New Results on Behavior of the Flash Point of Flammable Liquid Mixtures

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Background

The risk of corrosiveness, toxicity, radioactivity, flammability and irritation associated with the production and use of a vast variety of chemical substances in industry and laboratories have highlighted the need for the awareness of the potential dangers they can cause **(Faigle, 1997)**. Causes and treatments of injury from these substances are often found in Material Safety and Data Sheets (MSDS). A chemical finding serious usage is investigated to discover potential harmful effects since most chemicals can have very detrimental effects on the environment and also cause harm to humans. Among such concerns are fire hazards especially in chemical and petrochemical plants **(Belke, 1998)**. Incidents such as fire disasters have been reported to cost the chemical and petrochemical industries millions of dollars per year **(Fewtrell et al. 1998)**. The need to control or eliminate fire hazards led to the introduction of flash points of liquid chemicals being used as indicators of causing fire hazards.

The flash point of a liquid is the lowest temperature (corrected to atmospheric pressure) at which enough vapor is given off to form ignitable mixtures with air. At this temperature, the vapor burns only briefly. The flash point generally increases with increasing pressure **(Katrizky et al. 2001**). For a vapor-air mixture to ignite and burn, it must be defined over a well-bounded range of compositions. Thus, the flash point occurs between the lower flammability limit (LFL) and the upper flammability limit (UFL) for the substance, otherwise known as the explosive limits.

The flammability characteristics of these chemical substances are important safety considerations in storage, processing and handling. Knowledge of flash point behavior is very important as it is used to categorize flammable and combustible materials for handling, storage, and shipping, among other process operations. It is important for ensuring worker safety and loss prevention. Liquids with a flash point under 37.8^{o}C (100^{o}F) are considered flammable **(Wray, 1992)**.

Objective

Flash points information is lacking in the literature even for industrially important materials **(Katritzky et al. 2001)**. The increasing demand for safety in the chemical industry highlights the need for accurate flash points information for flammable material studies as well as processing. Estimation methods for the flash point of mixtures, particularly multi-component liquids, are of great interest to petroleum, paint, and other industries. Some work on mixtures has been reported previously **(Fujii and Herman, 1982)**, going back to some original work by Thiele in 1927 on lubricating oil blends. However, mixture data and estimation methods are particularly scarce. Hence, reports on the measurement and prediction of flash points for flammable liquid mixtures are both significant and needed. This study contribute to meeting that need, by (1) determining flash points for certain binary mixtures by direct measurement and (2) investigating how flash points vary with structure and composition of the constituents of the mixtures with the goal of developing prediction methods. Specific focus was on the categories of ideal and non- ideal behavior, and limited to binary mixtures. Of the millions of substances known, only a relative few of them have published flash points, thus making model for estimation very valuable for predicting flash points when experimental data is not available.

Available Data on Measured Flash Points

Flash point data corresponding to various compound solutions or mixtures appear to be scarce in the literature, with even those available (from an MSDS, typically) only valid for a specific mixture

composition. Much data on pure component flash points exist, however, and are available from a variety of sources.

- For this study, many literature sources of data were found using a computerized search of Compendex (the Comprehensive Engineering Index, a database inclusive of a broad range of engineering and scientific journals) and Science Direct.
- The Mary Kay O'Connor Process Safety Literature Database at Texas A&M University, contains a substantial amount of useful published data.
- Vapor-Liquid Equilibrium Data Collection; DECHEMA Chemistry Data Series, Vols.1, 9,20, was useful particularly for thermodynamic model interaction parameters.
- The handbook by the National Fire Protection Association **(NFPA 325, 1994)** contains much useful information, including flash points for thousands of pure compounds.
- Material Safety and Data Sheets also called (MSDS) are a standard source of information on substance characteristics, including flash point. MSDS are available online from a variety of sources, including vendor websites for the major sellers of chemicals.

Prediction Methods for Mixture Flash Points

We would like to be able to easily predict flash points for flammable mixture when only a small amount of basic data is available. Fortunately, there is prior work on which to build **(Liaw and Chiu, 2003).** Various models were developed as part of this work to predict flash points building on the work of Liaw and Chui, who developed thermodynamic models, based on Raoult's law, introducing activity coefficients where necessary, to predict flash points and then compared the model predictions to results from experiments.

