

Flashpoint of Battery Mixtures in Order to Improve their Safety

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The flammability of solvents and electrolytes is an important aspect of the thermal safety behavior of Li-ion batteries. The inherent safety of a cell is determined by the safety of each component as well as by the interactions between the single components. At present, most of the commercial lithium battery cells utilize organic solvents to dissolve the lithium salts. To obtain a complete picture of these chemical systems, safety should be assessed on multiple levels. The flashpoints have been measured according to the Abel closed-cup methods using the pure liquids and bottled propane-butane gas flame. The effect of the mixing of two-flammable solvents is analyzed. As an alternative to their experimental determination, the flashpoints of the pure solvents have been calculated from other physical and chemical properties of the substance, and the flashpoints of the solvent mixtures and electrolytes from the flashpoints of their flammable constituents. The most important results from evaluated experiments are the values of flashpoints for methanol-ethanol, methanol-1-propanol, methanol-1-butanol, ethanol-1-butanol, propanol-1-butanol-air mixtures. These values are used to be compared with the currently available physical-chemical models describe the effect of isomer blends on a deflagration process and to rate the effects of an explosion.

1. Introduction

Lithium-ion batteries have been widely used in electric vehicles, portable devices, grid energy storage, etc., especially during the past decades because of their high specific energy densities and stable cycling performance. Accidents related to fires and explosions of lithium-ion occur frequently worldwide, especially involving cell phones, laptops, electric vehicles, and airplanes. Some have caused serious threats to human life and health and have led to numerous products recalls by manufacturers. The organic liquid electrolyte inside lithium-ion battery is intrinsically flammable. The key parameter to characterize the flammability of the substances is flashpoint. The flashpoint is defined as the lowest temperature at which a liquid generates flammable vapours which can be ignited in air by a flame above its surface (Janès and Chaineaux, 2013). For the classification of flammable liquids data on flash point are needed. Data can be determined by testing, found in literature or calculated. If data are not available, the flash point and the initial boiling point shall be determined through testing. For flash point determination a closed-cup method shall be used (ECS, 2008). For a mixture containing non-volatile components the flash point is calculated from the volatile components. It is considered that a non-volatile component only slightly decreases the partial pressure of the solvents and the calculated flash point is only slightly below the measured value (ECS, 2008). Hess et al. (2015) discussed flammability of Li-ion battery electrolytes issues. Cui et al. (2018) reviewed materials for lithium-ion battery safety. Skřínský et al. (2015a) introduced the flashpoint prediction for binary mixtures of alcohols with water. Skřínský et al. (2015b) presented mathematical prediction of binary mixtures flash-points. Skřínský et al. (2015c) introduced flash-point prediction for industrial applications. Liaw and Lakzian, (2021) considered two-liquid (NRTL), Wilson, original universal quasi-chemical functional-group activity coefficients (UNIFAC) and UNIFAC-Dortmund models were used to predict the activity coefficients of the binary and ternary constituents. Liquid blends of solvents are more commonly used in industry. The flash point of the mixture could be lower than those of its pure components. The present article origins of lithium-ion batteries safety issues and highlight recent key progress in materials design.

2. Experimental

2.1 Procedure

The sample container is filled to the volume capacity requirement specified in (EN ISO 13736, 2021). The test cup is filled with the test specimen to the filling mark inside of the test cup. The temperature of the test cup and test specimen is at least 18°C below the expected flash point. If too much test specimen has been added to the test cup, the excess was removed using a syringe. The test cover has been placed on the test cup and the assembly have been placed into the apparatus. The temperature measuring device was inserted into its holder. The test flame was light and adjusted to a diameter of 3.2 to 4.8 mm. Gas pressure should not be allowed to exceed 3 kPa otherwise it will not ignite the vapors in the test cup, and the gas for the test flame that then enters the vapor space can influence the result. The heat has been applied at such a rate that the temperature, as indicated by the temperature measuring device, increases 5 to 6°C/min. The stirring device has been turned at 90 to 120 rpm, stirring in a downward direction. All details relating to the ignition source, size of test flame or intensity of the electric ignitor, rate of temperature increase, and rate of dipping the ignition source into the vapor of the test specimen is desirable for good results.

2.2 Apparatus

A typical assembly of the apparatus is shown in Figure 1.

