Lower Explosion Limits Measurements and Prediction for Binary Liquid Mixtures

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Abstract. The lower explosion limit (LEL) is an important physicochemical parameter for characterizing the flammable and explosive hazard potential of chemicals. In this study, the LEL values of 21 groups of binary liquid mixtures with different compositions and ratios were tested, and the change law of LEL with compositions and ratios were revealed. Then four different physicochemical parameters were employed as the input parameters for the LEL prediction of mixtures. Both the multiple linear regression (MLR) and multiple nonlinear regression (MNR) methods were employed to model the possible quantitative relationships between these parameters and the LEL of binary mixtures. The resulted models showed satisfactory prediction ability, with the average absolute error being 0.188% for the MLR model and 0.196% for the MNR model, respectively. Model validations were also performed to check the stability and predictivity of the presented models, and the results showed that both models were valid and predictive requiring only some common physicochemical parameters of the pure components. This study can provide a simple, yet accurate way for engineering to predict the LELs of binary liquid mixtures as applied in the assessment of fire and explosion hazards and the development of inherently safer designs for chemical processes.

1. Introduction
For the design of safe processes avoiding fire onset and explosion, the knowledge of the lower explosion limit (LEL) is the most important property employed to assess the overall flammable and explosive hazard potential of a chemical. The LEL which is usually in percentage volume (vol.%) at 298 K, is defined as the minimum concentration of a combustible substance that is capable of propagating a flame through a homogeneous mixture of the combustible and the air under the specified conditions of test. This parameter provides the knowledge necessary for understanding the fundamental physical and chemical processes of explosion, and is of importance in practice for safety considerations in storage, processing, and handling of given chemicals. LEL is one of the most important indices used to rate the flammability of chemicals in the chemical industries. Knowledge of LEL values is essential to maximize safety in process design and operational procedures, such as starting up a reactor without passing through a flammable range, and storing or shipping the flammable product safely. So, reliable and accurate LEL data are always required and also considered to be absolutely necessary in the practical industry process.

At present, the theoretical prediction of the LEL is mainly focused on pure component. However, there is less research on the prediction of the lower explosion limit of the mixture, and only a few explosive limit data were reported. The depth and breadth of the study are far from satisfying the practical needs. Albahri et al. [1] had predicted the lower explosion limit of 454 kinds of substances,
and the average error of the predicted results is 0.02%, which comparatively realized the prediction of the explosion limit of single component. F. van denschoor et al. [2] used two different methods to determine the explosion limit of methane / hydrogen / air mixtures in the normal temperature and pressure conditions. Kondo et al. [3] measured the lower explosion limit of nine binary and ternary combustible mixtures. Fuman Zhao [4] conducted an experimental study on the lower explosion limit of binary saturated and unsaturated hydrocarbon mixtures. He also proposed a method of calculating the flame temperature in the case of heat loss for predicting the lower explosion limit of the study system. In general, the factors that affect the lower explosion limit of flammable liquid mixtures are: the nature of the flammable mixture itself, the ambient state of the mixed gas (humidity, temperature, pressure, etc.), the extended performance of the test container (Container shape, linear scale etc.), ignition energy and flame propagation direction, etc. These factors interact with each other [5].

In this paper, ASTM E681-2009 standard method [6] is applied, and American FRTA explosion limit tester is used to test the lower explosion limit of binary flammable liquid mixtures which is commonly used in industrial production. On the one hand, the experimental data can be summed up to provide the necessary technical support for the industrial production, and on the other hand, based on the obtained experimental data and the physico-chemical parameters of the mixtures, the relevant empirical formulas are fitted which can provide scientific basis for the prediction of the lower explosion limit of flammable liquid mixtures.

2. Experiment Method

2.1 Experimental Apparatus and Reagents

FRTA explosion limit tester is used in this study; it was designed and manufactured by idea science company. Other equipment includes injectors, measuring cylinders, beakers, droppers, glass rods etc. The wide use of organic compounds in the chemical production industry is mainly considered in selecting experimental samples. Therefore, the more representative the chosen organic materials is, the more practical value the experimental results will have. All samples are provided by NanJing WanQing Chemical Classware Instrument CO.LTD, and the reagents used in the experiments include methanol, ethanol, isopropanol, n-pentane, n-hexane, acetone, methyl acetate, ethyl acetate (all are analytical pure).

