



C. Otoberise

Department of Chemistry, Delta State University, Abraka, Nigeria

otobrise@delta.edu.ng

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Abstract: A comparison of the capability of some group contribution methods (GCMs) in the estimation of pure compound properties of aliphatic alcohols was carried out. Four GCMs were tested in the prediction of three critical properties and two thermo physical properties of twenty aliphatic alcohols within the C₁-C₂₂ range. In the main, there was a good concord between predicted and experimental properties.

Keywords: Aliphatic alcohols, critical properties, group contribution, thermophysical properties

Introduction

Experimental data of the thermodynamic and critical properties are always required for various analyses and operations in chemistry, chemical engineering, and assessment of chemical impact on the environment and a host of other applications (Brauner *et al.*, 2008). Such experimental property data are usually not available for many compounds; it becomes inevitable to evolve methods or models to predict them (Brauner *et al.*, 2006; Shacham *et al.*, 2007; Hukkerikar *et al.*, 2012). Property prediction models are usually fitted into computer aided software and designs, provided such models are extrapolative (Hukkerikar *et al.*, 2012). Group Contribution Methods (GCMs) like the ones developed by Lydersen (1954), Ambrose (1978), Joback and Reid (1983), Constantinou and Gani (1994), Marrero and Gani (2001) are generally suitable for thermodynamic and critical properties estimation. They offer rapid estimates devoid of extensive computation.

GCMs for correlating pure component properties have been in use much longer than the Quantitative Structure-Property Relationships (QSPR) approach. The latter are essentially correlations between a compound or the property of a compound and a set of molecular or structural descriptors. On the other hand, GCMs are structural correlations that are widely used in estimating a wide range of thermodynamic and critical properties (Goodman, 2003). Group contributions are derived from the regression on serial combinations of chemically distinctive groups such as methylene groups (-CH₂-), methyl groups (-CH₃), hydroxyl groups (-OH), carboxylic acid groups (-COOH) and a host of others.

Gmelling *et al.* (2015) reviewed the status, flaws, merits and demerits, probable applications, and typical results of the different GCMs for the calculation of phase equilibria. Generally, the GCMs aided the prediction of the requisite phase equilibrium data by means of a small number of group interaction factors. Recently, Jhamb *et al.* (2018) developed a Group Contribution Method (GCM) for the estimation of physical properties of amino acids. Their model was adapted from the GCM of Marrero and Gani (2001). The method provided supplementary structural details for amino acids with bulky and intricate structures, consequently improving predictions of physical properties of amino acids. In the same vein, Renato (2017) evolved a semi-predictive approach, in which a one-parameter PC-SAFT model aided by a GCM was employed to estimate the phase behavior and properties of hydrocarbons. Analyses of the efficiency of this model revealed good results for extreme cases such as when only one vapor pressure data point is available for the fitting of the model parameter, whereas improved predictions may be achieved if more data are accessible.

Wang *et al.* (2017) undertook a comparative prediction of the refractive index of ionic liquids by GCM and Group

Contribution-Artificial Neural Network (GC-ANN) model. The two approaches yielded accurate and efficient results when the values were juxtaposed with over 2000 pieces of experimental data. The objective of this work is to undertake a comparative prediction, with acceptable accuracy, of some pure compound properties of aliphatic alcohols using four GCMs. Three critical properties; critical temperature (T_c), critical pressure (P_c), critical volume (V_c) and two thermodynamic properties; standard enthalpy of vaporisation (ΔH_{vap}) at 298 K and standard Gibbs Energy of formation (ΔG_f) at 298 K, were predicted by selected GCMs on the basis of their predictive capabilities.

