Thermodynamics of Lewis Acid-Base Mixtures

The associated perturbed-anisotropic-chain theory (APACT) has been applied to treat multicomponent mixtures, in which components exhibit Lewis acid-base interactions. Mixtures of amphoteric molecules (such as alcohols), acidic molecules (such as chloroform), and basic molecules (such as ketones) as well as nonassociating components (diluents) are treated. The acid-base version of the perturbed-anisotropic-chain theory (ABPACT) is a closed form equation of state that takes into account explicitly dispersion interactions, polar interactions, and hydrogen bonding interactions between components that self-associate or solvate. The equation fits binary VLE mixtures quite accurately. Calculated results also are compared with those obtained from the Peng-Robinson equation of state, UNIFAC and the original APACT. In all cases where there are mixtures of associating components, the ABPACT gives a better fit of experimental data than these other equations.

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Introduction

A number of different thermodynamic models have been used to calculate vapor–liquid equilibria in systems that contain hydrogen bonding components. Although the Peng–Robinson (PR) equation of state and UNIFAC are used widely to calculate the properties of associating systems, generally they can be used only over narrow ranges of conditions. Hydrogen bonding can be treated as an extreme case of dipolar interactions and use a dipole–dipole equation by simply increasing the value of the dipole moment (Prausnitz *et al.*, 1986). Another approach is to develop a perturbation theory based on a model potential that would be expected to mimic hydrogen bonding. This model developed by Wertheim (1986) and simplified by Gubbins and his coworkers (Chapman *et al.*, 1988; Jackson *et al.*, 1988) is quite accurate and results in expressions that are similar to the expressions developed in this work.

An approach that has been used successfully is to model hydrogen bonding as a series of equilibrium chemical reactions. In this approach, equations are written for the appropriate chemical equilibria in terms of temperature, density and composition of the species present. The equations can be solved simultaneously with the phase equilibria constraints (Weihe, 1967; Gmehling *et al.*, 1979; Neau and Peneloux, 1979; Baumgaertner *et al.*, 1980; Nagata, 1985). This, however, is a trial-and-error procedure that is cumbersome and calculation-intensive. An alternative method, first proposed by Heidemann and Prausnitz (1976), is to solve the chemical equilibria and combine them into the equation of state. The phase equilibria then are solved independently thus eliminating the trial-and-error aspect of the previous method. Ikonomou and Donohue (1986) applied this approach using the perturbed-anisotropic-chain theory (PACT) and arrived at a closed form equation of state for hydrogen bonding fluids, the associating PACT (APACT). Because of the assumptions used in the development of APACT, the resulting hydrogen bonding terms are very simple mathematically. In APACT, equations were presented for pure components and mixtures of associating components with diluents for the infinite equilibria chemical model. The infinite equilibria model alone, however, is not adequate for all types of hydrogen bonding fluid mixtures. For systems such as alcohol–ketone, treating the ketone as a diluent results in poor prediction of properties even with large values of binary interaction parameter because APACT does not take into account the solvation between ketone and alcohol. Recently, Anderko (1989) presented a closed-form equation of state for hydrogen bonding systems that uses an approach similar to that of Ikonomou and Donohue.

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Here, we extend the infinite equilibria model in APACT to a more general association scheme that accounts explictly for the acidic and basic properties of each component in the mixture. A Lewis acid is defined as a molecule capable of accepting electrons, whereas a Lewis base is a molecule capable of donating electrons. In the alcohol–ketone system, the alcohol is both a Lewis acid and base (amphoteric component), whereas the ketone is a Lewis base. Because of the importance of Lewis acid-base systems, considerable work has been done to quantitatively describe the acidity and basicity of different compounds. For example, Kamlet *et al.* (1983) proposed the solvatochromic parameters α and β to describe the acidity and the basicity of a component participating in a hydrogen bond. Drago *et al.* (1965) presented a double-scale equation for correlating enthalpies of Lewis acid-base interactions. The results of Drago's work are used here as a guide in determining values for equilibrium constants. APACT is extended to calculate properties of the following types of systems: amphoteric–amphoteric, amphoteric–acid, amphoteric–base, acid–base, and systems containing diluents. The new equation derived is briefly described in the following section. Properties of hydrogen bonding systems can be calculated accurately with small values of a binary interaction parameter.

Theory

In this paper, we use A to represent a Lewis acid, B to represent a Lewis base, M and N to represent amphoteric compounds (those that are both acidic and basic), and D to represent a diluent (a compound that is neither acid nor base). Since amphoteric molecules, and even chains of bonded amphoteric molecules, are both acidic and basic, we use the superscript a and b to indicate that these molecules are interacting as an acid and base, respectively. For example,

$$M^a + N^b \rightleftharpoons MN \tag{1}$$

indicates that the acidic portion of M is bonding to the basic portion of N, whereas

$$M^b + N^a \rightleftharpoons MN \tag{2}$$

indicates that the basic portion of M is bonding to the acidic portion of N. In general, for a mixture of components M and N, four types of chemical equilibria are possible. Two of them account for the self-association of components M and N:

$$(M_i)^a + M^b \rightleftharpoons M_{i+1} \tag{3}$$

$$(N_j)^a + N^b \rightleftharpoons M_{j+1} \tag{4}$$

and the other two account for the cross association between the two components:

$$(M_i)^a + (N_j)^b \rightleftharpoons M_iN_j \tag{5}$$

$$(M_i)^b + (N_j)^a \rightleftharpoons M_iN_j \tag{6}$$

where i and j denote the number of M and N monomers in the chain molecule M_iN_j, respectively; they can take any integer value from one to infinity. In Eq. 3, the acidic portion of the end M molecule of the chain is bonding to the basic portion of an M molecule. Similarly, in Eq. 4, the acidic portion of the end N molecule of the chain is bonding to the basic portion of an N molecule. Each time, only one interaction is taken into account. Free molecules M and N can react with other species by using either of their groups. In Eq. 3, monomer M reacts with the chain molecule using its basic group, since the end group of the chain molecule is an acidic one. In Eq. 5 the acidic portion of the end M molecule of the M i-mer is bonding to the basic portion of the end N molecule of the N j-mer. The notation in Eq. 6 is defined similarly.

Initially, the chemical reactions are described and material balances are written. To solve these material balances, an equation of state is needed—PACT is used. The change of enthalpy for these four reactions are $\Delta H_1^o = \Delta H_{Ma}^o + \Delta H_{Mb}^o$, $\Delta H_2^o = \Delta H_{Na}^o + \Delta H_{Nb}^o$, $\Delta H_3^o = \Delta H_{Ma}^o + \Delta H_{Nb}^o$, $\Delta H_4^o = \Delta H_{Mb}^o + \Delta H_{Na}^o$, respectively, where ΔH_{Ma}^o is the enthalpy change per mole of M accepting an electron and ΔH_{Mb}^o is the enthalpy change per mole of M donating an electron. ΔH_{Na}^o and ΔH_{Nb}^o are defined similarly. In addition, the change of entropy for these reactions are $\Delta S_1^o = \Delta S_{Ma}^o + \Delta S_{Mb}^o$, $\Delta S_2^o = \Delta S_{Na}^o + \Delta S_{Nb}^o$, $\Delta S_3^o = \Delta S_{Ma}^o + \Delta S_{Nb}^o$, $\Delta S_4^o = \Delta S_{Mb}^o + \Delta S_{Na}^o$, respectively, where ΔS_{Ma}^o is the entropy change per mole of M donating an electron and similarly for ΔS_{Mb}^o, ΔS_{Na}^o, and ΔS_{Nb}^o. The equilibrium constants for all four reactions are calculated as follows:

$$\ln K = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{7}$$

In addition, the equilibrium constants for M and N accepting or releasing an electron (K_{Ma}, K_{Mb} for M and K_{Na}, K_{Nb} for N, respectively) can be calculated similarly.

The overall material balance is written by defining n_T as the total number of moles of all components present in the system and n_0 as the total number of moles in the absence of association (i.e., the superficial number of moles). Similarly, the superficial number of moles of M and N are defined as n_1 and n_2 respectively:

$$n_0 = n_1 + n_2 \tag{8}$$

or

$$\frac{n_1}{n_0} + \frac{n_2}{n_0} = x_1 + x_2 = 1 \tag{9}$$

where x_1 and x_2, the superficial mole fractions of 1 and 2, are assumed to be known.

