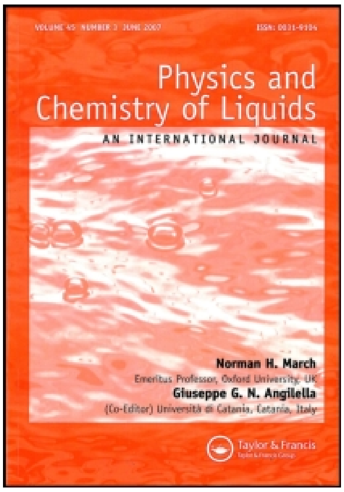

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

New Local Composition Model for Excess Gibbs Energy. I. Application for the Correlation of Isothermal VLE Data

Paweł Gierycz[a]
[a] Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland

To cite this Article Gierycz, Paweł(1990) 'New Local Composition Model for Excess Gibbs Energy. I. Application for the Correlation of Isothermal VLE Data', Physics and Chemistry of Liquids, 22: 3, 177 — 190
To link to this Article: DOI: 10.1080/00319109008028808
URL: http://dx.doi.org/10.1080/00319109008028808

Phys. Chem. Liq., 1990, Vol. 22, pp. 177–190
Reprints available directly from the publisher
Photocopying permitted by license only

NEW LOCAL COMPOSITION MODEL FOR EXCESS GIBBS ENERGY.
I. APPLICATION FOR THE CORRELATION OF ISOTHERMAL VLE DATA

PAWEŁ GIERYCZ*

Institute of Physical Chemistry, Polish Academy of Sciences,
Kasprzaka 44/52, 01-224 Warsaw, Poland.

(Received 5 June 1990)

A new local composition model for the excess Gibbs energy is derived from generalized lattice theory. The applicability of the model to the calculation of isothermal VLE data has been checked on a series of various binary systems. The results obtained show the superiority of the proposed model over previous proposals (the NRTL, Wilson, UNIQUAC) with the same number of adjustable parameters. Some recommendations about the use of the model have been made.

KEY WORDS: Lattice model, local composition, excess Gibbs energy calculation, correlation equation, correlation of VLE data.

INTRODUCTION

The complex nature of liquid mixtures is rather difficult to describe in detail. One of the popular methods is to describe the liquid as a well ordered lattice. The most important seems to be the Guggenheim quasichemical model[1] where the liquid is treated as a lattice with coordination number "z". Each lattice segment is in direct contact with z neighboring segments through "z" contact sites. All the segments are of equal size (unit segments) and each molecule in the liquid is built of such segments. Application of statistical mechanics to the simple lattice structure described above enables, in principle, calculation of the thermodynamic properties of the lattice.

This model however has too many arbitrary assumptions concerning the shape of the molecules (segments) and therefore is rather far from the reality. Let us attempt to derive the lattice model in the most general way.

---

* Address for correspondence until 20.05.1991, Dept. of Chemistry and Chem. Eng., Kanazawa University, Kanazawa, Ishikawa 920, Japan.

THE EXTENDED LATTICE MODEL

As previously the liquid is treated as a lattice but the molecules can act each on other according to their interaction potentials. It means that the molecular interactions are not reduced merely to those of neighboring molecules.

It has been assumed that the molecules can act on each other by their active sites and that the interaction potential for the same kind of interactions is always the same (i.e. u_{ij} potential is always constant independently of the position of "i" and "j" active sites). It has been assumed also that the lattice volume does not depend on the configuration of molecules (excess volume is equal to zero) and therefore the configurational contribution to the lattice partition function can be separated from other contributions (rotational, vibrational).

The configurational partition function Ω^* can be calculated from the following equation:

$$\Omega^* = \sum_i w_i \exp\left(\frac{u_i}{kT}\right) \tag{1}$$

where: the summation goes over all possible energy levels of the lattice, w_i is a combinational factor denoting the number of possible lattice configurations, for which the lattice has the energy u_i.

For the macroscopic system as the most probable energy level should be entirely dominant, one can justify the replacement of the sum in Eq. (1) by its maximum term (maximization):

$$\Omega^* = W^* \exp\left(\frac{U^*}{kT}\right) \tag{2}$$

where: * indicates the value for the maximum term. The remaining problem is to find an expression for W^* and U^*.

The total configurational energy of the lattice is assumed to be the sum of contributions from all the binary contact of active sites with u_{ij} being the pair potential for an interaction between sites and molecules i and j:

$$U^* = (\tfrac{1}{2}) \sum_i \sum_j N_{ji} u_{ji} \tag{3}$$

where: the factor $\frac{1}{2}$ reflects that two contact sites are involved in each contact, N_{ji} is the total number of contact sites on molecules i involved in contacts with sites belonging to molecules j.

