KINETIC STUDY ON THE TRANSESTERIFICATION PROCEEDING BY AZEOTROPIC DISTILLATION IN THE PRESENCE OF ALKALI METALLIC SALT

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КИНЕТИЧЕСКОЕ ИССЛЕДОВАНИЕ НА ПЕРЕЭТЕРИФИКАЦИИ ПРОТЕКАЮЩИЕ ПО АЗЕОТРОПНОЙ ПЕРЕГОНКЕ В ПРИСУТСТВИИ ЩЕЛОЧИ СОЛИ МЕТАЛЛА

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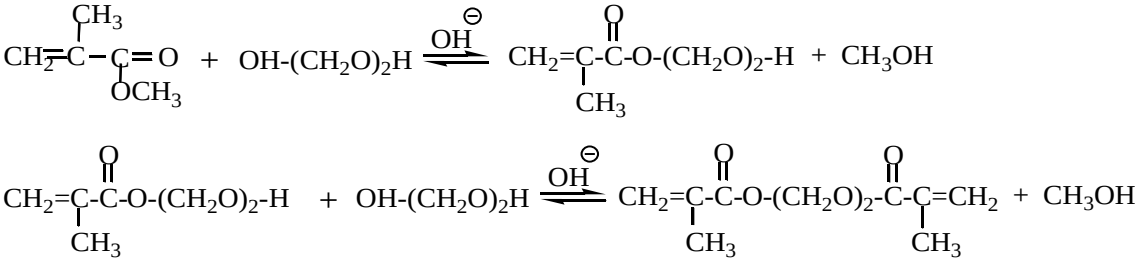
Abstract: *transesterification of methacrylate and diethyleneglycol proceeding by azeotropic distillation in the presence of alkali metallic salt have been investigated. In our study, the consumption rate of reactants for base-catalyzed transesterification process proc-eeding by azeotropic distillation was investigated in conjunction with the volumetric decrement with time, that is, decreasing rate in volume. It should be noted that this method is likely to be useful in studing the kinetic processes because of requiring so mild condition.The rate of transesterification process via azeotropic distillation is mainly attributed to volumetric decreme-nt with time. Namely, the consumption rate of reactants in transesterification process that is accompanied by change in volume is proportional to the intrinsic rate constant characterized by volumetric revision coefficient(ε).*

Аннотация*: трансэтерификация метакрилата и диэтиленгликоля производства путем азеотропной перегонки в присутствии щелочного соли металла исследованы. В нашем исследовании частота потребления реагентов для катализируемой основаниями переэтерификации PROC-eeding путем азеотропной перегонки была исследована в сочетании с объемной декремента со временем, то есть уменьшением скорости в объеме. Следует отметить, что этот метод может быть полезен в кинетических изучающих процессы из-за того, чтобы требовать столь мягкого состояния. Скорость процесса переэтерификации с помощью азеотропной перегонки в основном связана с объемной decreme-нт со временем. А именно, скорость потребления реагентов в процессе переэтерификации, который сопровождается изменением объема, пропорциональна константе коэффициента Лотки, характеризующейся коэффициентом объемного Revision(ε).*

Keywords: *azeotropic distillation, Transesterification, Alkali metal salt.*

Ключевые слова: *азеотропная перегонка, реакции переэтерификации, соли щелочных металлов.*

1. Mathematical modeling for kinetics based on the main principles



Transesterification of methylmethacrylate(MMA) and diethyleneglycol(DEG) was achieved in 2 stages as expressed below.[1,2]

For simplici-ty, it could be rewritten as

$$a + b \xrightarrow{k_1} c + e$$

$$a + c \xrightarrow{k_2} d + e$$

Where a , b , c , d , e represented methylmethacrylate(MMA),diethylene glycol(DEG), diethylene gly-col monomethacrylate(DEGMMA), diethylene glycol dimethacrylate(DEGDMA) and methanol, respect-ively.

