Kinetic Study on Propionic using Alamine 336 in Petroleum Ether by Reactive Extraction

B. Sarath Babu, Seerla Venkata Priyanka

Abstract: The growing demand for the production of propionic acid as it useful in chemical industry, pharmaceutical industry, preservations, drug delivery towards a more economical energy efficient technology. Reactive extraction is used over conventional method as conventional methods i.e., fermentation broth is expensive as well as unfriendly towards the environment. A specific extractant and various diluents are used in reactive extraction which gives us a promising technique for the acid extraction. Alamine 336 (TOA) was used with a combination of petroleum ether by varying concentrations. Physical and chemical extractions results are presented as equilibrium distribution, distribution co – efficient, extraction efficiency, loading ratio and volume percentage by varying concentrations. The propionic acid distribution between aqueous & organic phase reaches equilibrium over a concentration range of 0.04 $kmol/m^3$ – 0.22 $kmol/m^3$. The optimum TOA concentration is found to be 40% at which K_D value for petroleum ether is 0.73. In petroleum ether the modified separation and loading ratio increases with decrease in TOA acid concentration in petroleum ether.

Keywords: Carboxylic acids, propionic acid, petroleum ether, alamine – 336, reactive extraction, loading ration, equilibrium distribution, efficiency, modified separation.

Abbreviations: TOA, [B] – tri - n - octyl amine; [PA] – propionic acid; K_{D1} – distribution co – efficient; Z – loading ratio; S_f – Separation factor;

I. INTRODUCTION

Organic compounds which include carboxylic acids are widely utilized in the chemical, medicinal, and food sectors. Carboxylic acids are used in the manufacture of detergents, medications, polymers, textiles, dyes, fragrances, and animal feed [1], [2]. Carboxylic acids are currently used in sophisticated applications such as tissue engineering, medication delivery, and the manufacture of biopolymers. Chemical synthesis is used for synthesizing the majority of carboxylic acids on an industrial basis[3], [4]. Propionic acid, a major carboxylic acid, is used to preserve animal feed like hay, silage, and grains as well as human consumables like cheese and baked products.

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Along with these substantial uses, propionic acid and its derivatives have application in making plasticizers, solvents, tastes, perfumes, and mold inhibitors for hay and silage [5]. Due to their larger molecular weight, carboxylic acids like propionic acid have been reactively separated using effective solvating extractants that include aliphatic amines. Tertiary aliphatic amines are among the different extractants for reactive extraction that are frequently utilised in the reactive extraction of carboxylic acids. Without losing any extractant, long chain aliphatic amines have an extremely lower solubility in water. They are also thermally stable, making distillation a viable method for regeneration. In general, tertiary amines are preferred to secondary or primary amines [6]–[8]. For practical purposes, primary amines are too soluble in water. Carboxylic acid with secondary amines may potentially produce amides, losing both product and extractant in the process. Longer chains enhance the alkyl character of the solvent and lower the molar conc. of the extractant that is available for complexation, lowering extraction. Alamine 336 (TOA), Aliquat 336, & other aliphatic amines are frequently used to extract carboxylic acids such as lactic, propionic, citric, nicotinic, butyric, glyoxylic & glycolic acids [9], [10]. Several aspects in equilibrium research affect the reactive extraction system's properties. The four primary process variables are the nature and concentration of the acid to be extracted, the extractant concentration, the diluent utilised, and the temperature.[11]. Typically, diluent is added in addition to the extractant to improve its characteristics through general solvation and to affect the extractant's extraction power through specific interaction. One or more inert or active components are present in the diluent. The extraction is improved by a number of polar which are active and electron or proton donating diluents, including higher alcohols, ketones, nitro benzenes, and halogenated aliphatic/aromatic hydrocarbons. The solvent capacity, however, is constrained by long chain paraffins, benzene, etc. as they are inert [12], [13]. The many types of reactions governing the transfer, which are often exclusively dependent on the extractants and diluent employed, are what give rise to the variety of extraction processes. Tri-n-octylamine (TOA) was explored by Amit Keshav et al. (2009) studied using 1 – decanol and 2 – octanol as diluents for reactive extractions propionic acid[14]. From an acidic aqueous solution, physical and chemical extractions were presented. This study examines the propionic acid extraction from aqueous solutions utilising alamine 336 in petroleum ether.