The combinatorial factor w_i in Eq. (1) proposed by Guggenheim[1] represents the number of indistinguishable ways of arranging all the mutual contacts in the lattice, which means that they can be arranged independently of each other.

This is not the case and Larsen[2] proposed the modification of the factor w_i in order to obtain the correct value for random conditions:

$$W^* = w^0 \prod_i \prod_j \frac{((\frac{1}{2})N_{ji}^0)!}{((\frac{1}{2})N_{ij})!} \tag{4}$$

where the superscript ^{0} denotes random conditions.

Now it is possible to calculate the configurational partition function Ω^*. The maximum term in Eq. (2) is obtained by differentiation of $\ln \Omega^*$ with respect to the independent N_{ij}. For the maximum therm all these derivatives must be equal to zero.

In this differentiation Stirling's approximate formula is used:

$$\ln(n!) = n \ln(n) - n \tag{5}$$

The number of contacts on component i involved in contacts with sites on component j must be the same as the number of contacts of component j involved in contacts with sites on i (i.e. the contact balance must be fulfilled). This gives the following restrictions on N_{ji}'s:

$$N_{ji} = N_{ij} \tag{6}$$

$$N_i = \sum_j N_{ji} \tag{7}$$

where: N_i is the total number of contact of component i.

Selection of all N_{ji} with j larger than i as the independent variables and differentiation of $\ln \Omega^*$ with respect to these yields the following expression:

$$\begin{aligned}\frac{\partial \ln \Omega^*}{\partial N_{ji}} &= -(\tfrac{1}{2})(\ln N_{ij} + \ln N_{ji} - \ln N_{ii} - \ln N_{ij}) \\ &\quad -(\tfrac{1}{2})(u_{ij} + u_{ji} - u_{ii} - u_{jj})\end{aligned} \tag{8}$$

Setting Eq. (8) equal to zero we can calculate the values of N_{ji} corresponding to the maximum term in Eq. (2):

$$N_{ij}N_{ji} = N_{ii}N_{jj} \exp\left(-\frac{w_{ij}}{kT}\right) \tag{9}$$

with w_{ij} being the lattice interchange energy:

$$w_{ij} = u_{ij} + u_{ji} - u_{ii} - u_{jj} \tag{10}$$

If we assume that each molecule of type i may contact with molecules of type i by p active sites, and each j molecule may contact with j molecules by q active sites and each i molecule may contact with j molecules by z active sites than the total number of contacts of "$i - i$", "$j - j$" and "$i - j$" type can be written as follows:

$$N_{ii} = n_{ii}^p \tag{11}$$

$$N_{jj} = n_{jj}^q \tag{12}$$

$$N_{ij} = n_{ij}^z \tag{13}$$

where n_{ij} is a number of molecules of type i around a molecule j and can be calculated as a function of intermolecular distance r:

$$n_{ij} = 4\pi n_i/V \int_0^r r^2 g_{ij}(r) dr \tag{14}$$

where n_i is the total number of molecules i in the system, V is the volume of the system, and $g_{ij}(r)$ is the radial distribution function.

Substituting Eqs. (11, 12, 13) into Eq. (9) we obtain:

$$n_{ij}^{z} n_{ji}^{z} = n_{ii}^{p} n_{jj}^{q} \exp\left(-\frac{w_{ij}}{kT}\right) \tag{15}$$

If we define the local mole fractions x_{ji}:

$$x_{ij} = \frac{n_{ji}}{n_{ji} + n_{ii}} \tag{16}$$

where $x_{ji} + x_{ii} = 1$, then Eq. (15) can be rewritten into the following form:

$$\left(\frac{x_{ij}}{x_{jj}} \frac{x_{ji}}{x_{ii}}\right)^{z} n_{ii}^{z-p} n_{jj}^{z-q} = \exp\left(-\frac{w_{ij}}{kT}\right) \tag{17}$$

It is seen that if we introduce the assumptions corresponding to the Guggenheim lattice theory[1] that the number of active sites on molecule i which contact with active sites of i molecules is equal to the number of active sites on molecule i which contact with active sites of j molecules and equal to the number of active sites on molecule j which contact with active sites of j molecules ($z = p = q$), then Eqs. (17) reduce to those given by the Guggenheim model[1].

Now according to Wilson[3] we can define a general relation between local mole fraction x_{ii} of molecules i and local mole fraction x_{ji} of molecules j and between local mole fraction x_{jj} of molecules j and local mole fraction x_{ji} of molecules i:

$$\frac{x_{ji}}{x_{ii}} = \frac{x_j}{x_i} n_{ii}^{p/z-1} \exp\left(-\frac{u_{ji} - u_{ii}}{zRT}\right) \tag{18}$$

$$\frac{x_{ij}}{x_{jj}} = \frac{x_i}{x_j} n_{jj}^{q/z-1} \exp\left(-\frac{u_{ij} - u_{jj}}{zRT}\right) \tag{19}$$

Equations (18) and (19) show that local mole fraction are not only a function of the overall mole fractions and interaction energies (the Guggenheim model[1]) but also a function of the number of surrounding molecules which cannot be easily expressed by the concentration. That is why Eqs. (18), (19) cannot be used directly in such form for calculation of the local mole fractions in solutions.