Then the rate equation with respect to DEG could be rewritten as

$$\frac{-dn_b}{dt} = k_1 \cdot \frac{n_a \cdot n_b}{V} \qquad (1)$$

Herein, the number of moles of DEG present lies in the following defendent correlation with conversion of DEG x_b .

$$n_b = n_{b0}(1 - x_b) \qquad (2)$$

During reaction, lower boiling product-methanol was azeotropically removed with MMA

As the excess MMA should be withdrown in the form of azeotrope with methanol(azeotropic co-mposition: MMA:methanol=84.5:15.5 temperature (67-68℃) In addition to stoichiometric consumption, the attendant amount caused by azeotropic removal with methanol should be evaluated.[3,4]

$$n_a = n_{a0} - 2n_{b0}x_b - \frac{\frac{2n_{b0}x_b \cdot M_m}{100 - 84.5} \cdot 84.5}{M_a} = n_{a0} - 2n_{b0}x_b - 3.5n_{b0}x_b = n_{b0}(p - 5.5x_b) \qquad (3)$$

Where p represented the molar ratio of DEG and MMA at the beginning of reaction. $p = \frac{n_{a0}}{n_{b0}}$

And $\dfrac{\dfrac{2n_{b0}x_b \cdot M_m}{100-84.5}\cdot 84.5}{M_a}$ is the amount of loss of MMA by azeotropic removal

Herein, M_a, M_m are molecular weight of MMA and methanol, respectively.

Thus, Eq.(1) could be rewritten in conjunction with Eq.(2),(3).

$$\frac{dx_b}{dt} = k_1 \frac{n_{b0}(1-x_b)\cdot(p-5.5x_b)}{V} \qquad (4)$$

In this situation, since the volume of reactor contents, V decreases with time, it can be evaluated as a function of conversion, x_b.

$$V = V_0 \cdot (1-\varepsilon \cdot x_b)$$

Herein, ε so-called *volumetric revision coefficient* was expressed as.

$$\varepsilon = \frac{V_0 - V_1}{V_0} \qquad (5)$$

For a volume V, the differential material balance is $\int dV = \int (V_0 - V_1) dx_b$

Where V_0 represented initial volume and V_1 is final volume for 100% conversion.

When integrating, $V = (V_1 - V_0)x_b + C$ (6)

Therefore, the completed differential rate equation at variable V could be written as

$$\frac{dx_b}{dt} = k_1 \frac{n_{b0}(1-x_b)\cdot(p-5.5x_b)}{V_0\cdot(1-\varepsilon\cdot x_b)} \qquad (7)$$

When Eq.(7) was integrated,

$$\int \frac{V_0\cdot(1-\varepsilon\cdot x_b)}{n_{b0}(1-x_b)\cdot(p-5.5x_b)}\,dx_b = \int k\,dt$$

we obtain

$$\frac{p\varepsilon-5.5}{5.5(5.5-p)}\cdot \ell n(p-5.5x) + \frac{1-\varepsilon}{(5.5-p)}\cdot \ell n(1-x_b) = \frac{k_1 n_{b0}}{V_0}\cdot t + Q \qquad (8)$$

When t=0 and $x_b = 0$, where Q as integral constant was calculated as $Q = \dfrac{p\varepsilon-5.5}{5.5(5.5-p)}\cdot \ell np$

Substituting Q to Eq.(8), we obtain

$$\frac{p\varepsilon-5.5}{5.5(5.5-p)}\cdot \ell n(1-5.5x_b/p) + \frac{1-\varepsilon}{(5.5-p)}\cdot \ell n(1-x_b) = \frac{k_1 n_{b0}}{V_0}\cdot t \qquad (9)$$

Describing the left term of Eq.(9), we obtain

$$X = \frac{p\varepsilon - 5.5}{5.5(5.5-p)} \cdot \ell n(1-5.5x_b / p) + \frac{1-\varepsilon}{(5.5-p)} \cdot \ell n(1-x_b)$$

$$X = \frac{k_1 n_{b0}}{V_0} \cdot t \qquad (10)$$

Putting p=6, Eq.(9) could approximately be expressed as

$$t = \frac{V_0}{k_1 n_{b0}} \cdot \frac{\varepsilon}{5.5} \cdot \ell n(1-x_b) \qquad (11)$$

It could be clearly seen that ε plays main role in improving of the reaction rate and thus one possible way is for us to lessen ε

Hence we have performed another kinetic experiment in order to

Mathematical treatment was worked on the same manner as before.

