INTRODUCTION

Physico-chemical features of fluid systems are essential for recognizing different thermodynamic behaviours. Diverse physico-chemical characteristics such as density, molar volume, viscosity, surface tension and refractive index should be considered for optimizing and designing fluids [1,2].

Some published articles concerning the physico-chemical quantities of fluid show that the majority of them display non-ideal behaviour or not arranged in a straight line. Accordingly, the estimations of the above quantities or their variations necessitate empirical or semi-empirical formulae able to give a consistent estimation of their specific features [3-5].

The present research suggests an extension of Belda equation [5-7] giving dependable assessment of the special physico-chemical or thermodynamic quantities (density, viscosity, molar volume, surface tension and refractive index, etc.) of dual combinations of fluids against of mole composition. The judgment of the investigational data of those quantities versus Belda model and our proposed extension has been carried out.

Correlation equations: For most cases mixing operations in applied chemistry and in industrial engineering is difficult due to the non-straight line performance. Then, accurate statistics have to be obtainable with forms able to furnishing a consistent judgment of physical and chemical properties for different behaviours of liquid mixtures. In general, the theoretical description of concepts related to properties is therefore quite complex and exact explicit expressions are absent. This is the reason why several models have been suggested, extended and/or modified over the years referred on some theories, or empirical and semi-empirical equations which are constantly unrelated to every kind of binary liquid mixtures. Moreover, investigations on the physico-chemical quantities of dual mixtures show that a large amount of them reveal non-ideal or non-linear behaviours. Consequently, the search of these quantities or their excess or variations necessitates mathematical expressions eligible of giving a valid approximation of their behaviours [1-8].

In the present work, different properties (Y) were correlated with molar composition using the Belda [5] correlation equation and our proposed extension which uses a correcting factor to the linearity. The equation has been applied at least to 26 binary liquid mixtures. The validity versus the magnitude and accuracy of the adjustable parameters is compared and discussed for each property.
A general effective proceeding was used to determine the deviations $\Delta Y$ between the experimental values ($Y$) and the magnitudes which might be gained if the binary systems have been depicted straight line performance, expressed as follows:

$$\Delta Y = Y - (x_1 Y_1 + x_2 Y_2)$$  \hspace{1cm} (1)

where $Y_1$ and $Y_2$ are the properties of the pure constituent (1) and (2) forming the binary liquid mixture at given molar fraction ($x_1$, $x_2$).

Thus, these differences are subjected to non-linear regression correlation according to the famous polynomial Redlich-Kister equation [3]:

$$\Delta Y = Y^e = x_1 \cdot (1 - x_1) \sum_{p=0}^{n} A_{n,p,T} (2x_1 - 1)^p$$  \hspace{1cm} (2)

where $x_1$ is the molar composition of pure liquid constituent (1) and $A_{n,p,T}$ the adjustable coefficient for every degree $p$ of one-term expression $(2x_1 - 1)^p$ at absolute temperature $T$ and,

$$\Delta Y = Y^b = x_1 \cdot (1 - x_1) Q_{RK,Y}(x_1)$$  \hspace{1cm} (3)

where the reduced Redlich-Kister property $Q_{RK,Y}(x_1)$ is expressed as follows [9-20]:

$$Q_{RK,Y}(x_1) = \sum_{p=0}^{n} A_{n,p,T} (2x_1 - 1)^p = A_0 + A_1 (2x_1 - 1)$$  \hspace{1cm} (4)

**Belda equation:** Generally, the proposed correlation equations are based on the deviation on the linear or ideal behaviour ($Y_{mix} = \Sigma_i Y_i$) of binary liquid mixtures expressed as follows:

$$Y(x) = Y_2 + (Y_1 - Y_2) \cdot x_1$$  \hspace{1cm} (5)

So, Belda [5] proposed an empirical correlation equation (eqn. 6) with two adjustable parameters ($m_1, m_2$) for investigated four physico-chemical properties such as (density, viscosity, molar volume and refractive index) which introduces a correcting factor $F_{B,Y}(x_1)$ (i.e. fraction containing the two parameters) as an homographic function (eqn. 7) depending on the mole composition of one pure component of binary liquid system ($x_1$).

$$Y(x) = Y_2 + (Y_1 - Y_2) \cdot x_1 \cdot \frac{1 + m_1 (1 - x_1)}{1 + m_2 (1 - x_1)}$$  \hspace{1cm} (6)

where $Y_1$ is the larger magnitudes of the pure liquid constituents constituting the binary system with molar composition ($x_1$, $x_2$) and $m_1, m_2$ are two adjustable parameters to be fitted.

$$F_{B,Y}(x_1) = \frac{1 + m_1 (1 - x_1)}{1 + m_2 (1 - x_1)}$$  \hspace{1cm} (7)

It is known that the Belda equation responds to straight line attitude when $m_1 = m_2$, i.e. while the correction operator $F_{B,Y}(x_1) = 1$. In the case, where the correcting operator is $> 1$, positive synergy of the quantity has been recorded, whereas $F_{B,Y}(x_1) < 1$ such synergy proves negative. We add that more the difference between the Belda parameters are accentuated, more the system behaviour deviates to the linearity.

