A Surface Tension Model for Liquid Mixtures Based on NRTL Equation*

LI Chunxi(李春喜) and **WANG Wenchuan(汪文川)**
College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, China

Abstract A new equation for predicting surface tension is proposed based on the thermodynamic definition of surface tension and the expression of the Gibbs free energy of the system. Using the NRTL equation to represent the excess Gibbs free energy, a two-parameter surface tension equation is derived. The feasibility of the new equation has been tested in terms of 124 binary and 16 multicomponent systems(13-ternary and 3-quaternary) with absolute relative deviations of 0.59% and 1.55% respectively. This model is also predictive for the temperature dependence of surface tension of liquid mixtures. It is shown that, with good accuracy, this equation is simple and reliable for practical use.
Keywords model, surface tension, liquid mixtures, Gibbs free energy, NRTL equation

1 INTRODUCTION

Surface tension of a liquid mixture is very important in the process design, because it plays an important role in affecting the mass and heat transfer at the interface. Critically reviewed surface tensions of pure liquids ranging from the melting to critical temperatures are available for a great number of substances[1,2]. In contrast, experimental data for liquid mixtures are seriously scarce, especially for the ternary or multi-component mixtures. The method for calculating surface tensions of liquid mixtures can be divided into two categories: those based on empirical relations and those derived from thermodynamics. The former comprises the MacLeod-Sugden and the corresponding state[3] methods. For the latter case there are a variety of equations, such as the Butler equation[4], the expressions based on the gradient theory[5], the perturbation theory[6] and the Kirkwood-Buff's radial distribution function theory[7,8]. Among the thermodynamic-based equations, the Butler type equation is widely accepted by engineers and extensively developed to different forms[9–11], while the equations based on the gradient theory, the perturbation theory and the Kirkwood-Buff theory has not been widely used in practice for their complexity and limited accuracy. In Butler type equations, activity coefficients model is needed for calculating the activity of each component both at the surface and in the bulk phases. By substituting UNIFAC activity coefficient expression to the original Butler equation, Li et al.[12] predicted surface tensions for liquid mixtures with good accuracy. Similarly, by using P-R equation-of-state for calculating fugacity coefficients, Hu et al.[13] developed a predictive model for surface tensions of multicomponent liquid mixtures. However, an iteration procedure is necessary to solve the Butler type equation, which introduces some difficulties for multicomponent systems. The aim of the present work is to develop an explicit and universal surface tension equation which just relies on the thermodynamic definition of surface tension.

2 THEORY

For a multicomponent liquid mixture at system temperature T and pressure p, the molar Gibbs free energy of the system can be expressed as

$$g(T,p) = \sum_i x_i[g_i^0(T,p)RT \ln x_i] + g^{ex} \qquad (1)$$

where x_i and $g_i^0(T,p)$ are the mole fraction and the molar Gibbs free energy of pure component i at system temperature and pressure. Suppose that the molar excess Gibbs free energy of the liquid phase, g^{ex}, can be represented by the NRTL equation[14], then we have

$$g(T,p) = \sum_i x_i[g_i^0(T,p) + RT \ln x_i] +$$

$$RT \sum_i x_i \frac{\sum_j x_j G_{ji}\tau_{ji}}{\sum_l x_l G_{li}} \qquad (2)$$

$$\tau_{ij} = (U_{ij} - U_{ii})/RT, \quad G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \qquad (3)$$

where the non-random parameter is set to 0.2, *i.e.* $\alpha_{ji} = \alpha_{ij} = 0.2$.

