

Modeling the Surface Tension and the Interface of Ten Selected Liquid Mixtures: Correlation, Prediction, and the Influence of Using Partial Molar Volume

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ABSTRACT: *This work investigates the modeling of the surface tension and the interface of liquid mixtures. Nine binary liquid mixtures of (DMSO+alcohols), (2-Propanol+2,2,4-trimethylpentane), (Tetrahydrofuran+2-Propanol), (Tetrahydrofuran+2,2,4-trimethylpentane), and (ethano+glycerol) are considered. Additionally, one ternary liquid mixture of (Tetrahydrofuran+2-Propanol+2,2,4-trimethylpentane) is considered. Firstly, two correlations were used to model the surface tension. One of these correlations has one adjustable parameter, and the other has five fitting parameters. Then the model based on the equality of the chemical potentials at the interface and the liquid phase was used. The surface tension and interfacial composition are computed by using this model. This approach was used in two ways, including activity-based and fugacity-based models. The UNIFAC activity model and PSRK EOS equation of state were applied to compute activity and fugacity, respectively. Moreover, the effect of the partial molar volume on predictions was investigated. The results of the applied models show that the correlation with five adjustable parameters and the fugacity-based model have the best results. Also, the increase in the non-ideality of these systems results in a better performance of the fugacity-based model, therefore the application of the partial molar volume is necessary.*

KEYWORDS: *Surface tension; Liquid mixtures; Activity; Fugacity; Correlation.*

INTRODUCTION

Surface tension is known as a fundamental property that gives a thermodynamic description of the fluid-fluid interfaces. In recent years, the surface tension has drawn much attention because it has some applications in industrial processes, such as designing extraction processes, separation processes, and biological

membranes. Moreover, the composition of the surface layer is different from the bulk liquid phase. In fact, the adsorption of the component with a lower surface tension value results in a reduction of surface tension. The surface tension of the mixture depends not only on the surface layer but also on the bulk liquid phase.

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Therefore, the surface tension of a mixture should be related to the properties of the bulk liquid [1,2].

Different approaches have been applied to computing or measuring the surface tension and the composition of the surface layer. Several types of research have been dedicated to experimental measurements of the interfacial properties [3–7]. A group of modeling researchers have analysed the correlations. Many of these correlations are purely empirical, so there is the temptation to use them in all cases and forget the physical basis of the problem. A robust theoretical background usually results in a stable correlation. Therefore, using a correlation within a theoretical relation provides a powerful method for developing a reliable model. However, in many cases, no experimental data exist in a wide range of temperature. For this reason, some computational methods are required to predict data in such cases. To achieve this aim, thermodynamic models have been used: for example, the gradient theory [8–16] and activity coefficient [17–19]. The equality of chemical potentials of the components in the surface layer and bulk liquid phase is one of these approaches. These methods allow a researcher to calculate the surface tension and composition of liquid mixtures. This kind of model uses activity models such as UNIFAC to predict or reproduce the properties across the surface layer. Since properties of the surface layer depend on the volumetric properties, it would be advisable, the application of models with volumetric properties [1], including density or molar volume.

Based on the volumetric properties, *Khosharay et al.* [11,20–22] used the fugacity and equations of state instead of the activity model to compute the surface tension and composition of binary and ternary liquid mixtures. *Khosharay et al.* [11,20–22] used this model, mainly for the refrigerant family, (DMSO+methanol, ethanol, and propanol), and (water+ methanol, ethanol, propanol, and MEG). The model applied in [11,22] was predictive for refrigerant family and (DMSO+methanol, ethanol, and propanol. For (water+ methanol, ethanol, propanol, and MEG) [21], this model was a simple correlation. The performance of this model has not been yet compared with correlations and activity-based models for different mixtures. Additionally, in two of the previous investigations [11,20], the partial molar surface areas of components in the liquid mixture were considered the same as the molar surface areas of pure fluids.

This is not an appropriate assumption, especially for non-ideal liquid mixtures. Several disadvantages of this hypothesis were addressed by *Khosharay* [21]. It is known that the partial molar surface area is a function of partial molar volume [17]. By using an equation of state, the partial molar volumes can be calculated, so that partial molar surface areas of species will be available. This is the main advantage of using the equation of state and volumetric properties. In spite of these reasons, it is not clear how much partial molar volume can affect the accuracy of calculations for different kinds of mixtures. Therefore, when an equation of state is used, the influence of applying partial molar volume should be investigated.

From what stated above, nine binary liquid mixtures and one ternary liquid mixture were selected to investigate the influence of the partial molar volume on the model suggested by *Khosharay et al.* [11,20–22]. To achieve this aim, the PSRK EOS [23] was combined with the equality of the chemical potential of components at the surface layer and bulk liquid. Then the surface tension and composition were simultaneously predicted. The partial molar volume was computed by using PSRK EOS. Furthermore, the UNIFAC activity model [24] was utilized for simultaneous prediction of surface tension and composition. The results of these two models have been compared, and then was examined the influence of using the partial molar volume and fugacity on the predictions of the model. Furthermore, to understand the advantages of the present models, the results of these two models were compared with two correlations.

THE APPLIED MODELS

Correlation method of Di Nicola-Pierantozzi

In recent years, different approaches have been presented by *Di Nicola et al.* [26–34] to predict several physical properties. The aim of these models was to calculate the surface tension of pure compounds. All of these methods are based on the corresponding state principle. In 1873, *Van der Waals* [35] introduced this theory with a solid physical approach. He showed that properties at equilibrium depend on specific intermolecular forces. These properties are universally linked to the critical properties. The corresponding state's model works well for fluids with simple molecules, but it was not suitable for fluids in which molecular orientation is not significant,

for example, the molecules that are not strongly polar or hydrogen-bonded. In order to solve this problem, *Di Nicola* and *Pierantozzi* made a new equation (correlation) for refrigerant mixtures and applied it to 13 systems of refrigerants [36]. Following the same approach used for pure fluids, they proposed the following equation for binary refrigerant mixtures.

$$\sigma = 6.098 \times 10^{-8} \times \omega_m^{0.203} (3.285 \times 10^6 + P_{cm}^{3.4429}) T_{cm} (1 - T_r)^{1.258} \quad (1)$$

Where T_{cm} , P_{cm} , and ω_m are the critical properties of a liquid mixture defined by mole fraction averages of the pure-component properties, including T_{ci} , P_{ci} , and ω_i . There are several different techniques to establish the definition of critical properties. The most commonly used empirical methods are: (1) *Li* method [37] for T_{cm} ; (2) *Kreglewski* and *Kay* [38] method for P_{cm} and ω_m ; (3) *Chueh* and *Prausnitz* method [39] for V_{cm} . In this work, following the original method of *Di Nicola* and *Pierantozzi*, we computed the averages (T_{ci} , P_{ci} , and ω_i) by using mole fractions and the pure-component properties (T_c , P_c , and ω). In this way, all critical properties of mixtures were calculated using the following formula.

$$\xi_m = \sum_{i=1}^N \xi_i x_i \quad (2)$$

Where ξ is the general property, x is the mole fraction and N is the number of components.

