A New Vapor Pressure Equation

M. Edalat

Department of Chemical Engineering
Faculty of Engineering
Tehran University
Tehran — Iran

R. B. Bozarjomehri

Department of Chemical Engineering
Sharif University of Technology
Tehran — Iran

Abstract   The Wagner equation for prediction of vapor pressure has been modified in order to improve it accuracy . On the basis of this modification, development of a new equation for prediction of vapor pressure is outlined. Examples of the use of the equation for obtaining vapor pressure for a total of 94 pure substances are given. The proposed equation combines simplicity and accuracy and performs as well or better than the other correlations. This equation is tested and its advantages in obtaining vapor pressure are shown.

چکیده   معادله واگنربرای پیش بینی فشاربخارتعمیم داده شده است. براساس تغییرات داده شده معادله جدیدی برای محاسبه فشاربخارمواد ارائه گردیده است . نتایج حاصل ازمعادله جدید برای تعیین فشاربخار ۹۴ ماده با مقادیر تجربی آنها مقایسه شده که بیانگر دقت معادله می باشد. این معادله درعین سادگی از دقت خوبی برخوردار بوده وبرتری آن در مقایسه با سایر معادلات در این زمینه آزمایش ونشان داده شده است .

INTRODUCTION

Many authors have proposed several correlations for the prediction of vapor pressure. In general, vapor pressure correlations are classified in either empirical or corresponding states principle categories.

Among all types of empirical vapor pressure equations the more popular equations are due to Antione[1], Forst, et al. [2], and Wagner [3]. Among these equations, the Antione equation is older and simpler and has the following form:

$$LnP^{vp} = A - \frac{B}{(T+C)} \qquad (1)$$

where A, B, and C are constants which must be obtatined through experimental data. The applicability range of this correlation is limited and it is not recommended for extrapolation purposes beyond the temperature limit with which its parameters are correlated. The Wagner correlation on the other hand is more popular in this category and is as follows:

$$LnP_r^{vp} = \frac{a\tau + b\tau^{1.5} + c\tau^{3+} + d\tau^6}{1} \qquad (2)$$

where $\tau = 1 - Tr$, $Tr = T/Tc$, $Pr^{vp} = P^{vp}/Pc$, a, b, c, and d are constant, P^{vp} is the vapor pressure and Pc and Tc are the critical pressure and temperature, respectively. The Wagner equation predicts vapor pressure within acceptable accuracy down to reduced temperature (Tr) of 0.5. Generally, the accuracy of empirical correlations are better when they are used for interpolation purposes within the ranges of experimental data up on which they are based.

Among other corresponding states equations are the ones due to Riedel [4], Miller [5], Thek and Stiel [6], Lee and Kesler [7], Ambros [8], Gomez and Thodos [9], and Gupta and Daubert [10]. These equations

are developed through the use of the corresponding state principle. In this category of equations the ones which perhaps are more theoretically sound are the Lee-Kesler and Ambrose equations.

The Lee-Kesler equation expresses reduced vapor pressure as a sum of two terms: reduced vapor of simple fluids $f(T_r)^{(0)}$, and a deviation from simple fluids $\omega f(T_r)^{(1)}$ and has the following form:

$$Ln P_r^{vp} = f(T_r)^{(0)} + \omega f(T_r)^{(1)} \qquad (3)$$

where $f(T_r)^{(0)}$ and $f(T_r)^{(1)}$ are presented as:

$$f(T_r) = A_1 + B_1/T_r + C_1 Ln T_r + D_1 T_r^6 \qquad (4)$$

Equation 4 is the Riedel [4] equation for vapor pressure of simple fluids. The Lee-Kesler equation is recommended for hydrocarbons but vapor pressure of nonhydrocarbons and polar substances cannot be predicted accurately through the use of this equation.