Measurement of Mixture Flash Points

The work reported here was undertaken to obtain new flash point data for binary mixtures, to add to the existing body of knowledge and to provide measured results for model comparisons. Binary liquid mixtures, some expected to exhibit ideal solution behavior and while others non-ideal behavior, were mixed from stocks of the respective pure components. Samples of the mixtures created in the laboratory were examined using a flash point tester. Specifically a Normalab Pensky-Martens NPM-440 commercially available tester (shown in Figure 1) was used to measure flash points using the ASTM D93 protocol, which the tester performs automatically one sample at a time. Detailed description of the flash point tester is reported elsewhere, along with test procedures (**Kwabbi, 2005**).

Figure 1 The Normalab Analis automatic Pensky-Martens flash point tester.

Experimental Results for Pure Components

Several studies have been done on the relationship between flash points and molecular properties for pure organic compounds **(Lance et al 1979).** Hence, it is known that flash point is varies

directly with boiling point and inversely with vapor pressure at a given temperature. This linear relationship is observed for all different classes of hydrocarbons including paraffins, olefins, naphthenes and aromatics **(Albahri, 2003).** In a previous effort, to benchmark our method, we investigated pure component flash point for straight chain hydrocarbons and alcohols **(Sonaike, 2004).** The results (presented in Figure 2) confirm the linear dependency of flash point on alkyl chain length for these two families of compounds, having such simple structures.

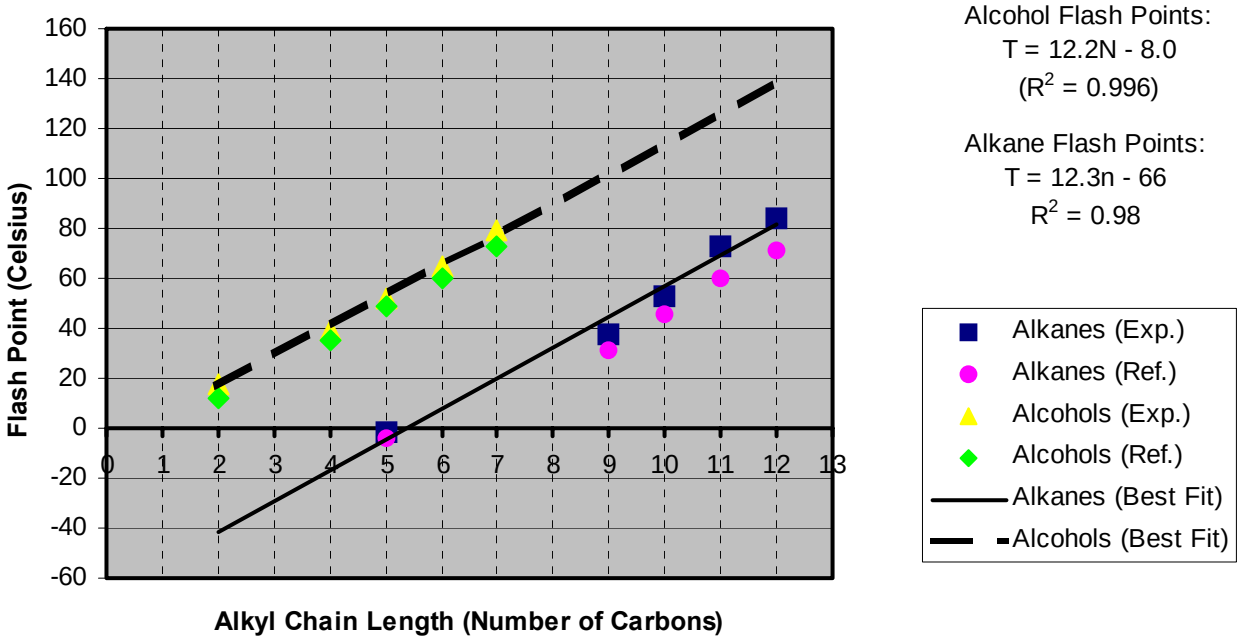


Figure 2 Comparison of the variation of flash point with alkyl chain length for series of normal alkanes and alcohols.