According to the surface thermodynamics, surface tension is defined as the Gibbs free energy required for the increase of unit area at constant temperature, pressure and composition, *i.e.*

$$\sigma = (\partial G^s/\partial A)_{T,p,\{n_i\}} = (\partial g^s/\partial A)_{T,p,\{x_i\}} \qquad (4)$$

where G^s and g^s related *via* $G^s = n_t^s g^s$ are the total and the molar Gibbs free energy in surface phase respectively, which are function of temperature, pressure, composition and surface area. In fact, the surface phase is of several 10^{-10} m thick and little is known a *priori* for the surface phase composition and properties. Hence it is assumed that the concentration and Gibbs free energy in surface phase are proportional to those in the bulk liquid phase, and Eq. (2) is suitable for representing Gibbs free energy in the surface phase. The approximations involved might be well adapted with the adjustable model parameters for a correlative equation for the binaries. With these assumptions and Eqs. (2)—(4), the expression for surface tension of a liquid mixture can be derived as

$$\sigma_{\mathrm{m}} = \sum_i x_i \sigma_i + RT \sum_i x_i$$
$$\left(\frac{\sum_j x_j G_{ji}[1 - \alpha_{ij}(\tau_{ji} - \bar{\tau}_i)]}{\sum_l x_l G_{li}} \left(\frac{\partial \tau_{ji}}{\partial A} \right)_{T,p,x} \right) \quad (5)$$

$$\left(\frac{\partial \tau_{ji}}{\partial A} \right)_{T,p,x} = \frac{1}{RT} \left[\frac{\partial(U_{ji} - U_{ii})}{\partial A} \right]_{T,p,x} \quad (6)$$

$$\bar{\tau}_i = \sum_l x_l G_{li} \tau_{li} / \sum_l x_l G_{li} \quad (7)$$

where the surface tension of pure component i at system temperature and pressure is defined as $\sigma_i = [\partial g_i^{0S}(T,p)/\partial A]_{T,p,x}$. Eq. (5) is the final expression for surface tension of a liquid mixture, and the adjustable model parameters for a binary system are $U_{ji} - U_{ii}$ and $[\partial(U_{ji} - U_{ii})/\partial A]_{T,p,x}$. The first term on the right hand side of Eq. (5) is the pure component contribution, and the second one is the excess surface tension $(\sigma^{\mathrm{ex}} = \sigma_{\mathrm{m}} - \sum_i x_i \sigma_i)$ arising from the cross interaction between species i and j. For an ideal solution the interaction energy between any species pair is identical, *i.e.* $U_{ii} = U_{jj} = U_{ij}$. In this case the excess surface tension term disappears and the surface tension of the ideal mixture equals to the mole fraction average of the surface tensions of pure components at system temperature and pressure. The physical meaning of the model parameters can be understood as follows: $U_{ji} - U_{ii}$ is directly related to the dimensionless parameter G_{ji}, which is used to account for the local composition effect in the liquid phase. On the other hand, $[\partial(U_{ji} - U_{ii})/\partial A]_{T,p,x}$ is a term which is analogical to the definition of the surface tension, hence it contributes to the excess surface tension.

3 CORRELATION OF BINARY SYSTEM

For the correlation of surface tensions for binary systems, there are 4 adjustable parameters, *i.e.*

$U_{12} - U_{11}$, $U_{21} - U_{22}$, $[\partial(U_{12} - U_{11})/\partial A]_{T,p,x}$ and $[\partial(U_{21} - U_{22})/\partial A]_{T,p,x}$. To reduce the number of the adjustable parameters, some postulates can be made. In this paper, we assume that the cross interaction energy is the arithmatic average of the pure components

$$U_{ij} = (U_{ii} + U_{jj})/2 \quad (8)$$

Then it follows

$$\tau_{ij} = -\tau_{ji} \quad (9)$$

$$(\partial \tau_{ij}/\partial A)_{T,p,x} = -(\partial \tau_{ji}/\partial A)_{T,p,x} \quad (10)$$

As a result, the surface tension equation for a binary system is given by

$$\delta^{\mathrm{ex}} = x_1 x_2 RT \left(\frac{\partial \tau_{21}}{\partial A} \right) \frac{G_{21} - 1 - \dfrac{\alpha_{12}\tau_{21}G_{21}}{x_1 + x_2 G_{21}}}{x_1 + x_2 G_{21}} \quad (11)$$

Note that for a binary system only two parameters are needed, *i.e.* $\dfrac{U_{12} - U_{11}}{R}$ and $\dfrac{\partial(U_{12} - U_{11})/\partial A}{R}$.

