

Development of a new form for the alpha function of the Redlich–Kwong cubic equation of state

Fatiha Souahi, Salim Sator, Samia Assia Albane, Fairuz Khalida Kies,
Chems Eddine Chitour *

*Laboratoire de Valorisation des Energies Fossiles, Département de Génie Chimique, Ecole Nationale Polytechnique, 10
avenue Pasteur, Hassan Badi, El Harrach, Alger, Algeria*

Received 30 September 1997; accepted 26 August 1998

Abstract

The dependence on temperature and acentric factor of the attractive term of the Redlich–Kwong equation of state has been modified. A new alpha function is expressed in a generalized form. The new equation allows a good representation of vapor pressure data of a great variety of compounds, as well as thermodynamic properties such as the enthalpy of vaporization and the entropy of vaporization. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Equation of state; Vapor pressure; Enthalpy; Hydrocarbons

1. Introduction

Since Van der Waals has proposed the first cubic equation of state (1873), a large number of equations has been proposed to predict thermodynamic properties of pure components and mixtures. The Redlich–Kwong cubic equation of state is the first equation which has been successfully applied to the prediction of the vapor phase properties [1]. It is the precursor of a family of simple and relatively precise equations of state.

$$P = \frac{RT}{V-b} - \frac{aT^{-0.5}}{V(V+b)} \quad (1)$$

P is the pressure, T the temperature, V the molar volume, R the gas constant. a and b are the Redlich–Kwong parameters. The development of the Redlich–Kwong cubic equation of state

* Corresponding author

(RK-CEOS) constituted a breakthrough in the beginning of the 1950s in the calculation of thermodynamic properties of the vapor phase. Chao and Seader adopted this equation for the calculation of vapor–liquid equilibrium of apolar or slightly polar mixtures [1]. Important deficiencies were found in the prediction of the vapor pressure by the RK-CEOS. Several works have attempted to modify this equation to improve the prediction of the vapor pressure. Wilson [2] proposed the introduction of the alpha function to force the Redlich–Kwong equation of state to reproduce the vapor pressure [3]. The alpha function depends on the reduced temperature and the acentric factor. The new form of the attractive term in the equation of state is expressed by:

$$a = a_c \cdot \alpha \quad (2)$$

where a_c is the value of the attractive term of the RK-CEOS in critical point and α the alpha function.

Following Wilson's approach, Soave [4] expressed the alpha function of the RK-CEOS according to:

$$\alpha [1 + m(a - T_r^{0.5})]^2 \quad (3)$$

Where T_r is the reduced temperature. This form has been proposed by Soave after having noticed that for a given substance the square root of alpha can be expressed with a good approximation as a linear function of the square root of the reduced temperature. The m parameter represents the slope and varies from one substance to another. Soave proposed to express it according to a second degree polynomial of the acentric factor ω :

$$m = 0.48 + 1.574\omega - 0.175\omega^2 \quad (4)$$

Where ω is the acentric factor. The Soave's modification of the RK-CEOS (SRK-CEOS) had great success in predicting the behaviour of apolar or slightly polar multicomponent systems. The main innovation brought by Soave was the introduction of a new form of the alpha function, improving the predicted vapor pressures. For its simplicity and precision, the Soave's equation has been used as a reference in the prediction of thermodynamic properties. However, the modification of Soave tends to diverge for low values of the reduced temperature [5]. He modified the alpha function according to:

$$\alpha = 1 + m(1 - T_r) + n(1 - T_r^{0.5})^2 \quad (5)$$

Parameters m and n of the above equation are determined from vapor pressure data generated by the Lee–Kesler equation [6].

$$m = 0.484 + 1.515\omega - 0.044\omega^2 \quad (6)$$

$$n = 2.756m - 0.700 \quad (7)$$

The new alpha function did not bring an improvement in the case of heavy hydrocarbons, because the Lee–Kesler equation diverges in the case of low values of the reduced temperature [7].

