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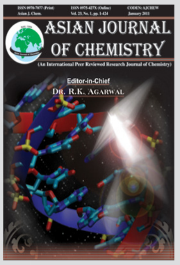

Studying of Different Activity Equations Effect for Estimate Binary Systems Pressure

T. AHMADI[1], F. ZAREEI[1], H. ZARE VALUEKOLAYI[2] and M. SOLEIMANI LASHKENARI[3,*]

[1]Islamic Azad University-Chalus Branch, Chalus, Iran
[2]Young Researchers Club, Babol Branch, Islamic Azad University, Babol, Iran
[3]Young Researchers Club, Chalus Branch, Islamic Azad University-Chalus Branch, Chalus, Iran

*Corresponding author: E-mail: mohammad.soleimani@hotmail.com

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The calculation of VLE's parameters in diverse system is important with assumed equality fugacity of two phases. In this study prediction binary system pressure by diverse activity equation was fitted by Matlab software and comparison of experimental and calculated pressure *versus* mole fraction was drawn (P-X). The vapour phase was assumed as an ideal gas. Finally error of calculated pressure was determined. Binary system studied are N-methyl pyrrolidone-1,3-butadiene. It can be concluded that optimization could be used for such systems.

Key Words: Activity equation, Binary mixture, Non-random two liquid, Wilson equation, Vanlar equation.

INTRODUCTION

Ideal liquid solution in which at constant pressure and temperature, fugacity of each part is consistent with proper scale of its condensation. Condensation is regarded as molar fraction[1]. It's mean that, constant pressure and temperature, for each ideal part $\gamma = 1$. In constant and definite temperature, mixed excess Gibbs energy (g^E) depend on combination and partially on pressure[2]. In low or medium pressures and away from critical conditions, pressure effect is little enough so that it can be neglected[3].

Binary mixture is represented in which excess properties is regarded as ideal solution and standard state for each pure liquid composition at mixture's temperature and pressure. In this case Gibbs energy should follow two boundary condition[4].

$$g^E = 0 \rightarrow X_1 = 0 \text{ and } X_2 = 0 \tag{1}$$

As an example, two-suffix margules equation, which is most valuable equation imitate from this boundary conditions is consisted of:

$$g^E = AX_1X_2 \tag{2}$$

A is tentative constant with energy dimension and 1, 2 component character that depend on temperature and independent of composition.

Within Gibbes-Duhem equation[5]:

$$RT\ln\gamma_i = \left(\frac{\partial n_T g^E}{\partial n_i}\right)_{T,P,n_j} \tag{3}$$

That:

$$\ln\gamma_1 = \frac{A}{RT}X_2^2 \tag{4}$$

$$\ln\gamma_2 = \gamma_2^\infty = \exp\left(\frac{A}{RT}\right) \tag{6}$$

This equation is good representation for simple liquid mixture, namely mixture of molecules, which is similar to each others in respect of size, shape and chemical nature[6]. If ln γ_1 and ln γ_2 drawn according to the X_2 (or X_1), both of infinite dilution, activities coefficients of both part is equal to[7]:

$$\gamma_1^\infty = \gamma_2^\infty = \exp\left(\frac{A}{RT}\right) \tag{6}$$

Modeling: As we know, equilibrium between two phases will be established if fugacities in two phases are the same[8]:

$$f_i^v = f_i^l \tag{7}$$

In which f^v and f^l are fugacity in vapour and liquid phase respectively.

$$f_i^l = x_i\gamma_i p_i^{sat} \tag{8}$$

$$f_i^v = py_i\phi_i \tag{9}$$

It is supposed that gas phase is ideal, so that:

$$\gamma_i^\infty = \lim_{x_i \to 0}\gamma_i = \lim_{x_i \to 0}\frac{p - x_j\gamma_j p_j^{sat}}{x_i p_i^{sat}} \tag{10}$$

Vanlar equation: Vanlar equation is proper for binary solutions that have no much difference chemically but have different molecule sizes; *e.g.*, solution of benzene and iso-octane. Basic equations obtained for activities coefficient consists of [8]:

$$\ln\gamma_1 = \frac{A}{\left[1 + \frac{AX_1}{BX_2}\right]^2} \tag{11}$$

$$\ln \gamma_2 = \frac{A}{\left[1 + \frac{AX_2}{BX_1}\right]^2} \qquad (12)$$

Derivation of vanlar equations shows that these equations should be used for relatively simple solutions preferly impolar liquid, but it is observed empirically that, these equations can represent more complicated mixtures activities coefficients.

