{22}\sigma_{22}x_2 \left(x_1 + \frac{\sigma_{21}}{\sigma_{22}}x_2 \right)}{\beta_{11}x_1^2 + 2\beta_{12}x_1x_2 + \beta_{22}x_2^2}$$

$$\sigma = \frac{\beta_{11}\sigma_{11}x_1(x_1 + \kappa_{12}x_2) + \beta_{22}\sigma_{22}x_2(x_1 + \kappa_{21}x_2)}{\beta_{11}x_1^2 + 2\beta_{12}x_1x_2 + \beta_{22}x_2^2}$$

The assumption made is that the β_{ij} and κ_{ij} are temperature-independent parameters. If successful, this modification increased the number of adjustable parameters of the EL model to four but this allows data correlation over a range of temperatures.

S1.9 Summary

Two Padé-type models appear to dominate in the literature concerned with the modelling of the surface tension of binary mixtures:

Connors and Wright (1989) model

$$\sigma = \frac{\beta_1 \sigma_{11} x_1^2 + 2\beta_{12} \sigma_{12} x_1 x_2 + \beta_2 \sigma_{22} x_2^2}{\beta_1 x_1 + \beta_2 x_2}$$

The Extended Langmuir model (Piñeiro et al., 2001)

$$\sigma = \frac{\beta_{11} \sigma_{11} x_1^2 + 2\beta_{12} \sigma_{12} x_1 x_2 + \beta_{22} \sigma_{22} x_2^2}{\beta_{11} x_1^2 + 2\beta_{12} x_1 x_2 + \beta_{22} x_2^2}$$

Several models proposed by other investigators were found to have the same mathematical form. The differences relate mostly to the combining rules that arose from theoretical considerations or which were applied to reduce the number of adjustable parameters.

Table S1.1 Combining rules proposed for the Connors and Wright (1989) model in its compact form

Expression for $2\beta_{12}\sigma_{12}$	Reference
$\beta_2(1+b)\sigma_1 + (\beta_1 - \beta_2 b)\sigma_2$	(Connors and Wright, 1989)
$\beta_1\sigma_1(1+m_1) + \sigma_2(\beta_2 - \beta_1 m_1)$	(Belda, 2009)
$(\beta_1 - \beta_2 m_1)\sigma_1 + (1+m_1)\beta_2\sigma_2$	(Belda, 2009)
$(2\beta_2 - \beta_1)\sigma_2 + (2\beta_1 - \beta_2)\sigma_1$	(Belda, 2009)

Table S1.2 Combining rules for the compact form of the Extended Langmuir model (Piñeiro et al., 2001)

$2\beta_{12}$	$2\beta_{12}\sigma_{12}$	Reference
$2\sqrt{\beta_1\beta_2}$	$[(2-\alpha)\sigma_1 + \alpha\sigma_2]\sqrt{\beta_1\beta_2}$	(Piñeiro et al., 2001)
$2\beta_{12}$	$(1+p)\beta_2\sigma_2 + [2\beta_{12} - \beta_2(1+p)]\sigma_1$	(Das and Bhattacharyya, 2003)
$1 + \beta_1\beta_2$	$\sigma_1 + \sigma_2 + \sigma_1 - \sigma_2 $	(Fu et al., 1986)

S1.10 References

- BELDA, R. 2009. A proposed equation of correlation for the study of thermodynamic properties (density, viscosity, surface tension and refractive index) of liquid binary mixtures. *Fluid Phase Equilibria*, 282, 88-99.
- CONNORS, K. A. & WRIGHT, J. L. 1989. Dependence of Surface Tension on Composition of Binary Aqueous-Organic Solutions. *Analytical Chemistry*, 61, 194-198.
- DAS, C. & BHATTACHARYYA, K. 2003. Modeling the variation of surface tension with composition for binary liquid mixtures. *Chemical Physics Letters*, 374, 676-683.
- EBERHART, J. G. 1966. The surface tension of binary liquid mixtures. *Journal of Physical Chemistry*, 70, 1183-1186.
- FU, J., LI, B. & WANG, Z. 1986. Estimation of fluid-fluid interfacial tensions of multicomponent mixtures. *Chemical Engineering Science*, 41, 2673-2679.
- PIÑEIRO, Á., BROCCOS, P., AMIGO, A., GRACIA-FADRIQUE, J. & LEMUS, M. G. 2001. Extended Langmuir isotherm for binary liquid mixtures. *Langmuir*, 17, 4261-4266.
- SHARDT, N. & ELLIOTT, J. A. W. 2017. Model for the Surface Tension of Dilute and Concentrated Binary Aqueous Mixtures as a Function of Composition and Temperature. *Langmuir*, 33, 11077-11085.
- SHARDT, N., WANG, Y., JIN, Z. & ELLIOTT, J. A. W. 2021. Surface tension as a function of temperature and composition for a broad range of mixtures. *Chemical Engineering Science*, 230.