Applying the general expression of Eq. (1), the following equation can be written for the surface tension of a liquid mixture.

$$\sigma = B_0 \omega_m^{B_1} (B_2 + P_{cm}^{B_3}) T_{cm} (1 - T_r)^{B_4} \quad (3)$$

This model has five adjustable coefficients for each mixture, including B_0 , B_1 , B_2 , B_3 , and B_4 .

The correlation with one adjustable parameter

When only rough approximations of surface tension are required for a mixture, one might use the following general form.

$$\sigma_m^r = \sum_{i=1}^N (x_i \sigma_i)^r \quad (4)$$

Where r is an adjustable parameter and x_i is the mole

the fraction of each component in the liquid phase and σ_i is the surface tension of each pure fluid.

Hadden [40] suggested $r = 1$ for most hydrocarbon mixtures, which would predict linear behavior in surface tension as a function of composition. To our knowledge, *Di Nicola* and *Pierantozzi* [36] used this correlation for binary refrigerant mixtures. In this study, this correlation has been extended to a multi-component liquid mixture.

The equality of chemical potentials

In this study, the equality of chemical potentials in the bulk liquid phase and the surface layer was considered to describe the interface of the liquid mixtures. All the details are given in [11,20].

By considering the phase equilibrium between the liquid phase and the surface layer, the required equations of a thermodynamic model can be obtained. The basic assumption of this model is that the surface layer is a separate phase in which both composition and density are uniform.

$$\mu_{i,B} = \mu_{i,B}^0 + RT \ln \left(\frac{a'_{i,B}}{a_i^0} \right) \quad (5)$$

$$\mu_{i,S} = \mu_{i,S}^0 + RT \ln \left(\frac{a'_{i,S}}{a_i^0} \right) - \sigma \bar{A}_i \quad (6)$$

or

$$\mu_{i,B} = \mu_{i,B}^0 + RT \ln \left(\frac{f_{i,B}}{f_i^0} \right) \quad (7)$$

$$\mu_{i,S} = \mu_{i,S}^0 + RT \ln \left(\frac{f_{i,S}}{f_i^0} \right) - \sigma \bar{A}_i \quad (8)$$

Eqs. (5) and (6) has been expressed in terms of an activity model and Eqs. (7) and (8) has been written based on the fugacity. In the above equations, μ shows the chemical potential, σ_i shows the surface tension of each pure fluid, σ shows the surface tension of a liquid mixture, a' is the activity, f indicates the fugacity, and \bar{A}_i belongs to a partial molar surface area of each type in a liquid mixture. Subscript S and B relate to the interface and the liquid bulk phase, respectively.

For pure fluids, the following equation exists [11]:

$$\mu_{i,S}^0 - \mu_{i,B}^0 = \sigma A_i \quad (9)$$

Based on these assumptions, when the chemical potentials of components in the bulk liquid phase and interface are equal, Eqs. (5) and (6) or Eqs. (7) and (8) can be expressed as follows:

$$\sigma \bar{A}_i = \sigma_i A_i + RT \ln \left(\frac{a'_{i,S}}{a'_{i,B}} \right) \quad (10)$$

$$\sigma \bar{A}_i = \sigma_i A_i + RT \ln \left(\frac{f_{i,S}}{f_{i,B}} \right) \quad (11)$$

In spite of the previous studies [11,20], when the fugacity-based model is used, the partial molar areas of components are not set equal to the molar surface areas of the pure fluids. In the present study, the effective surface has been expressed by the cross-sectional area:

$$A_i = V_i^3 N_0^{\frac{2}{3}} \quad (12)$$

$$\bar{A}_i = \bar{V}_i^3 N_0^{\frac{2}{3}} \quad (13)$$

In Eqs. (12) and (13), N_0 , V_i and \bar{V}_i belong to the Avogadro number, the molar volume of pure fluid, and the partial molar volume of each component in a liquid mixture, respectively. In this work, the partial molar volume of each component has been computed by using PSRK EOS [23].

The sum of interfacial mole fractions is one:

$$\sum_i x_{i,S} = 1 \quad (14)$$

The unknowns of the activity-based model are surface tension (σ) and interfacial compositions ($x_{i,S}$). Eqs.(10) and (14) are the main equations of this model. Eqs. (10) and (14) must be solved simultaneously to compute the surface tension and the interfacial compositions. To our knowledge, when the activity-based model is used, the partial molar area of the components is equal to the molar surface areas of the pure fluid. In this study, the UNIFAC activity model [24] was chosen for the modeling purpose.

In the case of using a fugacity-based model, one additional equation is needed because fugacity is a function of the molar volume in addition to

the temperature, surface tension and interfacial composition. Therefore, the simultaneous calculation of surface tension and composition of the interface is impossible by using Eqs.(11) and (14) alone. In this study, the *Laaksonen* and *Kulmala* (L-K) equation [41] has been considered as an additional equation.

$$\sigma = \sigma_1 \phi_1^S + \sigma_2 \phi_2^S \quad (15)$$

In Eq. (15), ϕ_1^S and ϕ_2^S are the surface volume fraction of component 1 and 2, respectively.

$$\phi_1^S = \frac{V_1 x_1^S}{V_1 x_1^S + V_2 x_2^S} = 1 - \phi_2^S \quad (16)$$

In order to extend this model to ternary mixtures, the following form of L-K model is used:

$$\sigma = \sigma_1 \phi_1^S + \sigma_2 \phi_2^S + \sigma_3 \phi_3^S \quad (17)$$

$$\phi_1^S = \frac{V_1 x_1^S}{V_1 x_1^S + V_2 x_2^S + V_3 x_3^S} \quad (18)$$

$$\phi_2^S = \frac{V_2 x_2^S}{V_1 x_1^S + V_2 x_2^S + V_3 x_3^S} \quad (19)$$

$$\phi_3^S = \frac{V_3 x_3^S}{V_1 x_1^S + V_2 x_2^S + V_3 x_3^S} = 1 - \phi_1^S - \phi_2^S \quad (20)$$

