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A Single-Parameter Equation for Isothermal Vapor-Liquid Equilibrium Correlations

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The Wilson equation is modified so that it contains only one adjustable constant per binary system. In describing binary behavior the new equation is inferior to the original Wilson but superior to the Van Laar equation. In developing ternary behavior from binary data, the new equation seems to be comparable to the original Wilson but definitely superior to the Van Laar equation.

Binary and ternary vapor-liquid equilibrium behavior has been successfully predicted from one γ° value per binary only.

Several expressions for the dependence of the activity coefficient on composition for binary and multicomponent systems have been suggested in the literature (*1, 2 10, 12, 17, 21, 25, 27*). Orye and Prausnitz (*17*) have shown that the Wilson equation (*27*) is superior to the Van Laar equation (*17, 20*), both in describing binary vapor-liquid equilibrium and in predicting multicomponent behavior from binary data only. More recently, Heil and Prausnitz (*12*) and Renon and Prausnitz (*21*) proposed two new expressions, based essentially on Wilson's concept of "local volume fractions," which seem to be superior to the original Wilson equation in describing highly nonsymmetrical and partially miscible systems (the Wilson equation cannot describe immiscible systems). All these equations contain a minimum of two adjustable constants per binary system, and therefore at least a pair of activity coefficients is needed for their evaluation so that the whole concentration range can be described. Furthermore, the constants are essentially of empirical nature and hence they cannot be predicted from pure component properties only.

A modified form of the Wilson equation, containing only one adjustable constant per binary system, is presented in this study. The new equation has been successfully tested both in describing binary vapor-liquid equilibrium and in predicting ternary behavior from binary data only. The new expression has also been compared with the original Wilson and Van Laar equations. In describing binary equilibrium, it is inferior to the Wilson, as should be expected, but better than the Van Laar equation. In predicting ternary equilibrium from binary data only, it appears to be as good as the Wilson equation and definitely superior to that of Van Laar. It can also describe the vapor-liquid equilibrium behavior of a binary system, based on the value of the activity coefficient of the one constituent at infinite dilution in the other, a task impossible for all other equations. Even though the adjustable constant is not purely empirical, no attempt is made in this paper to correlate it to pure component properties.

THE WILSON EQUATION AND THE PROPOSED MODIFICATION

Wilson (*27*) developed an expression for the free energy of mixing, from which the equation for the activity coefficient as function of composition is derived, based on the following assumptions:

1. The free energy of mixing is given by a relationship similar to the Flory-Huggins equation:

$$G^M = RT \sum_i^n x_i \ln \xi_i \qquad (1)$$

2. The distribution of molecules of kind j and k around a central molecule of type i is given by

$$\frac{x_{ji}}{x_{ki}} = \frac{x_j\, e^{-g_{ji}/RT}}{x_k\, e^{-g_{ki}/RT}} \qquad (2)$$

It follows from the second assumption that

$$\xi_i = \frac{x_i \bar{V}_i\, e^{-g_{ii}/RT}}{\sum_j^n x_j \bar{V}_j\, e^{-g_{ij}/RT}} \qquad (3)$$

Since values for $\bar{V}$ are not available in general, molar volume values can be used instead, without introduction of significant error. Substitution of Equation (3) into Equation (1) yields

$$G^M = RT \sum_i^n x_i \ln \frac{x_i V_i\, e^{-g_{ii}/RT}}{\sum_j x_j V_j\, e^{-g_{ij}/RT}} \qquad (4)$$

and hence

$$G^E = -RT \sum_i^n x_i \ln \sum_j^n x_j \frac{V_j}{V_i} e^{-(g_{ij}-g_{ii})/RT} \qquad (5)$$

From the last equation the following equation for the activity coefficient of component i is derived:

$$\ln \gamma_i = -\ln \left[1 - \sum_j^n x_j A_{ji} \right] + 1 - \sum_j^n \frac{x_j (1 - A_{ij})}{\left[1 - \sum_k^n x_k A_{kj} \right]} \qquad (6)$$

where

$$A_{ji} = 1 - \frac{V_j}{V_i} e^{-(g_{ji}-g_{ii})/RT} \qquad (7)$$

Notice that $g_{ij} = g_{ji}$ but $A_{ij} \neq A_{ji}$.

