

NOTE

Acentric factor estimation from the corresponding states principle

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Abstract: Acentric factor estimation from the corresponding states principle was conducted. The reported values, or analytical expressions, of the functions $f^{(0)}$, $f^{(1)}$ and $f^{(2)}$ are presented. The tabulated values of $f^{(0)}$, $f^{(1)}$ and $f^{(2)}$ by the Brandani relation of the Wagner type of vapor pressure equation are correlated. The estimation procedures are tested on 44 nonpolar substances. The Ambrose and Walton expressions have the best predictive characteristics.

Keywords: acentric factor, corresponding states principle, vapor pressure.

INTRODUCTION

Using the three-parameter corresponding states principle, the vapor pressure of a pure nonpolar substance is given by the following relation:¹

$$\ln(p_r^s) = f^{(0)}(T_r) + \omega f^{(1)}(T_r) \quad (1)$$

or including a quadratic term ω^2 :²

$$\ln(p_r^s) = f^{(0)}(T_r) + \omega f^{(1)}(T_r) + \omega^2 f^{(2)}(T_r) \quad (2)$$

where $T_r = T/T_c$ is the reduced temperature and $p_r^s = p^s/p_c$ is the reduced vapor pressure.

Pitzer *et al.*¹ (PLCHP), Chao *et al.*³ (CGOH), Carruth and Kobayashi⁴ (CK), and His and Lu⁵ (HL) have reported their values of $f^{(0)}$ and $f^{(1)}$ (Table I). Lee and Kesler⁶ (LK) have reported their analytical expressions of $f^{(0)}$ and $f^{(1)}$ in the form of a Riedel type of vapor pressure equation

$$f^{(0)}(T_r) = 5.92714 - 6.09648 / T_r - 1.28862 \ln(T_r) + 0.169347 T_r^6 \quad (3)$$

$$f^{(1)}(T_r) = 15.2518 - 15.6875 / T_r - 13.472 \ln(T_r) + 0.43577 T_r^6 \quad (4)$$

Ambrose and Walton⁷ (AW) have reported their analytical expressions of $f^{(0)}$, $f^{(1)}$ and $f^{(2)}$ in the form of a Wagner type of vapor pressure equation

$$f^{(0)}(T_r) = [-5.97616(1 - T_r) + 1.29874(1 - T_r)^{1.5} - 0.60394(1 - T_r)^{2.5} - 1.06841(1 - T_r)^5] / T_r \quad (5)$$

$$f^{(1)}(T_r) = [-5.03365(1 - T_r) + 1.11505(1 - T_r)^{1.5} - 5.41217(1 - T_r)^{2.5} - 7.46628(1 - T_r)^5] / T_r \quad (6)$$

$$f^{(2)}(T_r) = [-0.64774(1 - T_r) + 2.41539(1 - T_r)^{1.5} - 4.26979(1 - T_r)^{2.5} + 3.25259(1 - T_r)^5] / T_r \quad (7)$$

Schreiber and Pitzer⁸ (SP) have reported their analytical expressions of $f^{(0)}$ and $f^{(1)}$ by (Eq. 1) with common (base 10), instead of natural (base e) logarithm

$$f^{(0)}(T_r) = 0.90387412 - 3.8754024 / T_r - 10.021469 \log(T_r) + 2.9715283 T_r \quad (8)$$

$$f^{(1)}(T_r) = 2.0095293 - 8.6616276 / T_r - 30.391841 \log(T_r) + 6.6520983 T_r \quad (9)$$

Brandani⁹ has reported two sets of analytical expressions in the form of a Wagner type of vapor pressure equation, as follows. One for the relation (Eq. 1) (BI)

$$f^{(0)}(T_r) = [-6.25914(1 - T_r) + 2.33303(1 - T_r)^{1.5} - 2.53374(1 - T_r)^{2.5} + 3.09743(1 - T_r)^5 - 8.34044(1 - T_r)^{10}] / T_r \quad (10)$$

$$f^{(1)}(T_r) = [-4.27201(1 - T_r) - 1.79968(1 - T_r)^{1.5} - 0.49821(1 - T_r)^{2.5} - 24.37590(1 - T_r)^5 + 31.32263(1 - T_r)^{10}] / T_r \quad (11)$$

and the other for relation (Eq. 2) (BII)

