FLASH POINT FOR BINARY MIXTURES

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ABSTRACT

Three flammable binary systems were studied for flash point as a function of liquid mixture composition: 1) decane/dodecane, 2) O-xylene/cyclohexanol, and 3) 2-propanol/water. The vapor composition was estimated at each liquid mixture for which a flash point was obtained and these results were compared to the mixing rule proposed by Le Chatelier. This comparison shows that excellent agreement is obtained where the vapor composition can be accurately predicted, such as the nearly ideal case of system 1, but that for systems 2 and 3, where the composition calculations were made from the UNIFAC model and the Wilson model respectively, the agreement was not as good.

INTRODUCTION

Flash point is a widely used index of hazard for the manufacture, transportation, and utilization of flammable liquids. It can also be used to detect contamination of a liquid hydrocarbon by other more flammable liquids, e.g. gasoline contamination of diesel fuel.

The flash point test utilizes a standardized procedure and apparatus which conforms to ASTM D93. The primary components for the apparatus are the sample cup with stirrer, a heater, a pilot flame, and, for the case of the closed cup test, a shutter which can open and expose the vapor space above the sample to the pilot flame at specified intervals as the temperature of the sample is raised.

Although many manufactured liquids are refined to a high purity and are essentially a single component system, many other liquids, such as gasoline, crude oil, etc, are mixtures. Thus the flash point of mixtures represents a composite influence of each liquid present which exerts a vapor pressure. Le Chatelier, 1891, proposed a model for how the contributions of each component can be summed to contribute to the flammability of the mixture. This model was

experimentally verified by Affens, 1967, for binary mixtures which formed ideal solutions. Mullins, 1957, considered multi-component ideal mixtures, and while not explicitly utilizing Le Chatelier's rule, nevertheless obtained empirical correlations from the data which are consistent with that rule. Thorne, 1976, considered mixtures of flammables with non-flammables to understand the flame suppression effects of halogenated compounds. Gmehling and Rasmussen, 1982, applied the UNIFAC method to predict the flash point of several non-ideal binary mixtures and found significant improvement over Raoult's law predictions.

It is the objective of this paper to report data for three binary systems and investigate how well vapor composition models can be applied with Le Chatelier's rule to predict the flash point of binary systems in general.

MODEL

In order to discuss an analytic treatment of the problem, the events of the flash point test will be described. As the liquid sample in the cup is heated, its vapor will be more or less confined to the space above the liquid surface. Since the cup is not sealed, only restricted, ambient air will mix with these vapors. Until the composition reaches the lower flammability limit, ignition (or flash) will not be achieved. As heating of the sample continues, the vapor pressure of the liquid continues to rise until the lower flammability limit is reached and flash occurs when the vapor space is exposed to the pilot flame.

When the liquid is a mixture of two or more components, each will exert its own vapor pressure and the resulting flash point will be different from that of any of the pure constituents. Le Chatelier's rule for flammability of a solution can be written:

$$\sum_i \frac{y_i}{Y_i} - 1 \qquad (1)$$

where y_i is the actual vapor composition in air of component i at the flash point and Y_i is the lower flammability limit for pure component. For economy of expression in the rest of the paper, the summation on the left side of equation (1) will be written CSUM. (Since the flash point temperature will not normally be the same temperature at which the lower flammability limit or lfl has been measured, it is important to note that, in general, the temperature effect on lfl is not large and is frequently not available). To use equation (1), Y_i must be either measured or known from other sources and yi can be estimated from vapor-liquid equilibria. In the case of ideal mixtures, Raoult's law can be utilized, provided that vapor

pressures of the pure components can be obtained. However, for the general case, the vapor-liquid relationship will be described by

$$y_i \phi_i P = x_i \gamma_i P_i^{sat} \quad (i=1,2,....) \tag{2}$$

where ϕ_i = fugacity coefficient of component i in the vapor mixture
γ_i = activity coefficient of component i in the liquid mixture
P = total pressure
P_i^{sat} = vapor pressure of component i at the system temperature
x_i = mole fraction of component i in the liquid mixture

For flash point measurements, the total pressure is ambient, and the vapor phase can be treated as an ideal gas where $\phi_i = 1$ (see Smith and Van Ness, 1987). The vapor pressure P_i^{sat} may be available experimentally (see Perry's Handbook, 1984) or can be estimated from an equation such as Antoine's equation, if the required constants are known. Thus, in order to obtain a value for y_i, γ_i remains to be found.

In the simplest case, where the liquid mixture is ideal, the activity coefficient will be unity (as well as will be the fugacity coefficient) and equation (2) will reduce to Raoult's law. For non-deal mixtures, Margules, Van Laar, Wilson, NRTL or UNIQUAC models may be utilized provided that the appropriate parameters are available for the mixture of interest. Where they are not, parameters can be estimated using the UNIFAC group contribution method. Obviously, the accuracy in applying this procedure is limited by the accuracy of prediction of the vapor composition. If the model is accurate over the entire range of composition, then the prediction should be accurate.