Twu et al. [7] observed that by representing the alpha function as function of the acentric factor, a series of straight lines were obtained which slope varies with the reduced temperature. From this

observation, they proposed to represent the alpha function in mathematical analogy with Pitzer's corresponding states principle:

$$\alpha = \alpha^{(0)} + \omega(\alpha^{(1)} - \alpha^{(0)}) \quad (8)$$

where $\alpha^{(0)}$: value of the alpha function in the case of molecules supposed perfectly spherical ($\omega = 0$). This parameter is determined from intercept at the origin of the straight lines $\alpha = f(\omega)$; $\alpha^{(1)}$: value of the alpha function in the case of a hypothetical substance whose acentric factor is equal to 1. This parameter is determined from the slope of the straight lines $\alpha = f(\omega)$.

The mathematical form of functions $\alpha^{(0)}$ and $\alpha^{(1)}$ must be chosen judiciously to represent vapor pressure data of pure substances correctly. The general mathematical form of functions $\alpha^{(0)}$ and $\alpha^{(1)}$ adopted by Twu et al. [7] is the following:

$$\alpha = T_r^{N(M-1)} e^{L(1-T_r^{NM})} \quad (9)$$

Where L , N and M are the parameters of the Twu et al. α function. In this case, the $\alpha^{(0)}$ and $\alpha^{(1)}$ functions proposed par for the RK-CEOS (TRK-CEOS) are:

$$\alpha^{(0)} = T_r^{-0.1718352} e^{0.125283(1-T_r^{1.77634})} \quad (10)$$

$$\alpha^{(1)} = T_r^{-0.607352} e^{0.511614(1-T_r^{2.20517})} \quad (11)$$

In order to improve the prediction of thermodynamic properties for heavy hydrocarbons and petroleum fractions, the approach described here is to express alpha in a new generalized form.

2. Modification of RK-CEOS

The alpha function is expressed in a generalized form according to Eq. (8). The dependence of $\alpha^{(0)}$ and $\alpha^{(1)}$ on the temperature is modified by taking into account the constraint imposed by the critical point. The alpha function is closely linked to the vapor pressure [5]. The Wagner form has been adopted by different authors for the correlation of the vapor pressure [8,9]. However, the alpha function must be defined and be continuous in the entire temperature domain. The Wagner form does not satisfy this condition, as it is not applicable beyond the critical point. We propose to express the alpha function according to a modified form of the Wagner equation.

$$\alpha = 1 + \left[A(1 - T_r) + B(1 - T_r)^2 + C(1 - T_r)^3 + D(1 - T_r)^6 \right] / T_r \quad (12)$$

Where A , B , C and D are the parameters of Eq. (12). Pure component data are taken from the DIPPR data bank [10] and the data bank of Reid et al. [11]. To verify the linearity of alpha as a function of the acentric factor, the values of alpha for n -alkanes (from methane to the n -eicosane), benzene, toluene, cyclohexane, cyclopentane, argon, nitrogen and carbon dioxide have been calculated. The vapor pressure reference data are calculated using the equation of Twu et al. [8] which presents the advantage of having a large area of validity (from $T_r = 0.3$ until the critical point) and being applicable with a reasonable precision to light and heavy hydrocarbons. Alpha values have been determined for reduced temperatures ranging between 0.3 and 0.98 with an increment of 0.02.