THE LOCAL COMPOSITION MODEL

Equation (17) expresses the distribution of molecules in a solution as a function of interaction potentials (w_{ij}). To write Eq. (17) in the form expressed only by mole fractions and interaction potentials it is necessary to make some assumptions concerning the number of "$i - i$" and "$j - j$" active sites on one molecule.

For simplicity we can assume that the number of active sites on molecule i which contact with active sites of i molecules is smaller than the number of active sites on molecule i which contact with active sites of j molecules and the number of active sites on molecule j which contact with active sites of j molecules is greater than the number of active sites on molecule i which contact with active sites of j molecules and both these differences are equal to r:

$$p = z - r \quad \text{and} \quad q = z + r$$

Introducing these to Eq. (17) we obtain:

$$\left(\frac{x_{ij}}{x_{jj}}\frac{x_{ji}}{x_{ii}}\right)^{z}\left(\frac{n_{jj}}{n_{ii}}\right)^{r} = \exp\left(-\frac{w_{ij}}{kT}\right) \tag{20}$$

Now using the Eq. (14) and assuming that

$$\int_0^r r^2 g_{jj}(r)dr \simeq \int_0^r r^2 g_{ii}(r)dr \tag{21}$$

and that the overall mole fraction is given by the equation:

$$x_i = \frac{n_i}{n_i + n_j} \tag{22}$$

we can rewrite Eq. (18) in the following form:

$$\left(\frac{x_{ij}}{x_{jj}}\frac{x_{ji}}{x_{ii}}\right)^{z}\left(\frac{x_j}{x_i}\right)^{r} = \exp\left(-\frac{w_{ij}}{kT}\right) \tag{23}$$

Now we attempt to introduce the two-liquid theory of Scott[4]. The theory assumes that in the mixture of molecules i and j there are two kinds of cells containing molecules i and j at their centres. The residual Gibbs energy (compared with the ideal gas at the same temperature, pressure and composition) is the sum of all the residual Gibbs energies for two-body interactions experienced by the center molecule.

According to Scott[4] the residual Gibbs energy g^i for a cell containing a molecule i at the center is given by:

$$g^i = x_{ii}g_{ii} + x_{ji}g_{ji} \tag{24}$$

and for a cell containing a molecule j at the center by:

$$g^j = x_{jj}g_{jj} + x_{ij}g_{ij} \tag{25}$$

If we consider the pure liquid i, than $x_{ii} = 1$ and $x_{ji} = 0$ and the residual Gibbs energy g^i_p for the cell with i molecule in the center is:

$$g^i_p = g_{ii} \tag{26}$$

and similarly, for a cell containing a molecule j at the center:

$$g^j_p = g_{jj} \tag{27}$$

The molar excess Gibbs energy for a solution is the sum of two changes in residual energy: first caused by the transferring x_i molecules from a cell of the pure liquid into a cell of the solution equal to $x_i(g^i - g_p^i)$ and second by the transferring x_j molecules from a cell of the pure liquid into a cell of the solution equal to $x_j(g^j - g_p^j)$.

Thus

$$g^E = x_i(g^i - g_p^i) + x_j(g^j - g_p^j) \tag{28}$$

Substituting Eqs. (24, 25, 26, 27) into Eq. (28) and remembering that:

$$x_{ij} + x_{jj} = 1 \tag{29}$$

$$x_{ji} + x_{ii} = 1 \tag{30}$$

we obtain:

$$g^E = x_i x_{ji}(g_{ji} - g_{ii}) + x_j x_{ij}(g_{ij} - g_{jj}) \tag{31}$$

Now we can try to express the local mole fraction as a function of Gibbs energy. By definition we can write:

$$u_{ji} = g_{ji} - \Delta(pV)_{ji} + TS_{ji} \tag{32}$$

For isothermal and isobaric conditions we can rewrite Eq. (10) in the following form:

$$\begin{aligned} w_{ij} = {} & g_{ij} + g_{ji} - g_{ii} - g_{jj} \\ & - p(\Delta V_{ij} + \Delta V_{ji} - \Delta V_{ii} - \Delta V_{jj}) \\ & + T(S_{ij} + S_{ji} - S_{ii} - S_{jj}) \end{aligned} \tag{33}$$

The excess volume can be expressed by the following equation:

$$\Delta V^E = \sum_i \sum_j N_{ji} \Delta V_{ji} - \sum_i N_i \Delta V_{ii} \tag{34}$$