In the case of a binary system

$$\ln \gamma_1 = -\ln (1 - A_{21} x_2) + x_2 \left[\frac{x_2 A_{12}}{1 - A_{12} x_1} - \frac{x_1 A_{21}}{1 - A_{21} x_2} \right]$$
$$\ln \gamma_2 = -\ln (1 - A_{12} x_1) - x_1 \left[\frac{x_2 A_{12}}{1 - A_{12} x_1} - \frac{x_1 A_{21}}{1 - A_{21} x_2} \right] \qquad (8)$$

According to Wilson, g_{ii} is an adjustable constant proportional to the energy of interaction between molecules of type i. It is proposed in this paper that g_{ii} is substituted by the opposite of the energy of vaporization of pure i, under the same P and T as the solution, namely, Hildebrand's cohesive energy, based however on 1 mole rather than 1 cc. This assumption is valid if only two-body interactions are considered (*28*). This leaves only one adjustable constant per binary system, g_{12}, or three (g_{12}, g_{23}, g_{31}) per ternary. The original Wilson equation requires two adjustable constants (A_{12} and A_{21}) per binary and six (A_{12}, A_{21}, A_{23}, A_{32}, A_{31}, A_{13}) per ternary systems.

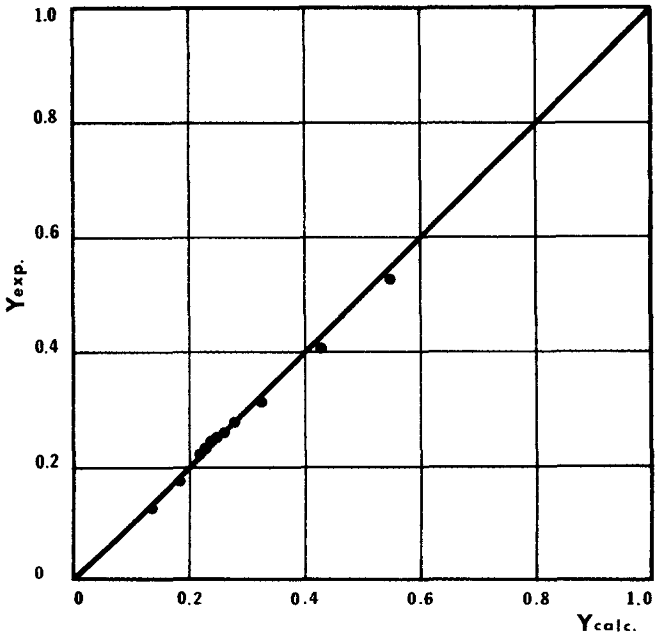

Fig. 1. Calculated versus experimental vapor compositions for the system nitromethane (1)-carbon tetrachloride at 318.15°K. (*20*).

DESCRIPTION OF BINARY VAPOR-LIQUID EQUILIBRIUM

Table 1 presents the results of a test of the one-parameter equation with 12 binary systems of varying degrees of nonideality. The results range from fair to excellent. It is worth noting that in the system acetone-chloroform all activity coefficients are less than unity.

Figure 1 presents experimental and calculated vapor-phase compositions for the system nitromethane-carbon tetrachloride (*20*). The average absolute deviation in y is 0.008 against 0.004 for the Wilson equation and 0.011 for the Van Laar equation (*20*).

BINARY VAPOR-LIQUID EQUILIBRIUM FROM ONE INFINITE DILUTION ACTIVITY COEFFICIENT

Since the new form of the Wilson equation contains one adjustable constant only (g_{12}), one of the infinite dilution activity coefficients per binary system is sufficient for the evaluation of this constant and hence the activity coefficients of the two constituents of the mixture for the whole concentration range. This was successfully tested with the

Table 1. Performance of the Modified and Wilson Equations with Systems of Varying Degree at Nonideality (g_{ij}-cal./g.-mole)

System (1) (2)	T, °C.	Root-mean-square average deviation in activity coefficients, × 100 Modified	Original	$-g_{11}$	$-g_{22}$	$-g_{12}$
n-Hexane–MEK	60	3.8	2.9	6,678.8	7,466.3	6,061.6
Nitromethane-carbon tet.	45	19.1	4.1	8,358.5	7,002.5	6,710.5
Acetone-chloroform	50	2.7	—	6,761.3	6,678.4	6,928.7
Chloroform-methanol	50	17.2	—	6,678.4	8,346.3	6,875.9
Methanol-acetone	50	7.9	—	8,346.3	6,761.3	7,312.1
Acetone-toluene	45	28.8	1.7	6,835	8,275	7,521
Acetonitrile-toluene	45	62.3	3.3	7,349	8,275	7,798
Nitromethane-carbon tet.	45	3.5	1.1	8,396	7,034	7,685
2-Propanol-ethyl acetate	60	19.4	3.8	10,720	7,343	8,872
1-Propanol-ethyl acetate	60	19.8	3.2	10,299	7,343	8,696
1-Propanol-water	60	36.5	23.9	10,408	9,543	9,966
Nitroethane-toluene	45	3.5	—	8,826	8,275	8,546

system n-hexane–MEK *(11)* by employing the value of the activity coefficient of MEK at infinite dilution in n-hexane. As it can be seen from Figure 2, the calculated values of the activity coefficients are in excellent agreement with the observed ones. It should be noticed that the average absolute deviation and the maximum deviation are essentially the same as those obtained when all observed activity coefficients were employed in evaluating g_{12}.