Prediction approach for critical properties

Three GCMs were selected to predict (T_c) (Lydersen, 1954; Ambrose, 1978; Marrero-Gani, 2001). The Lydersen relationship for the prediction of T_c in Kelvin units is expressed in equation (1).

$$T_c = T_b \left[0.567 + \sum \Delta_T - (\sum \Delta_T)^2 \right]^{-1} \quad [1]$$

Using the method of Ambrose, T_c in Kelvin can be calculated by means of Equations (2) and (3)

$$x = \frac{T_b}{T_c} = \frac{X}{1 + X} \quad [2]$$

$$X = a + \sum \Delta_X \quad [3]$$

Where $a = 1.242$ for all compounds except perfluoro carbons and monohydrogen substituted perfluorocarbons, and $\sum \Delta_X$

is the sum of the increments for each atom or group in the molecule. T_b is the experimental boiling temperature of the compound. The Marrero-Gani relationship for predicting T_c in Kelvin is portrayed in equation (4).

$$\exp(T_c / T_{co}) = \sum_i N_i T_{cli} + W \sum_j M_j T_{c2j} + Z \sum_k O_k T_{c3k} \quad [4]$$

Three GCMs were selected to predict (P_c) (Lydersen, 1954; Constantinou-Gani, 1994; Marrero-Gani, 2001). The relationships for the estimation of P_c in bar units are expressed in equation (5-7). All parameters in the equations have been described previously (Otoberise *et al.*, 2018).

$$P_c = M \left(0.34 + \sum \Delta_p \right)^{-2} \quad [5]$$

$$(P_c - p_{c1})^{-0.5} - p_{c2} = \sum_j N_j p_{c1j} + W \sum_j M_j p_{c2j} \quad [6]$$

$$(P_c - p_{c1})^{-0.5} - P_{c2} = \sum_j N_j P_{c1j} + W \sum_j M_j P_{c2j} + Z \sum_k O_k P_{c3k} \quad [7]$$

The methods of Lydersen (1954), Constantinou-Gani (1994) and Marrero-Gani (2001) were selected to predict V_c . The

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relationships are expressed in equation (8-10). V_c is in cubic centimeters per mole.

$$V_c = 40 + \sum \Delta v_i \quad [8]$$

$$V_c - v_{co} = \sum_i N_i v_{cli} + W \sum_j M_j v_{c2j} \quad [9]$$

$$V_c - V_{co} = \sum_i N_i V_{cli} + W \sum_j M_j V_{c2j} + Z \sum_k O_k V_{c3k} \quad [10]$$

Prediction approach for thermodynamic properties

The standard enthalpies of vaporisation at 298 K for the aliphatic alcohols were predicted by the GCM of Constantinou-Gani (1994) and Marrero-Gani (2001). Equations (11-12) present the correlations. Both methods were also employed in the standard Gibbs Energy of formation at 298 K. The correlations are presented in equations (13-14).

$$\Delta H_{vap} - h_{vo} = \sum_i N_i h_{vli} + W \sum_j M_j h_{v2j} \quad [11]$$

$$\Delta H_{vap} - H_{vo} = \sum_i N_i H_{vli} + W \sum_j M_j H_{v2j} \quad [12]$$

$$\Delta G_f - g_o = \sum_i N_i g_{li} + W \sum_j M_j g_{2j} \quad [13]$$

$$\Delta G_f - G_{fo} = \sum_i N_i G_{fli} + W \sum_j M_j G_{f2j} + Z \sum_k O_k G_{f3k} \quad [14]$$

Results and Discussions

The results of the critical and thermo physical properties of the aliphatic alcohols, predicted by the GCMs are presented on Tables 1 and 2. In the prediction of T_c , a comparison was made between the traditional temperature-dependence models namely; the methods of Lydersen and Ambrose and the structure-property dependence model of Marrero-Gani (M-G). The values of the predicted properties were also compared with experimental data that were available. The prediction of P_c and V_c followed a similar pattern. In this case the method of Lydersen, which required the molecular mass of the compounds for P_c , was juxtaposed with the structure-property dependence methods of Constantinou-Gani and Marrero-Gani (M-G). The latter were employed in the estimation of the thermo physical properties of the alcohols.

