Application of Molecular Corresponding States Theory to Highly Nonideal Liquid Mixtures

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There are four points of flexibility in present molecular formulations of the corresponding states idea. At these points the procedure followed or the numerical values can be tailored to achieve better agreement between predicted and experimental properties without violation of physical principles. These flexibilities are the exponent values used in the pair-potential function, the averaging procedure used to obtain an effective mixture pair-potential function, the combination rule for unlike-pair parameters, and the selection of a reference substance. The first two flexibilities are used in this paper to show that the conformal-parameter equations can correlate excess free energy and activity coefficient data of highly nonideal liquid mixtures. A pair-type-probability function is introduced in the averaging procedure used to obtain a mixture pair-potential function. Any macroscopic or molecular property may be used in this weighting function to improve mixture-property prediction.

Molecular theories of liquid mixtures fall into four main groups: lattice theories, cell theories, distribution-function theories, and corresponding states theory. The last of these appears at present to have the greatest potential for engineering use. The corresponding states principle has been used by engineers for many years; the equations that express the principle in molecular terms are simple in form and require assumptions which appear to be no more debilitating than those required by the other theories.

The formulation of the corresponding states idea in terms of molecular interactions is usually attributed to Pitzer (*22*). Longuet-Higgins (*15*), Brown (*4*), Scott (*33*), Prigogine et al. (*28*), and Wojtowicz et al. (*38*) have applied the molecular corresponding states equations to liquid mixtures that are almost ideal. An alternate corresponding states procedure has recently been presented by Flory and others (*6a*). The purpose of this paper is to show that results of engineering usefulness can be obtained from molecular corresponding states theory for highly nonideal liquid mixtures. These results are obtained by exploiting two points of flexibility in the corresponding states equations. Both flexibilities enter the theory through the effective pair-potential function. The first point of flexibility is the averaging procedure used to obtain effective pair-potential parameters for a mixture. The weighting function for this average is called a pair-type probability (PTP) function. The second point of flexibility is the pair of exponent values to be used in a Lennard-Jones type of pair-potential function.

This paper discusses some points of flexibility in molecular corresponding states theory and presents numerical results to show that the corresponding states equations can correlate the free energy of highly nonideal mixtures. A second paper will show how the idea of a PTP function unifies the major correlation and prediction equations now in engineering use, namely, the equations of Scatchard and Hildebrand; Wohl, Redlich, and Kister; Van Laar; and Margules.

EQUATIONS FOR EXCESS FREE ENERGY

The molecular corresponding states theory is based on the fact that for all fluids the interaction of molecular pairs can be represented fairly well by a pair-potential function $u = u^* f(r/r^*)$, where the function f is the same for all the fluids, and the parameters u^* and r^* are peculiar to each fluid (whether it is pure or a mixture). The corresponding states correlation of fluid properties may be improved by classifying fluids into groups i such that $u = u^* f_i(r/r^*)$, where each group has a different function f_i. Such classification is similar in content and effect to the classification parameter ω of Pitzer (*22*), α

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of Riedel (*30*), and Z_c of Meissner and Seferian (*19a*) and of Lydersen, Greenkorn, and Hougen (*16*). The principle of corresponding states is useful whenever a group of two or more fluids can have their molecular interaction portrayed by $u = u^* f(r/r^*)$, with the same f function for each fluid in the group.

The expression used for excess free energy in the work reported here was the second-order expansion form developed by Brown (*4*). Similar developments have been made by Prigogine et al. (*28*), Scott (*33*), and Wojtowicz, Salsburg, and Kirkwood (*38*).

$$\begin{aligned} F^E = {} & F_f[(f_{xx}-1) - \Sigma_a x_a (f_{aa}-1)] \\ & + F_h[(h_{xx}-1) - \Sigma_a x_a (h_{aa}-1)] \\ & + \tfrac{1}{2} F_{ff}[(f_{xx}-1)^2 - \Sigma_a x_a (f_{aa}-1)^2] \\ & + F_{fh}[(f_{xx}-1)(h_{xx}-1) - \Sigma_a x_a (f_{aa}-1)(h_{aa}-1)] \\ & + \tfrac{1}{2} F_{hh}[(h_{xx}-1)^2 - \Sigma_a x_a (h_{aa}-1)^2] + \ldots \end{aligned} \quad (1)$$

where

$$\begin{aligned} F_f &= E'_o \\ F_h &= pV_o - RT \\ F_{ff} &= -TC'_{po} - p^2 V_o K_o + 2pTV_o\alpha_o \\ F_{fh} &= -pTV_o\alpha_o + p^2 V_o K_o \\ F_{hh} &= RT - p^2 V_o K_o \end{aligned}$$

The pure-component *conformal* parameters f_{aa} and h_{aa} are defined in terms of the parameters, u^* and r^* of the intermolecular potential curves of the pure a, and some reference substance o.

$$f_{aa} = \frac{u^*_{aa}}{u^*_{oo}} \quad (2)$$

$$h_{aa} = (g_{aa})^3 = \left(\frac{r^*_{aa}}{r^*_{oo}} \right)^3 \quad (3)$$

If a and o do comply with the corresponding states principle [that is, if each of their intermolecular potentials are adequately represented by $u = u^* f(r/r^*)$ with the same f function for both o and a], their reduced p-V-T surfaces coincide and the following relations hold (*28*, *32*):

$$f_{aa} = (T_c)_a/(T_c)_o \quad (4)$$

$$g^3_{aa} = h_{aa} = f_{aa} \frac{(p_c)_o}{(p_c)_a} \quad (5)$$

Determination of the conformal parameters from critical constants requires no additional assumptions and broadens immensely the data base over which the theoretical forms may be tested for engineering usefulness.

