

Measurement of the rate constant and the activation energy of ethyl acetate saponification

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TABLE I. The fitting result of the reaction rate constant

$T/^{\circ}\text{C}$	25		30	35	40	45
k	0.09517	0.08650	0.1423	0.1609	0.2445	0.3392

Starting from

$$E_t = \frac{1}{ak} \frac{E_0 - E_t}{t} + E_{\infty} \quad (1)$$

It is deduced that

$$E_t = \frac{E_0 + akE_{\infty}t}{1 + akt} \quad (2)$$

Thanks to machine learning integrated in *Mathematica*, the coefficients can be derived out immediately:

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In[377]:= c1 /. (NonlinearModelFit[#, (-c2 + c1 c3 t)/(
  1 + c1 t), {c1, c2, c3}, t][
  "BestFitParameters"] & /@ (Transpose[{Range[Length
    [#]] +
    1, #]} & /@ react))

Out[377]= {0.000951675, 0.000865023, 0.00142327,
  0.0016089, \
  0.0024449, 0.00339182}
```

which is equivalent to the result shown in Table.I. The arrhenius fitting result is

$$k = 13.8186 - \frac{6211.05}{T/\text{K}} \quad (3)$$

giving $E_a = 51.64$ kJ/mol, which is much larger than that from the reference (41.4 ± 0.6 kJ/mol)[1]. This might result from the remainder of NaOH solution in the tube, which cannot be eliminated by just pressing the air into the apparatus. Such a mechanism of mixing the two solutions also allow a delay before forming a complete mixture, which contributes to a deviation of the dynamic equation that truly describes the system.

For a grand system with arbitrary concentration of two solutions,

$$\frac{dx_1}{dt} = \frac{dx_2}{dt} = kx_1x_2 \quad (4)$$

which has a solution according to *Mathematica*

$$\begin{cases} x_2(t) \rightarrow c_1 - \frac{e^{c_1 c_2} c_1}{e^{c_1 c_2} - e^{c_1 k t}} \\ x_1(t) \rightarrow -\frac{e^{c_1 c_2} c_1}{e^{c_1 c_2} - e^{c_1 k t}} \end{cases} \quad (5)$$

