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Extraction Kinetics of Pyridine, Quinoline, and Indole from the Organic Phase with Natural Deep Eutectic Solvents and Separation Study Using a Centrifugal Extractor

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Abstract: In this study, the kinetics of extracting pyridine, quinoline, and indole from model fuels using natural deep eutectic solvents (NaDES) composed of carboxylic acids, xylitol, and water were investigated under static conditions. This research marks the first examination of extraction kinetics in this context. The key kinetic parameters of the extraction process were identified. Notably, it was observed that the mass transfer coefficient for indole was in the range of 3.4×10^{-6} to 1.2×10^{-6}, depending on NaDES. That is significantly lower, by an order of magnitude, than for pyridine and quinoline under identical experimental conditions. The study revealed that, under specific conditions, where thermodynamic equilibrium for indole cannot be reached, it becomes possible to achieve kinetic separation of the components. The presented experimental data obtained on a centrifugal extractor showed a decrease in the degree of indole extraction with increasing flow: Extraction efficiency decreased from 63% at a flow rate of 0.05 L/h to 18% at 0.8 L/h. Moreover, the research indicated that, during indole extraction, the mass transfer coefficient in a centrifugal extractor was 1.3×10^{-4}, which is two orders of magnitude higher than under static conditions. The study underscores the potential utility of the proposed extraction systems based on environmentally friendly NaDES, comprised of carboxylic acids and xylitol, for the kinetic separation of various classes of heterocyclic compounds. Overall, the research provides valuable insights into the kinetics of extraction and the potential applications of 'green' NaDES in the separation of heterocyclic compounds from organic liquids.

Keywords: extraction kinetics; mass transfer; pyridine; quinoline; indole; natural deep eutectic solvents; centrifugal extractors

1. Introduction

Nitrogen-containing heterocyclic compounds exhibit diverse pharmacological effects, having antibacterial, antiviral, antitumor, anticonvulsant, anti-inflammatory, and analgesic properties, rendering them indispensable in pharmaceuticals and perfumery [1]. Pyridine, quinoline, isoquinoline, indole, imidazole, and other bases form the foundation of various drugs [2]. Notably, pyridine, quinoline, and indole serve as precursors for synthesizing essential compounds such as nicotinic acid, serotonin, tryptophan, and reserpine. Indole, in particular, plays a pivotal role in synthesizing biologically active compounds, such as sumatriptan, tadalafil, risatriptan, and fluvastatin [3,4]. Quinoline derivatives have antimalarial, antibacterial, antifungal, anthelmintic, cardiotonic, anticonvulsant, anti-inflammatory, and analgesic effects, so they are widely used in the pharmaceutical industry. Important commercially available alkylpyridine compounds are α, β, γ-picoline, lutidine, 5-ethyl-2-methylpyridine and 2,4,6-collidine. Pyridine has applications in the paint and pharmaceutical industries, as well as in the synthesis of herbicides, insecticides, fungi-

cides, and plant growth regulators [5]. The rationale behind their inclusion in medicinal formulations lies in the stability and efficacy of N-heterocycles within the human body [6].

The predominant methods for acquiring heterocyclic nitrogenous compounds involve chemical synthesis and extraction from coal tar or petroleum fractions, with the latter addressing environmental concerns related to harmful NOx gas emissions during fuel combustion. Therefore, the removal of these compounds from petroleum products such as gasoline, diesel fuel, and lubricants is imperative for enhancing oil quality and safeguarding the environment.

Traditionally, refineries use hydrogenitrogenation technology, which currently does not fully meet the increasing demand for nitrogen content in fuel. This is due to the inability to remove some N-containing compounds due to steric factors, which affect the performance of the catalyst. In addition, it has significant disadvantages in terms of operating conditions, requiring the use of high temperature and pressure and expensive catalysts. In this regard, other methods of fuel purification from nitrogen impurities are being developed today: extraction, adsorption, oxidation methods, and biodenitrogenation [7–10].

Recent research has concentrated on developing extraction methods for separating nitrogen-containing compounds from liquid petroleum fractions [11–18]. This dual-purpose approach involves creating an affordable and safe method for obtaining heterocyclic nitrogenous compounds for medical and pharmaceutical applications while simultaneously purifying fuel and reducing environmental impact.

