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ON BOUNDARY CONDITIONS BETWEEN CONSTANTS OF WILSON AND NRTL EQUATIONS IN THREE- AND MORE-COMPONENT SYSTEMS

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Certain restraining conditions between binary constants must be fulfilled if Wilson and NRTL equations, expressing the composition dependence of liquid phase activity coefficients in multicomponent systems, are to be consistent with the theoretical model.

Wilson[1] published a very useful equation which is based on a model for excess energy of mixing. He introduced the concept of nonrandomness and generalized in certain sense the Flory–Huggins theory. Wilson equation has two adjustable parameters per binary system and its flexibility and ability to predict the behaviour of multicomponent systems is very good[2]. Wilson equation is not applicable to partially miscible liquid mixtures. For this reason, he modified it by introducing the third empirical parameter. The modified equation cannot be, however, generalized for three-component systems unless the third binary constant is the same for all binary pairs. To overcome this difficulty, Renon and Prausnitz[3] combined Wilson's local mole fraction concept with Scott's two-liquid theory of mixtures[4] and obtained expressions for activity coefficients which have three adjustable parameters per binary system. Their NRTL equation can be used for systems with limited miscibility and extended to a mixture of more than two components using binary constants only. The suitability of NRTL equation is very good both for the correlation of experimental data and for the prediction of behaviour of multicomponent systems[3,5].

In this contribution it is shown that certain boundary conditions must be fulfilled between the constants of Wilson and NRTL equations if the expressions for the three- and more-component system are to be consistent with the theoretical model. The Wilson constants Λ_{ij} and Λ_{ji} are defined by the following equations

$$\Lambda_{ij} = (V_j/V_i) \exp \left[-(g_{ij} - g_{ii})/RT \right] , \quad (1)$$

$$\Lambda_{ji} = (V_i/V_j) \left[\exp -(g_{ij} - g_{jj})/RT \right] , \quad (2)$$

where V_i, V_j are liquid molar volumes of components i, j, R the gas constant, T absolute temperature, and $(g_{ij} - g_{ii})$, $(g_{ij} - g_{jj})$ denote the Wilson energy terms.

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According to Eqs (*1*) and (*2*) we can write for the ternary system

$$\ln(\Lambda_{ij}/\Lambda_{ji}) - 2\ln(\Lambda_j/V_i) = (g_{ii} - g_{jj})/RT, \tag{3}$$

and similarly

$$\ln(\Lambda_{ik}/\Lambda_{ki}) - 2\ln(V_k/V_i) = (g_{ii} - g_{kk})/RT, \tag{4}$$

$$\ln(\Lambda_{jk}/\Lambda_{kj}) - 2\ln(V_k/V_j) = (g_{jj} - g_{kk})/RT. \tag{5}$$

It is evident from Eqs (*3*), (*4*) and (*5*) that Wilson constants in ternary system are related by the equation

$$\ln(\Lambda_{jk}/\Lambda_{kj}) = \ln(\Lambda_{ik}/\Lambda_{ki}) - \ln(\Lambda_{ij}/\Lambda_{ji}) \tag{6}$$

which can be written in the form

$$\Lambda_{jk}/\Lambda_{kj} = (\Lambda_{ik}/\Lambda_{ki})(\Lambda_{ji}/\Lambda_{ij}). \tag{7}$$

The extension to four- and more-component systems is straightforward, and results are summarized in Table I, where number of restraining conditions in multicomponent systems is presented, too. NRTL equation characterises the binary system by means of the following constants:

$$\tau_{ij} = (g_{ij} - g_{jj})/RT, \quad \tau_{ji} = (g_{ij} - g_{ii})/RT, \qquad (8), (9)$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}), \quad G_{ji} = \exp(-\alpha_{ij}\tau_{ji}). \qquad (10), (11)$$

It is seen that three parameters (τ_{ij}, τ_{ji} and α_{ij}) are necessary for the description of the binary system. According to Eqs (*8*) and (*9*) we can write for the ternary system

$$\tau_{ij} = (g_{ij} - g_{jj})/RT, \quad \tau_{ji} = (g_{ij} - g_{ii})/RT, \qquad (12), (13)$$

$$\tau_{ik} = (g_{ik} - g_{kk})/RT, \quad \tau_{ki} = (g_{ik} - g_{ii})/RT, \qquad (14), (15)$$

$$\tau_{jk} = (g_{jk} - g_{kk})/RT, \quad \tau_{kj} = (g_{jk} - g_{jj})/RT. \qquad (16), (17)$$

It can easily be shown from Eqs (*12*)–(*17*) that NRTL constants in the ternary system are related by the equation

$$\tau_{jk} - \tau_{kj} = \tau_{ik} - \tau_{ki} - (\tau_{ij} - \tau_{ji}). \tag{18}$$

The extension to four- and more-component systems is evident and the results are summarized in Table I.

TABLE 1

Boundary Conditions between Constants of Wilson and NRTL Equations in Multicomponent System

Number: M components, C constants, F free constants, B boundary conditions.

M	C		F		B
	Wilson	NRTL	Wilson	NRTL	
2	2	3	2	3	0
3	6	9	5	8	1
4	12	18	9	15	3
5	20	30	14	24	6
6	30	45	20	35	10
.	.	.	.	.	.
.	.	.	.	.	.
.	.	.	.	.	.
M	$M(M-1)$	$1{\cdot}5M(M-1)$	$0{\cdot}5M(M+1)-1$	M^2-1	$0{\cdot}5M(M-3)+1$

It can be concluded: If we wish to be consistent with Wilson and Renon (NRTL) model, we cannot use constants evaluated from binary experimental data directly to the characterization of three- and more-component systems. The entire adjustment for the multicomponent system must be made in such a way that restraining conditions (7) or (*18*) are fulfilled.

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