Cohesion Factor Relations for Cubic Equations of State: Soave-Redlich-Kwong Equation of State

M.H.Joshipura, S.P.Dabke and N.Subrahmanyam

Abstract—**Cubic Equations of States (CEOS), a well celebrated tool for predicting phase equilibrium, can be compared based on the accuracy of the prediction of vapor pressure. Accurate vapor pressure prediction is completely dependent on cohesion factor used in CEOS. In the present work, six cohesion function models for Soave Redlich Kwong (SRK) Equations of State (EOS), available in literature have been compared. 313 compounds, compromising of 29 different classes of families, have been selected for the study. The reduced temperatures were studied in three regions; (i) $T_r < 0.7$ (ii) $T_r \geq 0.7$ and (iii) entire range from freezing point to critical point. It was observed that all the models compared here show the acceptable behavior except model proposed by Soave (Soave, 1992). Some families showed very high deviation in AAD, which can be attributed to more than one factor like polarity, acentricity, and association.**

Index Terms—**Alpha function; Cohesion Factor; Soave Redlich Kwong EOS; Vapor Pressure.**

I. INTRODUCTION

IN the present era of computational advancement the use of process simulators is inevitable. These simulators are like black box and if we do not provide them with the proper input the output generated are always doubtful. For getting the meaningful results from the simulator one needs to select a proper thermodynamic model. Amongst various available thermodynamic model options, equations of state (EOS) approach is widely acceptable. Ranging from molecular based SAFT EOS[1] to empirical cubic equations of state (CEOS) are available to be used. The simplicity and applicability of CEOS have made them top on the league and have attracted the process engineers for their continuous enhancement. Soave-Redlich-Kwong (SRK)[2] and Peng-Robinson (PR)[3] EOS are well recognized. They can, in principle, accurately represent the Vapor Liquid Equilibrium (VLE) relationship in binary and multicomponent mixtures, provided proper mixing rule is available and pure component vapor pressure is accurately reproduced. Any EOS is evaluated on different basis like estimation of saturated liquid density, prediction of critical constants, prediction of Joule Thomson inversion curves etc., but most important factor for comparing EOS is prediction of vapor pressure using proper cohesion/alpha function. In the present study SRK EOS is used for the estimation of vapor pressure of 313 compounds using six different cohesion factor

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models resulting in more than 95000 data points. SRK EOS is selected as it is widely accepted, two parameter EOS model, for the prediction of VLE.

II. EQUATION OF STATE AND COHESION FACTOR RELATIONSHIP

SRK EOS model is expressed as,

$$P = \frac{RT}{\nu - b} - \frac{a_i(T)}{\nu(\nu + b) + b(\nu - b)} \tag{1}$$

where

$$a_i(T) = \frac{\psi \alpha(T_r) R^2 T_c^2}{P_c} \tag{2}$$

and

$$b = \frac{\Omega R T_c}{P_c} \tag{3}$$

Values for α and ψ are characteristics constant for SRK EOS and the values are 0.08664 and 0.42748 respectively. $\alpha(T_r)$ represents the cohesion factor popularly known as alpha function. Its value was unity for the van der Waals EOS. Right from the introduction of the Redlich-Kwong (RK) EOS [4], the modification of cohesion function has been the subject of the interest. Many researchers have proposed different cohesion functions there after [5]-[15] It was first shown by Wilson in 1960 [10] that this cohesion factor is a function of temperature and acentric factor. RK and PR EOS improved the cohesion factor by expressing it as a polynomial in acentric factor. Soave [5] further modified the RK EOS cohesion factor. Correlations proposed for SRK EOS can be categorized in two basic types: Polynomial in acentric factor and Corresponding state type i.e. linear in acentric factor $\left(\alpha = \alpha^0 + \omega\left(\alpha^1 - \alpha^0\right)\right)$. Six popular models for cohesion factor were selected representing above mentioned two categories. Cohesion (alpha) function models with their parameters are listed in Table I .

III. VAPOR PRESSURE: ESTIMANT AND DATABASE

For present study total twenty nine different families of chemicals have been considered. Some important families are elements, oxides, halides, alkanes, cycloalkanes, alkenes, aromatic hydrocarbons, halogenated alkanes, alcohols, ethers, ketones etc. In all total three hundred and thirteen (313) compounds were considered in the present study. Compounds were selected such that their physical properties have a wide range. The ranges of all the properties are listed in Table II.