Table 1: Critical properties of the aliphatic alcohols

Alcohol	Nc	Tc/K			Pc/bar			Vc/cm ³ /mol		
		Lydersen	Ambrose	M-G	Lydersen	C-G	M-G	Lydersen	C-G	M-G
Methanol	1	512.99	495.50	448.96	82.58	65.09	72.94	113.00	109.66	106.91
Ethanol	2	521.33	512.65	489.42	64.01	55.57	60.24	168.00	165.42	163.19
1-Propanol	3	537.65	536.95	523.84	52.10	48.04	50.84	223.00	221.18	219.47
1-Butanol	4	556.11	562.82	553.80	43.89	41.97	43.69	278.00	276.94	275.75
1-Pentanol	5	574.05	587.55	580.32	37.91	37.01	38.12	333.00	332.7	332.03
1-Hexanol	6	591.26	610.85	604.11	33.34	32.91	33.70	388.00	388.46	388.31
1-Heptanol	7	607.60	632.53	625.68	29.94	29.48	30.13	443.00	444.22	444.59
1-Octanol	8	624.10	653.62	645.40	26.87	26.58	27.21	498.00	499.98	500.87
1-Nonanol	9	639.50	672.77	663.58	24.49	24.10	24.79	553.00	555.74	557.15
1-Decanol	10	655.08	691.32	680.43	22.50	21.98	22.76	608.00	611.5	613.43
1-Undecanol	11	666.18	704.33	696.13	20.80	20.13	21.04	663.00	667.26	669.71
1-Dodecanol	12	683.74	723.39	710.84	19.35	18.53	19.58	718.00	723.02	725.99
1-Tridecanol	13	698.96	739.18	724.66	18.08	17.12	18.31	773.00	778.78	782.27
1-Tetradecanol	14	712.82	752.76	737.71	16.97	15.88	17.22	828.00	834.54	838.55
1-Pentadecanol	15	726.46	765.31	750.06	15.99	14.78	16.26	883.00	890.3	894.83
1-Hexadecanol	16	739.70	776.69	761.78	15.11	13.80	15.43	938.00	946.06	951.11
1-Heptadecanol	17	752.85	787.20	772.94	14.33	12.92	14.69	993.00	1001.82	1007.39
1-Octadecanol	18	766.93	797.91	783.58	13.62	12.14	14.03	1048.00	1057.58	1063.67
1-Eicosanol	20	790.40	812.21	803.50	12.39	10.79	12.92	1158.00	1169.1	1176.23
1-Docosanol	22	554.80	561.37	821.84	11.37	9.68	12.03	1268.00	1280.62	1288.79

Table 2: Thermo physical properties of the aliphatic alcohols

Alcohol	Nc	$\Delta H_{vap}/\text{kJ/mol}$ (298 K)		$\Delta G_f/\text{kJ/mol}$ (298 K)	
		C-G	M-G	C-G	M-G
Methanol	1	35.47	36.19	-181.45	-176.14
Ethanol	2	40.12	41.10	-173.22	-168.08
1-Propanol	3	44.77	46.01	-164.99	-160.01
1-Butanol	4	49.42	50.92	-156.75	-151.95
1-Pentanol	5	54.07	55.83	-148.52	-143.88
1-Hexanol	6	58.72	60.74	-140.29	-135.82
1-Heptanol	7	63.37	65.65	-132.06	-127.76
1-Octanol	8	68.02	70.56	-123.83	-119.69
1-Nonanol	9	72.67	75.47	-115.60	-111.63
1-Decanol	10	77.32	80.38	-107.37	-103.56
1-Undecanol	11	81.97	85.29	-99.14	-95.50
1-Dodecanol	12	86.62	90.20	-90.91	-87.44
1-Tridecanol	13	91.27	95.11	-82.68	-79.37
1-Tetradecanol	14	95.92	100.02	-74.44	-71.31
1-Pentadecanol	15	100.57	104.93	-66.21	-63.24
1-Hexadecanol	16	105.22	109.84	-57.98	-55.18
1-Heptadecanol	17	109.87	114.75	-49.75	-47.12
1-Octadecanol	18	114.52	119.66	-41.52	-39.05
1-Eicosanol	20	123.82	129.48	-25.06	-22.92
1-Docosanol	22	133.12	139.30	-8.60	-6.80

