THERMODYNAMIC EQUILIBRIUM OF ETHYL ACETATE SYNTHESIS: VALIDATION OF OBTAINED DATA BY DIFFERENT TACKLED METHODOLOGIES AND TECHNIQUES

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Abstract - The esterification reaction between acetic acid and ethyl alcohol was examined over a temperature range of 298.15 to 328.15 K, utilizing both homogeneous and heterogeneous catalysts. Experimental conditions included equimolar reactant ratios and catalyst loadings of 40 g/L. Equilibrium was achieved within two days across all systems, with minimal temperature-dependent variation in equilibrium conversions. Catalyst characteristics significantly impacted equilibrium conversion, alongside temperature effects. The Modified UNIFAC-Dortmund model accurately predicted the system's non-idealities, with activity coefficients following the sequence: acid < alcohol < ester < water. Equilibrium constants (Ka) demonstrated a slight decrease with rising temperature. The average Ka values for sulfuric acid and various heterogeneous catalysts (Amberlyst 15, Amberlite IR-120, Dowex 50wx8) were 13.92, 8.16, 10.60, and 9.31, respectively. The catalyst type influenced equilibrium conversion, with Ka values for sulfuric acid comparable to those reported for para-toluene sulfonic acid. Theoretical equilibrium constants, sensitive to ΔG0 values, aligned closely with experimental results, particularly for the Amberlyst 15-catalyzed system.

I. INTRODUCTION

Ethyl acetate is a colorless, sweet-smelling liquid widely used as a polar aprotic solvent. It is valued for its low toxicity, cost-effectiveness, and versatile applications across various industries.

Applications

- Diluent: Commonly used due to its low toxicity and cost [1].
- Electronics: Employed as a cleanser for electronic boards [1].
- Varnish Remover: Used in paint and varnish removal processes [1].
- Paint Industry: Functions as an activator and hardener in paint formulations [2].
- Perfumes: A key ingredient in perfume manufacturing [2].
- Chromatography: Utilized in column chromatography for separations.
- Insect Study: Used in insect collection and preservation.

Availability & Demand

Ethyl acetate production grew significantly from 400,000 tons in 1985 to 1.3 million tons globally by 2004, with the Asia-Pacific region being the largest producer and consumer [3-5]. Key producers include China, India, Japan, the UK, and Brazil.

Production Methods

1. Fischer Esterification: The most common industrial method, reacting ethanol with acetic acid in the presence of an acid catalyst (e.g., sulfuric acid) [6].
2. Tishchenko Reaction: Produces ethyl acetate by reacting acetaldehyde with an alkoxide base [7].
3. Heterogeneous Catalysis: Emerging techniques using environmentally friendly catalysts (zeolites, metal oxides, cation-exchange resins) offer advantages such as non-corrosiveness and reusability [8-15].

Recent Studies

- Mazotti et al.: Investigated the cation-exchange resin (Amberlyst 15)-catalyzed esterification of ethanol and acetic acid, analyzing the equilibrium constant and reaction thermodynamics [16].
- Kang et al.: Examined vapor-liquid equilibrium (VLE) in ethyl acetate production, applying the UNIQUAC model to understand equilibrium constants and their temperature dependence [18].

This literature highlights ongoing research aimed at optimizing the production process, catalyst efficiency, and equilibrium modeling for industrial applications.

II. THEORY

Catalytic Esterification Reaction

The esterification of acetic acid with ethanol to form ethyl acetate and water is a reversible reaction, represented as:

$$CH_3COOH+CH_3CH_2OH \leftrightarrow CH_3COOCH_2CH_3+H_2O$$

The forward rate of esterification (r_f) and the backward rate of hydrolysis (r_b) are given by:

- $r_f=k\cdot C_{acid}\cdot C_{alcohol}$

- $r_b = k' \cdot C_{ester} \cdot C_{water}$

At equilibrium, $r_f = r_b$, leading to the equilibrium constant K=k/k' which depends on the specific acid and alcohol used and is determined experimentally. Though mildly temperature-dependent, the equilibrium constant is less sensitive to structural changes in the reactants.

Reaction Mechanism

The esterification mechanism involves protonation of acetic acid, nucleophilic attack by ethanol, water elimination, and ester formation. This stepwise mechanism is represented by a series of proton transfer and elimination reactions, which are influenced by both steric and electronic effects.

