

KINETICS OF ESTERIFICATION OF SALICYLIC ACID WITH N-AMYL ALCOHOL IN THE PRESENCE OF LEWATIT MONOPLUS S-100

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ABSTRACT

The kinetics of esterification of salicylic acid with amyl alcohol has been studied batchwise in the presence of Lewatit MonoPlus S-100 as heterogeneous catalyst. The kinetic behavior of the reaction has been tested by three different models: the quasi-homogeneous model, the Eley-Rideal model and the Langmuir-Hinselwood model. L-H model fits the experimental data best among the others.

Keywords: Esterification, Salicylic Acid, n-Amyl Alcohol, Kinetic modeling, Lewatit MonoPlus S-100

LEWATİT MONOPLUS S-100 VARLIĞINDA N-AMİL ALKOL İLE SALİSİLİK ASİDİN ESTERİFİKASYON KİNETİĞİ

ÖZET

Amil alkol ile salisilik asidin esterifikasyon kinetiği heterojen bir katalizör olan Lewatit MonoPlus S-100 varlığında kesikli bir sistemde incelenmiştir. Reaksiyon kinetik davranışı, üç farklı modelde tarafından test edilmiştir: yarı-homojen bir model, Eley-Rideal modeli ve Langmuir-Hinselwood modeli. Bütün modeller arasında en iyi deneysel verileri L-H modelinin sağladığı bulunmuştur.

Anahtar Kelimeler: Esterleştirme, salisilik asit, n-amil alkol, kinetik modelleri, Lewatit MonoPlus S-100

1. INTRODUCTION

Esters are substantially consequential organic compounds which are widely used in industries of pharmaceuticals, food flavor, cosmetics and perfumery. They are also used as emulsifiers in the food and cosmetic industries. Several synthetic routes given in literature are suitable for obtaining organic esters [1].

Generally, the esterification reaction rates are very slow so that the reactions usually take a long time to attain equilibrium in the absence of catalyst [2]. Formerly, the studies were carried out in the presence of homogeneous catalysts to reduce reaction time. However homogeneous catalysts are toxic, corrosive, pricy and often hard to remove from the products [3]. Thus, it is keenly desirable to improve new types of catalysts to replace them, since the catalysts are less toxic and facilitate the recovery and recycling of the catalysts [4, 5].

Many solid catalysts, e.g., new acids and bases, ion-exchange resins, zeolites and acidic clays were proposed in literature [6-14]. Among them, cation-exchange resins are the most known catalysts used in organic reactions [8-9]. Ion-exchange catalysis involves the use of ion-exchange resins to promote reactions that are normally catalyzed by mineral acids and bases. Additionally, ion-exchangers have been found to offer better selectivity towards the desired product(s) compared to homogeneous catalysts.

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Ion-exchange resins have been used in esterification as well as the hydrolysis of esters, such as methyl acetate distillation to produce acetic acid in a catalytic column [15]. Esterification reactions are realized by using many ion exchange resins. For instance, esterification of acetic acid with methanol and butanol [16-17], liquid-phase esterification of propionic acid with n-amyl alcohol [18], esterification of lactic acid with methanol [19], esterification of acrylic acid with propylene glycol [20] were investigated in the presence of Amberlyst-15. Amberlyst-35 was used in the study of liquid-phase esterification of propionic acid with n-butanol [21-22] and Amberlite IR-120 was employed in the esterification of acetic acid with iso-butanol [4], and the esterification of acetic acid with isoamyl alcohol was performed in the presence of Purolite CT-175 [23].

Some studies were found about salicylic acid esterification in literature. In a study, the esterification of acetic acid with salicylic acid over zeolites using dimethyl carbonate was investigated. Zeolites H β and HZSM5 are suitable catalysts for this reaction, whereas HY is not. The differences in the catalytic activity are attributed very much to the acid site strengths and their distribution. The energy of activation for the esterification reaction using DMC over H β and HZSM5 was calculated to be 25 and 36 kcal/mol, respectively. A reaction mechanism for the esterification of salicylic acid with dimethyl carbonate over zeolites is proposed. The deactivation is more pronounced when methanol is used as an esterifying agent compared to dimethyl carbonate [24].