S2. Data analysis

The data plots shown, in the Figures to follow, reflect data fits obtained with the P(2,2) Padé model using all the available information.

Table S2.1 Monoethanolamine (1) – 2-amino-2-methyl-1-propanol (2) – H₂O (3)

# Parameters	Objective	P(1,1)		P(1,2)		P(2,1)		P(2,2)	
		2	2	5	5	6	8	9	11
		Binary	All	Binary	All	Binary	All	Binary	All
MEA	β_{11}	7.27	7.52	23.46	22.23	18.65	17.41	19.11	19.52
AMP	β_{22}	29.57	26.98	60.41	62.36	48.57	49.70	45.41	46.17
water	β_{33}	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	β_{12}	18.42	17.25	41.93	45.70	33.61	33.56	32.26	155.82
	β_{13}	4.14	4.26	10.50	10.03	9.82	9.21	9.90	9.98
	β_{23}	15.28	13.99	25.43	26.03	24.79	25.35	24.58	24.66
	κ_{12}					1.00	-106.42	1.00	-95.23
	κ_{13}					0.60	0.74	0.59	0.65
	κ_{21}					1.00	59.94	1.00	72.46
	κ_{23}					0.57	0.49	0.62	0.54
	κ_{31}					7.99	5.81	8.11	7.30
	κ_{32}					13.92	16.12	13.55	14.95
	MAD,%	9.02	7.59	4.35	3.12	4.71	3.06	4.94	1.55
	AAD, %	3.28	3.15	0.47	0.43	0.30	0.34	0.31	0.18
	Δ AIC	0	11	490	546	519	587	495	779

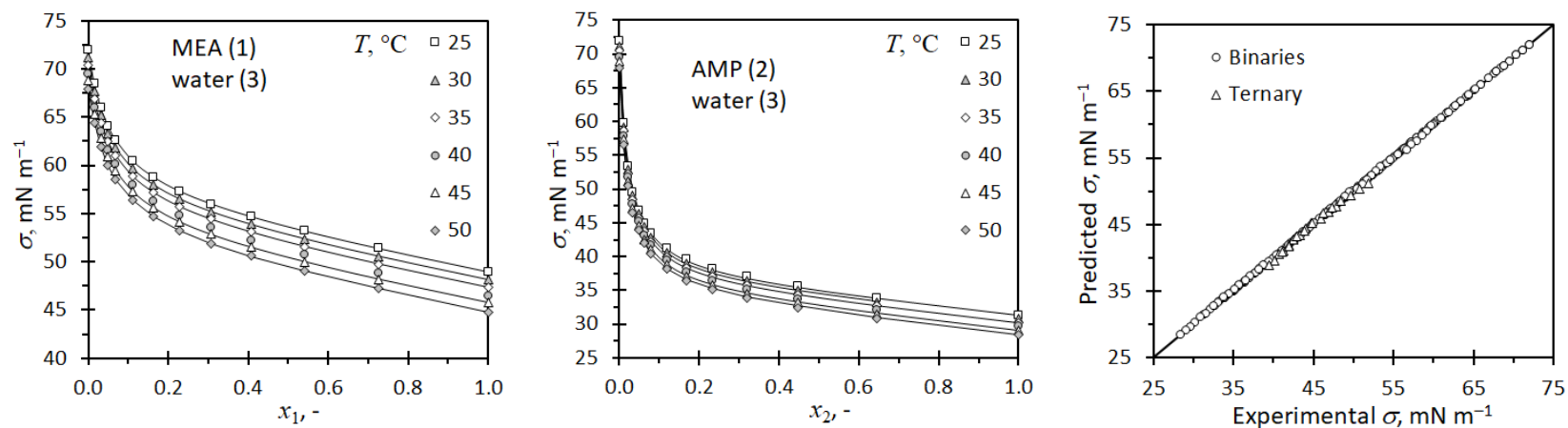


Figure S2.1 Monoethanolamine (1) - 2-amino-2-methyl-1-propanol (2) - H₂O (3)

Table S2.2 Water (1) – acetone (2) – toluene (3)