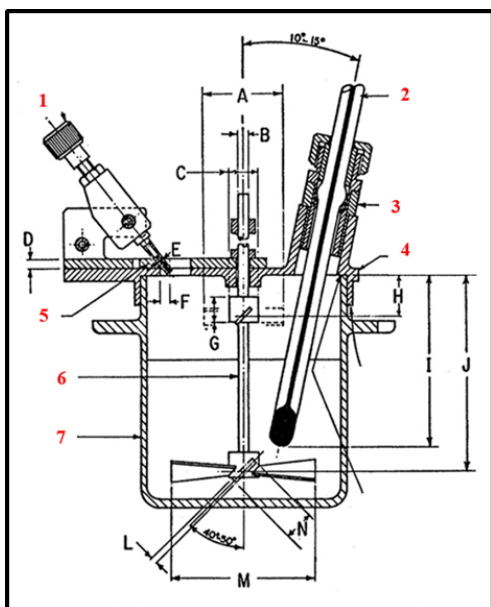


Figure 1: Test cup and cover assembly

Test cup and cover assembly consists of 1) flame-ignition device, 2) low-range thermometer, 3) adaptor, 4) cover proper, 5) shutter, 6) stirring Device, 7) test cup. A-N are dimensions given by the standard (EN ISO 13736, 2021). The test cup is of brass, and conforms to the dimensional requirements in standard (EN ISO 13736, 2021). The flange is equipped with devices for locating the position of the cup in the stove. A handle attached to the flange of the cup is a desirable accessory. The shutter is of brass and is so shaped and mounted that it rotates on the axis of the horizontal centre of the cover between two stops, so placed, that when in one extreme position, the openings A, B, and C in the cover are completely closed, and when in the other extreme position, these openings are completely opened. The mechanism operating the shutter is of the spring type and constructed so that when at rest the shutter shall exactly close the three openings. When operated to the other extreme, the three cover openings are exactly open and the tip of the exposure tube is fully depressed. The stirring device is mounted in the centre of the cover and carrying two 2-bladed metal propellers. In Figure 1 lower propeller is designated by the letters L, M, and N. This propeller measure approximately 38 mm from tip to tip, with each of its two blades 8 mm in width with a pitch of 45°. The upper propeller is designated by the letters A, C, and G. This propeller measures approximately 19 mm, tip to tip, each of its two blades is also 8 mm in width with a pitch of 45°. Both propellers are located on the stirrer shaft in such a manner that, when viewed from the bottom of the stirrer, the blades of one propeller are at 0 and 180° while the blades of the other propeller are at 90 and 270°. A stirrer shaft is coupled to the motor by a flexible shaft or a suitable arrangement of pulleys.

2.3 Materials tested

The apparatus was validated by Certified Reference Material (CRM, Rofa France). CRM is a stable, pure (> 99 moles % purity) hydrocarbon or other stable petroleum product with a method-specific flash point established by a method-specific interlaboratory study. The flammable solvents selected for these tests are listed in Table 1.

3. Calculations

Table 1: List of commercial materials used

Symbol	Chemical	Formula	Purity	Water	Company	Flashpoint
M	Methanol	CH ₄ O	≥ 99.8 %	< 0.05 %	Merck	11.0 ± 0.4 °C
E	Ethanol	C ₂ H ₆ O	≥ 99.0 %	< 0.10 %	Penta	13.0 + 0.3 °C
P	1-Propanol	C ₃ H ₈ O	≥ 99.5 %	< 0.10 %	Merck	21.0 ± 0.2 °C
B	1-Butanol	C ₄ H ₉ O	≥ 99.0 %	< 0.05 %	Sigma-Aldrich	37.0 ± 0.3 °C

4. Calculations

Table 2: Physical properties of the pure component (Skřínský, 2015a)

Parameters	Methanol	Ethanol	1-Propanol	1-Butanol
A	82.718	73.304	84.664	106.294
B	-6.90·10 ³	7.12·10 ³	-8.30·10 ³	-9.87·10 ³
C	-8.86	-7.14	-8.576	-1.165
D	7.47·10 ⁻⁶	2.56·10 ⁻⁶	7.51·10 ⁻¹⁸	1.08·10 ⁻¹⁷
E	2.00	2.00	6.00	6.00
ΔT [K]	175-512	159-514	146-536	183-563
R	1.4311	2.1055	2.7799	3.4543
q	1.432	1.972	2.512	3.052
ρ	0.7867	0.7850	0.8003	0.8097
MW	32.05	46.07	60.10	74.12
v _i	40.73	58.68	75.09	91.54

Table 3: Parameters of the Wilson, NRTL, and UNIQUAC equations (Skřínský, 2015a)

