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Improved equation to estimate flash points of organic compounds

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Abstract

An improved correlation, non-linear exponential type has been proposed for the estimation of flash points of organic compounds and petroleum fractions as a function of their boiling temperature. This correlation was tested with 1221 compounds and found to predict the flash points with less than 1% average absolute error, over a wide range of normal boiling temperature. The constants of the correlation for various classes of compounds are also presented.

Introduction

The global awareness of the importance of safety, risk assessment and emergency planning for industrial accidents and the stringent regulations of Governmental agencies of various countries have necessitated the search for better and accurate techniques for predictions in these areas. Flash point, one of the physical properties of chemical compounds, is useful to identify the flammable nature of the substance. It has received attention in recent years from the safety point of view. It is evident from the literature that thousands of new compounds are being synthesised every year and the flash point data of these compounds are essential for hazard classification of the substances. Experimental data are always desirable but when they are not available the recourse is taken to prediction methods.

Process plant designers, safety auditors, hazard study and risk assessment experts have to predict the flash points for many in plant stocks to check the compliance with safety requirements and for several other purposes. Many correlations have been reported in the literature [1–5] to estimate the flash points of organic compounds and their mixtures as a function of normal boiling temperature. All of these correlations fall either in the class of parabolic type or hyperbolic type. Both linear and parabolic types of equation [7] are used for

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estimating the flash points of different groups of organic compounds. A hyperbolic type of equation [6] is used for predicting the flash points of hydrocarbons and petroleum fractions. When these correlations [6, 7] were applied to predict the flash points for a wide range of organic compounds, notably larger deviations (>10 °C) were observed between the predicted and the reported experimental flash points. The reason is that either the correlations (Riazi and Daubert [6]) developed are based on a limited number of data points (<20 samples) or the correlation (Patil [7]) of a parabolic/hyperbolic nature does not represent the experimental data satisfactorily. So it is desirable to have a more accurate prediction method. In this paper, the applicability of a non-linear (exponential) type of equation is investigated to estimate the flash points for different classes of organic compounds and petroleum fractions as a function of normal boiling temperature.

Results and discussion

Reported experimental data of normal boiling and closed cup flash point temperatures of several organic compounds were taken from Lange's Handbook of Chemistry [8], Aldrich Catalogue Handbook of Fine Chemicals [9] and the Hazardous Chemical Data Book [10]. Twelve hundred organic compounds collected from the above sources have been divided into 12 groups as given in Table 1. Twenty-one data sets on petroleum fractions were obtained from the literature [6]. The materials contained in nitrogen group do not include the amines, which are considered separately. Care has been taken to include

TABLE 1

Values of constants in eq (3)

Group	No. of compounds	Source of data	*a*	*b*	*c*	AAE%[a]
Hydrocarbons	230	[8, 9]	225.10	537.60	2217.00	0.410
Alcohols	150	[9, 10]	230.80	390.50	1780.00	0.186
Amines	70	[9]	222.40	416.60	1900.00	0.200
Acids	40	[8, 9]	323.20	600.10	2970.00	0.531
Ethers	80	[9, 10]	275.90	700.00	2879.00	0.343
Sulphur	40	[10]	238.00	577.90	2297.00	0.484
Esters	120	[8, 9, 10]	260.80	449.20	2217.00	0.186
Ketones	80	[8]	260.50	296.00	1908.00	0.722
Halogens	200	[8, 9, 10]	262.10	414.00	2154.00	0.672
Aldehydes	45	[8]	264.50	293.00	1970.00	0.771
Phosphorus	20	[8, 9]	201.70	416.10	1666.00	0.815
Nitrogens	125	[8, 9, 10]	185.70	432.00	1645.00	0.622
Petroleum fractions	21	[6]	237.90	334.40	1807.00	0.294

[a]AAE%—Percentage of average absolute error in predicted flash point.

a greater number of compounds in each group, so as to increase the scope of applicability of correlation and minimise the deviations to result more accurate prediction.

As already stated, the general form of the parabolic and hyperbolic equations given below are not suitable for the estimation of flash points of different organic compounds.

$$T_f = a + bT_b + cT_b^2 \quad (1)$$

$$T_f = a + bT_b + c/T_b^2 \quad (2)$$

The best equation will obviously be one containing an exponential function. A possible candidate is:

$$T_f = a + b(c/T_b)\, e^{-c/T}/(1 - e^{-c/T})^2 \quad (3)$$

where T_f denotes the flash point temperature, K; T_b the normal boiling temperature, K; and a, b, c are constants in eqs. (1)–(3).