From the slope of the lines, there is clearly a 12°C rise in flash point for each methylene group added to the alkyl chain, both for alkanes and alkanols..

The flash point of organic compounds has been found to correlate well with the vapor pressure and boiling points **(Affens, 2002; Satyanarayana et al. 1992; Crowl and Louvar, 1990)**. This was confirmed by experiment, when measured flash points were plotted against published values of boiling point, for pure component alkanes and alkanols in this study. Also, the complexity of the molecular structure of the compound is another important factor affecting the flash point. Flash points of hundreds of hydrocarbons examined showed that their molecular structures were very significant. For example, the flash point of iso-paraffins depends not just on the number of carbon atoms in the alkyl chain, but also to a great extent on the degree of branching—on the number, length, and location of the branch along the hydrocarbon chain. This is easily seen by adding flash point values for branched alkyl chain alkanes and alkanols to the plot shown in Figure 2. In contrast, the flash point of straight chain hydrocarbons and alcohols are linear with respect to the number of carbon atoms, as we have seen.

Experimental Results for Binary Mixtures

Sonaike et al. reported previously on the behavior of binary mixtures for alkanes and alkanols, both mixes within each family series and mixtures across families. As expected from known vapor-liquid equilibrium behavior for these families of compounds, the flash point data corresponded well to predictions based on an ideal solution thermodynamic model for flash point prediction (**Sonaike, 2004**).

An example of this behavior is shown in Figure 3, for a binary mixture of *n*-butanol and *n*-pentanol. Some mixtures with non-ideal behavior were generated also by mixing members of the simple, straight chain, families with ethyl benzene, priopionic acid, or butyl acetate.

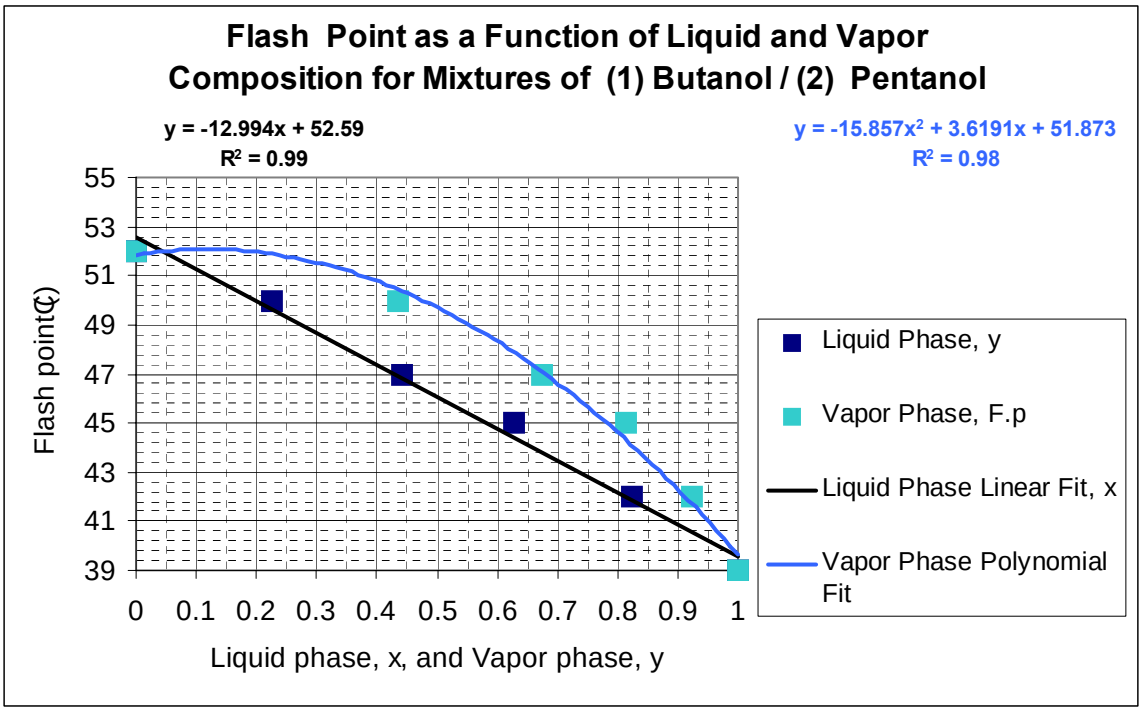
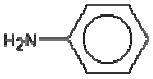
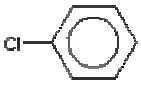
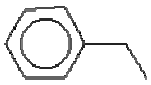