$$f^{(0)}(T_r) = [-6.25914(1 - T_r) + 2.33303(1 - T_r)^{1.5} - 2.53374(1 - T_r)^{2.5} + 3.09743(1 - T_r)^5 - 8.34044(1 - T_r)^{10}] / T_r \quad (12)$$

$$f^{(1)}(T_r) = [-5.65777(1 - T_r) + 1.91392(1 - T_r)^{1.5} - 3.75173(1 - T_r)^{2.5} - 18.16398(1 - T_r)^5 + 18.74981(1 - T_r)^{10}] / T_r \quad (13)$$

$$f^{(2)}(T_r) = [3.81370(1 - T_r) - 10.05038(1 - T_r)^{1.5} + 10.94146(1 - T_r)^{2.5} - 13.17857(1 - T_r)^5 + 0.18671(1 - T_r)^{10}] / T_r \quad (14)$$

Twu *et al.*¹⁰ (TCC) have reported their analytical expressions of $f^{(0)}$ and $f^{(1)}$ in the form of a Wagner type of vapor pressure equation

$$f^{(0)}(T_r) = [-5.96346(1 - T_r) + 1.17639(1 - T_r)^{1.5} - 0.559607(1 - T_r)^3 - 1.31901(1 - T_r)^6] / T_r \quad (15)$$

$$f^{(1)}(T_r) = [-4.78522(1 - T_r) + 0.413999(1 - T_r)^{1.5} - 8.91239(1 - T_r)^3 - 4.98662(1 - T_r)^6] / T_r \quad (16)$$

In order to avoid interpolation, the values of $f^{(0)}$ and $f^{(1)}$ from Table I were correlated by the Brandani type of Wagner relation for vapor pressure

$$f(T_r) = [A(1 - T_r) + B(1 - T_r)^{1.5} - C(1 - T_r)^{2.5} + D(1 - T_r)^5 - E(1 - T_r)^{10}] / T_r \quad (17)$$

TABLE I. Values of $f^{(0)}$ and $f^{(1)}$

T_r	$f^{(0)}$				$f^{(1)}$			
	PLCHP	CGOH	CK	HL	PLCHP	CGOH	CK	HL
0.250			-15.312				-36.611	
0.260			-14.690				-32.812	
0.270			-14.138				-30.164	
0.280			-13.608				-27.539	
0.290			-13.079				-25.144	
0.300			-12.549				-22.888	
0.310			-12.019				-20.677	
0.320			-11.524				-19.111	
0.330			-11.052				-17.615	
0.340			-10.592				-16.302	
0.350		-10.408	-10.154			-13.654	-15.289	
0.360			-9.717				-14.368	
0.370			-9.302				-13.539	
0.375		-9.279				-12.572		
0.380			-8.911				-12.802	
0.390			-8.520				-12.158	
0.400		-8.243	-8.151			-11.375	-11.536	
0.410			-7.794				-10.983	
0.420			-7.460				-10.454	
0.425		-7.391				-9.993		
0.430			-7.138				-9.947	
0.440			-6.839				-9.441	
0.450		-6.631	-6.562			-8.635	-8.980	
0.460			-6.286				-8.508	
0.470			-6.033				-8.174	
0.475		-5.964				-7.645		
0.480			-5.791				-7.622	
0.490			-5.556				-7.207	
0.500		-5.365	-5.330	-5.372		-6.701	-6.820	-6.507
0.510			-5.107				-6.475	
0.520			-4.905	-4.948			-6.125	-5.816
0.525		-4.858				-5.826		
0.530			-4.697				-5.761	