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1

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II. EXPERIMENTAL PROCEDURE

1.1 Material

Alamine 336 (TOA) is a colour less tertiary amine in liquid state, Without preliminary treatment, propionic acid (99%) and petroleum ether were utilised as diluents. The solutions were made with distilled water. For titration, NaOH and phenolphthalein indicator were used.

1.2 Apparatus

100 ml standard flask, 25 ml standard flask, 125 ml separating funnel, pH meter, rotating shakers, beakers, pipette, measuring jar.

1.3 Procedure

Experiments involving physical and chemical equilibrium were performed at 300°C, or normal temperature. Propionic acid's concentrations were adjusted from 0.05 to 0.4 $kmol/m^3$. Tri-octylamine concentrations of 10% (0.2066 $kmol/m^3$), 20% (0.4132 $kmol/m^3$), 30% (0.6198 $kmol/m^3$), and 40% in petroleum ether were studied at concentrations of 0.05, 0.1, 0.2, 0.3, and 0.4 $kmol/m^3$ of propionic acid.

Equal volumes (25 ml) of both aqueous and organic solutions are used in extraction experiments, which are run for 12 hrs at a constant room temperature. For at least two hours, at the same temperature, the mixture is allowed to settle. pH of the aqueous phase was determined using a pH metre. Propionic acid aqueous solutions range in pH from 2.65 to 3.13. Based on the differences in densities, the organic & aqueous phases were separated after settling. Using potentiometric titration with sodium hydroxide solutions of 0.05 N and phenolphthalein as an indicator, in the aqueous phase a sample of 2 ml is used to determine the acid concentration. By using mass balance, the acid concentrations in the organic phase are determined. The pH values used in the chemical equilibrium studies ranged from 3 to 7. [15]

1.4 Theory

Propionic acid ([PA]) is reactively extracted from liquid to liquid using tertiary amine i.e., tri octyl amine ([B]) that produces a complicated reaction known as B:(PA)n, which mostly takes place in organic phase. The distribution coefficient can be understood by the given series of equations, taking into account the fact that the precise chemistry involved in the uptake of additional acid is unknown [16]:
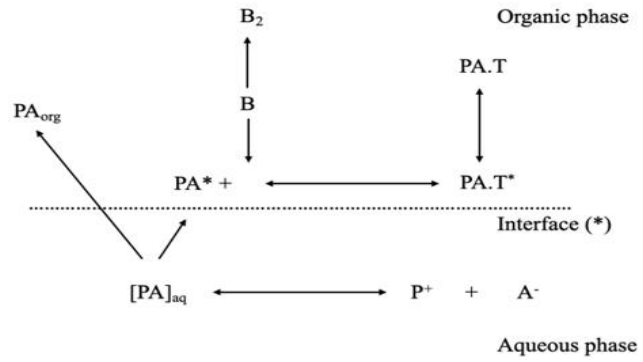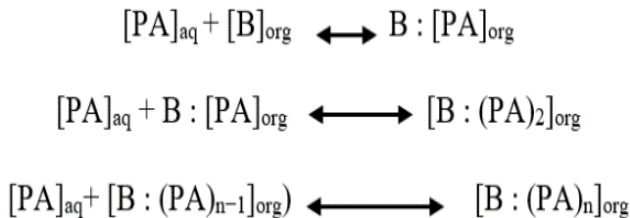
$$[PA]_{aq} + [B]_{org} \longleftrightarrow B : [PA]_{org}$$

$$[PA]_{aq} + B : [PA]_{org} \longleftrightarrow [B : (PA)_2]_{org}$$

$$[PA]_{aq} + [B : (PA)_{n-1}]_{org}) \longleftrightarrow [B : (PA)_n]_{org}$$

Fig. 1 Mechanism for extraction of propionic acid (PA) using TOA in petroleum ether (B) [13]

The degree of extraction & distribution coefficient were used to examine the extraction process. By assuming no change in volume at equilibrium, the degree of extraction is calculated as the ratio of the propionic acid (PA) concentration in the organic phase to the PA concentration in aqueous solution. With the stated connection, the distribution coefficient K_1 is determined.