Figure 3 Flash Points as a Function of Vapor Liquid Composition for the Binary Mixture of (1) Butanol / (2) Pentanol.

For this latest study, increased focus was placed on non-ideal mixtures. The components used to form binary mixtures are shown in Table 1.

Table 1 Compounds Used to Form Binary Mixtures for Flash Point Behavior Studies

Component	Molecular Structure	Stated Purity [a] %	Flash Point [b] °C
Acetonitrile C_2H_3N		99.9+	6
Aniline C_6H_7N		99.8+	70
Chlorobenzene C_6H_5Cl		-	28
Ethanol C_3H_5OH		-	13

Ethylbenzene C_8H_{10}		99.9+	21
Nitromethane CH_3NO_2		99.9+	35

[a] Information provided by the vendor, Fisher Scientific, Inc.
[b] Reported values obtained from MSDS or NFPA handbook.

These compounds were chosen because of their economic importance to process industry in combination with their availability and affordability. For each binary system chosen, several compositions selected to range across the mole fraction scale (from near zero to near 1) and mixtures were created, after which samples were taken and used to make flash point measurements with the test device. A typical set of results is shown in Figure 4, where experimental results (plotted points) are compared with predictions of the Van Laar thermodynamic model, using published interaction parameters. Other systems studied are shown in Table 2.

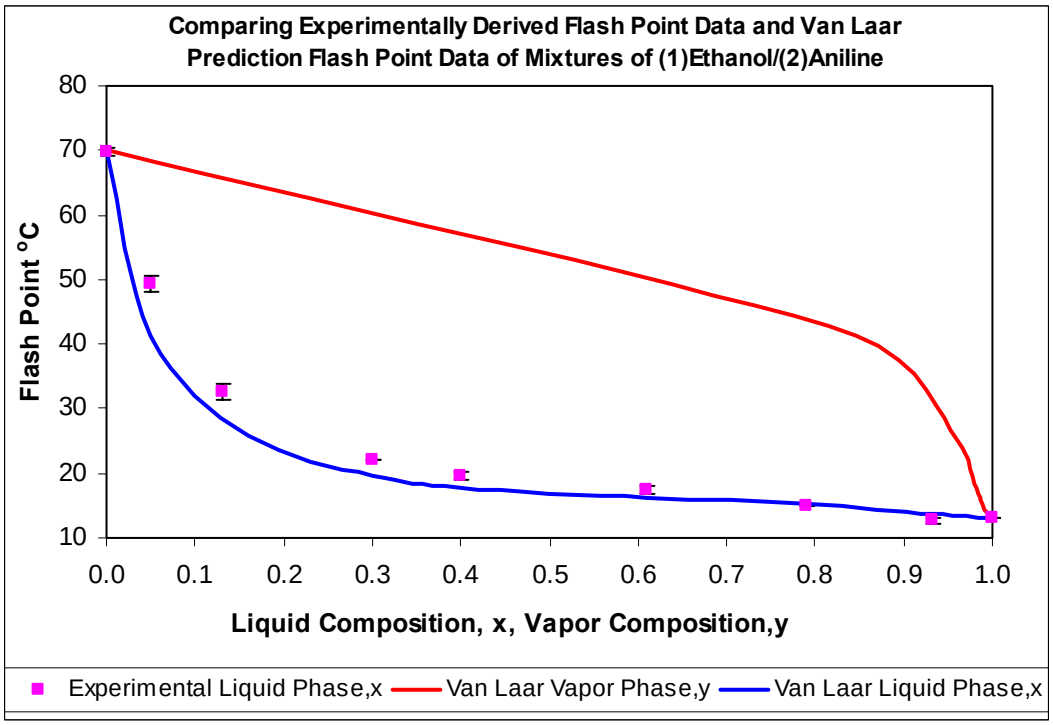


Figure 3 Flash Points as a Function of Vapor Liquid Composition for the Binary Mixture of (1) Butanol / (2) Pentanol.