Selected compounds cover almost entire range of the possible industrial important compounds. For all the compounds pseudo

TABLE I
COHESION FACTOR MODELS CONSIDERED IN THE PRESENT STUDY

| Model No.	$\alpha(T_r)$	
M1[4]	$\left[1 + \left(A + B\omega + C\omega^2\right)\left(1 - T_r^D\right)\right]^{1/E}$	A=0.48;B=1.574;C=-0.176; D=0.5;E=0.5
M2[5]	$\left[1 + \left(A + B\omega + C\omega^2 + D\omega^3\right)\left(1 - T_r^E\right)\right]^{1/F}$	A=0.47979;B=1.576;C=-0.1925; D=0.025;E=0.5;F=0.5
M3[6]	$T_r^A e^{\left(B\left(1 - T_r^C\right)\right)} + \omega\left(T_r^D e^{\left(E\left(1 - T_r^F\right)\right)} - T_r^A e\left(B\left(1 - T_r^C\right)\right)\right)$	A=0.012252;B=0.544;C=0.948247; D=-0.6142;E=0.544306;F=2.494152
M4[7]	$\left[1 + \left(A + B\omega + C\omega^2\right)\left(1 - T_r^D\right)\right]^{1/E}$	A=0.48508;B=1.55171;C=-0.15613; D=0.5;E=0.5
M5 [8]	$\left[1 + m1\left(1 - T_r\right) + n1\left(1 - T_r^0.5\right)\right]^2$	$m1 = 0.8484 + 1.515\omega - 0.44\omega^2$; $n1 = 2.756m1 - 0.7$
M6 [9]	$\alpha_0 + \omega\left(\alpha_1 - \alpha_0\right)$ $\alpha_0 = \left[1 + \frac{A_0(1-T_r) + B_0(1-T_r)_2 + C_0(1-T_r)^3 + D_0(1-T_r)^6}{T_r}\right]$ $\alpha_1 = \left[1 + \frac{A_1(1-T_r) + B_1(1-T_r)_2 + C_1(1-T_r)^3 + D_1(1-T_r)^6}{T_r}\right]$	$A_0 = 0.517224; B_0 = -0.428098$ $C_0 = -0.0551291; D_0 = 0.005803$ $A_1 = 1.92645451; B_1 = -0.635957$; $C_1 = -0.879041; D_1 = 0.1061225$
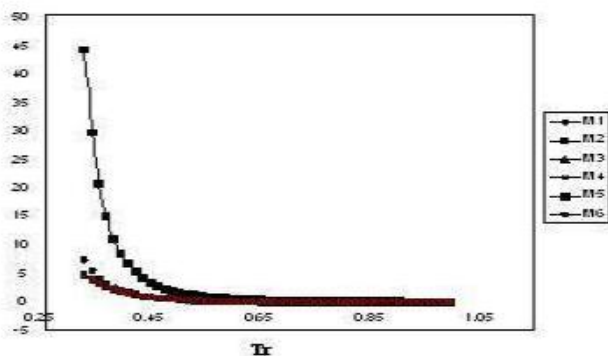
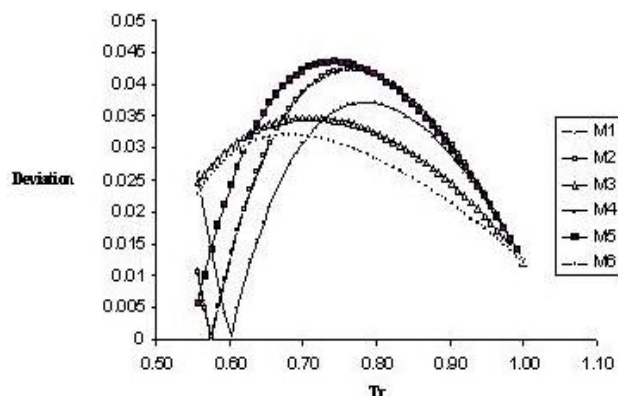Fig. 1.   Variation in deviation with temperature for 1-Pentenol