$$K_{D1} = \frac{[PA]_{Org}}{[PA]_{aq}}$$

Degree of extraction is calculated as

$$E\% = \frac{K_{D1}}{1+K_{D1}} \times 100$$

The loading ratio describes how much organic acid can be added to the organic phase (alamine 336 + petroleum ether). The loading of the extractant Z,

$$z = \frac{[PA]_{org}}{[B]}$$

The stoichiometric loading Factor Z_S

$$Z_S = \frac{[PA]_{org} - v[PA]_{org}^{diluent}}{[T]}$$

Modified Separation Factor S_f

$$S_f = \frac{[PA]_{org}}{[PA]_{org} + [PA]_{org}^{diluent}}$$

Experiments were conducted at different sets of conditions and the results obtained are presented and interpreted in the following sections:-

III. RESULTS & DISCUSSION

1.1. Physical equilibria

In figure 3 the equilibrium distribution of water – propionic acid – petroleum ether is shown. Petroleum ether is non – polar by nature. Equilibrium data is generated for physical extraction of propionic acid using diluent petroleum ether. The distribution of propionic acid between aqueous phase & organic phase reaches equilibrium over a conc. range of 0.04 $kmol/m^3$ – 0.22 $kmol/m^3$.
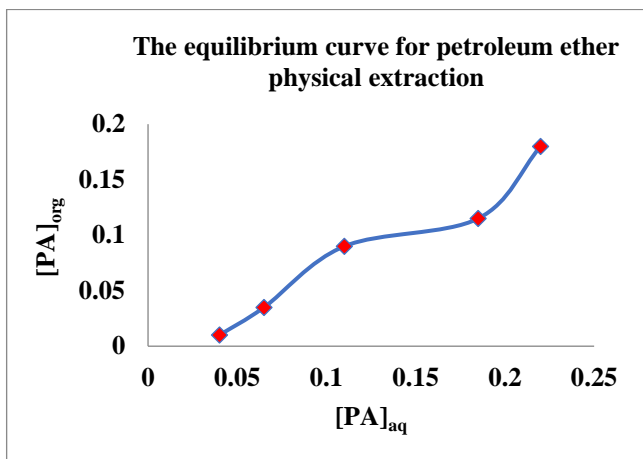
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Fig 2: Equilibrium distribution of (water - Propionic acid – Petroleum ether)
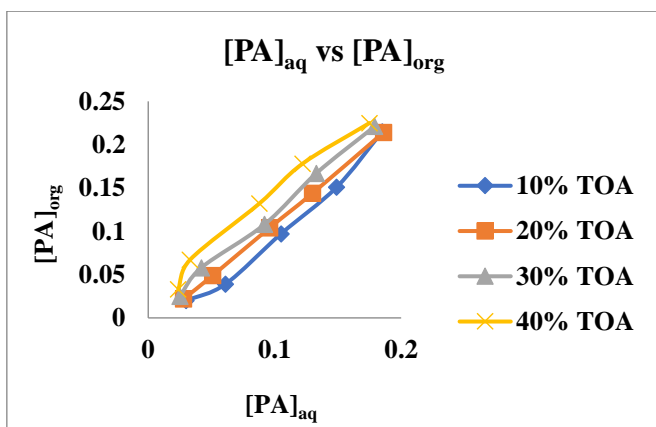

Fig 3: Equilibrium for Reactive Extraction

We can see the acid variation in organic phase with aqueous phase for different concentrations of propionic acid from 0.05 kmol/m^3 – 0.4 kmol/m^3 in petroleum ether. In both aqueous and organic phase, the acid concentration increases with increase initial concentration of propionic acid. We can observe the same trend for 10, 20, 30, 40 percentage TOA concentration.

