October 2007 Volume 2 Issue 3

Trade Science Inc.

Physical CHEMISTRY
An Indian Journal

Full Paper

PCAIJ, 2(3), 2007 [197-202]

Normal Boiling Point Prediction Of Carbocyclic Nitroaromatic Compounds

Mohammad Hossein Keshavarz*, Hamid Reza Pouretedal
Department of Chemistry, Malek-Ashtar University of Technology, Shahin-Shahr
P.O. Box-83145/115, (ISLAMIC REPUBLIC OF IRAN)
Tell : (0098)-0312-522-5071; Fax : (0098)0312-522-5068
Received: 6th August, 2007 ; Accepted: 11th August, 2007

ABSTRACT

A new approach has been introduced to predict boiling point of carbocyclic nitroaromatic compounds. This method is based on the number of carbon, hydrogen and oxygen as well as the contribution of specific polar group para to nitro group in disubstituted benzene ring and the number of alkyl or aryl group ortho to nitro group. Thirteen experimental data were used to predict the suitable correlation. Optimized correlation can be used to dinitro aromatic compounds which belong to energetic compounds. Predicted boiling points using the method described herein have been tested for 26 nitroaromatic carbocyclic compounds and compared with group-contribution method of Joback-Reid[K.G.Joback, R.C.Reid, Chem. Eng.Comm., 57, 233(1987)]. Predicted boiling temperatures have the average deviations for new and Joback-Reid procedures 3.0% and 13.1%, respectively.

KEYWORDS

Normal boiling point;
Carbocyclic nitroaromatic compounds;
Correlation;
Elemental composition;
Specific polar groups.

INTRODUCTION

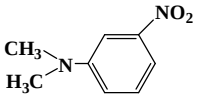
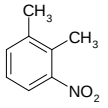
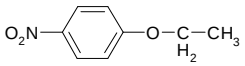
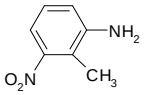
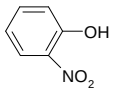
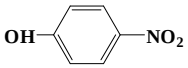
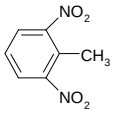
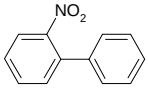
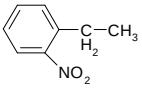
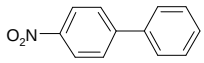
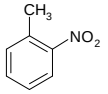
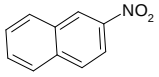
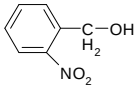
The basis for any design and simulation of chemical and environmental systems is a reliable set of physical and chemical properties of reactants. Since it is not always possible to find experimental values in the literature as well as measurement is expensive and time consuming or sometimes even difficult or impossible, estimation methods are generally of great value. Empirical methods complemented the computer output for desk calculations of performance and physicochemical properties of energetic compounds would be needed because the expenditure connected with the development and synthesis of a new energetic material.

One of the most comprehensive estimation procedures for boiling point, melting point, and vapor pressure is group contribution methods, where values assigned to atoms, bonds, and their placement in a molecule are used to estimate their contribution to the inherent physicochemical properties of that molecule[1]. Some of group contribution methods are Joback and Reid[2], Constantinou et al.[3,4], Prickett et al.[5], Constantinou and Gani[6]. Some new simple methods have been recently introduced for simple evaluation of thermochemical properties of energetic compounds, e.g. melting point[7,8] and heat of formation[9-11].

The normal boiling points reflect the strength of the intermolecular forces (among other forces present) that hold them together. However, the stronger the intermolecular forces, the more tightly the atoms will be held

Full Paper

TABLE 1 : Comparison of the calculated boiling point (K) of carbocyclic nitroaromatic compounds of new method and Joback-Reid (J-R) method[2] for training set with experimental data[13]

No.	Name	Molecular structure	Exp.	New method	%Dev	J-R method	%Dev
1	N,N-Dimethyl-N-(3-nitrophenyl)amine		556	576.9	-3.8	578.4	-4.0
2	1,2-Dimethyl-3-nitrobenzene		513	512.2	0.2	570.9	-11.3
3	1-Ethoxy-4-nitrobenzene		556	548.2	1.4	588.4	-5.8
4	2-Methyl-3-nitroaniline		578	556.7	3.7	620.6	-7.4
5	2-Nitrophenol		489	507.5	-3.8	595.7	-21.8
6	4-Nitrophenol		552	555.9	-0.7	595.8	-7.9
7	2-Methyl-1,3-dinitrobenzene		558	558.4	-0.1	699.9	-25.4
8	2-Nitro-1,1'-biphenyl		593	599.2	-1.1	684.1	-15.4
9	1-Ethyl-2-nitrobenzene		506	512.2	-1.2	565.9	-11.8
10	4-Nitro-1,1'-biphenyl		613	611.1	0.3	684.1	-11.6
11	1-Methyl-2-nitrobenzene		495	503.9	-1.8	543.1	-9.7
12	2-Nitronaphthalene		587	581.1	1.0	684.1	-16.5
13	(2-Nitrophenyl)methanol		543	515.8	5.0	635.2	-17.0
	Average deviation			2.4		12.7	

