

ESTIMATION OF WATER-ALCOHOL MIXTURE FLASH POINT

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ABSTRACT

Mixtures of water with alcohols are important in numerous engineering applications. Knowledge of mixture flash points is needed for their safe handling, storage and transportation. A procedure for the estimation of flash points of water-alcohol mixtures by using the equations of Margules, van Laar and Wilson is presented in this paper.

Keywords: flash point, mixture, water-alcohol.

INTRODUCTION

Flammable substances are commonly used in laboratories and industrial processes. The flash point is one of the most important physical properties used to determine the potential for fire and explosion hazards of liquids [1]. The flash point is also used for the classification and labelling of dangerous substances and preparation in accordance with Directive 67/548 EEC and 1999/45/EC respectively [2,3]. It should be noted that these Directives will be repealed and replaced with the EU Regulation on classification, labelling and packaging of substances and mixtures, implementing the Globally Harmonised System (GHS) in the EU [4].

The flash point of a given liquid is the experimentally determined temperature adjusted to standard sea level atmospheric pressure of 760 mmHg (0.1 MPa) at which a substance emits sufficient vapour to form a combustible mixture with air [5]. A lower flash point value indicates that a liquid is more hazardous relative to an analogue with a higher value [6].

Key to the definition of the flash point of a liquid is the specific test which has been used. Each individual test type may produce slightly differing flash points for the same liquid. When reporting the flash point, it is important to specify exactly which test has been used.

There are two methods for the measurement of the flash point value of a liquid - the closed-cup test and the open-cup test [6]. The open-cup flash point value is, typically, a few degrees greater than the closed-cup flash point value.

The flash point data for pure substances can be obtained from various sources, such as MSDS (Material Safety Data Sheets). MSDS are available online from a variety of sources, including vendor websites for the major sellers of chemicals.

Still flash point data for a variety of liquid mixtures are scarce in the literature. The total characterization of a mixture requires significant experimental work and time. If a flash point prediction model for a binary mixture could be successfully developed, the flash points

of various liquid solutions would be predicted relatively easily from a limited number of initial data.

Several methods have been developed for the prediction or estimation of the flash points of pure compounds and mixtures. We recently published a review of most of these methods [7].

The purpose of this work is to develop a procedure for the estimation of flash points of binary aqueous-organic solutions by using the equations of Margules, van Laar and Wilson as well as to estimate their advantages.

Mixtures of water with alcohols are important in numerous engineering applications. Aqueous solutions of various alcohols were selected for investigation in this study.

THEORETICAL

The properties of mixtures are difficult to predict, because a simple mixing rule will not work when interactions among the mixture components are strong [8]. The flash point of a liquid mixture depends on the composition of the mixture and on the types of chemical involved.

Mathematically, the flash point is the temperature at which the vapour pressure is equivalent to the lower flammable limit in air:

$$LFL_i = \frac{P_{i,fp}^{sat}(T_f)}{P} \quad (1)$$

where:

$P_{i,fp}^{sat}(T_f)$ - vapour pressure at the flash point temperature, $\kappa\Pi$ а;

Π - ambient pressure, $\kappa\Pi$ а.

The vapour pressure of a mixture and consequently - its flash point is affected by the predominant interactions (intermolecular forces) among the molecules.

The flash point of a binary mixture can be estimated by the model developed by Liaw et al. [9]:

$$\sum_{i=1}^2 \frac{x_i \gamma_i P_i^{sat}}{P_{i,fp}^{sat}} = 1 \quad (2)$$

where x_i , γ_i , P_i^{sat} , and $P_{i,fp}^{sat}$ are the mole fraction, activity coefficient, vapour pressure at temperature T , and vapour pressure at the flash point of the mixture components, respectively. This model is the result of combination of equation (1) with a Le Chatelier's rule for the flammable vapour-air mixture of two components with the assumption that the liquid and vapour phase of the mixture are in equilibrium, and the vapour phase is behaving as an ideal gas.

Thermodynamically, the relation between an ideal vapour and a non-ideal liquid is represented in equation (3):

$$y_i P = x_i \gamma_i P_i^{sat} \quad \text{or} \quad y_i = \frac{x_i \gamma_i P_i^{sat}}{P} \quad (3)$$

The flash point of a binary mixture can be estimated by equation (4):

$$\frac{x_1 \gamma_1 P_1^{sat}}{P_{1,fp}^{sat}} + \frac{x_2 \gamma_2 P_2^{sat}}{P_{2,fp}^{sat}} = 1 \quad (4)$$

The temperature that satisfies equation (4) is the flash point temperature of the mixture.

