PREDICTION OF SATURATED LIQUID DENSITIES OF HYDROCARBONS

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[Received: April 4, 1968]
[Revised manuscript received on September, 19, 1968]

ABSTRACT

A generalised method is developed for the prediction of the saturated liquid densities for hydrocarbons with the help of a reference substance. Using molecular weight or the normal boiling point of the substance and the saturated liquid densities at different reduced temperatures of the reference substance (Argon), saturated liquid densities of different hydrocarbons can be predicted within an average error of 2.0%

Corresponding state methods had been the basis for many correlations on saturated liquid density. The most successful among them is the Lyderson – Greenkorn – Hougen method[1] which uses many input data *viz.*, T_c, P_c and Z_c and above all it requires one experimental value of liquid density The other equally successful methods to correlate saturated liquid densities are due to Benson, Goldhammer and Mathias. Details of these methods are available in Reid and Sherwood[2]. These methods also require the knowledge of one experimental density value in addition to other critical properties. However, all these methods have wide application and predict the saturated liquid densities within an average error of 2.0% For hydrocarbons of high molecular weights, Bondi and Simkin[3] have proposed a correlation which does not require the knowledge of critical constants, but one must know other reduced properties and the molecular structure

Earlier to these successful correlations Antoine[4], Schmidt[5] and Dreisbach and Spencer[6] had suggested some estimation techniques to correlate saturated liquid densities. However these are not as useful as the methods based on corresponding state methods.

A method which does not require the knowledge of one experimental data of liquid density and which uses less number of input data which should be available easily without any uncertainty, is desirable. Using a reference substance plot and either molecular weight or the normal boiling point as a [illegible] parameter this has been achieved for predicting the saturated liquid densities of hydrocarbons. Earlier, this technique has been found useful to predict entropy of [illegible] of hydrocarbons[7] and inorganic gases[8].

Since Argon is nonpolar, non-reactive and devoid of any quantum mechanical effect, it was selected as the reference substance for all these correlations.

Saturated liquid densities of various hydrocarbons (d_{sl}) and of Argon $(d_{Al}$[9] from the literature[10-29] (various literature data have been collected and final recommendations have been made in these references. For methane[10], ethane[10] and propane[11] the basic data have been obtained from the works of Kuloor, Newitt, and Bateman[11], Tester[10] and Din[9] since there is not any difference in the data given by other workers[12, 13, 14]) were plotted against temperatures from which the smoothed values of d_{Sl} and d_{Al} at the required reduced temperatures were obtained. The statiscally estimated smoothened values were obtained from the work of Das and Kuloor[15, 18, 19-29]. The reduced temperatures for these liquids generally vary between 0.6 and 1.0. When these values of saturated liquid densities of Argon were plotted against the saturated liquid densities of one hydrocarbon at various reduced temperatures, in ordinary co-ordinates, a good linear relationship was observed. Similar good linear relationships were observed for all the twenty hydrocarbons considered in this work. The slopes and intercepts of these straight lines were obtained from these plots.

To arrive at a generalised equation to predict d_{sl} for all hydrocarbons and for all temperature ranges, attempts were made to correlate these slopes and intercepts with some easily accessible physical parameters of these substances. Following the successful correlations[7, 8] obtained for the case of entropy of vaporisation of hydrocarbons and inorganic gases, attempts were made to correlate these slopes and intercepts with molecular weights or the normal boiling points. On lagarithmic co-ordinates the slopes were well correlated with either one of these two parameters, namely the molecular weight or the normal boiling point. It was also observed that separate equations were required for saturated and unsaturated hydrocarbons. However, the intercepts failed to show any pattern of relationship with either molecular weight or the normal boiling point. The relations thus obtained do not correlate the saturated density data and hence a correction factor in the intercepts has to be added.

Introducing this correction factor which is also a function of molecular weight or normal boiling point as the case may be, the following equations were obtained to predict the saturated liquid densities of hydrocarbons.

