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PREDICTION OF THE SURFACE TENSION OF BINARY AND MULTICOMPONENT LIQUID MIXTURES BY THE UNIFAC GROUP CONTRIBUTION METHOD *

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ABSTRACT

In this paper, a new method for the prediction of the surface tension for both binary and multicomponent organic systems is derived by introducing the well-known UNIFAC group contribution approach used in phase equilibrium calculations into the Butler equation. Only pure component properties and UNIFAC parameters are needed, and the prediction is successful. The total average relative deviations of the calculated values from the experimental values are 2.6% and 2.0% for 23 binary and 5 ternary solutions, respectively. The maximum deviations may be found for the systems containing both water and alcohols.

INTRODUCTION

The surface tension of liquid mixtures of organic non-electrolytes is one of many important properties frequently required in the design of processes. A simple and reliable method for the prediction of this property is of engineering and physicochemical interest because surface tension of solutions plays an important role in interphase heat and mass transfer. Over the years, many attempts have been made to develop a reliable model for the prediction of solution surface tension [1-9]. There are many methods available for pure liquids and binary solutions, but very few for multicomponent systems. The prediction of surface tension for multicomponent systems is of greater interest than that for pure liquids or binary mixtures since most liquid streams in the chemical industry are usually multicomponent.

Goldsack et al. [6,7] used a Newton-Raphson iterative technique to solve the implicit Butler equation to predict the surface tension for binary systems of organic non-electrolytes. Starting from the Gibbs-Duhem equation, Rong

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et al. [8] derived a theoretical model to predict the surface tension of binary solutions successfully, although the calculation procedure was rather complicated. Furthermore, it can not be used for multicomponent systems.

Fu Jufu et al. [5,9] have developed an equation from the Hilderbrand–Scott equation combined with the local composition concept proposed by Wilson. The equation can be used not only for correlation of the surface tension data for binary systems, but also for the prediction of the surface tension of multicomponent solutions. Unfortunately, in general, the experimental data of binary mixtures are required to determine the model parameters involved in the equations. It is therefore desirable to develop a new method by which the surface tension of binary and multicomponent systems can be calculated with satisfactory precision, and only pure component properties are needed.

One of the well-known and successful group contribution methods used for the calculation of activity coefficients in the liquid phase is the UNIFAC model [10]. It has already been used successfully in many areas [11–13]. In this paper, a new method for the prediction of the surface tension of both binary and multicomponent organic systems is derived by introducing the UNIFAC model into the Butler equation derived in 1932 [14]. Only pure component properties and UNIFAC parameters, which are the same as for the calculation of the vapour–liquid equilibrium, are needed and the prediction precision can meet the requirement of engineering design.

THEORY

Based on the most fundamental assumption that the surface layer can be represented by a physical region of constant and uniform composition and treated thermodynamically as a separate phase located between the bulk liquid and vapour phases, the Butler equation was derived from thermodynamic theory in 1932

$$\sigma^{\mathrm{m}} = \frac{A_i}{\bar{A}_i}\sigma_i + \frac{RT}{\bar{A}_i}\ln\frac{a_i^{\mathrm{s}}}{a_i^{\mathrm{B}}} \tag{1}$$

where σ^{m} represents the surface tension of the mixture, σ_i is the surface tension of pure component i, A_i and $\bar{A}_i$ are the molar surface area and the partial molar surface area of component i, respectively, a_i^{B} is the activity of component i in the bulk phase, a_i^{s} is the activity of component i in the surface phase, and R and T are the gas constant and absolute temperature of the system, respectively.

Introducing the activity coefficients $\gamma_i^{\mathrm{B}} = a_i^{\mathrm{B}}/\chi_i^{\mathrm{B}}$ and $\gamma_i^{\mathrm{s}} = a_i^{\mathrm{s}}/\chi_i^{\mathrm{s}}$, eqn. (1) may be transformed to

$$\sigma^{\mathrm{m}} = \frac{A_i}{\bar{A}_i}\sigma_i + \frac{RT}{\bar{A}_i}\ln\frac{\gamma_i^{\mathrm{s}}\chi_i^{\mathrm{s}}}{\gamma_i^{\mathrm{B}}\chi_i^{\mathrm{B}}} \tag{2}$$

If the relations

$$\gamma_i^{s} = \gamma_i^{s}(\chi_i^{s})$$

and

$$\gamma_i^{B} = \gamma_i^{B}(\chi_i^{B})$$

are known, and A_i and $\bar{A}_i$ are obtained, eqn. (2), combined with the equation

$$\sum_{i=1}^{N} \chi_i^{s} = 1$$

can be solved to obtain the value of σ^{m}. Here, N is the number of components in the mixture.

For calculating the surface tension of a solution σ^{m} by eqn. (2), two fundamental assumptions are proposed.

(1) The partial molar surface area $\bar{A}_i$ is equal to the molar surface area A_i of the pure component i, which is calculated from the equation:

$$A_i = V_i^{2/3} N_0^{1/3} \tag{3}$$

where V_i is the liquid molar volume of pure component i and N_0 represents Avogadro's number.