2.2 Experimental Process

ASTM E681-2009 Standard Test Method is used in experiment. Firstly, extract the air from test vessel with vacuum pump and then check the air tightness after closing the pump. If the vacuum state can be maintained for five minutes, then the air tightness was good. Secondly, extract the appropriate amount of sample and inject them into test container, and then open the magnetic stirrer. Gasify the added liquid by constantly stirring, and the pressure value in the container is not recorded until the gas pressure in the bottle is no longer changed. Thirdly, open the intake valve and introduce the air until reaching the atmospheric pressure; then put it aside for five minutes to make flammable vapor and air mixed evenly. After that close the magnetic stirrer and ignite. If flame propagation reaches more than ten centimeters in the container or pressure curve increases significantly on the control panel, there is an explosion. At last, ventilate and record curves of pressure on the control panel. The test process requires repeated experiments until finding the minimum explosion pressure of the liquid vapor. And the lower explosion limit is calculated. In order to reduce the error, all experiments were carried out under the same conditions.

3. The Results and Discussions

3.1 Experimental Results

According to ASTM E681-2009 explosion limit test standard, under different ratios, the lower explosion limit of 21 sets of binary flammable mixed liquid were tested, a total of 92 data points, the experimental data were shown in table 1. In order to verify the accuracy of the experimental data, this
paper compares the experimental values of the lower explosion limit of single-component liquid vapor with values in Material Safety Data Sheet (MSDS) [7], the results were shown in table 2.

### Table 1. Experimental values of LELs

| No. | Component A-B | 0% | 20% | 40% | 60% | 80% | 100% |
|-----|---------------|----|-----|-----|-----|-----|------|
| 1   | Methanol-ethanol | 6.45 | 6.15 | 5.22 | 4.90 | 3.95 | 3.63 |
| 2   | Methanol-isopropyl alcohol | 6.45 | 5.80 | 5.19 | 3.92 | 3.31 | 2.36 |
| 3   | Methanol-methyl acetate | 6.45 | 6.16 | 5.53 | 4.90 | 4.26 | 3.62 |
| 4   | Methanol-ethyl acetate | 6.45 | 5.69 | 4.90 | 3.95 | 3.00 | 2.37 |
| 5   | Methanol-acetone | 6.45 | 6.16 | 4.89 | 4.26 | 3.63 | 2.72 |
| 6   | ethanol-isopropyl alcohol | 3.63 | 3.63 | 3.00 | 3.00 | 2.69 | 2.36 |
| 7   | Ethanol - n-pentane | 3.63 | 3.04 | 2.71 | 2.08 | 2.08 | 1.73 |
| 8   | ethanol-methyl acetate | 3.63 | 3.62 | 3.63 | 3.63 | 3.63 | 3.62 |
| 9   | ethanol-ethyl acetate | 3.63 | 3.49 | 3.01 | 2.69 | 2.69 | 2.37 |
| 10  | ethanol-acetone | 3.63 | 3.36 | 3.00 | 3.00 | 3.00 | 2.72 |
| 11  | Isopropyl alcohol-methyl acetate | 2.36 | 2.69 | 2.85 | 3.00 | 3.32 | 3.62 |
| 12  | Isopropyl alcohol-acetone | 2.36 | 2.55 | 2.71 | 2.71 | 2.70 | 2.72 |
| 13  | n-pentane - n-hexane | 1.73 | 1.44 | 1.44 | 1.28 | 1.28 | 1.12 |
| 14  | n-pentane-ethyl acetate | 1.73 | 1.73 | 1.76 | 1.91 | 2.08 | 2.37 |
| 15  | n-pentane-acetone | 1.73 | 1.75 | 1.91 | 2.23 | 2.71 | 2.72 |
| 16  | n-hexane-methyl acetate | 1.12 | 1.46 | 1.78 | 2.10 | 3.07 | 3.62 |
| 17  | n-hexane-ethyl acetate | 1.12 | 1.45 | 1.77 | 1.93 | 2.10 | 2.37 |
| 18  | n-hexane-acetone | 1.12 | 1.45 | 1.77 | 2.09 | 2.42 | 2.72 |
| 19  | Methyl acetate-ethyl acetate | 3.62 | 3.05 | 3.04 | 2.72 | 2.57 | 2.37 |
| 20  | Methyl acetate-acetone | 3.62 | 3.53 | 3.37 | 3.36 | 3.36 | 2.72 |
| 21  | Ethyl acetate-acetone | 2.37 | 2.41 | 2.73 | 2.74 | 2.73 | 2.72 |