When the fugacity-based model is applied for binary mixtures, surface tension (σ), compositions ($x_{i,S}$), and density (ρ^S) are unknown of the model. The fugacity-based model applies Eq. (11), Eq. (14), and Eq. (15) for the simultaneous calculation and prediction of the surface tension, composition, and density. These three equations are the main equations of the model. If a three-component mixture exists, Eq. (11), Eq. (14), and Eq. (17) should be simultaneously solved. Since this method uses equation state and the partial molar volumes can be computed, the partial molar area of a component is not set equal to the molar surface areas of a pure component.

The PSRK equation of state

To calculate the fugacities, an equation of state must be selected. The original SRK EOS [42] is expressed as follows:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v-b)} \quad (21)$$

The energy parameter, a , is defined as follows:

$$a_i(T) = 0.42747 \left(\frac{R^2 T_{ci}^2}{P_{ci}} \right) f'(T, T_{ci}, \omega_i) \quad (22)$$

$$f'(T, T_{ci}, \omega_i) = \quad (23)$$

$$\left[1 + (0.480 + 1.575\omega_i - 0.176\omega_i^2) \left(1 - \sqrt{\frac{T}{T_{ci}}} \right) \right]^2$$

For ethanol, 1-propanol, 2-propanol, and 1-butanol, this expression has been used [23].

$$f'(T, T_{ci}, \omega_i) = \quad (24)$$

$$\begin{cases} \left(1 + C_1(1 - \sqrt{T_{ri}}) + C_2(1 - \sqrt{T_{ri}})^2 + C_3(1 - \sqrt{T_{ri}})^3 \right)^2 & T_{ri} < 1 \\ \left(1 + C_1(1 - \sqrt{T_{ri}}) \right)^2 & T_{ri} \geq 1 \end{cases}$$

The covolume parameter, b , is computed as follows:

$$b_i = 0.08664 \left(\frac{RT_{ci}}{P_{ci}} \right) \quad (25)$$

The PSRK model [23] is stated as follows:

$$\alpha = -\frac{1}{0.647} \left(\frac{G_0^E}{RT} + \sum_i x_i \ln \left(\frac{b}{b_i} \right) \right) + \sum_i x_i \bar{\alpha}_i \quad (26)$$

$$\alpha = \frac{a}{bRT} \quad (27)$$

$$\bar{\alpha}_i = \frac{a_i}{b_i RT} \quad (28)$$

In Eqs. (20)-(23), G_0^E shows the excess Gibbs energy computed by using the UNIFAC model [24]. R belongs to the universal coefficient of gases. T is the temperature, P is the pressure, x_i is the mole fraction of each component. Subscript c shows critical. α is a parameter of the PSRK model.

RESULTS AND DISCUSSION

As mentioned in the introduction, one of the main aims of this study is to find the influence of the partial molar volume to predict surface tension, density, and composition. In order to prove our methodology valid, results were compared with two correlations. For all calculations of this study, The surface tension and

molar volumes of the pure fluids were taken from [25,43-45]. The first correlation is the one used by *Di Nicola and Pierantozzi* [36], based on the corresponding state principle. This correlation has five adjustable parameters. The second correlation is an empirical one with only one adjustable parameter [36]. This equation uses the surface tension of each pure fluid and the composition of the liquid phase. The ranges of surface tension and temperature of the applied mixtures have been presented in Table 1. The references to the experimental data [25,43-46] are shown in Table 1.

The parameters of both models, by minimizing the following objective function according to the chi-square minimization by using the quasi-Newton techniques [47].

$$AAD\% = \frac{1}{N_p} \sum_i \left| \frac{\sigma_i^{calc} - \sigma_i^{exp}}{\sigma_i^{exp}} \right| \times 100 \quad (29)$$

In Eq. (29), N_p shows the number of experimental points. Superscripts calc and exp indicate calculation and experimental, respectively.

The results of these two models are listed in Tables 2 and 3. Two types of systems were analysed in order to prove the overall performance of each correlative model. The first type belongs to the systems whose AAD% values are less than 5. These systems have a low AAD%. The second group is dedicated to the systems whose AAD% values are higher than 5. In this study, these systems were considered as the ones with high values of AAD%. According to the reported values of AAD% given in Table 3, it is found that the Di Nicola-Pierantozzi model has low deviations (AAD% < 5) for all systems. The one-parameter model has high deviations for three systems, namely DMSO+Propanol, DMSO+Hexanol, Ethanol+Glycerol.

After these two correlations, a model based on the equality of the chemical potential of components at the surface layer and the bulk liquid was used. The UNIFAC activity model [24] was chosen for calculations of activity-based approach. The second one was the fugacity-based model. The PSRK EOS [23] was used to compute the fugacities and molar volumes of the phases. The required coefficients of the PSRK EOS and critical properties of the fluid are listed in Table 4.

The results of correlations and the model based on the equality of chemical potentials are listed in Table 5.

Table 1: The systems studied and their ranges of surface tension and temperature.

System	Points	σ Range (mN/m)	T Range (K)	Ref.
2-propanol+2,2,4-trimethyl- Pentane	63	17.35-21.75	288.15-308.15	[43]
Dms0+methanol	55	20.548-39.628	288.15-328.15	[25,44]
Dms0+ethanol	105	19.83-42.51	293.15-313.15	[25,44]
Dms0+propanol	55	23.121-38.756	288.15-328.15	[25,44,45]
Dms0+butanol	105	20.48-42.93	293.15-313.15	[45]
Dms0+hexanol	139	20.278-42.48	288.15-328.15	[45]
Ethanol+glycerol	20	22.2-63.1	294.00-294.00	[46]
Tetrahydrofuran + 2,2,4-trimethyl- Pentane	63	17.35-28.37	288.15-308.15	[43]
Tetrahydrofuran + 2-propanol	63	20.17-28.37	288.15-308.15	[43]
Tetrahydrofuran +2-Propanol + 2,2,4-Trimethylpentane	55	18.55-28.85	298.15-298.15	[43]

Table 2: Summary of the results of calculations based on the corresponding state's model proposed by Di Nicola and Pierantozzi (Eq.(3)), including the adjustable parameters of the model and the percents of the average absolute deviation of surface tension (AAD γ %).