The conformal parameters f_{xx} and h_{xx} of a mixture x can be defined in the same way by

$$f_{xx} = u^*_{xx}/u^*_{oo} \qquad h_{xx} = r^*_{xx}/r^*_{oo}$$

The parameters u^*_{xx} and r^*_{xx}, of $u = u^*_{xx} f(r/r^*_{xx})$, are taken to be the same for the interaction of any two molecules of the mixture—alike or different. That is, if the behavior of the mixture is to be correlated by corresponding states, it is necessary that all the molecular interactions in the mixture be adequately portrayed by the single function of $u = u^*_{xx} f(r/r^*_{xx})$. And the f must correspond with that of the other fluids with which the given mixture is to be correlated. When these conditions are satisfied, the reduced pvT surface of the pseudo pure substance x coincides with that of the reference substance 0, and

$$f_{xx} = (T'_c)_x/(T_c)_o \qquad h_{xx} = (p_c)_o/(p'_c)_x$$

where $(T'_c)_x$ and $(p'_c)_x$ are pseudocritical constants of the mixture x.

The goal of this paper is to present an improved scheme for determining the mixture conformal parameters f_{xx} and h_{xx} or, equivalently, an improved scheme for determining pseudocritical constants $(T'_c)_x$ and $(p'_c)_x$.

MIXTURE POTENTIAL ENERGY AND THE PTP FUNCTION

The excess function given by Equation (1) is one measure of mixture nonideality. Mixture characteristics enter Equation (1) through the mixture potential function parameters (f_{xx}, h_{xx}). This fact focuses attention on the expression used for the potential energy of a mixture.

In existing molecular theories, and in this paper, the assumption is made that the potential energy of any mixture may be expressed in pairwise additive form, as follows:

$$U_x(\overline{r}) = \sum_{i<j}\sum u_{xx}(r_{ij}) \quad (6)$$

where $\mu_{xx}(r_{ij})$ denotes an effective, or average, pair interaction of molecules in a particular mixture. The form of μ_{xx} considered here is that given by the Lennard–Jones bireciprocal form

$$\mu_{xx}(r_{ij}) = \frac{-\mu_{xx}}{(r_{ij})^m} + \frac{\nu_{xx}}{(r_{ij})^n} \quad (7)$$

$$= \mu^*_{xx} \left[\frac{m}{n-m} \left(\frac{r^*_{xx}}{r_{ij}} \right)^n - \left(\frac{n}{n-m} \right) \left(\frac{r^*_{xx}}{r_{ij}} \right)^m \right] \quad (8)$$

where μ_{xx} and ν_{xx} are attraction and repulsion parameters, respectively, and (μ^*_{xx}, r^*_{xx}) give the coordinates of the potential energy minimum for interaction between a pair of mixture molecules. When Equation (7) or (8) is used, Equation (6) has the form of a pure-component potential energy function because the same parameters are used for every molecular pair in the mixture.

Attention will be focused here on the (μ_{xx}, ν_{xx}) parameters of Equation (7). These parameters represent in the theoretical expressions the interaction characteristics or properties of mixture molecules, so to speak. These parameters are the sole means available to a corresponding states theory for distinguishing between mixtures and pure components and between mixtures of different compositions. These parameters must reflect as accurately as possible the distinctive features of the molecular interactions that occur in any particular mixture. Therefore, the values used for these two parameters should be most strongly influenced by those pair interactions that tend to contribute most strongly to the mixture potential energy.

It may be well to note that there is nothing unreal (in any novel way) or theoretically reprehensible in use of pair-potential parameters that represent the interaction characteristics of mixture molecules. The pair-potential parameters presently in use are fitting constants and have been reported for mixtures, for example, air (*11*). Even if rigorous, quantum-mechanical values of the μ_{xx}, ν_{xx} parameters were available for every pair-interaction type, the mixture potential energy would still have to be expressed in terms of average mixture parameters, as long as the problem being attacked is the prediction of mixture properties from pure-component properties. Then, as now, some prescription would be needed to obtain the values for the μ_{xx}, ν_{xx} parameters that will cause theoretical expressions to reproduce experimental values of mixture properties.

In seeking a prescription for parameters that are useful in work with nonideal mixtures, it is noted first that there is little or no theoretical guidance available along the path from the pure-component parameters to the mixture parameters. It is reasonable, and customary, to assume that useful values of mixture parameters can be obtained by some sort of average over the parameters associated with all the different molecular pair types in the mixture. Having made this assumption, a decision must be made as to how the parameter averaging procedure will be carried out. The procedure used in the present work follows the approach of Brown (*4*) in that mixture parameters are obtained from an expression for the average attraction and repulsion parameters associated with the interaction of any two molecules in the mixture.

To obtain such average parameters, the pair interaction between two molecules of species a and b is written in the form of Equation (7); that is

$$u_{ab}(r_{ij}) = \frac{-\mu_{ab}}{(r_{ij})^m} + \frac{\nu_{ab}}{(r_{ij})^n} \tag{9}$$

where r_{ij} is the separation between the two molecules. Next, an average value of the potential energy between two molecules, separated by r_{ij}, is obtained by taking an average of Equation (9) to give

$$\begin{aligned} u_{xx}(r_{ij}) &= \sum_a \sum_b \text{PTP}\ (a,b)\ u_{ab}(r_{ij}) \\ &= -\sum_a \sum_b \text{PTP}\ (a,b) \frac{\mu_{ab}}{(r_{ij})^m} \\ &\quad + \sum_a \sum_b \text{PTP}\ (a,b) \frac{\nu_{ab}}{(r_{ij})^n} \end{aligned} \tag{10}$$

where Equation (10) is the same as Equation (7) with

$$\mu_{xx} \equiv \sum_a \sum_b \text{PTP}\ (a,b)\ \mu_{ab} \tag{11}$$

$$\nu_{xx} \equiv \sum_a \sum_b \text{PTP}\ (a,b)\ \nu_{ab} \tag{12}$$

The PTP symbol in Equations (10) to (12) denotes the weighting function used in averaging the pair-potential parameters. The purpose of the PTP weighting function is simply to permit the assignment of greater or lesser weights (in some averaging procedure) to each molecular pair type accordingly as the pair does, or does not, possess some recognizable tendency to contribute more to the total potential energy of a mixture than other pair types. In other words, the PTP function permits explicit allowance in the mixture equations for the differing ability of different molecular pairs to resist the disordering efforts of thermal motion.