### Table 2. Comparisons between the experimental and database values of LELs for pure chemicals

| Number | Material       | CAS     | LEL%  |
|--------|----------------|---------|-------|
|        |                |         | Database | Experimental |
| 1      | methanol       | 67-56-1 | 6.0    | 6.45     |
| 2      | ethanol        | 64-17-5 | 3.3    | 3.63     |
| 3      | isopropyl alcohol | 67-63-0 | 2.0    | 2.36     |
| 4      | n-pentane      | 109-66-0 | 1.5   | 1.73     |
| 5      | n-hexane       | 110-54-3 | 1.1   | 1.12     |
| 6      | acetone        | 67-64-1 | 2.5    | 2.72     |
| 7      | methyl acetate | 79-20-9 | 3.1    | 3.62     |
| 8      | ethyl acetate  | 141-78-6 | 2.2   | 2.37     |

In Table 2, the experimental values of single-component liquid vapor were compared with values in MSDS, the average absolute error was 0.29%. These errors were mainly caused by different experimental apparatus and test methods, such as the shape of the container, the purity of the sample, the initial temperature, the initial pressure, the mode of ignition etc. By comparison, under the ASTM E681-2009 standard, it is true and efficient to use the FRTA explosion limit tester to determine the lower explosion limit.

### 3.2 The Analysis of Lower Explosion Limit

Using FRTA explosion limit tester, under different ratio, lower explosion limit of 21 sets of binary combustible mixed liquid were tested. The initial temperature of the test was set to 25°C, and the initial pressure was one standard atmosphere. Figure 1 and Figure 2 respectively showed the changes
of curves of the lower explosion limit of the homogeneous binary liquid mixtures and inhomogeneous binary liquid mixtures explosion with the increase of volume fraction of matter A.

In the figure 1, with the increase of volume fraction of matter A, the experimental LEL values of the homogeneous binary liquid mixtures showed an upward trend. Such as methanol-isopropyl alcohol, with the volume fraction of methanol raised, the lower explosion limit of the mixture increased at a greater rate. However, for n-pentane and n-ethane, as the volume fraction of n-pentane increased, the experimental values rose at a smaller rate. When the volume fraction of methanol was 40% and 60% respectively, the growth rate of lower explosion limit of liquid vapor mixed with isopropanol was the highest. It could be seen from figure 2 that with the increase of the volume fraction of matter A, the experimental values of lower explosion limit of inhomogeneous binary liquid mixtures was almost declining. The experimental values of the mixture of ethanol and ethyl acetate were almost unchanged.

Taking the experimental values measured by mixing the same substances with different substances as the object of the research, and selects the groups of data, which were measured by respectively mixing the methanol with other substances as well as respectively mixing the n-hexane with other substances; the results were shown in figure 3 and figure 4.

Figure 3 and figure 4 showed the experimental LEL values of same substance which respectively mixed with the different substance, the income curve was a single upward or downward trend. In the figure 4, when the volume fraction of n-hexane was larger than 60%, the measured LEL value of the
liquid mixtures was basically the same. Because the n-hexane liquid was highly volatile, when its volume fraction exceeded 60%, the main component of the liquid mixtures was n-hexane vapor. At this point, the other liquid vapor could be seen as a dilution gas, since the lower explosion limit of n-hexane is very small, and once the mixed vapor concentration reaches the lower explosion limit of n-hexane, it will explode.

4. Materials and Methods

4.1 Data Sets and Determination of Input Parameters

In table 1, 22 data were randomly selected as test set to validate the prediction capability of the model, and the remaining 70 data points were used as training set to develop the model. In engineering thermodynamics, the basic method of studying the mixed gas is to calculate the thermodynamic properties of the gas based on the thermodynamic properties and composition of the constituent gas, and then take the mixed gas as a single gas to carry out various thermal calculations [8].