System	B ₀	B ₁	B ₂	B ₃	B ₄	AAD γ %
DMSO+Methanol	1.61×10 ⁻¹⁰	0.19	9.21×10 ⁸	7.99	1.32	0.53
DMSO+Ethanol	2.95×10 ⁻¹⁴	0.50	1.75×10 ¹⁴	15.32	1.32	0.27
DMSO+Propanol	10.45	-0.80	-4.80×10 ⁻³	-2.79	0.84	3.15
DMSO+Butanol	9.06	-1.44	-2.00×10 ⁻⁴	-3.68	0.86	1.18
DMSO+Hexanol	0.40	-2.07	-4.4×10 ⁻³	-2.31	0.78	1.69
Ethanol+Glycerol	4.00×10 ⁻³	-11.41	2.10×10 ⁻⁴	-3.17	-3.66	2.35
2-Propanol+2,2,4-Trimethylpentane	5.18×10 ⁻⁸	0.17	1.89×10 ⁶	8.16	1.09	0.35
Tetrahydrofuran+2-Propanol	106.06	-4.19×10 ⁻²	-1.0003	7.32×10 ⁻⁴	0.91	0.40
Tetrahydrofuran+2,2,4Trimethylpentane	1.78×10 ⁻³	-4.06	-0.052	-0.98	1.02	1.22
Tetrahydrofuran +2-Propanol + 2,2,4-Trimethylpentane	106.06	-4.19×10 ⁻²	-1.00	7.32×10 ⁻⁴	0.91	1.11

Table 3: Summary of the results of calculations based on the correlation with one adjustable parameter (Eq.(4)), including the adjustable parameter of the model and the percents of the average absolute deviation of surface tension (AAD γ %).

System	r	AAD γ %
DMSO+Methanol	0.994	0.93
DMSO+Ethanol	1.219	2.01
DMSO+Propanol	1.355	9.22
DMSO+Butanol	1.490	4.94
DMSO+Hexanol	1.630	7.68
Ethanol+Glycerol	2.897	12.97
2-Propanol+2,2,4-Trimethylpentane	1.084	0.96
Tetrahydrofuran+2-Propanol	0.992	0.60
Tetrahydrofuran+2,2,4Trimethylpentane	1.198	2.32
Tetrahydrofuran +2-Propanol + 2,2,4-Trimethylpentane	1.075	2.54

Table 4: The critical properties and coefficients of the PSRK EOS for the pure components applied in this study [23,24].

Fluid	T _c (K)	P _c (bar)	ω	C ₁	C ₂	C ₃
Methanol	512.5	8.084	0.565	-	-	-
Ethanol	513.9	61.5	0.644	1.4401	-0.1044	-0.0179
1-Propanol	536.7	51.7	0.620	1.3600	0.1917	0.0596
2-Propanol	508.4	47.6	0.664	1.4173	0.1903	0.0076
1-Butanol	563.0	44.1	0.590	1.2356	0.6834	0.0790
1-Hexanol	611.35	35.11	0.578	-	-	-
Tetrahydrofuran	540.15	51.9	0.225	-	-	-
DMSO	729	56.5	0.280	-	-	-
2,2,4-Trimethylpentane	543.8	2.57	0.303	-	-	-
Glycerol	850	75	0.512	-	-	-

Table 5: The absolute average deviations (AADs) of the activity-based and the fugacity-based models applied in this study.

System	Activity-based model (AAD%)	Fugacity-based model (AAD%)
2-Propanol+2,2,4-Trimethylpentane	0.97	0.86
Tetrahydrofuran+2-Propanol	1.98	1.33
Tetrahydrofuran+2,2,4-Trimethylpentane	2.67	1.16
DMSO+Methanol	3.79	2.33
DMSO+Ethanol	0.59	2.07
DMSO+Propanol	1.86	3.47
DMSO+Butanol	2.58	1.42
DMSO+Hexanol	7.93	1.55
Ethanol+Glycerol	12.27	1.71
Tetrahydrofuran +2-Propanol + 2,2,4-Trimethylpentane	2.54	1.54

Firstly, (2-Propanol+2,2,4-trimethylpentane), (Tetrahydrofuran+2-Propanol) and (Tetrahydrofuran+2,2,4-trimethylpentane) were studied. The difference between the surface tension of the pure components is less than 10mN/m for these three binary mixtures. The activity-based model was used in the previous study [20]. Therefore, this study took into account only the fugacity-based model. When the model based on the equality of chemical potentials was used, the applications of both activity and fugacity are predictive for these three binary mixtures. Also, it is found that the application of partial molar volumes is not so significant.

The results of the correlations show that AAD% is low for these three mixtures. The results of correlations

(with one and five adjustable coefficients) [36] were the same for these three systems. Therefore, the number of adjustable parameters did not affect the accuracy of the correlations. The accuracy of correlations and the model based on the equality of chemical potentials (activity-based and fugacity-based) was very close. Moreover, all of these applied methods were extended to the ternary mixture of tetrahydrofuran +2-propanol + 2,2,4-trimethylpentane for the first time. Similar to the binary mixtures, the results of are applied models are close. For these four mixtures, when the model based on the equality of chemical potentials was used, no adjustable parameters were required. According to the above explanations, when the information of the interface

is essential for a researcher or the experimental data do not exist for such liquid mixtures, the model based on the equality of chemical potentials should be considered. In other cases, both correlations and the model based on the equality of chemical potentials are applicable.

The second group contains the binary mixtures of (DMSO+alcohols). Although the fugacity-based model was applied to DMSO+methanol, ethanol, and 1-propanol [25], this model was used again to compare its performance with correlations and activity-based models. However, considering the previous study [25], the present model was applied to wider ranges of temperature and to DMSO+1-butanol and 1-hexanol. The difference between the surface tension of the pure DMSO and alcohol is about 20 mN/m. Firstly, the activity-based model was used for these binary mixtures. The results of calculations in Table 5 prove that using partial molar volume has no significant effect on (DMSO+methanol), (DMSO+ethanol), (DMSO+1-propanol), and (DMSO+Butanol). For (DMSO+methanol) and (DMSO+Butanol) mixtures, the fugacity-based model is a little better than the activity-based model. For (DMSO+ethanol) and (DMSO+1-propanol) systems, the activity-based model has a better performance than the fugacity-based model. The influence of applying partial molar volume and the fugacity-based model is more significant for (DMSO+hexanol) system in comparison with (DMSO+methanol), (DMSO+ethanol), (DMSO+1-propanol), and (DMSO+Butanol) mixtures.

