VAPOUR LIQUID EQUILIBRIUM PREDICTION FOR n-ALKANES USING THE GENERAL EQUATION OF STATE

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A general cubic equation of state was developed and presented in previous papers. The form of the equation we use in this paper has four parameters; among these, three are depending on the critical constants of the components and the fourth supplementary depends on three constants (C_1, C_2, C_3). Based on a database of PVT data for n-alkanes up to hexacontane there are proposed and comparatively discussed prediction functions for these three parameters.

Introduction

Describing the vapour – liquid equilibrium at high pressures is traditionally done using equations of state. A large group of them derives from the van der Waals equation of state and yield the dependence of pressure on volume as a third degree polynomial being therefore described as cubic equations of state. The initial equation has two parameters, with a molecular significance and is valid at low pressures. Most of the successors have two, three or four empiric parameters but maintain the original advantage of a simple, easy to handle, form.

A general cubic equation of state, GEOS, was developed and extended by Geană [1,2,3] and used by the authors [4,5] in describing vapour-liquid equilibrium in systems involving n-alkanes. The four parameters of GEOS (a, b, c, d) can be calculated based on the critical constants of the pure components (T_c, P_c, V_c) and, in the original form, on two additional constants (m and α_c).

Further papers, [6,7] introduced a new parameterisation, called GEOS3C which bases the calculation of the temperature dependent parameter "a" on three constants (C_1, C_2, C_3) instead of the parameter "m".

The C_1, C_2, C_3 parameters can be calculated, by matching points on the saturation curve together with the corresponding liquid volumes and details of the algorithm are presented by Geană and Feroiu [8,9]. Using this type of calculations, the parameters were calculated for n-alkanes up to eicosane and based on these results the paper presents some new correlation that are developed in order to predict their values for a broader group of n-alkanes. The results show that the polynomial dependencies on the accentric factor are suitable for VLE prediction for n-alkanes up to hexacontane.

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Equation of State Model

The General equation of state has the following form:

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

The four parameters are expressed for a pure component as:

$$a = \frac{R^2 T_c^2}{P_c} \Omega_a \beta(T_r) \tag{2a}$$

$$b = \frac{RT_c}{P_c} \Omega_b \tag{2b}$$

$$c = \frac{R^2 T_c^{\,2}}{P_c^{\,2}} \Omega_c \tag{2c}$$

$$d = \frac{RT_c}{P_c} \Omega_d \tag{2d}$$

The temperature function, $\beta(T_r)$, used in the new parameterisation GEOS3C is of Mathias and Copeman, [10], type:

$$\beta(T_r) = \left[1 + C_1\left(1 - T_r^{0,5}\right) + C_2\left(1 - T_r^{0,5}\right)^2 + C_3\left(1 - T_r^{0,5}\right)^3 \right]^2 \quad \text{for } T_r \leq 1 \tag{3}$$

and:
$$\beta(T_r) = \left[1 + C_1\left(1 - T_r^{0,5}\right) \right]^2 \quad \text{for } T_r > 1 \tag{4}$$

Based on the condition of critical point it results:

$$\Omega_a = (1 - B)^3 \tag{5a}$$

$$\Omega_b = (Z_c - B) \tag{5b}$$

$$\Omega_c = (1 - B)^2 (B - 0,25) \tag{5c}$$

$$\Omega_d = Z_c - (1 - B)/2 \tag{5d}$$

$$B = (1 + C_1) / (C_1 + \alpha_c) \tag{6}$$

The Riedl's criterion was calculated based on the accentric factor:

$$\alpha_c = 5.808 + 4.93\,\omega \tag{7}$$

Database

PVT experimental data are plenty for pure n-alkanes up to decane and scarce for higher members of the series. For n-alkanes over eicosane data are very few and on limited

domains. Therefore this paper uses pure P-T component data generated by the Ambrose correlation, in terms of the Wagner equation, [11], for n-alkanes up to eicosane and the correlation of Magoulas and Tassios, [12], for higher components.

Ambrose:
$$\ln P_r = \frac{a_1 q + a_2 q^{1,5} + a_3 q^{2,5} + a_4 q^5}{T_r} \tag{7},$$

$$q = 1 - T_r \tag{7a}$$

Magoulas and Tassios:
$$\ln\left(T_P^\infty - T\right) = t_1 + t_2 N^{2/3} \tag{8}$$

The V^l – T data are the result of the Daubert and Danner correlation formula, [13]:

$$V^l = \frac{b_2^x}{b_1} \tag{9}$$

$$x = 1 + \left(1 - \frac{T}{b_3}\right)^{b_4} \tag{9a}$$

All the parameters involved in eq. (7) and (9) are substance dependent and the parameters in eq. (8) depend on the saturation pressure. This paper uses the values recommended by the mentioned authors, obtained after regression calculations on the literature data.

Results and Discussions

Table 1 presents the result of the optimisation calculation of the parameters C_1, C_2, C_3 along with the absolute average deviation (AADP, AADV) and the maximum average deviation (MADP, MADV) in estimating the vapour pressure and the saturated liquid volume for the n-alkanes up to eicosane. The values in the table correspond to a pressure domain from 0,1 torr to the critical point.