In another study, Brønsted acidic ionic liquids were used as catalysts for the esterification of salicylic acid under microwave irradiation. The Brønsted acidity–catalytic activity relationships were also investigated and the results showed that the activity of the acidic ionic liquids was in excellent agreement with their acidity order [25].

In another study, inexpensive, eco-friendly, recyclable, and easily prepared Preyssler's anions have been used as catalysts for esterification of salicylic acid with aliphatic alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, t-butanol, 1-pentanol, and 2-pentanol) and benzylic alcohols (benzyl, 2-methylbenzyl, 2-chlorobenzyl, 4-bromobenzyl, 3-nitrobenzyl, and 4-methoxy benzyl alcohols). The results also suggest that the molar ratio, reaction time, temperature, and alcohol type are important factors. Preyssler catalyst can be recovered and reused without loss of structure and activity in both homogeneous and heterogeneous conditions [26]. The same research group studied the same reaction by using nano-SiO₂-supported Preyssler heteropolyacid catalyst both under thermal conditions and microwave irradiation. It has been found that the catalyst was highly active with 30 wt% loading and the yields were very high in esterification reactions. The use of nano-SiO₂-supported Preyssler heteropoly acid coupled with microwave irradiation allowed a solvent-free, rapid (3 min), and high-yielding reaction. This catalyst could be easily recovered and reused for many times without a significant loss in its activity [27].

In the last study, a series of functionalized mesoporous SBA-15 silica were synthesized with propylsulfonic groups by one-step method. The functionalized materials were characterized by various physico-chemical techniques and it was shown that the acid strength and acidity increased strongly with the concentration of sulfonic groups. The SBA-15-SO₃H was an efficient catalyst for esterification of salicylic acid with dimethyl carbonate to methyl salicylate [28].

In the present work, the aim was to obtain amyl salicylate which is known as the essence of the wildflowers. Amyl salicylate is generally used as supplement, in the cleanser and detergent production. Thus, in this work, the effects of temperature, reactant mole ratio, concentration of catalyst and mixing rate, in the presence of Lewatit MonoPlus S-100 as catalyst, was investigated and the kinetic models agreeable with the experimental data were developed.

2. MATERIALS

2.1. Materials

Salicylic acid (>99.5%) was obtained from Merck. Amyl alcohol (>99%), one of the reactants, dioxane, as the solvent, and Lewatit MonoPlus S-100, as the catalyst, were purchased from Sigma-Aldrich. The catalyst properties given by manufacturer are shown in Table 1.

Table 1. Properties of catalyst reported by manufacturer

Lewatit MonoPlus S-100		
Matrix		styrene-divinylbenzene (gel)
Standard ionic form		Na ⁺
Density	appx.g/ml	1.28
Moisture	%	~42-48
Particle size	mm	0.23-0.6
Cation exchange capacity	min. eq/L	2
uniform particle size	µm	575 ±50
Maximum operating temperature	K	393

2.2. Experiments

2.2.1. Apparatus

The reactor consists of a two-necked spherical Pyrex flask of 500 ml capacity fitted with a spiral coil condenser and a sample device. The temperature was controlled within ± 0.1 K by circulating water from a thermostat into the water jacket of the reactor. Mixing of the reaction fluid was performed by a magnetic stirrer.

2.2.2. Experimental procedure

The catalyst was kept in a water-dioxane solution containing 2 % water, representing the reaction mixture, for a night before using in the experiment. Thus the swelling effect of the catalyst was assumed to be eliminated during the reaction.

In a typical run, dioxane as the solvent and the reactant were placed in the reactor. A known amount of catalyst was added and the reactor contents were agitated thoroughly. After a steady value of desired temperature was attained, the second reactant was added and this was taken as zero time for the run. Two milliliters of the liquid sample were withdrawn from the reactor at regular intervals for analysis and immediately transferred to a crucible in an ice bath in order to ensure that no further reactions take place.

2.2.3. Analysis

Salicylic acid, in the reaction mixture, was determined by titration with 0.1 N standard sodium hydroxide solutions with phenolphthalein as an indicator. The water content in the reaction mixture was measured by Karl Fischer titration (Metrohm KF-784). After verifying that the measured water content corresponds to the calculated values based on stoichiometric equation, it has been concluded that there is no by product formation. Thus, the analysis was carried out by the determination of salicylic acid only and the other components of the mixture were calculated from stoichiometric mass balance equation.