To illustrate the PTP function idea, consider one form of the function.

$$\text{PTP}\ (a,b) = \frac{x_a x_b W_a W_b I(a,b)}{\sum_a \sum_b x_a x_b W_a W_b I(a,b)} \tag{13}$$

The $W_a W_b$ can be factors which give some numerical representation of the shape and size of the molecules of a and b in a pair. The $I(a,b)$ factor weights a molecular pair with some measure of its specific, or strong, interaction, strength relative to other pairs.

Any molecular or macroscopic properties, or any function of these properties, may be used for the W and I factors in Equation (13) and correlations made to see which properties produce better agreement between the predictions of Equation (1) and experimental values. The properties, and therefore the W and I factors, may be temperature dependent. The possibilities here seem not to have been extensively exploited. Random mixing theory, to which most theoretical corresponding states work has been confined (*4, 28, 32, 33, 38*), may be obtained by setting the W and I factors in Equation (13) to unity. This neglects size and interaction differences and gives equal weighting to all pairs in Equation (6) for the mixture potential energy. The Scatchard-Hildebrand equations (*10*) are equivalent (*37*) to a corresponding states approach which uses molar volumes for the W's to allow for the effect of molecular size differences on pair weightings. The Wohl equations (*37a*) may be obtained (*37*) by using Wohl's effective molar volumes for the W factors. In both equation schemes, the I factors are set to unity. In the work just referred to, molar volume is the only measured property whose usefulness in mixture-property correlations has been tested.

When the averages of Equation (10) are used, algebraic manipulation (*4, 36*) gives the following expression for the conformal parameters.

$$f_{xx} = \frac{[\Sigma_a \Sigma_b\ \text{PTP}\ (a,b)\ f_{ab} g_{ab}^{m}]^{\frac{n}{n-m}}}{[\Sigma_a \Sigma_b\ \text{PTP}\ (a,b)\ f_{ab} g_{ab}^{n}]^{\frac{m}{n-m}}} \tag{14}$$

$$h_{xx} = \left[\frac{\Sigma_a \Sigma_b\ \text{PTP}\ (a,b)\ f_{ab} g_{ab}^{n}}{\Sigma_a \Sigma_b\ \text{PTP}\ (a,b)\ f_{ab} g_{ab}^{m}} \right]^{\frac{3}{n-m}} \tag{15}$$

The following combination rules for the unlike-pair parameters are used in this work.

$$g_{ab} = \frac{g_{aa} + g_{bb}}{2} \tag{16}$$

$$f_{ab} = (f_{aa} f_{bb})^{1/2} \tag{17}$$

Before proceeding to a discussion of the restrictions on the PTP function, three items are worth explicit mention. First of all, the averaging procedure used in Equations (11) and (12) is perfectly arbitrary, in the sense that it has not been developed from the first principles of mechanics. Many averaging procedures are possible (*28, 36*). However, all averaging procedures known to the authors which are used to obtain effective pair-potential parameters for liquid mixtures are equally arbitrary in the sense just stated. Therefore, comparison of prediction with measurement is at present the only objective test of a prescription for obtaining mixture parameters.

Second, the average pair interaction of Equation (10) was selected because this average gives a mixture pair potential directly in terms of an average repulsion term and an average attraction term. Potential functions for forces of attraction and repulsion are basic quantities in particle mechanics, and fundamental developments (*11, 17*) express the interaction between molecules in terms of attraction and repulsion potentials. Therefore, use of average attraction and repulsion parameters seems potentially fruitful when a way is sought to correlate the effect on macroscopic mixture properties of molecular properties.

For example, in a methanol-benzene mixture, the methanol molecules interact strongly. On the basis of this knowledge alone, it would be reasonable to assign in Equation (10) a greater weighting to alcohol interactions than to hydrocarbon interactions when estimating an average interaction which characterizes the mixture. The numerical work discussed below indicates that this is a procedure that is consistent with measured macroscopic properties. These results and the possibility (*37*) of expressing the Scatchard–Hildebrand (*10*) and Wohl (*37a*) equations in terms of the PTP function make further investigation seem worthwhile.

Third, when the potential form in Equation (7) is used, specification or determination of the (m,n) exponents specifies the functional form of the effective pair potential that is being used to represent the mixture in the calculations. In other words, all substances with the same (m,n) exponents are in the same corresponding states class when the Lennard–Jones potential form is used. Therefore, corresponding states classes can be defined by effective (m,n) exponents which are determined from data fitting. The effective (m,n) exponents define corresponding states classes at the molecular level in the sense that the (m,n) exponents are used directly in the pair potential [Equation (7)] that represents the mixture in molecular corresponding states theory. This seems a consistent way to define corresponding classes in a theory that seeks its basis in molecular interactions.

It should be noted that the PTP function idea is not restricted to strong interactions between like molecules only. If unlike pairs interact strongly (for example, acetone and chloroform), the 1-2 pairs may be weighted to reflect this. Mixtures with negative deviations from Raoult's law may therefore be dealt with.

RESTRICTIONS ON PTP FUNCTION

A probability function is normalized. This requires that

$$\sum_{a}\sum_{d} \text{PTP}\,(\text{a,b}) = 1.0$$

This restriction, of course, has nothing to do with molecular properties.

Corresponding states theory requires that the PTP function be suitable for determining parameters for the pure-component form of the mixture potential function in Equation (6). The same parameters must be used in every term of the summation, and therefore the PTP function cannot depend upon molecular coordinates.