The moles of association species are defined as n_{ij} where i shows the number of moles from species M, and j the number of moles from species N, and the true mole fractions as: $z_{ij} = n_{ij}/n_T$. The overall material balance is given by:

$$n_T = \sum_{i=0}^{\infty}\sum_{j=0}^{\infty} n_{ij} = \sum_{i=1}^{\infty} n_{i0} + \sum_{j=1}^{\infty} n_{0j} + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} n_{ij} \tag{10}$$

Dividing the latter by n_T, yields:

$$1 = \sum_{i=1}^{\infty} z_{i0} + \sum_{j=1}^{\infty} z_{0j} + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} z_{ij} \tag{11}$$

In addition to the overall material balance, material balances over components M and N are written. For component M the material balance is:

$$n_1 = \sum_{i=1}^{\infty}\sum_{j=0}^{\infty} in_{ij} = \sum_{i=1}^{\infty} in_{i0} + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} in_{ij} \tag{12}$$

Dividing the latter by n_T, one obtains:

$$x_1 \frac{n_0}{n_T} = \sum_{i=1}^{\infty} iz_{i0} + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} iz_{ij} \tag{13}$$

Similarly for component N:

$$x_2 \frac{n_0}{n_T} = \sum_{j=1}^{\infty} jz_{0j} + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} jz_{ij} \tag{14}$$

In Eqs. 11, 13 and 14, all mole fractions z_{ij} are unknown and are temperature- and density-dependent as shown below. The chemical equilibria for self association of M (Eq. 3) are described by the following equation:

$$K_1 = \frac{\phi_{i+1,0}}{\phi_{i0}\phi_{10}P}\frac{z_{i+1,0}}{z_{i0}z_{10}} \tag{15}$$

where ϕ is the fugacity coefficient. Similarly, for self association of N (Eq. 4):

$$K_2 = \frac{\phi_{0,j+1}}{\phi_{0j}\phi_{01}P}\frac{z_{0,j+1}}{z_{0j}z_{01}} \tag{16}$$

For the cross association (solvation) equilibria in Eqs. 5 and 6:

$$K_3 = \frac{\phi_{ij}}{\phi^a_{i0}\phi^b_{0j}P}\frac{z_{ij}}{z_{i0}z_{0j}} \tag{17}$$

$$K_4 = \frac{\phi_{ij}}{\phi^b_{i0}\phi^a_{0j}P}\frac{z_{ij}}{z_{i0}z_{0j}} \tag{18}$$

where subscripts a and b in Eqs. 17 and 18 denote the acidic and basic species, respectively. Implicit in these equations is the assumption that these equilibrium constants are independent of the values of i and j. This assumption is not consistent with spectroscopic results. Barker (1952) discusses this problem for alcohols that are strongly associated. Nevertheless, the introduction of a chain-size dependence in the equilibrium constants increases the complexity of the problem considerably. To solve these equations, we need to make several additional assumptions. First, we need to choose an equation of state and mixing rules for that equation of state. Then the ratios of fugacity coefficients in the above equations are calculated using classical thermodynamics (Ikonomou, 1987). The equation used here is PACT:

$$\frac{PV}{n_T RT} = 1 + Z^{\text{rep}} + Z^{\text{iso}} + Z^{\text{ani}} \tag{19}$$

where the repulsive, isotropic and anisotropic terms, Z^{rep}, Z^{iso} and Z^{ani}, are given by Vimalchand and Donohue (1985). Ikonomou (1987) has shown that if certain assumptions are made about the variation of the equation of state parameters, a closed-form analytical equation of state can result for certain types of association processes. Here, we are interested in studying more complex mixtures and so we need to know additional information concerning the chemical equilibria that are occurring. In particular, we need to know the equilibrium constants K_3 and K_4 that cannot be determined from pure-component data alone. Rather than introducing additional parameters, we assume that we can estimate these if we know (or can estimate) the acidity and basicity of species M and N. In addition, instead of introducing additional parameters, we assume that the enthalpy and entropy of association are the sum of contributions for each molecule. In this paper, we make the additional assumption that amphoteric molecules are equally acidic and basic. Though this second assumption is not correct necessarily, it is a simple matter to redo the calculations with different values. The results are substituted back in Eqs. 15 through 18. From Eq. 15 and 16, an expression for z_{i0} in terms of z_{10} and for z_{0j} in terms of z_{01}, respectively, can be obtained by applying these equations to the formation of dimer, trimer, etc. The result is:

$$z_{i0} = \left(K_1 \frac{n_T}{n_0}\frac{RT}{v_0}\right)^{i-1} z^i_{10} \tag{20}$$

and similarly for component N:

$$z_{0j} = \left(K_2 \frac{n_T}{n_0}\frac{RT}{v_0}\right)^{j-1} z^i_{01}. \tag{21}$$

The term $(n_T/n_0)(RT/v_0)$ comes from evaluating the ratios of fugacity coefficients (see Ikonomou and Donohue, 1986). In Eqs. 20 and 21, it is assumed that i and j can take any value up to infinity. By evaluating the mole fractions z_{i0} and z_{0j} in Eqs. 20 and 21, one obtains the result that the mole fraction for a particular association species with more than a few (the exact number depends on the temperature and the particular component) monomeric species is extremely low. Ikonomou and Donohue (1986), in the calculation of the mole fraction of the association species in a mixture of ethanol–toluene, showed that the mole fraction of species larger than tetramers is very low. For the solvation equilibria, one can relate z_{ij} to the mole fractions of monomer of M and monomer of N (z_{10} and z_{01}, respectively) by generalizing the procedure leading to Eqs. 20 and 21. Since this derivation is cumbersome to discuss here, it is given in Appendix A. The result is:

$$z_{ij} = [D_{i,j}K_{\text{I}} + E_{i,j}(K_{\text{II}} + K_{\text{III}}) + F_{i,j}K_{\text{IV}}]\left(\frac{RT}{v_0}\frac{n_T}{n_0}\right)^{i+j-1} z^i_{10}z^j_{01} \tag{22}$$

where

$$D_{i,j} = \frac{(i+j-2)!}{(i-2)!j!},\ E_{i,j} = \frac{(i+j-2)!}{(i-1)!(j-1)!}$$

and

$$F_{i,j} = \frac{(i+j-2)!}{i!(j-2)!}.$$

Also,

$$K_{\text{I}} = K_{Ma}^{(i-1)}K_{Mb}^{(i-1)}K^j_{Na}K^j_{Nb} \tag{23}$$

$$K_{\mathrm{II}} = K_{Ma}^{(i-1)} K_{Mb}^{i} K_{Na}^{j} K_{Nb}^{(j-1)} \tag{24}$$

$$K_{\mathrm{III}} = K_{Ma}^{i} K_{Mb}^{(i-1)} K_{Na}^{(j-1)} K_{Nb}^{j} \tag{25}$$

$$K_{\mathrm{IV}} = K_{Ma}^{i} K_{Mb}^{i} K_{Na}^{(j-1)} K_{Nb}^{(j-1)} \tag{26}$$

Substituting the expressions for z_{i0}, z_{0j}, and z_{ij} back to Eqs. 13, 14 and 11, one obtains:

$$x_1 = \sum_{i=1}^{\infty} i\left(K_1 \frac{RT}{v_0}\right)^{i-1} W_1^i + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} i\overline{K}\left(\frac{RT}{v_0}\right)^{i+j-1} W_1^i W_2^j \tag{27}$$

$$x_2 = \sum_{j=1}^{\infty} j\left(K_2 \frac{RT}{v_0}\right)^{j-1} W_2^j + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} j\overline{K}\left(\frac{RT}{v_0}\right)^{i+j-1} W_1^i W_2^j \tag{28}$$

$$\frac{n_T}{n_0} = \sum_{i=1}^{\infty} \left(K_1 \frac{RT}{v_0}\right)^{i-1} W_1^i + \sum_{j=1}^{\infty} \left(K_2 \frac{RT}{v_0}\right)^{j-1} W_2^j + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} \overline{K}\left(\frac{RT}{v_0}\right)^{i+j-1} W_1^i W_2^j \tag{29}$$

where

$$W_1 = n_{10}/n_0,\ W_2 = n_{01}/n_0$$

and

$$\overline{K} = C_{i,j}(p_{i,j}K_{\mathrm{I}} + q_{i,j}(K_{\mathrm{II}} + K_{\mathrm{III}}) + r_{i,j}K_{\mathrm{IV}}) \tag{30}$$

with

$$C_{i,j} = \frac{(i+j)!}{i!j!}$$

the binomial coefficient,

$$p_{i,j} = \frac{i(i-1)}{(i+j)(i+j-1)},\ q_{i,j} = \frac{ij}{(i+j)(i+j-1)},$$

and

$$r_{i,j} = \frac{j(j-1)}{(i+j)(i+j-1)}.$$

The important difference between this formulation and the APACT is the following. If component M is not amphoteric but only a base, such as acetone, the APACT gave the result that K_{MN} is zero, since $K_{MN} = \sqrt{K_M K_N} = \sqrt{K_{Ma}K_{Mb}K_{Na}K_{Nb}}$. In the present formulation, however, Eq. 30 gives a nonzero $\overline{K}$ if K_{Ma} is zero as in the case of acetone.

For any real number a, where $0 \le a \le 1$, the two infinite single series converge as follows:

$$\sum_{i=1}^{\infty} a^i = \frac{a}{1-a},$$

$$\sum_{i=1}^{\infty} i a^i = \frac{a}{(1-a)^2}.$$

So finally, Eqs. 27 through 29 become:

$$x_1 = \frac{W_1}{(1-a_1W_1)^2} + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} i a_{12} W_1^i W_2^j \tag{31}$$

$$x_2 = \frac{W_2}{(1-a_2W_2)^2} + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} j a_{12} W_1^i W_2^j \tag{32}$$

$$\frac{n_T}{n_0} = \frac{W_1}{1-a_1W_1} + \frac{W_2}{1-a_2W_2} + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} a_{12} W_1^i W_2^j \tag{33}$$

where $a_1 = K_1RT/v_0$, $a_2 = K_2RT/v_0$, $a_{12} = \overline{K}(\mathrm{RT}/v_0)^{i+j-1}$. Equations 31 and 32 form a system of two algebraic equations with two unknowns, W_1 and W_2. n_T/n_0 can be obtained from Eq. 33 after Eqs. 31 and 32 have been solved.