The comparison between the correlations and predictive models carried out for (DMSO+alcohol) mixture. Figs. 1 and 2 compare the performance of correlations and predictive models. For (DMSO+methanol) and (DMSO+ethanol) mixtures, the performance of the correlations and predictive models are relatively close. Figs. 1 and 2 show that the modeling results and experimental data have a good agreement. The number of adjustable parameters has no significant influence on the accuracy of the model. Therefore, for these two mixtures, the application of a correlation or a predictive model depends on how much the information of the surface layer is important for a researcher. For (DMSO+1-propanol), (DMSO+Butanol), and (DMSO+hexanol) systems, the AADs% of the correlation with one adjustable coefficient is higher than the ones for (DMSO+methanol) and (DMSO+ethanol) mixtures.

Figs. 3-5 describe the results of all applied models for (DMSO+1-propanol), (DMSO+Butanol), and (DMSO+hexanol) mixtures. First of all, the AAD% of the correlation with one adjustable parameter (Eq.(4)) is 9.22 for (DMSO+1-propanol) mixture. Fig. 3 shows that the results of this correlation do not have a good agreement with experimental data, especially at higher concentrations of 1-propanol. Two ways were utilized for reducing AAD% of the surface tension. The AAD% of *Di Nicola-Pierantozzi* [36] correlation was 3.15. For (DMSO+1-propanol) system, the AADs% of the activity-based and fugacity-based models were 1.86 and 3.47, respectively, so the activity-based model has the best results. The better performance of these models is clear in Fig. 3.

The AADs% of the correlation with one adjustable parameter (Eq.(4)) are 4.64 and 7.68 for DMSO+butanol) and (DMSO+hexanol) mixtures, respectively. Fig.4 shows that the results of one-parameter correlation do not have a good agreement with experimental data. Similar to the (DMSO+1-propanol) mixture, firstly, the correlation of *Di Nicola-Pierantozzi* [36] and predictive models were used to decrease AAD% of the surface tension. AAD% of *Di Nicola-Pierantozzi* [36] correlation was 1.18 and 1.69 for (DMSO+butanol) and (DMSO+hexanol), respectively. The AADs% of the activity-based model are 2.58 and 7.93 while the AADs% of the fugacity-based model are 1.42 and 2.55 for (DMSO+butanol) and (DMSO+hexanol), respectively. As shown in Figs. 4 and 5 and Table 5, the fugacity-based model has very good predictions for these two systems. The activity-based model does not have good predictions for the (DMSO+hexanol) system. Also, the accuracy of the fugacity-based model is not significantly different from the correlation of *Di Nicola-Pierantozzi* [36]. Therefore, for these two binary mixtures, two ways are useful, including the fugacity-based model and the correlation of *Di Nicola-Pierantozzi* [36].

Moreover, the deviation of the surface tension from the ideal state was considered. At each temperature, over the whole composition range, this deviation is defined as follows:

$$\sigma^E = \sigma - \sigma_1 x_1 - \sigma_2 x_2 \quad (24)$$

Fig.6 shows the values of σ^E for the binary systems of (DMSO+alcohols) at 298.15 K. One can see that hexanol has the greatest deviations of the surface tension from

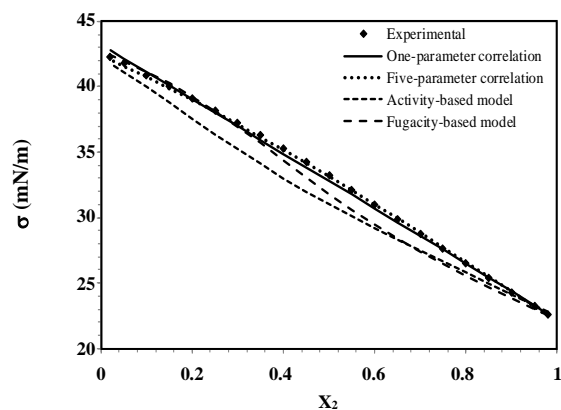


Fig. 1: The performance of four different models for the binary mixture of DMSO (1)+methanol (2) at the temperature of 298.15 K.

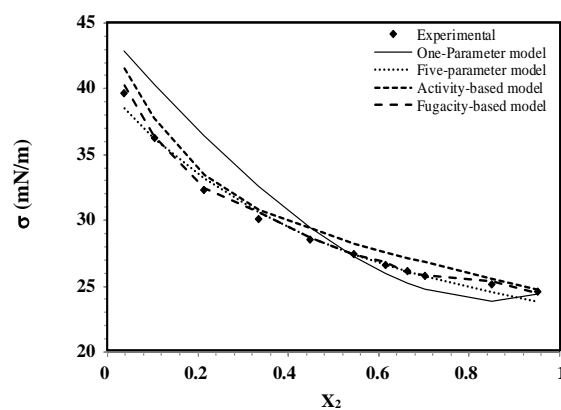


Fig. 4: The performance of four different models for the binary mixture of DMSO (1)+butanol (2) at the temperature of 288.15 K.

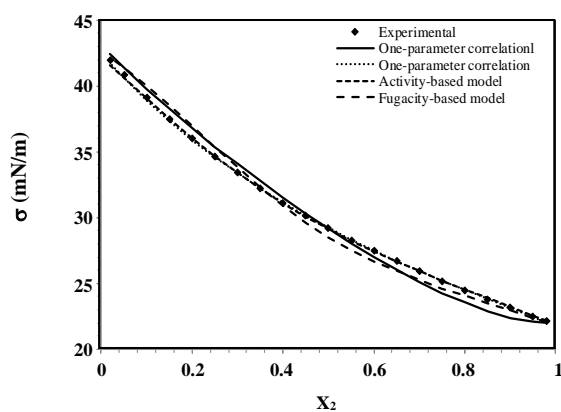


Fig. 2: The performance of four different models for the binary mixture of DMSO (1)+ethanol (2) at the temperature of 298.15 K.

