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Modification of Rk Equation of State for Liquid and Vapor of Ammonia by Genetic Algorithm

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***Abstract*—**Cubic equations of state like Redlich–Kwong (RK) EOS have been proved to be very reliable tools in the prediction of phase behavior. Despite their good performance in compositional calculations, they usually suffer from weaknesses in the predictions of saturated liquid density. In this research, RK equation was modified. The result of this study show that modified equation has good agreement with experimental data.

***Keywords*—**Equation of state, modification, ammonia, genetic algorithm.

I. Introduction

EQUATION of state (EOS) is an important and effective tool for calculations of thermodynamic properties and phase equilibrium of pure and fluid mixtures. The accurate and simple EOSs are widely used for theoretical and practical studies in chemical process design, petroleum industry, reservoir fluids, etc. Since the first cubic EOS was set out by van der Waals in 1873, hundreds EOSs have been proposed so far, in the three main categories of 1– Cubic EOSs, 2– Virial Expansion EOSs, and 3– Non-cubic or Complex EOSs. There are several review papers published on historical development of the EOSs [1]–[5]. Among various types of EOSs, the cubic EOSs are simple, flexible to handle and also reliable (according to its accuracy) in different practical applications. The main factors in developing a cubic EOS are its accuracy, flexibility (or simplicity) and generality. Logically there should be a balance between these factors for the applicability of any EOS [6]. Although in semi-empirical cubic EOSs, the parameters may not have sound theoretical basis, they are widely used by chemical engineers due to their simplicity. However, the accuracy of the results remains as the main concern. There has been considerable progress in the development of equations of state based on th1Asli,e molecular theory of statistical mechanics [1], [7]–[10], however, due to their complexity it is still worthwhile to make improvements on semi-empirical equations of state of industrial interest.

Cubic EOS models are the simplest class of EOSs that can be used to represent the vapor–liquid critical point, but these models are inaccurate for predicting liquid densities [11], [12].

This weakness can be relatively ascribed to the way in which the two EOS parameters, a and b, are calculated. For a pure compound, these parameters are calculated by using just critical temperature and pressure (Tc and Pc). The critical volume (vc) is not used because only two critical properties are needed to determine the values of the two EOS parameters. The critical temperature (Tc) and critical pressure (Pc) can be measured more accurately than the critical volume (vc). Moreover, the former also leads to give the EOS higher overall performance. As a result of excluding the experimental critical volume, the EOS ability to predict liquid volumetric properties is not satisfactory [13], [14]. Volume translation can be adopted in the EOS to overcome this deficiency.

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II. Redlich-Kwong Equation

Since Van der Waals has proposed the first cubic equation of state 1873, a large number of equations have 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 w1x. It is the precursor of a family of simple and relatively precise equations of state [15].

$$P = \frac{RT}{V-b} - \frac{a}{T^{\frac{1}{2}}V(V+b)} \quad (1)$$

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 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 [15], [16]. 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 w2x proposed the introduction of the alpha function to force the Redlich–Kwong equation of state to reproduce the vapor pressure [15], [16].

III. PVT Experimental Data of Ammonia

Specific density of liquid and vapor for ammonia is given by Perry et al [17]. This experimental data is given by Table I.

TABLE I
EXPERIMENTAL LIQUID AND VAPOR DATA OF PURE AMMONIA

Experiment number	Temperature (^oF)	Pressure (Psia)	Specific volume of liquid phase (ft^3/lb_m)	Specific volume of vapor phase (ft^3/lb_m)
1	-40	10.41	0.02322	24.86
2	-38	11.04	0.02327	23.53
3	-36	11.71	0.02331	22.27
4	-34	12.41	0.02336	21.1
5	-32	13.14	0.0234	20
6	-30	13.9	0.02345	18.97
7	-28	14.71	0.02349	18
8	-26	15.55	0.02354	17.09
9	-24	16.42	0.02359	16.24
10	-22	17.34	0.02364	15.43
11	-20	18.3	0.02369	14.68
12	-18	19.3	0.02373	13.97
13	-16	20.34	0.02378	13.29
14	-14	21.43	0.02383	12.66
15	-12	22.56	0.02388	12.06
16	-10	23.74	0.02393	11.5
17	-8	24.97	0.02398	10.97
18	-6	26.26	0.02403	10.47
19	-4	27.59	0.02408	9.991
20	-2	28.98	0.02413	9.541
21	0	30.42	0.02419	9.116
22	2	31.92	0.02424	8.714
23	4	33.47	0.0243	8.333
24	6	35.09	0.02435	7.971
25	8	36.77	0.02441	7.629
26	10	38.51	0.02446	7.304
27	12	40.31	0.02452	6.996
28	14	42.18	0.02457	6.703
29	16	44.12	0.02463	6.425
30	18	46.13	0.02468	6.161
31	20	48.21	0.02474	5.91
32	22	50.36	0.02479	5.671
33	24	52.59	0.02485	5.443
34	26	54.9	0.02491	5.227
35	28	57.28	0.02497	5.021
36	30	59.74	0.02503	4.825
37	32	62.29	0.02509	4.637
38	34	64.91	0.02515	4.459
39	36	67.63	0.02521	4.289
40	38	70.43	0.02527	4.126

