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## FUGACITY COEFFICIENT WITH MODIFIED CONSTANTS OF REDLICH-KWONG EQUATION OF STATE

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The adequacy of the modified constants of Redlich-Kwong equation of state suggested by various research workers has been studied on the criterion of equality of fugacity coefficients of vapour and liquid phases. The comparison with the data of twelve compounds showed that the approach of Medani and Hasan (1978) gave the least deviations. The values of constants, with their approach, for propane, argon, nitrogen, methane and methanol have also been reported.

### INTRODUCTION

It was shown by Medani and Hasan[9] that their modified Redlich-Kwong (R-K) equation of state predicted the volumetric properties and vapour-liquid equilibrium data of pure and binary mixtures of different complexities reasonably well. Their modification also offered advantages of simplicity and rapidity in converging the data to the required tolerance. In present work their approach is compared with other suggested modifications to R-K equation constants. Their method has also been analysed with data of few more compounds.

The method that is more popular for the improvement of R-K equation of state is the modification of the constants and thus retaining the original form of the equation, i.e.,

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

The values of the constants 'a' and 'b' could be evaluated by applying the equation to the critical conditions in the following form:

$$a = \Omega_a R^2 T_c^{2.5} / P_c \quad (2)$$

$$b = \Omega_b R T_c / P_c \quad (3)$$

The values of dimensionless constants  $\Omega_a$  and  $\Omega_b$  were originally proposed by Redlich and Kwong [10] as 0.4278 and 0.0867 respectively. Four possible ways have been reported in literature to modify the R-K equation constants for pure substance at their saturation conditions.

- 1)  $\Omega_a$  and  $\Omega_b$  are temperature independent. Chueh and Prausnitz [3] suggested to use two sets of constants by fitting R-K equation to the volumetric data of the saturated vapor and liquid phases separately.
- 2)  $\Omega_a$  is considered to be a temperature dependent while  $\Omega_b$  is kept constant and equal to 0.0867. This approach has been suggested by Wilson[13] and Soave[11].
- 3) Both  $\Omega_a$  and  $\Omega_b$  are considered as temperature dependents. This approach was followed by Chang *et al.* [1], Joffe *et al.* [5] and Chaudron *et al.* [2].
- 4)  $\Omega_b$  is considered as temperature dependent and  $\Omega_a$  is kept constant and equal to 0.4278. Medani and Hasan[9] followed this approach.

The methods of establishing the criterion to determine the best values of  $\Omega_a$  and  $\Omega_b$ , as reported in literature, include fitting of PVT data (Chueh and Prausnitz, [3]), fitting a pair of simultaneous equations (Wilson, [13]) and fitting for the equality of fugacity coefficients in the vapour and liquid phases (Joffe *et al.* [5]; Soave[11] and Medani and Hasan, [9]). Zudkevitch and Joffe[14] and Hasan[6] have shown that the first two methods of establishing the criterion of the best values of the constants were inadequate and did not yield equal fugacity coefficients for both phases. The equality of the fugacity coefficients is an essential thermodynamic requirement for an equilibrium state and hence the third method is now generally used in preference to other two methods. Moreover, the values of the constants obtained by this method also represent better thermodynamic data than others.

For the determination of the values of  $\Omega_a$  and  $\Omega_b$  a computer programme based on Newton-Raphson iterative method was used. The third method i.e. the criterion of equal fugacity coefficients for both phases, very similar to Joffe *et al.* [14] approach, has been followed in this

Table 1. Values of RMSD and R-K equation constants with different approaches for saturated propane.

Temperature K	Pressure k Pa	Wilson's approach	Soave's approach	Chaudron <i>et al.</i>			Medani & Hasan's approach
				This work	approach	This work	
198.5	10.132	0.4444	0.619007	0.426796	0.083837	0.420473	0.083473
231.1	101.325	0.4512	0.565294	0.424778	0.082201	0.427325	0.082390
259.33	303.975	0.4516	0.532812	0.424373	0.081491	0.425803	0.082267
275.24	506.624	0.4505	0.515682	0.424319	0.081232	0.423828	0.082375
286.9	709.275	0.4491	0.503612	0.424332	0.081108	0.421610	0.082541
296.3	911.924	0.4470	0.494160	0.424367	0.081048	0.419550	0.082726
317.42	519.875	0.4435	0.473769	0.424505	0.081043	0.413860	0.083328
341.71	2533.124	0.4437	0.451642	0.424732	0.081261	0.404643	0.084240
359.61	3546.374	0.4314	0.436160	0.424928	0.081575	0.400815	0.085261
367.18	4052.999	0.4288	0.429808	0.425015	0.081746	0.403731	0.085862
RMSD	—	0.02306	0.47422	0.02898	0.00090	0.00021	0.00009

 $\Omega_a = f(T)$  and  $\Omega_b = 0.0867$ 
 $\Omega_a = f(T)$  and  $\Omega_b = f(T)$ 
 $\Omega_b = f(T)$  &  
 $\Omega_a = 0.4278$ 

Table 2. Different values of RMSD with the three methods.

