알코올화합물의 폭발하한계 추산에 관한 연구

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A Study on Estimation of Lower Explosive Limits of Alcohol Compounds

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1. Introduction

Flammable compounds are indispensible in domestic as well as in industrial fields as fuel, solvent and raw materials. The fire and explosion properties necessary for safe storage, transport, process design and operation of handling flammable substances are lower explosive limits(LEL), upper explosive limits(UEL), flash point, fire point, AIT(auto ignition temperature), MIE(minimum ignition energy), MOC(minimum oxygen concentration) and heats of combustion[1].

Explosive limit is one of the major physical properties used to determine the fire and explosion hazards of the flammable substances[2]. Explosive limits are used to classify flammable liquids according to their relative flammability. Such a classification is important for the safe handling of flammable liquids which constitute the solvent mixtures.

The research on the explosive limits is one of fundamental fields of combustion process, and information on the explosive limits of mixture of fuel and oxidant, with or without additives, is very important for the prevention in industrial fire and explosion accidents. Therefore, the method to estimate the explosive limits of flammable materials have been of great concern of petroleum, paint, and other industries.

In this study, the new equation for predicting the lower explosive limits(LEL) of alcohol compounds by on the basis of flash points, statistics and mathematical method is proposed.

2. Relationship between explosion limits and flash points

The flash point is defined by the National Fire Protection Association (NFPA)[3] as the lowest temperature at which a flammable liquid gives off sufficient vapor to form an ignitable mixture with air near its surface or within a vessel. The the flash points are generally presented to values determined by tow apparatus. The open cup(O.C.) flash points are generally somewhat higher than the closed cup(C.C.) flash points for same materials. Special precautions should be taken when the product has a low flash point. Materials having a low flash point are a greater fire hazard than materials having a high flash point.

Explosion limits refer to the range of flammable gas or vapor concentrations between which ignition will occur if an ignition source is present. All concentrations between LEL and UEL are in the flammable range, and special precautions are needed to prevent ignition or explosion.

There exist close relationships between flash points and explosive limits. Therefore, the prediction of the explosive limits by flash points is an interesting field.

3. Development of the predictive models of explosive Limits by Flash points

3.1 Theory

The vapor pressure of a liquid increases as the temperature is elevated. A relationship of flash point to the lower explosive limits exists through the dependence of vapor pressure on temperature, given by Clausius-Clapeyron equation[4].

$$\ln\left(\frac{P_v}{P_T}\right) = \frac{\Delta H_v}{R}\left[\frac{1}{T_b} - \frac{1}{T}\right] \tag{1}$$

where ΔH_v is the enthalpy of vaporization of the liquid, P_v is the vapor pressure, P_T is the total pressure, T_b is the normal boiling point, R is the gas constant and T is the Kelvin temperature.

Turning now to the mole fraction of the flammable fuel x_v, with ideal gas approximation,

$$X_v = \frac{n_v}{n_T} = \frac{P_v V/RT}{P_T V/RT} = \frac{P_v}{P_T} \tag{2}$$

so that Eqn. (1) gives the mole fraction of the flammable fuel vapor in the space above the vaporizing liquid. The flammable fuel x_v has to exceed the lower explosive limit(L).

$$\ln(\frac{1}{L}) = \frac{\Delta H_v}{RT_B}[\frac{T_b}{T_F} - 1] + \alpha \tag{3}$$

3.2 Various possible prediction models

Multiple regression analysis[5,6] are applied to obtain the correlation for estimation of the explosive limits by using the flash points.

For the estimation of the explosive limits, the predicted equation which used Trouton rule[4] and various possible prediction models are as fellows :

$$\ln(\frac{1}{L}) = \frac{\Delta H_v}{RT_B}[\frac{T_b}{T_f} - 1] \tag{4}$$

$$\frac{1}{L} = a + b[\exp(\frac{T_b - T_f}{T_f})] \tag{5}$$

$$\frac{1}{L} = a + b[\exp(\frac{T_b - T_f}{T_f})] + c[\exp(\frac{T_b - T_f}{T_f})]^2 \tag{6}$$

where L is the lower explosive limits, T_b is the normal boiling points and T_f is the flash points.

3.3 Selection of data

All the explosive limits and the flash point data for this study were obtained from NFPA 325M "Fire Hazard Properties of Flammable Liquid, Gases, and Volatile solids[3]. The greater part of the heats of vaporization for alcohols were obtained from CRC Handbook[7] and Lange's Handbook of Chemistry[8]. If there were not the heats of vaporization of alcohol compound in these books, we were obtained from using the entropy values estimated by Vetere's equation[9].