To adequately test this treatment, three systems were chosen which exhibited a range in phenomenology: a very near ideal binary, a definitely non-ideal binary and finally a non-ideal binary which included a non-flammable component.

DATA
Decane/Dodecane

The first system studied was the nearly ideal binary system of decane-dodecane. Seven different liquid compositions were tested, varying form pure decane to pure dodecane. The flash point data for various x_i are shown in Table 1, along with computed values for P_i^{sat} from Antoine's equation, and y_i from Raoult's law. Also shown is the final calculated value for CSUM for each test.

Table 1: Flash Point Results for various Mixtures of Decane/Dodecane and Calculated Values of CSUM using Raoult's Law for Vapor Composition

No.	Flash Point (°C)	x_1	x_2	P_1^{sat} (mm Hg)	P_2^{sat} (mm Hg)	y_1	y_2	CSUM
1	51	1.000	0	6.83	0.90	0.00899	0	1.000
2	56	0.778	0.222	9.05	1.26	0.00926	0.00037	1.072
3	60	0.539	0.461	11.2	1.64	0.00797	0.00099	0.998
4	68	0.280	0.720	17.0	2.71	0.00627	0.00257	0.988
5	76	0.115	0.885	25.1	4.33	0.00380	0.00504	0.992
6	80	0.058	0.942	30.3	5.42	0.00231	0.00672	1.015
7	84	0	1.000	36.3	6.73	0	0.00886	1.000

Note: x_1 represents liquid mole fraction decane and y_1 represents vapor mole fraction decane

In comparison of the flash point in Table 1 for pure decane and pure dodecane to literature values, one finds some minor discrepancy. This discrepancy could arise from various sources but is most probably due to sample purity, the flammability limit being measured at a temperature different from the flash point and/or slight variations in the test procedure. Even amongst other values reported in the literature and by the manufacturer of the chemicals themselves, there is almost always found at least a small discrepancy.

O-xylene/Cyclohexanol

The second binary system studied was o-xylene/cyclohexanol. Although both are cyclic and somewhat polar, one is aromatic and the other is not. Therefore, a rather high degree of non-ideal behavior could be expected. Table 2 summarizes the results for six mixtures varying from pure o-xylene to pure cyclohexanol. The vapor composition was estimated by either of two methods: Raoult's law, and by the UNIFAC method as discussed in Smith and Van Ness, 1987. Vapor pressures were estimated using interpolation of experimental data for cyclohexanol, found in Perry's Handbook, 1984, and by Antoine's equation for o-xylene.

Again, some minor deviation of the flash points of Table 2 for the pure components with reported values can be noted.

2-propanol/water

The final binary system studied was 2-propanol/water. This combination was expected to be non-ideal, as was the second system, but with the added complication that one component was not flammable. Table 3 summarizes the results for seven mixtures, all for which ignition or flash, was achieved. The calculated values for CSUM were again based on 2 methods: Raoult's law, and a model for non-ideal mixtures. The model chosen is described by the Wilson equation because the needed parameters were available in Smith and Van Ness, 1987 for this combination. Again, Antoine's equation was utilized for the vapor pressures shown.

It is interesting to note that ignition of the 2-propanol/water system can be achieved to as low a concentration of 2-propanol as 0.72% (molar).

General

In collecting the data, each test was repeated at least once to verify reproductibility. If the flash point temperatures deviated by more than 1°C,

Table 2: Flash Point Results for Various Mixtures of O-Xylene/Cyclohexanol and Calculated Values of CSUM using Raoult's Law and the UNIFAC Method for Vapor Composition

No.	Flash Point (°C)	x_1	x_2	P_1^{sat} (mm Hg)	P_2^{sat} (mm Hg)	y_1^*	y_2^*	y_1^{**}	y_2^{**}	CSUM*	CSUM**
1	32	1.00	0	9.87	1.29	0.0130	0	0.0130	0	1.00	1.00
2	33	0.726	0.274	10.4	1.39	0.0100	0.00050	0.01144	0.00084	0.806	0.944
3	35	0.468	0.532	11.6	1.62	0.00717	0.00113	0.00950	0.00142	0.642	0.852
4	39	0.227	0.773	14.5	2.18	0.00432	0.00222	0.00791	0.00229	0.509	0.791
5	46	0.089	0.911	20.7	3.59	0.00242	0.00430	0.00514	0.00508	0.529	0.799
6	61	0	1.00	42.2	9.57	0	0.00126	0	0.0126	1.00	1.00

*   by Raoult's Law
**   by UNIFAC Method
Note: x_1 represents liquid mole fraction o-xylene and y_1 represents vapor mole fraction o-xylene