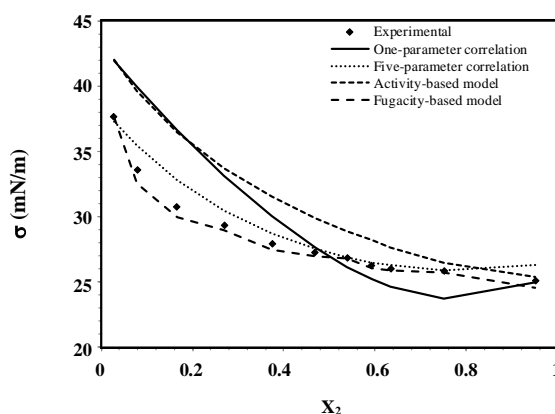


Fig. 5: The performance of four different models for the binary mixture of DMSO (1)+hexanol (2) at the temperature of 288.15 K.

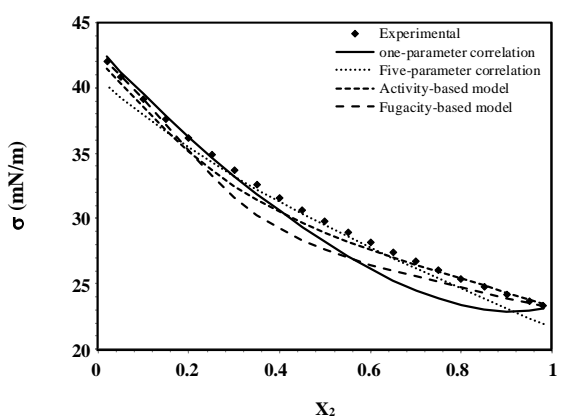


Fig. 3: The performance of four different models for the binary mixture of DMSO (1)+propanol (2) at the temperature of 298.15 K.

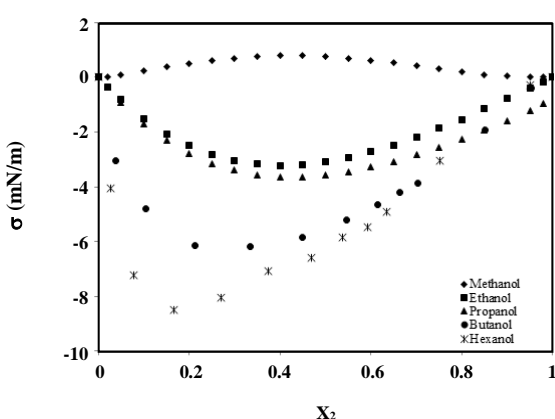


Fig. 6: Plot of surface tension deviation from the ideal state (σ^E) in terms of mole fraction of ethanol (x_2) for binary mixtures of DMSO (1)/ethanol (2) at the temperature of 298.15 K.

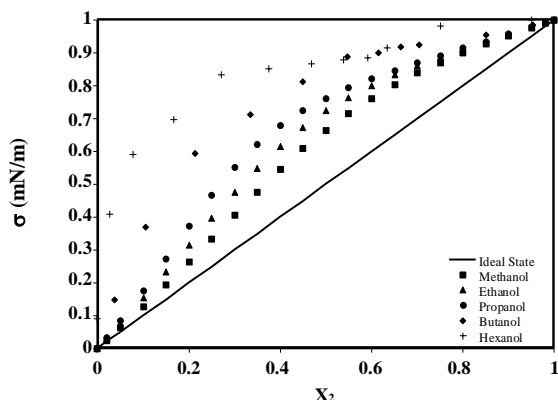


Fig. 7: Plot of the x_{2s} in terms of x_2 for the binary system of (DMSO (1)+alcohol (2)) at the temperature of 298.15 K.

the ideal state. This deviation decreases in the following order: butanol, propanol, ethanol, and methanol. As indicated in Fig.6, the absolute values of σ^E increase with increasing the mole fraction of alcohol. Then go through a minimum/maximum and decrease. Moreover, the slope of the σ^E diagram before the minimum/maximum is higher than the one after the minimum/maximum. These results show that the change of surface tension at a low concentration of alcohol is higher than these changes at high concentrations.

The excellent predictions of the fugacity-based model allow us to compute reliable interfacial mole fractions. Fig. 7 indicates that the interfacial mole fractions of alcohols (x_{2s}). Alcohols have lower surface tensions and their interfacial mole fractions are greater than the ones in the liquid phase (x_2). Therefore, the results of the model show that alcohol has expelled from the bulk to the surface layer. This results in the non-linear trend of the decrease in surface tension. Moreover, Fig. 8 shows the values of $(x_{2s}-x_2)$ for (DMSO+alcohols) over the whole composition and temperature of 298.15 K. The values of $(x_{2s}-x_2)$ increase when the mole fraction of alcohol increases. Then they reach a maximum and decrease. This trend is qualitatively the same as the one for σ^E . Consequently, the increase or decrease in the absolute values of σ^E can be attributed to the same changes $(x_{2s}-x_2)$. Moreover, Fig. 8 shows that hexanol has the greatest values of $(x_{2s}-x_2)$. The values of $(x_{2s}-x_2)$ reduce in the following order: butanol, propanol, ethanol, and methanol. Hence, it can be concluded that the greater σ^E is due to the greater $(x_{2s}-x_2)$.

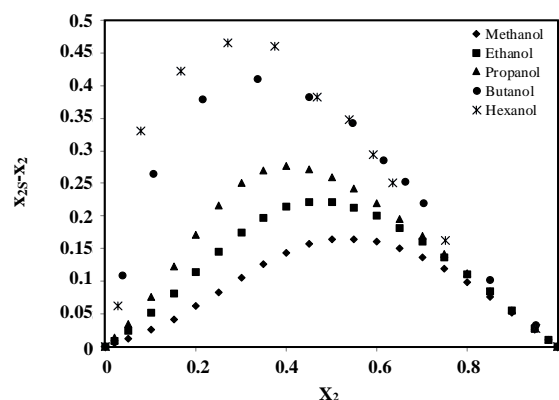


Fig. 8: Plot of the $(x_{2s}-x_2)$ in terms of x_2 for the binary system of (DMSO (1)+alcohol (2)) at the temperature of 298.15 K.