# Parameters	Objective	P(1,1)		P(1,2)		P(2,1)		P(2,2)	
		2	2	5	5	6	8	9	11
		Binary	All	Binary	All	Binary	All	Binary	All
Water(1)	β_{11}	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Acetone(2)	β_{22}	18.92	18.74	34.59	31.58	27.07	27.06	36.15	36.50
toluene(3)	β_{33}	17.39	19.86	61.18	197.32	101.06	44530.50	153.86	31818.64
	β_{12}	9.96	9.87	14.31	13.54	14.03	14.03	14.66	14.68
	β_{13}	9.20	10.43	107.75	107.75	51.03	22265.75	1.00	16400.05
	β_{23}	18.16	19.30	51.18	132.23	64.07	22278.78	62.98	12348.80
	κ_{12}					5.95	5.95	6.98	7.00
	κ_{13}					1.00	-8734.50	1.00	-6110.88
	κ_{21}					0.63	0.63	0.46	0.45
	κ_{23}					1.00	1113.73	1.00	483.41
	κ_{31}					1.00	1.54	1.00	1.54
	κ_{32}					0.85	0.25	0.48	0.16
	MAD,%	9.58	9.95	15.59	10.75	14.41	10.85	38.76	10.91
	AAD, %	1.70	1.64	3.74	1.21	1.34	0.83	4.47	0.80
	Δ AIC	0.00	4.76	-377	240	190	387	-541	400

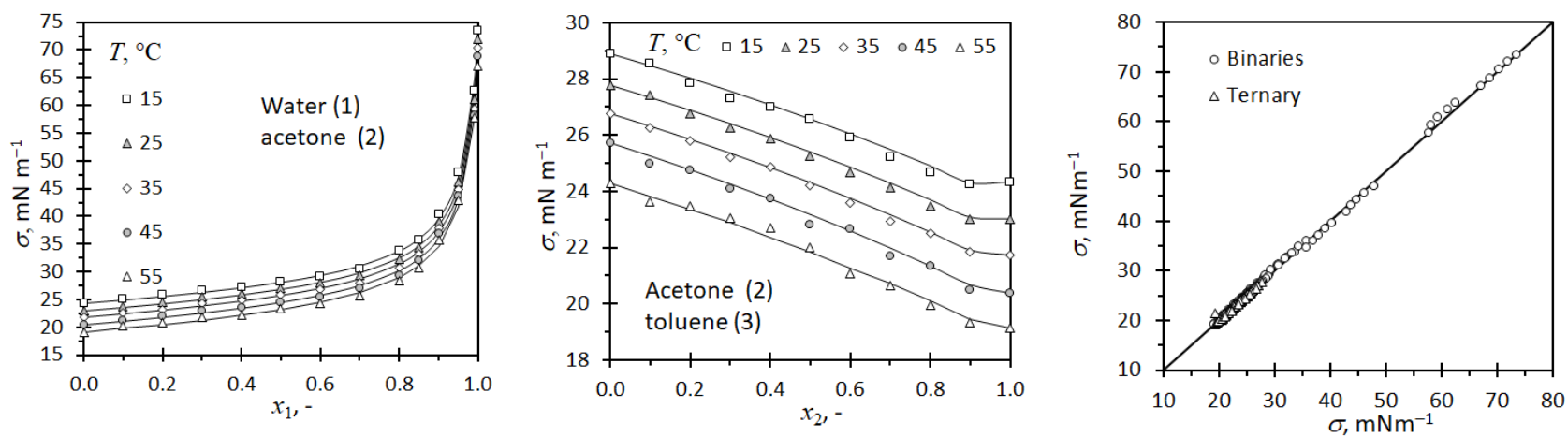


Figure S2.2 Water (1) – acetone (2) – toluene (3)

Table S2.3 2-Propanol (1) – 1,2-propanediol (2) – water (3)

# Parameters Objective		P(1,1)		P(1,2)		P(2,2)		P(3,2)	
		2	2	5	5	8	8	11	11
		Binary	All	Binary	All	Binary	All	Binary	All
2-propanol(1)	β_{11}	45.13	41.45	82.87	65.36	73.97	60.01	28.03	20.74
1,2- propanediol(2)	β_{22}	13.44	13.52	15.42	17.29	14.42	15.76	160.45	930.51
water	β_{33}	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	β_{12}	29.28	27.49	41.47	37.66	44.20	37.89	260.13	1428.91
	β_{13}	23.06	21.23	37.44	30.46	37.48	30.51	34.37	33.56
	β_{23}	7.22	7.26	7.82	8.51	7.71	8.38	17.09	60.78
	κ_{12}					-0.39	0.22	6.76	81.52
	κ_{13}					-0.22	1.10	-0.03	-0.04
	κ_{21}					5.68	3.00	1.26	0.77
	κ_{23}					0.66	0.25	0.01	-0.04
	κ_{31}					29.20	0.78	21.72	20.97
	κ_{32}					3.85	7.55	24.29	121.89
	MAD,%	8.21	11.06	11.47	8.30	12.50	8.28	11.47	4.88
	AAD,%	2.29	2.03	1.23	1.34	1.05	1.17	3.61	0.83
	Δ AIC	0	24	164	230	124	254	-468	502