Mixture	Wilson		NRTL		UNIQUAC		
	A ₁₂	A ₂₁	A ₁₂	A ₂₁	α ₁₂	A ₁₂	A ₂₁
M+E	68.350	-66.460	-13.178	9.519	0.300	-238.940	383.900
M+P	70.540	-66.790	110.500	-126.320	0.305	-187.480	280.610
M+B	253.800	707.800	-0.556	-0.071	0.304	513.740	-132.250
E+B	-341.320	1,159.440	2,4357.060	-17,972.670	0.043	3,602.950	-2,060.510
P+B	-35.220	56.870	4,151.270	-3,027.730	0.300	2,512.930	-1,793.080

$$\log p_i^s = A_i + \frac{B_i}{T} + C_i T + D_i T^{E_i} \quad (1)$$

$$G^E = \frac{g^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12} x_2) - x_2 \ln(x_2 + \Lambda_{21} x_1) \quad (2)$$

$$G^E = \frac{g^E}{RT} = x_1 x_2 \frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \quad (3)$$

$$\ln \gamma_i = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + \phi_i \left(l_i - \frac{r_i}{r_j} l_j \right) - q_i \ln(\theta_i + \theta_j \tau_{ji}) + \theta_j q_i \left[\frac{\tau_{ji}}{\theta_i + \theta_j \tau_{ji}} - \frac{\tau_{ij}}{\theta_j + \theta_i \tau_{ij}} \right] \quad (4)$$

5. Results

The present paper represents the flashpoint concentration temperature of binary alcohol mixtures by a physical-chemical calculation allowing flashpoint to be predicted when only the concentration of one flammable component (x_2) and flashpoint of pure substance is known. Binary alcohol mixtures are good examples of both ideal and non-ideal behaviours, allowing the flashpoints to be calculated by different thermodynamic models as prediction procedures. The procedure presented here for the estimation of the alcohol-alcohol binary mixture flashpoints useful for the assessment of flammability hazards because it saves time and effort by providing the user with techniques and resources that can be applied to estimate parameters and obtain input data that are needed for the determination of mixture flashpoints. The experimental data with the predictions is presented in Figures 2-6.

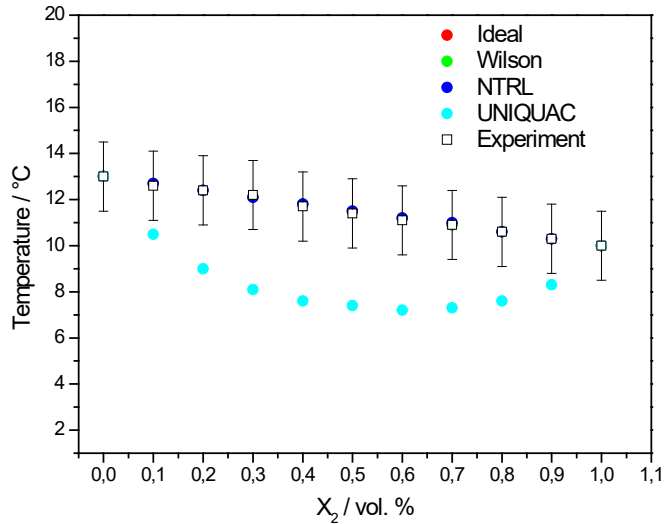


Figure 2: Comparison of predicted flashpoint and experimental data for methanol (1) + ethanol (2)

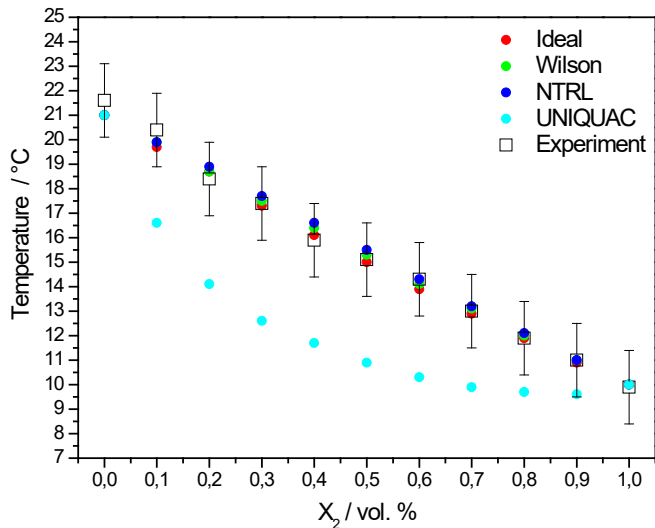


Figure 3: Comparison of predicted flashpoint and experimental data for methanol (1) + 1-propanol (2)

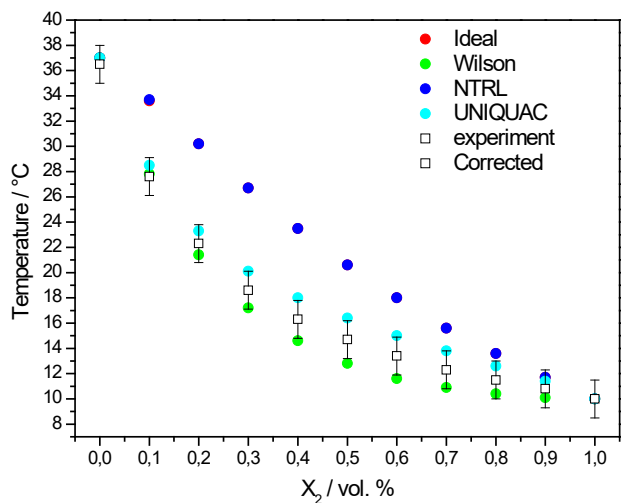


Figure 4: Comparison of predicted flashpoint and experimental data for methanol (1) + 1-butanol (2)