This is a very significant characteristic of the new equation. No other equation can generate activity coefficients for the whole concentration range, for both constituents of a binary mixture, solely from the activity coefficient of the one constituent at infinite dilution in the other. The two-suffix Margules equation can also accomplish this, but for symmetrical systems only. Infinite dilution activity coefficients can be obtained either experimentally, through static measurement (*9*) or gas-liquid chromatography measurements *(13* to *16, 19)*, or from empirical correlations (*18, 24, 26*). Since all these methods provide values for γ^0 that may include some error, it is desirable to examine the sensitivity of the new equation to the value of γ^0 employed. For this purpose values of γ^0, for the system n-hexane (1)–MEK (2), deviating as much as 16% from the value of γ^0 obtained from entrapolation, were employed in generating activity coefficients for the whole concentration range. The results are presented in Table 2 and suggest that the new expression provides satisfactory results for γ^0 values within the accuracy range of the aforementioned methods.

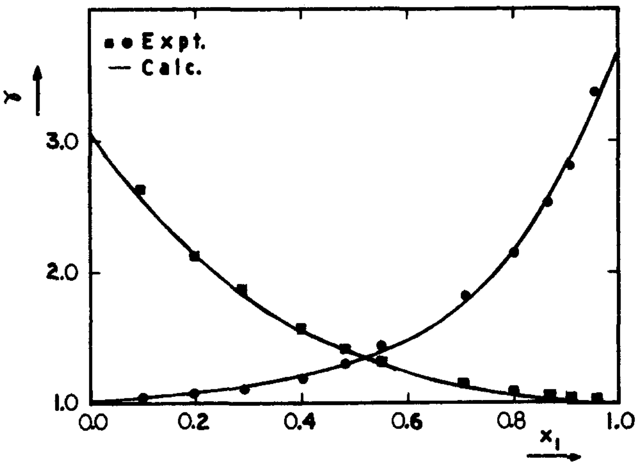

Fig. 2. The system n-hexane (1)-MEK (2) at 60°C. *(11)*.

TERNARY VAPOR-LIQUID EQUILIBRIUM FROM BINARY VAPOR-LIQUID EQUILIBRIUM DATA

Ternary, and generally multicomponent, vapor-liquid equilibrium is more often encountered in chemical engineering applications than binary ones. In addition, while the number of binary systems for which vapor-liquid equilibrium data are available is rather large, data for ternary systems are rather scarce, and for systems with more than three constituents are extremely scarce in the literature.

The Margules and Van Laar equations cannot, in general, adequately predict ternary vapor-liquid equilibrium from binary V-L equilibrium data only (*1, 3, 17, 20*). On the other hand the "local volume fraction" type equations —Wilson, Heil, or Renon—have very successfully predicted ternary equilibrium from binary data only (*12, 17, 20, 21*). Results of prediction of ternary vapor-liquid equilibrium from binary data by employing the new expression are presented in Table 3 along with results (*21*) of the NRTL, Heil, and Wilson equations. The performance of the new equation is remarkable, both in absolute terms as well as when compared with the other equations, if one bears in mind that it contains only three adjustable parameters per ternary as against at least six for the others. Calculated and experimental ternary vapor compositions for the system acetone-chloroform-methanol at 50°C. (*22*) are plotted against each other in Figure 3. When this plot is compared to the one presented by Orye and Prausnitz (*17*) for the same ternary system by employing the Van Laar equation, the new equation performs distinctly better than the Van Laar one.

Table 2. Effect of the $\gamma°$ Value on the Performance of the New Equation System: n-Hexane (1)-MEK (2) at 60°C.