While effective extractants such as sulfolane, N-formylmorpholine, N-methylpyrrolidone, acetonitrile, dimethyl sulfoxide, sulfuric acid, and trifluoroacetic acid were proposed in the middle of the 20th century and are still in use today, their toxicity renders them unsuitable for further use in industries such as pharmaceuticals and perfumery [19–22]. These substances have been used for decades, but their use results in heavy contamination, difficulty in their recovery, loss due to volatility and emissions to the environment, fire hazard, and toxicity of the process in general. Ionic liquids have long attracted great attention from researchers because they are non-volatile, non-flammable, and have high thermal stability and high extraction capacity with respect to nitrogen-containing compounds. However, the introduction of ionic liquids into industrial processes has never occurred due to their high mutual solubility with fuels and the risk of environmental pollution. Consequently, the urgent task is to develop environmentally safe yet equally effective extraction systems for separating nitrogen-containing compounds from petroleum fractions.

The emergence of deep eutectic solvents (DES) has provided a promising avenue for effective extraction processes in denitrification and desulfurization of hydrocarbon fractions [23–26]. Based on the hydrogen bond donor (HBD) structure, the solvents are classified into glycol, glycerol, organic acid, metal, aromatic, and imidazole-based DESs. As shown by previous studies, the extraction efficiency of sulfur- and nitrogen-containing substances largely depends on the components in the DES composition, which contain functional groups capable of interacting with the extracted components through the formation of intermolecular interactions (hydrogen bonds and/or p-p stacking) [27–29].

DES offers advantages such as tunable physico-chemical properties, accessibility, and simplicity of synthesis. DES often contains salts of ammonium bases (e.g., tetrabutylammonium bromide), which act as hydrogen bond acceptors that form when DES components interact with each other [30,31]. However, their use does not allow us to speak about the "green" nature of deep eutectic solvents. To address this, natural deep eutectic solvents (NaDES) have been introduced, consisting of liquid mixtures formed by combining natural substances such as sugars, polyalcohols, amino acids, organic acids, and bases at specific molar ratios [32–34]. In [35], the authors studied the efficiency of betaine and levulinic acid-based NaDES for the extraction of toluene, pyridine, and thiophene from a model diesel fuel (n-decane). The study showed that the extraction efficiency of pyridine was higher using NaDES betaine-levulinic acid at a molar ratio of 1:7 than using sulfolane under the same conditions. NaDES choline chloride-propylene glycol (1:3) was used for the extraction of sulfur- and nitrogen-containing compounds from a real gasoline fuel sample; the nitrogen content in the fuel decreased almost 2-fold, corresponding to an extraction efficiency of 45% [36].

Studies have demonstrated the effectiveness of NaDES in extracting compounds from model diesel fuel and real gasoline fuel, showcasing their potential in desulfurization, denitrification, and dearomatization of oil refining products [2,37].

This study specifically aimed to investigate the kinetics of extracting pyridine, quinoline, and indole using NaDES based on citric (CA) and malic (MA) acids, xylitol (Xyl) and water, (MA-CA-H_2O, CA-Xyl-H_2O and MA-Xyl-H_2O at a molar ratio of 1:1:10, respectively [38]), from a model fuel (n-hexane) under static conditions. The NaDES selected in this work for the extraction of heterocyclic compounds are stable over a wide temperature range and have low viscosity. Cheap and environmentally friendly components are also used for their preparation, which is important for scaling the process [39]. The primary objectives included establishing the main kinetic parameters of the extraction process and validating the proposed extraction separation of heterocycles using a centrifugal extractor.

2. Materials and Methods

Natural deep eutectic solvents were prepared according to the procedure described in the literature [38]. The water and solid NaDES components weighed on analytical scales were placed in a beaker and stirred on a magnetic stirrer US-4150D (ULAB, Hong Kong, China) at 60 °C for 30 min until a homogeneous mixture was formed. After cooling to room temperature, all obtained mixtures remained stable.

The experiments investigating the kinetics of pyridine, quinoline, and indole extraction were conducted using a Lewis cell with a constant phase contact surface area (5.31 cm^2). A schematic representation of the setup is shown in Figure 1. Initial solutions of nitrogen-containing heterocycles and NaDES, in a volume ratio of 1:1, at room temperature (20 °C), were agitated using an agitator Nanostar 7.5 (IKA, Staufen, Germany) equipped with an overhead drive running at a speed of 600 rpm. The concentration of pyridine, quinoline, and indole in n-hexane was detected using an optico-optical probe with an optical path of 2 nm every 15 s, connected to a Cary 60 UV-VIS spectrophotometer (Agilent Tech., Santa Clara, CA, USA). The wavelengths corresponding to the absorption maximum for pyridine, indole, and quinoline were 251, 266, and 271 nm, respectively. Control of the spectrophotometer and data collection were carried out using Cary WinUV 5.1.1 software (Agilent Tech., Santa Clara, CA, USA).