If the PTP function is to give the corresponding states framework any ability to predict mixture properties from those of pure components, it should not depend on mixture properties, but it need not forsake its role as a predictive device if it is made to depend [for example, by the $I(a,b)$ factors of Equation (13)] on known interaction tendencies of unlike molecular pairs.

The PTP function logically must include the concentration variables x_a, x_b, . . . x_C as the amount of a component present must affect its contribution to an effective pair interaction.

To apply the equations to a pure component, no averaging of the parameters is required and

$$\lim_{x_a \to 1.0} \text{PTP} = 1.0 \qquad (a = 1,2, \ldots C)$$

is a limitation to which any PTP function must conform.

OTHER POINTS OF FLEXIBILITY

There are four points of flexibility in the molecular formulation of the corresponding states idea where the procedure followed or the numerical values used can be tailored to achieve more perfect agreement between predicted and experimental values. These points of flexibility are (1) the combination rule used to obtain unlike-pair parameter values from pure-component values, (2) the (m,n) exponent values used in the pair potential function [Equation (7)], (3) the selection of a reference substance, and (4) the form of the PTP function and the type of averaging procedure in which it is used.

Combination Rules

The parameters in the pair potential function for unlike molecules must at present be approximated by an average of the pure component potential parameters. The most commonly used averaging procedures are shown in Equations (16) and (17) which, for our purposes, are written in terms of f and g rather than u^* and r^*.

Use of the arithmetic average for the length parameter g (or r^*) is based on the facts that it is exact for rigid sphere molecules, and it has been difficult to develop a better approximation which can be readily used in numerical work (*13*).

The form of the energy-parameter average in Equation (17) has some theoretical basis in the London expression for the attraction between two isolated, nonpolar molecules at large separations (*17*). No theoretical form for a repulsion force parameter seems to be in use (*21*).

Efforts to improve upon Equations (16) and (17) have proceeded along two lines. The first seeks to make maximum use of the London expression for the attraction of two widely spaced molecules and employs molecular properties (*9, 10, 12, 13, 18, 20, 29*). The second invokes the corresponding states idea and utilizes macroscopic properties (*1, 8, 13, 20, 24, 25*). Improved treatment of particular mixtures has often been accomplished, but it appears that alternate combination rules have not yet been developed to the point where consistent improvement over use of Equations (16) and (17) is achieved (*10, 12, 13*).

The combination rules used can affect sharply the values predicted by Equation (3) for any given liquid mixture (*36*). However, there seems to be no simple, reliable basis available at present to indicate what an optimum, or even helpful, modification of these rules should be for any given mixture. For this reason, the flexibility available in possible modifications of the combination rules was not utilized in the numerical work reported below and Equations (16) and (17) were used exclusively.

PAIR-POTENTIAL EXPONENT VALUES

The literature does give some indications of the manner in which the pair-potential exponent values m and n should be varied to give better results in liquid state work. First of all, it is relevant to note that neighboring molecules in the liquid state are separated by small distances on the order of r^* (*7, 23*). Davies and Coulson (*6, 11, 31*) examined the attraction forces between polyenes and found that the attraction exponent m was less, at small molecule separations, than the customary value of 6.

Another directional indication has to do with the pairwise additivity assumption (*11, 36*) that underlies Equation (3). Kihara (*14*) investigated nonadditive effects for three molecules in the gas state and concluded that when a pairwise-additive expression is used to express the potential energy of a three-molecule assembly, the pair-potential function (obtained from data fitting) should be accepted as the mean, or effective, additive intermolecular potential in a three-body system. Also, the bowl of the mean additive pair-potential curve in the three-body assembly was wider than that of the potential curve between two isolated molecules.

The two works just cited indicate that better agreement with experimental values might be anticipated in liquid state work if the (m,n) exponents were adjusted so as to widen the bowl of the pair-potential curve. If variation of (m,n) from the usual 6,12 values is required, no use can be made of literature values of u^* and r^*, obtained by fitting experimental data to the Lennard–Jones, 6-12 pair potential. However, a signal advantage of the conformal parameter approach is that the u^* and r^* values enter the theory only in ratios and can be replaced without further assumption by ratios of the critical constants, as done in Equations (4) and (5). The critical-constant ratios have of course no particular (m,n) set associated with them and so variation of these exponents can be explored when the conformal-parameter approach is used.

CHOICE OF REFERENCE SUBSTANCE

It has been noted (28, 32) that the numerical results obtained from molecular corresponding states theory often change appreciably with a change in the reference substance. This effect was noted for all mixtures investigated in connection with the present work. However, it was found that the effect on the calculations of reference-substance choice was sharply reduced when Equation (1) was made to agree with experiment by suitable choice of (m,n) exponents and PTP function in Equations (14) and (15). For example, consider the methanol-benzene binary. If the usual (6, 12) pair potential exponents and the random-mixture assumption (PTP $= x_a x_b$) are used to predict F^E for the equimolar mixture with methanol as reference, the error is 685 cal./mole. If benzene is used as reference, the error is 445 cal./mole, a change in prediction of 240 cal./mole. On the other hand, when using the preliminary nonrandom weighting-function procedure discussed below with an exponent set of (1, 19), the error in prediction with methanol as reference was 77 cal.; the error with benzene as reference was 2.1 cal., a change in prediction of 75 cal./mole. The effect of reference substance choice is reduced by a factor of three.

Since the predicted F^E values arise from a Taylor series expansion around the reference substance, the results may suffer if f_{xx} and h_{xx} differ too greatly from 1.0. The choice of reference substance for use in the second-order theory of Equation (1) might conceivably be governed by the size of the (f_{xx}, h_{xx}) parameters that result. In the systems studied, $(f_{xx} - 1)$ has never exceeded 0.2, but $(h_{xx} - 1)$ has been as great as 0.45. It is not yet known for what $(f_{xx} - 1)$, $(h_{xx} - 1)$ increment sizes the second-order Taylor series becomes inadequate. However, third-order terms were found to be entirely negligible for the ethanol-benzene binary (36), indicating that the increment sizes were sufficiently small for use of the second-order theory. The discussion of this and the preceding paragraph indicates the possibility that with good (m,n) values and a correctly formulated PTP function, the choice of reference substance can be based solely on the quality of the thermodynamic data that are available for the various substances that might be used as reference. Investigation of this possibility will be a part of future work.

