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A New Acentric Factor Correlation for Pure Hydrocarbons

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In this study, a vapour pressure equation is proposed to correlate saturated vapour pressure of pure compounds with higher accuracy. The acentric factor of 57 pure hydrocarbons is estimated based on this proposed equation for pure hydrocarbons. The results show that proposed equation is better than modified Wagner equation for estimating the acentric factor of pure hydrocarbons.

Key Words: Critical properties, Hydrocarbon, Vapour pressure, Acentric factor, Correlation.

INTRODUCTION

The acentric factor values are essential in estimating transport and thermodynamic properties for liquids and gases such as enthalpy of vapourization[1], saturated density or molar volume of liquids[2,3], compressibility factor[4-7], heat capacity of real gas[7], vapour pressure of pure liquid[7] and saturated liquid viscosity[8,9]. The acentric factor represents the acentricity or non- sphericity of a molecule.

In this work, a vapour pressure equation is suggested to correlate saturated vapour pressure of pure compounds and then the acentric factor is estimated according to the proposed equation for pure hydrocarbons and compared with modified Wagner. The average absolute error of proposed equation is 0.0507 while for modified Wagner's equation is 0.0847. The results show that the equation has good accuracy for estimating the acentric factor of pure hydrocarbon.

Proposed equation

The new saturated vapour pressure equation is proposed as follow:

$$\ln P_r^s = [(a + bt + ct^5 + d\exp(e(1-t)))\log(t)]/t \quad (1)$$

$$t = \frac{T}{T_c} \quad (2)$$

$$Pr^s = \frac{P}{P_c} \quad (3)$$

In this equation, P_c is the critical pressure, T_c is the critical temperature and a, b, c, d, e are constants.

According to the corresponding state principle, the saturated vapour pressure equation is defined as:

$$\ln P_r^s = f^{(0)}(t) + \omega f^{(1)}(t) \quad (4)$$

In the above equation, $f^{(0)}$ (t) and $f^{(1)}$ (t) are presented as below, based on the new equation:

$$f^{(0)} = \left[(a_1 + b_1 t + c_1 t^5 + d_1 \exp(e_1(1-t))\log(t)\right]/t \quad (5)$$

$$f^{(1)} = \left[(a_2 + b_2 t + c_2 t^5 + d_2 \exp(e_2(1-t))\log(t)\right]/t \quad (6)$$

The constants in eqns. 5 and 6 are calculated by minimization of the objective function:

$$ADD = \sum_i^N \left| \frac{P^{exp} - P^{model}}{P^{exp}} \right| \quad (7)$$

where p^{exp} is the experimental pressure, p^{model} is calculated by eqns. 4-6 and N is the number of the experimental data point.

The experimental saturated vapour pressure data for 30 hydrocarbons are obtained by Perry and Green[10]. The constant parameters (a, b, c, d and e) of eqns. 5 and 6 are shown in Table-1. These constant parameters are calculated by regression between experimental data and calculated data.

TABLE-1
CONSTANT PARAMETERS OF EQNS. 5 AND 6

Constant	a_i	b_i	c_i	d_i	e_i
i=1	-0.0389	4.3098	1.2712	1.0045	1.0650
i=2	2.4240	1.4458	-2.7831	1.1696	0.8115

The acentric factor (ω) of a pure substance is determined by using the Pitzer equation:

$$\omega = (-\log(P^s / P_c))_{(T/Tc)=0.7} - 1 \quad (8)$$

TABLE-2
PROPERTIES OF COMPOUNDS AND THE RESULTS OF THE PROPOSED MODEL, MODIFIED WAGNER'S MODEL FOR ESTIMATING ACENTRIC FACTOR