The degree of extraction of the i-th component (E_i, %) was determined by the formula:

$$E_i = \frac{n_{in}^i - n_{org}^i}{n_{in}^i} \tag{1}$$

when n_{in}^i—is the initial amount of substance of the i-th component in the organic phase, mol, n_{org}^i—the amount of substance of the i-th component in the organic phase after extraction, mol.

A number of experiments were performed with a centrifugal extractor (SOLVEX, Moscow, Russia) with a mixing chamber volume of 2.5 mL. The principle scheme of the unit is presented in Figure 2 and works in the following way: The phases are supplied by two peristaltic pumps BT-100M (Shenchen Pump, Baoding, China) with pump head YZ2515X (Shenchen Pump, Baoding, China) and Shenchen silicone tubing 15# (Shenchen Pump, Baoding, China) with varying flow rates given in Table 1.

Table 1. Flow rates of the organic phase and the NaDES phase in the experiment on centrifugal extractors.

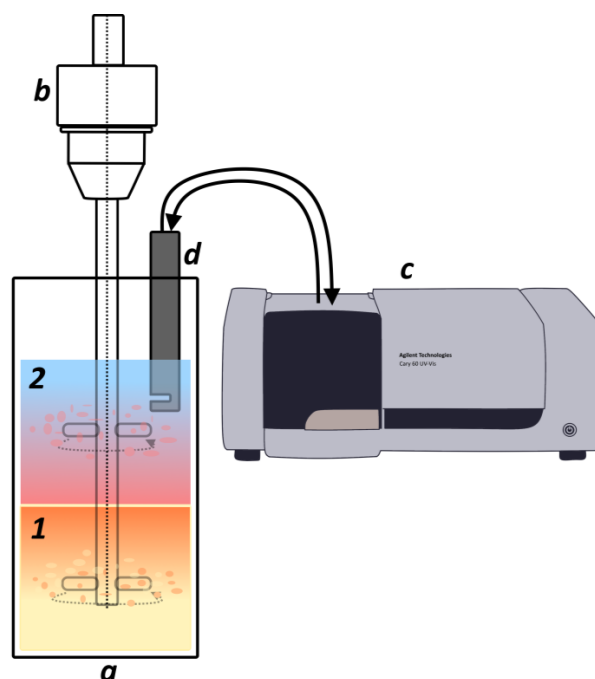| Experiment	1	2	3	4	5	6	7	8	9	10	11
NaDES flowrate, L/h	0.1	0.2	0.252	0.3	0.4	0.504	0.78	1.008	1.2	1.38	1.6
Organic phase flowrate, L/h	0.05	0.1	0.126	0.15	0.2	0.252	0.39	0.504	0.6	0.69	0.8