As the cosolvent-benzene should be withdrown in the form of azeotrope with methanol(azeotropic composition: benzene:methanol=60.5:39.5 temperature 58-59℃)

The number of moles of MMA referred to stoichiometry is

$$n_a = n_{a0} - 2n_{b0}x_b = n_{b0}(p - 2x_b) \qquad (12)$$

Thus, differential rate equation obtained in terms of Eq.(12) is

$$\frac{p\varepsilon - 2}{2(2-p)} \cdot \ell n(1-2x_b / p) + \frac{1-\varepsilon}{(2-p)} \cdot \ell n(1-x_b) = \frac{kn_{b0}}{V_0} \cdot t \qquad (13)$$

Defining $X = \frac{p\varepsilon - 2}{2(2-p)} \cdot \ell n(1-2x_b / p) + \frac{1-\varepsilon}{(2-p)} \cdot \ell n(1-x_b)$,the following linear correlation equation could be obtained.

From material balace, the amount of benzene to be added at the beginning of reaction is

$$n_M > \frac{\frac{2n_{b0}x_b \cdot M_m}{100-60.5} \cdot 60.5}{M_B} \qquad (14)$$

2. Experimental proof for the kinetic model based on the main principles

Fig.1 and Fig.2 represented the correlation of conversion x_b with time.

As shown in both figures, it could be clearly seen that linear correlation between $\frac{dx_b}{dt}$ and t is satisfactory within limited temperature.

From the above correlation, the following first order linearly dependent equation was obtained.

$$r = \frac{dx_b}{dt} = -0.0568t + 0.2746 \qquad (15)$$

Theses correlation suggested that this reaction is apparently first order with respect to DEG.

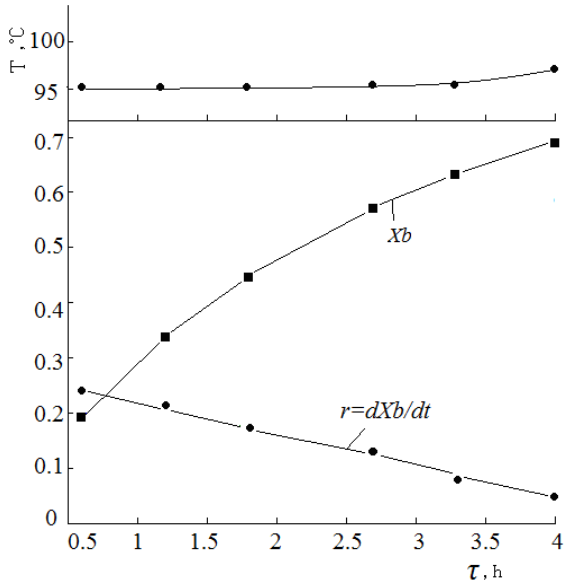


Fig .1. Correlation of x_b, $\frac{dx_b}{d\tau}$ *with time* τ

Under such a condition that the molar ratio of MMA and DEG is 6, the initial vlume of reactor contents, V_0 was given to be 789.58ml and the final volume for 100% conversion, namely, $x_b = 1$ was calculated to be 312.08ml.

Thus $\varepsilon = \frac{V_0 - V_1}{V_0}$ =0.6049

After calculating X from Eq.(9) in terms of experimental data, the correlation with time t was plotted ,shown in Fig. 2.

As shown in Fig. 2, the linear correlation of X with time is explanatory for proving the accuracy our chosen kinetic model.