I. Saturated Hydrocarbons :

$$[1.378 \times 10^3/T_b{}^{1.5055}]\, d_{Al} - 1.3158 \times 10^{-3}\, T_b + 0.4726 \qquad [1]$$

$$[20.95/M^{1.0111}]\, d_{Al} - 1.079 \times 10^4/M^{2.303} \qquad [2]$$

II. Unsaturated Hydrocarbons :

$$[1.378 \times 10^3/T_b{}^{1.5055}]\, d_{Al} - 0.4716 \times 10^{-2}\, T_b + 1.8846 \qquad [3]$$

$$[20.95/M^{1.0111}]\, d_{Al} - 2.871 \times 10^4/M^{2.641} \qquad [4]$$

Equations 1 and 2 were tested for 13 saturated hydrocarbons and equations 3 and 4 were tested for 7 unsaturated hydrocarbons (Table 2). Except methane all other hydrocarbons obeyed these equations well as can be seen from the results in Table 2. Being the first member of the family, the anamolus behaviour of methane can be expected for this type of correlation.

Except methane, the molecular weight predicts [Equations 2 and 4] the saturated liquid densities of hydrocarbons within 1.90% and unsaturated hydrocarbons within 1.72% over-all average. The normal boiling point, on the otherhand, predicts saturated liquid densities within 2.65% and the unsaturated liquid densities within 3.46%. Among these two parameters molecular weight seems to be the better parameter to predict the saturated liquid densities of hydrocarbons.

These averages are comparable to the existing correlations but using equations 1 and 2 or 3 and 4 one need to know only molecular weight or the normal boiling point in addition to the liquid densities of Argon. Table 1 groups the physical properties of the systems used in this work.

TABLE 1

Properties of the compounds and % Error

Compounds	Molecular weight (M)	%Error	Normal boiling point °K (T_b)	%Error	Slope (m)
Methane	16.04	19.71	111.76	49.97	1.3048
Ethane	30.07	5.13	184.56	1.62	2.0833
Propane	44.09	2.91	230.96	0.96	2.6396
n-butane	58.12	2.10	272.66	2.73	3.3636
iso butane	58.12	2.56	261.44	5.05	3.3749
n-pentane	72.15	1.62	309.23	2.99	......
iso-pentane	72.15	1.72	301.01	1.09	4.1493
neo-pentane	72.15	1.62	282.66	9.65	——
n-hexane	86.17	1.47	341.90	2.56	——
n-heptane	100.20	1.21	371.59	1.90	......
n-octane	114.22	0.77	398.83	1.31	5.9347
n-nonane	128.25	0.71	423.96	0.75	6.6006
n-decane	142.28	0.98	447.28	1.16	7.8003
Propylene	42.08	1.79	225.46	1.06	2.3843
1, 3-butadiene	54.09	3.83	268.75	8.50	——
1-butene	56.10	1.90	266.91	1.21	3.1665
cis-2-butene	56.10	0.88	276.88	6.88	2.8003
Trans-2-butene	56.10	1.40	274.04	4.69	......
[illegible]	56.10	1.23	266.16	1.13	3.0525
1-pentene	70.13	0.99	303.23	0.76	3.8669
Over-all average		1.81		3.05	

TABLE 2

Calculated and Experimental values of liquid densities for various Hydrocarbons

Hydrocarbons (Saturated)	T_r	d_{At} (Ref. 9)	d_{st} Lit.	d_{st} Calc. Eq. 1	°/₀ Div.	d_{st} Calc. Eq. 2	°/₀ Div.
Methane	0.96	21.15	16.56	24.37	47.16	8.70	47.46
(Ref. 10 & 13)	0.94	22.44	17.63	25.84	46.57	10.33	41.41
	0.92	23.85	18.46	27.44	48.65	12.12	34.34
	0.88	26.10	19.86	30.00	51.06	14.97	24.62
	0.84	27.84	21.05	31.98	51.92	17.17	18.43
	0.80	29.20	22.12	33.52	51.54	18.90	14.56
	0.76	30.38	23.12	34.87	50.82	20.39	11.81
	0.72	31.43	23.95	36.06	50.56	21.72	9.31
	0.68	32.42	24.74	37.19	50.32	22.98	7.11
	0.64	33.37	25.45	38.27	50.37	24.18	4.99
	0.60	34.36	26.14	39.39	50.69	25.43	2.72
				Average	49.47		19.71
Ethane	0.96	21.15	11.76	11.53	1.96	9.93	15.56
(Ref. 10 & 14)	0.94	22.44	12.50	12.22	2.24	10.80	13.60
	0.92	23.85	13.07	12.97	0.77	11.74	10.18
	0.88	26.10	14.03	14.17	1.00	13.25	5.56
	0.84	27.84	14.85	15.10	1.68	14.42	2.90
	0.80	29.20	15.54	15.83	1.87	15.33	1.35
	0.76	30.38	16.20	16.46	1.60	16.13	0.43
	0.72	31.43	16.76	17.02	1.55	16.83	0.42
	0.68	32.42	17.27	17.55	1.62	17.49	1.27
	0.64	33.37	17.76	18.05	1.63	18.13	2.08
	0.60	34.36	18.23	18.58	1.92	18.79	3.07
				Average	1.62		5.13