TABLE I. Continued

T_r	$f^{(0)}$				$f^{(1)}$			
	PLCHP	CGOH	CK	HL	PLCHP	CGOH	CK	HL
0.540			- 4.525	- 4.564			- 5.457	- 5.234
0.550		- 4.398	- 4.352			- 5.158	- 5.162	
0.560	- 4.223		- 4.186	- 4.198	- 4.789		- 4.881	- 4.746
0.570			- 4.023				- 4.651	
0.580	- 3.887		- 3.868	- 3.866	- 4.329		- 4.393	- 4.299
0.590			- 3.707				- 4.168	
0.600	- 3.574		- 3.555	- 3.553	- 3.914		- 3.937	- 3.887
0.610			- 3.419				- 3.749	
0.620	- 3.283		- 3.279	- 3.270	- 3.546		- 3.557	- 3.495
0.630			- 3.150				- 3.369	
0.640	- 3.012		- 3.012	- 3.009	- 3.201		- 3.201	- 3.092
0.650			- 2.878				- 3.039	
0.660	- 2.758		- 2.758	- 2.761	- 2.878		- 2.878	- 2.777
0.670			- 2.636				- 2.729	
0.680	- 2.524		- 2.524	- 2.531	- 2.579		- 2.579	- 2.482
0.690			- 2.411				- 2.441	
0.700	- 2.303		- 2.303	- 2.303	- 2.303		- 2.303	- 2.303
0.720	- 2.093			- 2.091	- 2.061			- 2.026
0.740	- 1.895			- 1.895	- 1.842			- 1.817
0.760	- 1.709			- 1.704	- 1.623			- 1.633
0.780	- 1.531			- 1.529	- 1.428			- 1.428
0.800	- 1.363			- 1.361	- 1.255			- 1.248
0.820	- 1.202				- 1.094			
0.840	- 1.048				- 0.933			
0.860	- 0.900				- 0.794			
0.880	- 0.760				- 0.656			
0.900	- 0.622				- 0.530			
0.920	- 0.488				- 0.414			
0.940	- 0.359				- 0.306			
0.950	- 0.297				- 0.251			
0.960	- 0.235				- 0.198			
0.970	- 0.175				- 0.147			
0.980	- 0.115				- 0.097			
0.990	- 0.058				- 0.048			
1.000	0.000				0.000			

Standard deviation and percent average errors were calculated as follows:

$$\sigma = \left\{ \left[\sum_{i=1}^n (\omega_{\text{exp},i} - \omega_{\text{cal},i})^2 \right] / (n - m) \right\}^{0.5} \quad (18)$$

$$p_{\text{av}} = (100/n) \sum_{i=1}^n |(\omega_{\text{exp},i} - \omega_{\text{cal},i}) / \omega_{\text{exp},i}| \quad (19)$$

The obtained parameters are presented in Table II.

The acentric factor ω can be determined from the normal boiling point from relation (Eq. 1) as follows:

$$\omega = \{-\ln(p_c / 1.01325) - f^{(0)}(T_{\text{br}})\} / f^{(1)}(T_{\text{br}}) \quad (20)$$

or from relation (Eq. 2):

$$\omega = [-f^{(1)}(T_{\text{br}}) - \sqrt{d}] / [2f^{(2)}(T_{\text{br}})] \quad (21)$$

$$d = [f^{(1)}(T_{\text{br}})]^2 - 4f^{(2)}(T_{\text{br}})\{f^{(0)}(T_{\text{br}}) + \ln(p_c[\text{atm}])\} \quad (22)$$

where $T_{\text{br}} = T_b/T_c$ is the reduced normal boiling point.

RESULTS AND DISCUSSION

All expression were tested on the selected substances from Table III. The values in this table are from Poling *et al.*¹¹ The results are presented in Table IV.

TABLE III. Experimental data reported in the literature¹¹

i	Substances	T_b/K	T_c/K	T_{br}	p_c	ω
n-Alkanes						
1	Methane	111.66	190.56	0.59	45.99	0.011
2	Ethane	184.55	305.32	0.60	48.72	0.099
3	Propane	231.02	369.83	0.62	42.48	0.152
4	Butane	272.66	425.12	0.64	37.96	0.200
5	Pentane	309.22	469.70	0.66	33.70	0.252
6	Hexane	341.88	507.60	0.67	30.25	0.300
7	Heptane	371.57	540.20	0.69	27.40	0.350
8	Octane	398.82	568.70	0.70	24.90	0.399
9	Nonane	423.97	594.60	0.71	22.90	0.445
10	Decane	447.30	617.70	0.72	21.10	0.490
11	Undecane	469.08	639.00	0.73	19.80	0.537
12	Dodecane	489.48	658.00	0.74	18.20	0.576
13	Tridecane	508.63	675.00	0.75	16.80	0.618
14	Tetradecane	526.76	693.00	0.76	15.70	0.644
15	Pentadecane	543.83	708.00	0.77	14.80	0.685
16	Hexadecane	559.98	723.00	0.77	14.00	0.718
17	Heptadecane	574.56	736.00	0.78	13.40	0.753