Table 1. Optimised GEOS3C parameters

N_c	C_1	C_2	C_3	AADP [%]	MADP [%]	AADV [%]	MADV [%]
1	0.1205	0.2193	0.1047	0.33	0.80	3.82	11.52
2	0.2408	0.3122	-0.0715	0.41	0.85	3.98	13.52
3	0.2597	0.4321	-0.1524	0.77	3.91	4.02	8.22
4	0.2454	0.4714	0.4147	0.81	5.22	5.62	15.07
5	0.2638	0.6136	0.1837	0.72	5.57	6.13	16.34
6	0.3246	0.7290	-0.4254	0.44	1.83	4.93	12.36
7	0.3069	0.9648	-0.7954	0.67	2.08	6.85	17.23
8	0.3527	1.1220	-1.7614	1.32	8.08	6.89	18.17
9	0.4258	0.9294	-0.6356	0.31	1.01	5.25	9.86
10	0.4091	1.1229	-0.9133	0.52	0.68	5.99	10.87
11	0.4380	1.1812	-0.9671	1.77	6.03	6.08	11.12

Table 1. (*continued*)

N_c	C_1	C_2	C_3	AADP [%]	MADP [%]	AADV [%]	MADV [%]
12	0.4506	1.2855	-1.1211	0.65	1.45	6.42	11.48
13	0.4244	1.4711	-1.3578	0.90	1.51	7.76	12.03
14	0.4458	1.5446	-1.4720	0.96	2.23	6.53	11.72
15	0.4233	1.7171	-1.7014	1.21	2.82	8.56	15.33
16	0.4134	1.8718	-1.9371	0.45	3.41	8.94	15.96
17	0.4822	1.7990	-1.8327	1.41	3.23	8.26	15.02
18	0.5103	1.8584	-1.9384	1.49	3.79	6.96	12.43
19	0.4876	1.9930	-2.0781	1.56	4.12	8.90	16.25
20	0.4814	2.1638	-2.3236	1.75	5.78	9.23	17.01
	Average			0.92	3.22	6.56	13.57

Some observations are common for the calculation of the PVT sets for the n-alkanes up to eicosane using GEOS3C: the highest deviations in vapour pressure estimation is registered at low temperatures, near the triple point, while the liquid volume estimation is less accurately predicted near the critical point. In both cases, an increase in the number of carbon atoms has as result an increase of the deviation.

Literature usually mentions two equation of state: Peng Robinson, [14] and Soave, [15] in the successful description of the vapour-liquid equilibrium in n-alkanes systems. The results obtained using GEOS3C are comparable in vapour pressure estimation with those obtained using these two equations and are of better quality regarding the liquid volume calculation. For example the molar saturated liquid volume of eicosane can be calculated using the Peng Robinson equation with an average absolute deviation of 18.23% and a maximum average deviation of 42.3%.

The next step is to identify the best correlation function for predicting the parameters C_1, C_2, C_3. The literature mentions both, for the Peng Robinson and for the Soave equation of state, a polynomial dependence of the parameters on the accentric factor [16÷18]. Therefore polynomials of different degrees were tested:

$$C_i = k_1 \omega^3 + k_2 \omega^2 + k_3 \omega + k_4; \ i = 1,2,3 \qquad (10)$$

In Table 2 there are presented the values $k_1 ÷ k_4$ obtained for different regression functions.

Table 2. Coefficients of the regression functions used in the prediction of the GEOS3C parameters

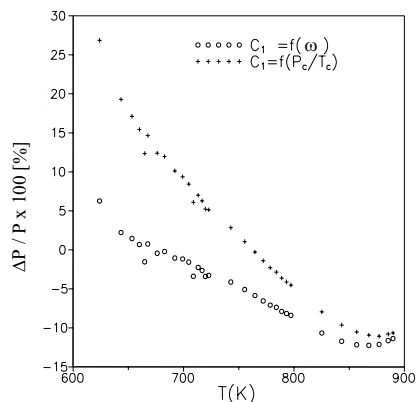| Parameter	k_1	k_2	k_3	k_4	Symbol of the dependence
	0.150108	-0.67047	0.877296	0.118333	C_1 (3)
C_1	0	-0.37223	0.722477	0.135053	C_1 (2)
	0	0	0.375285	0.191031	C_1 (1)
C_2	0	0.472185	1.80744	0.157308	C_2 (2)
	0	0	2.24784	0.086288	C_2 (1)
C_3	0	-0.696284	-2.29357	0.301397	C_3 (2)
	0	0	-2.94296	0.40603	C_3 (1)

Fig. 1: *Deviation in vapour pressure prediction of hexacontane.* $C_{60}H_{122}$ *using* GEOS3C.
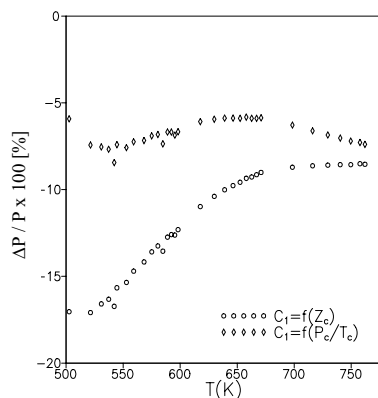

Fig. 2: *Deviation in vapour pressure prediction of pentatriacontane.* $C_{35}H_{72}$ *using* GEOS3C.