TABLE 2—(*contd*)

Hydrocarbons (Saturated)	T_r	d_{ll} (Ref. 9)	d_{sl} Lit.	d_{sl} Calc. Eq, 1	% Div.	d_{sl} Calc. Eq 2	% Div.
Propane	0.96	21.15	8.34	8.23	1.32	7.87	5 64
(Ref. 11)	0.94	22.44	8.90	8.72	2.02	8.46	4 94
	0 92	23.85	9.35	9.26	0.96	9.10	2.67
	0.88	26.10	10.08	10.12	0.40	10.13	0.50
	0.84	27.84	10.72	10.78	0 56	10.92	1.87
	0 80	29.20	11.27	11.30	0.27	11.54	2.40
	0.76	30.38	11.80	11.75	0.42	12.08	2.37
	0.72	31.43	12.24	12.15	0.74	12.56	2.61
	0 68	32.42	12.66	12.52	1.11	13 01	2.76
	0.64	33.37	13.06	12.89	1.30	13.44	3.91
	0.60	34.36	13.44	13.26	1.34	13.89	3.35
				Average	0.96		2.91
n-Butane	0 96	21.15	6.58	6.39	2.89	6.36	3.34
(Ref. 15)	0.94	22.44	7.05	6.77	3 97	6 80	3.55
	0 92	23.85	7.43	7.19	3 23	7 29	1.88
	0 88	26.10	8.03	7.86	2.12	8 06	0.37
	0.84	27.84	8.54	8.38	1.87	8.66	1.41
	0.80	29.20	8.97	8.78	2.12	9.13	2.23
	0.76	30.38	9.33	9.13	2.14	9.54	2.25
	0.72	31.43	9.71	9.44	2.78	9.90	1.96
	0.68	32.42	10.03	9.74	2.89	10.24	2.09
	0.64	33.37	10.36	10.02	3.28	10.56	1.93
				Average	2.73		2.10

TABLE 2—(*contd*)

Hydrocarbons (Saturated)	T_r	d_{Al} (Ref. 9)	d_{sl} Lit.	d_{sl} Calc. Eq. 1	% Div	d_{sl} Calc. Eq. 2	% Div.
iso-Butane	0.96	21.15	6.48	6.82	5.25	6.36	1.85
(Ref. 16)	0.94	22.44	6.97	7.23	3.73	6.80	2.44
	0.92	23.85	7.34	7.67	4.50	7.29	0.68
	0.88	26.10	7.93	8.38	5.67	8.06	1.64
	0.84	27.84	8.40	8.93	6.30	8.66	3.10
	0.80	29.20	8.85	9.36	5.76	9.13	3.16
	0.76	30.38	9.22	9.74	5.64	9.54	3.47
	0.72	31.43	9.57	10.07	5.22	9.90	3.45
	0.68	32.42	9.94	10.38	4.43	10.24	3.02
	0.64	33.37	10.27	10.68	3.99	10.56	2.82
				Average	5.05		2.56
n-Pentane	0.96	21.15	5.45	5.26	3.49	5.29	2.94
(Ref. 17)	0.94	22.44	5.82	5.58	4.12	5.65	2.92
	0.92	23.85	6.13	5.92	3.43	6.04	1.47
	0.88	26.10	6.63	6.48	2.26	6.66	0.45
	0.84	27.84	7.05	6.90	2.13	7.14	1.28
	0.80	29.20	7.41	7.24	2.29	7.52	1.48
	0.76	30.38	7.73	7.53	2.59	7.85	1.55
	0.72	31.43	8.03	7. 8	3.11	8.14	1.37
	0.68	32.42	8.32	8.03	3.49	8.41	1.08
				Average	2.99		1.62