Substituting Eqs. (6) and (7) into Eq. (34) and recalling our primary assumption, that the excess volume (ΔV^E) must be equal to zero, we obtain:

$$\Delta V_{ij} + \Delta V_{ji} - \Delta V_{ii} - \Delta V_{jj} = 0 \tag{35}$$

and Eq. (33) reduces to the following form:

$$\begin{aligned} w_{ij} = {} & g_{ij} + g_{ji} - g_{ii} - g_{jj} \\ & + T(S_{ij} + S_{ji} - S_{ii} - S_{jj}) \end{aligned} \tag{36}$$

Introducing an entropy factor:

$$A_{ji} = \exp\left(- \frac{S_{ji} - S_{ii}}{zk} \right) \tag{37}$$

which depends only on difference between shape of molecules i and j, Eq. (23) takes the following form:

$$\left(\frac{x_{ij}}{x_{jj}} \frac{x_{ji}}{x_{ii}} \right) = \left(\frac{x_i}{x_j} \right)^{r/z} A_{ij} A_{ji} \exp\left(- \frac{g_{ij} + g_{ji} - g_{ii} - g_{jj}}{zkT} \right) \tag{38}$$

Now we can define a relation between local mole fraction x_{ii} of molecules i and local mole fraction x_{ji} of molecules j and between local mole fraction x_{jj} of molecules j and local mole fraction x_{ij} of molecules i is expressed only by the interactions potentials and overall mole fractions:

$$\frac{x_{ji}}{x_{ii}} = \frac{(x_j)^{1-r/z}}{x_i} A_{ji} \exp\left(- \frac{g_{ji} - g_{ii}}{zRT} \right) \tag{39}$$

$$\frac{x_{ij}}{x_{jj}} = \frac{(x_i)^{1+r/z}}{x_j} A_{ij} \exp\left(- \frac{g_{ij} - g_{jj}}{zRT} \right) \tag{40}$$

If following Wilson[3] we assume that for interaction between two neighboring molecules $r = 0$, and $z = 1$, and that the A_{ij} parameter can be considered in the simplest way as a ratio of mole volume of component i and j:

$$A_{ij} = \frac{V_i}{V_j} \tag{41}$$

we obtain Wilson's[3] expression for local compositions:

$$x_{ii} = \frac{x_i}{x_i + x_j \frac{V_j}{V_i} \exp\left(- \frac{g_{ji} - g_{ii}}{RT} \right)}. \tag{42}$$

If we assume, as Renon and Prausnits[5] did, that we consider solution of the same molecules ($A_{ij} = 1$) interacting with the same number of molecules ($r = 0$) we retain the expression for local composition as in the NRTL equation:

$$x_{ji} = \frac{x_j \exp\left(-\alpha_{ij} \frac{g_{ji} - g_{ii}}{RT} \right)}{x_i + x_j \exp\left(-\alpha_{ij} \frac{g_{ji} - g_{ii}}{RT} \right)} \tag{43}$$

where: $$\alpha_{ij} = \frac{1}{z}$$

The form of Eqs. (39) and (40) for local compositions was confirmed also by Molecular Dynamics (MD) calculations. Gierycz *et al.*[6] have performed many calculations of local composition in binary mixtures with the same and different size of particles in the entire composition range. It was shown there that the NRTL equation could reproduce the MD data only for the mixtures with the same size of particle. In the case where the components had different sizes the agreement was rather poor. To get good agreement it was necessary to introduce a correction factor which was a measure of the difference of the size parameter of the particles. That correction factor appeared in the same place what A_{ij} and A_{ji} factor in the Eqs. (39) and (40).

Substituting Eqs. (39) and (40) into Eq. (31) we can get the general equation for excess Gibbs energy from the local composition concept:

$$\frac{g^E}{RT} = \frac{x_i(x_j)^{1-\beta}A_{ji}\exp(-\alpha\tau_{ji})}{x_i + (x_j)^{1-\beta}A_{ji}\exp(-\alpha\tau_{ji})}\tau_{ji} + \frac{x_j(x_i)^{1+\beta}A_{ij}\exp(-\alpha\tau_{ij})}{x_j + (x_i)^{1+\beta}A_{ij}\exp(-\alpha\tau_{ij})}\tau_{ij} \tag{44}$$

where: $\alpha = \frac{1}{z}, \beta = \frac{r}{z},$ and $\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT}$