1.2. Chemical equilibria

1.2.1. Effect of distribution co -efficient

The effect of TOA on extraction in petroleum ether is indicated in fig 4. With higher amine concentrations and reducing acid concentrations, from aqueous solutions more amount of acid was extracted at any initial acid conc.
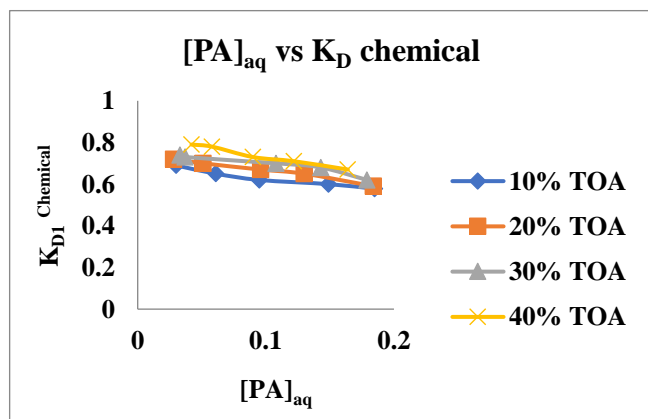

Fig 4: Effect of [PA]$_{aq}$ on K$_D$ with variable TOA concentration in Petroleum ether

1.2.2. Extraction efficiency

Fig 5 show how the conc. of propionic acid in the aqueous phase influences extraction efficiency. When the propionic acid concentration is reduced, the level of extraction dramatically increases. The influence of aqueous concentration on extraction efficiency has been studied using various TOA concentrations, and it has been found that the extraction efficiency improved as tri-n-octyl amine concentrations rose. This is driven by the fact that as TOA concentrations increases, the acid concentration in the aqueous phase decreases.
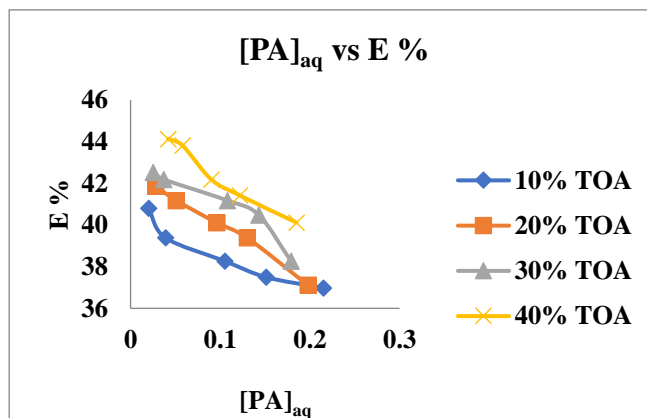

Fig 5: Effect of aqueous conc. on E%

1.2.3. Loading ratio

The equilibrium conc. of propionic acid in the aqueous phase for various concentrations of TOA in petroleum ether vs loading ratio, z in organic phase can be seen in Fig. 3.2.3.1. Also, it can be observed that the loading rate dropped as tri-n-octyl amine concentrations increased. Only when complexes are included formation of acid molecules is high at lower tri-n-octyl amine concentrations. It's obvious that complexes including a single amine develop since loading decreases as tri-n-octyl amine concentration increases.
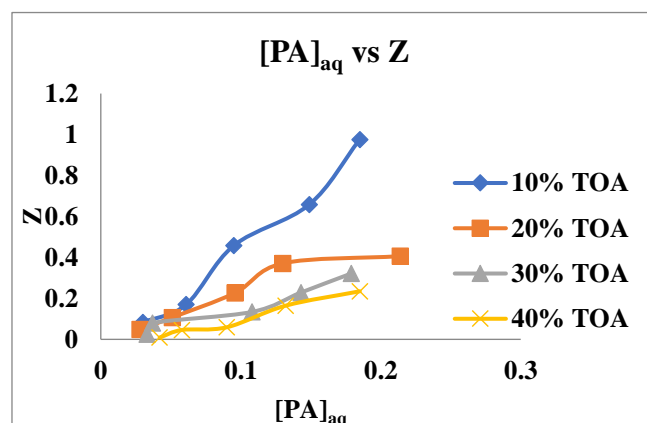

Fig 6: Effect of aqueous concentration on loading ratio

1.2.4. Effect of volume % of TOA (B)

To enhance the level of extraction, chemical extraction employing B (TOA) in these diluents can be used. The effect of TOA concentration in various diluents was investigated.