TABLE 2—(*contd.*)

Hydrocarbons (Saturated)	T_r	d_{sl} (Ref 9)	d_{sl} Lit.	d_{sl} Calc. Eq. 1	% Div.	d_{sl} Calc. Eq. 2	% Div.
Iso-Pentane	0.96	21.15	5.47	5.48	0.18	5.29	3.29
(Ref. 18)	0.94	22.44	5.84	5.81	0.51	5.65	3.25
	0.92	23.85	6.15	6.18	0.49	6.04	1.79
	0.88	26.10	6.64	6.75	1.66	6.66	0.30
	0.84	27.84	7.04	7.20	2.27	7.14	1.42
	0.80	29.20	7.43	7.54	1.48	7.52	1.21
	0.76	30.38	7.73	7.84	1.42	7.85	1.55
	0.72	31.43	8.03	8.11	1.00	8.14	1.37
	0.68	32.42	8.30	8.37	0.84	8.41	1.32
				Average	1.09		1.72
Neo-pentane	0.96	21.15	5.51	6.05	9.80	5.29	3.99
(Ref. 19)	0.94	22.44	5.93	6.41	8.09	5.65	4.72
	0.92	23.85	6.23	6.81	9.31	6.04	3.05
	0.88	26.10	6.70	7.44	11.04	6.66	0.60
	0.84	27.84	7.15	7.93	10.91	7.14	0.14
	0.80	29.20	7.55	8.31	10.07	7.52	0.40
	0.76	30.38	7.89	8.64	9.51	7.85	0.51
	0.72	31.43	8.17	8.94	9.42	8.14	0.37
	0.68	32.42	8.48	9.22	8.73	8.41	0.83
				Average	9.65		1.62

TABLE 2—(*contd*)

Hydrocarbons (Saturated)	T_r	d_{4l} (Ref 9)	d_{sl} Lit.	d_{sl} Calc. Eq. 1	% Div.	d_{sl} Calc. Eq. 2	% Div.
n-hexane	0.96	21.15	4.65	4.49	3.44	4.52	2.80
(Ref. 17)	0.94	22.44	4.96	4.76	4.03	4.82	2.81
	0.92	23.85	5.23	5.06	3.25	5.14	1.72
	0.88	26.10	5.64	5.53	1.95	5.66	0.35
	0.84	27.84	5.98	5.90	1.34	6.06	1.34
	0.80	29.20	6.30	6.19	1.75	6.38	1.27
	0.76	30.38	6.56	6.44	1.83	6.65	1.37
	0.72	31.43	6.84	6.66	2.63	6.90	0.88
	0.68	32.42	7.07	6.87	2.83	7.12	0.71
				Average	2.56		1.47
n-heptane	0.96	21.15	4.03	3.92	2.73	3.94	2.23
(Ref 17)	0.94	22.44	4.31	4.16	3.48	4.19	2.78
	0.92	23.85	4.53	4.42	2.43	4.47	1.32
	0.88	26.10	4.90	4.84	1.22	4.92	0.41
	0.84	27.84	5.20	5.17	0.58	5.27	1.35
	0.80	29.20	5.48	5.42	1.09	5.54	1.09
	0.76	30.38	5.73	5.64	1.57	5.77	0.70
	0.72	31.43	5.95	5.84	1.85	5.98	0.50
	0.68	32.42	6.15	6.02	2.11	6.18	0.49
				Average	1.90		1.21

TABLE 2—(*contd.*)