It is noticed that the Belda model generally success for numerous binary mixtures. Nevertheless, for some particular situations, we observe small discrepancy [6,7]. In fact, due to the few adjustable parameters ($m_1$ and $m_2$) and the homographic expression of $F_{B,Y}(x_1)$ which doesn’t present any change of curvature (inflection point), Belda equation exhibits low performance when the curves representing the binary mixture property ($Y$) indicates some peculiarities (inflection points, abrupt change of curvature, etc.) due to the existence of some strong correlation at particular compositions [6,7]. So, we observe that some small discrepancies between experimental data points and the fitted model, especially at the boundary limit of the composition domain and when the Belda factor exhibit a vertical asymptote very near or into the interval of composition (Figs. 1 and 2).

**Fig. 1.** Variation of Belda factor for the density $F_{B,Y}(x_1)$ for isobutyric acid (1) + water (2) systems against molar fraction $x_1$ at 308.15 K (●): experimental, (—): calculated by (eqn. 6) [Ref. 6]

**Fig. 2.** Variation of Belda factor for the molar volume $F_{B,V}(x_1)$ for 1,4-dioxanne (1) + water (2) systems against molar fraction $x_1$ at 298.15 K. (●): experimental, (—): calculated by (eqn. 6) [Ref. 7]
Proposed extended Belda equation: For the precedent reasons we understand about an addition of only one new parameter \( m_3 \) on the Belda model. Then, following the precedent mathematical analysis, we propose a supplementary adjustable \( m_3 \)-parameter associated to the mole fraction \( x_2 \) square and added on the numerator of the Belda factor which can be expressed as follows:

\[
Y(x) = Y_1 + (Y_1 - Y_2)x_2 + \frac{1 + m_1(1-x_1) + m_1(1-x_1)^2}{1 + m_2(1-x_1)}
\]

where \( Y_1 \) is the larger of the magnitudes of the pure liquid constituents constituting the binary system with molar composition \( (x_1, x_2) \) and \( m_1, m_2 \) and \( m_3 \) are three adjustable parameters to be fitted.

RESULTS AND DISCUSSION

To examine the suitability of the proposed correlation equation, 26 published systems in literature have been utilized [5,21-27] to investigate the density, viscosity and molar volume (Table-1) and 33 systems for refractive index (Table-2) of diverse dual liquids systems at 1 atmosphere with dissimilar temperature values. The results of these samples magnitudes have been compared with those achieved by the suggested formula, whereas Belda mathematical form arranging as comparing factor for the standard deviation \( \sigma \) assigned as:

\[
\sigma = \sqrt{\frac{\sum_{i=1}^{N} (Y_{i,\exp} - Y_{i,\text{cal}})^2}{N-K}}
\]

where \( N \) is the amount of outcome points of the sample and \( k \) is the amount of free adjustable factors of the proper equations 6 and 8 (\( N = k + 1 \)). The most selective factor \( m_3 \)-values (eqn. 8) and the corresponding standard deviation \( \sigma \) are given in Tables 3-6 for each physico-chemical property, separately. We have treated the same systems chosen by Belda to estimate the goodness of the suggested extension. The results of this study have been compared with those obtained with the Belda correlation model [4-9]. Figs. 3-6 show the variation of the obtained standard deviations values.

Tables 3-6 report the amounts of the optimal \( m_3 \)-parameters calculated through non-linear regression of the eqn. 8 and the corresponding standard deviations \( \sigma \), the mean standard deviation \( \bar{\sigma} \) and limiting standard deviations \( \sigma_{\text{max}} \) and \( \sigma_{\text{max}} \) of each set of the studied properties mentioned in Tables 1 and 2.