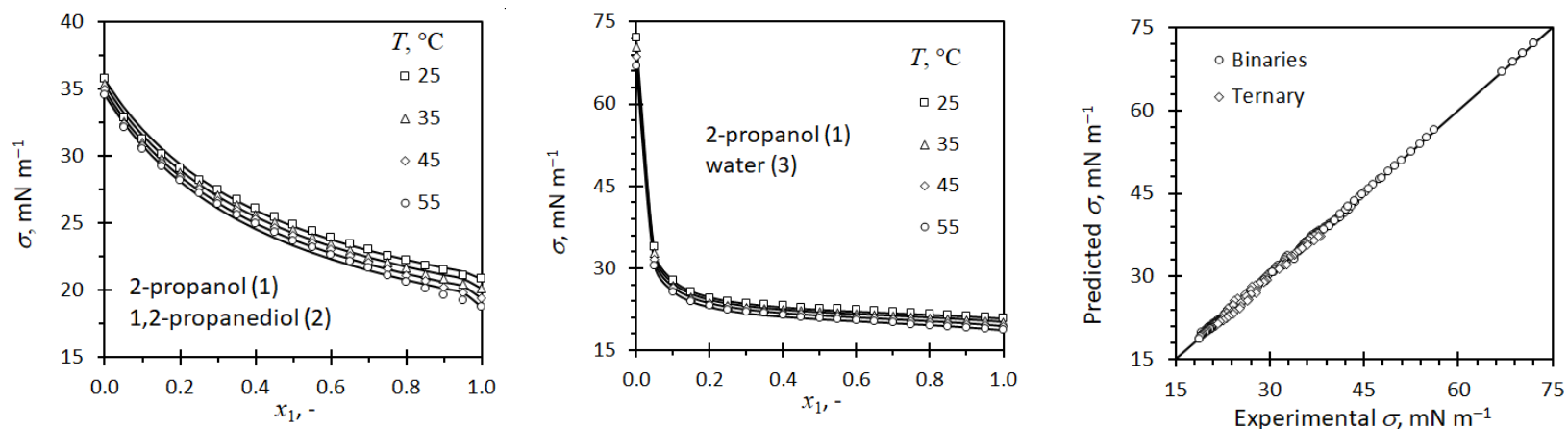


Figure S2.3 2-Propanol (1) – 1,2-propanediol (2) – water (3)

Table S2.4 Tetrahydrofuran (1) – 2-propanol (2) – 2,2,4-trimethylpentane

# Parameters	Objective	P(1,1)		P(1,2)		P(2,1)		P(2,2)	
		2	2	5	5	8	8	11	11
		Binary	All	Binary	All	Binary	All	Binary	All
Tetrahydrofuran	β_{11}	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2-propanol	β_{22}	1.03	1.02	0.94	1.33	1.22	1.73	0.15	0.20
2,2,4-trimethylpentane	β_{33}	4.07	4.08	5.01	4.55	4.98	4.81	2.11	2.88
	β_{12}	1.02	1.01	0.99	1.13	1.11	1.37	0.73	0.77
	β_{13}	2.54	2.54	2.89	2.71	2.99	2.90	2.52	2.56
	β_{23}	2.55	2.55	2.99	3.00	3.10	3.27	0.48	0.60
	κ_{12}					0.06	0.03	-0.29	-0.37
	κ_{13}					9.53	9.58	6.46	7.56
	κ_{21}					2.03	1.84	13.12	10.74
	κ_{23}					-1.14	-1.61	-0.46	-0.62
	κ_{31}					-1.49	-1.60	-1.98	-1.97
	κ_{32}					1.58	2.02	0.51	0.48
	MAD,%	1.85	1.85	2.27	1.92	2.17	1.54	1.71	1.61
	AAD, %	0.55	0.55	0.45	0.45	0.36	0.38	0.25	0.26
	Δ AIC	0.00	0.33	20.54	57.12	94.93	151.25	252.37	263.01