Properties of compounds						Modified Wagner		Proposed model	
Formula	m.w.	T_b (K)	T_c (K)	P_c (bar)	ω	ω_{cal}	AAD	ω_{cal}	AAD
CF_4	88.005	145.11	227.51	37.45	0.177	0.1769	0.0005	0.1728	0.0239
$CClF_3$	104.459	191.71	301.84	38.73	0.175	0.1737	0.0072	0.1700	0.0284
CCl_2F_2	120.913	243.45	385.10	41.30	0.179	0.1782	0.0044	0.1750	0.0223
CCl_3F	137.368	296.81	471.10	44.72	0.195	0.1910	0.0208	0.1882	0.0349
$CHClF_2$	86.468	232.14	369.28	49.86	0.221	0.2155	0.0251	0.2131	0.0357
$CHCl_2F$	102.923	281.97	451.52	51.87	0.207	0.2058	0.0058	0.2040	0.0144
CH_2O_2	46.026	374.04	588.00	58.07	0.316	0.3011	0.0473	0.2979	0.0572
CH_3F	34.033	194.88	315.00	55.48	0.204	0.1957	0.0409	0.1946	0.0461
CH_4O	32.042	337.69	512.64	80.97	0.565	0.5585	0.0115	0.5489	0.0285
CO	28.010	81.66	132.85	34.94	0.045	0.0528	0.1744	0.0505	0.1231
$C_2Cl_2F_4$	170.921	276.59	418.70	32.13	0.244	0.2492	0.0213	0.2401	0.0158
$C_2Cl_3F_3$	187.375	320.74	487.40	33.78	0.249	0.2520	0.0122	0.2436	0.0215
C_2H_2	26.038	188.40	308.30	61.14	0.189	0.1861	0.0154	0.1858	0.0168
$C_2H_4F_2$	66.051	249.10	386.41	45.16	0.276	0.2716	0.0158	0.2665	0.0344
$C_2H_4O_2$	60.053	391.04	594.45	57.90	0.445	0.4361	0.0199	0.4272	0.0399
C_2H_5F	48.060	235.43	375.28	50.27	0.217	0.2113	0.0264	0.2091	0.0364
C_2H_6	30.070	184.55	305.32	48.70	0.099	0.0969	0.0215	0.0960	0.0299
C_2H_6O	46.069	351.80	513.92	61.48	0.649	0.6688	0.0982	0.6452	0.0594
C_2H_7N	45.084	289.75	456.40	56.30	0.276	0.2846	0.0312	0.2816	0.0204
C_3H_4	40.065	238.77	394.00	52.50	0.122	0.1226	0.0053	0.1221	0.0004
$C_3H_6Cl_2$	112.187	369.43	578.00	46.50	0.255	0.2502	0.0187	0.2462	0.0345
C_3H_6O	58.080	329.22	508.10	47.00	0.307	0.3035	0.0115	0.2976	0.0306
$C_3H_6O_3$	90.084	363.24	557.00	48.00	0.33	0.3357	0.0010	0.3287	0.0217
C_3H_8	44.097	231.02	369.83	42.48	0.152	0.1502	0.0120	0.1478	0.0274
$C_4H_6O_3$	102.090	412.69	606.00	40.00	0.456	0.9537	1.0916	0.8811	0.9323
C_4H_8O	72.107	352.71	536.80	42.10	0.322	0.3217	0.0008	0.3134	0.0296
$C_4H_{10}S$	90.189	365.25	557.00	39.60	0.295	0.2929	0.0072	0.2850	0.0339
C_5H_5N	79.101	388.37	620.00	56.70	0.242	0.2409	0.0046	0.2391	0.0118
C_5H_8O	84.118	403.72	624.50	46.00	0.288	0.2879	0.0003	0.2824	0.0194
C_6H_5Cl	112.558	404.91	632.40	45.20	0.251	0.2476	0.0136	0.2433	0.0306
C_6H_6	78.114	353.24	562.05	48.95	0.21	0.2094	0.0029	0.2070	0.0142
C_6H_6O	94.113	455.04	694.25	61.30	0.442	0.4393	0.0061	0.4312	0.0244
$C_6H_{10}O$	98.144	428.59	653.00	40.00	0.299	0.2999	0.0029	0.2918	0.0241
C_7H_8	92.141	383.79	591.75	41.08	0.264	0.2643	0.0024	0.2573	0.0254
C_8H_8O	120.153	475.26	713.00	40.30	0.361	0.3670	0.0166	0.3554	0.0154
$C_8H_{16}O_2$	112.215	512.01	695.00	26.40	0.734	0.7904	0.0769	0.7196	0.0196
$C_8H_{19}N$	129.246	451.70	641.00	26.17	0.446	0.4699	0.0536	0.4390	0.0158
$C_9H_{20}O$	144.257	486.52	668.90	26.30	0.633	0.6838	0.0802	0.6278	0.0082
$C_{10}H_{20}O_2$	172.268	541.92	726.00	22.30	0.749	0.8049	0.0746	0.7223	0.0356
$C_{10}H_{22}O$	158.284	504.25	684.40	23.70	0.661	0.7276	0.1008	0.6603	0.0010
$C_{11}H_{24}$	156.312	469.08	639.00	19.80	0.537	0.5937	0.1056	0.5364	0.0012
$C_{11}H_{24}O$	172.311	521.24	705.00	22.40	0.656	0.7232	0.1024	0.6535	0.0038
$C_{12}H_{26}$	170.338	489.48	658.00	18.20	0.579	0.6470	0.1175	0.5774	0.0028
$C_{12}H_{26}O$	186.338	537.79	720.00	20.80	0.684	0.7665	0.1206	0.6859	0.0027
$C_{13}H_{12}$	168.238	537.65	760.00	27.10	0.481	0.5095	0.5095	0.4756	0.0112
$C_{13}H_{28}$	184.365	508.63	675.00	16.80	0.618	0.7061	0.7061	0.6221	0.0067
$C_{14}H_{22}$	190.330	510.43	708.00	23.00	0.506	0.5483	0.5483	0.5037	0.0045
$C_{14}H_{30}$	198.392	526.76	693.00	15.70	0.644	0.7406	0.7406	0.6461	0.0033
$C_{15}H_{32}$	212.419	543.83	708.00	14.80	0.685	0.8028	0.8028	0.6926	0.0110
$C_{16}H_{34}O$	242.446	597.53	770.00	16.10	0.818	0.9857	0.9857	0.8462	0.0345
$C_{17}H_{36}$	240.473	574.56	736.00	13.40	0.753	0.9062	0.9062	0.7668	0.0184
$C_{18}H_{38}$	254.500	588.30	747.00	12.90	0.800	0.9849	0.9849	0.8248	0.0233
$C_{19}H_{40}$	268.527	602.34	755.00	11.60	0.845	1.0666	1.0666	0.8761	0.0368
Br_2	159.808	331.90	584.10	103.00	0.119	0.1185	0.1185	0.1202	0.0098
HI	127.912	237.57	423.90	90.00	0.038	0.0606	0.5943	0.0614	0.6150
H_2O	18.015	373.15	647.14	220.64	0.344	0.3194	0.0715	0.3243	0.0572
NO	30.006	121.38	180.00	64.80	0.582	0.6016	0.0337	0.5846	0.0044
Average						0.0847		0.0507	