Because of the complex mathematical form of Eqs. 31 and 32, no analytical solution has been found. These equations, however, can be solved numerically. The only difficulty is to evaluate the two infinite series in i and j. The series are coupled in i and j because of the presence of a_{12}, so it is not clear that they can be solved analytically. Fortunately, the product $a_{12}W_1^i W_2^j$ is always less than unity for realistic values of K, T and v_0, and the series does converge. Numerical evaluation is possible by taking enough terms in the series. The number of terms that must be taken into account depends on temperature, density, and composition. At high temperatures and low densities only a few terms are needed for convergence, while at low temperatures and high densities many terms are needed. For the system of methanol–*i*-propanol at 55°C (70 × 70) terms are needed to obtain accurate results. This increases the computation time dramatically. For this reason, approximations to the exact solution are highly desirable. Two approximations that appeared recently in the literature (Ikonomou and Donohue, 1988; Anderko, 1989) and many others are discussed later in this paper.

Finally, the acid-base perturbed-anisotropic-chain theory (ABPACT) equation of state for a multicomponent associating mixture is given by:

$$\frac{PV}{n_0RT} = \frac{n_T}{n_0} + Z^{\mathrm{rep}} + Z^{\mathrm{iso}} + Z^{\mathrm{ani}} \tag{34}$$

where n_T/n_0 is given by Eq. 33, and Z^{rep}, Z^{iso}, and Z^{ani} are the same as in PACT and are given by Vimalchand and Donohue (1985). These three terms are independent of association parameters. ABPACT (as well as APACT) contains five parameters: T^*, v^*, c, ΔH^o, and ΔS^o. Values for these parameters are obtained by fitting the equation to experimental data for liquid density and vapor pressure. The parameters for the components examined in this work are shown in Table 1. T^*, v^*, and c for all

Table 1. Fitted Molecular Parameters for ABPACT

Molecule	T^*, K	v^* m^3/mol	c	ΔH^o kJ/mol	$\Delta S^o/R$
Methanol	195.5	22.03	1.195	−23.03	−9.88
Ethanol	268.9	32.97	1.338	−25.12	−11.32
i-Propanol	279.3	43.31	1.5456	−25.12	−11.59
n-Butanol	325.9	51.09	1.6486	−25.12	−11.48
Acetone	303.4	45.51	1.3628		
Chloroform	353.5	46.80	1.5638		

components, as well as ΔH^o and ΔS^o for the amphoteric components, were calculated by fitting the equations to experimental data for pure-component liquid density and vapor pressure. For the cross association, ΔH^o_{12} and ΔS^o_{12} were either obtained from the literature or calculated by fitting the equations to experimental VLE data for mixtures as shown in Table 2.

In the ABPACT, it is assumed that hydrogen bonding occurs only in linear chains. Branched chains and closed rings are not permitted. This is in contrast with some spectroscopic evidence showing that cyclic trimers and tetramers occur in alcohol mixtures. We have ignored the presence of these species to retain the mathematical simplicity of the equation of state. In addition, we assumed that for components like alcohols only two hydrogen bonding sites (one acidic and one basic) per molecule are available. This is not consistent with the atomic structure of the oxygen atom in the hydroxyl group of alcohol molecule. In fact, the oxygen has two lone pairs of electrons.

Mixtures containing one amphoteric component and one acidic or basic component

In a binary mixture of an amphoteric component M with a basic component B, M can self-associate or solvate, whereas B can only solvate with M. As a result, the following chemical equilibria are possible:

$$(M_i)^a + M^b \rightleftharpoons M_{i+1} \tag{35}$$

$$(M_i)^a + B \rightleftharpoons M_iB \tag{36}$$

Equation 35 takes into account the self-association of component M and Eq. 36 the solvation between the two components. Molecule B has only one site for interaction so that once a B monomer is added to the chain (Eq. 36) there is no available site for interaction in that end of the chain. The first chemical equilibrium is described by Eq. 15 and the second one by Eq. 17. Here, the cross association equilibrium constant is given by: $K_{12} = K_{Ma}K_B$, where K_{Ma} has been defined above and K_B is the equilibrium constant for B donating an electron. The material balances for M and B and the overall material balance can be obtained from Eqs. 13, 14 and 11, respectively, by considering the constraints that this system implies. The mole fractions z_{i0} and z_{i1} can be related to the mole fractions of monomer of M and monomer of B by repeating the procedure already applied for the general case. In Eqs. 23 through 26 for the equilibrium constants, $j = 1$ so that only K_{III} and K_{IV} are nonzero. In addition, $F_{i,j} = 0$ for $j = 1$. The material balances for M and B finally reduce to the expressions:

$$x_1 = \frac{W_1(1 + a_{12}W_2)}{(1 - a_1W_1)^2} \tag{37}$$

$$x_2 = \frac{W_2 - a_1W_1W_2 + a_{12}W_1W_2}{1 - a_1W_1} \tag{38}$$

where $W_1 = n_{10}/n_0$, $W_2 = n_{01}/n_0$, $a_1 = K_1RT/v_0$, and $a_{12} = K_{12}RT/v_0$.

The system of the nonlinear algebraic equations 37 and 38 is solved as follows. Equation 38 can be written as:

$$W_2 = \frac{x_2(1 - a_1W_1)}{1 - a_1W_1 + a_{12}W_1} \tag{39}$$

Substituting the latter back to Eq. 37, one obtains:

$$PW_1^3 + QW_1^2 + RW_1 + S = 0 \tag{40}$$

where $P = a_1^2x_1(a_{12} - a_1)$, $Q = x_1a_1(3a_1 - 2a_{12}) + a_1 - a_{12} + a_1a_{12}x_2$, $R = -3a_1x_1 + a_{12}(x_1 - x_2) - 1$, and $S = x_1$. Solving Eq. 40 for W_1 and substituting back to Eq. 39, one obtains W_2. The overall material balance for this system is given by the

Table 2. Parameters for Cross Association for ABPACT and k_{ij} Values for ABPACT, APACT and PR-EOS*

System	ΔH^o kJ/mol	$\Delta S^o/R$	k_{ij} ABPACT	k_{ij} APACT	k_{ij} PR-EOS
Acid—Base					
Acetone–chloroform	−30.73	−15.50	0.02	−0.0516	−0.051
Amphoteric–Acid					
Methanol–chloroform	−30.73	−15.36	−0.052	−0.095	
Ethanol–chloroform	−28.47	−14.90	−0.01	−0.037	
i-Propanol–chloroform	−28.47	−14.75	0.0	−0.03	
n-butanol–chloroform	−28.47	−15.10	0.0	−0.01	0.038
Amphoteric–Base					
Methanol–acetone	−23.87	−11.30	0.005	−0.08	0.0
Ethanol–acetone	−23.87	−12.80	0.0	−0.05	0.018
i-Propanol–acetone	−23.87	−12.90	0.0	−0.03	0.0362
n-Butanol–acetone	−24.08	−14.60	0.0	0.0	
Amphoteric–Amphoteric					
Methanol–ethanol	−24.08	−10.60	−0.01	−0.01	−0.0125
Methanol–*i*-propanol	−24.08	−10.74	−0.02	−0.02	−0.0271
Methanol–*n*-butanol	−24.08	−10.68	−0.02	−0.02	
Ethanol–*i*-propanol	−25.12	−11.46	−0.008	−0.008	
Ethanol–*n*-butanol	−25.12	−11.40	−0.01	−0.01	−0.0113
i-Propanol–*n*-butanol	−25.12	−11.54	−0.007	−0.007	

*For amphoteric–amphoteric systems the values for ΔH^o and $\Delta S^o/R$ are the same for both ABPACT and APACT.

expression:

$$\frac{n_T}{n_0} = \frac{W_1 + W_2 - a_1 W_1 W_2 + a_{12} W_1 W_2}{1 - a_1 W_1} \tag{41}$$

and n_T/n_0 is calculated by substituting the values for W_1 and W_2 to Eq. 41. From the three roots of Eq. 40, only one generally satisfies all the constraints: W_1 should be a real number and also $0 \leq W_1, W_2, n_T/n_0 \leq 1$. For a binary mixture of an amphoteric component and an acidic component, the derivation is identical.

Mixtures containing one acidic and one basic component

In the case where no amphoteric component is present, the complexity of the problem decreases. Assume a binary mixture where component A is only acidic and component B is only basic. Both A and B do not self-associate so that association occurs only after mixing them. Each molecule has only one site for association, either acidic or basic, so that only dimers of the form AB can exist in the mixture:

$$A + B \rightleftharpoons AB \tag{42}$$

The equilibrium constant for this reaction is $K_{12} = K_A K_B$ where K_A is the equilibrium constant for A accepting an electron and K_B has been defined before. The procedure here is similar to that described in the previous cases. The material balances for A and B are solved analytically:

$$W_2 = \frac{a_{12}(x_2 - x_1) - 1 + \sqrt{(a_{12}x_1 - a_{12}x_2 + 1)^2 + 4a_{12}x_2}}{2a_{12}} \tag{43}$$

$$W_1 = \frac{x_1}{1 + a_{12} W_2} \tag{44}$$

The overall material balance is reduced to the expression:

$$\frac{n_T}{n_0} = W_1 + W_2 + a_{12} W_1 W_2 \tag{45}$$

In all the mixtures so far, constituent components were amphoteric, acidic, or basic. In the case of a mixture of associating components where one of the species is a diluent (nonassociating component D), the material balance for the diluent reduces to the expression:

$$W_D = x_D \tag{46}$$

and no further complexity is introduced.

The mathematical formulation presented here is applicable to amphoteric components where the acidity and basicity can be measured independently (for example amino-acids). The reason such systems are not treated here is that the nonhydrogen bonding terms need to be developed further. An appropriate expression should be derived to take into account the polar and ionic interactions exhibited in these systems. In all the above derivations, only binary mixtures are treated. For multicomponent mixtures, the proper chemical equilibria and material balances should be set. The derivation is the same and only the algebra is more complicated; in Appendix B the equations for a ternary system are given as well as the equations for the general case of an N-component system.