Fig. 2.   Variation in deviation with temperature for Xenon

TABLE II
RANGE OF PROPERTIES OF SELECTED COMPOUNDS

Property(Unit)	Range	
	Minimum	Maximum
Critical Temperature (K)	33.18	1735
Critical Pressure (bar)	10.4	1608
Critical Compressibility Factor	0.184	0.628
Acentric factor	-0.22	2.389
Dipole Moment (dbye)	0	4.07

experimental vapor pressure data were generated using vapor pressure equation reported by Yaws [14]. The coefficients for vapor pressure equation were valid through out temperature range from freezing point to critical point for almost all the compounds. Vapor pressure prediction using SRK EOS was carried out with the help of equi-fugacity criteria algorithm [15] implemented using MATLAB. MATLAB code generated vapor pressure predictions at 51 various temperatures between freezing point and critical point for each of the 313 compounds studied.

IV.   RESULTS AND DISCUSSION

Variation of deviation (Deviation=$\sum \left| \frac{(vpcal - vpexp)}{vpexp)} \right|$ with reduced temperature is shown in figure 1-5 for some representative compounds. For 1-Eicosene Fig. 4 shows the effect of reduced temperature for all the models. Since deviation for model 5 is very high compared to other models, the deviation for other models are not visible. This can be observed separately as shown in Fig. 5. One can observe that the deviation in predicting vapor pressure is very high in the region of reduced temperature less than 0.7 for all compounds with all the models. Variation in the deviation was some random function of reduced temperature in the case of xenon but looking at the deviation values with 0.045 being the maximum, the profile can be considered as almost flat. The behavior at supercritical condition was studied earlier [16] and it was found that the cohesion factor with exponential form behave properly in supercritical region.

Percent Absolute Average Deviation $\%AAD = (100/N)\sum \frac{vpcal - vpexp}{vpexp}$, where N is number of data

TABLE III
GLOBAL %AAD FOR THE TWENTY FOUR FAMILIES FOR ALL THE MODELS

Sr. No.	Family	NC	NP	M1	M2	M3	M4	M5	M5
1	Elements	11	561	5.530465	5.487029	954.67	5.833413	4.248911	30.46954
2	NitrogenCompounds	2	102	6.494939	6.477105	6.216155	6.482561	5.941286	6.292116
3	Oxides	6	306	4.802966	4.894486	4.86573	4.790565	6.146633	4.903981
4	Sulfides	2	102	4.56952	4.563021	3.221615	4.680732	4.484693	3.9251
5	Chlorides	1	51	3.18553	3.169913	2.439712	3.406223	2.810688	2.399061
6	Oxyhelides	1	51	3.173488	3.18587	2.935781	3.130261	5.29759	2.125414
7	InorganicCompounds	2	102	10.54289	10.55172	10.95954	10.38885	9.665578	10.79923
8	Alkanes	56	2856	5.063944	5.021835	4.344802	5.080992	31.75321	4.651707
9	Cycloalkanes	28	1428	11.32668	11.40835	9.807308	11.14786	21.00557	9.191612
10	Alkenes	24	1224	8.300484	8.230618	6.723448	8.218378	64.38055	6.443619
11	Alkynes	3	153	5.057852	5.047834	5.17691	4.988396	4.519664	5.260537
12	Aromatic Hydrocarbons	43	2193	7.229732	7.267374	6.49371	7.209193	20.09188	6.601168
13	Halogenated Alkanes	18	918	6.625655	6.633071	6.605537	6.555804	7.79344	6.55358
14	Halogenated cycloalkanes	1	51	1.750407	1.798463	1.683846	1.785519	6.728683	2.123012
15	Halogenated aromatic hydrocarbons	6	306	3.35086	3.388715	3.263023	3.329795	11.95539	3.461717
16	Aldehydes	2	102	9.851131	9.808161	9.583923	9.86807	8.27609	9.764316
17	Ketones	8	408	8.95334	8.953088	8.948816	8.980401	13.25756	9.216453
18	Alkanoic Acid	2	102	6.738862	6.73266	5.645571	6.704222	32.28159	6.044308
19	Esters	3	153	3.179019	3.201067	3.630822	3.108809	8.377952	3.817685
20	Phenols	4	204	7.140333	6.763621	6.592857	6.757421	21.08847	10.80915
21	Heterocyclic Oxygen Compounds	3	153	7.130636	7.154224	7.46101	6.96686	8.355813	7.008239
22	Heterocyclic Nitrogen Compounds	3	153	4.713028	4.811935	5.102364	4.531199	10.77566	4.991803
23	Hydrocarbon Nitrogen Compounds	14	714	9.279721	9.281399	9.47755	9.231517	13.48429	9.634763
24	Sulfur Compounds	4	204	8.103672	8.095621	8.856863	7.916671	9.683429	8.889783
	Global	247	12597	6.337298	6.330299	45.61279	6.295571	13.85019	7.307413