A binary aqueous mixture contains water and a flammable component. Water is a non-flammable component, and therefore has no T_f . The lowest flash point that these mixtures can exhibit is the flash point of the flammable component. The prediction model for aqueous solutions is a reduced version of the original Liaw model [10]:

$$\frac{x_1 \gamma_1 P_1^{sat}}{P_{1,fp}^{sat}} + \frac{x_2 \gamma_2 P_2^{sat}}{P_{2,fp}^{sat}} = 1 \quad (5)$$

Water is assumed to be component 1 and the flammable compound is component 2. From equation (5) P_2^{sat} is:

$$P_2^{sat} = \frac{P_{2,fp}^{sat}}{x_2 \gamma_2} \quad (6)$$

Antoine's equation may be used to estimate vapour pressure:

Table 1. Parameters for the Margules, van Laar and Wilson equations [16].

System	Margules		van Laar		Wilson	
	A	B	A	B	cal/mol	cal/mol
Water (1) - Methanol (2)	0,5434	0,7923	0,5619	0,8041	520,6458	82,9876
Water (1) - Ethanol (2)	0,7947	1,6022	0,9227	1,6798	953,2792	325,0757
Water (1) - n-Propanol (2)	0,7172	2,7070	1,1572	2,9095	1396,638	906,5256
Water (1) - Isopropanol (2)	0,8976	2,3319	1,0938	2,4702	1230,208	659,5473

$$\log P_i^{sat} = A_i - \frac{B_i}{t + C_i} \quad (7)$$

The activity coefficient γ_2 can be estimated by the use of several equations, such as the Margules equation [11], the van Laar equation, the Wilson equation [12], the NRTL equation [13], or the UNIQUAC equation [14].

For an ideal solution, the activity coefficient of the liquid phase for any component is equal to unity, and equation (6) can be reduced to:

$$P_2^{sat} = \frac{P_{2,fp}^{sat}}{x_2} \quad (8)$$

FLASH POINT ESTIMATION PROCEDURE

The Liaw model was used to predict the flash point of the following binary aqueous solutions: water-

methanol, water-ethanol, water-n-propanol and water-isopropanol. The prediction results were compared with experimentally-derived data [10].

The information needed for the estimation of a binary mixture flash point is:

- flash points of the individual components of the mixture;
- vapour pressure of each mixture component;
- activity coefficient of each component.

The saturated vapour pressure of the pure substance, i , at its flash point, $P_{i,fp}^{sat}$, as presented in Eq. (5), can be estimated by substituting the flash point of component i into Antoine's equation.

The aqueous solutions are non-ideal solutions, and the activity coefficients are different than unity.

Each activity coefficient can be calculated by the Margules equation, van Laar equation or Wilson equation:

Table 2. Antoine coefficients for the involved components*.

Component	A	B	C
Methanol	8,0724	1574,99	238,7
Ethanol	8,2133	1652,05	231,48
n-Propanol	7,6192	1375,14	193,01
Izopropanol	8,1182	1580,92	219,62

$$* \lg P(\text{mmHg}) = A - \frac{B}{t[^\circ\text{C}] + C}$$

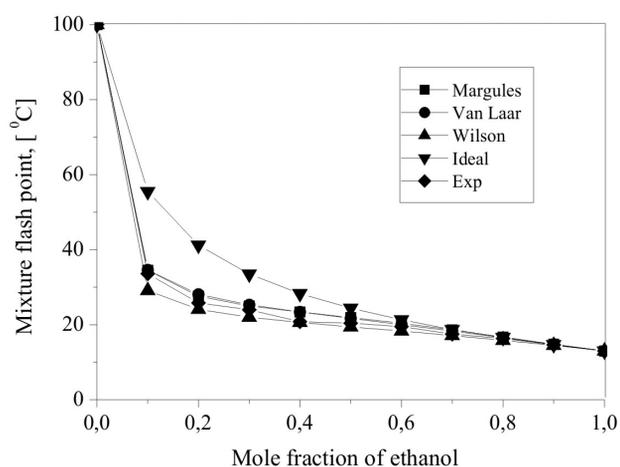


Fig. 1. Comparison of the estimated water (1)- methanol (2) mixture flash points with experimental data.

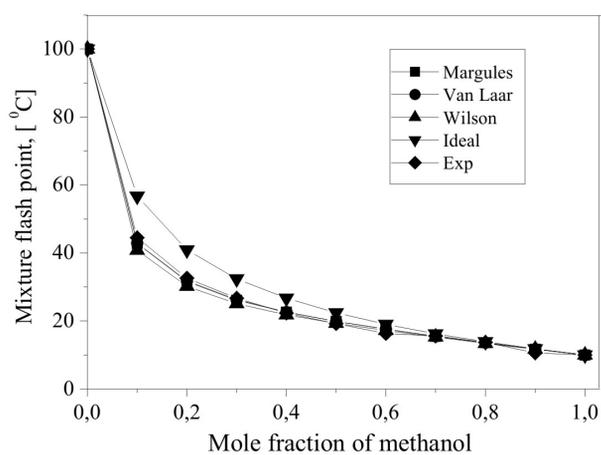


Fig. 3. Comparison of the estimated water (1)- propanol (2) mixture flash points with experimental data.