3. RESULTS AND DISCUSSION

3.1. Effect of Parameters on Reaction Rate

The effects of parameters such as catalyst type and loading, agitation speed, temperature and reactant mole ratio on the esterification reaction rate were studied.

Swelling effect of the catalyst was neglected since preliminary experiment showed that the swelling process reaches equilibrium in a few minutes. Thus, it was assumed that the reactions occurred in the presence of the reasonably stable catalyst. Therefore, the proposed model in this work comprises the effect of catalyst swelling.

3.1.1. Effect of catalyst loading

Experiments were carried out with different catalyst loadings of 30, 50, and 80 g/L catalyst under the constant reaction conditions of 358 K, 500 rpm and $M=1$ with $C_{A0}=2$ mol/L. The initial reaction rate was calculated from Eq. 1 by using a conversion not greater than 10%, since the reaction rate can be considered to be a linear function of time.

$$-r_{A,0} = \frac{C_{A,0}X_A}{t} \quad (1)$$

Applying Eq. 1 to the experimental data obtained at the conversion not higher than 10%, initial reaction rate was calculated. A plot of the initial reaction rate vs. catalyst loading is given in Figure 1.

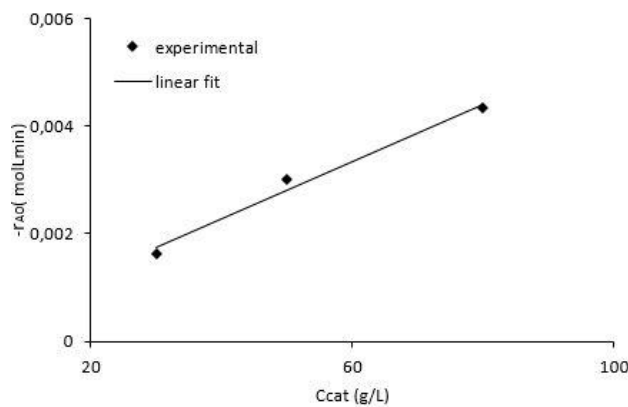


Figure 1. Effect of catalyst loading on the reaction rate at 358 K, 1/1 reactant mol ratio, 500 rpm

As seen in Figure 1, the reaction rate, as expected, is increasing linearly with catalyst loading since the active surface area is proportional to the amount of catalyst. Intersection of the line with ordinate will give the uncatalyzed reaction rate at given conditions. The mathematical expression relating the initial reaction rate to the catalyst loading can be derived from Figure 1 as follows;

$$-r_{A,0} = 0.0001 + 0.00005C_{cat} (g/L) \quad (2)$$

It should also be kept in mind that Eq. 2 is valid only at the given conditions of 358 K, 500 rpm and $M=1$ with $C_{A0}=2$ mol/L at which the experiments were performed. However, it does not alter the conclusion that the general reaction rate increases linearly with the catalyst loading.

3.1.2. Effect of agitation speed

To investigate the effect of agitation speed the experiments were carried out at 500 and 1000 rpm under the same reaction conditions of 358 K, $M=1$ with $C_{A0}=2$ mol/L, and catalyst loading of 50 g/L. Results are given in Figure 2. As seen in Figure 2, the reaction rate is not significantly differed by varying the stirring speed. Thereafter the experiments were carried out at constant stirring speed of 500 rpm. From this analysis it was concluded that the reaction is not external diffusion controlled.