Coward and Jones [9] established a correlate model of the explosion limit of organics with the stoichiometric concentration as the correlation parameter. Suzuki [10] established the corresponding nonlinear correlation model for the lower explosion limit of 112 kinds of organics and the upper explosion limit of 95 kinds of organics respectively with the standard combustion enthalpy as the correlation parameter, who got the predicted standard errors were 0.23% and 1.68% respectively. Subsequently, Suzuki and Ishida [11] used the artificial neural nets and multiple linear regression method to predict the lower explosion limit of organics, respectively, with the critical temperature, the critical pressure, the diffusion coefficient and combustion heat and other physicochemical properties as input parameters. Finally, good prediction results were obtained. Britton [12] established the formula for the lower explosion limit with the heat of oxidation as the correlation parameter.

Based on previous researches, in this work, four different physicochemical parameters, namely the heat of combustion, the critical pressure, the diffusion coefficient and the stoichiometric concentration were used as the input parameters of the model. The physicochemical parameter values of the pure component substances involved in the 22 data points were shown in table 3. All these values were obtained from the DIPPR databases.

| Chemicals     | Heat of combustion/(kJ·mol⁻¹) | Critical pressure/(bar) | Diffusion coefficient/(cm²/s) |
|---------------|-------------------------------|-------------------------|------------------------------|
| methanol      | -638.2                        | 79.5                    | 0.159                        |
| ethanol       | -1235                         | 63.8                    | 0.119                        |
| isopropyl alcohol | -1830                    | 47.6                    | 0.101                        |
| n-pentane     | -3244.9                       | 33.7                    | 0.084                        |
| n-hexane      | -3855.1                       | 30.9                    | 0.073                        |
| acetone       | -1659                         | 47.2                    | 0.105                        |
| methyl acetate| -1461                         | 46.9                    | 0.098                        |
| ethyl acetate | -2061                         | 38.3                    | 0.086                        |

The stoichiometric concentration \((C_{st})\) mix and combustion heat \((\Delta H_{C})_{mix}\) can be calculated using the sum formula and the composition of mixed gas, such as the calculation method for the combustion heat of the mixtures is:

\[
(\Delta H_{C})_{mix} = x_A \Delta H_{CA} + x_B \Delta H_{CB}
\]  

(1)

\(x_A\) and \(x_B\) respectively represent the amounts of matter A and matter B in the mixture; \(x_A + x_B = 1\); \(\Delta H_{CA}\) and \(\Delta H_{CB}\) respectively represent the heat of combustion of matter A and matter B in the mixture. Similarly, the critical pressure \((P_C)_{mix}\) and the diffusion coefficient \((D)_{mix}\) in the air can be calculated in the same way.
4.2 Modeling Methods

In this paper, both the multiple linear regression (MLR) and multiple nonlinear regression (MNR) methods are applied for the prediction models of the lower explosion limit.

4.2.1 MLR Model. The strong correlation variables are the combustion heat of the mixed gas ($X_1$), the critical pressure of the mixed gas ($X_2$), the diffusion coefficient of the mixed gas in the air ($X_3$), and the stoichiometric concentration of the mixed gas ($X_4$). The corresponding MLR model of the lower explosion limit of binary flammable liquid mixtures is present as follow:

$$LEL=-0.588+1.86 \times 10^{-4}X_1-0.040X_2+36.612X_3+0.425X_4$$

$$R^2=0.957, F=358.509, SE=0.249, P=0$$

$R^2$ is the squared correlation coefficient; $F$ is the significance test value of the equation and $SE$ and $P$ are the standard error of the model and the significance probability of the equation, respectively.

From the formula (2), we can see that the MLR model has a high correlation coefficient and a lower standard error, indicating that the model is reliable; significance probability is far less than 0.05, which indicates that the regression equation has significant statistical significance.