where $x_1(t), x_2(t)$ stands for the concentration of two solutions, c_1, c_2 being two constants. However, this solution fail to give proper solution to the system. Thus its approximation is considered, where the difference of the concentration between two solution is regarded as a constant perturbation, namely

$$\frac{dx}{dt} = -kx(x - \Delta x) \quad (6)$$

which leads to

$$x(t) = \frac{a\Delta x e^{kt\Delta x}}{ae^{kt\Delta x} - a + \Delta x} \quad (7)$$

Considering that Δx is comparatively small, the equation simplifies to

$$x(t) \sim \frac{a\Delta x e^{kt\Delta x}}{kt\Delta x + \Delta x} = \frac{a}{1 + kt} e^{kt\Delta x} \quad (8)$$

thus the term $e^{kt\Delta x}$ acts as a amplifier for k , which successfully explains the deviation of the result.

Microscopic perspective of the system may lead to another doubt that the reaction may not completely follow the second-order mechanism. Simulation of the molecular distribution of methanol and water is well studied, as shown in Fig.2, which reveals that the methanol molecules are not uniformly distributed in the water solution. It is of quite reasonable that the ethyl acetate is suffering the same situation in the water solution, which indicates that its practical concentration is over-estimated, which leads to exaggerated rate constant, which again explains the error.

[1] K. Das, P. Sahoo, S. B. Magapu, N. Murali, and P. Swaminathan, International Journal of Chemical Kinetics **19**, 648 (2011).

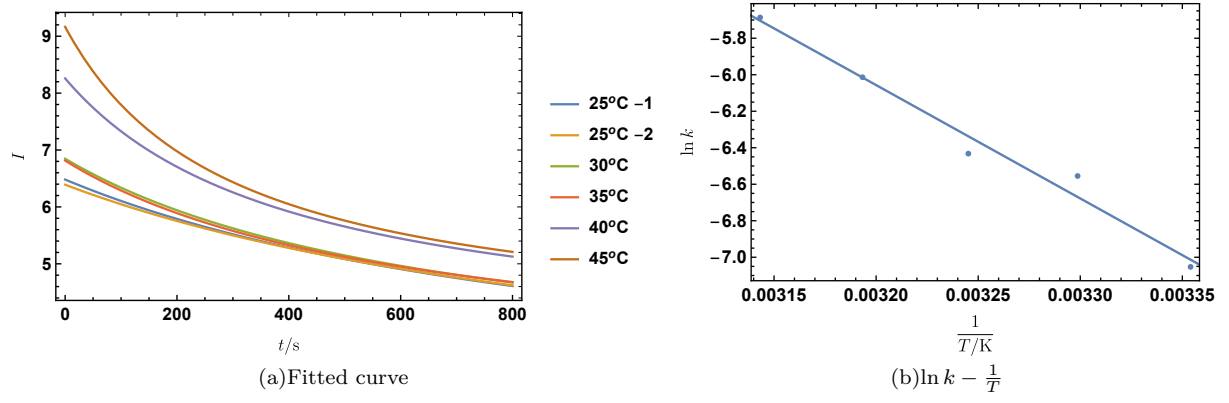


FIG. 1. The fitted curve of the reaction process with a fit of k according to Arrhenius equation

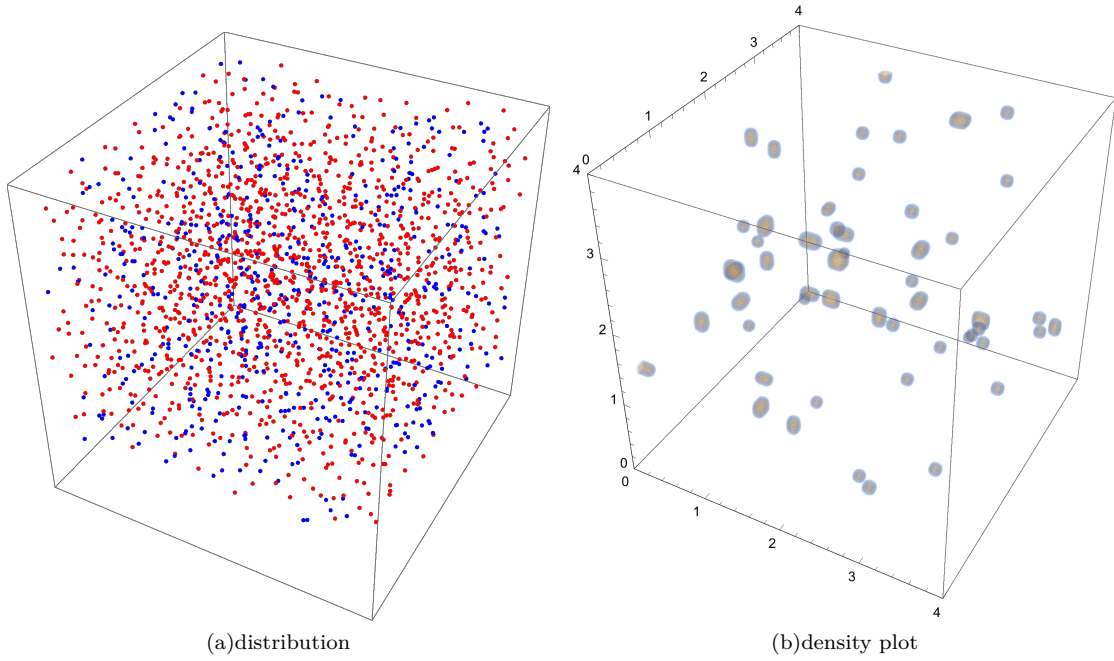


FIG. 2. The distribution of MeOH- H_2O mixed system with molar ratio of 3:7. Red dots in the first figure stands for the position of H_2O , while the stains in the second figure stands for the clusters of MeOH molecules.