

A New Surface Tension Model for Prediction of Interaction Energy between Components and Activity Coefficients in Binary Systems

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(Received 30 September 2017, Accepted 23 February 2018)

In this work, we develop a correlative model based on the surface tension data in order to calculate thermodynamic parameters, such as interaction energy between components (U_{ij}), activity coefficients, *etc.* In this new approach, using Li *et al.* (LWW) model, a three-parameter surface tension equation is derived for liquid mixtures. The surface tension data of 54 aqueous and 73 non-aqueous binary mixtures are correlated as a function of composition using the new model, then the interaction energy between two compounds (U_{ij}) of mixtures and their activity coefficients are calculated with the results of this model. The average relative error obtained from the comparison of experimental and calculated surface tension values for 127 binary systems is less than 2.8%. The obtained values using this method are comparable with those of the UNIFAC group contribution model.

Keywords: Correlation, LWW model, UNIFAC, Interaction energy, Activity coefficient

INTRODUCTION

An important part of each material (solid and liquid) is surface. The study of surfaces, as a region between two phases, represents the main field of research for many research activities. The surface tension, as one of the important thermophysical properties, reflects the valuable information about surface, intermolecular interactions and forces in the liquid, and also exerts a considerable influence on the transfer of mass and energy across the interface [1-2]. Thermodynamic properties of liquid mixtures involving excess properties, surface tension and surface activities are interesting from theoretical and experimental point of views. Knowledge of these properties is also helpful for understanding and interpreting the nature of interactions between the molecules of mixtures [3].

Surface tension and surface energy depend on variation in composition, molecular forces and density of packing or molecular size [4]. Therefore, it is important to know the

concentration dependence of the surface tension over the entire composition range.

A few empirical and thermodynamic-based equations have been presented to correlate the surface tension data of real liquid mixtures as a function of mole fraction such as the equations proposed by Fu *et al.* (FLW) [5], Myers-Scott (MS) [6] and Redlich-Kister (RK) [7]. Some of these equations have been recently proposed and are well-founded on thermodynamic bases. In 2000, Li *et al.* (LWW)[8] proposed a two-parameter model for liquid mixtures based on the Wilson equation for the excess Gibbs energy [9]. The experimental data of a large number of binary mixtures including the polar systems are very well correlated with LWW model.

In this study, we developed LWW model for correlating the surface tension data of numerous aqueous and non-aqueous binary mixtures with three adjustable parameters. A new equation was used for highly non-symmetrical binary systems with large values of surface tension deviation. The results of new equation can be used for predicting the interaction energy between components (U_{ij}) and activity coefficients of each component at the studied binary

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mixtures.

Activity coefficients and related thermodynamic quantities (*e.g.*, osmotic coefficients, water activities, changes in the standard Gibbs energy of transfer, standard solubility products, *etc.*) remain in constant demand by researchers in chemistry related disciplines, including potentiometry, polarography, voltammetry, biochemistry, geochemistry, industrial chemistry, pharmaceuticals, medicinal chemistry, water decontamination, purification and desalination treatments, petroleum recovery processes and electroanalytical methods [10].

Knowledge of activity coefficients is crucial to determine deviations from the ideal behavior of real solutions and predict vapor-liquid equilibrium (VLE). As known, activity coefficients can be determined using different methods [11-14].

To validate the proposed model, the activity coefficients obtained from this model were compared with those obtained from the original UNIFAC group contribution model, at fixed concentration of binary mixtures. There is a reasonable agreement between the results from new equation and the predictions of UNIFAC model for the estimation of activity coefficients in the liquid phase.

THEORETICAL SECTION

The deviation from ideal behavior can be determined by the surface tension deviations, $\Delta\sigma$, defined as

$$\Delta\sigma = \sigma - \sum_i^n X_i \sigma_i^* \quad (1)$$

where σ is the surface tension of the mixture, and σ_i^* is the surface tension of the pure component i , X_i is the mole fraction of the component i , and n is the number of components.

A surface tension deviation equation based on the thermodynamic definition of surface tension and the declaration of Gibbs energy is proposed by Li *et al.* (LWW) [8]:

$$\Delta\sigma = -RT \sum_i \frac{x_i}{\sum_j x_j \Lambda_{ij}} \sum_j x_j \left(\frac{\partial \Lambda_{ij}}{\partial A} \right)_{T,P,x} \quad (2)$$

where

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp \left(- \frac{U_{ij} - U_{ii}}{RT} \right) \quad (3)$$

and

$$\left(\frac{\partial \Lambda_{ij}}{\partial A} \right)_{T,P,x} = - \frac{\Lambda_{ij}}{RT} \left[\frac{\partial (U_{ij} - U_{ii})}{\partial A} \right]_{T,P,x} \quad (4)$$

and V_i is the molar volume of component i , $U_{ij} - U_{ii}$ the difference energy between molecular pair ij and ji and $[\partial(U_{ij} - U_{ii})/\partial A]_{T,P,x}$ reflects the energy change with the increase in surface area. Li *et al.* made the assumptions:

$$U_{ij} = (U_{ji} + U_{ji})/2 \quad (5)$$

$$(U_{ij} - U_{ii}) = -(U_{ji} - U_{jj}) \quad (6)$$

$$\left(\frac{\partial (U_{ij} - U_{ii})}{\partial A} \right)_{T,P,x} = - \left(\frac{\partial (U_{ji} - U_{jj})}{\partial A} \right)_{T,P,x} \quad (7)$$

and the ratio of molar volume for any two components is unity when calculating the parameter Λ_{ij} ; so the number of adjusted parameter is reduced from four to two for binary system; *i.e.*, $U_{12} - U_{11}$, $[\partial(U_{12} - U_{11})/\partial A]_{T,P,x}$; hence the resultant equation is given by:

$$\Delta\sigma = - \frac{x_1 x_2 RT}{x_2 + x_1 \Lambda_{21}} \left(\frac{\partial \Lambda_{21}}{\partial A} \right) \left[1 - \frac{1}{\Lambda_{21}} \right] \quad (8)$$

where $(\partial \Lambda_{21}/\partial A)$ and Λ_{21} are adjusted parameters (see Table 1).

In derivation of Eq. (8), Li *et al.* have used some incorrect assumptions; for example, the interaction energy between components in polar systems equalized the ideal conditions (Eqs. (5)-(6)). So, this assumption causes many errors in the calculations.

In the new approach, we have used Eq. (2) to obtain new equation with 3 parameters (finally) and better assumptions. For binary mixtures, Eq. (2) using Eq. (3) and Eq. (4) can be written as (without any approximation):

Table 1. The Models (Equation and Adjustable Parameters) for Correlation between Surface Tension Deviation and Concentration in Binary Mixtures

Model	Equation		
LWW	$\Delta\sigma = -\frac{x_1x_2RT}{x_2 + x_1\Lambda_{21}}\left(\frac{\partial\Lambda_{21}}{\partial A}\right)\left[1 - \frac{1}{\Lambda_{21}}\right]$		
Adjustable parameters	$\partial\Lambda_{21}/\partial A$	Λ_{21}	
New model	$\Delta\sigma = \left[\frac{x_1x_2}{x_1\frac{V_1}{V_2}\exp\left(\frac{U_{12}-U_{11}}{RT}\right) + x_2} \frac{\partial(U_{12}-U_{11})}{\partial A} + \frac{x_1x_2}{x_2\frac{V_2}{V_1}\exp\left(\frac{U_{21}-U_{22}}{RT}\right) + x_1} \frac{\partial(U_{21}-U_{22})}{\partial A} \right]$		
Adjustable parameters	U_{12}	$\partial(U_{12}-U_{11})/\partial A$	$\partial(U_{21}-U_{22})/\partial A$

$$\Delta\sigma = -RT \left[\frac{x_1}{\sum_j x_j \Lambda_{1j}} \sum_j x_j \left(\frac{\partial \Lambda_{1j}}{\partial A} \right)_{T,P,x} + \frac{x_2}{\sum_j x_j \Lambda_{2j}} \sum_j x_j \left(\frac{\partial \Lambda_{2j}}{\partial A} \right)_{T,P,x} \right]$$

or

$$\Delta\sigma = -RT \left[\frac{x_1}{x_1\Lambda_{11} + x_2\Lambda_{12}} \left(x_1 \left(\frac{\partial \Lambda_{11}}{\partial A} \right)_{T,P,x} + x_2 \left(\frac{\partial \Lambda_{12}}{\partial A} \right)_{T,P,x} \right) + \frac{x_2}{x_1\Lambda_{21} + x_2\Lambda_{22}} \left(x_1 \left(\frac{\partial \Lambda_{21}}{\partial A} \right)_{T,P,x} + x_2 \left(\frac{\partial \Lambda_{22}}{\partial A} \right)_{T,P,x} \right) \right] \quad (9)$$

$$\Delta\sigma = -RT \left[\frac{x_1x_2}{x_1 + x_2 \frac{v_2}{v_1} \exp\left(-\frac{(U_{12}-U_{11})}{RT}\right)} \left(-\frac{v_2}{v_1} \frac{1}{RT} \exp\left(-\frac{(U_{12}-U_{11})}{RT}\right) \left(\frac{\partial(U_{12}-U_{11})}{\partial A} \right) \right) + \frac{x_1x_2}{x_2 + x_1 \frac{v_1}{v_2} \exp\left(-\frac{(U_{21}-U_{22})}{RT}\right)} \left(-\frac{v_1}{v_2} \frac{1}{RT} \exp\left(-\frac{(U_{21}-U_{22})}{RT}\right) \left(\frac{\partial(U_{21}-U_{22})}{\partial A} \right) \right) \right] \quad (12)$$

therefore:

$$\Delta\sigma = -RT \left[\frac{x_1x_2}{x_1 + x_2\Lambda_{12}} \left(\frac{\partial\Lambda_{12}}{\partial A} \right) + \frac{x_1x_2}{x_2 + x_1\Lambda_{21}} \left(\frac{\partial\Lambda_{21}}{\partial A} \right) \right] \quad (10)$$

Then, by substitution of Eq. (3) into Eq. (12), we arrive at

$$\Delta\sigma = \left[\frac{x_1x_2\Lambda_{12}}{x_1 + x_2\Lambda_{12}} \frac{\partial(U_{12}-U_{11})}{\partial A} + \frac{x_1x_2\Lambda_{21}}{x_2 + x_1\Lambda_{21}} \frac{\partial(U_{21}-U_{22})}{\partial A} \right] \quad (13)$$

By substitution of Eqs. (3)-(4) into Eq. (10), one arrives at

$$\Delta\sigma = -RT \left[\frac{x_1x_2}{x_1 + x_2 \frac{v_2}{v_1} \exp\left(-\frac{U_{12}-U_{11}}{RT}\right)} \left(\frac{\partial\left(\frac{v_2}{v_1} \exp\left(-\frac{U_{12}-U_{11}}{RT}\right)\right)}{\partial A} \right) + \frac{x_1x_2}{x_2 + x_1 \frac{v_1}{v_2} \exp\left(-\frac{U_{21}-U_{22}}{RT}\right)} \left(\frac{\partial\left(\frac{v_1}{v_2} \exp\left(-\frac{U_{21}-U_{22}}{RT}\right)\right)}{\partial A} \right) \right] \quad (11)$$

or

$$\Delta\sigma = \left[\frac{x_1x_2}{x_1\frac{V_1}{V_2}\exp\left(\frac{U_{12}-U_{11}}{RT}\right) + x_2} \frac{\partial(U_{12}-U_{11})}{\partial A} + \frac{x_1x_2}{x_2\frac{V_2}{V_1}\exp\left(\frac{U_{21}-U_{22}}{RT}\right) + x_1} \frac{\partial(U_{21}-U_{22})}{\partial A} \right] \quad (14)$$

Using the thermodynamic functions for interaction energy between molecular pair ii, U_{ii} can be written as [15]:

$$U_{ii} = -\beta(\Delta H_{Vi} - RT) \quad (15)$$

where β is a proportionality factor and ΔH_{V_i} is the enthalpy of vaporization of pure component i at T . A similar equation is written for interaction energy between molecular pair jj , U_{jj} . Theoretical considerations suggest that $\beta = 2/Z$, where z is the coordination number (typically, $Z = 10$). This assumption, used by Wong and Eckert and Schreiber and Eckert, gives a good estimate for a variety of binary mixtures [16-17].