In special case in which constant A, B in vanlar equation are the same (equal to each other), they turn in two-suffix margules equation[9].

Wilson equation: For different combined mixture, Wilson equation represents excess Gibbs energy and it is useful especially for polar solution or gathering particles such as alcohol in non-polar solvent. Three-suffix margules equation and vanlar equation are not proper for such solutions. Margules equation and reformed vanlar equation can be applied for making consistency among data but such equilibriums need at least three parameters and importantly, these equilibriums don't generalize without additional assumption or three-part parameters for multi-part solutions[10].

$$\ln \gamma_1 = \ln(X_1 + A_{12}X_2) + X_2\left[\frac{A_{12}}{X_1 + A_{12}X_2} - \frac{A_{21}}{A_{21}X_1 + X_2}\right] \qquad (13)$$

$$\ln \gamma_2 = -\ln(X_2 + A_{12}X_1) - X_1\left[\frac{A_{12}}{X_1 + A_{12}X_2} - \frac{A_{21}}{A_{21}X_1 + X_2}\right] \qquad (14)$$

Wilson equation should be applied only for liquid systems, which are completely combining or limited areas of systems with little combination which have one liquid phase[11].

Non-random two liquid (NRTL) equation: Non-random two liquid equation is appropriated for systems, which have partial mixture such as for completely combining systems. For non-ideal intermediate systems, non-random two liquid equation has no advantage rather than simple vanlar equation and three-suffix margules equation[12].

$$\ln \gamma_1 = X_2^2\left[\tau_{21}\left(\frac{G_{21}}{X_1 + X_2G_{21}}\right)^2 + \frac{\tau_{21}G_{12}}{(X_2 + X_1G_{12})^2}\right] \qquad (15)$$

$$\ln \gamma_2 = X_1^2\left[\tau_{12}\left(\frac{G_{12}}{X_2 + X_1G_{12}}\right)^2 + \frac{\tau_{21}G_{12}}{(X_1 + X_2G_{12})^2}\right] \qquad (16)$$

$$G_{12} = \exp(-\alpha\tau_{12}) \qquad G_{21} = \exp(-\alpha_{12}\tau_{21}) \qquad (17)$$

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} \qquad \tau_{21} = \frac{g_{21} - g_{11}}{RT} \qquad (18)$$

The significance of g_{ij} is similar to that Wilson equation; g_{ij} is an energy parameter characteristic of the i-j interaction. The parameter α_{12} is related to no randomness in the mixture; when α_{12} is zero, the mixture is completely random .The non-random two liquid equation contains three parameters, but reduction of experimental data for a large number of binary systems indicates that α_{12} varies from about 0.2 to 0.47; when experimental data are scarce, the value of α_{12} can often be set arbitrarily; a typical choice is $\alpha_{12} = 0.3$.

RESULTS AND DISCUSSION

The empirical data for two systems have been examined and graph resulted from empirical pressure and calculated by activation equations will be obtained. In this system, pressure was given according to molar fraction at 288.15, 298.15 and 308.15 K (Table-1).

TABLE-1
EXPERIMENTAL DATA FOR N-METHYL PYRROLIDOONE-1,3-BUTADIENE SYSTEM (1,3-BUTADIENE IS FIRST COMPONENT)

T = 288.15 K		T = 298.15 K		T = 298.15 K	
P(atm)	X_1	P(atm)	X_1	P(atm)	X_1
0.083	0.026	0.097	0.021	0.172	0.028
0.123	0.039	0.205	0.044	0.290	0.048
0.182	0.058	0.339	0.072	0.373	0.062
0.267	0.084	0.546	0.123	0.474	0.079
0.491	0.155	0.779	0.177	0.696	0.117
0.758	0.251	1.000	0.228	0.944	0.157
0.966	0.332	1.250	0.292	1.250	0.227
1.250	0.449	1.500	0.359	1.500	0.276
1.500	0.587	1.750	0.447	1.750	0.341
1.750	0.758	2.000	0.553	2.000	0.402
–	–	2.250	0.680	2.250	0.404
–	–	2.500	0.834	–	–

By solving the equations with MATLAB's software in different activities equations, experimental and calculated pressures are shown in Figs. 1 and 2.