Approximate solutions for material balances

For the case of a binary mixture of two amphoteric components M and N, the computation time needed to solve the material balances in Eqs. 31 and 32 is very high so that approximate expressions are desirable. Ikonomou and Donohue (1988) have presented an approximate solution for a binary mixture of two amphoteric components that assumes linear interpolation between the pure component limits as follows:

$$W_1 = \frac{4x_1}{(1 + \sqrt{1 + 4K_1RT/v_0})^2} \tag{47}$$

$$W_2 = \frac{4x_2}{(1 + \sqrt{1 + 4K_2RT/v_0})^2} \tag{48}$$

$$\frac{n_T}{n_0} = \frac{2x_1}{1 + \sqrt{1 + 4K_1RT/v_0}} + \frac{2x_2}{1 + \sqrt{1 + 4K_2RT/v_0}} \tag{49}$$

where K_1 and K_2 have been defined above. Anderko (1989) makes an approximation that is somewhat more appealing intuitively. He assumes:

$$W_1 = \frac{4x_1}{[1 + \sqrt{1 + 4(RT/v_0)(K_1x_1 + K_{12}x_2)}]^2} \tag{50}$$

$$W_2 = \frac{4x_2}{[1 + \sqrt{1 + 4(RT/v_0)(K_2x_2 + K_{12}x_1)}]^2} \tag{51}$$

$$\frac{n_T}{n_0} = \frac{2x_1}{1 + \sqrt{1 + 4(RT/v_0)(K_1x_1 + K_{12}x_2)}} + \frac{2x_2}{1 + \sqrt{1 + 4(RT/v_0)(K_2x_2 + K_{12}x_1)}} \tag{52}$$

where K_{12} is defined as $K_{12} = (K_3 + K_4)/2 = (K_{Ma}K_{Nb} + K_{Mb}K_{Na})/2$. By using either of these approximations, computation time decreases dramatically. While both expressions give similar results, Ikonomou's approximation seems to work better for alcohol–alcohol mixtures. This is shown in Figure 1 for methanol–*i*-propanol at 55°C where both approximations and experimental data (Kogan, 1966) are plotted. It is apparent that the Ikonomou and Donohue approximation predicts experimental data more accurately than the Anderko approximation does. This has been also recognized by Elliott and Suresh (1990). Predictions obtained by solving the material balances numerically coincide with the results from the Ikonomou and Donohue approximation. Similar results have been obtained for other binaries such as *i*-propanol–*n*-butanol.

There has been an attempt to generalize the solution of the three cases presented in the above derivations (amphoteric–amphoteric, amphoteric–base, and acid–base). Since Eqs. 47 through 49 are only an approximate solution for the amphoteric–amphoteric mixture, they do not reduce to the exact solution when applied to the other two cases. If these equations are applied in the alcohol–ketone case, Eq. 47 will remain the same for the alcohol while Eq. 48 will reduce to $W_2 = x_2$ for the ketone. The expression for W_1 is correct only when $x_1 \rightarrow 1$, and

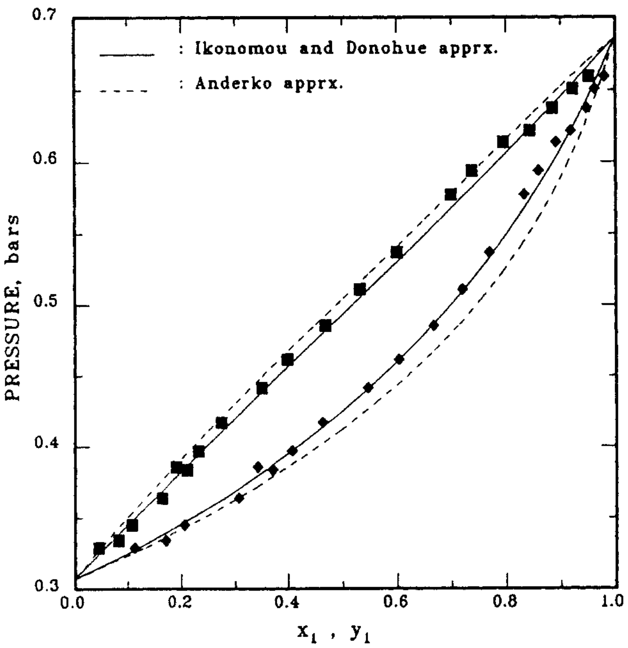

Figure 1. Experimental and ABPACT-predicted VLE for methanol (1)–*i*-propanol (2) at 55°C.

It is done by solving Eqs. 31 to 33 using the Ikonomou and Donohue and the Anderko approximations.

k_{ij} for the dispersion forces is -0.02 for the Ikonomou and Donohue approximation and -0.04 for the Anderko approximation. Predicted results from the numerical solution coincide with the Ikonomou and Donohue approximation. Experimental data are from Kogan (1966).

the expression for W_2 is correct only when $x_2 \rightarrow 1$, therefore no association occurs. This result is not surprising since Eqs. 47 through 49 were first derived from the APACT where nonself-associating components (e.g., ketone) are treated as diluents. For the case of chloroform–ketone mixture, Eqs. 47 and 48 reduce to $W_1 = x_1$ and $W_2 = x_2$, respectively, for the same reason as before. In that case, ABPACT reduces essentially to PACT since no association is considered.

The Anderko approximation (Eqs. 50 through 52) takes into account solvation between the two components explicitly; therefore, one expects that it should approximate the exact solution for the alcohol–ketone case better than Eqs. 47 through 49. In fact, Eq. 50 for the alcohol is a satisfactory approximation to the exact expression given from Eq. 40. Equation 51 reduces to the following expression for the ketone:

$$W_2 = \frac{4x_2}{(1 + \sqrt{1 + 4RT/v_0K_{12}x_1})^2} \tag{53}$$

which is a very bad approximation to the exact solution given from Eq. 39. When applied to the chloroform–ketone mixtures, Eqs. 50 through 52 give again very bad results. In general, Eqs. 50 through 52 go to the exact solution only in the limits, when $x_1 \rightarrow 1$ or $x_2 \rightarrow 1$.

We have attempted to generalize the solution of the material balances given from Eqs. 31 and 32 to find an expression that could be applicable to all cases: amphoteric–amphoteric, amphoteric–acid, acid–base, and mixtures containing diluents. Such an expression should meet the following constraints:

- It should accurately approximate the numerical solution for the amphoteric–amphoteric mixture, since we do not have an analytical solution for that case.
- It should be reduced to the exact solution under proper constraints, when applied to amphoteric–acid and amphoteric–base systems.
- It should be reduced to the exact solution under the proper constraints, when applied to acid–base systems.
- It should satisfy the limits in all cases when one of the components is in excess, when x_1 or $x_2 \rightarrow 1$.

Thus far, no single expression has been found to satisfy all four constraints. Many of the expressions applied meet the last three constraints but they fail to approximate the numerical solution for the amphoteric–amphoteric mixtue. A solution, which works well for the amphoteric–acid or base mixture and for the acid-base mixture, but is bad for the amphoteric–amphoteric mixture is:

$$W_1 = \frac{x_1}{\dfrac{1}{(1 - a_1W_1)^2} + \dfrac{a_{12}W_2}{(1 - a_2W_2)(1 - a_{21}W_1)(1 - a_1W_1)^2}} \tag{54}$$

$$W_2 = \frac{x_2}{\dfrac{1}{(1 - a_2W_2)^2} + \dfrac{a_{12}W_1}{(1 - a_1W_1)(1 - a_{21}W_2)(1 - a_2W_2)^2}} \tag{55}$$

For the amphoteric–acid case, Eqs. 54 and 55 reduce to the exact solution for $a_2 = a_{21} = 0$ and $a_{12} \neq 0$ and also for the acid-base case for $a_1 = a_2 = a_{21} = 0$. For the amphoteric–amphoteric mixture, Eqs. 54 and 55 do not correctly approximate the numerical solution.

The following expression works well for the amphoteric–amphoteric mixture and reduces to the exact solution for acid-base mixture but it is only an approximation for the amphoteric–acid (or base) mixture:

$$W_1 = \frac{2x_1}{a_{12}^D(x_2 - x_1) + 2a_1x_1 + 2a_{12}^{\infty}x_2 + R_1} \tag{56}$$

where

$$R_1 = \sqrt{[1 + a_{12}^D(x_1 - x_2)]^2 + 4a_{12}^Dx_2 + 4a_{12}^{\infty}x_2} + \sqrt{1 + 4a_1x_1}$$

and

$$W_2 = \frac{2x_2}{a_{12}^D(x_1 - x_2) + 2a_2x_2 + 2a_{12}^{\infty}x_1 + R_2} \tag{57}$$

where

$$R_2 = \sqrt{[1 + a_{12}^D(x_2 - x_1)]^2 + 4a_{12}^Dx_1 + 4a_{12}^{\infty}x_1} + \sqrt{1 + 4a_2x_2}.$$

For an amphoteric component $a_{12}^D = 0$ where D denotes dimer and $a^{\infty}_{12} = a_{12}$, whereas for an acid or a base $a^{D}_{12} = a_{12}$ and $a^{\infty}_{12} = 0$.