IV. GENETIC ALGORITHM

The optimization of process operations leads to the production of the best product or to the best operating performance, with respect to a specific situation. Different method can be employed to carry out the optimization. As the result of the work depends on the method of the optimization, it is important to determine which method should be used to find the optimum outcome.

GAs are computational search methods based on an optimization algorithm, gene structure, and chromosomes. They are effective search techniques for expansive search space. In these algorithms, the design space must change according to the genetic space; as such, GAs work with some encoded variables. Three important steps are associated with the implementation of a GA [17], [18]:

1) Identification of the objective function or cost function;
2) Identification and implementation of genetic space; and
3) Identification and implementation of the GA operator.

V. RESULT AND DISCUSSION

At first, (1) was written according to dimension of experimental data that is given in Table I.

$$P = \frac{\frac{10.73}{17}T}{V-b} - \frac{a}{T^{\frac{1}{2}}V(V+b)} \quad (2)$$

Then a function was defined to show deviation of (2) from experimental data. This equation is

$$\text{Function} = \left|1-\frac{P_V}{P_L}\right| + \left|1-\frac{P_L}{P_V}\right| + \left|1-\frac{P_V}{P}\right| + \left|1-\frac{P_L}{P}\right| \quad (3)$$

P_V : Calculated pressure of vapor phase

P_L : Calculated pressure of liquid phase

P : Experimental pressure

This function minimize by genetic algorithm. Figs. 1 and 2 show the results of minimization for (2).

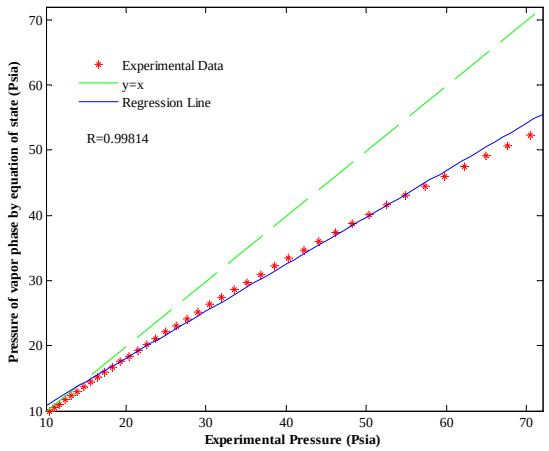

Fig. 1 Predicted pressure of vapor phase by RK equation versus experimental pressure

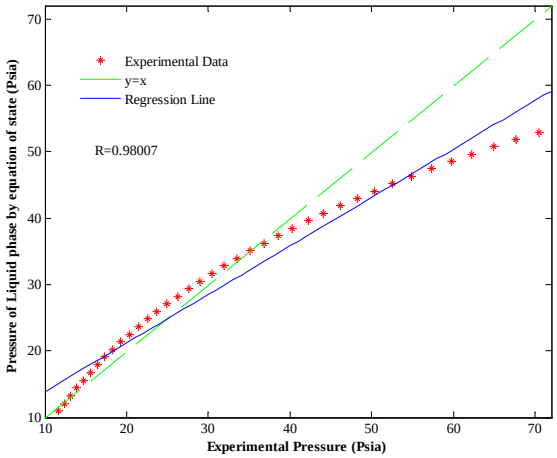

Fig. 2 Predicted pressure of liquid phase by RK equation versus experimental pressure

Figs. 1 and 2 show large deviation of equation 2 in upper experimental pressure. For decrease deviation, (4) replaces (2):

$$P = \frac{\frac{10.73}{17}T}{V-b} - \frac{AT+C}{T^{\frac{1}{2}}V(V+b)} \quad (4)$$

Constants of this equation were calculated by (3) and using genetic algorithm.

A = -0.2871

b = -0.8927

C = 4.5462

and deviation of (4) from experimental data is shown in Figs. 3 and 4.

