Comparison of van Laar and Wilson Equations for Isopropanol-Water Binary System

Parviz Davalloo
Department of Chemical Engineering, Pahlavi University, Shiraz, Iran

The validity of van Laar and Wilson equations is examined for the isopropanol–water binary system with a nonlinear curve fitting procedure. A detailed study is made to decide which set of equations would fit the experimental results better. Both equations predict the vapor-liquid equilibrium of this system with good accuracy; therefore, either of the two can be used for the design of isobaric distillation equipment.

To apply the computer for the design of a distillation column, it is necessary to use a mathematical correlation between vapor and liquid equilibrium. Such an equation is available for ideal solutions; however, for nonideal solutions the problem is more involved.

For a nonideal solution, the activity coefficient γ is used to indicate the deviation from ideality. At low pressures where the vapor phase can be assumed to follow the perfect gas law, the activity coefficient can be calculated from experimental vapor-liquid equilibrium data by Equation 1.

$$\gamma_i = \frac{\pi y_i}{p_i^\circ x_i} \tag{1}$$

Two relationships often used for correlating the activity coefficient as a function of liquid composition are the van Laar and the Wilson equations, which are compared for the isopropanol–water binary system at atmospheric and subatmospheric pressures.

Comparison of van Laar with Wilson Equations

A detailed study was made to test the applicability of the van Laar and the Wilson equations for the isopropanol–water binary system. The experimental vapor-liquid equilibrium data used for this purpose were reported in a previous paper (*1*). Both equations fit the experimental data satisfactorily. To find which equation is better for this system, a critical comparison was necessary. A computer program based on the "Gradient Search Optimization" as proposed by Zellnik et al. (*3*) was applied to obtain the best values of the van Laar and the Wilson constants. The program utilizes the steepest descent method to minimize the value of an objective function. The objective function considered is the deviation of the vapor compositions from the predicted values, squared and summed over all the experimental runs.

Results and Conclusions

Table I compares the experimental vapor composition with the calculated value based on activity coefficients predicted by the van Laar and the Wilson equations.

The detailed comparison of the van Laar and the Wilson equations indicates that both equations can be used for the design of isobaric distillation equipment with confidence.

Table II. Constants of van Laar and Wilson Equations

	van Laar constants		Wilson constants	
Press, mm Hg	*A*	*B*	A_{12}	A_{21}
$757.7^{+8.7}_{-9.5}$ [a]	1.09771	0.45757	0.07800	0.74395
760[b]	1.04792	0.49179	0.10714	0.64506
760[c]	1.000	0.483	...	...
$381.2^{+0.8}_{-1.1}$ [a]	1.08487	0.49445	0.05693	0.70236
380[b]	1.08271	0.50589	0.09222	0.63176
380[c]	0.966	0.520	...	...
$192.2^{+1.2}_{-1.4}$ [a]	1.10964	0.50208	0.08581	0.63065
190[b]	0.98139	0.52322	0.13633	0.59454
190[c]	0.930	0.532	...	...
$94.8^{+0.9}_{-0.9}$ [a]	1.04175	0.51490	0.10240	0.63948
95[b]	0.97186	0.53445	0.13827	0.58923
95[c]	0.918	0.546	...	...

[a] "Gradient Search Optimization" program and data reported in reference *1*. The experimental pressure of each run was considered in this computation. [b] "Gradient Search Optimization" program and data of Wilson and Simons (2) were used in this computation. [c] Constants reported by Wilson and Simons (2).

Table I. Comparison of Experimental Vapor Composition with Calculated Value Based on Activity Coefficients Predicted by van Laar and Wilson Equations

Press, mm Hg	$757.7^{+8.7}_{-9.5}$		$381.2^{+0.8}_{-1.1}$		$192.2^{+1.2}_{-1.4}$		$94.8^{+0.9}_{-0.9}$	
No. of exptl data, *N*	27		14		20		16	
Range of exptl x_i	0.01537–0.99994		0.06103–0.99851		0.00913–0.99627		0.00915–0.99917	
Range of exptl y_i	0.23495–0.99974		0.46571–0.99891		0.18986–0.99445		0.15571–1.00000	
Type of equation	van Laar	Wilson	van Laar	Wilson	van Laar	Wilson	van Laar	Wilson
Max positive dev	0.03168	0.03366	0.02129	0.01551	0.02647	0.02370	0.01131	0.02939
Min negative dev	−0.01720	−0.04692	−0.03006	−0.01537	−0.01974	−0.01697	−0.01170	−0.02286
x_i with positive dev, %	66.2	27.1	72.4	23.7	77.3	32.2	49.9	23
x_i with negative dev, %	33.8	72.9	27.6	76.3	22.7	67.8	50.1	77
Av positive dev	0.00797	0.01500	0.00680	0.00458	0.01155	0.00526	0.00485	0.00382
Av negative dev	−0.00805	−0.01003	−0.01400	−0.00400	−0.01087	−0.00876	−0.00515	−0.00994
$\sum_{i=1}^{N} (y_{i,\text{exptl}} - y_{i,\text{calcd}})^2$	0.00434	0.00859	0.00251	0.00096	0.00267	0.00234	0.00074	0.00348