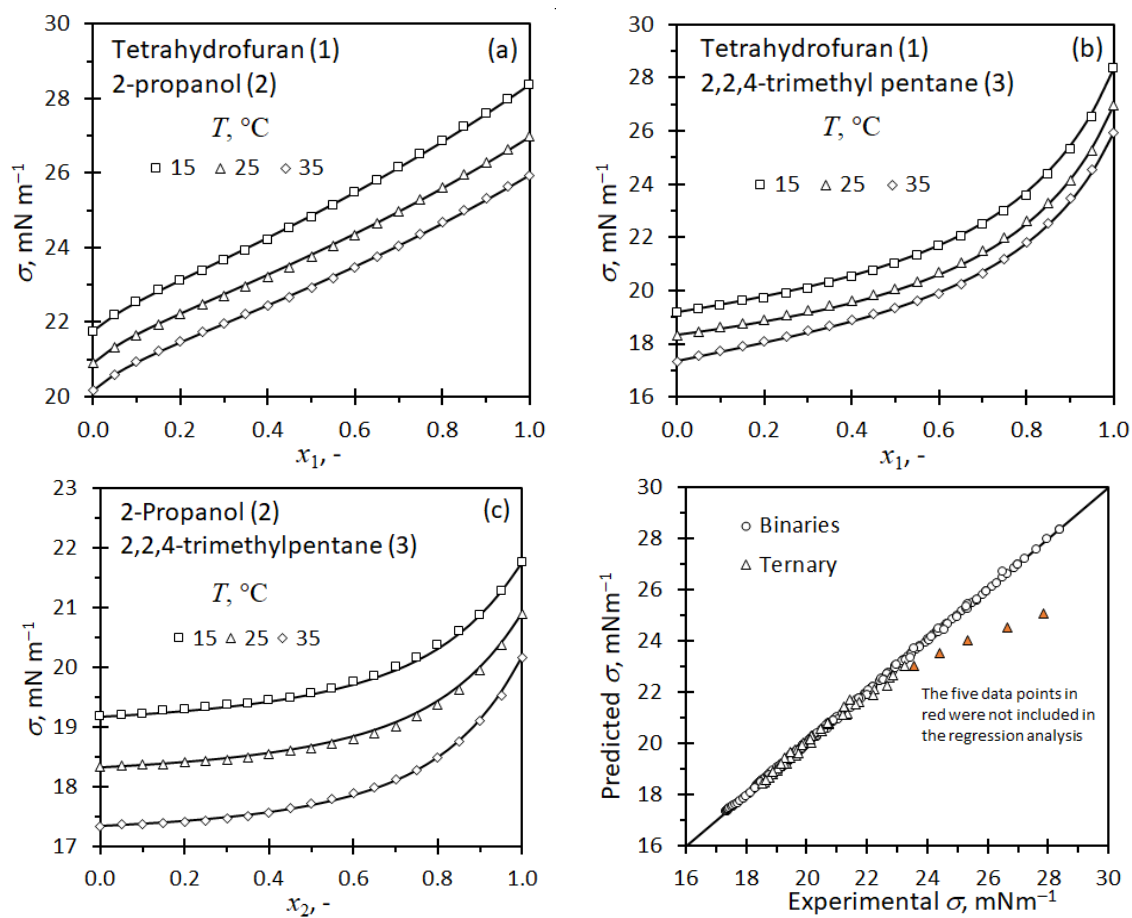


Figure S2.4 Tetrahydrofuran (1) – 2-propanol (2) – 2,2,4-trimethylpentane

Table 2.5 2-Propanol (1) – tetrahydropyran (2) – 2,2,4-trimethylpentane

# Parameters	Objective	P(1,1)		P(1,2)		P(2,1)		P(2,2)	
		2	2	5	5	8	8	11	11
		Binary	All	Binary	All	Binary	All	Binary	All
2-propanol	β_{11}	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Tetrahydropyran	β_{22}	1.00	1.02	0.65	0.59	0.90	0.67	1.61	1.24
2,2,4-Trimethylpentane	β_{33}	2.97	3.09	2.13	1.86	2.82	2.08	2.82	6.09
	β_{12}	1.00	1.01	0.78	0.75	0.95	0.84	1.10	0.94
	β_{13}	1.99	2.04	1.65	1.52	1.91	1.54	1.76	1.47
	β_{23}	1.98	2.05	1.36	1.21	1.86	1.38	2.95	2.95
	κ_{12}					0.27	0.04	0.49	0.25
	κ_{13}					-0.72	-0.82	-0.05	-0.06
	κ_{21}					1.65	2.21	0.94	1.17
	κ_{23}					5.81	5.44	4.47	7.25
	κ_{31}					1.64	1.91	1.26	0.50
	κ_{32}					-1.23	-1.09	-1.47	-1.03
	MAD,%	2.77	2.66	1.15	1.17	1.17	1.15	1.11	1.17
	AAD, %	0.56	0.56	0.34	0.34	0.31	0.30	0.26	0.23
	Δ AIC	0	6	278	286	312	352	359	454