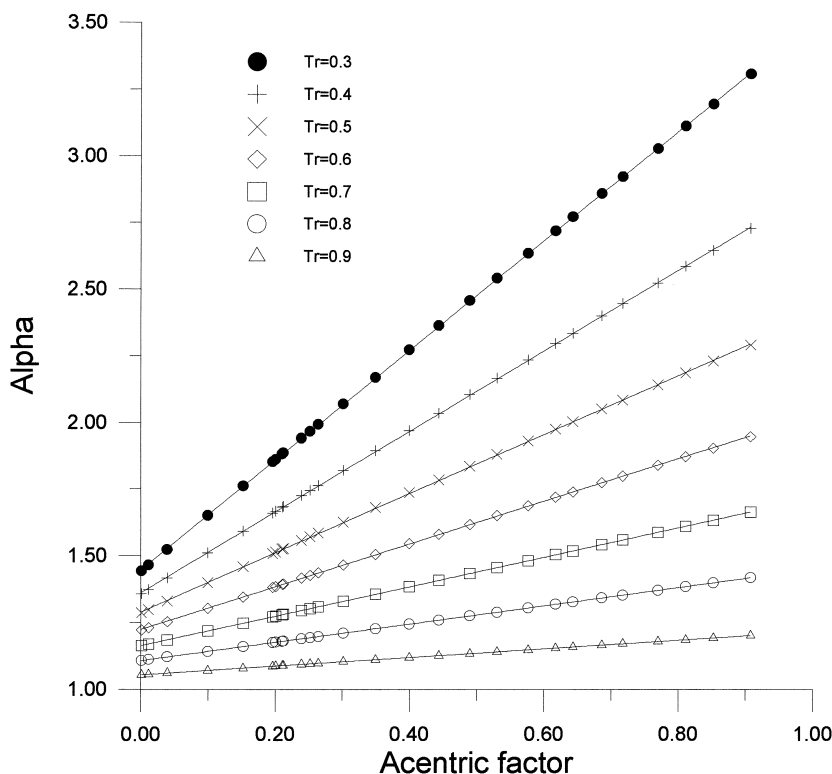


Fig. 1. Dependence of alpha on the acentric factor for different values of the reduced temperature.

The variation of alpha for some values of the reduced temperature is represented in Fig. 1. Alpha is linearly dependent on the acentric factor, which is in agreement with the observations of Twu et al. [7]. In this case, Eq. (8) is perfectly applicable to the vapor pressure reference data.

The next stage consists of the determination of $\alpha^{(0)}$ and $\alpha^{(1)}$. From the values of $(\alpha^{(0)}, T_r)$ and $(\alpha^{(1)}, T_r)$ pairs, $\alpha^{(0)}$ and $\alpha^{(1)}$ have been correlated according to Eq. (12). The resulting equations are:

$$\alpha^{(0)} = 1 + \left(0.517224(1 - T_r) - 0.428098(1 - T_r)^2 - 0.0551291(1 - T_r)^3 + 0.005803(1 - T_r)^6 \right) T_r \quad (13)$$

$$\alpha^{(1)} = 1 + \left(1.92645451(1 - T_r) - 0.635957(1 - T_r)^2 - 0.879041(1 - T_r)^3 + 0.1061225(1 - T_r)^6 \right) / T_r \quad (14)$$

These two last functions are represented in Fig. 2.

3. Application of the modification of RK-CEOS to the calculation of thermodynamic properties

The new equation of state has been applied to estimate thermodynamic properties of pure compounds. The first property studied is the vapor pressure. About 114 hydrocarbons have been