Performances of this model for calculating surface tensions of binary systems at ambient temperatures are extensively tested with 124 systems, and part of the results are listed in Table 1. For 124 binary systems studied, some are highly asymmetric in molecular interaction or in molecule size such as alcohol-alkane systems and some are of large difference in surface tension between pure components such as water-containing systems. The total average absolute relative deviation(AAD) is found to be 0.59%. Figs. 1 and 2 show some typical results for aqueous and non-aqueous binary systems. It is found that except for the systems with a turning point on the plot of excess surface tension *versus* mole fraction, *e.g.* the acetone-methanol system in Fig. 2, the new model can be applied to all kinds of binary systems even to aqueous solutions, for which many models failed.

4 PREDICTION FOR MULTICOMPONENT SYSTEMS

In order to test the applicability of the new equation to multicomponent systems, prediction has been made for 13 ternary and 3 quaternary systems. The average absolute relative deviations of our model (AAD1) and the ideal solution approximation (AAD2) are listed in Table 2. The overall AAD's for the 16 multi-component systems predicted with the above two methods are 1.55% and 15% respectively. Comparison of the present model with other Butler type equations has been made and the result is listed in Table 3. It is seen that the accuracy of the present model is comparible to that of Wang-Fu model[11], and a little bit superior to that of UNIFAC model[12] and Hu's model[13]. Fig. 3 shows a comparison between

Table 1   Correlation results and the model parameters for binary systems

| Component		T, K	$\dfrac{U_{12} - U_{11}}{R}$	$\dfrac{\partial(U_{12} - U_{11})}{R\partial A \times 10^{-5}}$	AAD, %
1	2				
1,3-propanediol	water	303	−2178.7	−178.95	0.65
acetic acid	acetone	298	−1218.5	39.25	0.2
acetic acid	benzene	308	−18.9	21099.6	0.12
acetic acid	cyclohexane	303	960	60.656	0.58
acetic acid	ethanol	298	11.56	−2405.98	0.66
acetic acid	water	298	−3367.8	−386.31	1.6
acetone	carbon disulfide	298	−5655.3	−56.71	0.9
acetone	ethanol	298	580.6	8.1935	0.23
AMP	water	298	−3841.2	−294.68	2.4
benzene	cyclohexane	293	764.2	46.223	0.13
benzene	n-hexane	293	1396.7	66.913	0.16
benzene	ethanol	298	−32.59	−930.75	0.14
benzene	methanol	298	−220.1	−77.132	0.08
benzene	acetone	298	−45.44	133.518	0.49
benzene	n-propanol	298	−65.2	−11.624	0.2
benzyl alcohol	ethyl acetate	298	1228.8	57.596	0.23
cyclohexane	n-hexane	293	379.4	102.914	0.23
ethyl acetate	acetic acid	298	49.78	240.03	0.39
ethyl acetate	benzene	298	−11.44	−762.84	0.22
ethyl acetate	ethanol	298	83.18	−76.970	0.85
ethanol	water	303	−3051.8	−390.73	0.85
formic acid	water	298	−1936.5	−264.57	0.5
iso-propanol	furfural	298	−1776.1	−147.48	0.13
iso-propanol	toluene	298	−372.1	−82.056	0.3
MDEA	water	298	−3675.5	−211.22	2.6
MEA	water	298	−2904.5	−133.16	0.38
methanol	acetone	308	−112.9	119.81	0.33
nitromethane	benzene	298	−127.7	−351.95	0.25
nitromethane	n-propanol	298	−183.5	−1057.5	0.32
toluene	1-propanol	298	−769.2	−80.563	0.71
toluene	benzyl alcohol	298	157.15	481.76	1.4
toluene	ethyl acetate	298	789.4	8.3468	0.11
toluene	furfural	298	−1253.2	−106.72	0.26
total average relative deviation(for 124 systems)				0.59	
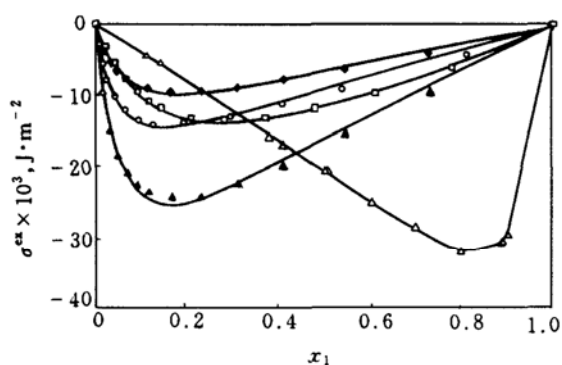
Figure 1   Comparison of excess surface tensions for binary aqueous solutions at 298.15 K
◆ MEA-H$_2$O; ▲HAc-H$_2$O; □ HCOOH-H$_2$O;
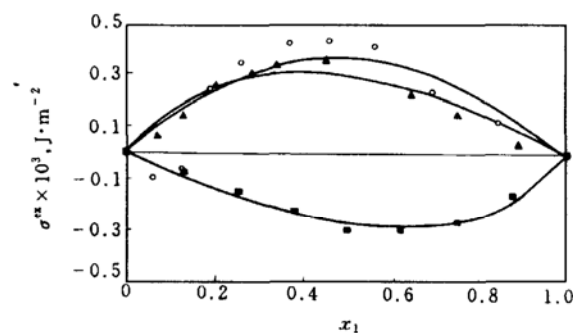△H$_2$O-acetone; ○ 1,3-propanediol-water; ——calculated