Several thermodynamic models were investigated. These range of models includes an ideal solution model; zero-parameter, structure based models; and one-, two-, and three-parameter models requiring measured or estimated parameter data. The models are used for VLE of the mixtures being studies. The models used are listed below.

- Rault's Law
- Two –Suffix Margules Equation
- NRTL Equation
- UNIQUAC Equation

- Van Laar Equation
- Wilson Equation
- Scatchard-Hildebrand Solution Theory
- One-parameter Regular Solution Model

Summary of Results Using Regular Solution Model

Comparison of model predictions with measured mixture flash point data for the several models studies, using literature values for model parameter where required, showed varied results; with no one model able to model the entire range of behavior, from ideal solution behavior to systems showing lard deviations from ideal solution theory predictions. One model was successful in correlating behavior for all for systems. The regular solution theory, formulated based on one system-specific parameter was used to provide a good fit to data for all systems. The resulting parameter (*W*) values, for all six systems studied, are tabulated in an increasing order of W values. These are shown in Table 2.

Table 2 Regular Solution Parameter Results for Non-Ideal Mixtures Based on Best Model Fit to Measured Flash Point Data

Binary Mixture	**Parameter W cal/mol°K**
(1) Acetonitrile/ (2) Aniline	-350
(1) Acetonitrile/ (2) Nitromethane	50
(1) Chlorobenzene/ (2) Ethylbenzene	51
(1) Chlorobenzene/ (2) Aniline	450
(1) Ethanol/ (2) Aniline	650
(1) Ethanol/ (2) Nitromethane	880

Discussion of Results

The one-parameter regular solution model casts the excess free energy of mixing as the parameter reflecting the degree of departure from ideality (**Osborne-Lee, 1985**). For the ideal solution, there is no excess free energy of mixing and thus the parameter *W* is zero. For the current study, no attempt has been made to predict the quantitative value of W; to do so is an interesting challenge, which we now leave for future work. Rather, the value of W is obtained from best fits of the model to measured flash point data in the case of each binary mixture system. The values thereby obtained give information on the relative degree of non-ideality of each system, with a quantitative measure of "distance" from ideality. Hence, the most ideal system shown in Table 2 is acetonitrile/nitromethane or chlorobenzene/ethylbenzene (since the *W* values are so close, the difference of 1 Cal/mol°K.is not meaningful), while the most non-ideal system is clearly ethanol/nitromethane.

Further, the one-parameter regular solution model is obtained by assuming no excess entropy of mixing. Since $\Delta G = \Delta H - T\Delta S$, then $\Delta S = 0$ means that W is equivalent to ΔH, which in this case is the excess enthalpy of mixing. Thus the values obtained in Table 2 represent a measure of the excess enthalpy occurring on the mixing of the respective binary systems.

Conclusions

This study has provided new measured flash point data for systems not previously reported, in addition to confirming some previously reported findings. Various models were studied, with mixed results. One clear finding is that the one-parameter regular solution model is very useful for describing flash point behavior in binary mixtures, with the added value of there being clear significance to the single parameter. While found in this study by adjustment to fit a series of experimental measurements,

in future the potential exists to predict this parameter, $W = [\Delta H^{Mixing}]_{Excess}$ based on such a familiar quantity.

Acknowledgements

The authors gratefully acknowledge the assistance of the State of Texas Coordinating Board, for valuable support in the form of a grant through the Applied Technology Program. We also express appreciation for our partners in this project at Texas A&M University, in the Chemical Engineering Department and the Mary Kay O'Conner Process Safety Center, particularly Dr. Bill Rodgers.

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