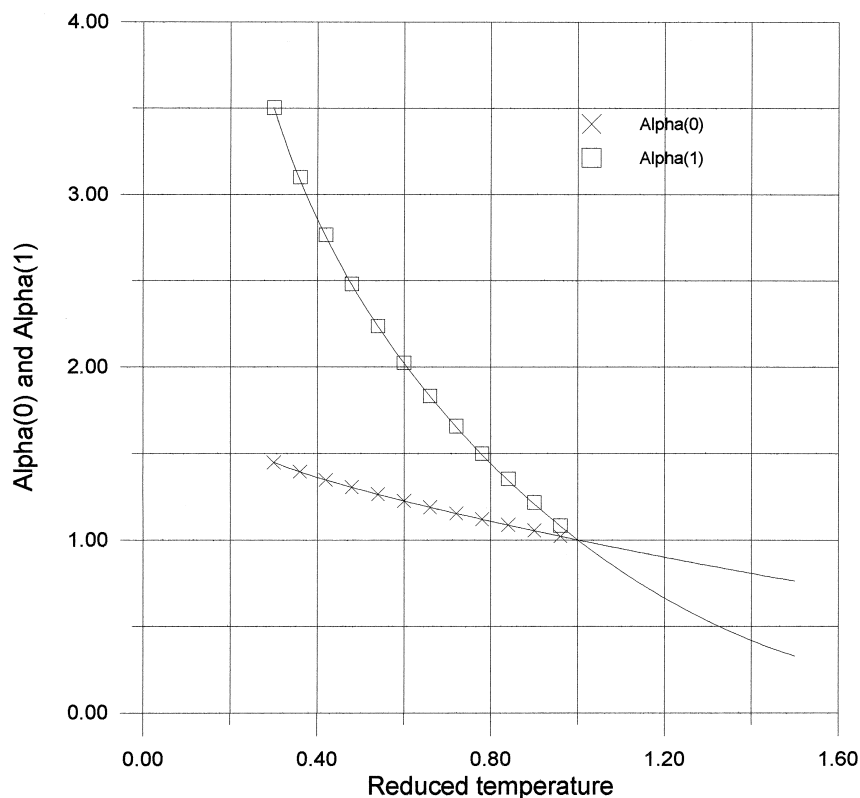


Fig. 2. $\alpha^{(0)}$ and $\alpha^{(1)}$ versus the reduced temperature.

considered (critical properties and acentric factor given in the database of Reid et al. [11] and the DIPPR database [10]. Vapor pressure data of hydrocarbons are obtained from the Wagner equation with coefficients given by Reid et al. [11]. In the case of heavy hydrocarbons, the vapor pressure equation of the DIPPR [10] is used. The vapor pressure is calculated between the minimal reduced temperature of the application of the equations and the critical point with an increment of 0.01. The average absolute deviation expressed in percent (AAD%) is given in the Table 1.

Table 1

AAD% obtained in the prediction of hydrocarbon vapor pressures from triple point to critical point for RK-CEOS type equations

Hydrocarbures	Number of hydrocarbons	Number of points	AAD%		
			This work	TRK-CEOS	SRK-CEOS
<i>n</i> -Alkanes	22	1330	2.00	2.42	2.58
Branched alkanes	37	1969	0.94	0.86	1.38
Alkylcyclopentanes	11	511	2.29	2.28	2.35
Alkylcyclohexanes	11	552	7.16	6.27	8.03
Alkylbenzenes	33	1795	4.71	6.19	5.08
Global	114	4198	2.94	3.35	3.39

Table 2

AAD% obtained in prediction of enthalpy of vaporization for RK-CEOS type equations

Hydrocarbons	Number of hydrocarbons	Number of points	T_r range	AAD%		
				This work	TRK-CEOS	SRK-CEOS
<i>n</i> -Alkanes	17	850	0.5–0.99	2.34	2.47	2.41
<i>n</i> -Alkylcyclohexanes	5	250	0.6–0.99	3.36	3.28	3.17
<i>n</i> -Alkylbenzenes	19	950	0.5–0.99	2.64	2.89	2.98
Global	41	2050		2.60	2.76	2.77

These results show that the new equation of state allows a better reproduction of the vapor pressure of the *n*-alkanes and the alkylbenzenes than the SRK-CEOS and the TRK-CEOS. It gives comparable results with the other equations for the branched alkanes and cyclopentanes. For the alkylcyclohexanes, TRK-CEOS gives the smallest deviations. The new equation of state gives good results compared to the other equations of the RK-CEOS type with reasonable average absolute deviations.

The new equation of state has been used to estimate the enthalpy of vaporization and the entropy of vaporization. The reference enthalpy of vaporization is obtained from DIPPR [10] for reduced temperatures ranging between 0.5 and 0.99 with an increment of 0.01. The values of the enthalpy of vaporization have been calculated as function of temperature for 41 hydrocarbons. Obtained deviations are given in Table 2. In the case of the entropy of vaporization, experimental data have been obtained from Perry and Chilton [12] for several compounds. For methane and ethane, the experimental data are taken from Raznjevic [13]. The results are given in Table 3.

The results of the enthalpy of vaporization predicted by the new equation of state are satisfactory. Despite the sophistication brought by Twu et al. [7] in the establishment of the function α , the

Table 3

AAD% obtained in prediction of entropy of vaporization for RK-CEOS type equations