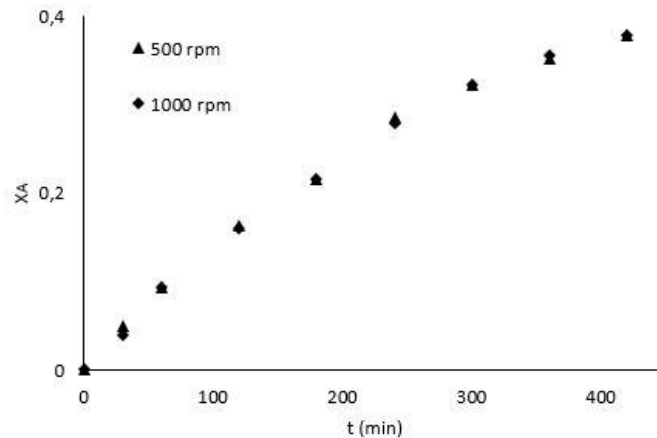


Figure 2. Effect of stirring speed on the reaction rate

3.1.3. Effect of temperature

Esterification reaction was realized at different temperatures of 338, 348 and 358 K under the constant reaction conditions of $M=1$ with $C_{A0}=2$ mol/L, 500 rpm and catalyst loading of 50 g/L as given in Figure 3. As seen in Figure 3, reaction rate is highly temperature sensitive. Therefore, it is reasonable to accept that the overall reaction is controlled by the surface reaction since internal and external diffusions, as the physical steps, are not strongly temperature dependent.

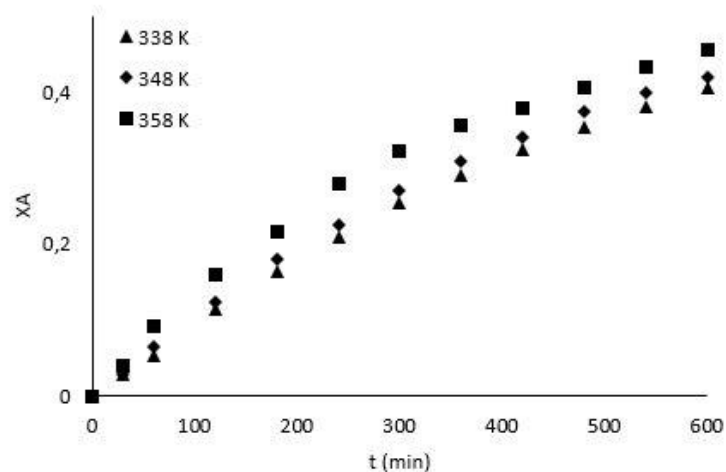


Figure 3. Effect of temperature on reaction rate

3.1.4. Effect of initial alcohol concentration

Initial reaction rate was determined by altering the concentration of alcohol while keeping that of acid constant at 358 K, $C_{A0}=2$ mol/L and catalyst loading 50 g/L. The results are shown in Figure 4. The ordinate values of these figures were obtained from Eq. 1 by using the experimental data. It is evident from this figure that n-amyl alcohol is adsorbed on the catalyst since the initial reaction rate is becoming nearly independent of the alcohol after certain values [29].

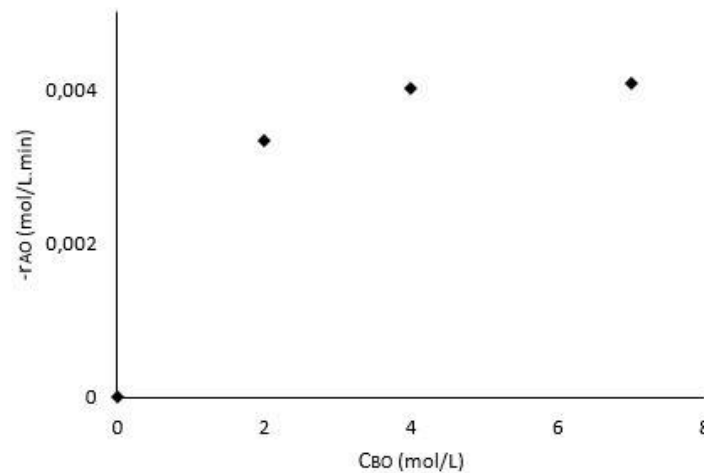


Figure 4. Effect of initial alcohol concentration on the initial reaction rate

3.2. Determination of the Equilibrium Constant

To determine the equilibrium conversion, X_e , reaction was carried out until the last two conversions calculated with 24 hr intervals was equal to each other at different temperatures of 338, 348 and 358 K. The equilibrium constant of the reaction can be found from the equilibrium conversions, as follows;

$$K_e = \frac{X_{A,e}^2}{(1 - X_{A,e})(M - X_{A,e})} \quad (3)$$

In Eq. 3 the equilibrium constant is stated in terms of concentration instead of activities since activity can be defined as $a_i = \gamma_i c_i$ and the coefficient γ_i can readily be combined with the equilibrium constant. Furthermore, the usage of concentrations is more practical than that of activities.