together which results the higher the normal boiling point. The purpose of this work is to present a new approach for obtaining boiling point of carbocyclic nitroaromatic compounds as an important class of organic materials which can be used as reactants or intermediates for synthesis of carbocyclic polynitroaromatic explosives. Although some of polynitro compounds decompose at temperatures below their normal boiling points, the new method can be applied for some energetic compounds that have normal boiling points, e.g. dinitro carbocyclic aromatic compounds. New correlation will be optimized with experimental data of some carbocyclic nitroaromatic compounds and, then, will be tested against experimental values as well as Joback-Reid method[2].

RESULTS AND DISCUSSION

Determination of physicochemical properties of nitro compounds is the essential of somewhat more practical importance to the chemist. The study of boiling point for various carbocyclic nitroaromatic organic compounds shows that it is possible to correlate boiling point

TABLE 2 : Comparison of the calculated boiling point (K) of carbocyclic nitroaromatic compounds of new method and Joback-Reid (J-R) method[2] for test set with experimental data[13]

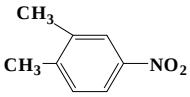
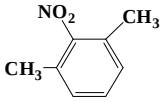
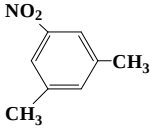
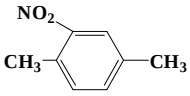
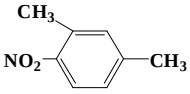
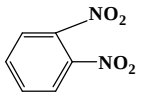
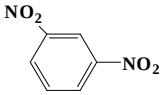
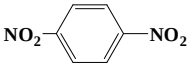
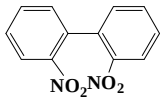
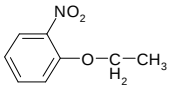
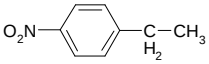
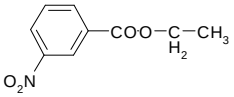
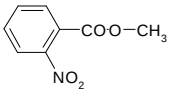
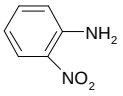
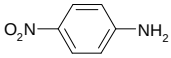
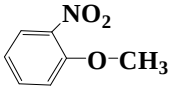
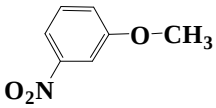
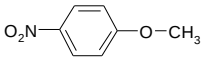
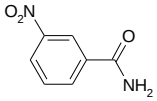
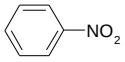
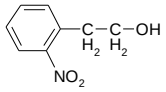
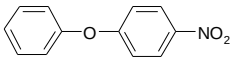
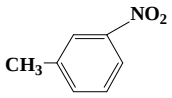
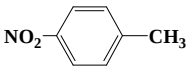
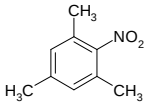
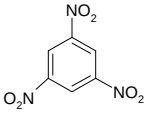
No.	Name	Molecular structure	Exp.	New method	%Dev	J-R method	%Dev
1	1,2-Dimethyl-4-nitrobenzene		524	524.0	0.0	570.9	-9.0
2	1,3-Dimethyl-2-nitrobenzene		499	476.6	4.5	570.9	-14.4
3	1,3-Dimethyl-5-nitrobenzene		547	524.0	4.2	570.9	-4.4
4	1,4-Dimethyl-2-nitrobenzene		514	500.3	2.7	570.9	-11.1
5	2,4-Dimethyl-1-nitrobenzene		520	500.3	3.8	570.9	-9.8
6	1,2-Dinitrobenzene		591	573.8	2.9	672.0	-13.7
7	1,3-Dinitrobenzene		564	573.8	-1.7	672.0	-19.1
8	1,4-Dinitrobenzene		570	573.8	-0.7	672.0	-17.9
9	2,2'-Dinitro-1,1'-biphenyl		578	630.0	-9.0	840.9	-45.5
10	1-Ethoxy-2-nitrobenzene		540	524.0	3.0	588.4	-9.0
11	1-Ethyl-4-nitrobenzene		518	524.0	-1.2	565.9	-9.2
12	Ethyl 3-nitrobenzoate		570	545.8	4.2	647.0	-13.5
13	Methyl 2-nitrobenzoate		548	537.5	1.9	624.1	-13.9
14	2-Nitroaniline		557	560.3	-0.6	597.0	-7.2
15	4-Nitroaniline		605	560.3	7.4	597.0	1.3
16	1-Methoxy-2-nitrobenzene		550	515.8	6.2	565.5	-2.8
17	1-Methoxy-3-nitrobenzene		531	515.8	2.9	565.5	-6.5