If the effect of reference substance choice cannot be eliminated, some empirical basis for the choice will be required. Two possible ways of deciding upon a reference substance are to use some physical property as a criterion, and to use an hypothetical reference substance whose properties are obtained from the properties of the pure components by some specified calculation procedure. As an example of a physical property criterion, better predictions of F^E were obtained for all systems discussed below when the component with the smaller acentric factor (22) was used as reference.

Turning to the hypothetical reference substance possibility, it is not necessary on theoretical grounds that the reference substance be one of the mixture components. The theoretical expressions require only that the potential parameters (or critical constants) and the macroscopic properties of the reference substance be unambiguously defined. However, a given set of pair-potential parameters *implies a unique set of macroscopic properties* when all other specifications such as (m,n) values, combination rules, pair-potential form, and PTP function form have been fixed. Agreement would be fortuitous between (1) the reference-substance macroscopic properties determined by some recipe from the pure-component macroscopic properties, and (2) the reference-substance macroscopic properties that are associated with the potential parameters obtained from a second recipe. In this sense, *use of an hypothetical reference substance is almost certain to be inconsistent.*

In future work, the possibility of reducing or eliminating the effect of reference substance choice will be explored before any further effort is devoted to developing bases for this choice.

PTP WEIGHTING FUNCTION

The form of the PTP function shown in Equation (13) utilizes the usual double-sum average. This form has the disadvantage of counting unlike pairs twice; that is, unlike pairs are weighted by a factor of 2.0 in addition to whatever other weighting is assigned. This means that as the proper molecular weighting factors *W*'s and *I*'s are developed, it will always be necessary to allow for this 2.0.

If the $I(a,b)$ factors in Equation (13) are set equal to 1.0, molecular *pairs* will (aside from composition effects) be weighted only by products of weights that have been assigned to molecular *species*. In the double summation of Equation (13), the unlike (1-2) pairs will be given a weighting which is the geometric mean of the weightings given the (1-1) and (2-2) pairs. This is not a consequence of the parameter combining rule used but is a separate assumption. This characteristic makes it impossible to include pair-interaction terms in the W factors. If the $I(a,b)$ factors are omitted, the PTP function in Equation (13) is therefore restricted to mixtures where the unlike pairs interact less strongly than one of the pure pairs, that is, to mixtures which exhibit positive deviations from Raoult's law. To handle negative deviation systems, where unlike pairs must be weighted more heavily than like pairs, the pair interaction terms must fall outside of the geometric average. The separation of the pair interaction weighting factor $I(a,b)$ from the pure-component shape and size factors W_a and W_b permits this.

One other flexibility in the formulation of the PTP function which may merit future work is that of weighting the attraction and repulsion coefficients by different amounts. The PTP (a,b) can be written more generally as PTP (μ_{ab}) in the numerator of Equation (14) and denominator of Equation (15). Similarly, in the denominator of Equation (14) and numerator of Equation (15), PTP (a,b) may be replaced by PTP (ν_{ab}), where μ and ν are the parameters in the attraction and repulsion terms, respectively, of the pair potential. This double averaging might be used to test the assumptions, for example, that the repulsion term in a mixture pair potential depends primarily on molecular size and shape, while the attraction term depends primarily upon the dipole moment and polarizability of the molecules involved. Application of this idea is not used in our work other than to note that the predictions of Equation (1) vary strongly with the pair weightings used. It is felt that systematic exploration of the double-averaging procedure should be deferred until the single-average approach has been more fully developed.

NUMERICAL APPLICATIONS

This paper will not present a final (m,n,W,I) set for any system. The full development of the correlational and predictive ability of the weighting function approach will be deferred until later papers. The present work is concerned with the answers to preliminary questions which had to be answered before a more complete study could be regarded as potentially fruitful.

TABLE 1. CORRELATION BY VARIATION OF (m,n) IN RANDOM-MIXING THEORY

System	Data source	(m,n)	Predicted F^E (exp. F^E) $X_1 = 0.25$	$X_1 = 0.50$	$X_1 = 0.75$
$CO\text{-}CH_4$	*19*	3, 58.0	20.8 (20.6)	28.0 (28.0)	21.5 (21.4)
$C_6H_6\text{-}CCl_4$	5	3, 30.5	11.8 (11.6)	16.8 (18.3)	13.6 (13.5)
$CyC_6H_{12}\text{-}CCl_4$	5	4, 6.75	10.4 (9.2)	13.2 (13.2)	9.46 (10.2)
$CO_2\text{-}C_3^{=}$	9	1, 13.0	44.5 (44.5)	67.2 (68.5)	63.3 (61.2)
$C_6H_6\text{-}CyC_6H_{12}$	5	6, 8.3	49.7 (52.5)	72.2 (71.5)	59.5 (53.2)
$CH_3OH\text{-}C_6H_6$	5	6, 4.5	208 (268)	325 (323)	383 (245)
$nC_7\text{-}C_2OH$	*34*	3, 3.6	346 (275)	355 (355)	219 (292)
$C_2OH\text{-}CyC_6H_{12}$	*35*	6, 5.0	212 (285)	331 (338)	307 (222)

Random-mixture theory (PTP $= x_a x_b$), plus Lennard-Jones pair potential parameters obtained from gas data with (m,n) values of (6, 12), does not provide satisfactory prediction of F^E for even moderately nonideal mixtures (*36*). One of the first questions arising in the present approach is if random-mixture theory will give acceptable F^E predictions if the (m,n) pair potential exponents are allowed to vary. Table 1 shows the best (m,n) set for eight systems, the first five of which are almost ideal while the last three are highly nonideal. The almost ideal systems can be correlated fairly well by (m,n) variation alone but rather unusual values of m and n are often required. No (m,n) set could be found to represent the alcohol-hydrocarbon systems adequately. Therefore, a PTP function of $x_a x_b$ plus exponent variation is not a useful correlating device.