The obtained statistical data are also illustrated in Figs. 3-6. It is observed that globally the standard deviations (\( \sigma \))-values of the extended model (eqn. 8) are less than those of the Belda model (eqn. 6) especially for high values of standard deviations related to Belda model. Nevertheless, it is noticed that for some rare cases for low standard deviation values, Belda

**TABLE-1**

<table>
<thead>
<tr>
<th>System</th>
<th>T (K)</th>
<th>Binary mixture</th>
<th>Component (1)</th>
<th>Component (2)</th>
<th>N</th>
<th>Ref.</th>
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<td>Ethanol</td>
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<td>[21]</td>
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Fig. 3. Comparison of standard deviations $\sigma$ for density (Table-3) calculated by eqn. (9), related to ($\bullet$): Belda model (eqn. 6) and that (○): calculated by proposed equation (eqn. 8)

Fig. 4. Comparison of standard deviations $\sigma$ for viscosity (Table-4) calculated by eqn. (9), related to ($\bullet$): Belda model (eqn. 6) and that (○): calculated by proposed equation (eqn. 8)
model excels. This can be explained in the case of monotonous variation of the studied properties against molar composition, the two parameter model is optimal, while the statistical analysis of a model with more than two adjustable parameters can give absurd parameters values or doesn’t well converge in the iterations calculation by the used software. So, when there are no special phenomena occurring in the binary system, we prefer the Belda model than our extended model. Nevertheless, when there are strong curvatures, singular points or change of curvature, our extended models provided better results. Figs. 7-10 show how the excellent agreement between experimental data points and the calculated values of physico-chemical properties in the whole range of molar compositions of the some studied binary liquid mixtures.

Physical meaning of Belda parameters: Comparing the Redlich-Kister expression (eqns. 2-4) and the Belda model (eqn. 6), we can deduce the following relationship:
In relation with previous works [9-20] we have demonstrated the correlation among the reduced Redlich-Kister function $Q_{RK,Y}(x_i)$ and the apparent molar thermodynamic quantities ($Y_i, \phi$) for one component ($i$) as follows:

$$Q_{RK,Y}(x_i) = \frac{Y_1 - Y_2}{1+m_2(1-x_i)} [(m_1 - m_2) + m_3(1-x_i)]$$  \hspace{1cm} (10)

We can write then:

$$Q_{RK,Y}(x_i) = \frac{Y^f - Y^c}{x_i(l-x_i)} = \frac{Y^f_1 - Y^c_1}{1-x_i} = \frac{Y^f_2 - Y^c_2}{x_i}$$  \hspace{1cm} (11)

Replacing eqn. 10 into eqns. 12 and 13, we obtain:

$$Y_{1,\phi}(x_i) = Y_1 + x_i Q_{RK,Y}(x_i)$$  \hspace{1cm} (12)

$$Y_{2,\phi}(x_i) = Y_2 + x_i$$  \hspace{1cm} (13)

Likewise, we can obtain the limiting excess partial molar thermodynamic quantities ($\bar{Y}_{i,\phi}$) as follow:
We have treated the same systems chosen by Belda due to the goodness of the suggested extension. Using the two different expressions of Belda model (the original one with two parameters and our suggested extended equation using three adjustable parameters) in 26 or 33 samples of binary mixtures identified indicated above and comparing the standard deviation, we see that the proposed model offer better results than those of Belda especially for high standard deviation.

We have also concluded that due to the few adjustable Belda parameters (m₁ and m₂) and the homographic shape of the correcting Belda factor which doesn’t present any change of curvature (inflection point). Belda equation exhibited low performance when the curves representing the binary mixture property indicating some peculiarities (inflection points, abrupt change of curvature, etc.) due to the existence of some strong correlation at particular compositions. So, we have observed some small discrepancies between experimental data points and the fitted model, especially at the high dilution and when the Belda factor exhibited a vertical asymptote very near or into the range of composition. Nevertheless, when there are strong curvatures, singular points or change of curvature, our extended models gives better results. Excellent agreement has been obtained between experimental data points and the calculated values of physico-chemical properties in the whole range of molar compositions of the some studied binary liquid mixtures. Due the obtained improvements, we can ascertain that the suggested extended model can be used to correlate several physico-chemical properties in binary liquid mixtures, more than the fourth properties tested by Belda.

We have demonstrated that the adjustable parameters have some physical significance and they are in relationship with the apparent molar thermodynamic quantities and the limiting excess partial molar thermodynamic quantities. As a result, the Belda model can be upgraded and considered as a semi-empirical equation and can be used as new techniques to determine these thermodynamic quantities with a reliable estimation. The Belda model and our extended suggested equation can be used with reliable correlation for any physico-chemical properties other tested by Belda. In future works, we will study about the supplementary third adjustable parameter which can be added in the denominator of the correcting Belda factor and compare the goodness of different models.

REFERENCES