Table 3: Available experimental properties of the aliphatic alcohols

Alcohol	Nc	Tc/K	Pc/bar	$\Delta H_{vap}/\text{kJ/mol}$
Methanol	1	512.50 ^a	80.94 ^b	37.83 ^c
Ethanol	2	514.00 ^a	61.68 ^b	42.46 ^c
1-Propanol	3	536.80 ^a	51.79 ^b	47.50 ^c
1-Butanol	4	563.00 ^a	44.25 ^b	51.42 ^c
1-Pentanol	5	588.10 ^a		57.04 ^c
1-Hexanol	6	610.30 ^a		61.61 ^c
1-Heptanol	7	632.60 ^a	30.60 ^b	66.81 ^c
1-Octanol	8	652.50 ^a		70.98 ^c
1-Nonanol	9	670.70 ^a		76.86 ^c
1-Decanol	10	687.30 ^a		81.50 ^c
1-Undecanol	11	703.60 ^a		85.80 ^c
1-Dodecanol	12	719.40 ^a		90.80 ^c
1-Tridecanol	13			94.70 ^c
1-Tetradecanol	14			98.90 ^c
1-Pentadecanol	15			103.50 ^c
1-Hexadecanol	16			107.70 ^c
1-Heptadecanol	17			112.50 ^c
1-Octadecanol	18			116.80 ^c
1-Eicosanol	20			125.90 ^c
1-Docosanol	22			135.90 ^c

Source: ^aBrauner, 2008; ^bGil *et al.*, 2008; ^cNichols *et al.*, 2005

Experimental data that were found in the literature are shown in Table 3. The critical temperatures were sourced from the work of Brauner (2018); the critical pressures were obtained from the work of Gil *et al.* (2008) and the enthalpies of vaporisation were got from the work of Nichols *et al.* (2005). The deviations of predicted properties from experimental properties are presented in Table 4. The deviations are evidently connected to the number of carbon atoms in each molecule and were calculated by the relationship in equation (15). The Average Relative Deviations (ARD) which is

indicative of the predictive capability of the GCMs is included at the last row of Table 4. They were computed by the relation in equation (16).

$$D = \frac{\text{Predicted}_{(data)} - \text{Experimental}_{(data)}}{\text{Predicted}_{(data)}} \times 100 \quad [15]$$

$$\text{ARD}\% = \frac{\sum \text{Deviation}}{N} \quad [16]$$

Table 4: Deviations of predicted properties from available experimental properties

Alcohols	T_c (%)			P_c (%)			ΔH_{vap} (%)	
	Lydersen	Ambrose	M-G	Lydersen	C-G	M-G	C-G	M-G
Methanol	0.10	-3.43	-14.15	1.99	-24.35	-10.97	-6.65	-4.53
Ethanol	1.41	-0.26	-5.02	3.64	-11.00	-2.39	-5.83	-3.31
1-Propanol	0.16	0.03	-2.47	0.60	-7.81	-1.87	-6.10	-3.24
1-Butanol	-1.24	-0.03	-1.66	-0.82	-5.43	-1.28	-4.05	-0.98
1-Pentanol	-2.45	-0.09	-1.34				-5.49	-2.17
1-Hexanol	-3.22	0.09	-1.02				-4.92	-1.43
1-Heptanol	-4.11	-0.01	-1.11	-2.20	-3.80	-1.56	-5.43	-1.77
1-Octanol	-4.55	0.17	-1.10				-4.35	-0.60
1-Nonanol	-4.88	0.31	-1.07				-5.77	-1.84
1-Decanol	-4.92	0.58	-1.01				-5.41	-1.39
1-Undecanol	-5.62	0.10	-1.07				-4.67	-0.60
1-Dodecanol	-5.22	0.55	-1.20				-4.83	-0.67
1-Tridecanol							-3.76	0.43
1-Tetradecanol							-3.11	1.12
1-Pentadecanol							-2.91	1.36
1-Hexadecanol							-2.36	1.95
1-Heptadecanol							-2.39	1.96
1-Octadecanol							-1.99	2.39
1-Eicosanol							-1.68	2.76
1-Docosanol							-2.09	2.44
ARD (%)	-2.88	-0.17	-2.69	0.64	-10.48	-3.61	-4.19	-0.41

The GCMs generally, under predicted T_c , with an ARD of -2.88, -0.17 and -2.69 for the methods of Lydersen, Ambrose and M-G, respectively. The GCM of Ambrose yielded better predictions of T_c than the other two. The contribution of the OH group in this method is specific for each compound unlike the other GCMs. This makes it particularly suitable for T_c prediction in compounds with OH functional group.