The final question addressed in the work reported here was if exponent variation together with use of the PTP function idea provides a potentially useful correlation, and possibly prediction, procedure for highly nonideal mixtures. Work was done primarily with the alcohol-hydrocarbon systems, which are all positive deviation systems; that is, unlike pairs interact less strongly than the alcohol pairs. The attempt was made to correlate such systems with

$$\text{PTP}\ (a,b) = \frac{x_a x_b W_a W_g}{\Sigma_a \Sigma_b x_a x_b W_a W_b} \tag{18}$$

The W factors were assumed for these calculations to include the strong-interaction effects as well as shape and size effects. This lumping together of distinct factors which influence molecular interactions is not regarded as potentially fruitful practice. It was done, in the preliminary calculations reported here, to establish the overall ability of the algebraic expressions to reproduce nonideal data. Equation (18) depends, for a binary only, on composition and the ratio of W_1 to W_2.

The procedure followed (*36*) was to specify (m,n) and the W ratio (W_1/W_2) and to calculate F^E at $x_1 = 0.25$, 0.5, and 0.75. The calculations were repeated for several (m,n) pairs with several W ratios for each (m,n) pair. The results were plotted to obtain the minimum value for the sum of the absolute values of the prediction error at the three compositions.

The best $(m,n,\ W_1/W_2)$ sets were obtained for the following binaries: methanol-benzene, ethanol-benzene, ethanol cyclohexane, and n-heptane–ethanol. The hydrocarbon was always used as the reference substance. For methanol-benzene, the $(m,n,\ W_1/W_2)$ set was (1, 19, 1.88) and the sum-of-absolute errors at the three compositions was 6 cal./mole. Ethanol-benzene gave (2, 17, 1.78) with a sum of errors of 2 cal./mole. Ethanol-cyclohexane gave (4, 5, 1.77) and a sum of errors of 9 cal./mole. For ethanol–n-heptane $(m,n,\ W_1/W_2)$ was (1, 8, 1.82) and the error sum was 12 cal./mole. The sum of experimental F^E values at the three compositions is 835 cal./mole for methanol benzene, 682 cal./mole for ethanol benzene, 845 cal./mole for ethanol-cyclohexane, and 822 cal./mole for ethanol–n-heptane. The error sums are approximately 1% of these latter figures. Satisfactory correlation of these highly nonideal is therefore possible using Equation (3) as a three-constant $(m,n,\ W_1/W_2)$ fitting equation.

Activity coefficients were calculated for the four systems just discussed and compared with experimental values. The activity coefficient expression for component r developed from Equation (1) is the following, when the PTP function of Equation (18) is used.

$$\begin{aligned} RT \ln \gamma_r = {} & F_f \left[(f_x - 1) - (f_{rr} - 1) + \frac{\partial}{\partial x_r} (f_x - 1) \right] \\ & + F_h \left[(h_x - 1) - (h_{rr} - 1) + \frac{\partial}{\partial x_r} (h_x - 1) \right] \\ & + \frac{1}{2} F_{ff} \left[(f_x - 1)^2 - (f_{rr} - 1)^2 \right. \\ & \left. + 2(f_x - 1) \left[\frac{\partial}{\partial x_r} (f_x - 1) \right] \right] \\ & + F_{fh} \left[(f_x - 1)(h_x - 1) - (f_{rr} - 1)(h_{rr} - 1) \right. \\ & \left. + (f_x - 1) \frac{\partial}{\partial x_r} (h_x - 1) + (h_x - 1) \frac{\partial}{\partial x_r} (f_x - 1) \right] \\ & + \frac{1}{2} F_{hh} \left[(h_x - 1)^2 - (h_{rr} - 1)^2 \right. \\ & \left. + 2(h_x - 1) \frac{\partial}{\partial x_r} (h_x - 1) \right] \end{aligned} \tag{19}$$

where the F_f, F_h, . . . coefficients are those in Equation (1), and

$$\frac{\partial}{\partial x_r} (f_x - 1) = \frac{2 f_x W_r}{S^2} \left\{ \frac{-n C_r}{n-m} + \frac{\sum_a x_a W_a B_{ra}}{N} - S \right\}$$

$$\frac{\partial}{\partial x_r} (h_x - 1) = \frac{6\, h_x W_r}{(n-m) S^2} C_r$$

$$C_r = \frac{\sum_a x_a W_a B_{ra}}{N} - \frac{\sum_a x_a W_a A_{ra}}{M}$$

$$S = \sum_a x_a W_a$$

$$A_{ra} = f_{ra}\, g_{ra}^m$$

$$B_{ra} = f_{ra}\, g_{ra}^n$$

$$M = \sum_a \sum_b \text{PTP}\,(a,b)\,A_{ab}$$

$$N = \sum_a \sum_b \text{PTP}\,(a,b)\,B_{ab}$$

Using Equation (19) and the $(m,n,W_1/W_2)$ values found by fitting Equation (1) to data, we calculated activity coefficients for the four alcohol-hydrocarbon binaries discussed above and compared them with experimental results. For the methanol-benzene system, the methanol activity coefficients were calculated to be 2.93, 1.56, and 1.15 at methanol compositions of 25, 50, and 75 mole %, respectively. These calculations differed from measured values (2.91, 1.56, 1.17) by 0.7, 0, and −1.7%, respectively, to give a sum of absolute errors of 2.4% for the three compositions considered. Similarly, the benzene activity coefficients had a sum of absolute errors of 4.6%. For ethanol-benzene, the sums of absolute errors in calculated activity coefficients were 2.9% for ethanol and 6% for benzene. For ethanol-cyclohexane, the sums of errors were 12.9% for ethanol and 10.1% for cyclohexane. The sum of three absolute errors was 7% for *n*-heptane and 11.1% for ethanol in the *n*-heptane–ethanol system. The figures just quoted indicate that the closeness of correlation to free energy values is retained in the calculation of activity coefficients from the equations of molecular corresponding states theory for highly nonideal mixtures.