Heterogeneous Catalytic Process

Esterification in the presence of a heterogeneous catalyst involves multiple steps, including external and internal diffusion, adsorption of reactants, surface reactions, and desorption of products. The overall reaction rate is controlled by the slowest of these steps, typically surface reactions or diffusion processes. In cases where diffusion limitations occur, strategies such as reducing catalyst particle size can mitigate these effects.

Modelling the Reaction

For simplification, esterification reactions can be modeled using the Pseudo-Homogeneous Model when no significant adsorption or desorption steps are involved. The reaction rate is then governed by the activities of the species, influenced by the forward rate constant and the equilibrium constant, both of which follow the Arrhenius equation.

Thermodynamics of Esterification

The equilibrium constant KKK is a key parameter that describes the balance between reactants and products at equilibrium. It is derived from the standard Gibbs free energy change (ΔG∘\Delta G^\\circΔG∘) and is linked to the temperature through the van 't Hoff equation. The temperature dependence of KKK is used to predict how equilibrium shifts with temperature changes.

Non-Ideal Behavior and Activity Coefficients

In real systems, deviations from ideal behavior necessitate the use of activity coefficients. The UNIFAC model is employed to account for non-idealities, with the activity coefficient consisting of combinatorial and residual parts. This model aids in predicting equilibrium in non-ideal mixtures by factoring in molecular interactions and surface area parameters.

III. EXPERIMENTAL

Materials

The reagents and catalysts for this study were procured from Sigma-Aldrich and Fluka. The details are provided below:

Reagent/Catalyst	Catalog Number	Supplier
Sulfuric Acid	39741	Aldrich
Amberlyst® 15	16380	Sigma-Aldrich
Amberlite® IR120	216534	Aldrich
Dowex® 50WX8 (200-400 mesh)	217514	Sigma-Aldrich
Ethanol	4852	Sigma-Aldrich
Acetic Acid	320099	Sigma-Aldrich
Sodium Hydroxide Solution (0.1 N)	319481	Fluka
Phenolphthalein Solution	74760	Fluka

The sulfuric acid catalyst was used as supplied, while the cation exchange resins (Amberlyst® 15, Amberlite® IR120, Dowex® 50WX8) were dried at 343.15 K under vacuum to remove moisture without affecting their catalytic activity.

Equilibrium Runs

The equilibrium experiments were conducted as follows:

1. Preparation: Equimolar amounts (0.5 mol each) of ethanol and acetic acid were added to a water-jacketed glass reaction cell, totaling approximately 58 mL of reactants.
2. Catalyst Addition: Calculated amounts of catalyst were introduced to achieve a catalyst loading of 40 g/L or its equivalent.
3. Temperature Control: The reaction temperatures studied were 298.15 K, 313.15 K, 321.15 K, and 328.15 K.
4. Mixing: The reaction mixtures were stirred continuously using magnetic stirrers.
5. Sampling: Samples were collected at the start of the reaction and subsequently once a day for seven days.
6. Reaction Monitoring: The progress of the reaction was tracked using two methods:

- Titration: A 0.3 mL sample was titrated against 0.1 N sodium hydroxide (NaOH) solution.
- Gas Chromatography: A 1 μL sample was injected into an Agilent gas chromatograph with a Porapak-QS 1.25 m × 1/8 in. column, using a temperature program (390 K for 2 min, 10

K.min^{-1} ramp to 443 K, held for 8 min). Retention times were: water (2.3 min), ethanol (5.2 min), ethyl acetate (10.2 min), and acetic acid (11.7 min)

IV. RESULTS & DISCUSSION

UNIFAC Parameters

The Modified UNIFAC (Dortmund) model was employed to predict activity coefficients for the components in the system. Table 1 presents the r_k and Q_k parameters used.

Catalyst Influence on Conversion

The conversion rates of acetic acid to ester for systems catalyzed by sulfuric acid, Amberlyst 15, Amberlite IR-120, and Dowex 50WX8 were plotted in Figures 1 through 16. Equilibrium conversions were reached within 2 days for all systems. The average percentage conversions were as follows:

- Sulfuric Acid: 65.57%
- Amberlyst 15: 59.56%
- Amberlite IR-120: 64.42%
- Dowex 50WX8: 61.83%

These results align with previous findings, indicating that catalyst type influences equilibrium conversion [16].

Effect of Temperature

Tables 2 through 5 show that the equilibrium constants (k_x) for sulfuric acid and Amberlyst 15 systems increased slightly with temperature, suggesting mild endothermic behavior. In contrast, the Amberlite IR-120 and Dowex 50WX8 systems exhibited a slight decrease in k_x with temperature, indicating mild exothermic behavior. The corresponding enthalpy change (ΔH) values confirm this behavior, in line with previous research [29, 30].