From this correlation, the following first order equation was obtained as

$$X = 0.06134\,t \qquad (16)$$

With a slobe of straight line, the apparent rate constant was evaluated as

$$k_1 = \frac{V_0}{n_{b0}} \cdot 0.06134 = (4.84 \pm 0.02) \times 10^{-2}, \ell/(mol \cdot h) \qquad (17)$$

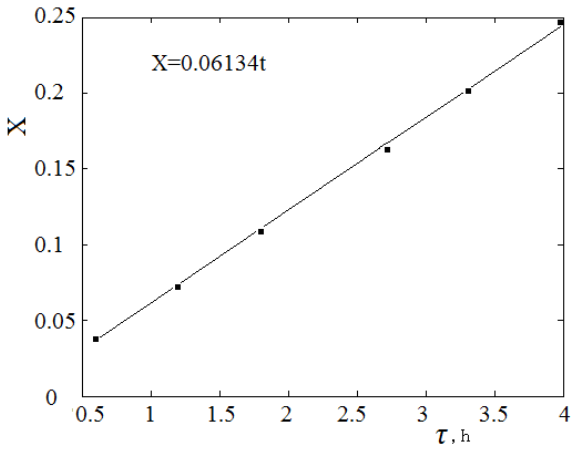


Fig. 2. Correlation of X with time τ

3. Eexperimental proof for the kinetic model in the presence of a cosolvent

On the other hand, the reaction was achieved by adding benzene as a cosolvent.

Herein, 1.5mol of MMA and 0.6mol of DEG was taken part in the reaction corresponding to the molar ratio of 2.5 and benzene was added as much as calculated from Eq.(14)

In this case, the *volumetric revision coefficient* ε was calculated in the same manner as before.

As shown in Fig. 3, the correlations of $\frac{dx_b}{dt}$ and X with t are of satisfactory linear within nearly constant temperature, agreed with the previous case.

Therefore, the equation obtained from above correlation is

$$X = 0.09233t \qquad (18)$$

The rate constant k can be calculated by a slobe of straightline.

$$k = \frac{V_0}{n_{b0}} \cdot \tan\alpha = (4.55 \pm 0.02) \times 10^{-2}, \ell/(mol \cdot h)$$

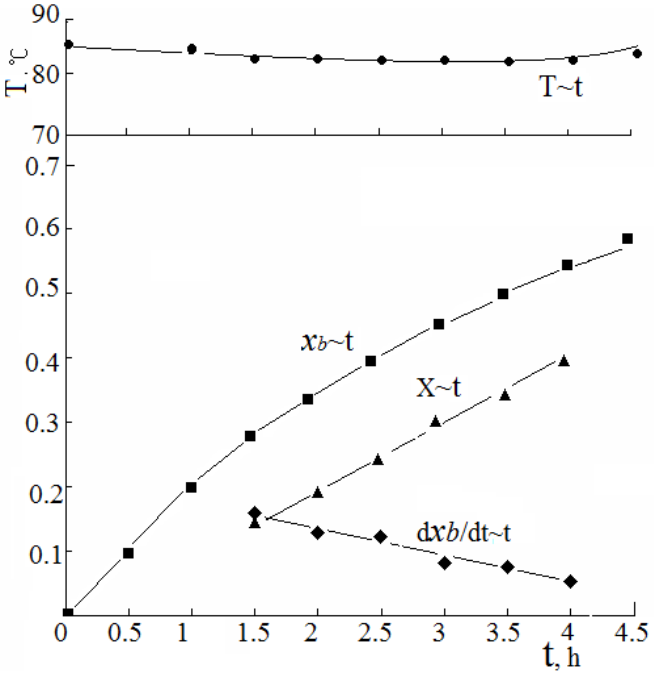


Fig. 3. Change of T, x_b, X *with time when adding benzol*

In order to predict time necessary for reaching conversion to a maximum at constant T, Eq.(1) and Eq.(2) were modified in the following forms and plotted, respectively.

$$t = \frac{V_0}{k_1 n_{b0}} \cdot \frac{\varepsilon}{5.5} \cdot \ell n(1 - x_b) \qquad x_b = 1 - \exp(-2 \cdot \frac{k_1 n_{b0}}{V_0 \varepsilon} \cdot t)$$