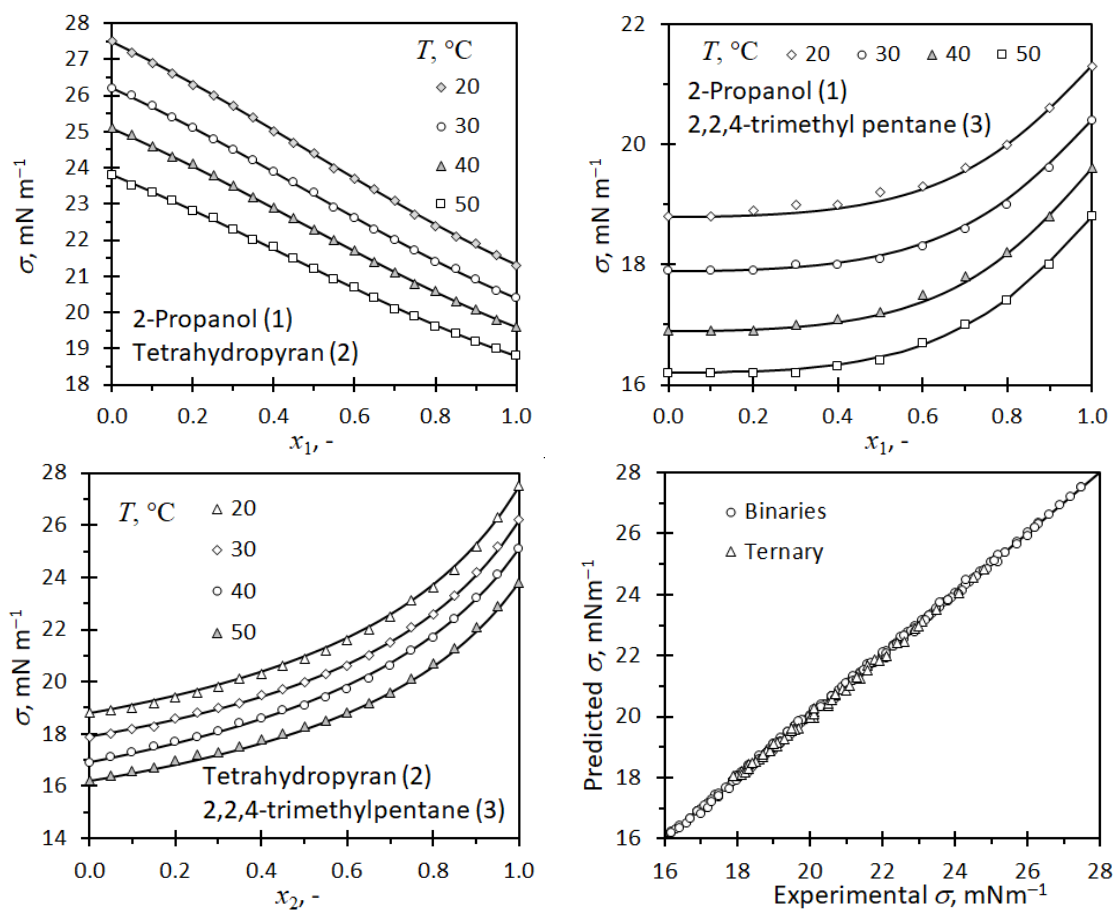


Figure 2.5 2-Propanol (1) – tetrahydropyran (2) – 2,2,4-trimethylpentane

Table 2.6 Ethanol (1) – benzyl acetate (2) – benzyl alcohol (3)

# Parameters	Objective	P(1,1)		P(1,2)		P(2,1)		P(2,2)	
		2	2	5	5	8	8	11	11
		Binary	All	Binary	All	Binary	All	Binary	All
Ethanol (1)	β_{11}	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Benzyl Acetate (2)	β_{22}	0.86	0.86	3.06	1.42	0.34	0.30	3.12	1.52
Benzyl alcohol (3)	β_{33}	1.23	1.23	0.78	0.77	0.31	0.31	2.01	2.03
	β_{12}	0.93	0.93	2.65	1.36	0.67	0.65	-0.13	1.47
	β_{13}	1.11	1.12	0.77	0.77	0.65	0.66	1.60	1.19
	β_{23}	1.04	1.05	1.83	1.06	0.32	0.31	0.92	1.77
	κ_{12}					-1.47	-1.27	2.21	-1.42
	κ_{13}					0.75	0.83	1.54	2.78
	κ_{21}					5.97	6.33	0.21	1.97
	κ_{23}					3.14	3.55	1.52	4.29
	κ_{31}					2.65	2.48	0.33	0.11
	κ_{32}					-1.21	-1.28	-1.29	-1.30
	MAD, %	2.61	2.64	2.59	2.41	2.19	2.29	2.61	2.25
	AAD, %	0.67	0.68	0.57	0.46	0.45	0.43	0.43	0.40
	Δ AIC	0	1	6	128	170	179	112	197