4.2.2 MNR Model. The main performance parameters of the second and third order nonlinear models were given in table 4.

Table 4. The performance parameters of different orders of nonlinear models

| Model        | Training set $R^2$ | Test set $Q^2$ | Maximum absolute error/% | Average absolute error/% |
|--------------|--------------------|----------------|--------------------------|--------------------------|
| Second order | 0.964              | 0.961          | 0.54                     | 0.226                    |
| Third order  | 0.978              | 0.953          | 0.61                     | 0.248                    |

Considering the performance parameters of each nonlinear model, this paper selects the second order polynomial as the final prediction model, which is present as follows:

$$LEL = 3.680 - 0.477 \left( \sum c_i X_i \right) + 0.027 \left( \sum c_i X_i \right)^2$$

$$\sum c_i X_i = -0.004 X_1 + 0.145 X_2 - 115.271 X_3 - 0.070 X_4$$

$$R^2=0.964, F=1911.921, P=0$$

$R^2$ is the squared correlation coefficient; $F$ is the significance test value of the overall linear equation.

4.3 Model Validation

Model validation is an important step to ensure the establishment of the MLR model and MNR model. And in the models the stability, predictive capability and generalization capability should be tested through model validation. The squared correlation coefficient ($R^2$) which can provide a reliable indication of the fitness of the models is the most widely used in the model validation. Thus, $R^2$ was employed in the present study to determine the calibration capability of the model. When the squared correlation coefficient ($R^2$) is closer to 1, the fitting ability of the models will be stronger. The model predictive capability is evaluated by an external sample set (test set), the results can directly reflect the extrapolation capability of the model. Therefore, this paper uses the model to predict the test set samples which do not involved in modeling so as to evaluate the true predictive capability of the model for external samples. The average absolute error ($AAE$) and root mean square error ($RMSE$) were determined to evaluate the predictive capability of the developed models. As the values of $AAE$
and $RMSE$ become smaller, the predictive capability of the model is stronger. The squared correlation coefficient for external validation ($Q^2$) was employed as a traditional external validation criterion, which can be calculated as follows: [13]:

$$Q^2 = 1 - \frac{\sum_{i=1}^{\text{prediction}} (y_{\text{obs}} - y_{\text{pred}})^2}{\sum_{i=1}^{\text{prediction}} (y_{\text{obs}} - \bar{y})^2}$$ (4)

### 4.4 Result of Prediction

In order to further analyse the prediction models, the training set samples were corrected by using the formula (2) and (3) respectively to evaluate the fitting ability of the model. What’s more, 22 samples of the test set were predicted to verify the model's external predictive capability. The values were shown in table 5. By calculating, the main performance parameters of the models were shown in table 6. The correlation between the predicted and experimental LEL values for both training and test set of two models was showed in the figure 5 and figure 6.

**Table 5.** The predicted LEL values for the test set by developed models

| Number | Binary mixtures       | Volume fraction | Experimental value/% | Predicted value/% |
|--------|-----------------------|-----------------|---------------------|------------------|
|        | A         | B      |                      |                  |
| 1      | methanol | ethanol | 0.8 | 0.2 | 6.15 | 6.09 | 6.23 |
| 2      | methanol | ethanol | 0.4 | 0.6 | 4.9 | 4.78 | 4.82 |
| 3      | methanol | isopropanol | 0.4 | 0.6 | 3.92 | 4.01 | 3.87 |
| 4      | methanol | methyl acetate | 0.6 | 0.4 | 5.53 | 5.15 | 5.09 |
| 5      | methanol | ethyl acetate | 0.4 | 0.6 | 3.95 | 3.61 | 3.53 |
| 6      | methanol | acetone | 0.6 | 0.4 | 4.89 | 5.12 | 4.91 |
| 7      | ethanol  | isopropanol | 0.6 | 0.4 | 3 | 3.3 | 3.31 |
| 8      | ethanol  | ethyl acetate | 0.2 | 0.8 | 2.69 | 2.56 | 2.59 |
| 9      | isopropanol | acetone | 0.6 | 0.4 | 2.71 | 2.96 | 2.95 |
| 10     | n-pentane | n-hexane | 0.2 | 0.8 | 1.28 | 1.63 | 1.18 |
| 11     | n-pentane | ethyl acetate | 0.4 | 0.6 | 1.91 | 1.92 | 2.01 |
| 12     | n-hexane | ethyl acetate | 0.8 | 0.2 | 1.45 | 1.58 | 1.26 |
| 13     | n-hexane | acetone | 0.8 | 0.2 | 1.45 | 1.56 | 1.37 |
| 14     | n-hexane | acetone | 0.4 | 0.6 | 2.09 | 1.96 | 2.1 |
| 15     | methyl acetate | acetone | 0.6 | 0.4 | 3.37 | 3.28 | 3.24 |
| 16     | ethanol  | 1 | 0 | 3.63 | 3.72 | 3.8 |
| 17     | isopropanol | 1 | 0 | 2.36 | 2.78 | 2.79 |
| 18     | n-pentane | 1 | 0 | 1.73 | 1.59 | 1.64 |
| 19     | n-hexane | 1 | 0 | 1.12 | 1.7 | 1.07 |
| 20     | acetone | 1 | 0 | 2.72 | 3.27 | 3.21 |
| 21     | methyl acetate | 1 | 0 | 3.62 | 3.29 | 3.28 |
| 22     | ethyl acetate | 1 | 0 | 2.37 | 2.35 | 2.38 |