Figure 2   Comparison of excess surface tensions for non-aqueous binary solutions at 298.15 K
■ hexane-ethanol; ▲ethyl acetate-methanol;
○ methanol-acetone; ——calculated

Table 2 Predictions of surface tensions for multi-component systems

System				T, K	AAD1, %	AAD2, %	Ref.
cyclo-hexane	benzene	n-hexane		293	0.71	6.4	15
iso-propanol	toluene	furfural		293	1.5	11.7	16
nitromethane	benzene	n-propanol		298	1.4	9.1	16
benzyl alcohol	toluene	ethyl acetate		293	2.3	4.4	16
carbon bisulfide	methanol	acetone		298	1.1	11	17
water	benzene	acetone		303	2.2	24.9	18
acetic acid	acetone	ethanol	water	298	2.7	47.6	19
ethyl acetate	ethanol	acetic acid	benzene	298	2	1.9	19
ethyl acetate	ethanol	benzene		298	1.4	0.3	19
ethyl acetate	methanol	benzene		298	2.34	0.96	19
ethyl acetate	methanol	ethanol	benzene	298	0.97	0.79	19
ethyl acetate	methanol	ethanol		298	0.55	0.96	19
methanol	ethanol	benzene		298	1.75	1.47	19
MDEA	AMP	water		298	2.3	41.5	20
MDEA	MEA	water		298	0.65	26.7	21
MEA	AMP	water		298	1.1	50.5	21
total average relative deviation(for 16 systems)					1.55	15.0	

Table 3 Comparison with Butler type equations

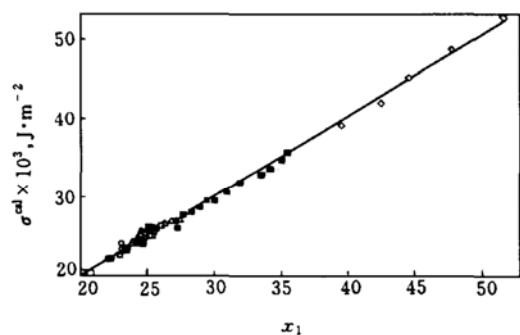| Model	Binary systems					Multicomponent systems		
	Type of calculation	No. of systems	Required data	No. of parameters	AAD, %	Type of calculation	No. of systems	AAD, %
This paper	Corr.	124	σ_i, σ_m^{exp}	2	0.59	Pred.	13	1.55
Wang Z.[19]	Corr.	253	σ_i, σ_m^{exp}	2	0.46	Pred.	12	2.90
Hu Y.[13]	Corr.	73	σ_i, V_i, σ_m^{exp}	1	1.35	Pred.	8	1.28
	Pred.	73	σ_i, V_i	0	3.31			
UNIFAC[12]	Pred.	100	σ_i, V_i, group parameter	0	2.53	Pred.	12	2.36