Hydrocarbons (saturated)	T_r	d_{si} (Ref. 9)	d_{st} Lit.	d_{st} Calc. Eq. 1	% Div	d_{st} Calc. Eq. 2	% Div.
n-octane	0.96	21.15	3.56	3.49	1.97	3.49	1.97
(Ref. 20)	0.94	22.44	3.78	3.70	2.12	3.71	1.85
	0.92	23.85	4.00	3.94	1.50	3.96	1.00
	0.88	26.10	4.33	4.32	0.23	4.35	0.46
	0.84	27.84	4.63	4.61	0.43	4.65	0.43
	0.80	29.20	4.86	4.84	0.41	4.89	0.62
	0.76	30.38	5.07	5.03	0.79	5.09	0.39
	0.72	31.43	5.27	5.21	1.14	5.28	0.19
	0.68	32.42	5.47	5.38	1.65	5.45	0.37
	0.64	33.37	5.64	5.53	1.95	5.61	0.53
	0.60	34.36	5.83	5.70	2.23	5.79	0.69
				Average	1.31		0.77
n-nonane	0.96	21.15	3.06	3.14	2.61	3.12	1.96
(Ref. 21)	0.94	22.44	3.34	3.34	–	3.32	0.60
	0.92	23.85	3.55	3.56	0.28	3.54	0.28
	0.88	26.10	3.86	3.90	1.04	3.89	0.78
	0.84	27.84	4.11	4.17	1.46	4.16	1.22
	0.80	29.20	4.34	4.37	0.69	4.37	0.69
	0.76	30.38	4.53	4.55	0.44	4.55	0.44
	0.72	31.43	4.71	4.71	–	4.72	0.21
	0.68	32.42	4.86	4.87	0.21	4.87	0.21
				Average	0.75		0.71

TABLE 2—(*contd.*)

Hydrocarbons (Saturated)	T_r	d_{Al} (Ref. 9)	d_{sl} Lit	d_{sl} Calc Eq. 1	% Div.	d_{sl} Calc. Eq. 2	% Div.
n-decane	0.96	21.15	2.85	2.86	0.35	2.83	0.70
(Ref. 22)	0.94	22.44	3.09	3.04	1.62	3.01	2.59
	0.92	23.85	3.31	3.24	2.11	3.21	3.02
	0.88	26.10	3.56	3.56	–	3.52	1.12
	0.84	27.84	3.76	3.81	1.33	3.76	–
	0.80	29.20	3.95	4.00	1.27	3.95	–
	0.76	30.38	4.13	4.16	0.73	4.12	0.24
	0.72	31.43	4.27	4.31	0.94	4.26	0.23
	0.68	32.42	4.36	4.45	2.06	4.40	0.92
				Average	1.16		0.98

Hydrocarbons (unsaturated)	T_r	d_{Al} (Ref. 9)	d_{sl} Lit.	d_{sl} Calc. Eq. 3	% Div.	d_{sl} Calc. Eq. 4	% Div.
Propylene	0.96	21.15	9.02	9.18	1.77	8.63	4.32
(Ref. 23)	0.94	22.44	9.62	9.69	0.73	9.24	3.95
	0.92	23.85	10.13	10.24	1.08	9.92	2.07
	0.88	26.10	11.02	11.13	1.00	10.99	0.27
	0.84	27.84	11.74	11.82	0.81	11.82	0.68
	0.80	29.20	12.30	12.36	0.49	12.47	1.38
	0.76	30.38	12.84	12.82	0.16	13.04	1.56
	0.72	31.43	13.35	13.24	0.82	13.54	1.42
	0.68	32.42	13.83	13.63	1.45	14.01	1.30
	0.64	33.37	14.33	14.00	2.30	14.47	0.98
				Average	1.06		1.79

TABLE 2—(*contd.*)

Hydrocarbons (unsaturated)	T_r	d_{ll} (Ref. 9)	d_l Lit.	d_{st} Calc. Eq. 3	% Div.	d_{st} Calc. Eq. 4	% Div.
	0.96	21.15	7.63	7 03	7.86	7.08	7.21
1,3 – butadiene	0.94	22.44	8.14	7.43	8.72	7.56	7.13
(Ref. 24)	0.92	23 85	8.54	7 85	8.08	8.08	5.39
	0.88	26.10	9.23	8 54	7.45	8.91	3.47
	0.84	27.84	9.79	9.06	7.46	9.56	2.35
	0.80	29.20	10.31	9.48	8.05	10 06	2.42
	0.76	30.38	10.75	9.83	8 56	10 50	2.33
	0.72	31.43	11.17	10.15	9.13	10 89	2.51
	0.68	32.42	11.56	10.45	9.60	11.25	2.68
	0 64	33.37	11.94	10 74	10 05	11.61	2 76
				Average	8 50		3.83
1 – butene	0.96	21.15	7 02	7.11	1.28	6.86	2.28
(Ref. 25)	0 94	22.44	7.52	7.50	0.27	7.32	2.66
	0 92	23.85	7.88	7 94	0.76	7 83	0.63
	0.88	26.10	8.48	8.63	1.77	8.63	1.77
	0.84	27.84	9.02	9.16	1.55	9.25	2.55
	0.80	29.20	9.46	9.58	1.27	9 74	2 96
	0.76	30.38	9.94	9 94	—	10.16	2.21
	0.72	31.43	10.39	10.26	1.25	10.53	1.35
	0.68	32.42	10.76	10.56	1.86	10.89	1.21
	0.64	33.37	10.08	10.85	2.08	11.23	1.35
				Average	1.21		1.90