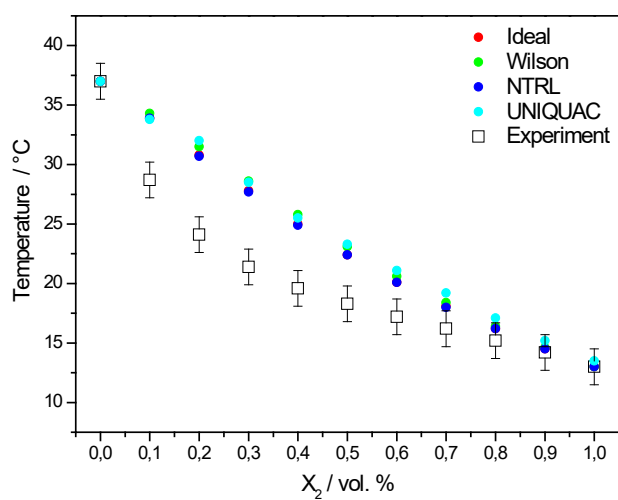


Figure 5: Comparison of predicted flashpoint and experimental data for ethanol (1) + 1-butanol (2)

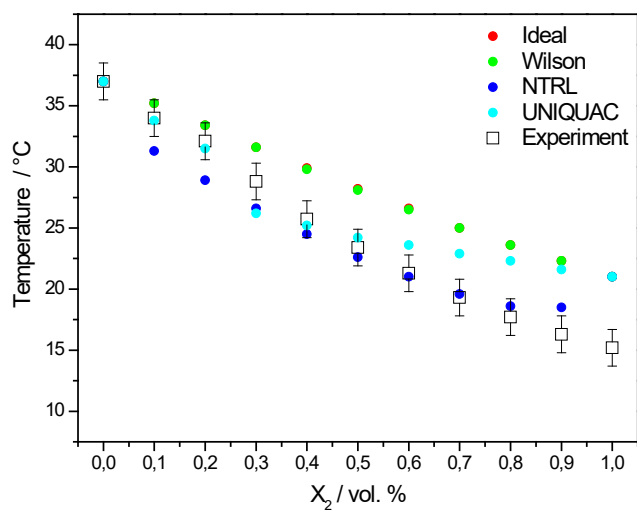


Figure 6: Comparison of predicted flashpoint and experimental data for 1-propanol (1) + 1-butanol (2)

6. Conclusions

This work has been aimed to the study of the battery solvents flammability as some common flammable solvents, by characterizing their flashpoints at various mutual concentrations. The procedure presented here for the estimation of binary mixture flashpoint is very useful for the assessment of flammability hazards, because it saves time and effort by providing the user with techniques and resources that can be used to estimate parameters and obtain input data that are needed for determination of mixture flash points. This procedure also allows for the estimation of a mixture flash point when experimental data are limited or no experimental vapour–liquid equilibrium data are available for the mixture of interest. Compared to estimation, experimental flash point data are always preferred; however, even for experimental tests estimates of flash point values are needed. Also, a tool to predict minimum flash point behaviour is a resource that can be used by the experimenter to perform experiments in a safer way, because the possibility of a lower flash point value at a certain composition will then not be ignored. The present investigation completed the series of studies by vapour-liquid equilibrium of the 1-monoalcohol-substituted com-pounds $C_nH_{2n+1}OH$ with $n= 1-4$ in a water solution. An extensive set of flashpoint values was obtained, allowing a systematic comparison of the miscible and partially miscible behaviour properties to be made among the entire series. The approximation function constants of $C_nH_{2n+1}OH$ with $n= 1-4$ alcohol – alcohol mixtures were accurately determined for the first time, and the results of the approximation compare well with the thermodynamic calculations and experimental value. While the flash point can be used to indicate the flammability of liquid materials for certain end uses, flash point does not represent the minimum temperature at which a material can evolve flammable vapours.

Nomenclature

A, B, C, D, E – Antoine coefficients, -	x – liquid phase composition, -
A_{ij} – binary parameter, K	α_{ij} – NRTL parameter, -
MW – molecular weight of component i , kg/kmol	λ – parameters of Wilson equation, J/mol
P – saturated vapor pressure, kPa	ρ – molecular density i , g/cm ³
q – measure of molecular surface, -	η – specific volume i , cm ³ /mol
r – molecular van der Waals volume, -	
R – gas constant, J/mol ¹ K ¹	
ΔT – temperature, K	

Acknowledgments

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