The enthalpy of vaporization for alcohol compounds were predicted by the use of the entropy of vaporization calculated by Vetere's method. Vetere's equation is as follow:

$$\Delta S_{vb} = 81.119 + 13.083 \log T_b - 25.769 \frac{T_b}{M} + 0.146528 \frac{T_b^2}{M} - 2.1362 \times 10^{-4} \frac{T_b^3}{M} \quad (7)$$

$$\Delta H_{vb} = \Delta S_{vb} T_b \quad (8)$$

where ΔH_{vb} is the enthalpy of vaporization, ΔS_{vb} is the entropy of vaporization and M is molecular weight.

3.4 Optimum seeking of the predictive model

Optimization in selecting the predictive models of the functional relationship between the lower explosive limits and the flash points are attempted.

Prior selection was made based on an A.A.P.E.(average absolute percent errors) and A.A.D.(average absolute deviations)[10,11], namely the difference of the reported value $L_{exp.}$ and estimated value $L_{est.}$.

$$A.A.P.E. = \frac{\sum \left| \frac{L_{est.} - L_{exp.}}{L_{exp.}} \right|}{N} \times 100 \quad (9)$$

$$A.A.D. = \frac{\sum | L_{est.} - L_{exp.} |}{N} \quad (10)$$

4. Comparison with reported and estimated values

Statistical analysis of these 22 compounds resulted in best-fit empirical equation for predicting the lower explosive limits of alcohol compounds.

Empirical equation is as fellows :

$$\frac{1}{L} = -16.95703 + 22.24219[\exp(\frac{T_b - T_f}{T_f})] - 6.66211[\exp(\frac{T_b - T_f}{T_f})]^2 \quad (11)$$

The experimental values compared with the predicted values according to the optimized equation in table 1.

Equation (11) is in agreement with the predicted LEL values of 22 alcohol compounds, average absolute percent error is 17.77 %, average absolute deviation is 0.315 vol%. The values calculated by the proposed equations were a good agreement with literature data within a few percent.

Table 1. Comparison with the predicted and estimated LEL values for alcohol compounds

No.	Components	T_b[K]	T_f[K]	H_v[KJ/ mol K}	H_v/RT_b	LEL exp.	Trouton rule	This Work
1	Methanol	337	285	35.20	12.56	6.00	10.11	7.08
2	Ethanol	351	286	38.26	13.21	3.30	4.97	2.15
3	n-Propanol	370	296	41.44	13.47	2.20	2.16	1.62
4	i-Propanol	355	285	39.85	13.50	2.00	3.63	1.70
5	n-Butanol	390	302	43.29	13.35	1.70	2.04	1.14
6	i-Butanol	373	301	40.75	13.14	1.68	3.18	1.43
7	2-Methyl-1-propanol	380	310	41.52	13.14	1.70	5.15	2.20
8	2-Methyl-2-propanol	357	277	39.07	13.16	1.90	2.24	1.16
9	1-Pentanol	411	311	44.36	12.98	1.20	1.54	0.96
10	2-Pentanol	392	307	41.40	12.70	1.20	2.79	1.27
11	3-Pentanol	391	313	43.01	13.23	1.20	3.70	1.63
12	2-Methyl-1-butanol	403	316	43.90*	13.10	1.20	2.71	1.28
13	2-Methyl-2-butanol	375	294	39.04	12.52	1.40	3.19	1.28
14	3-Methyl-1-butanol	403	319	44.07	13.15	1.20	3.14	1.42
15	3-Methyl-2-butanol	385	300	41.40*	12.93	1.20	2.56	1.21
16	1-Hexanol	430	333	41.40	12.45	1.20	2.66	1.13
17	3-Methyl-1-pentanol	423	332	46.30*	13.17	1.10	2.34	1.29
18	4-Methyl-2-pentanol	405	314	45.60*	13.45	1.20	1.98	1.15
19	1-Heptanol	449	347	48.10*	12.89	0.89	2.26	1.12
20	1-Octanol	469	354	46.90*	12.09	0.79	1.97	0.94
21	2-Octanol	452	344	47.34**	12.06	0.80	2.14	0.99
22	1-Nonanol	487	349	54.40*	13.44	-	0.49	-
23	1-Decanol	504	355	48.78**	11.88	0.7	0.76	0.68
A.A.P.E.							100.38	17.77
A.A.D.							1.43	0.315

*Lange's Handbook of Chemistry

**The predicted enthalpy of vaporization by the use of Vetere's method

By using the proposed equations, it is possible to predict the other properties. It is hoped eventually that this method will permit the estimation of the explosive

limits of alcohol with improved accuracy and the broader application for other compounds.

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