TOA was varied in petroleum ether from 10 to 60%. It was found that distribution co efficient first increased and then decreased, it increased for chemical extraction ($K_D^{Chemical}$) from 10–40% and decreased from 40-60% TOA.
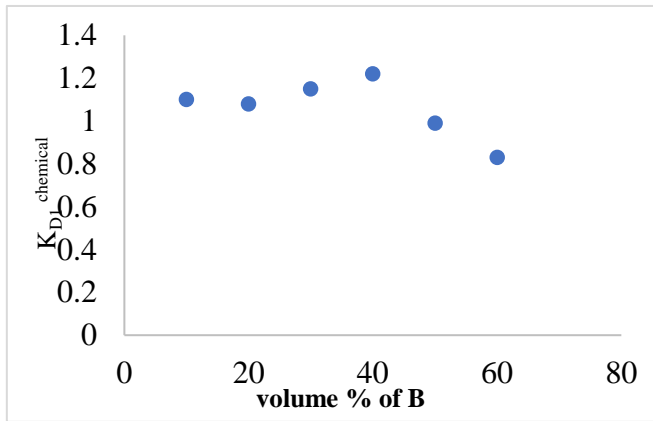

Fig 7: Effect of volume % of B in Petroleum ether for 0.2 kmol/m³

1.2.5.   Effect of pH

Propionic acid extraction employing 40% TOA in 1-octanol is shown in fig. 8. Since the pH of the fermentation broth changes as acid is created, it is crucial to research how pH affects the extraction of propionic acid at varied pH values. It is discovered that extraction is relatively low at pH 5 of acid when pH is changed from 3.0 to 7. , $K_D^{Chemical}$ decreases sharply when pH is raised above natural pH; beyond that, the reduction is more gradual and slower. The most likely explanation for this is that when pH rises, the proportion of undissociated acid decreases. The excessive amount of TOA present caused the existing bonding sites to become cluttered, which resulted in a very low acid partition from the aqueous phase.
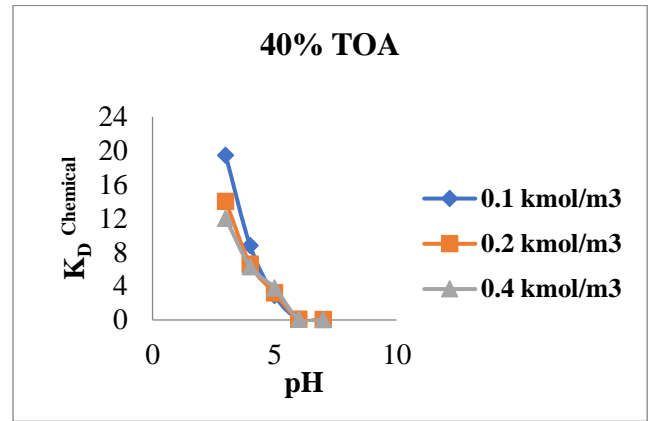

Fig. 8: Effect of pH

1.2.6.   Modified separation factor

From fig. 9 the S_f observed is 0.5454 at initial concentration of acid 0.1 kmol/m³ for TOA conc. of 40% in petroleum ether. We can observe that effect of S_f is less.
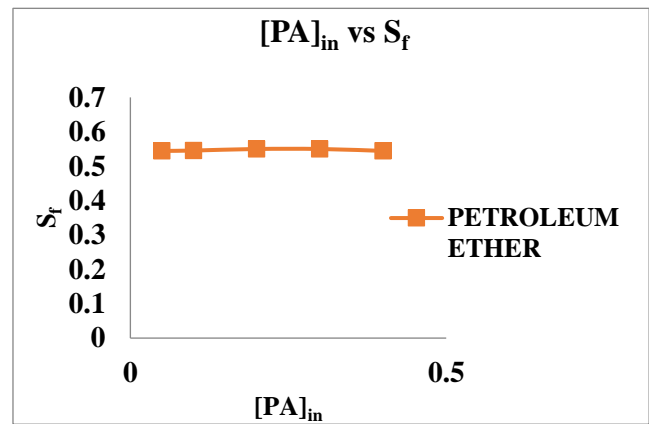

Fig. 9: Effect of acid concentration ([PA]ₙ) on (Sf) using 40% alamine

Table 1: Equilibrium for reactive extraction of propionic acid with various concentrations of TOA (B) in Petroleum Ether