TABLE III. Continued

i	Substances	T_b/K	T_c/K	T_{br}	p_c	ω
<i>n-Alkanes</i>						
18	Octadecane	588.30	747.00	0.79	12.90	0.800
19	Nonadecane	602.34	755.00	0.80	11.60	0.845
20	Eicosane	616.84	768.00	0.80	10.70	0.865
<i>i-Alkanes</i>						
21	2,2-Dimethylbutane	322.87	488.70	0.66	30.80	0.233
22	2,3-Dimethylbutane	331.12	499.90	0.66	31.30	0.248
23	2,2,3-Trimethylbutane	354.01	531.10	0.67	29.50	0.250
24	2,2,3,3-Tetramethylbutane	379.44	567.80	0.67	28.70	0.248
25	2-Methylpentane	333.40	497.50	0.67	30.10	0.278
26	3-Ethylhexane	391.69	565.40	0.69	26.10	0.362
27	4-Methylheptane	390.86	561.70	0.70	25.40	0.371
28	3,3,5-Trimethylheptane	428.83	609.60	0.70	23.20	0.383
<i>Cycloalkanes</i>						
29	Cyclopropane	240.34	398.25	0.60	55.75	0.130
30	Cyclobutane	285.64	460.00	0.62	49.90	0.185
31	Cyclohexane	353.93	553.50	0.64	40.73	0.211
32	Cyclooctane	424.31	647.20	0.66	35.70	0.254
<i>Alkylcycloalkanes</i>						
33	Ethylcyclopentane	376.59	569.50	0.66	33.97	0.270
34	Methylcyclohexane	374.09	572.19	0.65	34.71	0.235
<i>Alkenes</i>						
35	Propene	225.46	364.90	0.62	46.00	0.142
36	1-Butene	266.92	419.50	0.64	40.20	0.194
37	1-Hexene	336.63	504.00	0.67	31.43	0.281
38	1-Octene	394.44	567.00	0.70	26.80	0.393
<i>Alkynes</i>						
39	Ethyne	188.40	308.30	0.61	61.14	0.189
<i>Aromatics</i>						
40	Benzene	353.24	562.05	0.63	48.95	0.210
41	Toluene	383.79	591.75	0.65	41.08	0.264
42	1,4-Dimethylbenzene	411.53	616.20	0.67	35.11	0.322
43	Naphthalene	491.16	748.40	0.66	40.50	0.304
44	Anthracene	614.39	869.30	0.71	28.70	0.501

From the values for T_{br} from Table III it follows that the Chao *et al.*³ expressions (Table II) are not applicable to any of the substances from this Table, while the Carruth

and Kobayashi⁴ expressions (Table II) are not applicable to some of the substances. From the results presented in Table IV, it can be concluded that the Ambrose and Walton⁷ expressions (Eqs. 5–7) have the best predictive characteristics.

TABLE IV. Comparison of the predicted and literature values of ω

Expressions	$p_{av}/\%$	Expressions	$p_{av}/\%$	Expressions	$p_{av}/\%$
PLCHP	1.96	LK	1.59	BI	1.14
CGOH	–	AW	0.42	BII	0.80
CK	1.41	SP	1.39	TCC	0.88
HL	2.02				

NOTATION

n	Number of data points
m	Number of parameters
T	Temperature, K
p	Pressure, bar
p_s	Vapor pressure, bar
p_{av}	Percentage average error, %
p_{max}	Maximum percent error, %

Greek letters

ω	Acentric factor
σ	Standard deviation

Subscripts

b	Boiling property
c	Critical property
r	Reduced property
exp	Experimental value
cal	Calculated value

ИЗВОД

ОДРЕЂИВАЊЕ ФАКТОРА АЦЕНТРИЧНОСТИ НА БАЗИ ПРИНЦИПА КОРЕСПОНДЕНТНИХ СТАЊА

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У овом раду размотрене су могућности предсказивања вредности фактора ацентричности на бази принципа кореспондентних стања. Приказане су предложене функције, $f^{(0)}$, $f^{(1)}$ и $f^{(2)}$, како у дискретној, тако и аналитичкој форми. Дискретне вредности су корелисањем преведене у аналитичке изразе. Предсказивање вредности фактора ацентричности тестирано је на 44 неполарне супстанце. Најбоље предиктивне особине показао је модел који су предложили Ambrose и Walton.

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