The activity coefficients (γ_i and γ_j) can be found by differentiation of Eq. (44) and they have the following form:

$$\ln \gamma_i = \tau_{ji}\frac{x_j^{1-\beta}Z_{ji}(x_j^{1-\beta}Z_{ji} + \beta x_i^2)}{(x_i + x_j^{1-\beta}Z_{ji})^2} + \tau_{ij}\frac{x_j^2 x_i^{\beta}Z_{ij}(1 + \beta x_j)}{(x_j + x_i^{1+\beta}Z_{ij})^2} \tag{45}$$

$$\ln \gamma_j = \tau_{ij}\frac{x_i^{1+\beta}Z_{ij}(x_i^{1+\beta}Z_{ij} - \beta x_j^2)}{(x_j + x_i^{1+\beta}Z_{ij})^2} + \tau_{ji}\frac{x_i^2 x_j^{-\beta}Z_{ji}(1 - \beta x_i)}{(x_i + x_j^{1-\beta}Z_{ji})^2} \tag{46}$$

where: $Z_{ij} = A_{ij}\exp(-\alpha\tau_{ij})$

Equations (44), (45), (46) can be easily generalized to solutions containing any number of components. The generalization requires no additional assumption. We further consider only two-body intermolecular interactions and therefore the assumptions needed for multicomponent solutions are the same as those for binary solutions.

For multicomponent solutions, the excess Gibbs energy is as follows:

$$\frac{g^E}{RT} = \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{x_j x_i^{1-\beta_{ij}}A_{ji}\exp(-\alpha_{ij}\tau_{ji})}{x_i + x_j^{1-\beta_{ij}}A_{ji}\exp(-\alpha_{ij}\tau_{ji})}\tau_{ji} + \frac{x_i x_j^{1+\beta_{ij}}A_{ij}\exp(-\alpha_{ij}\tau_{ij})}{x_j + x_i^{1+\beta_{ij}}A_{ij}\exp(-\alpha_{ij}\tau_{ij})}\tau_{ij} \tag{47}$$

where: N is the number of components.

APPLICATION TO THE CALCULATION OF VLE DATA

Equations (44)–(47) can be used for calculation of phase equilibria in binary and multicomponent systems. The equation for binary mixtures has two energetic parameters ($g_{ij}-g_{jj}$, $g_{ji}-g_{ii}$), two parameters dependent on shape of interacting molecules (A_{ij} and A_{ji}) and two parameters depending on the number of two-body interactions in a solution (α and β). But four of these parameters (A_{ij}, A_{ji}, α and β) can be calculated from pure substance properties and only two energetic parameters are to be adjusted using the experimental data.

The entropic A_{ij} parameters (Eq. 37) for mixtures of nonpolar molecules account for both size and shape differences. For more complex mixtures they account for molecular orientation in the intermolecular interaction of a polar or hydrogen bonding. For simple cases A_{ij} parameters can be assumed to be equal to one but for more complicated systems they should assume different values.

The expression for A_{ij} parameters can be derived from our lattice model in the following way. We can imagine that our lattice is divided into very many cells which are so small that by far the greater part are empty. As a result of the thermal agitation the occupied cells are continuously changing.

Now we can assume that we partition our lattice into two parts where in the first part there are p cells and n_1 molecules of "i" kind and in the second part q cells and n_2 molecules of kind "j". Since the interchange of either two empty or two occupied cells does not alter an arrangement, the total number of configurations is given by:

$$m = \frac{p!}{n_1!(p-n_1)!}\,\frac{q!}{n_2!(q-n_2)!} \tag{48}$$

After the partition has been removed (n_1+n_2) molecules are distributed over $(p+q)$ cells. The number of different configurations m' is now given by:

$$m' = \frac{(p+q)!}{n_1!n_2!(p+q-n_1-n_2)!} \tag{49}$$

Now we can calculate the increase in entropy S_{ij} due to mixing of two kinds of molecules "i" and "j":

$$S_{ij} = k\ln\frac{m'}{m} \tag{50}$$

$$S_{ij} = k\ln\left(\frac{(p+q)!(p-n_1)!(q-n_2)!}{(p+q-n_1-n_2)!p!q!}\right) \tag{51}$$

In the same way we can consider the increase in entropy S_{jj} due to mixing of molecules "j" which had occupied two parts of the lattice with p cells ($n_2/2$-molecules) and q cells ($n_2/2$-molecules) and then were distributed over $(p+q)$ cells. The number of configurations m'' before and m''' after removing of the partition is given by:

$$m'' = \frac{p!q!}{(n_2/2)!(p-n_2/2)!(n_2/2)!(q-n_2/2)!} \tag{52}$$

$$m''' = \frac{(p+q)!}{(n_2/2)!(n_2/2)!(p+q-n_2)!} \tag{53}$$

and the increase of entropy S_{jj} by:

$$S_{jj} = k \ln\left(\frac{(p+q)!(p-n_2/2)!(q-n_2/2)!}{(p+q-n_2)!p!q!}\right) \tag{54}$$