The ARD in the prediction of P_c by the GCMs of Lydersen, C-G and M-G are 0.64, -10.48 and -3.61, respectively. The method of Lydersen which required the molecular weight of the compounds as input parameter, yielded better P_c values than the other GCMs that are entirely structure-property dependent. The advantage of the latter over the method of Lydersen is that they can differentiate between isomers, while Lydersen's GCM produces the same P_c values for isomers.

For the other critical property considered in this work, i.e. V_c , experimental data could not be sourced in the open literature. Analysis among the selected GCMs was carried out in relation to the trends observed in their predicted values. Fig. 1 illustrates the estimated values for the critical volumes of the alcohols as a function of the number of carbon atoms in each compound. It can be observed from Fig. 1 that the three GCMs predicted similar V_c values for the alcohols. As the number of carbon atoms increased the values became closer.

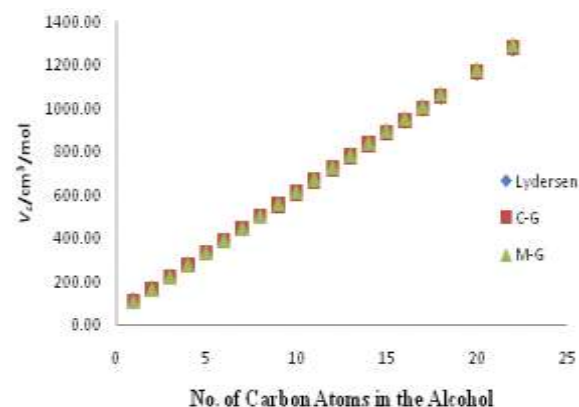


Fig. 1: Plot of critical volumes estimated by different GCMs with respect to number of carbon atoms of the alcohols

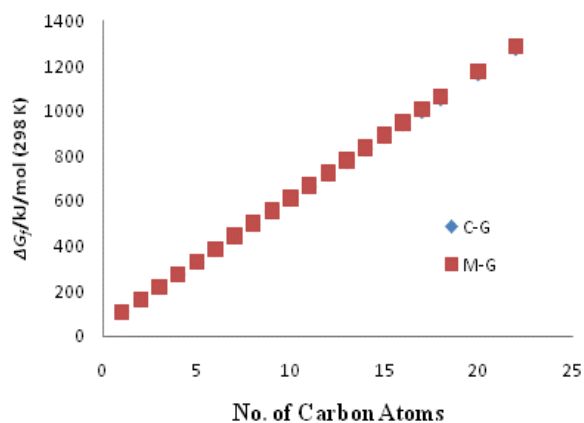


Fig. 2: Plot of enthalpies of formation estimated by different GCMs with respect to the number of carbon atoms of the alcohols

Thermo physical properties of the alcohols predicted by the GCMs of C-G and M-G were similar for the most part. However, the method of M-G yielded better ΔH_{vap} values with an ARD of -0.41%. Fig. 2 is a comparative plot of the ΔG_f values calculated by the two GCMs in relation to the carbon chain length of the alcohols. The results are identical from C₁–C₂₂.

Conclusion

Some important properties of aliphatic alcohols required for analyses and process design can be acceptably predicted by GCMs. The appropriate method(s) to opt for is an essential factor on accurateness of the ultimate estimation result. Minimum deviations observed between experimental data and estimations carried out by the GCMs selected for this study substantiate the applicability of using prediction models on engineering problems.

Conflict of Interest

Author declares that there is no conflict of interest reported in this work.

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