Figure 1. Scheme of an installation for studying the kinetics of extraction of nitrogen-containing heterocyclic compounds. a—Lewis cell, b—an agitator, c—spectrophotometer, d—optico-optical probe, 1—NaDES phase, 2—organic phase.
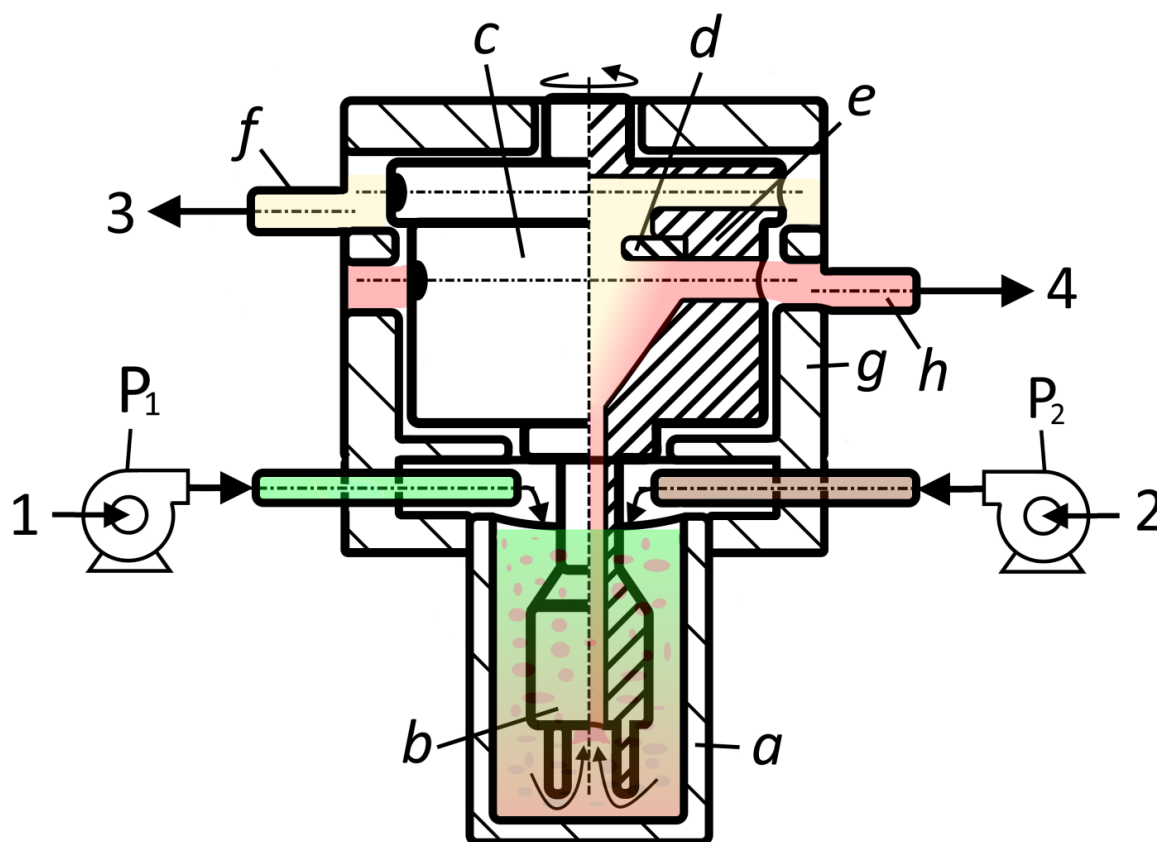

Figure 2. The extraction scheme implemented on a centrifugal apparatus: a—mixing chamber, b—agitator, c—general view of separation chamber and agitator, d—PTFE ring, e—split view of separation chamber and agitator, f—organic phase drain, g—split view of the external body of apparatus, h—NaDES phase drain, P—peristaltic pump, 1—initial NaDES phase, 2—light hydrocarbon fractions model solution, 3—light hydrocarbon fractions model solution raffinate, 4—NaDES extract.

We prepared 1 L NaDES CA-Xyl-H$_2$O and a solution of three components, quinoline, pyridine, and indole, in n-hexane with concentrations of 0.008, 0.005, and 0.003 mol/L, respectively. This solution was a model of a real solution of light hydrocarbon fractions. To ensure the phase ratio V$_{NaDES}$/V$_{org}$ = 2/1, the NaDES phase flow rate was set 2 times higher in relation to the flow rate of the model solution. In Figure 2, yellow is the phase flow of pure extractant NaDES CA-Xyl-H$_2$O, and pink is the phase flow of the model solution of light hydrocarbon fractions—in this case, a solution of quinoline, pyridine, and indole in n-hexane. Both streams flow through the connections into the interior of the extractor, where they are mixed in the mixing chamber with the help of a stirrer. Figure 2 shows how the formed emulsion enters the upper part of the shaft, which is the drum of the separation chamber, where the emulsion is stratified due to the centrifugal force generated by rotating the shaft of the unit at a speed of 3000 rpm. It is worth noting that the 3000 rpm rotation speed of this unit allows it to achieve a mixing efficiency of more than 99.9%, which has been determined on test systems recommended by [40]. Centrifugal force creates a concentration of heavy phase on the periphery of the drum, after which it is discharged through drain holes leading to the peripheral channel; the light phase is concentrated in the middle part of the drum and overflows through the polytetrafluoroethylene ring into the channel, where the light phase is concentrated, after which it is discharged through drain holes. After extraction and stratification, a stream of extract contaminated with heterocyclic nitrogenous compounds—quinoline, pyridine, and indole, colored orange, and a stream of raffinate, colored blue in the figure, are formed, which are discharged from the apparatus.