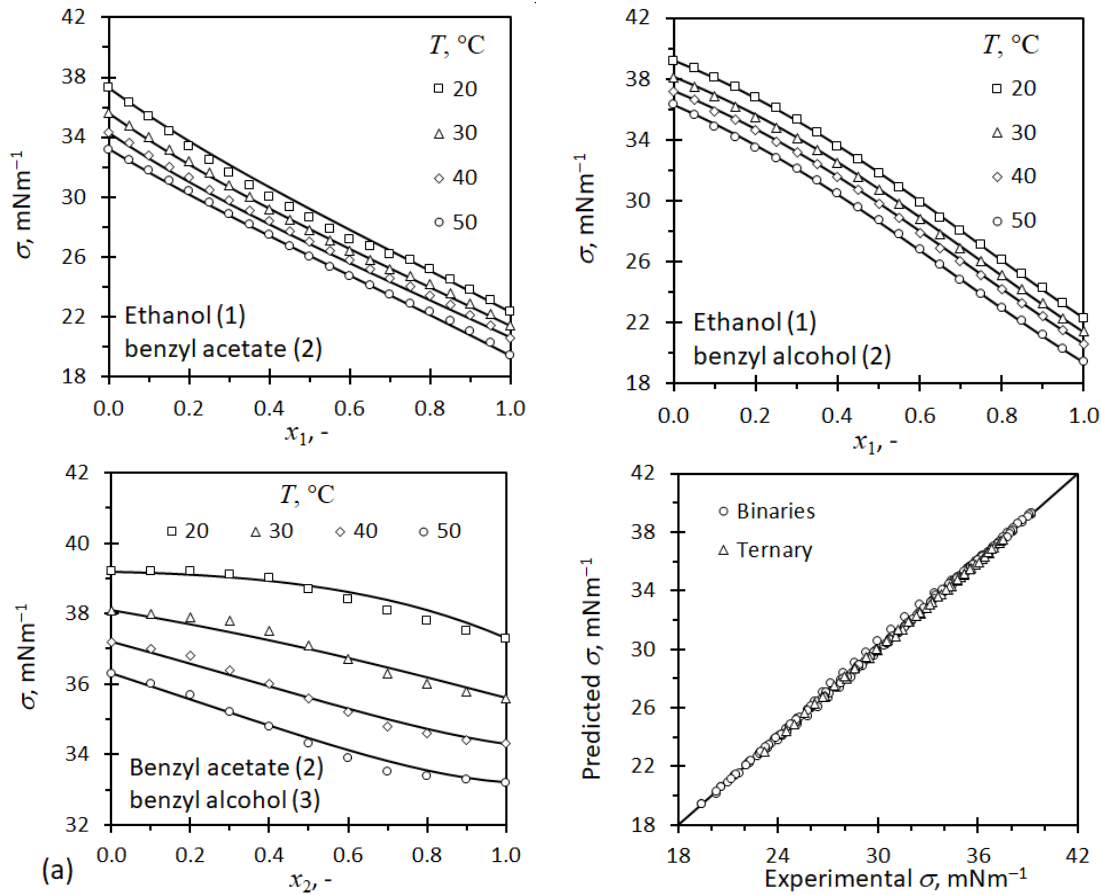


Figure 2.6 Ethanol (1) – benzyl acetate (2) – benzyl alcohol (3)

Table 2.7 2-Propanol (1) – benzyl alcohol (2) – 2-phenylethanol (3)