Figure 3 Comparison of predicted and experimental excess surface tensions for multicomponent systems at 298.15 K
■ iso-propanol-toluene-furfural;
△ ethylacetate-methanol-benzene;
○ carbon disulfide-methanol-acetone;
□ benzene-n-cyclohexane-n-hexane;
◇ MEA-AMP-H₂O; ——calculated

calculated and experimental results for some multi-component systems studied. As a whole, the predic-

tion results are quite satisfactory, and the model is of good accuracy and reliablility.

As can be seen from Table 1 that most of our correlation for the binary systems is around room temperature, this is restricted by the available experimental data. Now the problem is whether the model parameters obtained from correlating experimental data at room temperature is useful in predicting surface tension at other temperatures only with the temperature dependence consideration involved in the NRTL expression. In order to test this ability of the present model, surface tension is predicted by using the temperature independent model parameters and by using the ideal solution assumption which reflect the non-ideality of the solution. The overall prediction results with these two assumptions and the average relative deviations noted as AAD1 and AAD2 respectively are listed in Table 4. It is shown that the present model can satisfactorily represent the variation of surface tension with temperature for the liquid mixture and the AAD is found to be 1.9%.

Table 4 Surface tension prediction for liquid mixtures at higher temperatures

System			T, K	AAD1, %	AAD2, %	Ref.
AMP	water		323	3.2	26.5	20
			313	2.55	44.1	20
MEA	water		323	0.87	11.0	20
MEA	AMP	water	308	1.7	42.0	20
			323	3.1	45.0	20
MDEA	water		323	0.51	27.5	21
MDEA	AMP	water	323	2.1	52.0	21
propionic acid	water		323	4.2	71.4	22
			313	3.9	70.0	22
acetic acid	water		323	2.1	40.9	22
			313	1.67	40.0	22
formic acid	water		313	0.57	16.4	22
			323	0.77	16.6	22
ethylene glycol	water		373	1.9	11.6	23
			323	0.51	11.2	23
methanol	water		323	1.41	39.7	24
ethanol	water		323	2.8	68.9	24
Total average relative deviation				1.9	37.3	

As mentioned in the theory part of this paper, the NRTL equation is only one of many potential choices for representing the excess Gibbs free energy of the liquid phase. If the NRTL equation is replaced with a group contribution model, e.g. ASOG or UNIFAC, then it is possible to establish a predictive model, even for binary systems, which is attractive for practical engineering problems. This part of work is in process, and the results will be reported in our future work.

5 CONCLUSIONS

A new surface tension equation is proposed, which is different from the existing equations with respect to the theoretical background and formulation. In the derivation of the new model only the thermodynamic definition of surface tension and the expression of Gibbs free energy are used. In this study, the NRTL equation is chosen to represent the excess Gibbs free energy among many other options. The applicability of the new equation is exetensively tested with 124 binary, 13 ternary and 3 quaterny systems. The AAD for the correlation of binary and the prediction of multicomponent systems are 0.59% and 1.55% respectively. Further, the present model is able to account for the temperature dependence of surface tension of liquid mixtures. It is shown that, with good accuracy, this equation is simple and reliable for practical use.

NOMENCLATURE

A surface area, m^2

G Gibbs free energy, J

g molar Gibbs free energy, $J \cdot mol^{-1}$

n_i mole number of component i

n_t total mole number

p pressure, Pa

R gas constant, $8.314\,J \cdot mol^{-1} \cdot K^{-1}$

T temperature, K

U interaction energy, J

x_i mole fraction of component i

τ parameter in NRTL equation

α 0.2, non-random parameter

σ surface tension, $J \cdot m^{-2}$

Superscripts

ex   excess property

s   surface phase

0   pure component property

Subscripts

i, j, l component indices

m   mixture

x mole fraction concentration

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