All components of the device are made of stainless steel. The mixing chamber has a volume of 2.5 mL. High productivity of the extractor was achieved due to the combined action of intensive stirring created by the stirrer rotating coaxially with the centrifugal drum at a speed of 3000 rpm, which leads to high dispersion, i.e., to the formation of dispersed phase droplets with a small diameter, which creates a high value of the ratio of the contact surface area of the phases to the volume and a high mass transfer rate. The emulsion obtained in the process was sucked into the central hollow channel of the agitator due to the vortex flow created by a special design of the device and from the mixing chamber was transferred through the inner channel to the centrifugal drum, which acted as a separation chamber. Due to the rapid rotation of the system from the agitator and drum, the emulsion fell into the field of centrifugal force, which led to the separation of phases. The main volume of the emulsion was concentrated and separated in the lower part of the drum, where the heavy phase was formed along the periphery of the device and the light phase in the center. Thus, the NaDES phase was discharged through the channels of the outer ring of the drum, while the organic phase overflowed through the polytetrafluoroethylene ring through the center into the cavity of the inner ring of the drum, from where it was exited from the agitator/drum system through the channels of the inner ring to the drain shelves of the apparatus body, connected to welded fittings. Phases were introduced into the cells through inlet fittings "a" (see Figure 3). After the separation in the drum, NaDES phases were extracted from the cell through outlet fittings "b", while the organic phase was extracted through outlet fittings "c" (see Figure 3).
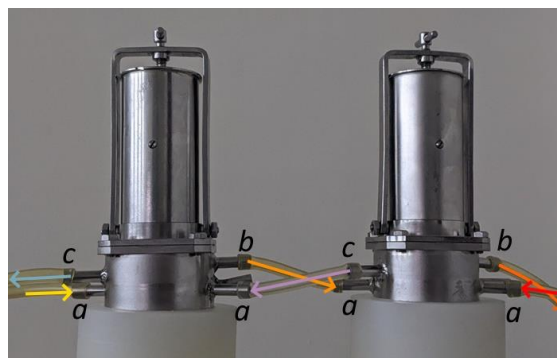

Figure 3. Outlet and inlet fittings for the centrifugal extraction equipment cell: a—inlets for the organic/NaDES phase, b—outlets for the NaDES phase, and c—outlets for the organic phase.

3. Results and Discussion

3.1. Extraction Kinetics Study

This study focused on investigating the kinetics of heterocyclic compound extraction in systems using NaDES. The examination of extraction kinetics under static conditions is crucial for the subsequent application of the process in extraction equipment. An experiment was conducted to explore the kinetics of extraction using Lewis cells. This experiment facilitated the determination of the kinetic parameters of the extraction process by using spectrophotometric detection to monitor the concentration of nitrogen-containing compounds in real time within the raffinate (n-hexane) phase.

Figure 4 shows data that illustrate the kinetics of nitrogen-containing compound extraction from n-hexane using deep eutectic solvents MA-CA-H_2O, CA-Xyl-H_2O, and MA-Xyl-H_2O. In the case of pyridine and quinoline extraction, there was virtually no significant difference in equilibrium time based on the NaDES selected. Given that pyridine is a stronger base, with a lower pKa, than quinoline (4.8 vs. 5.17, for a bound base) [41], pyridine extraction occurred more rapidly, taking only 4 min, compared with 5 to 7 min for quinoline. These observations, coupled with an understanding of the acid-base interaction extraction mechanism, suggest that extraction is likely to occur in a diffusion-limited regime.

In contrast, indole extraction required a longer equilibrium time for all NaDES, specifically 30 min. The formation of an extractable compound between indole and the extractant involves the creation of weak hydrogen bonds, resulting in a significantly slower reaction rate compared with acid-base interactions. Consequently, extraction, in this case, proceeds in a mixed regime, combining both diffusion-limited and chemical reaction-limited aspects. This distinct kinetic behavior of indole can be strategically utilized for its kinetic isolation from a mixture of heterocyclic compounds.

The mass transfer across the boundary between two liquids in a liquid-liquid system can be explained using the two-film theory, which is based on Fick's First Law [42]. The process is mathematically described by Equation (2) for the respective phase j (j—NaDES) [43]:

$$V_j \times \frac{d_{c_j}}{dt} = k_j \times a \times (c_{j,\infty} - c_j) \tag{2}$$

V_j—volume of the corresponding phase, k_j—mass transfer coefficient, a—interfacial surface, $c_{j,\infty}$ equilibrium concentration of the component in phase j, c_j—concentration of the component in phase j at time t.