$\gamma_2°$	% Deviation from expt.	$-g_{12}$	Root mean square avg. deviation in γ_1 and γ_2	% Avg abs. error γ_1	γ_2	Max. error % γ_1	γ_2
3.195	15.8	6,673.8	0.187	5.03	5.08	14.8	14.9
3.395	10.5	6,649.8	0.130	3.56	3.27	11.2	10.3
3.595	5.5	6,625.8	0.075	2.06	1.43	7.6	5.5
3.795	0.0	6,603.8	0.038	1.04	0.90	4.1	3.0
3.995	−5.5	6,581.8	0.061	0.96	2.26	2.7	7.1

TABLE 3. PREDICTION OF TERNARY VAPOR-LIQUID EQUILIBRIUM

System	Temp., °C.	Average absolute deviation in y, × 1,000	Mean arithmetic deviation in y, × 1,000			
			New equation	Wilson	Heil	NRTL
Acetone	50	15	9	−5	−5	−5
Methanol		14	−8	8	8	8
Chloroform		20	−1	−3	−3	−3
Acetone	50	6	−1	−4	−4	−4
Me acetate		17	−9	3	3	3
Methanol		20	10	1	1	1
Acetone*	50	15	8			
Methanol		10	−13			
Chloroform		20	6			
Acetone†	50	15	6			
Methanol		10	−12			
Chloroform		18	6			

* From γ^* values only, set A.
† From γ^* values only, set B.

TERNARY V-L EQUILIBRIUM FROM ONE INFINITE DILUTION ACTIVITY COEFFICIENT PER BINARY SYSTEM

The V-L equilibrium data on the same system: acetone-chloroform-methanol were employed in testing the ability of the equation to predict ternary V-L equilibrium from the value of one infinite dilution activity coefficient per binary system.

Two sets of infinite dilution activity coefficients, presented in Table 4 along with the corresponding values for g_{ij}, were employed. Set A includes the values for γ^0 reported by Severns et al. (*22*). Set B includes γ^0 values obtained by extrapolation of activity coefficients calculated by the method of Prausnitz et al. (*20*). The purpose was to test not only the ability of the equation to predict ternary V-L equilibrium behavior, but also its sensitivity to the employed values of the infinite dilution coefficients.

The calculated vapor-phase compositions for sets A and B along with the experimental values are presented in Table 5. The overall accuracy in predicting ternary vapor compositions is incorporated in Table 3. It can be seen that employment of one γ^0 value per binary provides essentially the same accuracy as the employment of the complete sets of binary data. Again it is worth noticing that the predicted ternary vapor compositions are definitely superior to those of the Van Laar equation.

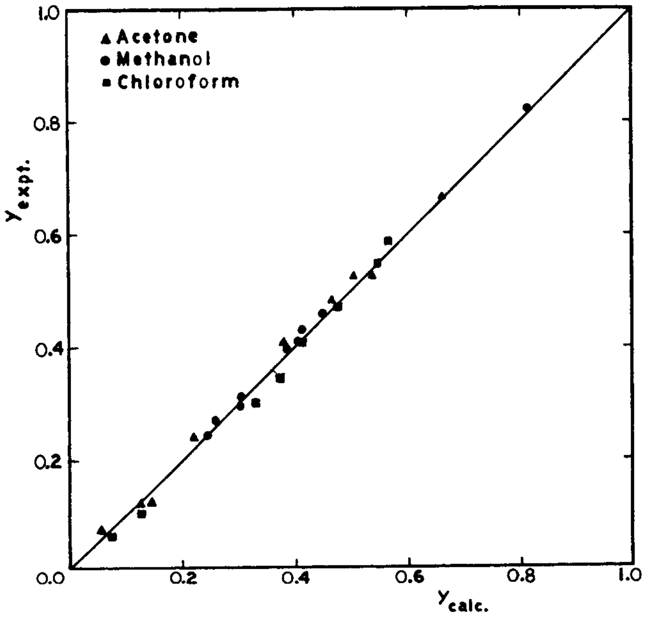

Fig. 3. Comparison of calculated and experimental results.

Finally, a comparison of the predicted vapor compositions for sets A and B shows very small differences, suggesting again that the new equation is not strongly sensitive to the γ^0 values employed.

CALCULATION OF g_{ii}

From thermodynamics

$$\Delta U = \Delta H - RT \tag{9}$$

Since heats of vaporization (ΔH) are not always available, the Clausius-Clapeyron equation can be employed:

$$\frac{d\ln P}{dT} = \frac{\Delta H}{RT^2} \tag{10}$$

TABLE 4. INFINITE DILUTION ACTIVITY COEFFICIENTS AND VALUES FOR THE BINARY CONSTANT (g_{ij}) OBTAINED FROM THEM FOR THE SYSTEM ACETONE (1)-CHLOROFORM (2)-METHANOL (3)