Non-Ideality and Activity Coefficients

Activity coefficients calculated by the Modified UNIFAC (Dortmund) model increased in the following order: $\gamma_{acid}<\gamma_{alcohol}<\gamma_{ester}<\gamma_{water}$ The activity equilibrium constant (K_a) for each system was approximately 3.8 times the corresponding mole-fraction-based constant (K_x). The average K_x values were:

- Sulfuric Acid: 13.92
- Amberlyst 15: 8.16
- Amberlite IR-120: 10.60
- Dowex 50WX8: 9.31

For the Amberlyst 15 system, the back-calculated Gibbs free energy (ΔG^0) was -5.04 kJ/mol, slightly differing from previously reported values due to the activity coefficient model used.

Comparison with Theoretical Data

Theoretical calculations for the activity equilibrium constant at 298.15 K yielded values between 7.43 and 7.11 across the studied temperature range. These values are consistent with those reported by earlier studies [18, 19], though significantly different when compared to data from Stull et al. [20]. This highlights the sensitivity of calculated K_a values to ΔG^0 values.

The theoretically calculated K_a values confirm that the esterification reaction is mildly exothermic, and the theoretical equilibrium constant is comparable to the experimental value obtained for the Amberlyst 15 system.

This revised version simplifies the detailed analysis while retaining critical information, making it clearer and more concise for a professional audience. Let me know if you'd like any further adjustments or additions!

V. CONCLUSIONS

1. The average equilibrium percentage conversions for sulfuric acid, Amberlyst 15, Amberlite IR-120, and Dowex 50WX8-catalyzed systems were 65.57%, 59.56%, 64.42%, and 61.83%, respectively.
2. The esterification of ethanol with acetic acid was mildly endothermic for the sulfuric acid and Amberlyst 15-catalyzed systems, and mildly exothermic for Amberlite IR-120 and Dowex 50WX8-catalyzed systems, as indicated by K_x values.
3. The activity coefficients, calculated via the Modified UNIFAC (Dortmund) method, increased in the order of $\gamma_{acid}<\gamma_{alcohol}<\gamma_{ester}<\gamma_{water}$.
4. The K_y values decreased slightly with increasing temperature.
5. The K_y values were at least three times greater than the corresponding K_x values for all systems.
6. The average equilibrium constant values (K_a) for sulfuric acid, Amberlyst 15, Amberlite IR-120, and Dowex 50WX8-catalyzed systems were 13.92, 8.16, 10.60, and 9.31, respectively.
7. The average K_a values for homogeneous catalysts like sulfuric acid (13.9, this study) and para-toluene sulfonic acid (13.4, earlier study [18]) were comparable.
8. Theoretical calculations for the equilibrium constant showed a weak dependence on temperature and yielded values in agreement with experimental data.
9. The theoretical K_a values (7.4 to 7.1) are comparable to those reported by earlier studies (7.1 to 8.2).

10. The average theoretical K_a value (7.19) closely matches the experimental value for the Amberlyst 15-catalyzed system (8.16) and is consistent with other heterogeneous systems.

NOMENCLATURE

- $a_{acetic\ acid}$: Activity of acetic acid in the liquid phase
- $a_{alcohol}$: Activity of alcohol in the liquid phase
- a_{ester} : Activity of ester in the liquid phase
- a_{water} : Activity of water in the liquid phase
- F_i : Area fraction of component i
- K_y : Activity coefficient reaction equilibrium constant
- K_a : Activity reaction equilibrium constant
- K_a ,298.15 : Activity reaction equilibrium constant at 298.15 K
- K_i : Adsorption equilibrium constant for component i
- K_x : Mole fraction reaction equilibrium constant
- M_{cat} : Mass of the catalyst (g)
- n : Total number of moles in the system
- N : Number of data points
- q_i : Area parameter of component iii
- Q_k : Area parameter of the UNIFAC group k
- Q_m : Group parameter
- R^2 : Coefficient of determination of fitted values
- R_g : Universal gas constant (kJ/mol/K)
- r_i : Volume parameter of component iii
- R_k : Volume parameter of the UNIFAC group k
- T : Temperature (K)
- V_i' : Modified volume parameter fraction of component iii used in the Modified UNIFAC (Dortmund) method

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