Temperature dependency of the equilibrium constant was also determined by applying van't Hoff equation. The result is shown in Figure 5. From Figure 5, the equilibrium constant was found to be

$$K_e = \exp(3191/T - 11.324) \quad (4)$$

where T is absolute temperature in Kelvin.

The heat of reaction, assuming independent of temperature ranging from 338 K to 358 K, was calculated to be $\Delta H_r = 3.191 \times 8.314 = 26.53$ kJ/mol.

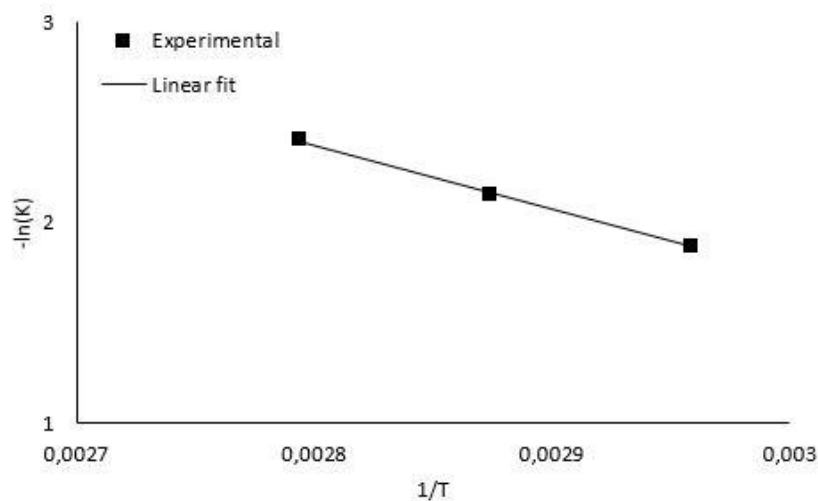


Figure 5. Temperature dependency of the equilibrium constant

3.3. Kinetic Modeling

As seen in Figure 3, reaction rate is highly temperature sensitive. It is almost doubling in every temperature rising of 10 K. Therefore, it is reasonable to accept that the overall reaction is controlled by the surface reaction since internal and external diffusion, as the physical steps, are not strongly temperature dependent. This conclusion was further confirmed by literature stating that the influence of external and internal diffusion can be neglected for most of the reactions catalyzed by the strongly acidic cation exchange resins [30-37].

For the kinetic behavior of heterogeneously catalyzed esterification reactions, three different models have been applied: the quasi-homogeneous model (Q-H), the Eley–Rideal model (E–R) and the Langmuir–Hinselwood model (L–H) [26]. The quasi-homogeneous first- and second order models are applicable for many reactions catalyzed by ion-exchange resins. In the E–R and L–H mechanisms, it is assumed that the surface reaction controls the overall process. The L–H model is applicable for the reaction between adsorbed molecules. On the other hand, the E–R model can be applied to the reactions between an adsorbed and a non-adsorbed reactants in the bulk phase.

It is reported that the affinity of Lewatit MonoPlus S-100 resin towards water and amyl alcohol are stronger than that towards salicylic acid and amyl acetate and thus the adsorption terms for salicylic acid and amyl salicylate are neglected in the LHHW and ER models [38-39].

Since the general reaction stoichiometry is given by



The kinetic model for Q-H, E-R and L-H will be in the form of

$$-r_A = k_1 \left(C_A C_B - \frac{C_E C_W}{K} \right) \quad (6)$$

$$-r_A = \frac{k_1 K_B \left(C_A C_B - \frac{C_E C_W}{K} \right)}{(1 + K_B C_B + K_W C_W)} \quad (7)$$

$$-r_A = \frac{k_1 K_B \left(C_A C_B - \frac{C_E C_W}{K} \right)}{(1 + K_B C_B + K_W C_W)^2} \quad (8)$$

respectively, where K_B and K_W are the respective adsorption equilibrium constants for amyl alcohol and water.

The estimation of the constants appearing in the models was performed by applying nonlinear regression analysis in MATLAB 7.0 program to the experimental data obtained at different temperatures. In this fitting the mean square differences between calculated and experimental values of rate was minimized as shown in Eq.9.

$$\min \phi = \sum_{allsamples} (r_{cal} - r_{exp})^2 \quad (9)$$

The constants with their standard deviation at 95% confidence interval are given in Table 2. Experimental results were then compared with those of the model prediction through the values of the mean relative deviation (MRD) between experimental and calculated conversions.

$$MRD = \frac{1}{n} \left(\sum_{allsamples} \left| \frac{X_{A,cal} - X_{A,exp}}{X_{A,exp}} \right| \right) \times 100 \quad (10)$$

The MRDs calculated by Eq. 10 are also given in Table 2.