The experimental data are usually between the values predicted by the van Laar and the Wilson equations. Thus, it may be advisable to average these equations for some critical design problems.

The van Laar constants A and B and the Wilson constants A_{12} and A_{21} are presented in Table II for the different pressures investigated. The constants reported by Wilson and Simons (2) are also shown in this table. The data of these authors are used to calculate the van Laar and the Wilson parameters by means of the "Gradient Search Optimization" program. The results of these computations are presented in Table II.

A noticeable difference in the values of the van Laar and the Wilson parameters is observed. This is more significant for Wilson than van Laar parameters. The reasons for such a discrepancy may be explained as follows: The criteria used for the approach to the minimum by various authors and the different programs do not coincide. It appears that the objective function has a rather flat minimum; therefore, a rather wide range of parameters for the van Laar and Wilson equations can be obtained to fit the experimental data.

The nature of the objective function which has been considered by different authors will affect the best values of the constants of the van Laar and Wilson equations.

The range of experimental data to which the equations are fitted also has some effect on the values of the constants.

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Nomenclature

p_i° = vapor pressure of component i, mm Hg absolute
x_i = mole fraction of isopropanol in liquid phase
y_i = mole fraction of isopropanol in vapor phase
γ_i = activity coefficient of component i
π = total pressure, mm Hg absolute

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Application of Hard Sphere Equation of State to Real Fluids

Aleksander Kreglewski,[1] **Randolph C. Wilhoit, and Bruno J. Zwolinski**
Thermodynamics Research Center, Texas A&M University, Department of Chemistry, College Station, Tex. 77843

Several variations of an equation of state formed by combining a hard sphere term with an attractive term are tested by comparison with *PVT* data for gaseous argon, six alkanes, tetrafluoromethane, and perfluorocyclobutane. The parameters are evaluated by a nonlinear regression calculation, and the two best equations are described in detail. Both fit well up to near the critical density and hold for nonspherical molecules as well as for spherical molecules. The equation with the attractive term derived from the Barker-Henderson theory is better than the van der Waals approximation. However, it is still not suitable for precise correlations above the critical density.

A few years ago, Reiss et al. (*11*) and Thiele (*14*) derived the following equation of state of the classical hard sphere fluid:

$$P/(\rho kT) = \Phi_1(y) = (1 + y + y^2)/(1 - y)^3 \qquad (1)$$

where

$$y = \tfrac{1}{6}\pi\sigma^3\rho \qquad (2)$$

and where $\rho = N/V$ is the number density, and σ is the diameter of the spheres.

Equation 1 reproduces closely the exact virial series obtained from molecular dynamics experiments of Alder and Wainwright (*11*) up to the fourth virial coefficient.

Carnahan and Starling (*2*) noted that the numerical coefficients of the virial series are close to the integral numbers,

$$P/(\rho kT) = 1 + 4y + 10y^2 + 18y^3 + 28y^4 + 40y^5 + \ldots \qquad (3)$$

and, therefore, the series can be expressed by

$$P/(\rho kT) = \Phi_2(y) = (1 + y + y^2 - y^3)/(1 - y)^3 \qquad (4)$$

The seventh virial coefficient resulting from this treatment agrees with the value calculated by Ree and Hoover (*10*). Hence, $\Phi_2(y)$ may be expected to be valid up to the densities corresponding to the liquid state.

To demonstrate the application of the hard sphere equation of state, modified to allow for intermolecular attraction, to the correlation of the thermodynamic properties of fluids, a series of equations obtained by combining the two functions from Equations 1 and 4 with various types of attractive terms has been tested by comparison of the observed and calculated compressibility factors for nine gases over a wide range of temperature and pressure. These gases contain molecules of various sizes and shapes but exhibit weak intermolecular forces. The "observed" data for argon and the hydrocarbons have already been smoothed, but we feel that they represent the real values accurately. The parameters were evaluated by a nonlinear least-squares method, and the root-mean-square deviations, as well as individual deviations, were examined and compared for the different equations. The results for the two best equations are given below.

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[1] To whom correspondence should be addressed.