By assuming that $U_{12} = U_{21}$ (it is reasonable) and the calculations of U_{11} and U_{22} from Eq. (15), the number of adjustable parameters is reduced from four to three for binary system *i.e.* $p = U_{12}$, $q = \partial(U_{12} - U_{11})/\partial A$ and $r = \partial(U_{21} - U_{22})/\partial A$ (see Table 1).

In this paper, in order to estimate the adjustable parameters, the Levenberg-Marquardt method (as a non-linear regression algorithm for fitting data) is used.

After estimating the adjustable parameters ((from Eq. (14)) and then the calculation of Λ_{12} and Λ_{21} (from Eq. (3)), the Wilson equations used for obtaining liquid phase activity coefficients at any concentration of components in binary systems [9]:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right) \quad (16)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) + x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right) \quad (17)$$

In order to compare the results obtained (the activity coefficients) from new model, the UNIFAC model is employed to determine the activity coefficients of component i , γ_i , from the knowledge of the bulk mole fractions at various temperatures. The model has a combinatorial contribution to the activity coefficient, $\ln \gamma_i^C$, essentially due to differences in size and shape of the molecules, and a residual contribution, $\ln \gamma_i^R$, essentially due to energetic interactions [18-26]:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (18)$$

In this work, the original UNIFAC model was used for

calculation of the activity coefficients of component mixtures. Also, this method can be applied at various mole fractions of the organic solvents from the diluted to concentrated region and was the most widely used before several revisions and extensions were developed [18-26].

RESULTS AND DISCUSSION

The surface tension of all studied binary solution were fitted with new model (Eq. (14)) for 115 binary organic solutions and 32 binary aqueous solutions, and then, the activity coefficients of each component were calculated using obtained adjustable parameters and Wilson equation over a wide range of composition and temperature. Some properties of pure components in this work are shown in Table 2. The calculated value of the molar volume of component i (V_i) and the interaction energy between molecular pair (U_{ii}) (calculated by Eq. (15)) are listed in columns 6 and 9 of Table 2, respectively. The values of U_{ii} , V_i and surface tension data of binary mixtures are input data for correlation with Eq. (14).

Also the obtained fitting results from this new model have been presented in Tables 3-6. In the 5th column of Tables (3-1, 4-1, 5-1, 6-1 and 7-1) are presented the values of adjusted parameter $p = U_{12}$ (the most parameter) obtained from Eq. (14). The interaction energy differences $U_{12} - U_{11}$ and $U_{12} - U_{11}$ are shown in 6th and 7th columns.

In the 1th column of Tables (3-2, 4-2, 5-2, 6-2 and 7-2), the standard deviations (S) are reported computed by applying the following equation:

$$S = \left[\sum_{i=1}^M \frac{(Y_{i,\text{exp}} - Y_{i,\text{cal}})^2}{M - P} \right]^{1/2} \quad (19)$$

where Y stands for $\Delta\sigma$, M the number of data points and P the number of adjustable parameters used for fitting the experimental data. Considering the obtained standard deviation data in all binary systems, it is clear that there is a good agreement between experimental data and the obtained results by new model. The observed difference between experimental and calculated surface tension deviation values is small, therefore, it can be said that the proposed model is a capable model for reproducing surface tension data of all

Table 2. The Density (ρ), Surface Tension (σ), Enthalpy of Vaporization (ΔH_{vap}), Interaction Energy between Pair Molecules (U_{ii}) from Eq.(15) at Various Temperatures of Pure Components

No.	Component	T (K)	M (g mol ⁻¹)	ρ (g cm ⁻³)	V_m (cm ³ mol ⁻¹)	σ (mN m ⁻¹)	ΔH_{vap} (J mol ⁻¹)	U_{ii} (J mol ⁻¹)
1	Water	293.15	18.015	0.99820	18.04743	72.75 _{28,29}	44046.95	-8321.94
2	Water	298.15	18.015	0.99704	18.06843	72.01 _{28,29,30,31} , 71.95 ₃₁ , 71.97 ₃₂	43868.87	-8278.01
3	Water	303.15	18.015	0.99565	18.09380	71.21 _{28,29}	43687.94	-8233.51
4	Water	308.15	18.015	0.99403	18.12321	70.42 _{28,29}	43504.08	-8188.42
5	Water	313.15	18.015	0.99221	18.15640	69.52 _{28,29}	43317.17	-8142.73
6	Water	318.15	18.015	0.99021	18.19315	68.84 _{28,29}	43127.13	-8096.41
7	Water	323.15	18.015	0.98803	18.23325	67.92 _{28,29}	42933.85	-8049.44
8	Methanol	293.15	32.042	0.79438	40.33585	22.95 ₂₈ , 22.78 ₃₃	37936.48	-7099.85
9	Methanol	298.15	32.042	0.78961	40.57940	22.51 ₂₈ , 22.13 ₃₄ , 28.10 ₃₅	37643.75	-7032.99
10	Methanol	303.15	32.042	0.78479	40.82878	22.01 ₂₈	37346.45	-6965.21
11	Methanol	308.15	32.042	0.77991	41.08426	21.52 ₂₈	37044.39	-6896.49
12	Methanol	313.15	32.042	0.77497	41.34613	21.13 ₂₈ , 19.99 ₃₆	36737.39	-6826.77
13	Methanol	318.15	32.042	0.76997	41.61471	20.61 ₂₈	36425.23	-6756.03
14	Methanol	323.15	32.042	0.76490	41.89034	20.21 ₂₈	36107.69	-6684.20
15	Ethanol	288.15	46.068	0.79469	57.96978	22.64 ₂₈	43147.86	-8150.44
16	Ethanol	293.15	46.068	0.79031	58.29105	22.31 _{28,33} , 22.35 ₃₆	42847.10	-8081.97
17	Ethanol	298.15	46.068	0.78588	58.61979	21.82 ₂₈ , 21.83 ₃₄ , 21.74 _{37,38}	42541.61	-8012.56
18	Ethanol	303.15	46.068	0.78139	58.95634	21.41 ₂₈ , 21.23 ₃₆	42231.23	-7942.17
19	Ethanol	308.15	46.068	0.77685	59.30106	21.04 ₂₈ , 20.34 ₃₆	41915.74	-7870.76
20	Ethanol	313.15	46.068	0.77225	59.65434	20.62 ₂₈ , 19.48 ₃₆	41594.94	-7798.28
21	Ethanol	318.15	46.068	0.76759	60.01662	20.22 ₂₈	41268.59	-7724.70
22	Ethanol	323.15	46.068	0.76286	60.38834	19.82 ₂₈	40936.47	-7649.96
23	1-Propanol	293.15	60.095	0.80377	74.76624	23.69 ₂₈ , 23.40 ₃₆ , 23.78 ₃₃	48323.98	-9177.35
24	1-Propanol	298.15	60.095	0.79950	75.16608	23.28 ₂₈ , 22.49 ₃₉ , 23.39 _{37,38}	47937.08	-9091.65
25	1-Propanol	303.15	60.095	0.79518	75.57452	22.89 ₂₈ , 22.76 ₃₆	47544.83	-9004.89
26	1-Propanol	308.15	60.095	0.79081	75.99193	22.51 ₂₈ , 22.45 ₃₆	47146.94	-8917.00

Table 2. Continued

27	1-Propanol	313.15	60.095	0.78639	76.41870	22.11 ₂₈	46743.12	-8827.92
28	1-Propanol	318.15	60.095	0.78192	76.85525	21.69 ₂₈	46333.05	-8737.59
29	1-Propanol	323.15	60.095	0.77741	77.30201	21.31 ₂₈	45916.39	-8645.94
30	Isopropanol	293.15	60.095	0.78671	76.38765	21.74 ₂₈	46230.41	-8758.63
31	Isopropanol	298.15	60.095	0.78183	76.86431	21.22 ₂₈ , 20.95 ₃₅	45768.64	-8657.96
32	Isopropanol	303.15	60.095	0.77690	77.35265	20.72 ₂₈	45300.96	-8556.11
33	Isopropanol	308.15	60.095	0.77190	77.85323	20.23 ₂₈	44826.97	-8453.00
34	Isopropanol	313.15	60.095	0.76684	78.36666	19.71 ₂₈	44346.27	-8348.55
35	Isopropanol	318.15	60.095	0.76172	78.89358	19.21 ₂₈	43858.42	-8242.66
36	Isopropanol	323.15	60.095	0.75653	79.43470	18.69 ₂₈	43362.98	-8135.26
37	1-Butanol	293.15	74.122	0.80822	91.71052	24.21 ₄₀ , 24.67 ₄₁	54043.23	-10321.20
38	1-Butanol	298.15	74.122	0.80404	92.18733	24.30 ₃₁ , 24.23 ₄₁ , 24.02 _{37, 38}	53535.30	-10211.30
39	1-Butanol	303.15	74.122	0.79982	92.67342	23.78 ₄₁	53021.89	-10100.30
40	1-Butanol	308.15	74.122	0.79556	93.16915	22.79 ₄₀	52503.04	-9988.22
41	Butane-2-ol	298.15	74.122	0.80230	92.38686	23.3 ₃₁	49931.68	-9490.57
42	Butane-2-ol	303.15	74.122	0.79742	92.95235	22.61 ₄₁	49362.00	-9368.32
43	1,2-Butanediol	298.15	90.121	0.99920	90.19277	31.16 ₃₂	69101.04	-13324.45
44	1,3-Butanediol	298.15	90.121	1.00157	89.97943	37.09 ₃₂	26311.54	-4766.55
45	Pentan-1-ol	293.15	88.148	0.81604	108.01985	25.457 ₃₃	57639.68	-11040.49
46	Pentan-1-ol	298.15	88.148	0.81214	108.53847	24.97 _{37, 38}	57097.02	-10923.64
47	Hexane-1-ol	288.15	102.175	0.82315	124.12741	26.08 ₄₀	65058.79	-12532.62
48	Hexane-1-ol	293.15	102.175	0.81957	124.66974	25.61 ₄₀	64442.03	-12400.96
49	Hexane-1-ol	298.15	102.175	0.81596	125.22093	25.73 _{37, 38} , 25.69 ₄₂ , 25.67 ₃₄	63815.92	-12267.42
50	Hexane-1-ol	303.15	102.175	0.81232	125.78124	24.74 ₄₀	63180.98	-12132.12
51	Hexane-1-ol	308.15	102.175	0.80866	126.35097	24.19 ₄₀	62537.70	-11995.15
52	Heptan-1-ol	298.15	116.201	0.82098	141.53996	26.47 _{37, 38} , 26.39 ₄₂ , 26.44 ₄₃	69632.62	-13430.76
53	Octane-1-ol	288.15	130.228	0.83351	156.24041	27.41 ₄₀	73496.09	-14220.08
54	Octane-1-ol	293.15	130.228	0.82974	156.95052	26.94 ₄₀	72905.07	-14093.56
55	Octane-1-ol	298.15	130.228	0.82595	157.67109	27.1 ₃₇ , 26.52 ₄₀ , 27.04 ₄₂ , 27.02 ₄₃	72301.29	-13964.49