The difficulty in decoupling the two infinite series in Eqs. 31 and 32 arises from the presence of the binomial coefficient $C_{i,j}$ in the expression for $\overline{K}$ (see Eq. 30). To overcome this problem we used the following approach. Initially we take into account only the self-association of the two amphoteric components M and N, and the resulting associated species M_i and N_j are treated as monomers so that a monomer–dimer chemical equilibrium is assumed for the solvation similar to the chemical equilibrium in the acid-base mixture. As a result, in the material balances for the two components the binomial coefficient is approximated with the term ij and the two series are decoupled. The two nonlinear equations are solved with a numerical technique using the Ikonomou and Donohue approximation for the initial estimate. The results obtained from this procedure for the amphoteric–amphoteric mixture were bad because of the approximate expression used for the binomial coefficient. Nevertheless, this numerical technique gave very good results in the case of amphoteric-base mixture. In that case, an initial estimate for W_1 obtained from the Ikonomou and Donohue approximation is used in Eq. 38 to solve for W_2, and the result is substituted back to Eq. 37 to solve for W_1. The new result is used to calculate a new value for W_2, and so on until convergence.

It is interesting to compare the variation of n_T/n_0 with x for the different mixtures. In Figure 2, n_T/n_0 is plotted vs. x for the case of amphoteric–amphoteric, amphoteric–acid, acid-base and amphoteric-diluent mixture, respectively. For the amphoteric–amphoteric, amphoteric-acid and amphoteric-diluent mixtures x is the amphoteric component, whereas for the acid-base mixture, n_T/n_0 is symmetric with respect to x, and so x can be either the acid or the base. For the amphoteric–amphoteric mixture $K_1 = 0.8$ and $K_2 = 0.5$, for the amphoteric-acid mixture $K_1 = 0.8$ and $K_{12} = 0.63$, for the acid-base mixture $K_{12} = 0.63$, and for the amphoteric-diluent mixture $K_1 = 0.8$. In all cases, $RT/v_0 = 10$. For the mixtures where one of the components (component 2) is not self-associating, $n_T/n_0 = 1$ for $x_2 = 1$, as expected.

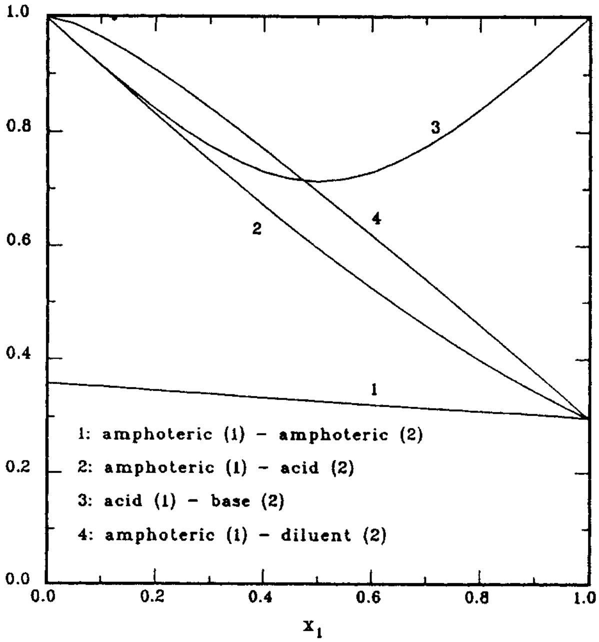

Figure 2. n_t/n_0 vs. x_1 predictions from ABPACT for amphoteric (1)–amphoteric (2), amphoteric (1)–acid (2), acid (1)–base (2), and amphoteric (1)–diluent (2) mixture.

Results and Discussion

The ABPACT was applied to a number of binary and ternary mixtures exhibiting acid-base interactions. Since the equations allow for each component to be acidic and/or basic (*i.e.*, amphoteric), the various permutations of these types of components were examined. The parameters needed for a mixture calculation are the pure-component parameters for each component (see Table 1), and the equilibrium constants for self-association and solvation where appropriate. The temperature dependence of each K is given by Eq. 7:

$$\ln K = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$

In some cases, an adjustable mixture parameter k_{ij} is used in the dispersion term, and its magnitude is reported for each mixture calculation. In this paper, we have concentrated only on VLE. No attempt was made to apply the equation of state to LLE.

The following combinations are possible for a binary mixture: *a-b, a-ab, b-ab, ab-ab,* where *a, b,* and *ab* refer to acidic, basic, and amphoteric, respectively. To evaluate the capabilities of ABPACT, alcohols were chosen as amphoteric components, acetone as a basic component, and chloroform as an acidic component. Calculated results from the ABPACT are compared with experimental data and with other equations: the APACT (Ikonomou and Donohue, 1986), UNIFAC (Fredenslund *et al.*, 1977), and the PR-EOS (Robinson *et al.*, 1977). For a mixture of the type *a-b,* Figure 3 shows the ABPACT-calculated, PACT-calculated and experimental VLE behavior (Kogan, 1966) of acetone–chloroform at 1 atm. In that case, PACT predictions can be obtained from ABPACT by using the Ikonomou and Donohue approximation for the material balances, as mentioned before. Predictions obtained from ABPACT are quite accurate and similar to the predictions from PACT. The solvation enthalpy, ΔH^o_{12}, is taken as the value reported by Drago *et al.* (1965), while the entropy, ΔS^o_{12}, is fitted to the mixture VLE data. ΔH^o and ΔS^o values for the solvation equilibria and k_{ij} values are given in Table 2 for all mixtures. For the case of amphoteric-acid and amphoteric-base mixtures, ΔS^o for the solvation is obtained by fitting the equation to experimental VLE data so that k_{ij} is zero for most of the cases. For amphoteric–amphoteric mixtures ΔH^o and ΔS^o for the solvation are calculated as a mean average of ΔH^o and ΔS^o of association of the pure components so that a nonzero k_{ij} is needed to fit accurately the experimental VLE data. In general, ABPACT gives reasonably good agreement.

For *ab-a* type of binary mixtures, ABPACT fit, APACT fit and experimental VLE data (Gmehling and Onken, 1981) of chloroform with methanol at 1 atm are given in Figure 4. In this calculation, chloroform was treated as a diluent in APACT neglecting the solvation equilibrium. As shown, significant improvement has been achieved by including the acid-base interactions which lead to solvation equilibrium. Similarly, good results have been obtained using ABPACT for other systems

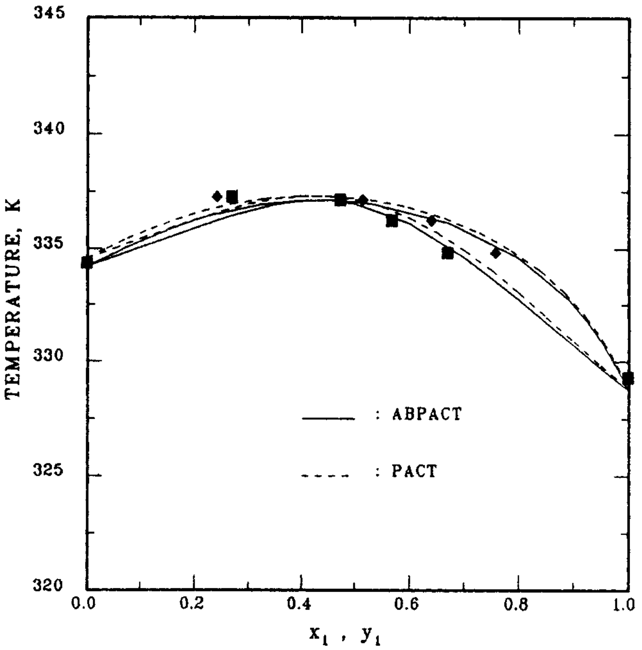

Figure 3. Experimental ABPACT- and PACT-predicted VLE for acetone (1)–chloroform (2) at 1 atm.

PACT calculations are obtained from ABPACT using the Ikonomou and Donohue approximation; experimental data are from Kogan (1966).

such as ethanol–chloroform, *i*-propanol–chloroform, and *n*-butanol–chloroform. The magnitude of the improvement between ABPACT and APACT becomes smaller as the size of the alochols increases. For the methanol–chloroform mixture, an azeotrope is observed because the boiling points of the pure components are very close to each other and so a nonzero k_{ij} is needed in ABPACT to accurately fit the azeotrope. This azeotrope disappears for mixtures of chloroform with higher alcohols such as *i*-propanol and *n*-butanol, and as a result APACT can fit these experimental data accurately. For *n*-butanol–chloroform, the difference between the two equations is very small. In Figure 5 comparisons are made between ABPACT and PR-EOS for *n*-butanol–chloroform mixture at 1 atm. Best fits to experimental data (Kogan, 1966) for the *k* factor are shown using these two equations. The fit obtained from ABPACT is better and also PR-EOS fit fails to calculate the minimum in the curve that is fitted very accurately by ABPACT. PR-EOS does not consider hydrogen bonding explicitly; to accurately fit phase equilibrium data for such systems it needs more than one temperature-dependent binary parameter (Robinson *et al.*, 1985).

For mixtures of acetone with alcohols, ABPACT gives very good fits. In Figure 6 ABPACT, APACT, and UNIFAC-calculated VLE are compared with experimental data (Gmehling and Onken, 1981) for the ethanol–acetone mixture at 1 atm. UNIFAC activity coefficient model does not take into account hydrogen bonding explicitly. Two sets of parameters were used for the UNIFAC calculations. The original parameters given by Fredenslund *et al.* (1977) are based on VLE data, whereas the more recent parameters (Bastos *et al.*, 1988) are based on infinite dilution activity coefficient data. The original parameters fit the data much better than the recent ones. The recent parameters predict the existence of an azeotrope that does not exist. The improvement of ABPACT over APACT and UNIFAC is apparent. Good results were obtained also from ABPACT for methanol–acetone, *i*-propanol–acetone and *n*-butanol–acetone mixtures.