TABLE 4

Hydrocarbons (unsaturated)	T_r	d_{Al} (Ref. 9)	d_{sl} Lit.	d_{sl} Calc. Eq. 3	% Div.	d_{sl} Calc Eq. 4	% Div.
Cis-2-butene	0.96	21.15	6.83	6.71	1.76	6.86	0.44
(Ref. 26)	0.94	22.44	7.46	7.09	4.96	7.32	1.88
	0.92	23.85	7.95	7.49	5.79	7.83	1.51
	0.88	26.10	8.72	8.15	6.54	8.63	1.03
	0.84	27.84	9.27	8.65	6.69	9.25	0.22
	0.80	29.20	9.74	9.05	7.08	9.74	–
	0.76	30.38	10.20	9.39	7.94	10.16	0.39
	0.72	31.43	10.63	9.69	8.84	10.53	0.94
	0.68	32.42	11.03	9.98	9.52	10.89	1.27
	0.64	33.37	11.36	10.26	9.68	11.23	1.14
				Average	6.88		0.88
Trans-2-butene	0.96	21.15	7.07	6.82	3.54	6.86	2.97
(Ref. 27)	0.94	22.44	7.56	7.20	4.76	7.32	3.17
	0.92	23.85	7.96	7.62	4.27	7.83	1.63
	0.88	26.10	8.63	8.28	4.06	8.63	–
	0.84	27.84	9.16	8.79	4.04	9.25	0.98
	0.80	29.20	9.63	9.19	4.57	9.74	1.14
	0.76	30.38	10.06	9.54	5.17	10.16	0.99
	0.72	31.43	10.44	9.85	5.65	10.53	0.86
	0.68	32.42	10.80	10.14	6.11	10.89	0.83
				Average	4.69		1.40

TABLE 2—*(concld)*

Hydrocarbons (unsaturated)	T_r	d_{Ai} (Ref. 9)	d_l Lit.	d_{sl} Calc. Eq 3	% Div.	d_{sl} Calc Eq. 4	% Div.
Isobutylene	0.96	21.15	6.97	7.14	2.44	6.86	1.58
(Ref. 28)	0.94	22.44	7.48	7.53	0.67	7.32	2.14
	0.92	23.85	7.92	7.97	0.63	7.83	1.14
	0.88	26.10	8.56	8.66	1.17	8.63	0.82
	0.84	27.84	9.13	9.20	0.77	9.25	1.31
	0.80	29.20	9.62	9.61	0.10	9.74	1.25
	0.76	30.38	10.03	9.98	0.50	10.16	1.30
	0.72	31.43	10.43	10.30	1.25	10.53	0.96
	0.68	32.42	10.79	10.61	1.67	10.89	0.93
	0.64	33.37	11.13	10.90	2.07	11.23	0.90
				Average	1.13		1.23
1-pentene	0.96	21.15	5.65	5.80	2.66	5.64	0.18
(Ref. 29)	0.94	22.44	6.11	6.13	0.33	6.01	1.64
	0.92	23.85	6.46	6.49	0.46	6.41	0.77
	0.88	26.10	7.03	7.06	0.43	7.05	0.28
	0.84	27.84	7.46	7.50	0.54	7.55	1.21
	0.80	29.20	7.84	7.84	–	7.94	1.28
	0.76	30.38	8.16	8.14	0.24	8.27	1.35
	0.72	31.43	8.47	8.40	0.83	8.57	1.18
	0.68	32.42	8.77	8.65	1.37	8.86	1.03
				Average	0.76		0.99

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