Table 2. Continued

56	Octane-1-ol	303.15	130.228	0.82213	158.40240	26.07 ₄₀	71685.31	-13832.98
57	Octane-1-ol	308.15	130.228	0.81830	159.14475	25.52 ₄₀	71057.67	-13699.14
58	Nonane-1-ol	298.15	144.255	0.82443	174.97634	27.55 ₄₂	78521.66	-15208.57
59	Decane-1-ol	298.15	158.281	0.82080	192.83717	27.95 ₄₂ , 28.12 ₄₃	80759.02	-15656.04
60	Formic acid	293.15	46.026	1.21973	37.73472	37.58 ₂₉	19824.30	-3477.41
61	Formic acid	298.15	46.026	1.21365	37.92368	37.03 ₂₉	19952.42	-3494.72
62	Formic acid	303.15	46.026	1.20752	38.11608	36.47 ₂₉	20083.35	-3512.59
63	Formic acid	308.15	46.026	1.20135	38.31205	35.94 ₂₉	20216.85	-3530.98
64	Formic acid	313.15	46.026	1.19512	38.51171	35.39 ₂₉	20352.67	-3549.83
65	Formic acid	318.15	46.026	1.18884	38.71520	34.87 ₂₉	20490.54	-3569.09
66	Formic acid	323.15	46.026	1.18250	38.92265	34.34 ₂₉	20630.17	-3588.70
67	Acetic acid	293.15	60.052	1.04706	57.35305	27.61 ₂₉	23414.01	-4195.35
68	Acetic acid	298.15	60.052	1.04200	57.63136	27.12 ₂₉	23420.44	-4188.33
69	Acetic acid	303.15	60.052	1.03691	57.91461	26.63 ₂₉	23430.65	-4182.05
70	Acetic acid	308.15	60.052	1.03177	58.20296	26.11 ₂₉	23444.36	-4176.48
71	Acetic acid	313.15	60.052	1.02659	58.49659	25.64 ₂₉	23461.35	-4171.56
72	Acetic acid	318.15	60.052	1.02137	58.79570	25.13 ₂₉	23481.34	-4167.25
73	Acetic acid	323.15	60.052	1.01610	59.10048	24.66 ₂₉	23504.06	-4163.48
74	Propionic acid	293.15	74.079	0.99317	74.58861	26.66 ₂₉	30954.70	-5703.49
75	Propionic acid	298.15	74.079	0.98821	74.96273	26.17 ₂₉	30969.02	-5698.04
76	Propionic acid	303.15	74.079	0.98322	75.34330	25.68 ₂₉	30984.84	-5692.89
77	Propionic acid	308.15	74.079	0.97819	75.73056	25.18 ₂₉	31001.93	-5687.99
78	Propionic acid	313.15	74.079	0.97313	76.12470	24.69 ₂₉	31020.03	-5683.30
79	Propionic acid	318.15	74.079	0.96802	76.52599	24.19 ₂₉	31038.88	-5678.76
80	Propionic acid	323.15	74.079	0.96288	76.93465	23.68 ₂₉	31058.23	-5674.31
81	Butyric acid	298.15	88.105	0.95160	92.58642	26.19 ₃₀	40177.03	-7539.64
82	Hexane	298.15	86.175	0.65601	131.36244	17.89 ₃₇ , 17.93 ₄₄	31539.11	-5812.06
83	Heptane	287.81	100.202	0.69021	145.17586	20.70 _{45, 46}	37228.96	-6967.22
86	Heptane	298.15	100.202	0.68154	147.02388	19.68 ₃ , 19.73 ₄₄ , 19.69 _{30, 47}	36629.67	-6830.17

Table 2. Continued

87	Heptane	303.15	100.202	0.67728	147.94660	18.93 ₄₀	36334.25	-6762.77
88	Heptane	307.86	100.202	0.67325	148.83408	18.68 _{45, 46}	36052.45	-6698.58
89	Heptane	308.15	100.202	0.67300	148.88932	18.93 ₄₀	36034.99	-6694.61
90	Heptane	317.86	100.202	0.66456	150.78050	17.76 ₄₆	35442.35	-6559.93
91	Heptane	327.88	100.202	0.65568	152.82178	16.68 _{45, 46}	34813.94	-6417.59
92	Octane	298.15	114.229	0.70269	162.56075	21.19 _{30,15,47} , 21.17 ₃₈	41464.21	-7797.08
93	Nonane	298.15	128.255	0.71695	178.88973	22.37 ₄₄ , 22.30 _{30,47}	46172.08	-8738.65
94	Decane	298.15	142.282	0.72789	195.47188	23.33 ₄₄ , 23.26 _{30,47}	50869.54	-9678.14
95	Cyclopentane	298.15	70.133	0.74127	94.61215	22.06 ₄₈	28380.85	-5180.41
96	Cyclopentane	313.15	70.133	0.72779	96.36501	19.76 ₄₈	27644.17	-5008.13
97	Cyclohexane	287.81	84.159	0.78232	107.57555	25.34 ₄₅	33515.80	-7221.42
98	Cyclohexane	297.82	84.159	0.77342	108.81453	24.20 ₄₅	33006.98	-7108.06
99	Cyclohexane	298.15	84.159	0.77312	108.85621	24.73 ₄₈	32990.00	-6102.24
100	Cyclohexane	307.86	84.159	0.76434	110.10745	23.02 ₄₅	32484.46	-6992.29
101	Cyclohexane	327.88	84.159	0.74575	112.85220	20.71 ₄₅	31402.90	-6754.71
102	Acetonitrile	293.15	41.052	0.78197	52.49827	29.25 ₃₃ , 29.20 ₄₁	33281.95	-6168.94
103	Acetonitrile	298.15	41.052	0.77665	52.85772	28.10 ₃₆ , 28.16 ₄₁	33051.20	-6114.48
104	Acetonitrile	303.15	41.052	0.77129	53.22491	27.71 ₄₁	32817.39	-6059.40
105	DMSO	293.15	78.133	1.10106	70.96164	43.36 ₃₆	53729.82	-10258.51
106	DMSO	298.15	78.133	1.09619	71.27698	42.179 ₃₉	53477.23	-10199.68
107	DMSO	303.15	78.133	1.09130	71.59620	42.05 ₃₆	53222.90	-10140.50
108	DMSO	308.15	78.133	1.08640	71.91937	40.95 ₃₆	52966.80	-10080.97
109	DMSO	313.15	78.133	1.08148	72.24661	39.83 ₃₆	52708.89	-10021.07
110	THF	298.15	72.106	0.87997	81.94168	26.73 ₄₄ , 26.75 ₄₂	31971.24	-5898.48
111	Toluene	297.82	92.138	0.86421	106.61507	27.76 ₄₆	38016.38	-7108.06
112	Toluene	307.86	92.138	0.85497	107.76713	26.60 ₄₆	37520.97	-6992.29
113	Toluene	317.86	92.138	0.84564	108.95647	25.46 ₄₆	37016.57	-6874.78
114	Toluene	327.88	92.138	0.83615	110.19311	24.29 ₄₆	36499.52	-6754.71
115	1,4-Dioxane	298.15	88.105	1.02850	85.66350	32.51 _{30,47} , 33.23 ₄₈	38603.58	-7224.95
116	1,4-Dioxane	313.15	88.105	1.01170	87.08605	31.23 ₄₈	37830.99	-7045.49

Table 3-1. The Value of Adjustable Parameter of New Model ($p = U_{12}$), the Difference in Interaction Energy between Molecules 1 and 2 ($U_{12} - U_{11}$ and $U_{21} - U_{22}$), the Mean Relative Standard Deviations (MSRD%) for Studied Binary Mixtures (Using Eq. (14))

Mixture No.	Ref.	Component		T (K)	$p = U_{12}$ (J mol ⁻¹)	$U_{12} - U_{11}$ (J mol ⁻¹)	$U_{21} - U_{22}$ (J mol ⁻¹)	MSRD (%)
		1	2					
1	[28]	Water	Methanol	293.15	-3819	4503.39	3281.30	1.32
2	[28]	Water	Methanol	298.15	-3749	4529.09	3284.07	1.24
3	[28]	Water	Methanol	303.15	-3666	4567.77	3299.47	1.18
4	[28]	Water	Methanol	308.15	-3566	4622.19	3330.25	1.17
5	[28]	Water	Methanol	313.15	-3543	4599.74	3283.79	1.22
6	[28]	Water	Methanol	318.15	-3433	4663.42	3323.04	1.14
7	[28]	Water	Methanol	323.15	-3354	4695.83	3330.59	0.90
8	[28]	Water	Ethanol	293.15	-3089	5233.39	4993.42	1.07
9	[28]	Water	Ethanol	298.15	-3025	5252.99	4987.54	1.07
10	[28]	Water	Ethanol	303.15	-2958	5275.93	4984.59	1.05
11	[28]	Water	Ethanol	308.15	-2880	5308.67	4991.00	0.99
12	[28]	Water	Ethanol	313.15	-2820	5323.01	4978.56	0.97
13	[28]	Water	Ethanol	318.15	-2735	5361.03	4989.32	0.97
14	[28]	Water	Ethanol	323.15	-2647	5402.05	5002.57	0.96
15	[28]	Water	1-Propanol	293.15	-1431	6890.72	7746.12	1.31
16	[28]	Water	1-Propanol	298.15	-1322	6955.64	7769.28	1.32
17	[28]	Water	1-Propanol	303.15	-1216	7017.72	7789.10	1.30
18	[28]	Water	1-Propanol	308.15	-1111	7077.91	7806.49	1.28
19	[28]	Water	1-Propanol	313.15	-1005	7138.22	7823.41	1.28
20	[28]	Water	1-Propanol	318.15	-884	7212.69	7853.87	1.30
21	[28]	Water	1-Propanol	323.15	-768	7281.58	7878.08	1.28
22	[28]	Water	2-Propanol	293.15	-2860	5461.77	5898.46	1.75
23	[28]	Water	2-Propanol	298.15	-2740	5537.53	5917.49	1.74
24	[28]	Water	2-Propanol	303.15	-2639	5594.09	5916.69	1.77
25	[28]	Water	2-Propanol	308.15	-2524	5664.28	5928.86	1.88
26	[28]	Water	2-Propanol	313.15	-2420	5722.67	5928.49	1.90
27	[28]	Water	2-Propanol	318.15	-2302	5794.85	5941.10	1.84
28	[28]	Water	2-Propanol	323.15	-2180	5869.15	5954.97	1.85
29	[31]	Water	1-Butanol	298.15	412	8689.99	10623.28	6.01

Table 3-2. The Value of Standard Deviation (S), the Parameters of Wilson Equation (Eq. (3)) that Obtained Using the Adjusted Parameter (p) of New Model (Λ_{21} and Λ_{12}), Activity Coefficient of Components 1 and 2 (γ_1 and γ_2) that Obtained from New Model and UNIFAC Model at Equimolar Composition of the Binary Mixtures ($x_1 = x_2 = 0.5$)

Mixture No.	S	Λ_{21}	Λ_{12}	γ_1		γ_2	
				Model	UNIFAC	Model	UNIFAC
1	1.34E-01	1.16E-01	3.52E-01	1.729	1.199	1.532	1.114
2	1.30E-01	1.18E-01	3.61E-01	1.723	1.201	1.525	1.116
3	1.30E-01	1.20E-01	3.68E-01	1.719	1.202	1.519	1.117
4	1.24E-01	1.20E-01	3.73E-01	1.717	1.204	1.515	1.119
5	1.11E-01	1.24E-01	3.89E-01	1.706	1.205	1.501	1.120
6	1.01E-01	1.24E-01	3.92E-01	1.704	1.207	1.499	1.122
7	7.85E-02	1.26E-01	4.00E-01	1.700	1.208	1.493	1.123
8	2.15E-01	3.99E-02	3.77E-01	1.838	1.498	1.520	1.200
9	2.12E-01	4.12E-02	3.90E-01	1.831	1.497	1.510	1.204
10	2.14E-01	4.25E-02	4.02E-01	1.824	1.496	1.500	1.207
11	2.04E-01	4.36E-02	4.12E-01	1.819	1.495	1.493	1.211
12	1.97E-01	4.50E-02	4.25E-01	1.811	1.494	1.483	1.214
13	1.98E-01	4.60E-02	4.35E-01	1.806	1.492	1.476	1.217
14	1.99E-01	4.69E-02	4.43E-01	1.801	1.491	1.469	1.219
15	3.45E-01	1.01E-02	2.45E-01	1.936	1.726	1.642	1.231
16	3.43E-01	1.05E-02	2.51E-01	1.934	1.724	1.636	1.236
17	3.39E-01	1.09E-02	2.58E-01	1.931	1.721	1.629	1.240
18	3.38E-01	1.13E-02	2.65E-01	1.928	1.719	1.622	1.243
19	3.34E-01	1.18E-02	2.71E-01	1.925	1.717	1.616	1.246
20	3.35E-01	1.22E-02	2.76E-01	1.923	1.714	1.610	1.250
21	3.28E-01	1.26E-02	2.82E-01	1.920	1.712	1.605	1.253
22	4.76E-01	2.10E-02	4.50E-01	1.843	1.727	1.466	1.232
23	4.63E-01	2.16E-02	4.56E-01	1.840	1.724	1.462	1.236
24	4.64E-01	2.24E-02	4.65E-01	1.835	1.722	1.456	1.240
25	4.83E-01	2.30E-02	4.71E-01	1.831	1.720	1.452	1.243
26	4.84E-01	2.38E-02	4.79E-01	1.826	1.718	1.446	1.247
27	4.77E-01	2.44E-02	4.85E-01	1.823	1.715	1.442	1.250
28	4.70E-01	2.50E-02	4.90E-01	1.820	1.713	1.439	1.253
29	2.91E-01	2.70E-03	1.53E-01	1.975	1.945	1.751	1.256