For *ab-ab* mixtures, ethanol–*n*-butanol mixture at 1 atm is shown in Figure 7. ABPACT fits experimental data (Kogan, 1966) very accurately. Since it is very difficult experimentally to accurately measure the acidic and basic contributions to K_{12}, it

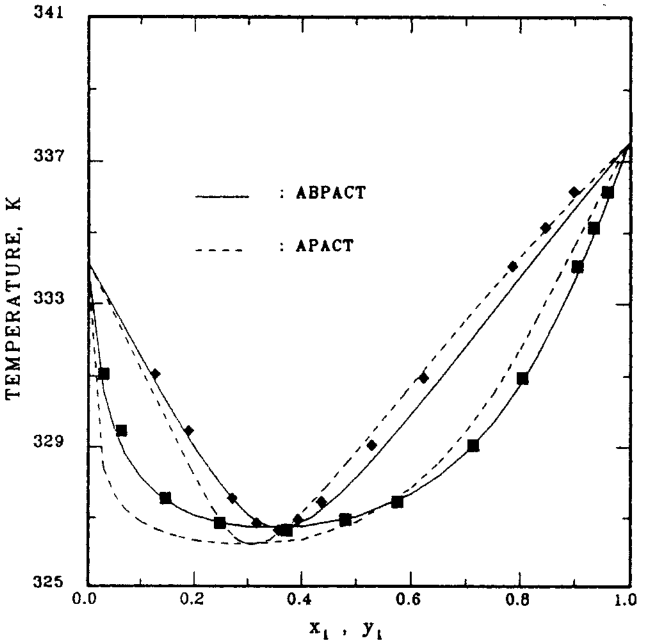

Figure 4. Experimental ABPACT- and APACT-predicted VLE for methanol (1)–chloroform (2) at 1 atm.

Experimental data are from Gmehling and Onken (1981).

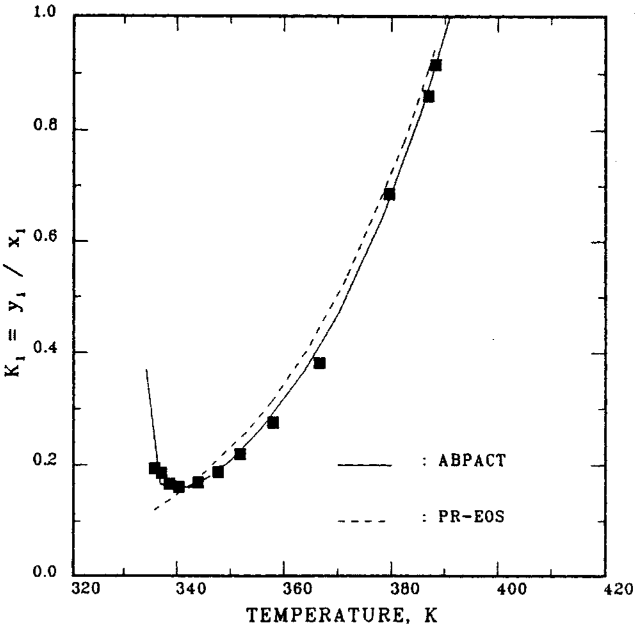

Figure 5. Experimental ABPACT- and PR-EOS-predicted VLE for *n*-Butanol (1)–Chloroform (2) at 1 atm.

Experimental data are from Kogan (1966).

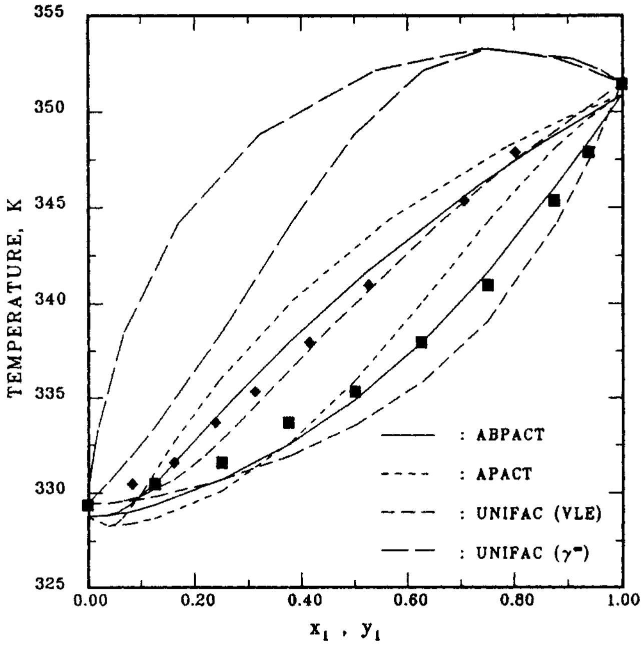

Figure 6. Experimental ABPACT-, APACT-, and UNIFAC-predicted VLE for ethanol (1)–acetone (2) at 1 atm.

Two sets of parameters were used for UNIFAC. The original parameters (Fredenslund *et al.*, 1977) were based on VLE data, whereas the more recent parameters (Bastos *et al.*, 1988) were based on infinite dilution activity coefficient data. Experimental data are from Gmehling and Onken (1981).

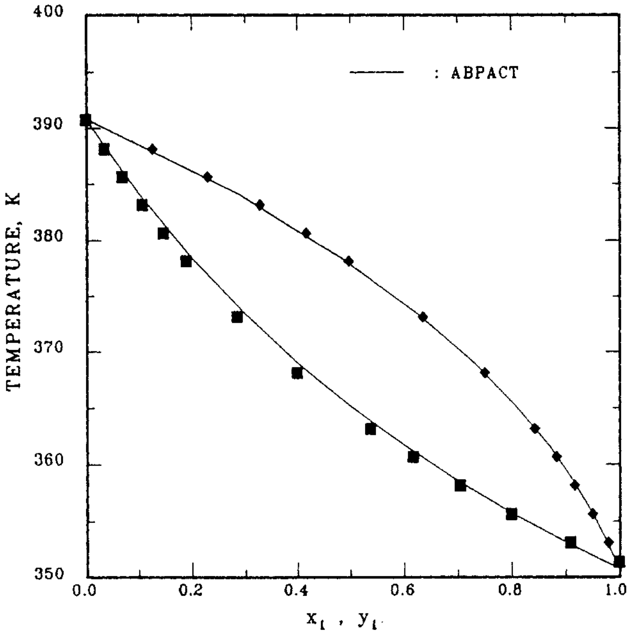

Figure 7. Experimental and ABPACT-predicted VLE for ethanol (1)–*n*-butanol (2) at 1 atm.

Experimental data are from Kogan (1966).

is simply taken as the geometric mean of K_1 and K_2 (this corresponds to taking the arithmetic mean both for ΔH^o_{12} and S^o_{12}). Attempts to separate the acidic and basic contributions to ΔH^o and ΔS^o for binary mixtures of alcohols based on the solvatochromic parameters of Kamlet *et al.* (1983) gave no significant improvement in the results. Therefore, the APACT and the ABPACT have the same mathematical form, and no comparison between the two is possible. Binaries of two alcohols, in addition to those reported by Ikonomou and Donohue (1988), have been examined using the new equation, and good agreement with the experimental data has been observed in all cases.

The values for ΔH and ΔS for the Lewis acid-base interactions in Table 2 are obtained either from the literature or by fitting experimental data. The ideal way would be to obtain all these values experimentally from spectroscopic data. In practice, it is difficult to obtain values that are accurate or even unique. Literature values vary widely. For example, Prausnitz *et al.* (1986) give $\Delta H = -22.61$ *kJ/mol of product* for the acetone–chloroform system, whereas using Drago's method a value of -30.73 *kJ/mol of product* is obtained. Several attempts have been made to calculate the enthalpy of a reaction using characteristic parameters for the reactants. Drago *et al.* (1965) have proposed a double-scale equation to calculate the enthalpy of a Lewis acid-base reaction assigning two constants to the acid and another two to the base. In Table 3, experimental data (Becker, 1961) for ΔH^o and ΔS^o are compared to the values obtained using Drago's method as well as values fitted for the ABPACT. The consistency between the values used in ABPACT and these obtained using Drago's method is remarkable. In addition, the difference between the experimental values reported by Becker and the values obtained from ABPACT are within the range of experimental error (± 1.67 *kJ/mol of reactant* as estimated by Becker).

Table 3. Values for ΔH^o and $\Delta S^o/R$*

	ΔH^o (kJ/mol of Product)			$\Delta S^o/R$	
System	Expt.	Drago	ABPACT	Expt.	ABPACT
Methanol—Methanol		−23.61	−23.03		−9.88
Methanol—Ethanol		−24.08	−24.08		−10.60
Methanol—Acetone	−21.10	−20.94	−23.87	−7.30	−10.65
Methanol—Chloroform		−34.33	−30.73		−15.36
Ethanol—Ethanol		−25.12	−25.12		−11.32
Ethanol—Acetone	−28.97	−23.28	−23.87	−11.20	−12.80
Ethanol—Chloroform		−33.08	−28.47		−14.90
Acetone—Chloroform		−30.73	−30.73		−15.50

*Experimental values are from Becker (1961); those marked Drago are calculated using his method (1965). Values for ABPACT are calculated as discussed in the text.