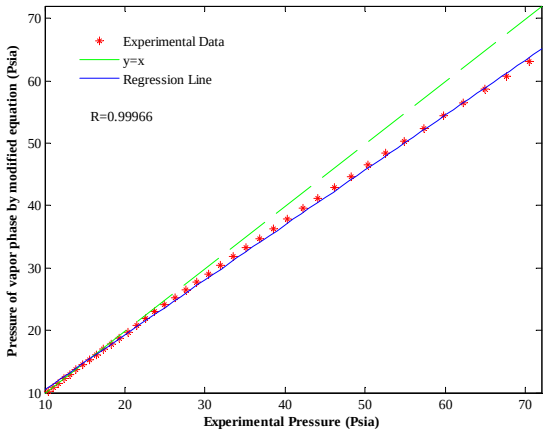

Fig. 3 Predicted pressure of vapor phase by modified RK equation versus experimental pressure

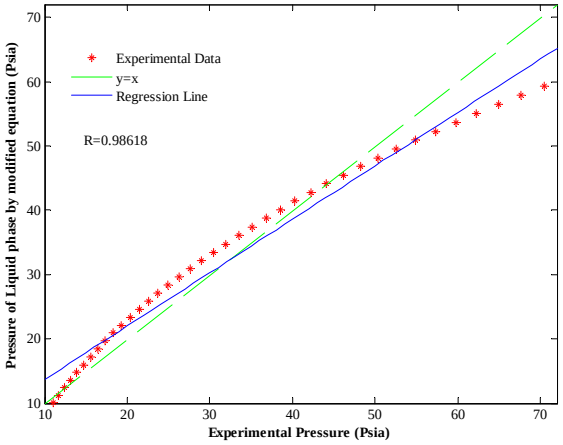

Fig. 4 Predicted pressure of liquid phase by modified RK equation versus experimental pressure

Figs. 3 and 4 show that modified equation has less deviation from experimental data.

REFERENCES

[1] A.H. Farrokh-Niae, H. Moddarress, M. Mohsen-Nia," A three-parameter cubic equation of state for prediction of thermodynamic properties of fluids", J. Chem. Thermodynamics 40 (2008) 84–95.

[2] J.J. Martin, Ind. Eng. Chem. Fundam. 18 (1979) 81–97.

[3] S. M. Walas, in: Phase Equilibria in Chemical Engineering, Butterworths, London, 1985, pp. 42–59.

[4] J.V. Sengers, R.F. Kayser, C.J. Peters, H.J. White Jr., in: Experimental Thermodynamics, first ed. Equations of State for Fluids and Fluids Mixtures. Part I, vol. V, Elsevier, Amsterdam, 2000, pp. 75– 86.

[5] W.Y. Song, R.J. Sadus, AIChE J. 46 (2000) 169–196.
[6] J.M. Yu, B.C.-Y. Lu, Fluid Phase Equilibr. 34 (1987) 1–19.
[7] S. Beret, J.M. Prausnitz, AIChE J. 21 (1975) 1123–1132.
[8] M.D. Donohue, J.M. Prausnitz, AIChE J. 24 (1978) 849–860.
[9] W.G. Chapman, J. Chem. Phys. 93 (1990) 4299–4304.
[10] W.G. Chapman, K.E. Gubbins, G. Jackson, M. Radosz, I&EC Res.29 (1990) 1709–1721.
[11] Kurt Frey, Chad Augustine, Rocco P. Ciccolini, Scott Paap, Michael Modell, Jefferson Tester." Volume translation in equations of state as a means of accurate property estimation", Fluid Phase Equilibria 260 (2007) 316–325.
[12] G. Schmidt, H. Wenzel, Chem. Eng. Sci. 35 (1980) 1503–1512.
[13] Milad Nazarzadeha, Mahmood Moshfeghian." New volume translated PR equation of state for pure compounds and gas condensate systems", Fluid Phase Equilibria 337 (2013) 214– 223.
[14] K. Frey, M. Modell, J. Tester, Fluid Phase Equilib. 279 (2009) 56–63.
[15] Fatiha Souahi, Salim Sator, Samia Assia Albane, Fairuz Khalida Kies,Chems Eddine Chitour," Development of a new form for the alpha function of the Redlich–Kwong cubic equation of state", Fluid Phase Equilibria 153 _1998. 73–80.
[16] G. Soave, Fluid Phase Equilibria 82 _1993. 345–359.
[17] Perry RH. Perry's chemical engineer's handbook. 7th ed. New York: McGraw-Hill companies; 1999.
[18] A. R. Moghadassi, F. Parvizian, B. Abareshi ,F. Azari, I. Alhajri," Optimization of regenerative cycle with open feed water heater using genetic algorithms and neural networks", J Therm Anal Calorim (2010) 100:757–761.