Table 4-1. The Value of Adjustable Parameter of New Model ($p = U_{12}$), the Difference in Interaction Energy between Molecules 1 and 2 ($U_{12} - U_{11}$ and $U_{21} - U_{22}$), the Mean Relative Standard Deviations (MSRD%) for Studied Binary Mixtures (Using Eq.(14))

Mixture No.	Ref.	Component		T (K)	$p = U_{12}$ (J mol ⁻¹)	$U_{12} - U_{11}$ (J mol ⁻¹)	$U_{21} - U_{22}$ (J mol ⁻¹)	MSRD (%)
		1	2					
30	[31]	Water	2-butanol	298.15	995	9272.92	10485.48	2.36
31	[32]	Water	1,2-butanediol	298.15	-7897	381.43	5427.87	0.07
32	[32]	Water	1,3-butanediol	298.15	63	8340.58	4829.11	8.64
33	[29]	Water	Formic acid	293.15	-355	7967.26	3122.73	1.75
34	[29]	Water	Formic acid	298.15	-389	7889.48	3106.19	0.99
35	[29]	Water	Formic acid	303.15	-329	7904.92	3184.00	0.95
36	[29]	Water	Formic acid	308.15	-316	7872.08	3214.64	1.02
37	[29]	Water	Formic acid	313.15	-303	7839.43	3246.53	1.02
38	[29]	Water	Formic acid	318.15	-251	7845.74	3318.42	1.02
39	[29]	Water	Formic acid	323.15	-256	7793.50	3332.76	0.97
40	[29]	Water	Acetic acid	293.15	677	8998.97	4872.39	0.30
41	[29]	Water	Acetic acid	298.15	741	9018.95	4929.27	0.47
42	[29]	Water	Acetic acid	303.15	871	9104.05	5052.59	0.19
43	[29]	Water	Acetic acid	308.15	957	9145.03	5133.08	0.29
44	[29]	Water	Acetic acid	313.15	1057	9199.63	5228.47	0.31
45	[29]	Water	Acetic acid	318.15	1163	9259.68	5330.52	0.23
46	[29]	Water	Acetic acid	323.15	1266	9315.42	5429.46	0.35
47	[29]	Water	Propionic acid	293.15	1032	9354.02	6735.57	0.53
48	[29]	Water	Propionic acid	298.15	1131	9408.86	6828.89	1.14
49	[29]	Water	Propionic acid	303.15	1304	9537.56	6996.94	0.64
50	[29]	Water	Propionic acid	308.15	1419	9607.29	7106.86	0.65
51	[29]	Water	Propionic acid	313.15	1547	9690.20	7230.77	0.70
52	[29]	Water	Propionic acid	318.15	1689	9785.21	7367.56	0.70
53	[29]	Water	Propionic acid	323.15	1817	9866.06	7490.94	0.83
54	[30]	Water	Butyric acid	298.15	1861	10139.31	9400.94	15.85

Table 4-2. The Value of Standard Deviation (S), the Parameters of Wilson Equation (Eq. (3)) that Obtained Using the Adjusted Parameter (p) of New Model (Λ_{21} and Λ_{12}), Activity Coefficient of Components 1 and 2 (γ_1 and γ_2) that Obtained from New Model and UNIFAC Model at Equimolar Composition of the Binary Mixtures ($x_1 = x_2 = 0.5$)

Mixture No.	S	Λ_{21}	Λ_{12}	γ_1		γ_2	
				Model	UNIFAC	Model	UNIFAC
30	1.55E-04	2.85E-03	1.21E-01	1.982	1.946	1.795	1.256
31	8.52E-03	2.24E-02	4.28E+00	0.834	1.333	0.889	1.053
32	7.29E-02	2.86E-02	1.72E-01	1.922	1.333	1.726	1.053
33	1.27E-01	1.33E-01	7.95E-02	1.774	1.035	1.844	1.007
34	8.38E-02	1.36E-01	8.70E-02	1.768	1.037	1.832	1.008
35	8.18E-02	1.34E-01	9.15E-02	1.770	1.039	1.825	1.010
36	8.52E-05	1.35E-01	9.79E-02	1.768	1.041	1.815	1.011
37	8.40E-02	1.35E-01	1.04E-01	1.767	1.043	1.806	1.013
38	8.01E-02	1.34E-01	1.10E-01	1.768	1.045	1.798	1.014
39	7.61E-02	1.36E-01	1.17E-01	1.764	1.047	1.787	1.016
40	5.97E-02	4.26E-02	7.92E-02	1.914	1.311	1.857	1.112
41	9.74E-02	4.29E-02	8.39E-02	1.913	1.311	1.849	1.114
42	3.14E-02	4.21E-02	8.64E-02	1.914	1.312	1.846	1.116
43	4.90E-02	4.20E-02	9.05E-02	1.914	1.312	1.839	1.117
44	5.29E-02	4.17E-02	9.41E-02	1.914	1.313	1.834	1.119
45	4.52E-02	4.12E-02	9.75E-02	1.914	1.313	1.828	1.120
46	5.96E-02	4.10E-02	1.01E-01	1.914	1.314	1.823	1.122
47	1.14E-01	1.53E-02	8.90E-02	1.963	1.545	1.843	1.158
48	3.33E-01	1.53E-02	9.32E-02	1.962	1.544	1.836	1.160
49	1.36E-01	1.50E-02	9.46E-02	1.963	1.543	1.834	1.162
50	1.38E-01	1.49E-02	9.83E-02	1.962	1.543	1.829	1.164
51	1.47E-01	1.48E-02	1.01E-01	1.962	1.542	1.824	1.165
52	1.47E-01	1.47E-02	1.04E-01	1.962	1.542	1.820	1.167
53	1.72E-01	1.46E-02	1.07E-01	1.962	1.541	1.815	1.169
54	9.26E-01	4.40E-03	8.57E-02	1.985	1.779	1.848	1.189

Table 5-1. The Value of Adjustable Parameter of New Model ($p = U_{12}$), the Difference in Interaction Energy between Molecules 1 and 2 ($U_{12} - U_{11}$ and $U_{21} - U_{22}$), the Mean Relative Standard Deviations (MSRD%) for Studied Binary Mixtures (Using Eq. (14))

Mixture No.	Ref.	Component		T (K)	$p = U_{12}$ (J mol ⁻¹)	$U_{12} - U_{11}$ (J mol ⁻¹)	$U_{21} - U_{22}$ (J mol ⁻¹)	MSRD (%)
		1	2					
55	[44]	THF	Hexane	298.15	-3686	2212.25	2125.82	0.61
56	[44]	THF	Heptane	298.15	-5208	690.71	1622.39	2.93
57	[44]	THF	Octane	298.15	-5480	418.15	2316.75	1.27
58	[44]	THF	Nonane	298.15	-5660	238.04	3078.21	1.15
59	[44]	THF	Decane	298.15	-6864	-965.38	2814.28	2.23
60	[42]	THF	Hexane-1-ol	298.15	-5265	633.43	7002.36	3.19
61	[42]	THF	Heptane-1-ol	298.15	-5968	-69.50	7462.78	14.12
62	[42]	Octan1-ol	THF	298.15	-5176	8788.75	722.74	6.37
63	[42]	Nonane-1-ol	THF	298.15	-5457	9751.68	441.59	3.03
64	[42]	Decane-1-ol	THF	298.15	-4383	11273.52	1515.97	9.18
65	[33]	Ac	Methanol	293.15	-5557	612.21	1543.12	4.27
66	[33]	Ac	Ethanol	293.15	-7094	-924.86	988.17	7.63
67	[33]	Ac	1-Propanol	293.15	-7632	-1463.39	1545.01	6.54
68	[35]	Ac	Isopropanol	298.15	-4376	1738.24	4281.73	15.57
69	[41]	Ac	Butane-1-ol	293.15	-3091	3078.27	7230.52	2.43
70	[41]	Ac	Butane-1-ol	298.15	-2374	3740.08	7836.90	6.51
71	[41]	Ac	Butane-1-ol	303.15	-1675	4384.23	8425.13	10.77
72	[41]	Ac	Butane-2-ol	303.15	-7671	-1611.24	1697.68	11.70
73	[33]	Ac	Pentan-1-ol	293.15	-7688	-1518.85	3352.70	6.92
74	[36]	DMSO	Methanol	313.15	-3987	6033.61	2839.31	8.99
75	[36]	DMSO	Ethanol	293.15	-5031	5227.74	3051.20	1.76
76	[36]	DMSO	Ethanol	303.15	-5673	4467.84	2269.51	3.64
77	[36]	DMSO	Ethanol	308.15	-6134	3946.51	1736.30	10.61
78	[36]	DMSO	Ethanol	313.15	-6604	3417.24	1194.45	12.78
79	[36]	DMSO	1-Propanol	293.15	-6378	3880.41	2799.24	2.03

Table 5-2. The Value of Standard Deviation (S), the Parameters of Wilson Equation (Eq. (3)) that Obtained Using the Adjusted Parameter (p) of New Model (Λ_{21} and Λ_{12}), Activity Coefficient of Components 1 and 2 (γ_1 and γ_2) that Obtained from New Model and UNIFAC Model at Equimolar Composition of the Binary Mixtures ($x_1 = x_2 = 0.5$)

Mixture No.	S	Λ_{21}	Λ_{12}	γ_1		γ_2	
				Model	UNIFAC	Model	UNIFAC
55	1.05E-02	2.65E-01	6.57E-01	1.456	1.098	1.312	1.068
56	2.18E-02	2.90E-01	7.35E-01	1.407	1.088	1.271	1.051
57	1.64E-02	1.98E-01	8.13E-01	1.464	1.035	1.258	1.004
58	1.21E-02	1.32E-01	8.94E-01	1.506	1.055	1.238	1.018
59	1.15E-02	1.35E-01	9.77E-01	1.473	1.035	1.211	1.004
60	6.52E-03	3.88E-02	1.18E+00	1.517	1.138	1.162	1.047
61	1.24E-02	2.85E-02	1.78E+00	1.329	1.090	1.054	1.021
62	1.19E-02	1.44E+00	1.50E-02	1.109	1.046	1.458	0.999
63	9.03E-03	1.79E+00	9.16E-03	1.053	1.006	1.350	0.980
64	3.08E-02	1.28E+00	4.5E-03	1.142	0.970	1.532	0.964
65	1.61E-02	6.91E-01	6.25E-02	1.327	1.258	1.678	1.256
66	1.70E-02	6.00E-01	1.62E-01	0.974	0.880	0.980	0.744
67	2.13E-02	3.73E-01	6.98E-01	1.354	0.902	1.267	0.755
68	9.49E-02	1.22E-01	4.20E-01	1.698	0.903	1.478	0.759
69	4.40E-02	2.95E-02	3.82E-01	1.854	0.928	1.517	0.765
70	7.58E-02	2.43E-02	2.97E-01	1.893	0.929	1.590	0.769
71	1.41E-01	2.03E-02	3.36E+00	0.972	0.930	0.925	0.773
72	6.02E-02	2.92E-01	3.19E+00	0.815	0.930	0.906	0.773
73	5.34E-02	1.23E-01	2.06E+00	1.149	0.956	1.014	0.773
74	1.77E-02	5.87E-01	5.64E-02	1.380	0.791	1.729	0.745
75	1.94E-02	3.84E-01	9.62E-02	1.539	0.796	1.759	0.716
76	1.77E-02	4.94E-01	1.40E-01	1.425	0.806	1.648	0.725
77	3.23E-05	6.16E-01	1.77E-01	1.349	0.810	1.559	0.730
78	2.71E-05	7.65E-01	2.22E-01	1.272	0.814	1.457	0.735
79	2.49E-05	3.01E-01	2.14E-01	1.559	0.844	1.624	0.753

Table 6-1. The Value of Adjustable Parameter of New Model ($p = U_{12}$), the Difference in Interaction Energy between Molecules 1 and 2 ($U_{12} - U_{11}$ and $U_{21} - U_{22}$), the Mean Relative Standard Deviations (MSRD%) for Studied Binary Mixtures (Using Eq. (14))