Combinations of the correlation functions were used to predict VLE data for n-alkanes up to hexacontane. The use of a single type of dependence for all the parameters (linear, quadratic) leads to poor results. Better results are obtained when C_1 is considered as a polynomial of third degree because the calculations are more sensitive to this parameter.

Table 3. Correlation calculations using GEOS3C and predicted C_1, C_2, C_3 parameters

N_C	AADP [%]					
	$C_1(1). C_2(1). C_3(1)$	$C_1(2). C_2(2). C_3(2)$	$C_1(2). C_2(1). C_3(1)$	$C_1(2). C_2(2). C_3(1)$	$C_1(3). C_2(1). C_3(2)$	$C_1(P_c/T_c) C_2(1). C_3(2)$
1	2.42	1.21	0.61	1.68	2.40	3.70
2	2.67	1.45	1.37	3.25	1.41	7.92
3	2.25	1.03	1.29	2.23	0.98	4.56
4	1.29	1.24	1.17	1.30	1.39	5.65
5	0.42	0.65	1.03	0.36	2.03	5.53
6	0.77	0.23	0.84	0.68	2.13	4.49
7	0.92	0.27	1.15	0.75	2.60	3.60
8	2.18	0.98	0.51	1.89	1.85	0.91
9	1.69	0.44	0.97	1.33	2.42	1.35
10	1.67	0.57	1.18	1.27	2.36	0.90
11	1.77	0.71	1.13	1.30	1.76	1.90
12	1.84	0.86	1.11	1.46	1.74	2.74
13	1.39	1.11	1.40	1.08	1.78	3.83
14	1.61	1.24	1.36	1.38	1.53	5.37
15	1.48	1.50	1.55	1.44	1.57	6.33

Table 3. (*continued*)

N_C	$C_1(1).\ C_2(1).\ C_3(1)$	$C_1(2).\ C_2(2).\ C_3(2)$	$C_1(2).\ C_2(1).\ C_3(1)$	$C_1(2).\ C_2(2).\ C_3(1)$	$C_1(3).\ C_2(1).\ C_3(2)$	$C_1(P_c/T_c)\ C_2(1).\ C_3(2)$
16	1.92	1.92	1.90	1.94	1.89	7.76
17	2.35	2.27	2.19	2.36	2.30	8.48
18	2.88	2.71	2.63	2.95	3.23	9.84
19	2.56	2.51	3.20	2.74	4.66	11.41
20	2.92	2.91	4.33	3.16	6.34	13.31
23	30.81	26.35	22.64	28.00	19.61	11.71
24	31.40	26.12	18.29	29.13	18.45	10.75
26	33.29	37.68	20.63	28.88	17.42	10.49
28	35.10	15.48	18.29	29.13	15.69	9.66
32	37.88	29.91	14.28	28.45	11.70	7.89
35	39.81	23.13	9.29	31.58	8.44	6.55
36	40.30	22.21	7.10	26.67	7.47	6.22
40	42.22	17.88	4.66	23.43	3.30	4.34
44	43.93	12.06	18.66	18.91	4.22	3.26
60	--	29.31	156.9	18.39	5.31	8.57
Average	12.81	8.86	10.72	9.91	5.25	6.30

In Table 3 there are presented the results of estimating the vapour pressure using GEOS3C and different combinations of regression functions for predicting the C_1, C_2, C_3 parameters.

Considering as variable the accentric factor, the best prediction results correspond to a cubic equation for C_1, a linear dependence for C_2 and a quadratic dependence for C_3.

Other regression variables for the parameter C_1 lead to no significant improvement in tests that consider the critical compression factor (Z_c) and the number of carbon atoms (N_c and $N_c^{2/3}$).

Using the ratio P_c / T_c as regression variable the results were of quite good quality as the last column in Table 3 shows. Data plotted in Fig. 1 and Fig. 2 also underline the superiority of the new correlation proposed.

$$C_1 = -1.32672 \frac{P_c}{T_c} + 0.427528 \tag{11}$$

Conclusions

A set of correlation functions is presented for the parameters C_1, C_2 and C_3 used in the new parameterization of the general equation of state, GEOS3C. These functions are valid for pure n-alkane systems up to hexacontane.

Vapor pressure and molar liquid volume are well predicted using the accentric factor as variable, in a cubic dependence for C_1, a linear dependence for C_2 and a quadratic

dependence for C_3. By using the same functions for C_2 and C_3 quality results may be obtained using C_1 values predicted by a linear dependence on P_c / T_c.

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