Solving Equation (2) at t = 0, $c_j = c_{j,0}$, where $c_{j,0}$ is the initial concentration, yields Equation (3):

$$\ln \frac{(c_{j,\infty} - c_{j,0})}{(c_{j,\infty} - c_j)} \times \frac{V_j}{a} = k_j \times t \tag{3}$$

Figure 5 shows graphs depicting the dependence of $\ln \frac{(c_{j,\infty} - c_{j,0})}{(c_{j,\infty} - c_j)}$ on time for the extraction of pyridine, quinoline, and indole by NaDES. The mass transfer coefficients for the compounds investigated were calculated based on the slope of the established dependencies, and the results are summarized in Table 2.

Table 2. Mass transfer coefficients (cm/s) for pyridine, quinoline, and indole during extraction by the proposed NaDES.

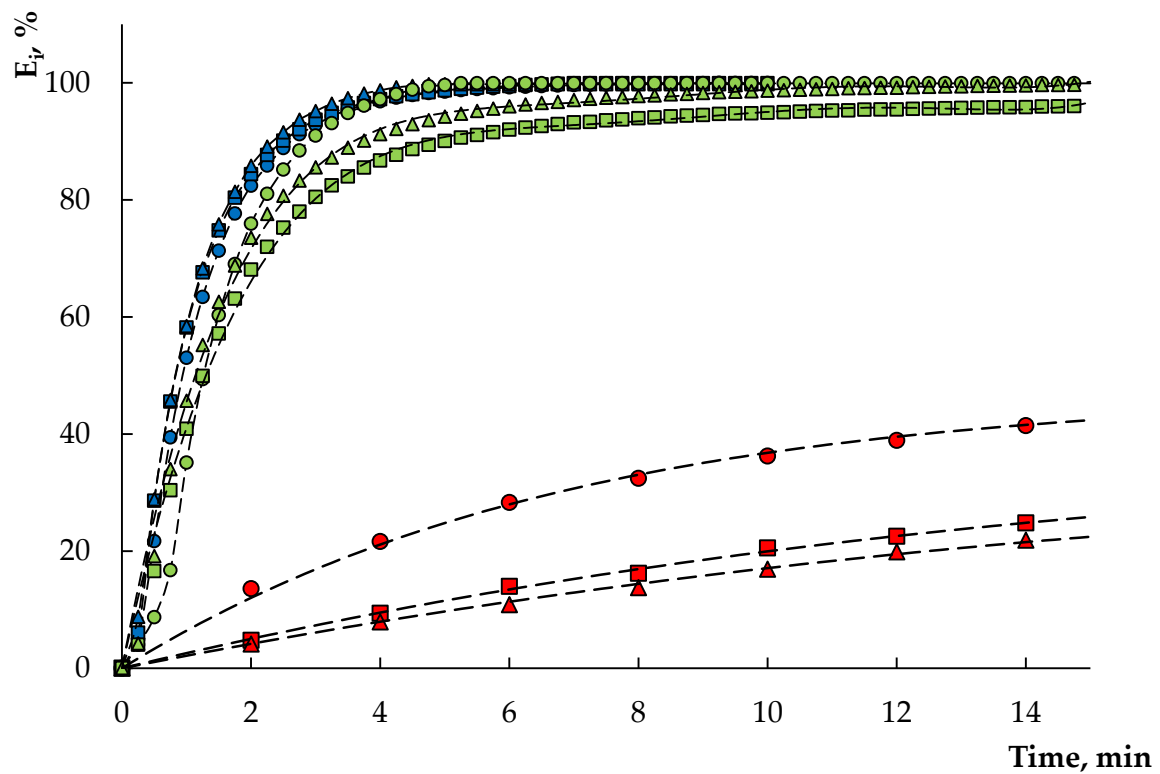|	CA-Xyl-H_2O	MA-Xyl-H_2O	MA-CA-H_2O
Pyridine	3.8×10^{-5}	2.8×10^{-5}	2.7×10^{-5}
Quinoline	2.0×10^{-5}	1.9×10^{-5}	2.5×10^{-5}
Indole	3.4×10^{-6}	2.9×10^{-6}	1.2×10^{-6}