Mixture No.	Ref.	Component		T (K)	$p = U_{12}$ (J mol ⁻¹)	$U_{12} - U_{11}$ (J mol ⁻¹)	$U_{21} - U_{22}$ (J mol ⁻¹)	MSRD (%)
		1	2					
80	[39]	DMSO	1-Propanol	298.15	-5155	5045.03	3937.00	7.14
81	[36]	DMSO	1-Propanol	303.15	-7359	3762.40	2626.79	2.22
82	[36]	DMSO	1-Propanol	308.15	-8116	1965.45	801.48	4.15
83	[38]	Ethanol	Octane	298.15	-5613	2399.26	2183.78	4.78
84	[38]	Propan-1-ol	Octane	298.15	-6869	2222.62	928.04	2.38
85	[38]	Butan-1-ol	Octane	298.15	-8570	1641.20	-773.02	1.49
86	[38]	Pentan-1-ol	Octane	298.15	-7378	3546.00	419.43	1.59
87	[38]	Hexane-1-ol	Octane	298.15	-7034	5233.49	763.15	3.43
88	[38]	Heptan-1-ol	Octane	298.15	-6841	6949.89	1316.21	1.21
89	[44]	THF	Octane	298.15	-5496	402.88	2301.47	1.30
90	[37]	Ethanol	Hexane	298.15	-5709	2303.24	102.73	5.44
91	[37]	1-Propanol	Hexane	298.15	-7104	1987.58	-1292.01	3.75
92	[37]	Butan-1-ol	Hexane	298.15	-6326	3885.60	-513.64	3.61
93	[37]	Pentan-1-ol	Hexane	298.15	-5726	5198.00	86.41	4.71
94	[37]	Hexane-1-ol	Hexane	298.15	-5130	7136.97	681.60	3.29
95	[37]	Heptan-1-ol	Hexane	298.15	-6428	7002.83	-615.88	15.84
96	[37]	1-Octanol	Hexane	298.15	-6199	7765.90	-386.53	5.90
97	[40]	Butan-1-ol	Heptane	293.15	-8170	2150.74	-1273.63	8.57
98	[40]	Butan-1-ol	Heptane	308.15	-8268	1720.28	-1573.33	14.81
99	[40]	Hexane-1-ol	Heptane	293.15	-5930	6470.99	966.86	8.93
100	[40]	Hexane-1-ol	Heptane	298.15	-6015	6251.99	814.74	14.12
101	[40]	Hexane-1-ol	Heptane	303.15	-6079	6053.43	684.09	12.36
102	[40]	Hexane-1-ol	Heptane	308.15	-5200	6794.84	1494.30	9.78

Table 6-2. The Value of Standard Deviation (S), the Parameters of Wilson Equation (Eq. (3)) that Obtained Using the Adjusted Parameter (p) of New Model (Λ_{21} and Λ_{12}), Activity Coefficient of Components 1 and 2 (γ_1 and γ_2) that Obtained from New Model and UNIFAC Model at Equimolar Composition of the Binary Mixtures ($x_1 = x_2 = 0.5$)

Mixture No.	S	Λ_{21}	Λ_{12}	γ_1		γ_2	
				Model	UNIFAC	Model	UNIFAC
80	1.07E-01	1.94E-01	1.38E-01	1.687	0.849	1.746	0.757
81	1.38E-02	3.34E-01	2.37E-01	1.524	0.853	1.590	0.762
82	1.70E-02	6.92E-01	4.91E-01	1.239	0.857	1.280	0.767
83	1.12E-02	1.49E-01	1.05E+00	1.429	1.880	1.186	1.926
84	1.22E-02	3.18E-01	8.82E-01	1.334	1.696	1.209	1.864
85	8.37E-03	7.75E-01	9.10E-01	1.090	1.570	1.083	1.806
86	1.18E-02	5.64E-01	3.58E-01	1.337	1.477	1.409	1.752
87	1.11E-02	5.66E-01	1.57E-01	1.379	1.404	1.600	1.700
88	9.03E-03	5.12E-01	9.96E-02	1.422	1.346	1.739	1.651
89	1.76E-02	1.99E-01	1.69E+00	1.181	1.035	1.051	1.004
90	4.08E-02	4.28E-01	8.85E-01	1.257	1.587	1.182	1.912
91	2.27E-02	9.64E-01	7.84E-01	1.065	1.442	1.072	1.814
92	1.89E-02	8.63E-01	2.97E-01	1.220	1.343	1.357	1.725
93	2.97E-02	7.98E-01	1.49E-01	1.271	1.271	1.523	1.645
94	1.90E-02	7.24E-01	5.89E-02	1.312	1.215	1.670	1.572
95	4.13E-02	1.38E+00	5.50E-02	1.118	1.170	1.424	1.505
96	3.89E-02	1.40E+00	3.63E-02	1.115	1.134	1.441	1.444
97	2.61E-02	1.06E+00	6.59E-01	1.072	1.408	1.092	1.773
98	5.77E-02	1.16E+00	8.17E-01	1.009	1.403	1.012	1.739
99	5.65E-02	5.74E-01	8.24E-02	1.385	1.268	1.696	1.631
100	4.72E-02	6.13E-01	9.43E-02	1.362	1.267	1.663	1.621
101	3.72E-02	6.48E-01	1.07E-01	1.343	1.266	1.633	1.611
102	5.97E-02	4.74E-01	8.31E-02	1.466	1.264	1.733	1.602

Table 7-1. The Value of Adjustable Parameter of New Model ($p = U_{12}$), the Difference in Interaction Energy between Molecules 1 and 2 ($U_{12} - U_{11}$ and $U_{21} - U_{22}$), the Mean Relative Standard Deviations (MSRD%) for Studied Binary Mixtures (Using Eq. (14))

Mixture No.	Ref.	Component		T (K)	$p = U_{12}$ (J mol ⁻¹)	$U_{12} - U_{11}$ (J mol ⁻¹)	$U_{21} - U_{22}$ (J mol ⁻¹)	MSRD (%)
		1	2					
103	[40]	Octan-1-ol	Heptane	288.15	-5262	8958.53	1701.22	11.96
104	[40]	Octan-1-ol	Heptane	293.15	-5434	8659.75	1463.01	7.26
105	[40]	Octan-1-ol	Heptane	298.15	-4894	9070.39	1936.07	7.59
106	[40]	Octan-1-ol	Heptane	303.15	-4751	9081.86	2011.65	11.05
107	[40]	Octan-1-ol	Heptane	308.15	-4256	9443.58	2439.04	6.63
108	[45]	Cyclohexane	Heptane	287.81	-6451	-226.39	516.24	15.62
109	[45]	Cyclohexane	Heptane	297.82	-6388	-282.25	446.16	9.07
110	[45]	Cyclohexane	Heptane	307.86	-5661	323.62	1037.22	10.96
111	[45]	Cyclohexane	Heptane	327.88	-4364	1371.75	2053.96	10.95
112	[46]	Toluene	Heptane	297.82	-5370	1737.63	1464.16	2.62
113	[46]	Toluene	Heptane	307.86	-5028	1964.51	1670.81	1.73
114	[46]	Toluene	Heptane	317.86	-4273	2602.03	2287.18	2.07
115	[46]	Toluene	Heptane	327.88	-5030	1724.40	1387.29	1.86
116	[47]	1,4-Dioxane	Heptane	298.15	-2560	4664.48	4269.70	2.86
117	[47]	1,4-Dioxane	Octane	298.15	-3969	3255.72	3827.84	3.98
118	[47]	1,4-Dioxane	Nonane	298.15	-4508	2717.05	4230.75	3.24
119	[47]	1,4-Dioxane	Decane	298.15	-4895	2329.93	4783.12	2.01
120	[48]	1,4-Dioxane	Cyclopentane	298.15	-2659	4566.40	2521.85	5.39
121	[48]	1,4-Dioxane	Cyclopentane	313.15	-2837	4208.56	2171.20	6.40
122	[48]	1,4-Dioxane	Cyclohexane	298.15	-2713	4512.18	3389.46	13.20
123	[34]	1,4-Dioxane	Methanol	298.15	-3337	3888.31	3696.34	2.98
124	[43]	1,4-Dioxane	Hexan-1-ol	298.15	-9625	-2400.44	2642.03	2.39
125	[43]	1,4-Dioxane	Heptan-1-ol	298.15	-8412	-1187.10	5018.70	1.59
126	[43]	1,4-Dioxane	Octan-1-ol	298.15	-10495	-3269.83	3469.72	12.51
127	[43]	1,4-Dioxane	Decan-1-ol	298.15	-8727	-1501.63	6929.46	2.83

Table 7-2. The Value of Standard Deviation (S), the Parameters of Wilson Equation (Eq. (3)) that Obtained Using the Adjusted Parameter (p) of New Model (Λ_{21} and Λ_{12}), Activity Coefficient of Components 1 and 2 (γ_1 and γ_2) that Obtained from New Model and UNIFAC Model at Equimolar Composition of the Binary Mixtures ($x_1 = x_2 = 0.5$)

Mixture No.	S	Λ_{21}	Λ_{12}	γ_1		γ_2	
				Model	UNIFAC	Model	UNIFAC
103	7.17E-02	5.29E-01	2.21E-02	1.415	1.180	1.809	1.519
104	4.37E-02	5.89E-01	2.67E-02	1.380	1.179	1.777	1.510
105	4.29E-02	4.91E-01	2.40E-02	1.438	1.178	1.821	1.502
106	5.33E-02	4.82E-01	2.54E-02	1.444	1.177	1.822	1.493
107	4.91E-02	4.13E-01	2.35E-02	1.493	1.176	1.853	1.485
108	6.25E-02	5.97E-01	1.48E+00	1.007	1.001	1.001	1.000
109	4.00E-02	6.18E-01	1.51E+00	0.992	1.001	0.992	1.000
110	3.62E-02	4.93E-01	1.19E+00	1.130	1.001	1.082	1.000
111	6.34E-02	3.48E-01	8.19E-01	1.333	1.001	1.225	1.000
112	4.53E-02	4.02E-01	6.83E-01	1.339	0.500	1.266	0.820
113	2.51E-02	3.77E-01	6.41E-01	1.370	0.500	1.292	0.820
114	3.33E-02	3.04E-01	5.17E-01	1.468	0.500	1.377	0.820
115	2.31E-02	4.33E-01	7.37E-01	1.301	0.500	1.235	0.820
116	6.21E-02	1.04E-01	2.61E-01	1.775	1.397	1.618	1.280
117	8.69E-02	1.12E-01	5.10E-01	1.678	1.440	1.419	1.213
118	6.04E-02	8.69E-02	6.98E-01	1.640	1.432	1.321	1.235
119	5.43E-02	6.36E-02	8.91E-01	1.596	1.440	1.246	1.213
120	4.01E-02	3.27E-01	1.75E-01	1.544	1.261	1.661	1.316
121	4.26E-02	3.93E-01	2.20E-01	1.481	1.249	1.590	1.299
122	7.14E-02	2.00E-01	2.06E-01	1.665	1.313	1.660	1.311
123	2.02E-02	4.75E-01	9.87E-02	1.443	1.172	1.710	1.118
124	1.90E-02	2.36E-01	3.85E+00	0.754	1.203	0.886	1.123
125	1.31E-02	7.99E-02	2.67E+00	1.048	1.186	0.964	1.100
126	4.16E-02	1.34E-01	6.88E+00	0.540	1.169	0.829	1.080
127	1.71E-02	2.71E-02	4.13E+00	0.850	1.137	0.894	1.046

studied binary mixtures. The calculated standard deviations data are presented in Tables (3-2, 4-2, 5-2, 6-2 and 7-2).

The values of Λ_{21} and Λ_{12} were calculated from Eq. (3) based on U_{12} or U_{21} obtained from fitting results (see Tables (3-2, 4-2, 5-2, 6-2 and 7-2)), and then substituting these values into Eqs. (15) and (16) (Wilson equations) can predict activity coefficients for the whole concentration range of the components in binary mixtures. In continue, these results were compared with the obtained activity coefficients from the UNIFAC model, based on the application of the group contribution [18-26].

The activity coefficients (γ_1 and γ_2) obtained from two methods (new model and UNIFAC model) at equimolar composition of the binary mixtures ($x_1 = x_2 = 0.5$) are shown in Tables 3-2, 4-2, 5-2, 6-2 and 7-2.