Based on these explanations, for DMSO+alcohols, it is found that the application of the correlation, the activity-based, or the fugacity-based model depends on the non-ideality of the systems. When the non-ideality of the system increases (the values of σ^E or $x_{2s}-x_2$ increases), the correlation needs more adjustable parameters. Moreover, the increase in the non-ideality of these systems leads to better performance of the fugacity-based model and the application of partial molar volume is necessary.

The other binary mixture is (ethanol+glycerol). The experimental data are from [46]. The difference between the surface tension of the pure glycerol and ethanol is about 40 mN/m. The activity-based and fugacity-based models were applied to this binary mixture. To our knowledge, such models have not been used for the binary mixture of (ethanol+glycerol). Moreover, only one investigation [40] was dedicated to the surface tension of (ethanol+glycerol) system at the temperature of 294 K. Except (ethanol+glycerol) system, no experimental data exist for (alcohol+glycerol) systems, so investigation about the application of correlative and predictive methods is useful.

The results of calculations in Table 5 prove that using partial molar volume has a significant influence on the performance of the model. Fig. 9 shows that the results of the correlations and activity based model do not have a good agreement with experimental data, while the results fugacity-based model has a very good agreement with experimental data. AAD% of activity-based and fugacity-based models 12.27 and 1.71. Therefore, the activity-based model is not a predictive model

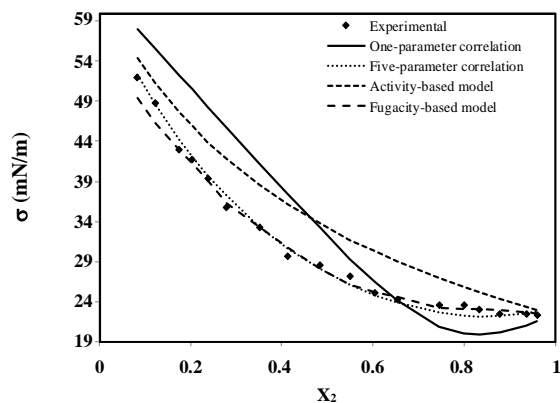


Fig. 9: The performance of four different models for the binary mixture of glycerol (1)+ethanol (2) at the temperature of 294K.

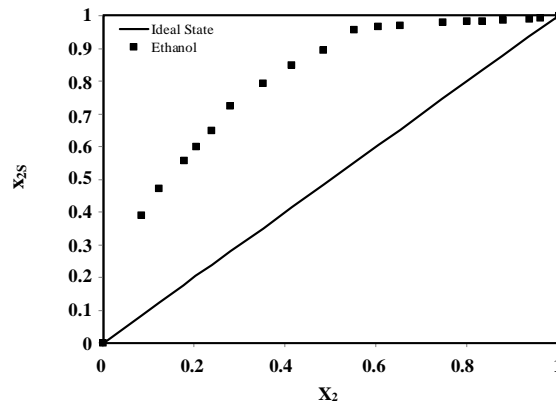


Fig. 11: Plot of the x_{2s} in terms of x_2 for the binary system of (glycerol (1)+ethanol (2)) at the temperature of 294 K.

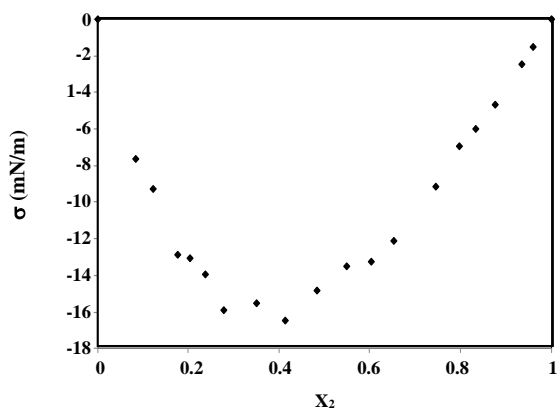


Fig. 10: Plot of surface tension deviation from the ideal state (σ^E) in terms of mole fraction of ethanol (x_2) for a binary mixture of glycerol (1)/ethanol (2) at the temperature of 294 K.

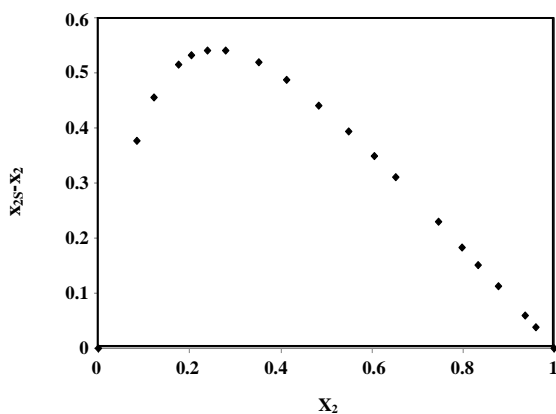


Fig. 12: Plot of the $(x_{2s}-x_2)$ in terms of x_2 for the binary system of (glycerol (1)+ethanol (2)) at the temperature of 294 K.

for (ethanol+glycerol) system. These explanations prove that using partial molar volumes is necessary for (ethanol+glycerol) system.

Fig. 9 compares the results of correlative and predictive approaches. For (glycerol+ethanol) mixture, the performances of the correlative and predictive models are different. The number of adjustable parameters has a significant effect on the accuracy of the model. The AAD% of the correlative model with one adjustable parameter (Eq.(4)) is 12.97 for (glycerol+ethanol) mixture. This deviation is very high. Similar to (DMSO+alcohols), two ways can be used for decreasing the AAD% of the surface tension. The first one is the correlation between Di Nicola-Pierantozzi [36]. AAD% of this method was 2.35. Therefore, more than one adjustable parameter is required for (glycerol+ethanol). The other way is

the fugacity-based model. AAD% of this model was 1.71. This AAD% is even less than the one for correlation of Di Nicola-Pierantozzi [36] which has five adjustable parameters. According to these results, the partial molar volume is absolutely necessary for (glycerol+ethanol) mixture. Since experimental data are very limited for (glycerol+alcohols), the predictive fugacity-based model is the best choice for such mixtures.

Fig. 10 shows the values of σ^E for the binary systems of (glycerol+ethanol) at 294 K. One can notice that this mixture has the greatest deviations from the ideal state. Furthermore, Fig. 11 shows the interfacial mole fractions of ethanol (x_{2s}). Since ethanol has lower surface tension, its interfacial mole fractions are much greater than the ones in the liquid phase (x_2). Fig. 12 shows the changes of $(x_{2s}-x_2)$ as a function of x_2 .