The correlation of excess free energy obtained from Equation (1) and the three-constant $(m, n, W_1/W_2)$ fitting procedure can be summarized by use of the contour plots shown in Figure 1. The curves in Figure 1 delineate contours on the (m, n) plane, within which the *sum function* (the sum of the absolute deviations (experimental F^E − predicted F^E) at the three compositions) is less than 20 cal. The W_1/W_2 ratio used for each (m, n) point was the ratio that gave the minimum sum function for that (m, n) point. The 20-cal. value was chosen arbitrarily as giving a satisfactory fit of the data. Equation (1) is symmetrical in m and n, and so a mirror image of each contour exists in the lower octant of the $m > o$, $n > o$ quadrant.

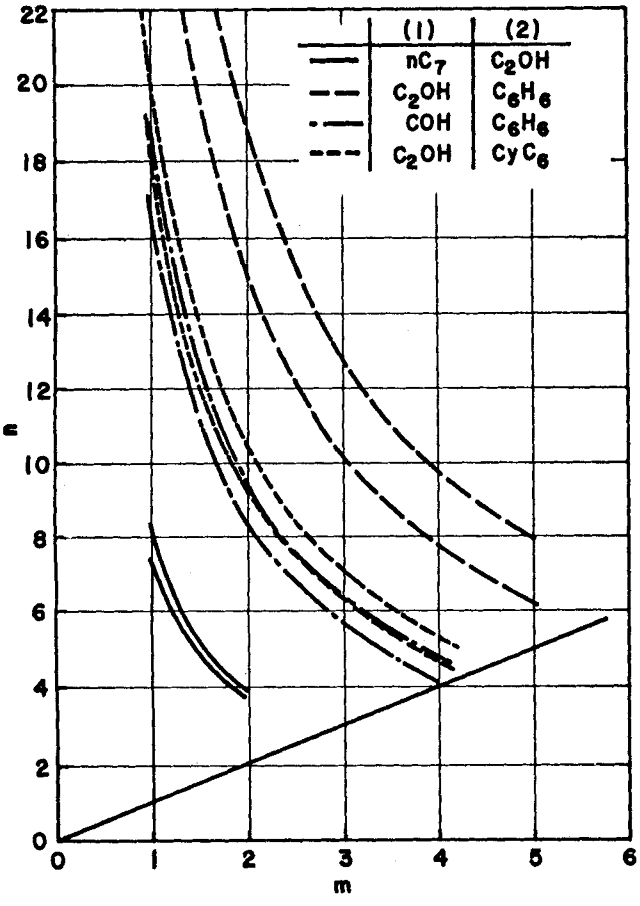

Fig. 1. Twenty-calorie sum function.

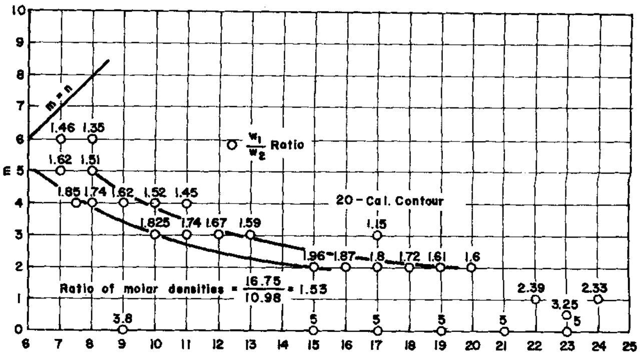

Fig. 2. Ethanol-benzene (40°C.).

These are two features of these contour plots that are of interest. First, the calculations indicate that a minimum-error point exists within the contours. In support of this indication, a 10-cal. contour for the ethanol-benzene system was found to close at an n value of around 96. A minimum-error point would be used to determine the best parameter values in whatever form of PTP pair-type-probability function was being investigated.

The second feature of the contour plots is that, for any (m, n) exponent pair within a contour, the two components and all mixtures formed from them may be treated —with useful accuracy—as members of the same corresponding states class. Note, for example, that all mixtures of methanol and benzene and all mixtures of ethanol and cyclohexane can be treated here as members of the same corresponding states class, that is, the class defined by $m = 1.5$ and $n = 14$.

However, these particular plots would also put benzene in two different classes, depending on the other component. This does not spoil the correlation achieved, but a goal of future work will be to find a more descriptive PTP function that will cause the contours of large classes of mixtures to overlap in the manner observed here. If mixtures of several pure substances can be shown to have a common set of exponent values, then all mixtures formed from these substances—multicomponent as well as binary—can be treated as a single class in corresponding states theory.

The numerical work gives some encouragement that contour overlap may be possible for classes of mixtures, while retaining the PTP function that was determined from minimum correlation error. This is because, within a 20-cal. error tolerance, a wide range of exponent values may be associated with a given value of the W_1/W_2 ratio. Figure 2 shows the 20-cal. contour for ethanol and benzene. The best exponent values were (2, 17) with a W ratio of 1.78 and an error sum of 2 cal. However, if a 20-cal. sum of errors is permitted, exponent pairs of (3, 10.5), (4, 7.5), etc., may also be used while retaining the same W_1/W_2 ratio. The possibility is indicated of selecting exponent values so that the constituent binaries of a multicomponent mixture will have overlapping contours and can therefore be treated as members of the same corresponding states class. This could be done without altering the weighting factors for individual pair types and without departing from a close fit of the data.

