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COMPARING OF SEVERAL EOS FOR EVALUATION OF NARMS' THERMODYNAMIC PROPERTIES

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ABSTRACT

The paper at first, analyzes three equations of state—MH equation, RKS equation, SHBWR equation for their adaptation in liquid state. The equations are solved with special mixing regulation on the condition of vapor-liquid equilibrium (VLE) for NARMs and then the paper evaluates thermodynamic properties of this mixture for four conditions by method of the complementary function. This paper considers that there are enough experimental data, the precision of MH equation is higher and the adaptable region is larger than the other equations with optimizing the constants of MH equation. SHBWR equation could also be used for preliminary evaluation. RKS equation is simple so that it is easy to be solved, but the results is not good.

NOMENCLATURE

a	Free energy (KJ/Kmol)	Subscript
f	Freedom	
h	Specific enthalpy (KJ/Kmol)	C Critical
P	Pressure (KPa)	
R	The constant of gas	Superscript
S	Specific entropy (KJ/K · Kmole)	
T	Temperature (K)	L Liquid
V	Specific volume (m ³ /Kmol)	V Vapor
x	Molar fraction of liquid	* Ideal point
y	Molar fraction of vapor	

INTRODUCTION

The use of NARMs has been paid attention to by more and more researchers because of their specific characteristics. The experimental method has been adopted by most of the researchers who are interested in NARMs to look for and analyze working-pair. It took the researchers higher price and longer time

to finish this process. Theoretical evaluation can make up the loss of the experimental method and supply direction to the experimental research.

The evaluation of thermodynamic properties problem about NARM is actually about how to utilize data of pure refrigerant. Since there are enough data in certain region to most of the refrigerants, the thermodynamic properties of NARMS can be calculated according to the data of pure refrigerants and mixing regulation if there were proper mixing regulation. However, the thermodynamic properties of pure refrigerants used now for example specific volume, specific enthalpy and specific entropy, are obtained through specialized equations within some special region. On the basis of this, there will be difficulties to solve the constants of many special equations and the process of the calculation will be very troublesome. To reduce the work load, a single equation which can describe the characteristics of liquid and vapour state must be found. If this equation can be used in calculation for most refrigerants, thermodynamic properties of NARMS can be evaluated after determining constants of the equation to pure refrigerants and adopting proper mixing regulation. In the meanwhile, it is more identical and reasonable to describe the characteristics of refrigerants from the physical feature.

Most of EOS describe poorly about characteristic of liquid state and they could not be used in calculation of VLE. This paper compares and analyze three equations of state — MH, SHBWR and RKS equation.

CALCULATION METHOD OF THE THREE EOS

The form of MH equation ⁽¹⁾:

$$P = \frac{RT}{V-b} + \frac{A_2+B_2T+C_2e^{-KT/T_c}}{(V-b)^2} + \frac{A_3+B_3T+C_3e^{-KT/T_c}}{(V-b)^3} + \frac{A_4+B_4T}{(V-b)^4} + \frac{B_5T}{(V-b)^5} \quad (1)$$

Where A_n , B_n , C_n ($n=2, 3, 4, 5$) and b are constants of equation. $K=5.475$.

There is one more constant B_4 in this equation while it is compared with the initial MH equation. The precision of liquid state is greatly improved when the precision of vapour state is not changed.

The appropriate mixing regulation:

$$L_m = \sum \sum y_i y_j L_{ij}$$

Where L_m is constant of NARMS, $L_{11}=L_1$, $L_{jj}=L_j$, they are the constants of pure refrigerants. For L_{ij} ($i \neq j$), there are

$$(A_2)_{ij} = (1-Q_{ij}) \left[\frac{(A_2)_i + (A_2)_j}{2} \right] \quad (A_n)_{ij} = \frac{(A_n)_i + (A_n)_j}{2} \quad (n=3, 4, 5)$$

$$(B_n)_{ij} = \frac{(B_n)_i + (B_n)_j}{2} \quad (n=2, 3, 4, 5) \quad b_{ij} = \frac{b_i + b_j}{2}$$

$$(C_n)_{ij} = \left[\frac{(C_n)_i^{1/3} + (C_n)_j^{1/3}}{2} \right]^3 \quad (n=2, 3, 4, 5) \quad (T_c)_{ij} = [(T_c)_i \cdot (T_c)_j]^{1/2}$$

Where Q_{ij} is parameter of action each other.