Table 2. The average values of the constant with 95% confidence interval and MRDs at different temperatures for each model

Model	T (K)	$k_1 (x10^3)$ (L/mol.min)	K_B (L/mol.min)	K_W (L/mol.min)	MRD (%)
Q-H	338	0.2826±0.004	-	-	3.388
	348	0.3102±0.002	-	-	2.951
	358	0.3594±0.076	-	-	4.481
E-R	338	0.537±0.085	100.66±11.443	18.583±8.833	0.997
	348	0.568±0.084	75.145±15.33	18.786±13.616	2.299
	358	0.732±5.142	38.210±4.049	30.019±11.061	2.267
L-H	338	5.948±0.486	6.448±0.383	3.424±0.499	0.824
	348	7.739±0.997	5.816±0.672	3.386±0.865	1.263
	358	9.874±0.584	3.383±0.191	3.346±0.561	1.265

As seen in Table 2, although the rate constants for three models are close to each other, the L-H model is the most preferable one because of low MRD. This conclusion can also be seen in Fig. 6.

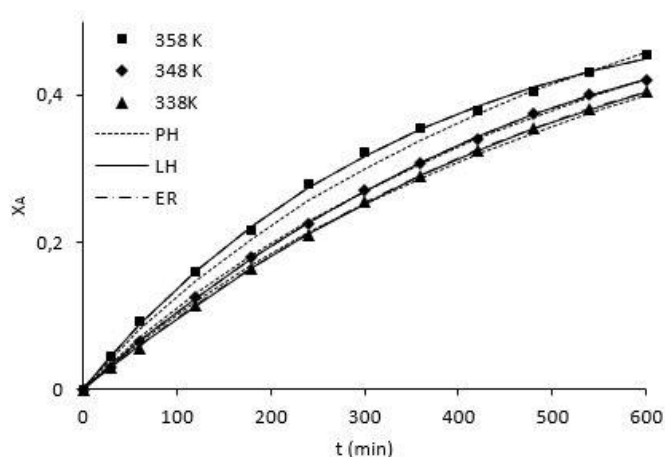


Figure 6. Conversion-time curves based on the three models with the experimental data

The curves obtained by applying the Runge-Kutta method to the Eqs. 6, 7 and 8 are given in Fig 6 together with the experimental data. As seen in Figure 6, L-H model fits the experimental data best among the others.

Therefore, applying the Arrhenius equation to the values given in Table 2 for L-H model, the temperature dependency of the constants as well as their corresponding activation energies and adsorption heats were found to be;

$$\begin{aligned} k_1 &= \exp(4.349 + 3211/T) & E &= 26.70 \text{ kJ/mol} \\ K_A &= \exp(7.109 - 3050/T) & \Delta H &= -25.36 \text{ kJ/mol} \\ K_W &= \exp(0.818 - 139.6/T) & \Delta H &= -1.17 \text{ kJ/mol} \end{aligned}$$

4. CONCLUSIONS

The kinetics of esterification of salicylic acid with amyl alcohol has been studied batchwise in the presence of Lewatit MonoPlus S-100 as heterogeneous catalyst. The kinetic behavior of the reaction has been tested by three different models: the quasi-homogeneous model, the Eley-Rideal model and the Langmuir-Hinselwood model. By applying nonlinear regression analysis in MATLAB 7.0 program to the experimental data at different temperatures, it has been shown that L-H model fits the experimental data best among the others.

The temperature dependencies of the constants appearing in the model were also determined from Arrhenius equation. These are:

$$\begin{aligned} k_1 &= \exp(4.349 + 3211/T) & E &= 26.70 \text{ kJ/mol} \\ K_A &= \exp(7.109 - 3050/T) & \Delta H &= 25.36 \text{ kJ/mol} \\ K_W &= \exp(0.818 - 139.6/T) & \Delta H &= 1.17 \text{ kJ/mol} \end{aligned}$$

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