Conclusions

The APACT has been extended to treat multicomponent mixtures where Lewis acid-base interactions occur. All interactions are taken into account explicitly. The new equation works better than APACT in predicting VLE between amphoteric and acidic or basic components. Other commonly used models that calculate hydrogen bonding implicitly like UNIFAC and PR-EOS gave satisfactory results in calculating VLE for hydrogen bonding systems, but in all cases ABPACT was superior than these models.

In the future, our theory will be generalized to treat components with more than two hydrogen bonding sites per molecule. We expect to retain the simplicity of the hydrogen bonding term in the resulting equation of state. In addition, we hope to be able to independently calculate the acidic and the basic contribution of the two molecules in the enthalpy and entropy of reaction in the formation of a hydrogen bond.

Acknowledgment

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Notation

A = acidic component
a_1, a_2, a_{12} = association parameters defined in Eq. 33
B = basic component
c = 1/3 number of external (density-dependent) degrees of freedom
$C_{i,j}$ = binomial coefficient
D = diluent component
$D_{i,j}, E_{i,j}, F_{i,j}$ = coefficients defined in Eq. 22
$\Delta H^o, \Delta H^o_{12}$ = standard enthalpy of association
k_{ij} = binary interaction parameter
$K_1, K_2, K_3, K_4, K_{12}$ = association equilibrium constants
$K_I, K_{II}, K_{III}, K_{IV}$ = association equilibrium constants defined in Eqs. 23–26
K = association equilibrium constant defined in Eq. 30
k, l, m, n = exponents in the equilibrium constant expression defined in Appendix A
M, N = amphoteric components
n = number of moles
P = pressure
P, Q, R, S = coefficients in Eq. 40
$p_{i,j}, q_{i,j}, r_{i,j}$ = coefficients defined in Eq. 30
R = gas constant
$\Delta S^o, \Delta S^o_{12}$ = standard entropy of association
T = temperature
T^* = characteristic energy molecular parameter
V = total volume
v = molar volume
v^* = characteristic size molecular parameter
W_1, W_2 = association variables defined in Eq. 29
x = mole fraction calculated ignoring association
Z = compressibility
z = true mole fraction

Greek letters

β = association parameter defined in Eq. A3
ϕ = fugacity coefficient

Subscripts

0 = quantity calculated ignoring association
a = acidic
b = basic
$i0$ = association species of pure M
$0j$ = association species of pure N
ij = association species of components M and N in a binary
N_i = component in a mixture of N components in Appendix B
T = true association species

Superscripts

a = acidic
ani = anisotropic
b = basic
D = dimer
iso = isotropic
rep = repulsive
∞ = infinite equilibria

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Appendix A: Evaluation of the Expression for z_{ij}

In a mixture of two amphoteric components M and N, there are four distinguishable species: M^b (M acting as a base), M^a (M acting as an acid), N^b and N^a. The bonds that are permitted for these species are of the type acid base or base acid. Bonds of the type acid acid or base base are not permitted. Two molecules M and N can form a hydrogen bond in two different ways as follows:

$$M^b + N^a \rightleftarrows MN, \tag{A1}$$

$$M^a + N^b \rightleftarrows MN. \tag{A2}$$

From the chemical equilibria that describe these two reactions, the mole fraction z_{11} can be calculated as:

$$z_{11} = (K_{Mb}K_{Na} + K_{Ma}K_{Nb})\beta z_{10}z_{01} \tag{A3}$$

where the term $\beta = (n_T/n_o)(RT/v_o)$ comes from evaluating the ratios of fugacity coefficients in the chemical equilibria as already has been shown in the theory. In the case of trimer, there are two possibilities: either $i = 1$ and $j = 2$ or $i = 2$ and $j = 1$, where i corresponds to the number of M monomers in the trimer and j to the number of N monomers in the trimer. For $i = 1$ and $j = 2$ the following species are possible: $^a(MNN)^b$, $^b(MNN)^a$, $^a(NMN)^b$, where the difference between $^a(MNN)^b$ and $^b(MNN)^a$ is that in species $^a(MNN)^b$ the M molecule has used its basic portion for bonding with N whereas in species $^b(MNN)^a$ the M molecule has used its acidic portion for bonding. As a result, z_{12} can be calculated from the chemical equilibria and an expression can be obtained for z_{12} with respect to the monomeric species z_{10} and z_{01}:

$$z_{12} = (K_{Mb}K_{Na}K_{Nb}K_{Na} + K_{Ma}K_{Nb}K_{Na}K_{Nb} + K_{Nb}K_{Ma}K_{Mb}K_{Na})\beta^2 z_{10}z_{01}^2. \tag{A4}$$

For the case where $i = 2$, $j = 1$, the following species are possible: $^a(MMN)^b$, $^b(MMN)^a$, $^a(MNM)^b$, and

$$z_{21} = (K_{Mb}K_{Ma}K_{Mb}K_{Na} + K_{Ma}K_{Mb}K_{Ma}K_{Nb} + K_{Mb}K_{Na}K_{Nb}K_{Ma})\beta^2 z_{10}^2 z_{01}. \tag{A5}$$

For the tetramer there are three possible combinations in terms of the number of monomers from each component: $i = 1, j = 3$ ($C_{1,3} = (4!/1!3!) = 4$ possible configurations), or $i = 2$, ($C_{1,2} = 6$ possible configurations), or $i = 3$, $j = 1$ ($C_{3,1} = 4$ possible configurations). The expressions for the z_{13}, the z_{22} and the z_{31} are quite long and they are not presented. The number of different configurations increases as the size of the i-mer increases. By analyzing the chemical equilibria step by step, calculation of z_{ij} with respect to z_{10} and to z_{01} is possible.

In all the above expressions, the term $K^k_{Ma}K^l_{Mb}K^m_{Na}K^n_{Nb}$ exist with different values for the k,l,m, and n. The exponents k,l,m, and n correspond to the number of acidic and basic monomers of species M and N, respectively, bonded to the association species. For a linear species M_iN_j, the following constraints should be satisfied:

- Number of acids = number of bases, so $k + m = l + n$.
- Each substituent monomer contributes two equilibrium constants (one acidic and one basic) except for the end groups. Thus, it is: $k + l + m + n = 2(i + j) - 2$.
- Each substituent monomer may be in an end position or in a middle one. In the end it contributes one equilibrium constant, whereas in the middle two. For M^a having i M monomers, the number of equilibrium constants K_{Ma} may be i (thus $k = i$) if there is no M^a in the end, or $i - 1$ if there is an M^a in one end (it is impossible both ends to be acidic, one should be basic). So, $k = i$ or $k = i - 1$ and similarly $l = i$ or $l = i - 1$.
- k and l depend on i only; m and n depend on j only.
- Once the relations $k = f(i)$ and $l = g(i)$ are established, m and n are calculated using the first two constraints.

So finally there are four possible configurations that meet all the constraints:

I. $k = i - 1, l = i - 1, m = j, n = j$
II. $k = i - 1, l = i, m = j, n = j - 1$
III. $k = i, l = i - 1, m = j - 1, n = j$
IV. $k = i, l = i, m = j - 1, n = j - 1$

So for a specific pair of i and j there are four different equilibrium constants: K_{I}, K_{II}, K_{III}, and K_{IV}. The last step is to examine how many different species can exist for each of the four configurations. Again by starting from the dimer and going to trimer, tetramer, etc., all the different species are calculated. Finally, the following number of species are possible for each of the four configurations for a specific pair of i and j: for configuration I with equilibrium constant K_{I}, $[(i + j - 2)!/(i - 2)!j!]$ different species can exist; for configuration II with constant K_{II} and for configuration III with constant K_{III} $[(i + j - 2)!/(i - 1)!(j - 1)!]$ species for each can exist; and for configuration IV with constant K_{IV} $[(i + j - 2)!/i!(j - 2)!]$ different species can be found. For example, for $i = 1$ and $j = 2$ we have calculated in the beginning of this section the different species that can exist. Using the formalism developed here, for configuration I no species can be found, for the configuration II one species is available, and the equilibrium constant for this species corresponds to the first term inside the parenthesis in the righthand side of Eq. A4. Similarly, for configurations III and IV, one species is available for each one corresponding to the second and third term, respectively, inside the parenthesis in the right hand side of Eq. A4. Similarly, one can calculate the possible species for $i = 2$ and $j = 1$ and compare the results with Eq. A5.