The trends of σ^E and $(x_{2S}-x_2)$ diagrams are the same as the ones for (DMSO+alcohols). Both of these diagrams show very high deviations from the ideal state, so (glycerol+ethanol) is detected as a very non-ideal system. The high non-ideality of this system can be connected to the high differences between the surface tension of pure components (about 40 mN/m). This leads to the high absorption of ethanol at the interface. Because of this high non-ideality, the partial molar volume is required for calculations and has a significant influence on the accuracy of the model.

CONCLUSIONS

This work investigated different methods to model the surface tension and interface of different liquid mixtures. The binary liquid mixtures of (DMSO+alcohols), (2-Propanol+2,2,4-trimethylpentane), (Tetrahydrofuran+2-Propanol), (Tetrahydrofuran+2,2,4-trimethylpentane), and (ethano+glycerol) were studied. Also, one ternary liquid mixture of (Tetrahydrofuran+2-Propanol+2,2,4-trimethylpentane) was used. The first approach uses correlations, and the second one is based on the equality of chemical potential at the interface and liquid phase. The second method carried out in two different ways: containing activity-based and fugacity-based methods. Subsequently, the effect of using partial molar volume was studied. According to the results and analysis presented throughout this work, the following main conclusion can be drawn. The best results are obtained with the 5 parameters correlation and the fugacity-based model. The fugacity model with the usage of the partial molar volume achieves the best performances for mixtures with high non-ideality. Future work will involve the application of the proposed methods to data from different families for a better explanation of the connections between selected models and the chemical composition.

Nomenclature

A	Molar surface area
B_i	Adjustable parameters of Eq. (3)
a	Parameter in the energy term
a'	Activity
a''_{mn}	Parameter for interaction in a binary mixture of groups
b	Covolume parameter

AAD	Average Absolute Deviation
Calc	Calculated from model
EOS	Equation of state
Exp	Experimental
f	Fugacity
f'	Coefficient of the PSRK model
G_0^E	Excess Gibbs energy
N	Number of experimental points
N_0	Avogadro's number
q	Pure-component area parameter
Q_k	Area parameter of group k
R	Ideal gas constant
r	Pure component volume parameter
R_k	Volume parameter of group k
v	Molar volume
X_m	The mole fraction of group m in the mixture
x,y	Mole fraction
Z	Compressibility factor
z'	Lattice coordination number

Subscripts

B	Bulk
i, j	Components i and j
S	Surface

Greek letters

γ	Activity coefficient
Γ_k	The group residual activity coefficient
ρ	Mole density
θ	Area fraction
Θ_m	The area fraction of group m
μ	Chemical potential
σ	Surface tension
ν_k^i	The number of group k in the molecule i.
Φ	Segment fraction
φ	Volume fraction
Ψ_{mn}	Group interaction parameter

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Appendix A

A.1. UNIFAC activity model and fugacity coefficient

The UNIFAC model has two terms for the activity coefficient of component i (γ_i), including combinatorial term (γ_i^C) and residual term (γ_i^R).

$$\ln(\gamma_i) = \ln(\gamma_i^C) + \ln(\gamma_i^R) \quad (\text{A-1})$$

The combinatorial term is expressed as follows:

$$\ln(\gamma_i^C) = \ln\left(\frac{\Phi_i}{x_i}\right) + \frac{z'}{2} q_i \ln\left(\frac{\theta_i}{x_i}\right) + l_i - \frac{\Phi_i}{x_i} \sum_j x_j l_j \quad (\text{A-2})$$

In Eq. (A-2), the parameters are computed as follows:

$$l_i = \frac{z'}{2} (r_i - q_i) - (r_i - 1) \quad z' = 10 \quad (\text{A-3})$$

$$D\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad (\text{A-4})$$

$$\Phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad (\text{A-5})$$

In the above equations, θ_i is the area fraction, and Φ_i is the segment fraction, z' shows the lattice coordination number. Parameters r_i and q_i are computed based on the group volume (R_k) and area (Q_k) parameters.

$$r_i = \sum_k v_k^{(i)} R_k \quad (\text{A-6})$$

$$q_i = \sum_k v_k^{(i)} Q_k \quad (\text{A-7})$$

In the above equations, v_k^i shows the number of group k in the molecule i .

The residual term of the activity coefficient is computed as follows:

$$\ln(\gamma_i^R) = \sum_k v_k^{(i)} \left(\ln(\Gamma_k) - \ln(\Gamma_k^{(i)}) \right) \quad (\text{A-8})$$

In Eq. (A-8), Γ_k indicates the group residual activity coefficient. $\Gamma_k^{(i)}$ shows the residual activity coefficient of group k . The group activity coefficient is computed as follows:

$$\ln(\Gamma_k) = Q_k \left(1 - \ln\left(\sum_m \Theta_m \psi_{mk}\right) - \sum_m \frac{\Theta_m \psi_{mk}}{\sum_n \Theta_n \psi_{nm}} \right) \quad (\text{A-9})$$

Θ_m is the area fraction of group m computed as follows:

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad (\text{A-10})$$

In Eq.(A-10), X_m is the mole fraction of group m in the mixture. The group interaction parameter, ψ_{mn} , is computed as follows:

$$\psi_{mn} = \exp\left(-\frac{a_{mn}''}{T}\right) \quad (\text{A-11})$$

a_{mn}'' is a parameter for interaction in a binary mixture of groups. The values R_k , Q_k , and a_{mn}'' are taken from [24].

Also, $\frac{G_0^E}{RT}$ is computed as follows:

$$\frac{G_0^E}{RT} = \sum_i x_i \ln(\gamma_i) \quad (\text{A-12})$$

The fugacity coefficient of PSRK EOS is computed as follows:

$$f_i = P x_i \exp\left(\frac{b_i}{b} (Z-1) - \ln\left(Z - \frac{Pb}{RT}\right) - \right) \quad (\text{A-13})$$

$$\alpha_i' \ln\left(\frac{Z + \frac{Pb}{RT}}{Z}\right)$$

in which

$$\alpha_i' = -\frac{1}{0.647} \left(\ln(\gamma_i) + \ln\left(\frac{b}{b_i}\right) + \frac{b_i}{b} - 1 \right) + \frac{a_i}{b_i RT} \quad (\text{A-14})$$