As can be seen from Figs. 1-8, accuracy of the correlated surface tensions data by new LWW model with 3 adjusted coefficients for all studied mixtures is reasonable. The calculated $\Delta\sigma$ values using new model are negative over the entire concentration range and at all studied temperatures in polar binary mixtures of water/alkanols (see Figs. 1-3). As Figs. 1 and 2 show, the values of absolute $\Delta\sigma$ for mixtures of alcohol (methanol, ethanol, 1-propanol and 2-propanol)/water increase with decreasing temperature and increasing alkyl chain length of the alcohol but slope of changes is sharper in latter. As can be seen from Figs. 1-2 and Tables 3-7, the LWW model with three adjusted parameters correlates the surface tensions of these polar binary mixtures well, even for binary mixtures of 1-propanol/water and 2-propanol/water, which are highly nonsymmetrical with large values of $\Delta\sigma$. The calculated absolute deviations from ideal behavior ($|\Delta\sigma|$) for alcohol/water systems using new model are presented in Fig. 3 at 298.15 K. The order of data is as follows (in the low concentrations of alcohol): 1,3-butanediol < 1,2-butanediol < 2-butanol < 1-butanol

Also, negative values of $\Delta\sigma$ were obtained for all binary systems over the whole composition range (see Figs. 4-6). In binary mixtures of water/carboxylic acid and alkane/THF, the absolute values of $\Delta\sigma$ increase with increasing alkyl chain length of the carboxylic acid and decrease with increasing temperature and alkyl chain length of the alkane, respectively (see Fig. 4 and Fig. 6).

In addition, Figs. 7 and 8 show the behavior of our other

studied binary mixtures and capability of our proposed model to correlate surface tension data. It is clear that this model correlates the surface tension of these systems well.

The correlation results using new LWW model (with three adjusted parameter) and the relevant results such as the difference in interaction energy between molecule pairs ij and ii and pairs ji and jj ($U_{ij} - U_{ii}$ and $U_{ji} - U_{jj}$) for binary systems are presented in Table 3.

In this section, we show another advantage of the adjusted parameters of new LWW model to explain the influence of temperature on interaction energy values between components. According to Eq. (14), the surface tension deviation ($\Delta\sigma$) arises from the cross interaction between species i and j . For an ideal solution, the interaction energy between any two species is practically equal; *i.e.*, $U_{ii} = U_{jj} = U_{ij}$. In this case, the surface tension deviation term disappears and the surface tension of the ideal mixture is equal to mole fraction average of the surface tension of pure components at the system temperature and pressure [8].

The LWW parameters have physical significance which can be explained as follow: $U_{12} - U_{11}$ is specifically identified with the dimensionless parameter Λ_{ij} *via* Eq. (14), which is utilized to represent the local composition impact, and the term $[\partial(U_{12} - U_{11})/\partial A]_{T,P,X}$ reflects the energy change with increasing in surface area, and hence, it contributes to the surface deviation.

The values of $U_{12} - U_{11}$, $U_{21} - U_{22}$, $[\partial(U_{12} - U_{11})/\partial A]_{T,P,X}$ and $[\partial(U_{21} - U_{22})/\partial A]_{T,P,X}$ acquired by new LWW model are presented in Tables 3-2, 4-2, 5-2, 6-2 and 7-2. Inasmuch as $U_{12} - U_{11}$ depends mainly on variation in intermolecular interactions between two components in contact, if interaction energies between dissimilar molecules (U_{12}) are stronger than those between similar molecules (U_{11}), positive values of $U_{12} - U_{11}$ will be observed.

In polar binary systems consisting of water/alcohols (methanol, ethanol, 1-propanol and 1-butanol), due to the molecular structure of alcohols demonstrates that strength of hydrogen bond (the interaction energy) between OH group of alcohols and water molecules increase with increasing the alkyl chain length of alcohols (from methanol to 1-propanol) at studied temperatures. It is obvious that the value of $U_{11}(U_{\text{water-water}})$ is equal in this four mixtures, So, it appears that the major reason for difference mentioned above is absolute measure of $U_{12}(U_{\text{water-alcohol}})$. Therefore, at constant

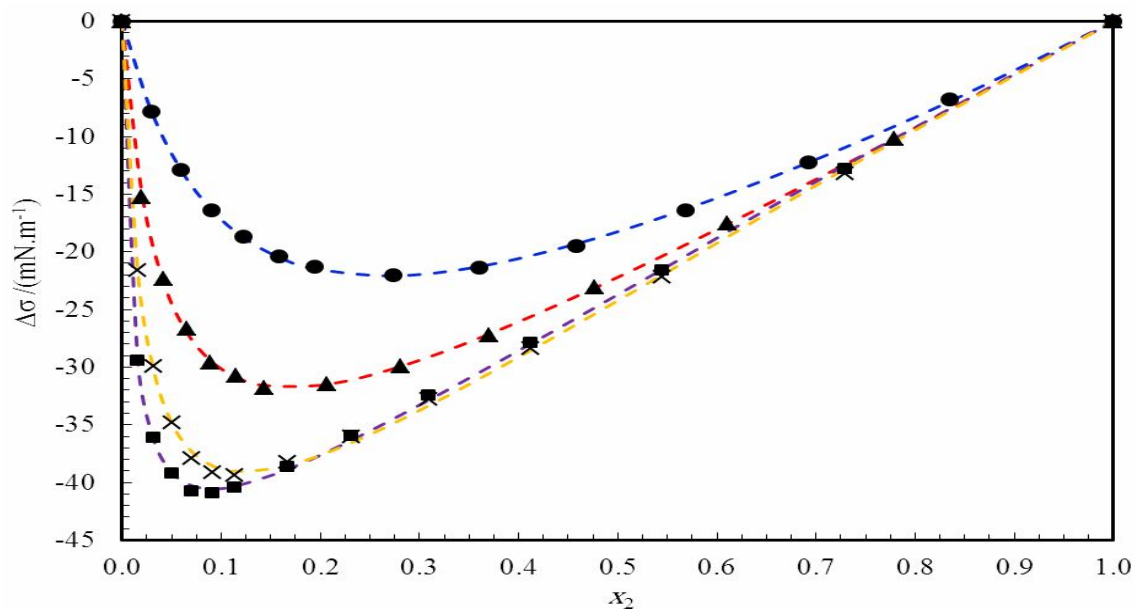


Fig. 1. Surface tension deviation, $\Delta\sigma$, against mole fraction, x_2 , for the binary systems of alkanol (2)/water (1) at 298.15 K. The symbols refer to the experimental data, the dashed curves represent the correlation with equation (14): (●) methanol, (▲) ethanol, (■) 1-propanol and (×) 2-propanol.

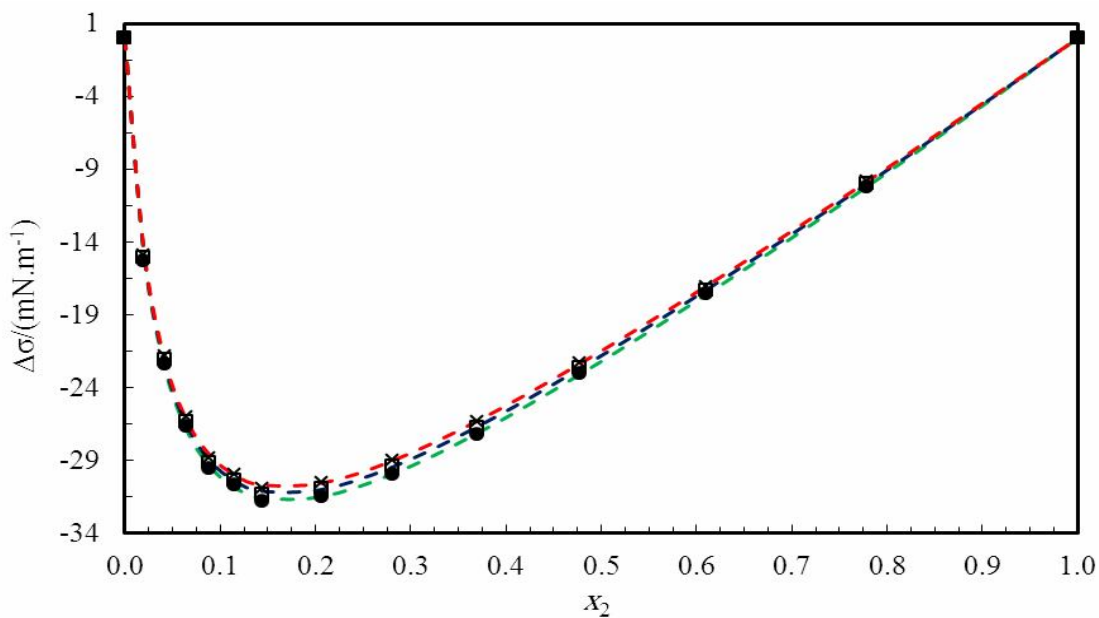


Fig. 2. Plot of surface tension deviation, $\Delta\sigma$, against mole fraction for ethanol (2)/water (1) system. The symbols refer to the experimental data at various temperatures, the dashed curves represent the correlation with equation (14): (●) 298.15 K, (□) 308.15 K and (×) 318.15 K.

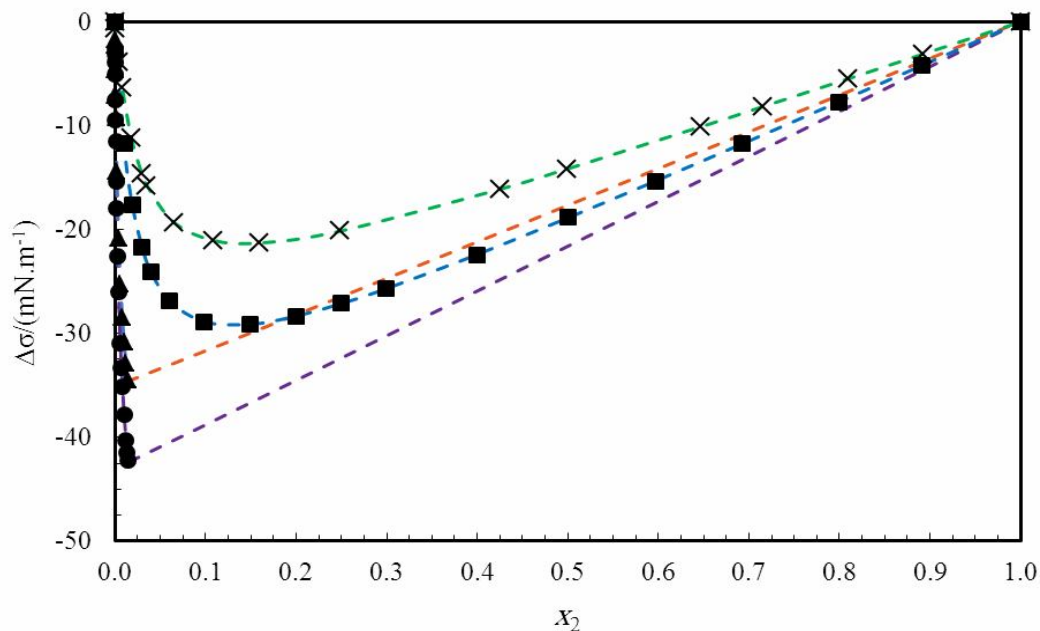


Fig. 3. Surface tension deviation, $\Delta\sigma$, against mole fraction, x_2 , for the binary systems of alkanol (2)/water (1) at 298.15 K. The symbols refer to the experimental data, the dashed curves represent the correlation with equation (14): (●)1-butanol, (▲) 2-butanol, (■) 1,2-butanediol and (×) 1,3-butanediol.