(2) The relations $\gamma_i^{s} = \gamma_i^{s}(\chi_i^{s})$ and $\gamma_i^{B} = \gamma_i^{B}(\chi_i^{B})$ can be described by the UNIFAC group contribution model used in phase equilibrium calculations. That is to say, the surface activity coefficients (γ_i^{s}) and the bulk activity coefficients (γ_i^{B}) can all be calculated by the UNIFAC model with the same interaction parameters as used for the phase equilibrium calculation.

CALCULATION METHOD

From the first assumption, eqn. (2) can be changed to

$$\sigma^{m} = \sigma_i + \frac{RT}{A_i} \ln \frac{\gamma_i^{s}\chi_i^{s}}{\gamma_i^{B}\chi_i^{B}} \tag{4}$$

Then, by use of the second assumption, the values of σ^{m} and χ_i^{s} can be calculated from eqn. (4) and $\sum_{i=1}^{N}\chi_i^{s} = 1$.

A computerized method suitable for solving these equations may contain the following steps.

(1) Calculating the bulk activity coefficients γ_i^{B} and molar surface area A_i for a system containing N components at temperature T and bulk mole fraction χ_i^{B} by use of the UNIFAC model and eqn. (3), respectively.

(2) Estimating the first approximations of σ^{m} and χ_i^{s} from

$$\sigma^{m}(\text{est}) = \sum_{i=1}^{N} \chi_i^{B}\sigma_i \tag{5}$$

and

$$\chi_i^{\mathrm{s}}(\mathrm{est}) = \chi_i^{\mathrm{B}} \exp\left(\frac{A_i[\sigma^{\mathrm{m}}(\mathrm{est}) - \sigma_i]}{RT}\right) \tag{6}$$

(3) Normalizing $\chi_i^{\mathrm{s}}(\mathrm{est})$ by

$$\chi_i^{\mathrm{s}}(\mathrm{est}) = \frac{\chi_i^{\mathrm{s}}(\mathrm{est})}{\sum_{i=1}^{N} \chi_i^{\mathrm{s}}(\mathrm{est})} \tag{7}$$

(4) Calculating the surface activity coefficients $\gamma_i^{\mathrm{s}}(\mathrm{est})$ by the UNIFAC model [10].

(5) Calculating the surface tension of the mixture $(\sigma^{\mathrm{m}})_i(\mathrm{est})$ from the surface tension of the i component σ_i by use of

$$(\sigma^{\mathrm{m}})_i(\mathrm{est}) = \sigma_i + \frac{RT}{A_i} \ln \frac{\gamma_i^{\mathrm{s}}(\mathrm{est})\chi_i^{\mathrm{s}}(\mathrm{est})}{\gamma_i^{\mathrm{B}}\chi_i^{\mathrm{B}}} \tag{8}$$

taking

$$\sigma^{\mathrm{m}}(\mathrm{est}) = \frac{\sum_{i=1}^{N} (\sigma^{\mathrm{m}})_i(\mathrm{est})}{N} \tag{9}$$

(6) Calculating the new surface mole fraction $\chi_i^{\mathrm{s}}(\mathrm{est})$ from the new value of $\sigma^{\mathrm{m}}(\mathrm{est})$ by

$$\chi_i^{\mathrm{s}}(\mathrm{est}) = \frac{\gamma_i^{\mathrm{B}}\chi_i^{\mathrm{B}}}{\gamma_i^{\mathrm{s}}(\mathrm{est})} \exp\left(\frac{A_i[\sigma^{\mathrm{m}}(\mathrm{est}) - \sigma_i]}{RT}\right) \tag{10}$$

(7) Taking

$$\sigma^{\mathrm{m}} = \sigma^{\mathrm{m}}(\mathrm{est}) \text{ and } \chi_i^{\mathrm{s}} = \chi_i^{\mathrm{s}}(\mathrm{est}) \tag{11}$$

and finishing the calculation the value of $|\Sigma_{i=1}^{N}\chi_i^{\mathrm{s}}(\mathrm{est}) - 1|$ is less than or equal to ϵ, the convergence criterion, or returning to step (3) and carrying out a new calculation run until convergence is reached.

RESULTS AND DISCUSSION

The surface tensions of 23 binary organic systems and 5 ternary systems have been predicted by the new method proposed by the authors. The results obtained are tabulated in Tables 1 and 2, respectively. The binary systems involve a variety of organic compounds: alkanes, aromatic hydrocarbons, halohydrocarbons, alcohols, ketones, ethers, organic acids, amines, water and so on. The five ternary systems are (1) benzene–cyclohexane–*n*-hexane, (2) nitromethane–benzene–*n*-propyl alcohol, (3) isopropyl alcohol–