Equation (3) was used to fit the flash points of 1200 organic compounds and 21 petroleum fractions as a function of normal boiling temperature. The constants in eq. (3) were evaluated by non-linear regression using the Gauss–Newton iteration method. Similarly, the values of the constants in eqs. (1) and (2) were also determined by polynomial and multiple regression analysis, respectively, for each group of compounds.

The results of the calculations for the twelve groups of organic compounds and the group of the 21 petroleum fractions are summarised in Table 1. A maximum percentage of average absolute error (AAE%) of 0.815 was observed in the case of the phosphorus group. Using eqs. (1) and (2) only gave an AAE% of 1.014 and 1.18, respectively, for the phosphorus group. Equation (3) results were also compared with those of eqs. (1) and (2) for the other groups. The sample calculations of two compounds in each group are shown in Table 2. Reasonably accurate results are obtained by the use of (3) with most of the groups. But in case of the phosphorus group, the deviation with experiment of predicted values from eq. (3) are slightly greater than found in the other groups. However, the deviations of predicted values of flash points from eqs. (1) and (2) with experiment are still higher. Table 2 indicates that the classical parabolic/hyperbolic equations give substantially inaccurate results. It is clear from Tables 1 and 2 that (3) gives more reliable predictions of flash points for all of the materials investigated.

Conclusions

The suggested non-linear correlation gave satisfactory agreement between the predicted and reported experimental data of flash points. It is further suggested that this correlation can be applied over a wide range of normal

TABLE 2

Comparison of performance of (3) with eqs. (1) and (2) for two example components in each group

Group	Compound	T_f, °C (Data from literature)	T_b, °C	Predicted T_f, °C		
				Eq. (1)	Eq. (2)	Eq. (3)
Hydrocarbons	1. *p*-Cumene	320.00	449.00	324.00	323.08	320.40
	2. Undecane	333.00	469.00	335.83	335.09	333.35
Alcohols	1. 2-Propanol	296.00	355.00	315.57	317.79	296.10
	2. 2-Phenylethanol	375.00	494.00	369.82	370.35	375.92
Amines	1. Decylamine	358.00	491.00	355.29	355.86	358.17
	2. 1-Hexadecylamine	413.00	603.00	422.64	423.28	415.67
Acids	1. 4-Methylvaleric acid	370.00	474.00	366.61	367.11	369.81
	2. Octanoic acid	383.00	510.00	382.70	382.96	383.12
Ethers	1. Hexyl ether	351.00	502.00	375.36	373.32	350.89
	2. *N*-Propyl ether	294.00	363.00	281.60	283.38	292.00
Sulphurs	1. Ethyl disulphide	313.00	426.00	319.43	385.60	315.20
	2. Cyclohexanethiol	316.00	431.00	322.28	379.97	318.33
Esters	1. Benzyl benzoate	420.00	596.00	425.83	425.12	419.04
	2. 2-Butoxy ethyl acetate	349.00	465.00	346.45	346.60	349.08
Ketones	1. Octanophenone	383.00	563.00	375.79	375.52	383.36
	2. 2-Methoxycyclo-hexanone	342.00	458.00	345.39	345.49	342.73
Halogens	1. 1-Bromo-2-propanol	327.00	421.00	329.15	329.19	327.89
	2. 1-Iodooctane	368.00	499.00	365.38	365.09	367.85
Aldehydes	1. Benzaldehyde	335.00	452.00	340.00	339.91	337.21
	2. 3,4-Dimethoxy-benzaldehyde	373.00	554.00	367.54	367.83	376.60
Phosphorus	1. Triethylphosphite	327.00	429.00	212.88	340.19	336.33
	2. Trimethylphosphate	300.00	385.00	290.32	317.56	307.35
Nitrogens	1. 3-Ethoxybenzonitrile	383.00	517.00	378.87	380.00	383.31
	2. 4-Nitrotoluene	379.00	511.00	375.31	376.09	379.94
Petroleum fractions	1. —	361.89	499.11	364.02	365.60	361.79
	2. —	364.11	507.44	369.33	369.86	365.52

boiling temperatures of organic compounds to estimate flash point temperature, especially when the parabolic/hyperbolic equations fail.

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