The Ambrose vapor pressure equation is derived based on two reference fluids corresponding states. It is considered a linear relationship in the following form:

$$\frac{Ln (P_r^{vp}) - Ln (P_r^{vp})^{R_1}}{\omega - \omega^{R_1}} =$$

$$\frac{Ln (P_r^{vp})^{R_2} - Ln (P_r^{vp})^{R_1}}{\omega^{R_2} - \omega^{R_1}}$$

where superscripts R_1 and R_2 refer to the two reference fluids and $Ln(P_r^{vp})^{R_1}$ and $Ln (P_r^{vp})^{R_2}$ are in exact form of the Wagner equation. Equation 5 is recommended for non-hydrocarbons and polar substances. In using Equation 5 knowledge of two reference fluids is required. Ambrose has specified the two referance fluids but it is obvious that a more reliable estimate will be obtained if acentric factors of the two reference fluids are chosen such that the following constrain is held.

$$\omega^{R_1} < \omega < \omega^{R_2} \qquad (6)$$

The use of two reference fluids makes the applicability or usage of Equation 5 more difficult.

In the present paper, an equation for prediction of vapor pressure is presented which is simple, accurate and takes into account non-ideality of fluids. It estimates vapor pressures of hydrocarbons, as well as non-hydrocarbons and polar fluids accurately when the results are compared with the other corresponding states correlations.

Formulation of the Equation

Study of semi-empirical vapor pressure equations generally, and corresponding states vapor pressure equations such as the Lee-Kesler and Ambrose correlation particularly, reveals that vapor pressure of fluids must be a function of T_r and ω. Ambrose used the Wagner equation for simple fluids along with the two reference fluids for taking into account the non-ideality of fluids. Although, the Wagner equation gives vapor pressure accurately it is not simple and accurate enough to be suitable for engineering design calculations. Thus to develop a vapor pressure equation applicable to wide ranges of temperature and non-ideal fluids without neglecting the

advantage of simplicity, the Wagner equation should be considered as a basis for construction of such an equation.

Our study of the Wagner equation indicates that its coefficients are not actually constants but they are functions of acentric factor. These constants were treated somehow by Ambrose and Lee-Kesler to be linear with respect to ω.

We have compiled the vapor pressure data of 94 fluids and the coefficient data of Equation 2 reported by McGarry [11]. From this compilation we have produced Figures 1-4 which indicate that constants a and c of

Equation 2 are linear functions of ω but b and d of the same equation are non-linear with respect to ω. Therefore, based on this observation the following relation is proposed:

$$LnP_r^{vp} \qquad (7)$$

$$\frac{a(\omega)\tau + b(\omega)\tau^{1.5} + C(\omega)\tau^3 + d(\omega)\tau^6}{1 - \tau}$$

where a(ω), b(ω), c(ω), and d(ω) are assumed to be functions of acentric factor.
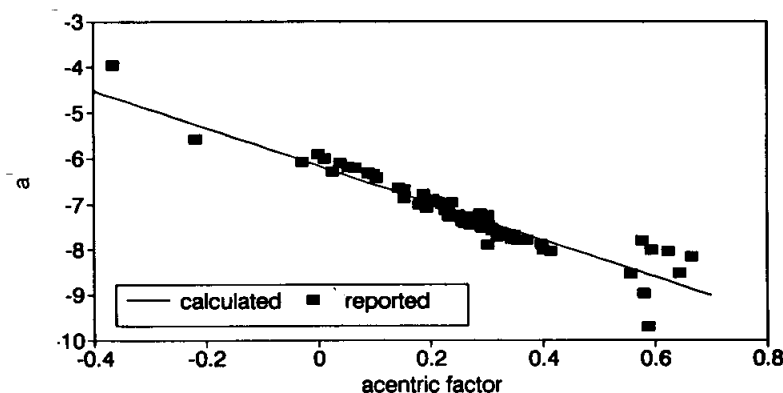

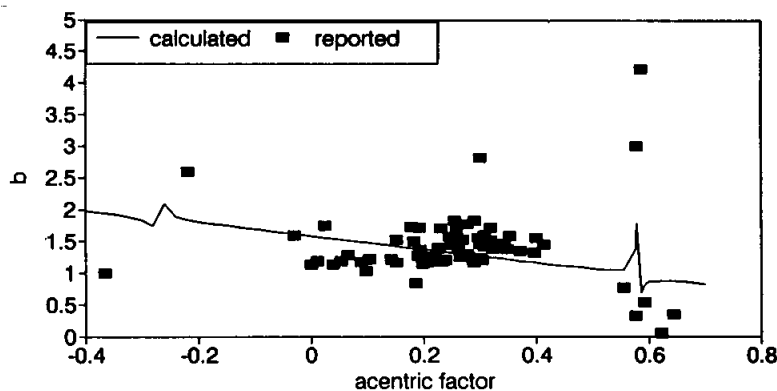Figure 1. First coefficient in Equation 7 versus acentric factor