CONCLUSIONS

The results discussed above give some indication that a predictive procedure of considerable usefulness and generality might be fashioned from the PTP function approach. In the four alcohol-hydrocarbon binaries, OH. . .O hydrogen bonds are formed between alcohol molecules. Intuitively one would anticipate that the best agreement with experimental values would be obtained with a PTP function which (aside from concentration effects) weighted the alcohol pairs more heavily than the hydrocarbon pairs. In each case, the best fits occurred at alcohol pair weightings of 2.5 to 3.5 times those given the hydrocarbon. The 1.6 to 1.9 spread in the $W_{\text{alc.}}/W_{\text{hyd.}}$ ratios does not seem excessive in view of the differences in the molecules involved (aromatics, naphthenes, paraffins).

It seems reasonable to conclude that the PTP function idea, *plus exponent variation*, permits the corresponding states equations to correlate highly nonideal systems. The impression can be gained from the literature that the corresponding states idea can be used only for spherical molecules that interact weakly. However, the essential assumption required for use of the existing theory is that the pair-potential function, Equation (8), is of the same form (has the same exponents) for the molecules of that *group* of substances whose properties are to be correlated or predicted by the corresponding states approach. The potential energy between *any* two molecules may be expressed to some approximation in terms of a pair potential function such as Equation (8). This is because any molecular pair has a reasonably well-defined mass-center separation, and the parameters in the potential function can be (as always) obtained by data fitting. This fact sustains the anticipation of a single pair-potential form that will serve for any group of molecules. When molecules of different shape, polarity and/or specific interaction tendencies are investigated, a single pair-potential form (m, n pair) cannot be expected to represent with perfect accuracy the potential energy of all molecular pair types. This latter fact need not, however, restrict the usefulness of the molecular form of corresponding states theory to simple molecules of little industrial interest if it is possible to develop corresponding classes of molecules on the basis of empirical values for the pair-potential exponents.

The question of practical interest here is whether or not there exist large molecular classes whose molecules interact in a manner that can be characterized by a single pair of exponents together with individual attraction and repulsion parameters [μ, ν in Equation (8)]. The work of Lydersen et al. (*16*) and the corresponding class parameters of Pitzer (*23*), Riedel (*30*), and Rowlinson (*32*) indicate that pure substances of vastly different molecular structure (from argon to water) may be given useful classification via three macroscopic parameters. It seems reasonable therefore to explore the possibility that mixtures of widely differing molecules may be given useful classification in terms of parameters arising in molecular theory as long as the procedure used is not explicitly prohibited by mechanical or statistical theory. The PTP function procedure presented above is one possibility. It makes possible the correlation of nonideal mixtures and opens the possibility of developing a predictive scheme that can use molecular properties and known intermolecular interaction strengths to weight the contribution of various pair types to an effective pair-potential function for a mixture. In determining the relative weights, it is possible to make use of as much information about molecular structure as is available for the species that enter the mixture being considered.

NOTATION

C = number of components in a mixture
C_p = heat capacity at constant pressure
E' = configurational internal energy
f_{aa} = conformal energy parameter for pure species a
f_{xx} = mixture conformal parameter
F_f, F_h, F_{ff}, F_{fh}, F_{hh} = partial derivatives in Equation (1)
F^E = excess Gibbs free energy of mixing
g_{aa} = conformal length parameter
g_{xx} = mixture conformal parameter
h = Planck's constant
h_{aa} = conformal length parameter
$I(a,b)$ = pair interaction strength factor
K_o = isothermal compressibility
m = pair potential attraction exponent
n = pair potential repulsion exponent
p = pressure
PTP = pair-type-probability function
$\bar{r}$ = set of mass-center position vectors for all molecules of an assembly
r_{ij} = distance between molecules i and j
r^* = pair potential length parameter
R = gas constant
T = temperature
$u(r_{ij})$ = potential energy of molecules i and j
u^* = pair potential energy parameter
U = total potential energy of a molecular assembly
V = volume of a mole of a substance
W_a = numerical shape and size factor
x_a = mole fraction of species a in the liquid phase

Greek Letters

α_o = thermal expansion coefficient
γ = activity coefficient
μ = pair-potential attraction parameter
ν = pair-potential repulsion parameter

Subscripts

a,b,r = mixture components
o = reference substance
x = mixture function

Superscripts

E = excess function
= configurational property

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Development of the Scatchard-Hildebrand and Wohl Equations in Terms of Pair and Triplet Weighting Functions

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A previous paper introduced the pair-type-probability (PTP) function for use in molecular corresponding states theory. The present paper develops the predictive equations of Scatchard and Hildebrand and the correlation equations of Wohl from particular pair and triplet weighting functions for clusters of two and three molecules in a liquid mixture. The cluster-weighting idea therefore unifies the major prediction and correlation schemes now in engineering use.

In a previous paper (*15*) the idea of a pair-type-probability (PTP) function was introduced and preliminary numerical results were given to show that use of this idea, together with other flexibilities in molecular corresponding states theory, enabled the theoretical equations to serve as correlating expressions for the thermodynamic properties of highly nonideal mixtures. The purpose of this paper is to show that the predictive excess free energy equations of Scatchard and Hildebrand (*4*) and the correlation equations of Wohl (*17, 18*) may be developed from the idea of a probability weighting function for clusters of 2, 3, . . . molecules in a liquid mixture, and therefore that the cluster-weighting idea underlies the majority of prediction and correlation schemes now in engineering use.

The cluster-weighting (or cluster-probability function) idea enters the various molecular formulations of the corresponding states idea (*1, 10, 11, 13, 15, 19*), the Scatchard–Hildebrand equations, and the Wohl equations at the same point. This point is the expression for the potential energy of a mixture. All the equation schemes referred to above employ for the mixture a pure-component form of the potential energy function. Except for Wohl equations of third and higher order (see the discussion below), the expression used for the mixture potential energy is the pairwise-additive form,

$$U_x = \sum_{i<j}\sum u_{xx}\,(r_{ij}) \qquad (1)$$

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