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Table 3: Flash Point Results for varous Mixtures of 2-Propanol/Water and Calculated Values of CSUM using Raoult's Law and the Wilson Equation for Vapor Composition

No.	Flash Point (°C)	x_1	x_2	P_1^{sat} (mm Hg)	P_2^{sat} (mm Hg)	y_1^*	y_2^*	y_1^{**}	y_2^{**}	CSUM*	CSUM**
1	14	1.000	0	22.2	11.7	0.0292	0	0.0292	0	1.000	1.00
2	19	0.415	0.585	30.8	16.1	0.0168	0.0124	0.0277	0.0185	0.525	0.947
3	22	0.191	0.809	37.2	19.5	0.00936	0.0207	0.0290	0.0236	0.320	0.992
4	28	0.0730	0.927	53.7	27.9	0.00515	0.0341	0.0312	0.0354	0.176	1.07
5	41	0.0256	0.974	111.8	57.8	0.00377	0.00741	0.0344	0.6744	0.129	1.18
6	53	0.0123	0.988	206.9	106.0	0.00335	0.138	0.0340	0.138	0.115	1.17
7	63	0.0072	0.993	332.1	170.0	0.00315	0.223	0.0325	0.223	0.108	1.11

* by Raoult's Law
** by Wilson Equation
Note 1: x_1 represents liquid mole fraction 2-propanol and y_1 represents vapor mole fraction 2-propanol
Note 2: Values of CSUM include 2-propanol only since water is not a flammable component

additional tests were conducted until reproducible results were obtained. The reported values for flash point temperature are the average of the consistent set of raw data, rounded to the nearest degree.

In Tables 1,2, and 3, the value utilized for Y_i was taken as the value of y_i for the pure component test. This value of Y can be compared to the lower flammability limit found in the literature. Where the literature data were available, the agreement was quite reasonable, e.g. for 2-propanol, literature values of 2.0% to 2.3% are reported, which compares to a value of 2.9% from Table 3. Similarly, the reported values of flash point temperature vary from 12°C to 22°C, compared to the value in Table 3 of 14°C. Again, these variations probably result from variable sample purity, test temperature differences and/or variations in the test method. More specifically, the flash point test procedure/apparatus differs somewhat from those for determination of the lower flammability limit, which follows ASTM E 681.

In performing the calculations for liquid and vapor composition, air was assumed to be of negligible solubility in the liquid phase, so that $x_1 + x_2 = 1$. However, $y_1 + y_2 \neq 1$ because the third component was air, whose concentration can be calculated by $y_3 = 1-y_1-y_2$.

DISCUSSION

In order to address the objective of this study, that is to determine the applicability of Le Chatelier's rule to the general case, the value of CSUM for each test should be compared to unity, i.e. as in equation (1).

For the case of decane/dodecane, excellent agreement is found. Of course, the mixture is expected to be very nearly ideal, and the vapor composition can apparently be accurately calculated using Raoult's law. This observation, as stated previously, was also made by Affens, 1967.

For the system of 0-xylene/cyclohexanol, very large departures of CSUM from unity are noted when the vapor composition is calculated using Raoult's law. The agreement is much improved, however, when the UNIFAC method was utilized to calculate vapor composition. The deviation which remains is tentatively attributed to the fact that the UNIFAC method is based on summation of group contributions and not on experimental data for this binary system. Were the required data for applying one of the other VLE equations available, then better agreement would be expected.

For the system 2-propanol/water, the vapor composition was again estimated using Raoult's law and very significant departures of CSUM from unity were again found, particularly at the dilute concentrations of 2-propanol. For this binary, the required data were available for the Wilson equation (see Smith and Van Ness, 1987) and the results based on this vapor composition calculation are much improved over the ideal system calculation. In fact, the sum of the positive and negative departure of CSUM from unity appears to be nearly zero over this range of values.

Now, how do these observations impact the objective of this study? By returning to the assumption previously made for the vapor phase, that the fugacity coefficient is unity, the implication is that the vapor phase can be treated as an ideal gas. Since Le Chatelier's rule makes no assumption as to how the vapor composition is achieved, then it should be valid, regardless of the ability to calculate vapor phase composition from liquid phase composition. This then, is the limitation to the general application of the rule. Although the general applicability of Le Chatelier's law has not been "proven" by either the arguments above or by the data presented here, it is easy to observe that the comparison of CSUM to unity is improved as the description of the vapor phase composition has improved, i.e. Wilson equation (with experimental parameter) gives better results than UNIFAC (with estimated parameter) which in turn is better than Raoult's law (which assumes that the activity coefficients are all unity for non-ideal mixtures).

If the premise is accepted that Le Chatelier's rule has general utility, then the flash point test may be a simple and valid method for obtaining the binary interaction parameters for non-ideal liquid mixtures. A more exhaustive future study should be designed to focus specifically on this issue.

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