The form of SHBWR equation ⁽²⁾:

$$P = \frac{RT}{V} + (B_0 RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4}) / V^2 + (bRT - a - \frac{d}{T}) / V^3 + \alpha (a + \frac{d}{T}) / V^6 + \frac{c}{T^2 V^3} (1 + \frac{\gamma}{V^2}) \exp(-\frac{\gamma}{V^2}) \quad (2)$$

where A_0 , B_0 , D_0 , E_0 , C_0 , a , b , c , d , α , γ are constants of equation.

It is revised BWR equation by Starling and Han on the basis of a lot of experiment data. The application region of it is enlarged and the precision is improved. The model of VLE on the basis of SHBWR equation is often adopted in chemical engineering.

The appropriate mixing regulation:

$$\begin{aligned} A_0 &= \sum \sum y_i y_j A_{0i}^{1/2} A_{0j}^{1/2} (1 - k_{ij}) & B_0 &= \sum y_i B_{0i} \\ C_0 &= \sum \sum y_i y_j C_{0i}^{1/2} C_{0j}^{1/2} (1 - k_{ij})^3 & D_0 &= \sum \sum y_i y_j D_{0i}^{1/2} D_{0j}^{1/2} (1 - k_{ij})^4 \\ E_0 &= \sum \sum y_i y_j E_{0i}^{1/2} E_{0j}^{1/2} (1 - k_{ij})^5 & a &= (\sum y_i a_i^{1/3})^3 \\ b &= (\sum y_i b_i^{1/3})^3 & c &= (\sum y_i c_i^{1/3})^3 \\ d &= (\sum y_i d_i^{1/3})^3 & \gamma &= (\sum y_i \gamma_i^{1/2})^2 & \alpha &= (\sum y_i \alpha_i^{1/3})^3 \end{aligned}$$

Where k_{ij} is parameter of action each other.

The form of RKS equation ⁽³⁾:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V-b)} \quad (3)$$

Where

$$a(T) = \frac{\Omega_a R^2 T_c^2}{P_c} \alpha \quad b = \frac{\Omega_b R T_c}{P_c}$$

$$\alpha^{0.5} = 1 + m(1 - T_r^{0.5}) \quad m = 0.48 + 1.57\omega - 0.176\omega^2$$

ω is eccentricity factor. $\Omega_a = 0.42748$, $\Omega_b = 0.08664$

It is revised RK equation by Soave. The precision of VLE calculation is improved compared with initial equation.

The appropriate mixing regulation:

$$a = (\sum y_i a_i^{0.5})^2 \quad b = \sum y_i b_i$$

For VLE, there is $f_i^V = f_i^L$

So $y_i P \varphi_i^V = x_i P \varphi_i^L$ (4)

Where

$$\varphi_i = \exp \left(\frac{RT}{P} \int_0^P \left[\left(\frac{\partial V}{\partial n_i} \right)_{T, P, n_j} - \frac{RT}{P} \right] dP \right)$$

To solve above simultaneous equations (1), or (2), or (3) and (4), the thermodynamic properties P, V or T could be obtained. For enthalpy and entropy, the complementary function method⁽³⁾ is adopted.

Complementary free energy: $a_r = a^* - a$
 Complementary entropy: $S_r = S^* - S$
 Complementary enthalpy: $h_r = a_r + TS_r + RT(1 - Z)$
 Z is compression factor. $Z = PV/RT$

RESULTS AND DISCUSSIONS

According to above method, this three EOS are adopted separately to evaluate the thermodynamic properties of NARMs — R12-R22, R22-R142. Because there is lack of experimental data of NARMs to be compared with calculation results. Pure refrigerants — R12, R22 and R142 results by this method are compared with data of ASHRAE in order to test and verify this method. (Pure refrigerant could be looked upon as an example when Y = 1). Table 1, 2 and 3 are results compared with data of ASHRAE.