TABLE IV
COMPARISON OF THE MODELS FOR THE FAMILIES SHOWING HIGHER %AAD

Sr. No.	Family	NC	NP	M1	M2	M3	M4	M5	M5
1	Alkadiens	9	459	106.9955	107.2222	114.7703	106.1511	135.9766	109.8751
2	Halogenated lkenes	2	102	20.04912	20.12007	19.48645	19.75882	22.83724	18.22654
3	Alcohols	32	1632	137.1214	136.5753	103.531	140.1646	608.2656	106.156
4	Ethers	8	408	40.13992	40.22085	40.95173	39.78387	48.3108	39.94715
5	Others	15	765	18.6932	17.35986	15.82237	17.99158	2943.318	16.21999
	Global	66	3366	64.5996	64.2996	58.9129	64.3361	751.7416	58.0849

points) between predicted and pseudo experimental vapor pressures was used for comparison of various models for alpha function. Since, some of the families showed very high AAD their results are reported separately. Table III reports the family wise AAD for all the models as well as Global AAD for twenty four families where as Table IV reports the same for remaining five families (for which AAD was observed to be high). Both the tables show that M5 (Soave 1992) model has the highest deviation compared to all other models. Model M3 (Twu et al) show high deviation as can be seen in Table III. However, a closer look at AAD values of Model M3, will show that very high deviation in elements family makes the Global AAD of model M3 very high. Analysis of compounds considered in elements showed that mercury (which is considered to associate) was responsible for very high deviation in elements family for all most all the models especially in model M3. Except that all the models show acceptable behavior for vapor pressure predictions.

The results were also analyzed for two regions of reduced temperature. Region-I: Tr <0.7 region II: $Tr \geq 0.7$. Results were grouped in various ranges of AAD and are reported in

TABLE V
NUMBER OF COMPOUNDS SHOWING VARIOUS RANGE OF %AAD FOR SIX MODELS FOR REGION-I TR <0.7

Models	<10%	10%to 20%	20% to 30%	30% to 50%	50% to 100%	>100%
M1	181	60	20	24	11	15
M2	182	58	20	25	11	15
M3	189	53	19	24	9	17
M4	178	65	18	25	10	15
M5	84	66	37	40	32	52
M6	187	58	19	20	10	17

Table V and VI. Table V reports the number of compounds in various groups for all the six models for Tr <0.7 and it can be seen that almost 40% compounds are having more than 10 AAD. Model M5 has the lowest number of compounds having less than 10% AAD. For the other region ($T_r \geq 0.7$) for all the models except M5 more than 95% compounds were having less than 10% AAD. It confirms that all the models have acceptable behavior for any of the compound if the reduced temperature is greater than 0.7. However for reduced temperature less than 0.7, proper selection of cohesion factor is a must for accurate prediction of vapor pressure and hence for VLE prediction.