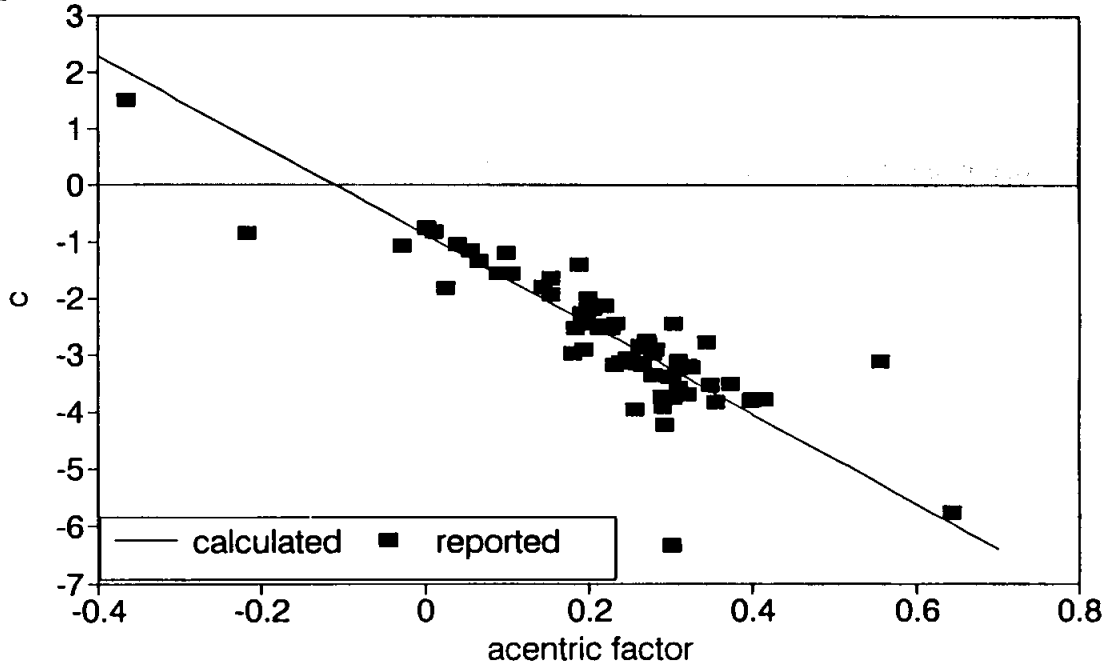Figure 2. Sencond coefficient in Equation 7 versus acentric factor

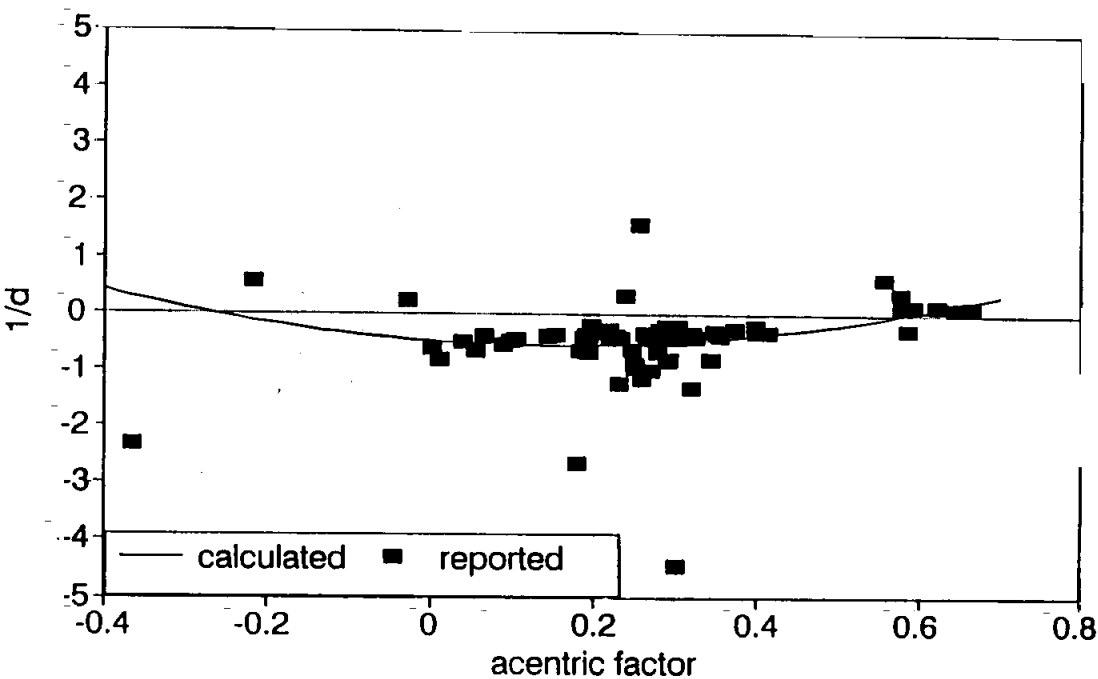*Figure 3. Third coefficient in Equation 7 versus acentric factor*