Figure 4. Dependence of the degree of extraction of pyridine (blue), quinoline (green), and indole (red) NaDES MA-CA-H_2O (circle), MA-Xyl-H_2O (square), CA-Xyl-H_2O (triangle) on the time of phase contact.
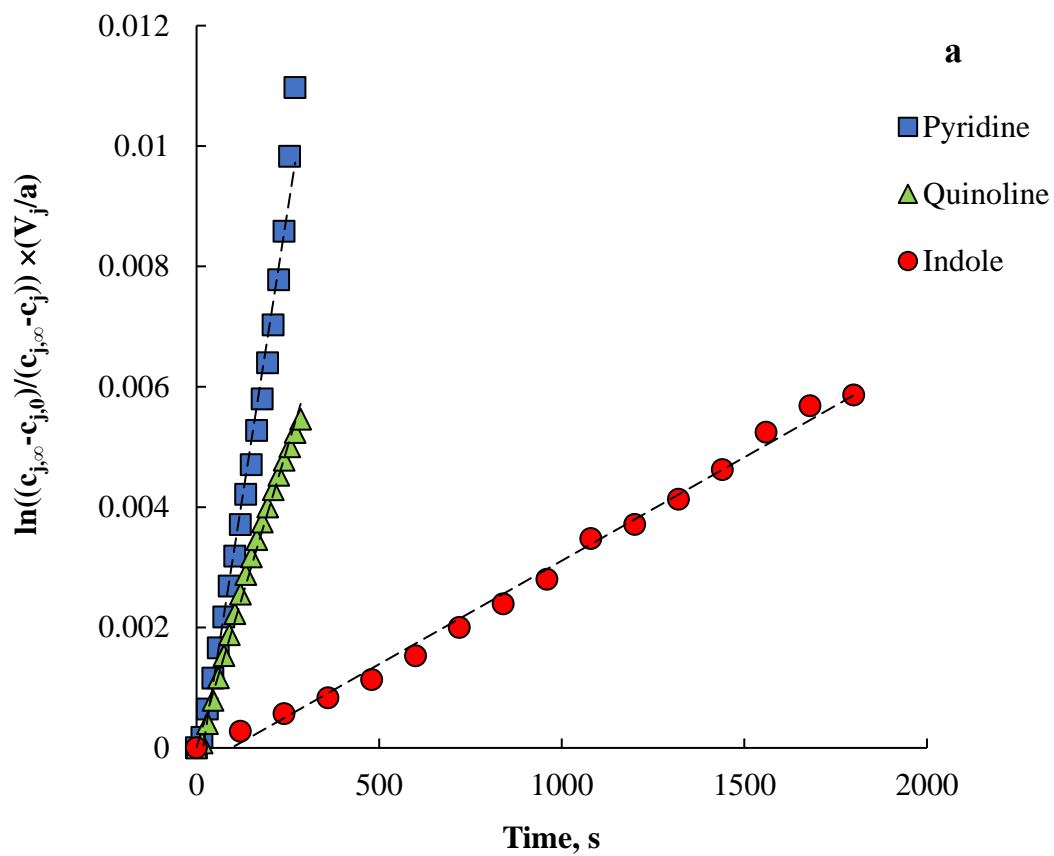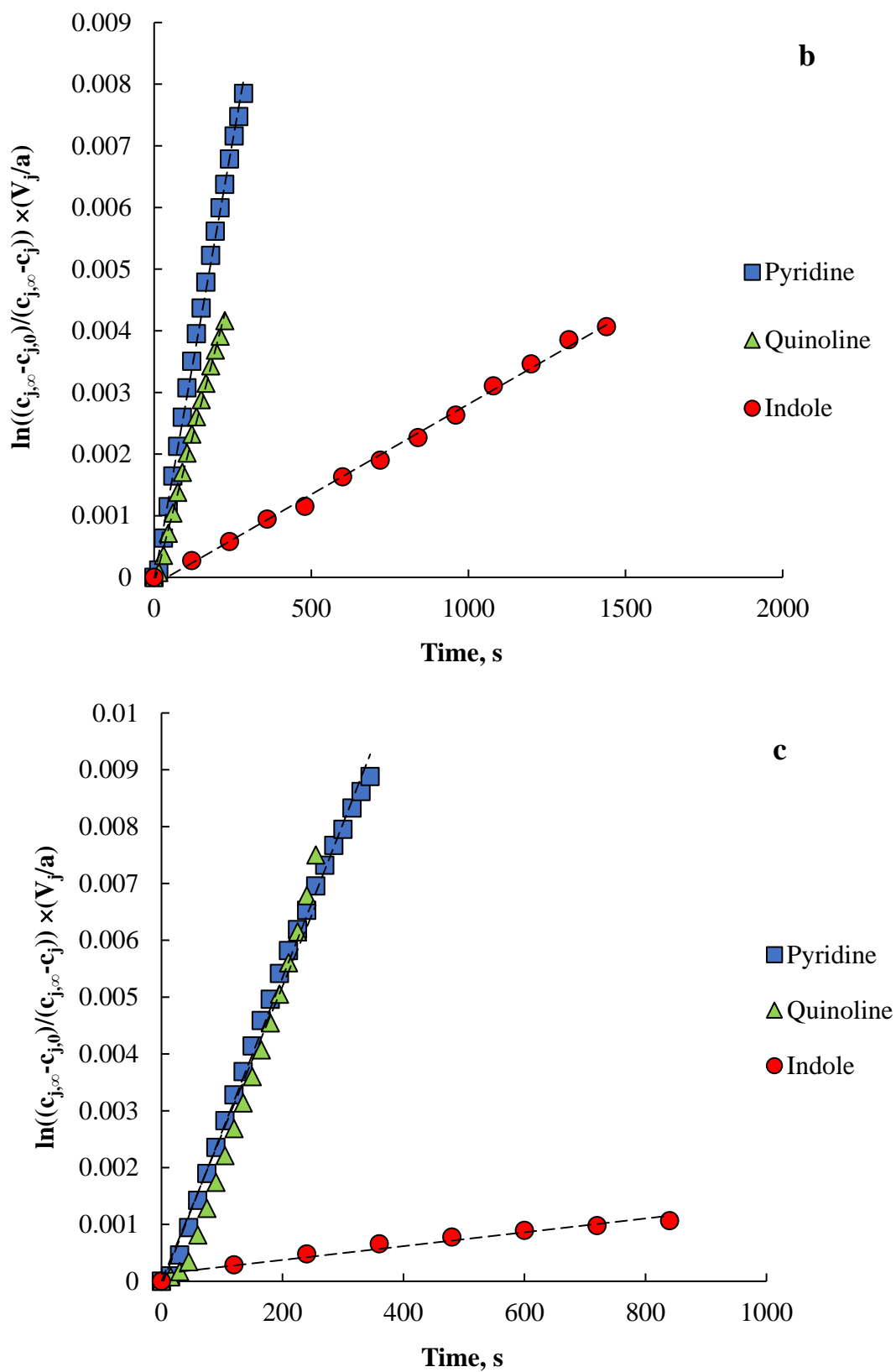