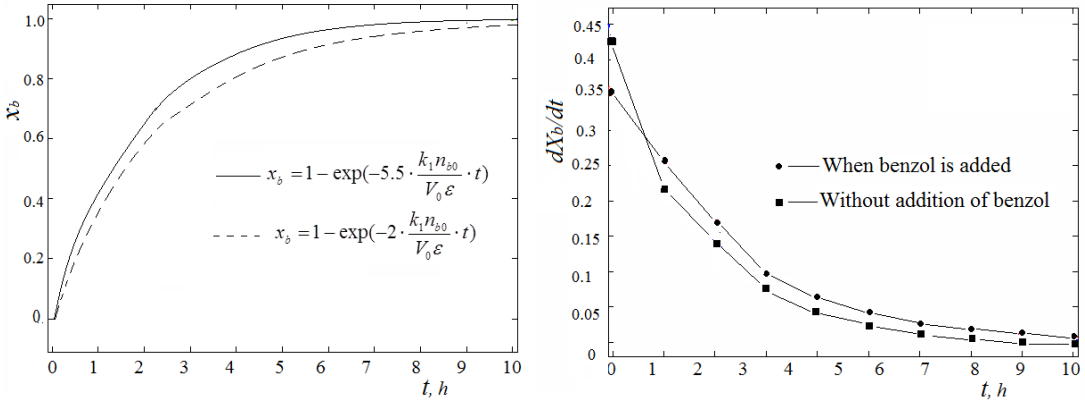


Fig. 4. Simulation results between $x_b \sim \tau$ *and* $\frac{dx}{dt} \sim \tau$ *according to the solvation method*

As shown in Fig. 4, the reaction rate tend to be linearly decreasing obeyed the law of mass action within 4h,

regardless of which cases.

In particular,

This shows that solvent condition being such that they allow high yields in DEGDMA production. For this reason, it is certain that the tendency of two curves of rate to be saturated never differs greatly

In a word, this is caused by the law of mass action.

That is, the results of kinetic observation for transesterification were summarized in the table.

Table 1. Kinetic experiment results of exchange reaction

Character	solventless	solvent
$k,\ \ell/(mol\cdot h)$	$(4.84\pm0.2)\times10^{-2}$	$(4.55\pm0.2)\times10^{-2}$
$\frac{n_{b0}}{V_0\varepsilon}$	2.098	4.69

Relatively low value in rate constant for solventless process caused by the decrease of reaction temperature owing to addition of benzene. Nevertheless, reaching to a maximum conversion within same time can be found to be the result ofincrease.

This is substantially caused by $\frac{n_{b0}}{V_0\varepsilon}$ the increase of rea-ction rate from the increase in conce-ntration of participates, namely molecularity of reactants per unit volume according to the law of reaction rate.

Thus, it is clear that for the latter case, the chemical affinity become larger rather than the former.

Herein, $\frac{n_{b0}}{V_0}$ as molar concentration of DEG is used to be defined so long as certain process.

Eventually, we arrived at the conclusion that the main factor obeying the conversion of DEG is none other than ε and thus the instric rate constant of the transesterification via azeotropic distillation is $\frac{k_1}{\varepsilon}$. In other words, the smaller ε is, the larger rate becomes

Thus reaction design must to be oriented to the direction of increasing K_{rel}.

On the other hand , in virtue of solvolysis by benzene, it was probably found to the contribution to the decrease of activation energy, namely selectivity of forward reaction.

$$K_{\text{rel}} = \frac{k_1}{\varepsilon} \qquad (19)$$

Similarly, this model could be found to be applicable to other situation.

Thus, for general transesterification processes, equation of mathematical physics in bounded domain could be expressed as

$$\frac{p\varepsilon - m}{m(m-p)} \cdot \ell n(1-\frac{mx_b}{p}) + \frac{1-\varepsilon}{(m-p)} \cdot \ell n(1-x_b) = \frac{k_1 n_{b0}}{V_0} \cdot t \qquad (20)$$

Hence

m is theoretical number of loss moles of MMA by different reason

V_0 -initial volume of reactor contents,Mℓ, n_{b0} -,initial number of moles of DEG, mol

p -molar ratio of ester and alcohol at the beginning of reaction(=$\frac{n_{a0}}{n_{b0}}$) ,

n_{a0} -initial number of moles of ester,mol

ε -volumetric revision coefficient(for 100% conversion)

Conclusion

In the kinematic consideration process, DEGDMA synthesis reaction has a smaller and lower reactant volume in the case of addition of benzene than in the case of no addition of benzene, and a higher production rate of the desired product within the temperature and time limit, The method is more innovative in terms of productivity and power.

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