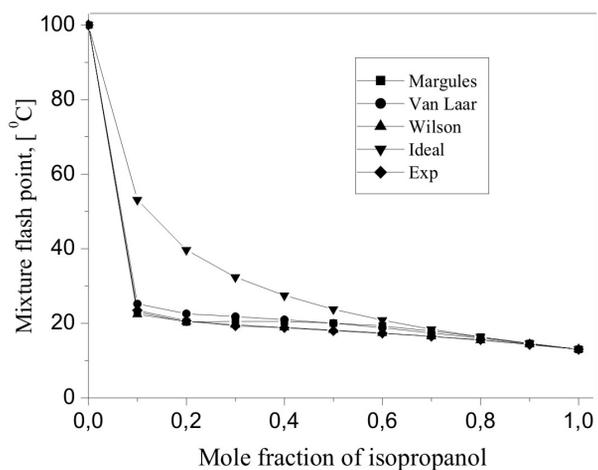


Fig. 2. Comparison of the estimated water (1)- ethanol (2) mixture flash points with experimental data.

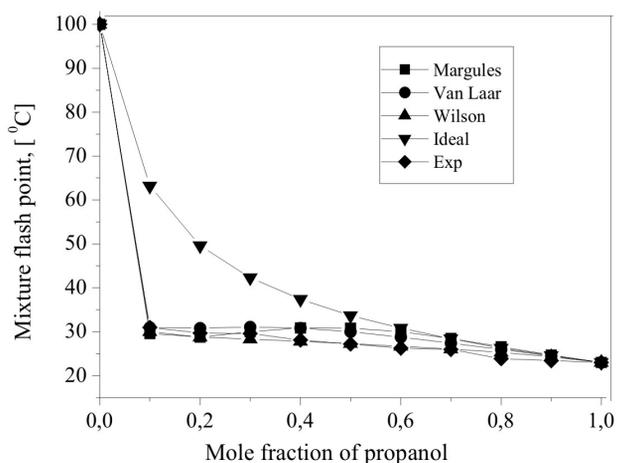


Fig. 4. Comparison of the estimated water (1)- isopropanol (2) mixture flash points with experimental data.

Table 3. Characteristics of the studied alcohols.

Component	CAS number	T_{fp} (°C)	T_{boil} (°C)	M (kg/kmol)	ρ (g/cm ³)	(cm ³ /mol)
Methanol	67-56-1	10,0	64,7	32,04	0,7867	40,73
Ethanol	64-17-5	13,0	78,4	46,07	0,789	58,68
n-Propanol	71-23-8	23,0	97,2	60,1	0,8003	75,09
Isopropanol	67-63-0	13,0	82,3	60,1	0,7853	76,53

$$V_i^* = M/\rho$$

Margules

$$\ln \gamma_2 = (B + 2(A - B)x_2)x_1^2 \quad (9)$$

van Laar

$$\ln \gamma_2 = B \left[\frac{Ax_1}{Ax_1 + Bx_2} \right]^2 \quad (10)$$

Wilson

$$\ln \gamma_2 = -\ln(x_1\Lambda_{21} + x_2) - x_1 \left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_1\Lambda_{21} + x_2} \right) \quad (11)$$

$$\Lambda_{12} = \frac{V_2}{V_1} \exp\left(\frac{-A_{12}}{RT}\right); \quad \Lambda_{21} = \frac{V_1}{V_2} \exp\left(\frac{-A_{21}}{RT}\right) \quad (12)$$

where V_i - molar volume in cm^3/mol
 R - universal gas constant cal/mol
 T - temperature in K .

RESULTS AND DISCUSSION

Flash point predictions assuming non-ideal behaviour using the different G^{ex} (an excess free Gibbs energy) models were performed by iterative calculations in MathLab.

The relevant parameters for the equations to calculate the activity coefficients from literature are listed in Table 1. The Antoine coefficients for these substances were adopted from literature sources [15] and are listed in Table 2. Table 3 presents the parameters for the pure components, needed for the application of the Wilson equation.

The predictions for the water-alcohol mixtures are presented in Figs. 1-4. Calculated flash points by using the different equations for activity coefficients are comparable with the experimental data obtained from Liaw et al [10]. Larger deviations between the ideal predicted values and experimental data are obtained with increasing water content ($x_1 > 0.8$) for the mixtures water-methanol and water-ethanol. The flash point of the water-ethanol mixture, predicted by the ideal solu-

tion model is higher - approximately 20°C , when $x_1 = 0.9$. For the water-propanol and water-isopropanol mixtures, the ideal solution model predicts higher flash points values for $x_1 > 0.4 - 0.5$. Wilson's equation is more effective for dilute compositions than Margules or van Laar equations.

CONCLUSIONS

The calculated flash points of water-alcohol mixtures are in a good agreement with experimental data. Equations for activity coefficients estimations are widely used because of their flexibility, simplicity, and ability to fit many systems. Wilson's equation is more effective for dilute compositions than the equations of Margules or van Laar.

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