TABLE 1

Predicted results of the surface tension for binary systems

No.	System	Temperature (K)	No. of data points	$\bar{\Delta}$
1	(1) Benzene	293.15	8	2.45
	(2) *n*-Heptane	313.15	8	2.11
		333.15	8	1.80
2	(1) Benzene	293.15	10	2.34
	(2) Cyclohexane	313.15	11	2.41
		333.15	11	2.73
3	(1) Acetone	293.15	7	0.17
	(2) Carbon tetrachloride	313.15	7	0.48
4	(1) Ethanol (2) Water	298.15	15	9.90
5	(1) Ethanol (2) *n*-Hexane	295.15	5	1.51
6	(1) Ethanol (2) Cyclohexane	298.15	5	1.41
7	(1) Ethanol (2) Benzene	298.15	9	1.69
8	(1) Methanol (2) Water	298.15	9	5.73
9	(1) Methanol	293.15	11	0.14
	(2) Ethanol	313.15	11	0.00
		333.15	11	0.00
10	(1) Acetone (2) Benzene	291.15	9	0.19
11	(1) Ethyl ether (2) Chloroform	291.15	9	1.59
12	(1) Acetone (2) Water	293.15	13	4.80
13	(1) Acetone (2) Chloroform	291.15	9	0.53
14	(1) Formic acid (2) *n*-Hexane	293.15	4	3.49
15	(1) Isopropyl alcohol (2) Benzene	293.15	10	0.53
16	(1) *n*-Hexane (2) Benzene	293.15	5	1.07
17	(1) Acetic acid (2) Benzene	293.15	5	3.78

TABLE 1 (continued)

No.	System	Temperature (K)	No. of data points	$\bar{\Delta}$
18	(1) Ethanol (2) Carbon tetrachloride	293.15	5	3.28
19	(1) Ethanol (2) Chloroform	293.15	4	1.60
20	(1) Ethanol (2) *p*-Dichlorobenzene	328.15	9	4.28
21	(1) Carbon tetrachloride (2) Chloroform	293.15	4	4.02
22	(1) Carbon tetrachloride (2) Benzene	293.15	5	0.21
23	(1) Aniline (2) Cyclohexane	305.15	9	3.37

toluene–furfural, (4) toluene–benzyl alcohol–ethyl acetate, and (5) water–benzene–acetone. The average relative deviation, $\bar{\Delta}$, is given by

$$\bar{\Delta} = 100\left[\sum_{j=1}^{C} \frac{|\sigma_{\mathrm{cal}}^{\mathrm{m}} - \sigma_{\mathrm{exp}}^{\mathrm{m}}|}{\sigma_{\mathrm{exp}}^{\mathrm{m}}} \Big/ C\right] \tag{12}$$

TABLE 2

Predicted results of the surface tension for multicomponent systems

No.	System	Temperature (K)	No. of data points	$\bar{\Delta}$
1	(1) Benzene (2) Cyclohexane (3) *n*-Hexane	293.15	35	3.27
2	(1) Toluene (2) Benzyl alcohol (3) Ethyl acetate	298.15	16	0.53
3	(1) Nitromethane (2) Benzene (3) *n*-Propyl alcohol	298.15	16	1.28
4	(1) Isopropyl alcohol (2) Toluene (3) Furfural	298.15	16	1.75
5	(1) Water (2) Benzene (3) Acetone	303.15	29	2.93

where C is the number of data points, and $\sigma_{\mathrm{cal}}^{\mathrm{m}}$ and $\sigma_{\mathrm{exp}}^{\mathrm{m}}$ represent the calculation and experimental values of the surface tension of the solution, respectively.

For the 23 binary and the 5 ternary systems, the total average relative deviations shown in Tables 1 and 2 are 2.6% and 2.0%, respectively. As we know, water usually possesses a much larger surface tension than organic compounds and the surface tension plots of organic aqueous solutions show a rapid surface tension drop with concentration at very low concentrations of solute for a wide variety of organic solutes. This is difficult to describe quantitatively. However, the new method proposed by the authors can predict the surface tension of aqueous non-electrolyte systems well. At the same time, the calculation procedure established in this paper can rapidly converge, not only for binary systems but also for multicomponent systems. Multipeak phenomena do not occur in the calculation. All of these show that the new method is reliable and efficient.

It is also noted that there is still a substantial deviation for the water–ethanol system which may result from the large difference between the water molecules and the ethanol molecules. This large difference makes the two assumptions on which the new method is based less valid for this system, although the second assumption gives a certain reasonable consideration to the non-ideality of the bulk and surface phases.

CONCLUSIONS

The method combining the Butler equation with the UNIFAC model can predict the surface tension of a variety of organic solutions successfully. Only pure component properties and UNIFAC parameters are needed. The iterative calculation procedure of this new method can rapidly converge. It can be applied not only to binary systems but also to multicomponent systems with acceptable precisions in engineering design. It is shown that the new method proposed by the authors is simple, reliable, practical and efficient. At the same time, the new method has extended the application of the UNIFAC model, which has been used widely in phase equilibrium calculations.

However, somewhat larger deviations are encountered for the systems containing both water and alcohols. Hence, further work needs to be done on improving the precision of the prediction of the surface tensions for these systems.

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