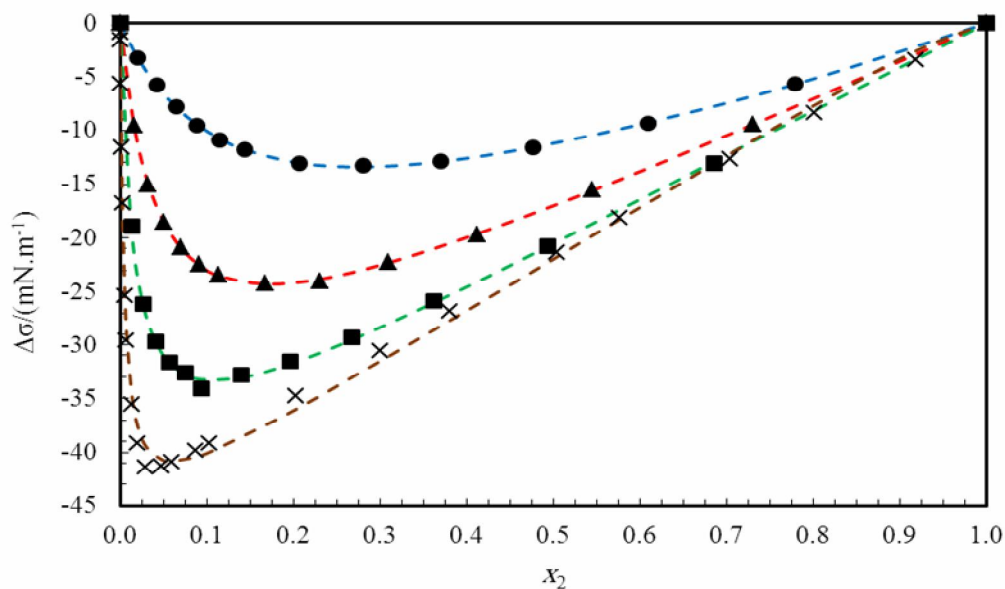


Fig. 4. Surface tension deviation, $\Delta\sigma$, against mole fraction, x_2 , for the binary systems of carboxylic acid (2)/water (1) at 298.15 K. The symbols refer to the experimental data; the dashed curves represent the correlation with equation (14): (●) formic acid, (▲) acetic acid, (■) propionic acid and (×) butyric acid.

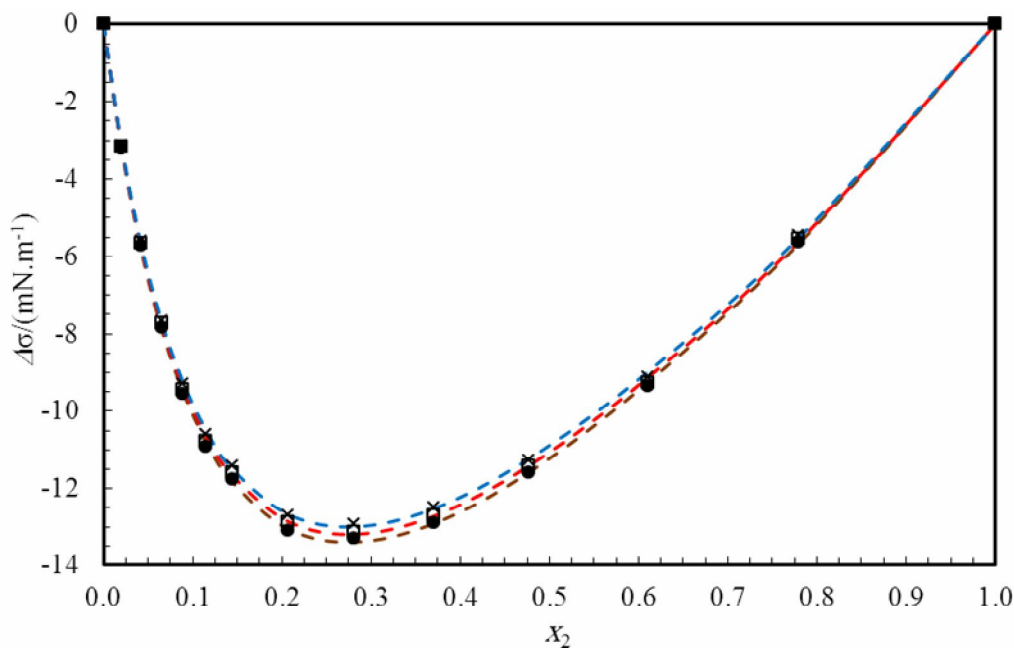


Fig. 5. Plot of surface tension deviation, $\Delta\sigma$, against mole fraction for formic acid (2)/water (1) system. The symbols refer to the experimental data at various temperatures: (●) 298.15 K, (□) 308.15 K and (×) 318.15 K.

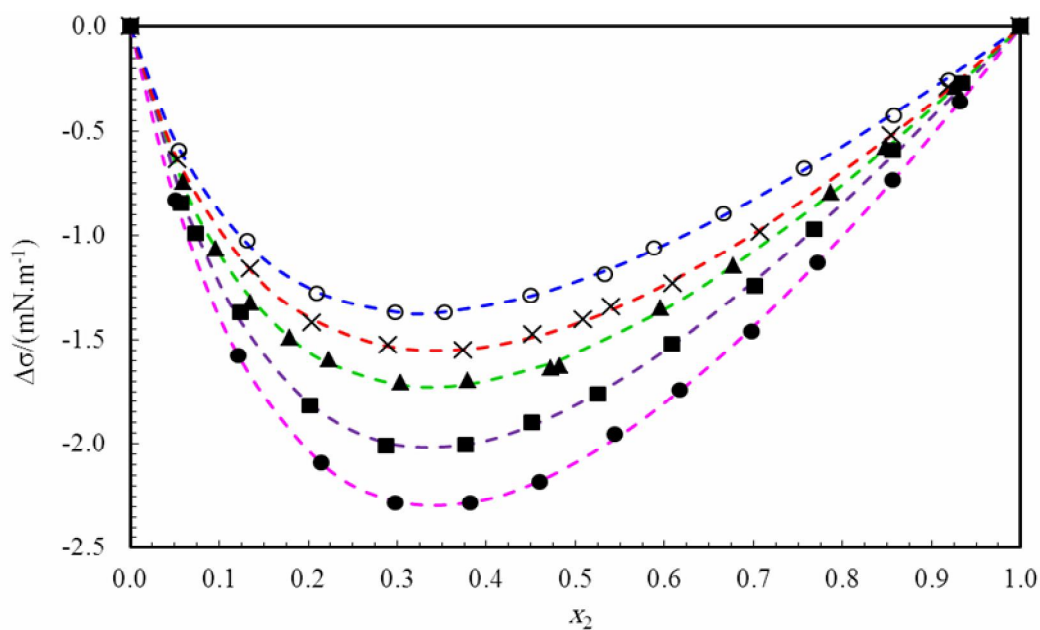


Fig. 6. Surface tension deviation, $\Delta\sigma$, against mole fraction, x_2 , for the binary systems of alkane (2)/THF (1) at 298.15 K. The symbols refer to the experimental data; the dashed curves represent the correlation with equation (14): (●) hexane, (■) heptane, (▲) octane, (×) nonane and (○) decane.

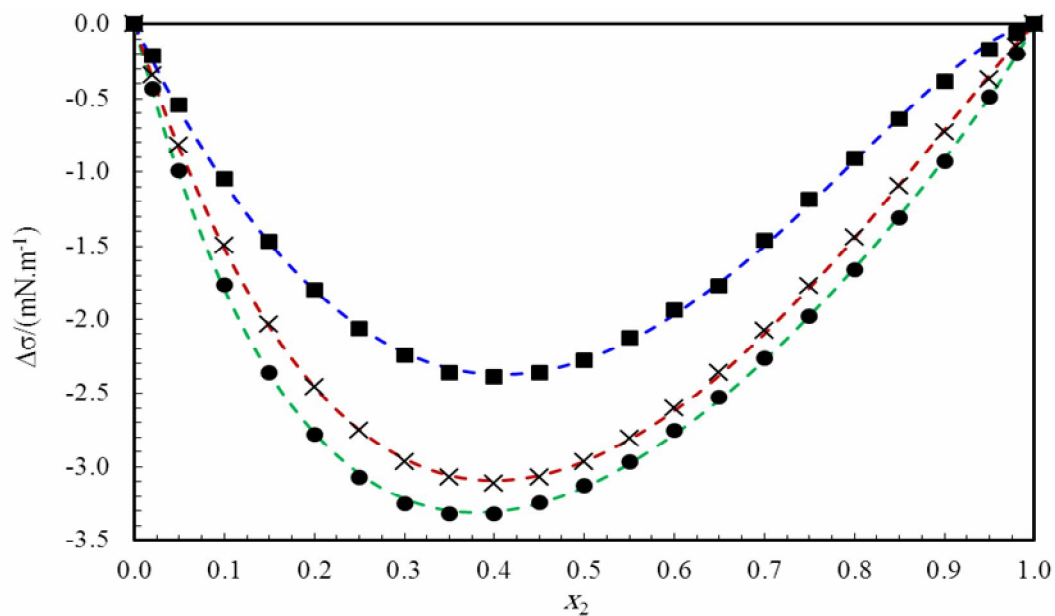


Fig. 7. Plot of surface tension deviation, $\Delta\sigma$, against mole fraction for ethanol (2)/DMSO (1) system. The symbols refer to the experimental data at various temperatures: (●) 298.15 K, (×) 308.15 K and (■) 318.15 K.

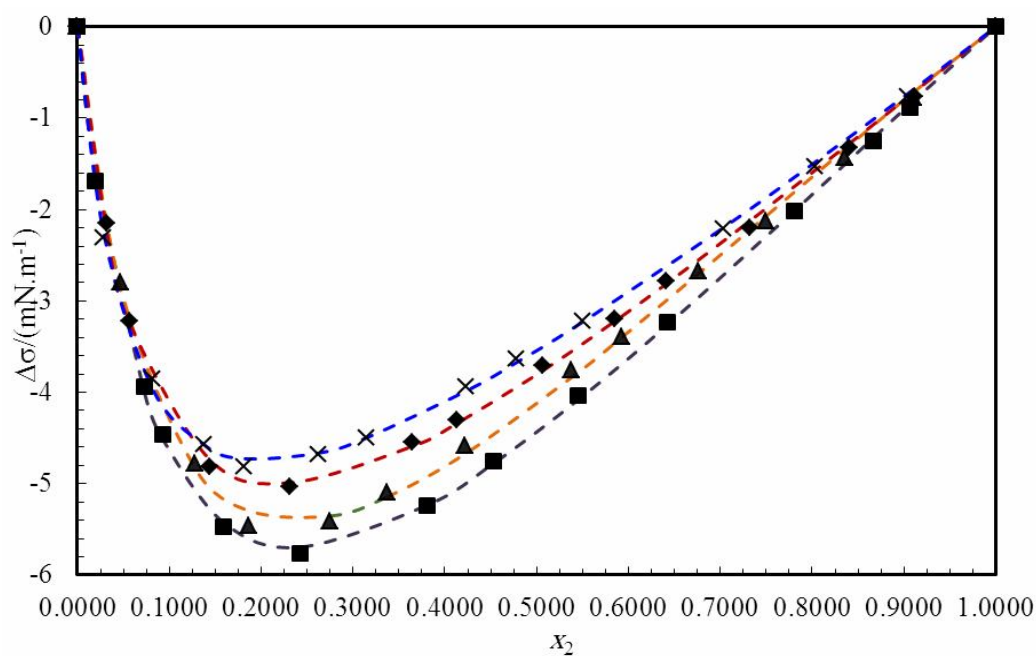


Fig. 8. Surface tension deviation, $\Delta\sigma$, against mole fraction, x_2 , for the binary systems of alkane (2)/1,4-dioxane (1) at 298.15 K. The symbols refer to the experimental data, the dashed curves represent the correlation with equation (14): (■) heptane, (▲) octane, (◆) nonane and (×) decane.