Hydrocarbons	Number of points	T_r range	AAD (%)		
			This work	TRK-CEOS	SRK-CEOS
Methane	19	0.50–0.97	2.08	1.95	3.41
Ethane	26	0.57–0.98	2.63	2.27	3.30
Propane	27	0.52–0.87	0.54	0.46	1.17
<i>n</i> -Butane	29	0.33–0.99	2.08	2.43	2.16
<i>n</i> -Heptane	19	0.37–0.74	1.92	2.53	1.72
<i>n</i> -Octane	17	0.42–0.98	4.08	4.75	4.44
<i>n</i> -Nonane	14	0.44–0.87	4.80	5.26	4.89
<i>n</i> -Decane	18	0.42–0.97	2.23	2.70	2.25
<i>iso</i> -Butane	22	0.29–0.98	1.31	1.45	1.51
Benzene	25	0.52–0.98	1.45	1.26	1.52
Toluene	22	0.46–0.98	0.97	1.67	1.94
Ethylene	12	0.39–0.96	2.04	1.73	2.66
Propylene	21	0.44–0.99	1.40	1.51	2.25
Global	271		1.98	2.15	2.42

SRK-CEOS gives better results than the TRK-CEOS. However, the deviation obtained by the proposed equation of state is smaller than other RK-CEOS type of equations.

In the case of the entropy of vaporization, deviations obtained by the new equation are in general smaller than obtained from the other RK-CEOS, although being comparable to TRK-CEOS.

4. Conclusion

The use of the modified Wagner form to express the alpha function in the Redlich–Kwong equation of state allows the estimation of thermodynamic properties such as the vapor pressure, the enthalpy of vaporization and the entropy of vaporization.

The alpha function for the Redlich–Kwong equation of state is expressed according to Pitzer's corresponding states principle. The new equation of state is applied to estimate the vapor pressure. The results are acceptable in most cases and compare favourably with those of the literature. The mean absolute deviations are smaller than those for other Redlich–Kwong type equation of state.

Furthermore, the new cubic equation of state is established from vapor pressure data of *n*-alkanes, and has been successfully applied to hydrocarbons of different chemical structures (branched alkanes, alkylcyclopentanes, alkylcyclohexanes et alkylbenzenes).

The same conclusions apply to the prediction of thermodynamics properties such as enthalpy of vaporization and entropy of vaporization. This demonstrates that the new cubic equation of state is a useful tool for predicting different thermodynamical properties with the same precision as other equations of state of Redlich–Kwong type.

5. List of symbols

a, b	Redlich–Kwong equation of state parameters
A, B, C, D	parameters in Eq. (12)
L, M, N	parameters in the TRK-CEOS α function
P	pressure
T	temperature
V	molar volume

Greek letters

α	alpha function defined in Eq. (2)
ω	acentric factor

Subscripts

c	critical property
r	reduced property

Superscripts

(0)	reference fluid ($\omega = 0.0$)
(1)	reference fluid ($\omega = 1.0$)

References

- [1] W.C. Edmister, B.I. Lee, *Applied Hydrocarbons Thermodynamics*, Vol. 1, 2nd edn., Gulf Publishing, Houston, 1984.
- [2] G.M. Wilson, *Adv. Cryog. Eng.* 9 (1964) 168–176.
- [3] G. Soave, *Fluid Phase Equilibria* 82 (1993) 345–359.
- [4] G. Soave, *Chem. Eng. Sci.* 27 (1972) 1197–1203.
- [5] G. Soave, *Fluid Phase Equilibria* 84 (1993) 339–342.
- [6] B.I. Lee, M.G. Kesler, *AIChE J.* 21 (1975) 510–527.
- [7] C.H. Twu, J.E. Coon, J.R. Cunningham, *Fluid Phase Equilibria* 105 (1995) 61–69.
- [8] C.H. Twu, J.E. Coon, J.R. Cunningham, *Fluid Phase Equilibria* 96 (1994) 19–31.
- [9] B.E. Poling, *Fluid Phase Equilibria* 106 (1996) 102–109.
- [10] Design Institute for Physical Properties Research, *Data Compilation of Pure Compounds Properties*, Standard Reference Data, National Institute of Standards and Technology, Gaithersburg, 1995.
- [11] R.C. Reid, J.M. Prausnitz, B.E. Poling, *The Properties of Gases and Liquids*, 3rd edn., McGraw-Hill, New York, 1987.
- [12] M.S. Perry, J.C. Chilton, *Chemical Engineering Handbook*, McGraw-Hill, New York, 1990.
- [13] S. Raznjevic, *Handbook of Thermodynamics Tables and Charts*, Addison-Wesley, New York, 1976.