From Eqs. (51) and (54) using Stirling's approximation (5) we can calculate the difference $S_{ij} - S_{jj}$:

$$\frac{S_{ij} - S_{jj}}{k} = \ln\left(\frac{(p-n_1)^{p-n_1}(q-n_2)^{q-n_2}}{(p+q-n_1-n_2)^{p+q-n_1-n_2}}\right) + \ln\left(\frac{(p+q-n_2)^{p+q-n_2}}{(p-n_2/2)^{p-n_2/2}(q-n_2/2)^{q-n_2/2}}\right) \tag{55}$$

Now assuming according to our investigations that $n_1 = p - z$ and $n_2 = q - z$ and substituting these to the Eq. (55) together with our previous definitions of p, q, α, β ($p = z - r$, $q = z + r$, $\alpha = (1/z)$, $\beta = (r/z)$) we find the following expression for the difference $S_{ij} - S_{jj}$:

$$\frac{S_{jj} - S_{ij}}{zk} = \ln\left(\frac{[(2+\beta)/\alpha]^{1+\beta/2}}{[(2-\beta)/\alpha]^{1-\beta/2}}\right) \tag{56}$$

In an analogous way we can derive the expression for the difference $S_{ji} - S_{ii}$ and it will have the following form:

$$\frac{S_{ii} - S_{ji}}{zk} = \ln\left(\frac{[(2-\beta)/\alpha]^{1-\beta/2}}{[(2+\beta)\alpha]^{1+\beta/2}}\right) \tag{57}$$

Thus the entropic parameters (Eq. 37) assume the following form:

$$A_{ij} = \frac{[(2+\beta)/\alpha]^{1+\beta/2}}{[(2-\beta)/\alpha]^{1-\beta/2}} \tag{58}$$

$$A_{ji} = \frac{[(2-\beta)/\alpha]^{1-\beta/2}}{[(2+\beta)/\alpha]^{1+\beta/2}} \tag{59}$$

The α parameter (Eq. 44) according to its definition should assume value from the range 0–0.3, but rather close to zero. The β parameter (Eq. 44) can be assumed to be equal to α ($r = 1$) or $-\alpha$ (if we make an opposite assumption concerning the difference in the number of contacts of molecule i and j: $p = z + r$ and $q = z - r$—Eqs. (20), (23)) or to be a multiplicity of α ($r = 2, 3, \ldots$) or $-\alpha$. The β parameter can be assumed also to be independent of α value close to zero because the relations between z, p, and q can be different than these assumed in Eq. (44), and by the β value we can approximate the true relation for local mole fractions (Eq. 18, 19). Finally the β parameter can be equal to zero and in this case Eqs. (44)–(47) reduce to the NRTL equation[5] with extra size parameters A_{ij}.

The α and β parameters can be treated also as adjustable parameters which can improve the results but in this case we cannot give a physical meaning to the values of these parameters.

We have checked the applicability of the proposed model on VLE binary data for systems formed by hydrocarbons (systems with physical interactions), and hydrocarbons and strong associating systems (systems with physical and strong chemical interactions).

These two groups of systems have been selected as the most interesting from point of view of our previous investigations[8,9,10,11].

Selection of the systems have been performed in the same way as previously[8,9,10] i.e. selecting the systems we wanted to fullfill two conditions. The first one was the wide representation of various kinds of hydrocarbons interacting with strong associating systems and second one it was the selection of good consistent VLE data.

As previously[8] to avoid the problems with the temperature dependence of parameters which seems to be discussible we limited our interests to isothermal data only. Additionally to have a possibility of comparison with our previous investigations we based mostly on the data selected previously[8,9,10].

Finally we have selected 18 isothermal binary VLE data:

1) benzene-2-propanol at $T = 313.15$, 328.15 K[12]
2) benzene-cyclohexane at $T = 313.15$, 328.15 K[13]
3) cyclohexane-2-propanol at $T = 313.15$, 328.15 K[12]
4) cyclohexane-ethanol at $T = 323.15$ K[13]
5) cyclohexane-benzene at $T = 323.15$ K[13]
6) ethanol-benzene at $T = 323.15$ K[13]
7) ethanol-benzene at $T = 328.15$ K[14]
8) *n*-hexane-benzene at $T = 328.15$ K[14]
9) *n*-hexane-ethanol at $T = 328.15$ K[14]
10) cyclohexane-methanol at $T = 328.15$ K[13]
11) benzene-cyclohexane at $T = 328.15$ K[13]
12) benzene-methanol at $T = 328.25$ K[13]
13) cyclohexane-ethanol at $T = 323.15$ K[15]
14) benzene-cyclohexane at $T = 323.15$ K[15]
15) benzene-ethanol at $T = 323.15$ K[15]
16) acetone-2,2,4-trimethylpentane at 325.15 K[16]
17) carbon tetrachloride-hexadecane at 298.15 K[17]
18) carbon tetrachloride-hexadecane at 328.15 K[17]

We have performed our calculations using the NRTL[5] equation with $\alpha = 0.2$ and the proposed model in three versions: I—with the assumption that A_{12} and A_{21} parameters are equal to 1 and $\alpha = \beta$, II—where the A_{ij} parameters are equal to one and α and β parameters assume different values but are close to 0, III—where the A_{12} and A_{21} parameters are calculated according to Eqs. (58) and (59) and $\alpha = \beta$. For all versions the α and β values were chosen arbitrarily and the models used had only two adjustable parameters (energetic parameters: $g_{12} - g_{22}$ and $g_{21} - g_{11}$).