To adopt MH equation, the deviation from its constants calculation could produce a great effect to solve simultaneous equations, especially in calcula-

tion process of liquid state. So optimization of the constants is adopted. The object function:

$$\min f = \sum_N | (1 - f_T / f_Y) | / N$$

A set of optimum constants could be obtain at some range of temperature. To adopt SHBWR equation, the same problem come across in the calculation process so that the same method is used to obtain optimum constants. Compared with the precision of MH equation results, that of SHBWR equation results is low because SHBWR equation is not good to describe polar mixtures.

To adopt RKS equation, the calculation is the simplest and speed of calculation is the fastest, but the precision is the lowest. The constants of RKS equation are obtained when the eccentricity factor ω_1 is known only. The description of RKS equation is bad, especially in liquid state so that the precision of liquid state is even lower.

CONCLUSIONS

According to above results, it is evident for the three equations that the precision of vapour state is higher than that of liquid state. The reason is that EOS is bad to describe characteristic of liquid state. MH equation is the best, SHBWR equation comes second, RKS equation is the worst. MH equation could be used to evaluate thermodynamic properties of NARM in order to provide the condition of cycle analysis. Before this process, constants of MH equation must be optimized at some range of temperature. SHBWR equation could also be used for preliminary evaluation, but the precision is not high. RKS equation, though it is simple to use, it is difficult to qualify for this character.

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Tab. 1 Deviation of MH equation results

	$\frac{\Delta P}{P}$ %	$\frac{\Delta V_L}{V_L}$ %	$\frac{\Delta V_v}{V_v}$ %	$\frac{\Delta h_L}{h_L}$ %	$\frac{\Delta h_v}{h_v}$ %	$\frac{\Delta S_L}{S_L}$ %	$\frac{\Delta S_v}{S_v}$ %	Temperature range °C
R-12	1.55	7.01	0.27	5.17	1.37	2.86	0.63	-40 — 40
R-22	0.78	5.58	0.21	4.64	1.52	2.36	0.74	-20 — 60
R-142b	1.72	5.02	0.21	5.43	1.94	2.94	0.92	-30 — 40

Tab. 2 Deviation of SHBWR equation results

	$\frac{\Delta P}{P}$ %	$\frac{\Delta V_L}{V_L}$ %	$\frac{\Delta V_v}{V_v}$ %	$\frac{\Delta h_L}{h_L}$ %	$\frac{\Delta h_v}{h_v}$ %	$\frac{\Delta S_L}{S_L}$ %	$\frac{\Delta S_v}{S_v}$ %	Temperature range °C
R-12	1.95	8.32	0.88	9.20	2.74	4.47	0.91	-40 — 40
R-22	1.22	7.11	0.81	8.89	2.74	3.73	1.12	-20 — 60
R-142b	2.07	7.19	1.00	9.99	3.08	4.36	1.13	-30 — 40

Tab. 3 Deviation of RKS equation results

	$\frac{\Delta P}{P}$ %	$\frac{\Delta V_L}{V_L}$ %	$\frac{\Delta V_v}{V_v}$ %	$\frac{\Delta h_L}{h_L}$ %	$\frac{\Delta h_v}{h_v}$ %	$\frac{\Delta S_L}{S_L}$ %	$\frac{\Delta S_v}{S_v}$ %	Temperature range °C
R-12	6.39	18.46	5.81	20.32	9.00	12.85	6.64	-40 — 40
R-22	5.85	17.74	5.43	19.87	7.67	14.59	5.99	-20 — 60
R-142b	5.96	20.14	6.02	22.43	8.24	13.27	6.97	-30 — 40

Where
$$\frac{\Delta X}{X} = \frac{1}{n} \sum \frac{|X - X_{cal}|}{X} \times 100\%$$
 X — Data of ASHRAE
Xcal — Data of calculation