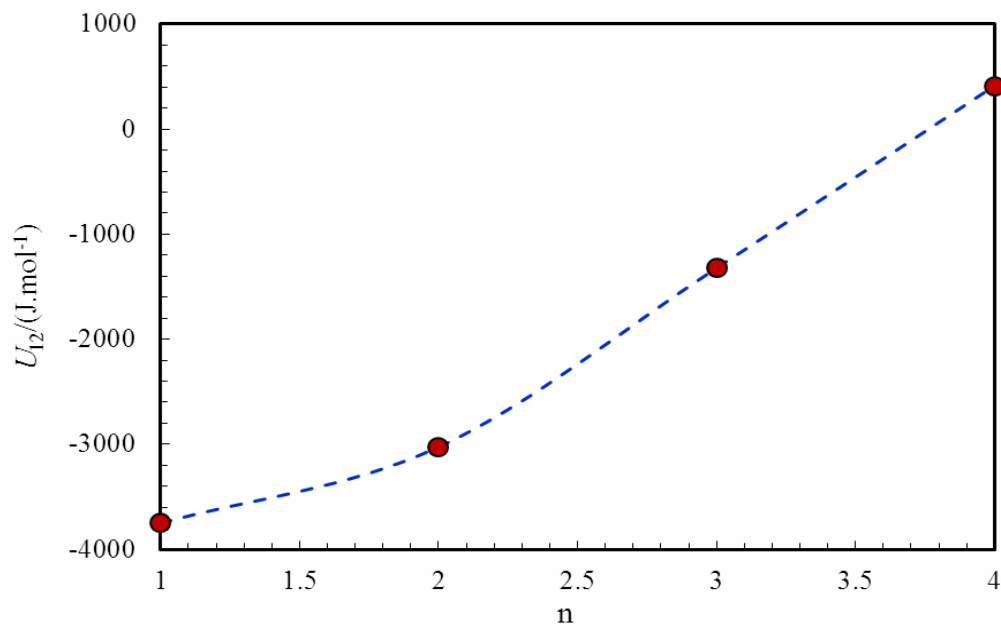


Fig. 9. The interaction energy, U_{12} , against number of carbon atom in hydrocarbon chain of alcohol at 298.15 K.

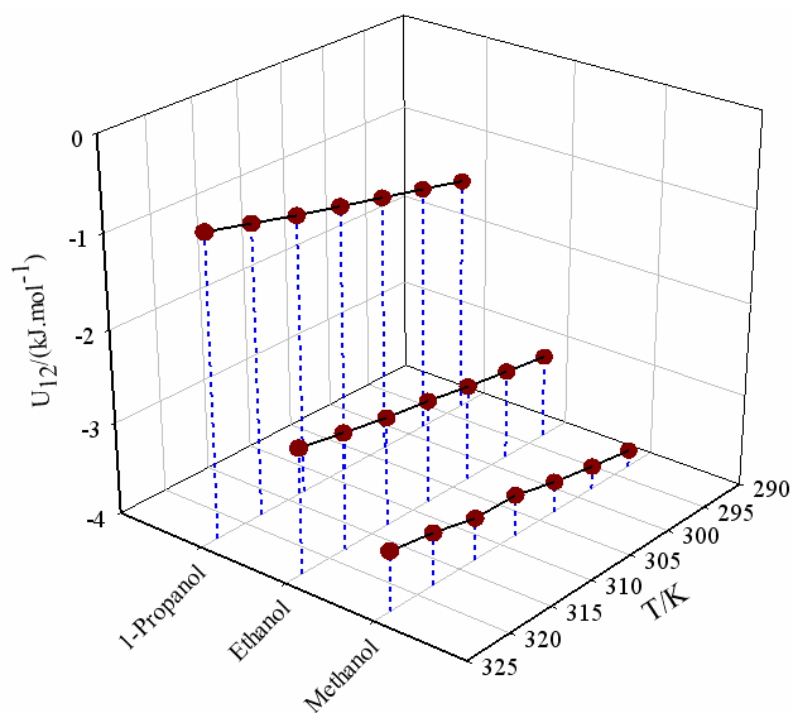


Fig. 10. Three dimensional representation of U_{12} (kJ mol⁻¹) for alcohol/water systems at various temperatures, calculated using parameters of Eq. (14) (The effect of temperature on the interaction energy).

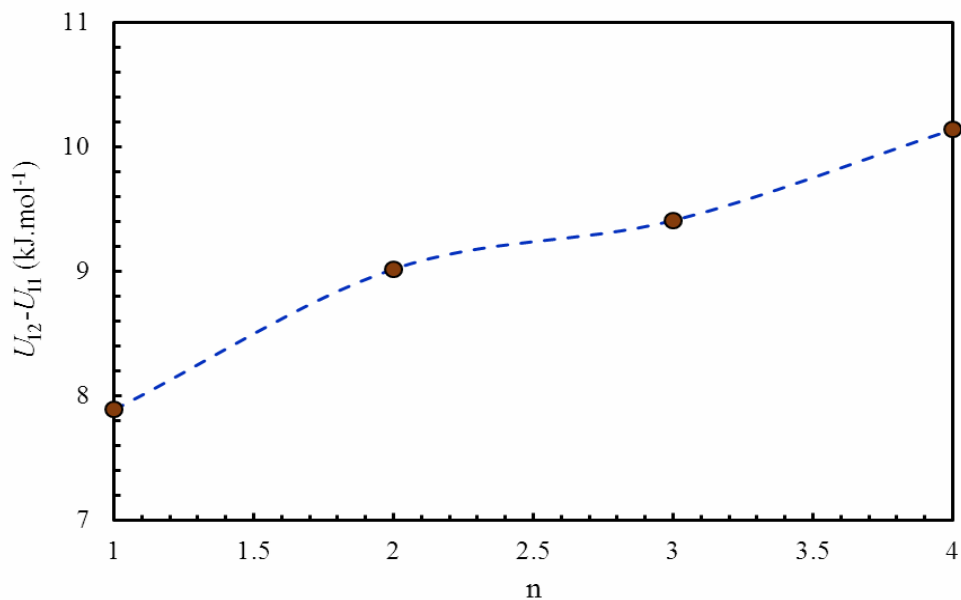


Fig. 11. The interaction energy, $U_{12} - U_{11}$, against number of carbon atom in hydrocarbon chain of carboxylic acid at 298.15 K.

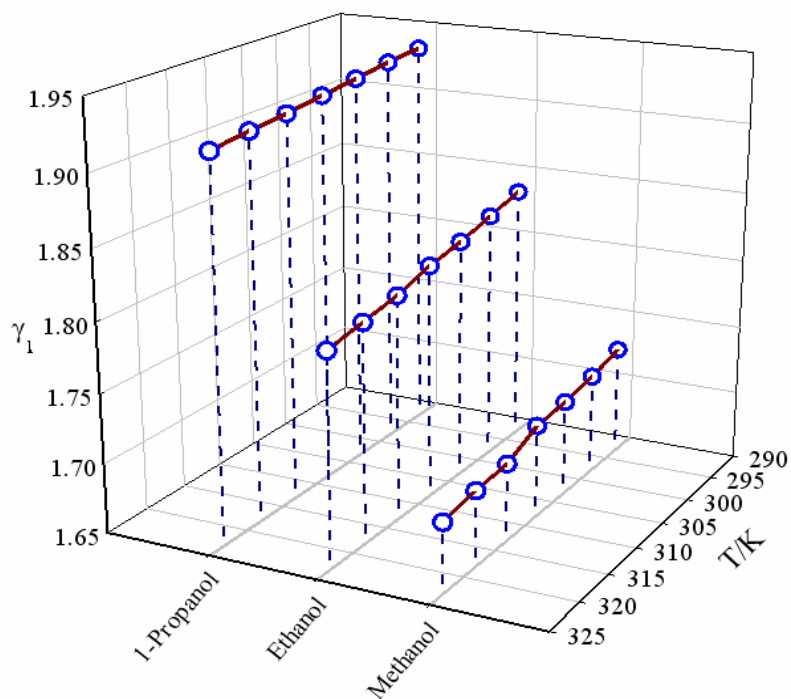


Fig. 12. Three dimensional representation of γ_1 in alcohol (2)/water (1) systems at various temperatures (The effect of temperature on the activity coefficient). The symbols refer to the calculated data using parameters of Eq. (14), and the solid curve is a guide for the eyes.

value of $U_{\text{water-water}}$ and at any studied temperature, the variation of $U_{\text{water-alcohol}}$ is as follow:

$$U_{\text{water-methanol}} < U_{\text{water-ethanol}} < U_{\text{water-1-propanol}} < U_{\text{water-1-butanol}}$$

Because of the less interaction energy between alcohol and water, the interaction energy between the studied alcohols and water (U_{12}) increased with increasing alkyl chain length of alcohol (from methanol to 1-butanol at 298.15 K) (see Figs. 9 and 10).

In binary solution of water/alcohols (methanol, ethanol, 1-propanol and isopropanol), the U_{12} values increased with increasing temperature over the studied temperatures from 298.15 K to 323.15 K (see Fig. 10 and Tables (3-1, 4-1, 5-1, 6-1 and 7-1)).

Also, this trend observed for obtained values of $U_{12} - U_{11}$ and U_{12} in binary mixtures of water (1)/carboxylic acid (2) (formic acid, acetic acid, propionic acid and butyric acid); these values increased with increasing the alkyl chain length of carboxylic acid at given temperatures (see Tables (3-1, 4-1, 5-1, 6-1 and 7-1) and Fig. 11).

It can be seen that in polar binary systems of water/studied carboxylic acid, due to molecular structure of organic acids demonstrates that strength of hydrogen bond between -COOH group of acid and water molecules (the interaction energy) increases with increasing the alkyl chain length of organic acid from formic acid to butyric acid at studied temperature.

The present dipoles in carboxylic acid structures allow these compounds to participate in energetically favorable hydrogen bonding (H-bonding) interaction with water, functioning as both H-bond donor and acceptor [27].

The surface tension of binary mixtures including DMSO and alcohols are extremely fascinating in light of the fact that DMSO provides a O=S group and alcohols provide an -OH group for interaction. In a section of this work, surface tension deviation of binary systems consisting of DMSO/(methanol, ethanol, 1-propanol, isopropanol, 1-butanol and 1-hexanol) were measured over the whole range of composition at the studied temperatures. In all studied systems of DMSO/alcohols, the values of $U_{12} - U_{11}$ are positive indicating that the intermolecular interactions between unlike molecules ($U_{\text{DMSO-alcohol}}$) in contact, are stronger than those between like molecules ($U_{\text{DMSO-DMSO}}$).

The results for other studied systems have been presented in Tables (3-7).

The functionality of the new model was evaluated by comparing the calculated surface tension deviation values with experimental values. The mean relative standard deviations (MRSDs) were calculated from Eq. (20)) (see 8th column of Tables 3-1, 4-1, 5-1, 6-1 and 7-1).

$$MRSD = 100 \times \left[\frac{1}{N} \sum_i \left(\frac{\sigma_{i,\text{exp}} - \sigma_{i,\text{cal}}}{\sigma_{i,\text{exp}}} \right)^2 \right]^{1/2} \quad (20)$$

Where N is the number of experimental data.

The obtained overall MRSD% (less than 4.5%, except for few binary mixtures) confirms that this proposed model is a reliable model to estimate the surface tension values according to the experimental behavior observed by different types of binary systems in this work. The value of MRSD% for almost half of our studied systems is less than 1%. These observed results show that there is a propensity of the average relative error to increase as deviation from linearity increases for some of the studied systems. The comparison between experimental and calculated values for some studied binary systems are graphically shown in Figs. 1-8.

Tables (3-2, 4-2, 5-2, 6-2 and 7-2), the activity coefficients of components (1 and 2) obtained by new model and UNIFAC model are presented.

In binary mixtures of water (1)/alcohols (2), the obtained values of γ_1 and γ_2 using new model decrease with increasing temperature. Figure 12 shows the γ_1 values as a function of temperature in three systems (water/methanol, ethanol and 1-propanol):

The values of activity coefficient of component 1 (water) increased with decreasing temperatures and increasing the alkyl chain of component 2 (alcohol). Therefore, considering the obtained activity coefficients data by two models, a great correlation of the experimental surface tensions data by this proposed model is caused to this new model to be a powerful model for predicting the activity coefficient just with having surface tensions data.

CONCLUSIONS

In this paper, in a new approach, LWW model with three adjusted parameters for calculating the surface tension

deviations of both organic and aqueous binary solutions is presented. The calculated values of surface tension deviation by this new model is remarkably well comparable with experimental data. The performance of the model is evaluated with 127 binary systems. The calculated overall MRSD value for the studied binary systems was found to be less than 2.8%. It is shown that, with a good accuracy, the proposed equation is simple and reliable for use and it has the best performance among the studied models. Then, using Wilson equations, the activity coefficients of components of all binary studied mixtures were calculated. These values were also compared with those of UNIFAC model. This model has the unique feature that only with having surface tension values of binary mixtures, the activity coefficients of components could be obtained. This is an exclusive power of this model compared to the other models used for correlating the surface tension deviation of binary mixtures. The present study also shows that correlation model based on surface tension data can be a promising method to calculate the thermodynamic parameters. Consequently, all predicted data verify high efficiency of the proposed model.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support received for this research work from the Research Council of Semnan University.

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