# Parameters	Objective	P(1,1)		P(1,2)		P(2,1)		P(2,2)	
		2	2	5	5	8	8	11	11
		Binary	All	Binary	All	Binary	All	Binary	All
2-propanol	β_{11}	1.25	1.26	1.10	1.14	1.28	1.28	0.35	0.39
benzyl alcohol	β_{22}	1.00	1.00	1.00	1.00	1.00	1.00	1.15	1.00
2-phenylethanol	β_{33}	0.94	0.95	0.72	0.72	1.60	1.57	1.00	0.43
	β_{12}	1.13	1.13	1.09	1.10	1.14	1.14	0.88	0.80
	β_{13}	1.10	1.10	0.87	0.88	1.44	1.43	0.75	0.40
	β_{23}	0.97	0.97	0.87	0.87	1.30	1.28	1.11	0.72
	κ_{12}					-1.36	-1.36	0.00	-1.38
	κ_{13}					-0.75	-0.75	0.00	-0.79
	κ_{21}					2.62	2.62	0.94	1.29
	κ_{23}					1.05	1.05	0.50	0.11
	κ_{31}					1.50	1.53	0.88	1.62
	κ_{32}					0.93	0.93	1.60	3.00
	MAD, %	1.57	1.54	1.52	1.55	0.81	0.76	0.82	0.83
	AAD, %	0.42	0.41	0.32	0.32	0.19	0.19	0.18	0.17
	Δ AIC	0	1	93	96	332	334	320	348

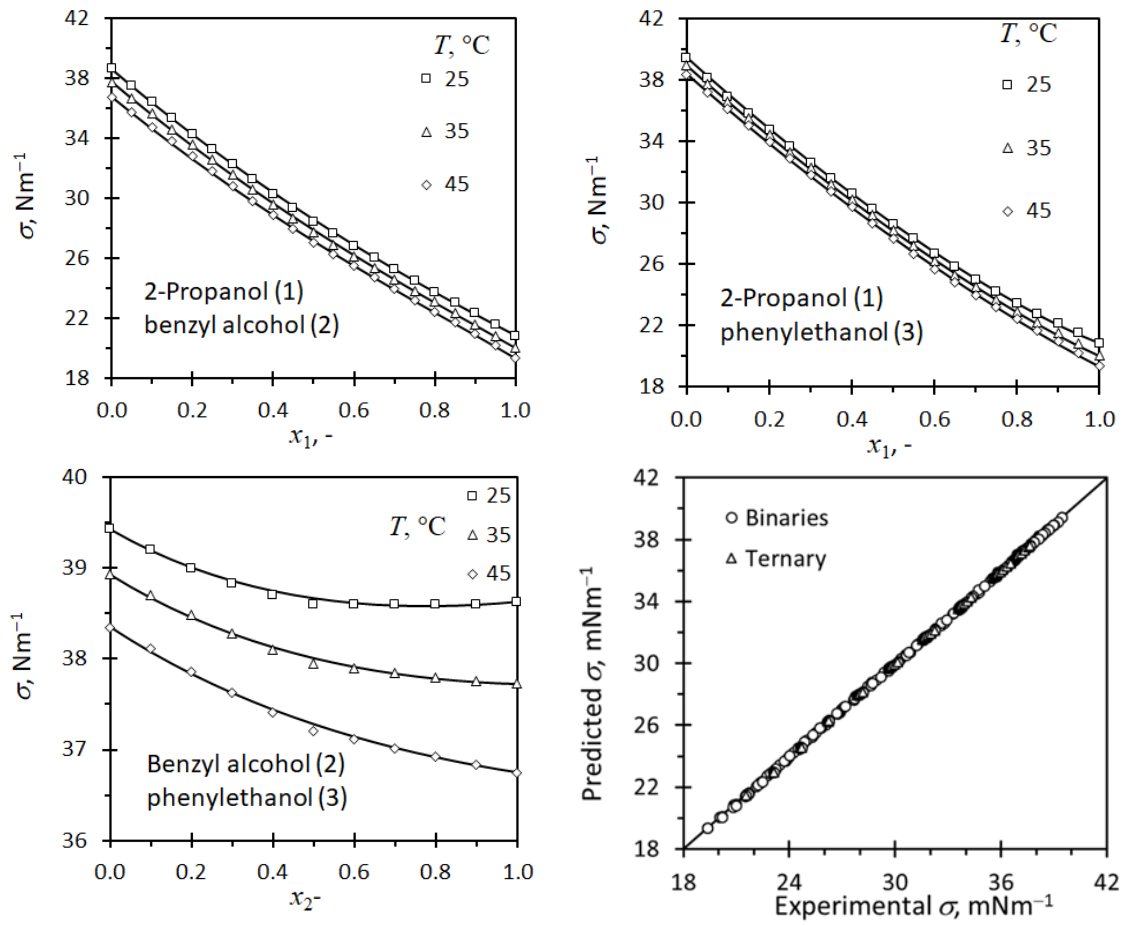


Figure 2.7 2-Propanol (1) – benzyl alcohol (2) – 2-phenylethanol (3)