Table 1 Results of correlation by means of the NRTL equation and the proposed method in three versions (I, II, III) for all binary systems investigated.

System	*T/K*	*D(P)/kPa* *NRTL*	*I*	*II*	*III*
Benzene 2-propanol	313.15	0.021	0.020	0.012	0.019
Cyclohexane 2-propanol	313.15	0.279	0.107	0.006	0.060
Benzene cyclohexane	313.15	0.046	0.046	0.046	0.046
Benzene 2-propanol	328.15	0.046	0.033	0.021	0.030
Cyclohexane 2-propanol	328.15	0.205	0.101	0.094	0.093
Benzene cyclohexane	328.15	0.144	0.059	0.059	0.056
Benzene ethanol	323.15	0.164	0.101	0.096	0.095
Benzene cyclohexane	323.15	0.166	0.134	0.134	0.115
Cyclohexane ethanol	323.15	0.304	0.145	0.143	0.132
n-hexane ethanol	328.15	2.414	0.952	0.871	0.774
Ethanol benzene	328.15	0.738	0.407	0.407	0.401
n-hexane benzene	328.15	0.196	0.133	0.133	0.132
Benzene cyclohexane	328.15	0.144	0.058	0.058	0.056
Methanol cyclohexane	328.15	2.490	0.948	0.948	0.414
Methanol benzene	328.15	0.756	0.309	0.224	0.167
Acetone 2,2,4-trimethylpentane	325.15	2.582	0.469	0.469	0.446
Carbon tetrachloride hexadecane	298.15	0.058	0.041	0.041	0.038
Carbon tetrachloride hexadecane	328.15	0.160	0.151	0.150	0.100

For computation of the vapour phase nonideality the Hayden–O'Connell[18] correlation was applied. The computed values of the root mean square deviations of the total pressure $D(P)$ (Eq. 60) for all investigated systems and models are given in Table 1.

$$D(P) = \left(\frac{\sum_i^n (P_i^{\text{exp}} - P_i^{\text{cal}})^2}{n - m - 1} \right)^{1/2} \tag{60}$$

where: P_i^{exp}, P_i^{cal} are the experimental and calculated total vapour pressures, respectively, n is the number of experimental data points and m is the number of adjustable parameters.

Table 2 shows the values of α and β parameters obtained for all investigated systems during the calculations.

CONCLUSIONS

Examining the results obtained (Table 1) one can see that in all cases the proposed method (version I) gave much better results of correlation of VLE data (sometimes even 3–4 times) than the NRTL equation.

Table 2 The values of α and β parameters in three versions of calculations for all binary systems investigated.

System	*T/K*	*The proposed method*			
		I	*II*		*III*
		$\alpha = \beta$	α	β	$\alpha = \beta$
Benzene 2-propanol	313.15	0.001	0.001	0.0005	0.001
Cyclohexane 2-propanol	313.15	0.05	0.05	0.08	0.05
Benzene cyclohexane	313.15	0.001	0.001	0.001	0.001
Benzene 2-propanol	328.15	0.001	0.05	0.012	0.001
Cyclohexane 2-propanol	328.15	0.01	0.01	0.012	0.01
Benzene cyclohexane	328.15	0.01	0.01	0.01	0.005
Benzene ethanol	323.15	0.01	0.01	0.008	0.01
Benzene cyclohexane	323.15	0.01	0.01	0.01	0.005
Cyclohexane ethanol	323.15	0.05	0.05	0.056	0.02
n-hexane ethanol	328.15	0.08	0.08	0.09	0.05
Ethanol benzene	328.15	0.01	0.01	0.01	0.005
n-hexane benzene	328.15	0.001	0.001	0.001	0.001
Benzene cyclohexane	328.15	0.05	0.05	0.05	0.01
Methanol cyclohexane	328.15	0.2	0.2	0.2	0.1
Methanol benzene	328.15	0.1	0.1	0.11	0.1
Acetone 2,2,4-tri-methylpentane	325.15	0.1	0.1	0.1	0.1
Carbon tetrachloride hexadecane	298.15	0.08	0.08	0.08	0.08
Carbon tetrachloride hexadecane	328.15	0.1	0.1	0.08	0.05

It is seen also that the assumption that the α parameter is equal to the β parameter can be accepted as true; this is confirmed by the second version of calculations (Tables 1 and 2). The improvement obtained by assumption of different values of α and β was in most cases rather small and the obtained value of α parameter differed only slightly from the β parameter (Table 2).