TABLE 2 is continue on next page

Full Paper

No.	Name	Molecular structure	Exp.	New method	%Dev	J-R method	%Dev
18	1-methoxy-4-nitrobenzene		547	540.0	1.3	565.5	-3.4
19	3-Nitrobenzamide		540	582.1	0.7	669.5	-14.2
20	Nitrobenzene		518	507.5	-4.9	515.0	-6.4
21	2-(2-Nitrophenyl)ethanol		570	524.0	3.0	658.1	-21.9
22	1-Nitro-4-phenoxybenzene		548	611.1	-3.1	706.6	-19.2
23	1-Methyl-3-nitrobenzene		557	515.8	-2.1	543.1	-7.5
24	1-Methyl-4-nitrobenzene		605	515.8	-0.9	543.1	-6.3
25	1,3,5-Trimethyl-2-nitrobenzene		550	532.3	-0.8	598.8	-13.4
26	1,3,5-Trinitrobenzene		531	616.5	-4.8	828.8	-41.0
	Average deviation				3.0		13.1

with some specific structural parameters. The results show that the numbers of carbon, hydrogen and oxygen atoms as well as the contribution of specific polar group para to nitro group in disubstituted benzene ring and the number of alkyl or aryl group ortho to nitro group are important structural parameters to derive a new correlation. One set of carbocyclic nitroaromatic compounds containing **(13)** compounds of different molecular structures was selected as training set, which is given in TABLE 1. The suitable form for predicting boiling point of $C_aH_bN_cO_d$ carbocyclic aromatic compounds based on multiple linear regression as a function of mentioned parameters can be written as follows:

$$\mathbf{T_b = z_1 + z_2 a + z_3 b + z_4 d + z_5 C_{p,-OR} + z_6 n_{o,-R(or-Ar)}} \quad \mathbf{(1)}$$

where T_b is boiling point, a, b and c are the number of carbon, hydrogen and oxygen atoms, $C_{p,-OR}$ shows the existence of specific polar groups including alkoxy and -OH para to nitro group in disubstituted benzene ring, $n_{0,-R(or-Ar)}$ is the number of alkyl or aryl groups ortho to nitro group, and z_1 to z_6 are adjustable parameters which can be found from experimental data given in TABLE 1. Since the equation set is overdetermined[12] to find adjustable parameters, the left-division method for solving linear equations uses the least squares method in multiple linear regression method. However, the following optimized correlation can be obtained:

$$\mathbf{T_b\,(K) = 351.03 + 21.771a - 6.7522b + 59.597d + 24.201C_{p,-OR} - 11.856n_{o,-R(or-Ar)}} \quad \mathbf{(2)}$$

Due to various inter- and intra-molecular forces, R-squared values or the coefficients of determination of Eq.(2) is 0.90[12]. As seen in Eq.(2), the coefficient of the $C_{p,-OR}$ has positive sign which shows extra intermolecular forces for the presence of this term in disubstituted benzene ring. Due to the presence of hydrogen bonding for –OH group, it can be expected that the contribution of the $C_{p,-OR}$ for -OH is more than the alkoxy group. However, the value of $C_{p,-OR}$ is 1.0 and 2.0 for alkoxy and –OH groups, respectively. The percent of error, [(measured-predicted)/measured]×100, are given in TABLE 1. As seen in TABLE 1, the average deviation for Eq.(2) is 2.4% which is much lower than Joback-Reid procedure, i.e. 12.7%.