Compounds	$\Omega_a = f(T)$ & $\Omega_b = 0.0867$	$\Omega_a$ and $\Omega_b$ $= f(T)$	$\Omega_b = f(T)$ & $\Omega_a = 0.4278$
Acetylene	0.00008	0.00001	0.00001
Ammonia	0.00013	0.00005	0.00001
Argon	0.00009	0.00003	0.00001
Benzene	0.00098	0.00028	0.00021
Ethane	0.00011	0.00002	0.00001
n-Hexane	0.00076	0.00022	0.00008
Hydrogen sulphide	0.00011	0.00001	0.00001
Methane	0.00010	0.00004	0.00002
Methanol	0.00094	0.00042	0.00014
Nitrogen	0.00011	0.00003	0.00002
n-pentane	0.00009	0.00003	0.00001

work. The data were taken from literature (Timmermans, [12]; Din[4] and Eubank[5]). The deviations of the fugacity coefficients in the two phases are expressed in the term of root mean square deviation:

$$RMSD = \left[ \frac{\sum(\text{Difference in fugacity coefficients})^2}{\text{Number of observations}} \right]^{2.5} \quad (4)$$

For the sake of comparison, different methods suggested by various research workers have been applied to the data of saturated propane. The values of RMSD and the R-K equation constants were calculated and are shown in Table 1. The approaches of keeping  $\Omega_a$  or  $\Omega_b$  or both of them as temperature dependent have also been compared with the data of eleven more compounds and are reported in Table 2. The results of both the comparative studies indicate that the modification by Medani and Hasan[9] gave more nearly equal values of the fugacity coefficients

Notation:

- a, b = Constants of the Redlich-Kwong equation
- P = Pressure, vapour pressure
- R = Gas constant
- RMSD = Root mean square deviation, Equation(4)
- T = Absolute temperature
- V = Molar volume
- $\Omega_a, \Omega_b$  = Dimensionless parameters
- Subscript c = Critical phase.

Table 3. The value of  $\Omega_b$  as a function of temperature ( $\Omega_a = 0.4278$ )

Argon		Nitrogen		Methane		Methanol	
Temp. K	$\Omega_b$	Temp. K	$\Omega_b$	Temp. K	$\Omega_b$	Temp. K	$\Omega_b$
83.7	0.093253	63.1	0.091898	100	0.093276	383.15	0.068911
87.2	0.092691	65.8	0.091407	105	0.092936	393.15	0.069570
94.4	0.091442	68.4	0.090959	110	0.092244	403.15	0.070284
99.2	0.090652	71.9	0.090278	115	0.091565	413.15	0.071080
105.9	0.089666	74.4	0.089803	120	0.090895	423.15	0.071925
110.9	0.089000	77.3	0.089323	125	0.090257	433.15	0.072815
116.8	0.088277	83.3	0.088265	130	0.089651	443.15	0.073776
124.2	0.087482	88.0	0.087819	135	0.089094	453.15	0.074829
130.0	0.086956	94.0	0.087263	140	0.088572	463.15	0.076006
134.8	0.086672	98.6	0.086878	145	0.088110		
139.0	0.086457	103.8	0.086492	150	0.087703		
146.1	0.086190	110.5	0.086124	155	0.087351		
		115.8	0.085961	160	0.087069		
		120.1	0.085962	165	0.086818		
		123.8	0.086058	170	0.086587		
				175	0.086531		

of the two phases than the other methods. Medani and Hasan [8-9] have also shown the adequacy of their suggested modification to represent a unified treatment for the estimation of phase equilibria as well as physical properties and enthalpy departures to a reasonable tolerance. In view of their work and the present study on the comparison of different proposed methods (on the basis of equality of fugacity coefficients of both the phases) their approach of modifying the constants of R-K equation appears to be more justifiable than others. The values of  $\Omega_b$  with their proposed method for the compounds, ethane, hydrogen-sulphide, benzene and n-hexane have already been mentioned by them. The values of  $\Omega_b$  for few more compounds studied in this work are being reported in Table 3.

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