So, in general, the mole fraction z_{ij} is given by:

$$z_{ij} = \frac{(i+j-2)!}{(i-2)!j!} K_{Ma}^{(i-1)} K_{Mb}^{(i-1)} K_{Na}^{j} K_{Nb}^{j} + \frac{(i+j-2)!}{(i-1)!(j-1)!} [K_{Ma}^{(i-1)} K_{Mb}^{i} K_{Na}^{j} K_{Nb}^{(j-1)} + K_{Ma}^{i} K_{Mb}^{(i-1)} K_{Na}^{(j-1)} K_{Nb}^{j}] + \frac{(i+j-2)!}{i!(j-2)!} K_{Ma}^{i} K_{Mb}^{i} K_{Na}^{(j-1)} K_{Nb}^{(j-1)}. \quad (A6)$$

Appendix B: Evaluation of the Equations for Multicomponent Mixtures

In the case of ternary mixtures where all three components (M, N, and L) are amphoteric, the following species would exist in the mixture: M_i, N_j, L_k, M_iN_j, M_iL_k, N_jL_k, and $M_iN_jL_k$ and the chemical equilibria can be described using the approach developed for the binary mixture. Following the same procedure, the material balances finally yield to the equations:

$$x_1 = \sum_{i=1}^{\infty} i \left(K_1 \frac{RT}{v_0}\right)^{i-1} W_1^i + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} i\overline{K}_{12} \left(\frac{RT}{v_0}\right)^{i+j-1} W_1^i W_2^j + \sum_{i=1}^{\infty}\sum_{k=1}^{\infty} i\overline{K}_{13} \left(\frac{RT}{v_0}\right)^{i+k-1} W_l^i W_3^k + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\sum_{k=1}^{\infty} i\overline{K} \left(\frac{RT}{v_0}\right)^{i+j+k-1} W_1^i W_2^j W_3^k \quad (B1)$$

$$x_2 = \sum_{j=1}^{\infty} j \left(K_2 \frac{RT}{v_0}\right)^{j-1} W_2^j + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} j\overline{K}_{12} \left(\frac{RT}{v_0}\right)^{i+j-1} W_l^i W_2^j + \sum_{j=1}^{\infty}\sum_{k=1}^{\infty} j\overline{K}_{23} \left(\frac{RT}{v_0}\right)^{j+k-1} W_2^j W_3^k + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\sum_{k=1}^{\infty} j\overline{K} \left(\frac{RT}{v_0}\right)^{i+j+k-1} W_1^i W_2^j W_3^k \quad (B2)$$

$$x_3 = \sum_{k=1}^{\infty} k \left(K_3 \frac{RT}{v_0}\right)^{k-1} W_3^k + \sum_{i=1}^{\infty}\sum_{k=1}^{\infty} k\overline{K}_{13} \left(\frac{RT}{v_0}\right)^{i+k-1} W_l^i W_3^k + \sum_{j=1}^{\infty}\sum_{k=1}^{\infty} k\overline{K}_{23} \left(\frac{RT}{v_0}\right)^{j+k-1} W_2^j W_3^k + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\sum_{k=1}^{\infty} k\overline{K} \left(\frac{RT}{v_0}\right)^{i+j+k-1} W_1^i W_2^j W_3^k \quad (B3)$$

$$\frac{n_T}{n_0} = \sum_{i=1}^{\infty} \left(K_1 \frac{RT}{v_0}\right)^{i-1} W_1^i + \sum_{j=1}^{\infty} \left(K_2 \frac{RT}{v_0}\right)^{j-1} W_2^j + \sum_{k=1}^{\infty} \left(K_3 \frac{RT}{v_0}\right)^{k-1} W_3^k + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} \overline{K}_{12} \left(\frac{RT}{v_0}\right)^{i+j-1} W_l^i W_2^j + \sum_{i=1}^{\infty}\sum_{k=1}^{\infty} \overline{K}_{13} \left(\frac{RT}{v_0}\right)^{i+k-1} W_1^i W_3^k + \sum_{j=1}^{\infty}\sum_{k=1}^{\infty} \overline{K}_{23} \left(\frac{RT}{v_0}\right)^{j+k-1} W_2^j W_3^k + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\sum_{k=1}^{\infty} \overline{K} \left(\frac{RT}{v_0}\right)^{i+j+k-1} W_1^i W_2^j W_3^k \quad (B4)$$

where

$$\overline{K} = A(K_{\rm I} + K_{\rm VII}) + B(K_{\rm II} + K_{\rm VIII}) + C(K_{\rm III} + K_{\rm V}) + DK_{\rm IV} + EK_{\rm VI} + FK_{\rm IX} \quad (B5)$$

$$K_{\rm I} = K_{Ma}^{i} K_{Mb}^{(i-1)} K_{Na}^{(j-1)} K_{Nb}^{j} K_{La}^{k} K_{Lb}^{k} \quad (B6)$$

$$K_{\rm II} = K_{Ma}^{i} K_{Mb}^{(i-1)} K_{Na}^{j} K_{Nb}^{j} K_{La}^{(k-1)} K_{Lb}^{k} \quad (B7)$$

$$K_{\rm III} = K_{Ma}^{i} K_{Mb}^{i} K_{Na}^{(j-1)} K_{Nb}^{j} K_{La}^{k} K_{Lb}^{(k-1)} \quad (B8)$$

$$K_{\rm IV} = K_{Ma}^{i} K_{Mb}^{i} K_{Na}^{j} K_{Nb}^{j} K_{La}^{(k-1)} K_{Lb}^{(k-1)} \quad (B9)$$

$$K_{\rm V} = K_{Ma}^{i} K_{Mb}^{i} K_{Na}^{j} K_{Nb}^{(j-1)} K_{La}^{(k-1)} K_{Lb}^{k} \quad (B10)$$

$$K_{\rm VI} = K_{Ma}^{(i=1)} K_{Mb}^{(i-1)} K_{Na}^{j} K_{Nb}^{j} K_{La}^{k} K_{Lb}^{k} \quad (B11)$$

$$K_{\rm VII} = K_{Ma}^{(i-1)} K_{Mb}^{i} K_{Na}^{j} K_{Nb}^{(j-1)} K_{La}^{k} K_{Lb}^{k} \quad (B12)$$

$$K_{\rm VIII} = K_{Ma}^{(i-1)} K_{Mb}^{i} K_{Na}^{j} K_{Nb}^{j} K_{La}^{k} K_{Lb}^{(k-1)} \quad (B13)$$

$$K_{\rm IX} = K_{Ma}^{i} K_{Mb}^{i} K_{Na}^{(j-1)} K_{Nb}^{(j-1)} K_{La}^{k} K_{Lb}^{k} \quad (B14)$$

and

$$A = \frac{(i+j+k-2)!}{(i-1)!(j-1)!k!},\quad B = \frac{i+j+k-2)!}{(i-1)!j!(k-1)!},\quad C = \frac{(i+j+k-2)!}{i!(j-1)!(k-1)!},$$

$$D = \frac{(i+j+k-2)!}{i!j!(k-2)!},\quad E = \frac{(i+j+k-2)!}{(i-2)!j!k!},\quad F = \frac{(i+j+k-2)!}{i!(j-2)!k!}$$

and $\overline{K}_{12}$, $\overline{K}_{13}$, and $\overline{K}_{23}$ are obtained from $\overline{K}$ by setting $k = 0, j = 0$, and $i = 0$, respectively. In the case where one or more of the components is only acidic, only basic or diluent, the complexity of the above equations decreases considerably. Based on pure components and on constituent binary parameters, ABPACT fairly accurately predicted VLE for various ternary mixtures such as methanol–*i*-propanol–acetone, methanol–ethanol–acetone, and methanol–chloroform–acetone. For example, for the mixture methanol–ethanol–acetone, we have performed flash calculations to obtain the compositions of the two phases at 1 *atm*. The % *AAD* of the ABPACT predictions from the experimental data for the equilibrium compositions was 6.0%. Calculations using the PR-EOS gave a % *AAD* of 5.0% from the experimental data. In both calculations, binary parameters were obtained from the constituent binary mixtures (Table 2).

Finally, in the general case for an N-amphoteric components system, the $N + 1$ nonlinear algebraic equations describing the association among the various components are:

$$\begin{aligned} x_{N_i} = {} & \sum_{i=1}^{\infty} i \left(K_{N_i}\frac{RT}{v_0}\right)^{i-1} W^i_{N_i} + \sum_{\substack{N_j=1\\N_j\neq N_i}}^{N} \left[\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} i\overline{K}_{N_iN_j}\left(\frac{RT}{v_0}\right)^{i+j-1} W^i_{N_i}W^j_{N_j}\right] + \sum_{\substack{N_j=1\\N_j\neq N_i}}^{N-1}\ \sum_{\substack{N_k=N_j+1\\N_k\neq N_i}}^{N} \\ & \cdot\left[\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\sum_{k=1}^{\infty} i\overline{K}_{N_iN_jN_k}\left(\frac{RT}{v_0}\right)^{i+j+k-1} W^i_{N_i}W^j_{N_j}WS^k_{\mathrm{N_k}}\right] + \cdots + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\cdots\sum_{l=1}^{\infty}\sum_{m=1}^{\infty}\cdots\sum_{n=1}^{\infty} i\overline{K}\left(\frac{RT}{v_0}\right)^{i+j+\cdots+l+m+\cdots+n-1} \\ & \cdot W^i_{N_i}W^j_1\cdots W^l_{\mathrm{N_i}-1}W^m_{N_i+1}\cdots W^n_N \end{aligned} \tag{B15}$$

where $N_i = 1,2,\ldots,N$ and:

$$\begin{aligned} \frac{n_T}{n_0} = {} & \sum_{N_i=1}^{N}\left[\sum_{i=1}^{\infty}\left(K_{N_i}\frac{RT}{v_0}\right)^{i-1} W^i_{N_i}\right] + \sum_{N_i=1}^{N-1}\ \sum_{N_j=N_i+1}\left[\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\overline{K}_{N_iN_j}\left(\frac{RT}{v_0}\right)^{i+j-1} W^i_{N_i}W^j_{N_j}\right] \\ & + \cdots + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\cdots\sum_{n=1}^{\infty}\overline{K}\left(\frac{RT}{v_0}\right)^{i+j+\cdots+n-1} W^i_1W^j_2\cdots W^n_N \end{aligned} \tag{B16}$$

where $\overline{K}_{N_iN_j} = f(K_{N_ia}, K_{N_ib}, K_{N_ja}, K_{N_jb})$, and $\overline{K} = f(K_{1a}, K_{1b}, K_{2a}, K_{2b}, \ldots, K_{Na}, K_{Nb})$. It is obvious that these equations for $N = 2$ reduce to the ones described in the theory and those for $N = 3$ reduce to the equations presented in the beginning of this section.

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