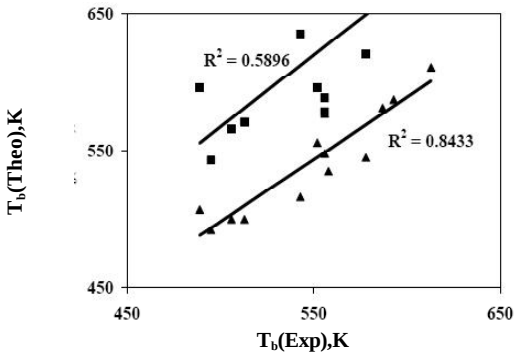


Figure 1 : Filled triangle and square denote predictions for training set by new and Joback-Reid methods, respectively

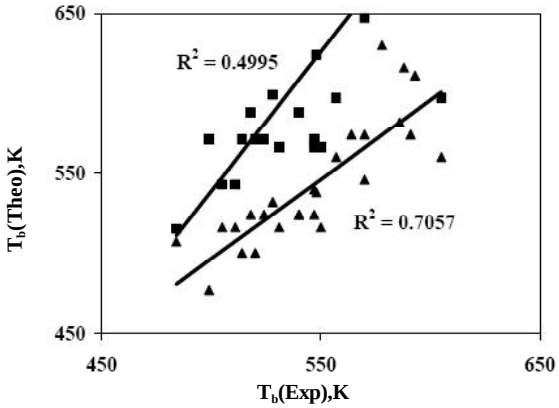


Figure 2. Filled triangle and square denote predictions for test set by new and Joback-Reid methods, respectively

To test the validity of the new correlation, boiling point of 26 carbocyclic nitroaromatic compounds are calculated and compared with the experimental values as well as Joback-Reid[9] method, which are given in TABLE 2. As indicated in TABLE 2, the same as the results of training set, the predictions of new method are in good agreement with experimental values (average deviation=3.0%) as compared to Joback-Reid[2] method (average deviation=13.1%). Of 39 calculated values of normal boiling points, which are given in TABLES 1 and 2, deviations for only five compounds are higher than 5.0%.

A visual comparison of the predictions for training and test sets by new and Joback-Reid methods with experiment are also given in figures 1 and 2. As evident in figures 1 and 2, the new method shows much better agreement with experimental data than Joback-Reid procedure.

CONCLUSIONS

This work has introduced a simple method for predicting normal boiling point of carbocyclic nitroaromatic compounds. Two sets were used as training and test sets to derive appropriate correlation and it application. As shown in TABLES 1 and 2, the calculated results have shown good agreement with experimental data as compared to Joback-Reid[2]. This may be taken as appropriate validation of the new procedure for carbocyclic nitroaromatic compounds because the new procedure exhibits an improved accuracy and simple applicability with respect to Joback-Reid method, which confirms the accuracy is not necessarily enhanced by greater complexity.

ACKNOWLEDGENT

We would like to thank the research committee of Malek-ashtar University of Technology (MUT) for supporting this work.

REFERENCES

[1] R.C.Reid, J.M.Prausnitz, B.E.Poling; The Properties of Gases and Liquids, 4th ed., McGraw-Hill, New York, **(1987)**.
[2] K.G.Joback, R.C.Reid; Chem.Eng.Comm., **57**, 233 **(1987)**.
[3] L.Constantinou, S.E.Prickett, M.L.Mavrovouniotis; Ind.Eng.Chem.Res., **32**, 1734 **(1993)**.
[4] L.Constantinou, S.E.Prickett, M.L.Mavrovouniotis; Ind.Eng.Chem.Res., **33**, 395 **(1994)**.
[5] S.E.Prickett, L.Constantinou, M.L.Mavrovouniotis, Mol.Simul., **11**, 20 **(1993)**.
[6] L.Constantinou, R.Gani; AIChE J., **40**, 1697 **(1994)**.
[7] M.H.Keshavarz, J.Hazard.Mat., **A138**, 448 **(2006)**.
[8] M.H.Keshavarz, H.R.Pouretedal, J.Hazard.Mat.A, in press.
[9] M.H.Keshavarz, M.Oftadeh; High Temp High Press., **35/36**, 499 **(2003/2006)**.
[10] M.H.Keshavarz; J.Hazard.Mater., **A136**, 145 **(2006)**.
[11] M.H.Keshavarz; J.Hazard.Mater, **A136**, 425 **(2006)**.
[12] W.J.Palm; 'Matlab for Engineering Applications', WBC/McGraw-Hill, **(1999)**.
[13] D.R.Lide, ed.; 'CRC Handbook of Chemistry and Physics', CRC Press, Inc., **(2005)**.