It is interesting to notice that the α and β parameters assume for non- or weak-associating components very small values (0.0002–0.005) and for strong-associating higher values (0.01–0.2). This is in agreement with our liquid model where for non-associating components each molecule interacts with many other molecules (high values of z and p and q, small values of α and β) and association causes that molecules are grouping. Instead of many interactions there are only few interations between groups of molecules (α assumes higher value Table 2).

Such interpretation is confirmed by version III of our calculations. For strong association the entropy factors (A_{ij}) become important (high value of α and β) and taking them into account improves significantly correlation results (Table 1—systems with methanol).

Looking at the form of A_{ij} parameters (Eqs. (58) and (59)) one can see that for small values of α and β they are close to one and have no influence on correlation results. They attain values significantly different from one and are important when association is occurring (higher values of α and β).

It is necessary to point out that for some systems the values of $\alpha = \beta$ parameters obtained for version I and III of our model are different. It is caused by the fact that when we assume the A_{ij} parameters equal to 1, the $\alpha = \beta$ parameters are influenced by the shape effects. Therefore they have different values from those in the situation where the entropy factors are taken into consideration.

Concluding we can say that the proposed model in version III ($\alpha = \beta$ and A_{ij} parameters calculated from Eqs. (58) and (59)) can be recommended for correlation of VLE data and leads to better results than the NRTL equation. The model has the same number of adjustable parameters as the NRTL equation (two energetic parameters for binary systems) and as all local composition models can be applied for calculation of any kind of phase equilibria in multicomponent systems.

Moreover for some systems very difficult to be correlated the description (flexibility of the equation) can be improved by the use of slightly different values for α and β parameters.

The approach presented here and the formulae obtained for local composition fractions (Eqs. (18), (19), (39), (40)) have been used for Scott's two fluid theory[4]; that is why the model obtained is in fact a generalized NRTL equation. Based on the proposed formulae for the local composition fractions, any local composition model can be assessed and modified.

Acknowledgement

This work was carried out within the Polish Academy of Sciences Research Project CPBR 3.20.61.

References

1. E. A. Guggenheim, *Mixtures*, Clarendon Press, Oxford, 1952.
2. B. L. Larsen, *Prediction of Phase Equilibria and Heat Effects of Mixing with a Modified UNIFAC Model*, Institut for Kemiteknik, Denmarks Tekniske Hojskole, Lyngby, Denmark, 1986.
3. G. M. Wilson, *J. Am. Chem. Soc.*, **86**, 127 (1964).
4. R. L. Scott, *J. Chem. Phys.*, **25**, 193 (1956).
5. H. Renon, J. M. Prausnitz, *AIChE J.*, **14**, 135 (1968).
6. P. Gierycz, K. Nakanishi, *Fluid Phase Equilibria*, **16**, 255 (1984).
7. A. Bondi, *Physical Properties of Molecular Liquids, Crystals and Glasses*, Wiley, New York, 1968.
8. P. Gierycz, J. Rauk, J. Gregorowicz, *Thermochimica Acta*, **142**, 59 (1989).
9. P. Gierycz, J. Rauk, J. Gregorowicz, *Thermochimica Acta*, **154**, 287 (1989)
10. P. Gierycz, J. Rauk, *Thermodynamica Acta*, in print, 1990.
11. P. Gierycz, B. Wisniewska, *Thermochimica Acta*, in print, (1990).
12. A. V. Storonkin, A. G. Morachevsky, *Zh. Prikl. Khim.*, **30**, 1297 (1956).
13. A. G. Morachevsky, E. G. Komarova, Vestnik, Leningrad. Univ. 12. *Ser. Fiz. Khim.*, **1**, 118 (1957).
14. K. L. Young, R. A. Mentzer, R. A. Greenkorn, *J. Chem. Thermodyn.*, **9**, 979 (1977).
15. V. T. Zharov, A. G. Morachevsky, L. G. Shapil, T. A. Buevich, *Zh. Prikl. Khim.*, **41**, 2443 (1968).
16. J. L. Edwards, K. Schaefer, *Z. Naturforsch.*, **19A**, 136 (1964).
17. D. V. S. Jain, B. S. Lark, *J. Chem. Thermodyn.*, **5**, 455 (1973).
18. J. G. Hayden, J. P. O'Connell, *Ind. Eng. Chem. Proc. Des. Dev.*, **14**, 209, 1975.