TABLE VI
NUMBER OF COMPOUNDS SHOWING VARIOUS RANGE OF %AAD FOR SIX
MODELS FOR REGION-II $T_R >0.7$

Models	<10%	10%to 20%	20% to 30%	30% to 50%	50% to 100%	>100%
M1	300	7	2	3	0	0
M2	301	7	2	2	0	0
M3	303	5	2	2	0	0
M4	300	7	2	3	0	0
M5	241	52	12	4	1	2
M6	302	6	2	2	0	0

V. CONCLUSIONS

In present study six different alpha/cohesion factor models have been compared. Using SRK EOS, vapor pressures of total 313 compounds have been computed and compared with the pseudo experimental data generated from freezing point to critical point. From the results obtained it was very clear that different models show more or less same behavior in terms of prediction of vapor pressure with some specific model not suitable for specific class of compounds. Proper selection of model representing cohesion factor must be done in order to accurate prediction of VLE. Two most important criteria for the selection of models are the family of the compound and the temperature range. It is observed that it is not any one factor that contributes to the deviation in vapor pressure estimation. It can be the effect of any one or combination of polarity acentricity and association. To take care of all the features that contribute to higher %AAD the remedy is to introduce a compound specific parameter. The future work is aimed at introducing compound specific parameter in cohesion function model to improve vapor pressure prediction.
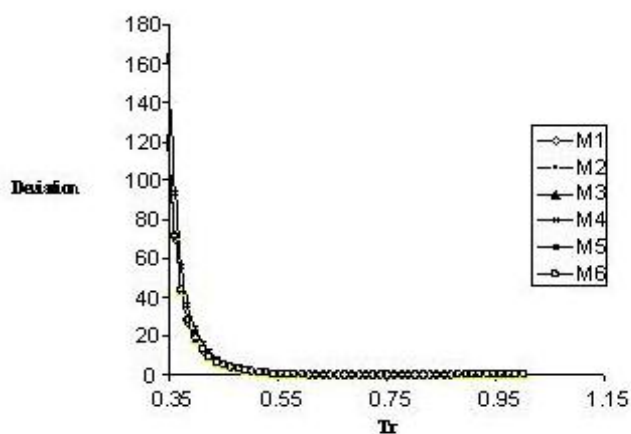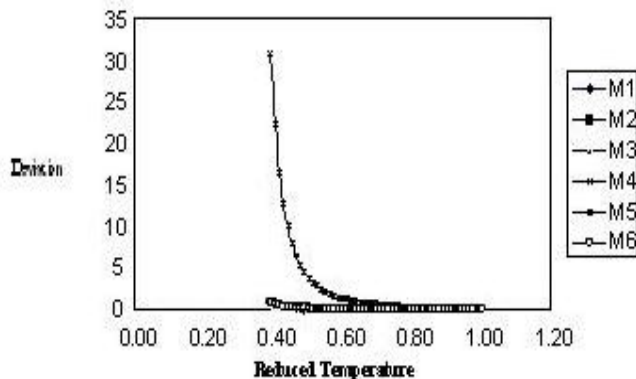

Fig. 4. Variation in deviation with temperature for 1-Eicosene for all the models
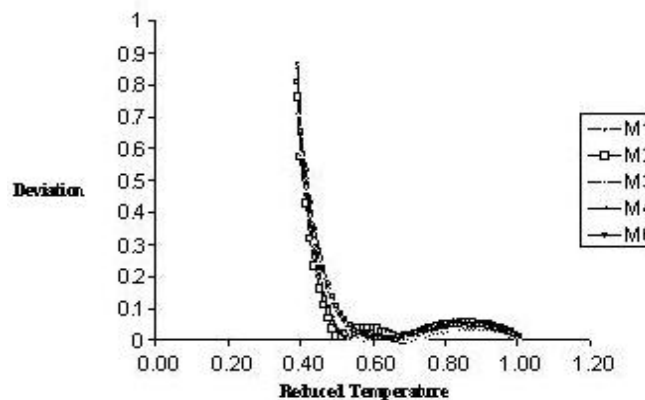

Fig. 5. Variation in deviation with temperature for 1-Eicosene for models excluding M5

A. Greek Letters

$\alpha(T_r)$ Cohesion factor
$\beta, \epsilon, \Omega, \psi$ Equation of state parameters
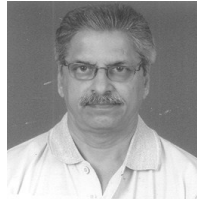ω Acentric factor

Fig. 3. Variation in deviation with temperature for Propadiene

VI. NOMENCLATURE

$a_i(T)$ Attraction parameter, bar cm^3/mol
b   Molecular co volume, cm^3/mol
ν Molar volume, cm^3/mol
%AAD   Percent Absolute Average Deviation

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