It should be noted that Vanlar and Wilson equations can't predict pressure similar to non-random two liquid equation, and their useful parameters (A_{12}, A_{21}) for Wilson equation and (A_i, B_i) for vanlar equation will be obtained by related data. Finally by using of these parameters γ_1, γ_2 will be obtained for calculating pressure for obtaining above-mentioned parameters, infinity activity coefficients should be calculated in infinite dilution. For this purpose, γ with X_1 (molar fraction of first substance) is obtained in form of function then γ in point of $X_1 = 0$ is obtained by first degree and second-degree regression this is the same γ in infinite dilution. This practice should be carried out for both parts.

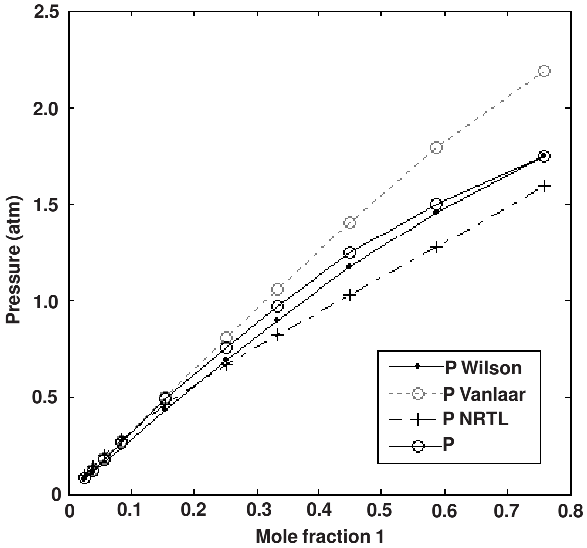

Fig. 1. Experimental and calculated pressure for N-methyl pyrrolidone-1,3-butadiene system in 15 ºC

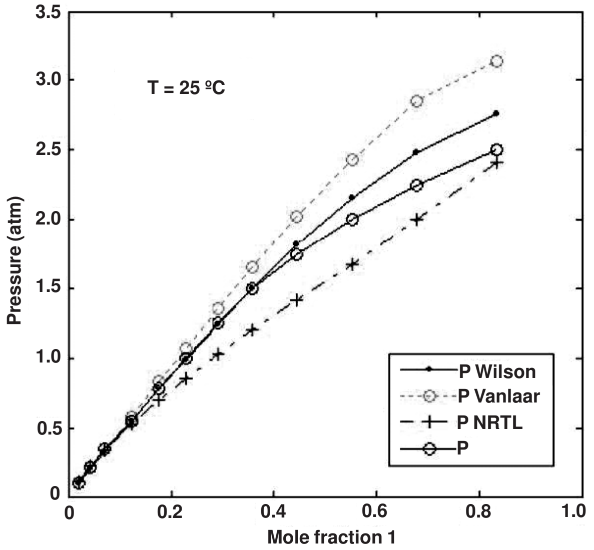

Fig. 2. Experimental and calculated pressure for N-methyl pyrrolidone-1,3-butadiene system in 25 ºC

So that, use of above-mentioned methods namely vanlar and Wilson equations need to have empirical data (system pressure according to molar fraction), while use of activation equation non-random two liquid satisfy/meet our need for having these empirical data of course it needs data calculate for every pair previously (HYSYS can be applied for obtained these data Table-2).

TABLE-2
PREDICTED PRESSURE WITH ACTIVITIES
EQUATION IN T = 288.15 ºC

Mole Fraction	P-Wilson	P-Vanlar	P-NRTL
0.026	0.0846	0.0848	0.0973
0.039	0.1265	0.1271	0.1421
0.058	0.1875	0.1887	0.2034
0.084	0.2702	0.2728	0.2808
0.155	0.4916	0.5010	0.4631
0.251	0.7788	0.8054	0.6675
0.026	1.008	1.0574	0.8206
0.332	1.3129	1.4101	1.0301

Conclusion

In this system, non-random two liquid equation predicted pressure lower than real pressure in all temperatures. There is good consistency between calculated pressure in all of temperatures in molar fraction lower than 0.2, but by increasing molar fraction, deviation from real quantity increases and it becomes divergent, although non-random two liquid has more deviation from real quantity suddenly, it converges to real rate sooner than other curves and by more power in higher molar fractions. Wilson equation in 25 ºC temperature has high precision to 0.4 from low molar fraction and it is consistent with empirical quantity almost completely. Finally in this system Wilson equation has lowest error in order to predict pressure. Calculation error in pressure estimation for Wilson, Vanlar and non-random two liquid equations was 0.0023, 0.0135 and 0.0172, respectively.

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