**Table 6.** The main statistical parameters of the obtained models

| Model | Training set | Test set |
|-------|--------------|----------|
|       | $R^2$ | $AAE$ | $RMSE$ | $Q^2$ | $AAE$ | $RMSE$ |
| MLR   | 0.957 | 0.189 | 0.248 | 0.971 | 0.185 | 0.236 |
| MNR   | 0.964 | 0.181 | 0.227 | 0.961 | 0.226 | 0.274 |

It can be seen from Table 6 that the $Q^2$ of the test sets of the MLR and MNR are 0.971 and 0.961 respectively, which indicates that the MLR model can predict better. At the same time, the comparison of the results from $AAE$ and $RMSE$ of the training and test set shows that the prediction error of the two subsets is not only low, but also relatively close which means that the two models have better generalization performance. As can be seen from the figure 5 and figure 6, the predicted values and
the experimental values were close to each other in both training set and test set for two models. And the results showed that the two models had predictive ability and generalization performance. Subsequently, the prediction error of all 92 binary liquid mixtures in the sample concentration was calculated, and the average absolute errors of the prediction of the MLR and MNR model were 0.188% and 0.196% respectively, which indicates that the MLR model has better prediction performance.

4.5 Stability Analysis of the Models
The predicted residual distributions of the MLR and MNR models are shown in figure 7 and figure 8. It can be seen from these figures that the prediction residuals are distributed on both sides of the baseline randomly, and no obvious regularity exists. It indicates that there are no systematic errors in the development of the MLR and MNR models. It can be reasonably concluded that both presented models are valid models and can be effectively used to predict the lower explosion limit of binary mixtures.

4.6 Comparison between MLR and MNR Models
It can be seen from table 6 that the accuracy of the two prediction models is satisfactory, in which the external verification value $Q^2$ of the MLR model is 0.971, which is larger than the MNR model, and for both models, the AAE values for the test set are within the experimental error of LEL determination.
(around ±0.5%), which again demonstrated the satisfactory predictivity of the developed models. At the same time, the prediction error of training set and test set is compared, and the results are not only small and similar, which shows that the two models are also ideal in generalization performance. This phenomenon strongly suggests that a simple linear relationship may exist between the selected physicochemical parameters and the lower explosion limit of binary organic liquid mixtures.

As for the performance parameters of the models, the AAE value for the test set of the MLR model has dropped by 18.14% compared with the MNR model. It indicated the better performance of the MNR model. At the same time, the MLR model also has the advantages of application simplicity.

5. Conclusions
In the present work, two empirical models were presented for prediction of the LEL of binary liquid mixtures based on a dataset consisted of a variety of experimental LEL values for binary mixtures. Four characteristic physicochemical parameters for mixtures were used as the input parameters for both the MLR and MNR modelling for LEL prediction. The resulted models are two empirical equations both with four common-used physicochemical parameters. The model validation results showed that both models are valid and predictive. A general comparison between the two models showed that the MLR model possess some obvious superiorities, such as computationally simple, easy to apply, and more representative. This study can provide a quick and reliable pathway to predict LEL of binary liquid mixtures for which experimental values are unknown. Additionally, potential application for this method concerns the classification of flammable liquid mixtures as well as the design of inherently safer chemical process.

6. Acknowledgments
This research was supported by National Program on Key Basic Research Project of China (2016YFC0801502, 2017YFC0804801) and National Natural Science Fund of China (No. 21576136, 21436006). Yong Pan acknowledges the sponsorship of Qing Lan Project.

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