Figure 4. Fourth coefficient in Equation 7 versus acentric factor

To find appropriate correlations for $a(\omega)$, $b(\omega)$, $c(\omega)$, and $d(\omega)$, a total of seventy three data points of acentric factor are used. Based on coefficient data of the Wagner equation which are reported by [11], and applying a regression method considering Pitzer's definition of acentric factor, i. e:

$$\omega = - \text{Log } P^{vp}_r \quad Tr = 0.7$$

then the following correlations are obtained.

$$a(\omega) = -6.1559 - 4.0855\,\omega \qquad (7-1)$$

$$b(\omega) = 1.5737 - 1.0540\,\omega \qquad (7-2)$$
$$- 4.4365 \times 10^{-3}\,d(\omega)$$

$$c(\omega) = -0.8747 \quad 7.8874\,\omega \qquad (7-3)$$

$$d(\omega) = (-0.4893 - 0.9912\,\omega \qquad (7-4)$$
$$+ 3.1551\,\omega^2)^{-1}$$

Equation 7 joined with Equations 7-1—7-4 constitutes a new correlation for vapor pressure. In what follows the applicability of this equation is tested for a variety of fluids.

RESULTS AND DISCUSSION

The calculation results show that Equation 7 can predict vapor pressure of hydrocarbons, non-hydrocarbons and polar fluids more accurately than the other vapor pressure equations. In Table 1 average percent error of the substances which are predicted through the Ambrose, Lee-Kesler correlations and the present work are compared. It is shown that the present equation predicts vapor pressure more

Table 1. Average Percentage of Error of Substances

Number of data	Number of components	Lee—Kesler equation	Ambrose equation	Present equation
		n—Alkane and Alkene		
177	16	6.41	6.13	5.53
		Aromatics		
85	7	2.66	8.47	2.40
		Non—hydrocarbons		
96	7	9.82	11.97	8.63
		Halogens		
49	3	2.98	13.69	2.49
		Nobel Gases		
25	2	2.08	2.08	1.65
		Alcohols		
140	11	6.19	20.37	14.73

Table 2. Over All Percentage of Error

number of data	Number of components	Lee–Kesler equation	Ambrose equation	Present equation
1106	94	6.87	11.63	6.06

accurately than the Ambrose equation. The present equation is also superior than Lee-Kesler equation for all substances excluding alcohols.

In Table 2 the overall average percent error for prediction of vapor pressure by the present equation, Ambrose and Lee-Kesler equation for 94 substances with a total of 1106 vapor pressure data points reported [12]. According to this table, the overall prediction of vapor pressure by the present equation is more accuratle than those of Ambrose or Lee-Kesler equations.

In summary, the Ambrose Equation 5 requires the knowledge of two reference fluids in accordance with constraint, Equation 6,which makes applicability of the equation more difficult. While the present equation is accurate and it is suitable for engineering design calculations.

NOMENCLATURE

A, B, and C — Antoine constants
$A_1, B_1, C_1,$ and D_1 — Riedel constants
a, b, c, and d — Wagner constant
P^{vp} — Vapor pressure
P_r^{vp} — Reduced vapor pressure
P_c — Critical pressure
T — Temprature, K
T_r — Reduced temperature
T_c — Critical temperature
ω — Acentric factor

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