The saturated vapour pressure at T/Tc = 0.7 is required for estimating the acentric factor.

The acentric factor is calculated by using the values at the normal boiling point:

$$\text{at} \quad T = T_b \qquad \Rightarrow P = 1.01325\,\text{bar} \tag{9}$$

Thus, eqn. 4 is changed to:

$$\omega = -(\ln(P_c / 1.01325) + f^{(0)}(v)) / f^{(1)}(v) \tag{10}$$

where

$$f^{(0)}(v) = \frac{[-0.0389 + 4.3098v + 1.2712v^5 + 1.0045\exp(1.065(1-v))]\log(v)}{v} \tag{11}$$

$$f^{(1)}(v) = \frac{[2.424 + 1.4458v - 2.7831v^5 + 1.1696\exp(0.8115(1-v))]\log(v)}{v} \tag{12}$$

$$v = \frac{T_b}{T_c} \tag{13}$$

where T_b is boiling temperature.

RESULTS AND DISCUSSION

Acentric factor is estimated for 57 pure hydrocarbons by eqn. 10. The normal boiling temperature (T_b for P_b = 1.01325 bar), the critical properties, acentric factor and the average absolute deviations of new model and modified Wagner model[11] are presented in Table-2.

The modified Wagner equation has the following form:

$$\ln P_r^s = (-5.462t + 0.0666t^{1.5} + 0.9311t^3 - 5.8487t^6) / (1-t) + \omega(1.9892t - 13.4124t^{1.5} + 1.9574t^3 + 9.2168t^6) / (1-t) \tag{14}$$
$$t = 1 - T / T_c$$

According to Table-2, the average absolute deviation of new model for 57 pure hydrocarbons is 0.0507 and for modified Wagner model (eq. 14) is 0.0847. This result shows that the new model has a better accuracy than modified Wagner model.

Conclusion

The saturated vapour pressure is calculated for 30 hydrocarbons according to the proposed equation. In addition, acentric factor (ω) is calculated for 57 pure hydrocarbon based on the corresponding state principle. Based on the average absolute deviation values, the proposed equation has good accuracy for estimating acentric factor.

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