Set	System	i	$\gamma_i{}^0$	$-g_{ij}$, cal./g.-mole
A	1-2	2	0.495	6,918.68
	2-3	3	6.000	6,924.90
	3-1	3	1.675	7,362.12
B	1-2	2	0.495	6,918.68
	2-3	3	6.000	6,924.90
	3-1	3	1.800	7,344.12

TABLE 5. EXPERIMENTAL AND CALCULATED VAPOR-PHASE COMPOSITION FOR THE SYSTEM ACETONE-CHLOROFORM-METHANOL AT 50°C. FROM ONE γ^0 VALUE PER BINARY

	y_a			y_c		
	Expt.	Calcul.		Expt.	Calcul.	
x_a		A	B		A	B
0.190	0.120	0.1266	0.1274	0.589	0.5725	0.5702
0.215	0.133	0.1463	0.1472	0.553	0.5496	0.5470
0.450	0.529	0.5336	0.5362	—	0.0528	0.0516
0.037	0.0735	0.0559	0.0578	0.102	0.1307	0.1303
0.232	0.242	0.2162	0.2195	0.298	0.3331	0.3301
0.635	0.669	0.6670	0.6654	0.060	0.0777	0.0762
0.498	0.528	0.5060	0.5052	0.406	0.4168	0.4154
0.433	0.486	0.4648	0.4674	0.115	0.1496	0.1470
0.427	0.410	0.3811	0.3811	0.347	0.3780	0.3748
0.154	0.105	0.1152	0.1171	0.478	0.4744	0.4721

Combining Equations (9) and (10)

$$\Delta U = RT^2 \left[\frac{d\ln P}{dT} \right] - RT \tag{11}$$

The expression $(d\ln P/dT)$ can be evaluated by employing the proper equation for the dependence of P on T. As such, the following equation is recommended (*20*):

$$\ln P \text{ (atm)} = C_1 + \frac{C_2}{C_3 + T} + C_4 T + C_5 T^2 + C_6 \ln T \tag{12}$$

Notice that if $C_4 = C_5 = C_6 = 0$, Equation (14) becomes the familiar Antoine equation:

$$\ln P = C_1 + \frac{C_2}{C_3 + T} \tag{13}$$

Evaluation of $(d\ln P/dT)$ from Equation (12) and substitution in Equation (13) yields

$$\Delta U = RT^2 \left[\frac{-C_2}{(C_3 + T)^2} + C_4 + \frac{C_6 - 1}{T} + 2\, C_5 T \right] \tag{14}$$

Values for the constants in Equation (12) for a variety of chemical compounds are given by Prausnitz et al. (*20*). Values for the constants in the Antoine equation are also available (*4* to *7*, *23*).

DISCUSSION

The performance of this new, one adjustable constant, equation in describing binary vapor-liquid equilibrium and predicting ternary vapor-liquid equilibrium from binary data is remarkable, especially if it is kept in mind that only two-body interactions are considered in its development.

The replacement of the g_{ii} constants by the energies of vaporization, and the successful performance of the resulting equation, should make the new expression less empirical in nature than the original Wilson equation or the Heil and NRTL equations. If, however, g_{ii} is the energy of vaporization of pure i, it follows that $g_{ij,\, i \neq j}$ should be the energy of vaporization of the binary mixture of some unknown composition. From the order of the magnitude of the values of g_{12}, Table 1, this conclusion seems reasonable and it will be further investigated in the future. A better understanding of the physical meaning of g_{12} might provide leads to a better knowledge of liquid mixtures and to prediction of their properties from pure component properties.

Finally, it should be mentioned that the new expression has the same shortcomings of the original Wilson equation, that is, it does not describe partially miscible systems and maxima in the concentration dependence of the activity coefficient.

NOTATION

$A_{ij,\, i \neq j}$ = constant defined by Equation (7)
C_1, C_2, C_3, C_4, C_5, C_6 = constants in Equation (12)
ΔH = heat of vaporization
ΔU = energy of vaporization
G^M = free energy of mixing
g_{ii} = energy of interaction between molecules of type i equal to the energy of vaporization
$g_{ij,\, i \neq j}$ = constant
n = number of components
P = pressure, atm.
R = gas constant
T = temperature, °K.
x_i = mole fraction in the liquid phase, component i
x_{ij} = local mole fraction of component j around component i
y_i = mole fraction in the vapor phase, component i
$\overline{V}_i$ = partial molar volume of i
V_i = volume of pure i

Greek Letters

γ_i = activity coefficient of component i in the liquid phase
ξ = local volume fraction
γ^0 = infinite dilution activity coefficient

Subscripts

a = acetone
c = chloroform
m = methanol

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