10% B		20% B		30% B		40% B	
$[PA]_{aq}$	$[PA]_{org}$	$[PA]_{aq}$	$[PA]_{org}$	$[PA]_{aq}$	$[PA]_{org}$	$[PA]_{aq}$	$[PA]_{org}$
0.03	0.02	0.028	0.022	0.033	0.017	0.042	0.008
0.061	0.039	0.051	0.049	0.037	0.063	0.058	0.042
0.095	0.105	0.096	0.104	0.108	0..92	0.09	0.11
0.149	0.151	0.13	0.17	0.143	0.157	0.122	0.178
0.185	0.215	0.214	0.186	0.179	0.221	0.164	0.236

Units: $[PA]_{aq}$, $[PA]_{org}$ – Kmol/m³

Table 2: Effect of aqueous concentration on K_D with variable TOA (B) concentration in Petroleum Ether

10% B		20% B		30% B		40% B	
$[PA]_{aq}$ Kmol/m³	$K_{D1}^{chemical}$	$[PA]_{aq}$ Kmol/m³	$K_{D1}^{chemical}$	$[PA]_{aq}$ Kmol/m³	$K_{D1}^{chemical}$	$[PA]_{aq}$ Kmol/m³	$K_{D1}^{chemical}$
0.03	0.69	0.028	0.72	0.033	0.74	0.042	0.79
0.061	0.65	0.051	0.7	0.037	0.73	0.058	0.78
0.095	0.62	0.096	0.67	0.108	0.7	0.09	0.73
0.149	0.6	0.13	0.65	0.143	0.68	0.122	0.71
0.185	0.578	0.214	0.59	0.179	0.62	0.164	0.67

Table 3: Effect of aqueous conc. on E% with variable TOA (B) conc. in Petroleum Ether

10% B		20% B		30% B		40% B	
$[PA]_{aq}$ Kmol/m^3	E%	$[PA]_{aq}$ Kmol/m^3	E%	$[PA]_{aq}$ Kmol/m^3	E%	$[PA]_{aq}$ Kmol/m^3	E%
0.03	40.8	0.028	41.86	0.033	42.53	0.042	44.13
0.061	39.39	0.051	41.18	0.037	42.19	0.058	43.82
0.095	38.27	0.096	40.11	0.108	41.18	0.09	42.19
0.149	37.5	0.13	39.39	0.143	40.48	0.122	41.42
0.185	36.98	0.214	37.11	0.179	38.27	0.164	40.12

Table 4: Effect of aqueous conc. on loading ratio with variable TOA (B) conc. in Petroleum Ether

10% B		20% B		30% B		40% B	
$[PA]_{aq}$ Kmol/m^3	Z	$[PA]_{aq}$ Kmol/m^3	Z	$[PA]_{aq}$ Kmol/m^3	Z	$[PA]_{aq}$ Kmol/m^3	Z
0.03	0.0873	0.028	0.048	0.033	0.025	0.042	0.00873
0.061	0.170	0.051	0.1069	0.037	0.0917	0.058	0.04585
0.095	0.458	0.096	0.2271	0.108	0.1339	0.09	0.05895
0.149	0.6594	0.13	0.3711	0.143	0.2285	0.122	0.1943
0.185	0.9368	0.214	0.4061	0.179	0.3216	0.164	0.2347

IV. CONCLUSION

Propionic acid reactive extraction from the aqueous stream was conducted using TOA dissolved in petroleum ether. Physical and chemical equilibria for propionic acid by Tri – n octyl amine in petroleum ether as a diluent have been determined. The extent to which organic phase (amine + petroleum ether) may be loaded with propionic acid ratio is expressed as $z = \frac{[PA]_{org}}{[T]}$. In this experiment loading ratio for 10%, 20%, 30%, 40% TOA is observed to be maximum at 0.4 when z value is 0.9368, 0.4061, 0.3216, 0.2347 respectively. Maximum S_f observed is 0.5454 at initial concentration of acid 0.1 kmol/m^3 for TOA concentration of 40% in petroleum ether. Extraction efficiency increases with increase in TOA concentration. In future different carboxylic acids can be extracted using alamine 336 in petroleum ether due to the high applications of carboxylic acids in various different fields.

DECLARATION

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Conflicts of Interest/ Competing Interests	No conflicts of interest to the best of our knowledge.
Ethical Approval and Consent to Participate	No, the article does not require ethical approval and consent to participate with evidence.
Availability of Data and Material/ Data Access Statement	Not relevant
Authors Contributions	All authors have equal participation in this article.

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