Figure 5. *Cont.*

Figure 5. Dependence of $\ln \frac{\left(c_{j,\infty} - c_{j,0}\right)}{\left(c_{j,\infty} - c_j\right)} \times \frac{V_j}{a}$ on time for pyridine, quinoline, and indole by NaDES extraction CA-Xyl-H_2O (**a**), MA-Xyl-H_2O (**b**) and MA-CA-H_2O (**c**).

It can be seen that the mass transfer coefficient for indole is an order of magnitude smaller than for pyridine and quinoline under the same experimental conditions. Thus, it was determined that when reaching a regime in which the thermodynamic equilibrium is not reached for indole, it is possible to realize the kinetic separation of components since pyridine and quinoline will still reach equilibrium under these conditions.

3.2. Separation Study on Centrifugal Extractors

With a constant volume of the mixing chamber of classical types of extractors such as sump mixer, centrifugal extractor, and extraction column, the phase contact time can be varied by varying the volume flow rate. Increasing the volume flow rate leads to a decrease in the phase contact time, but rapid emulsion formation under such conditions leads to improper operation of the equipment. Due to the resulting obstacle to achieving a good stratification, penetration of one phase into the other can occur, and a persistent emulsion can form, resulting in an upper limit of the volume flow rate. The way out of this situation can be a reduction in the speed of rotation of the agitators, reducing the diameter of the blades, or simplifying its shape. This technique does lead to a reduction in emulsification but reduces the mixing efficiency, which ultimately does not solve the problem. The advantage of centrifugal extractors is the combination of intensive mixing with high productivity. The high shaft speed of the apparatus not only leads to powerful mixing and emulsification but also creates a centrifugal force in the drum, which enables quality stratification in the same system. Thus, even with small mixing chamber volumes, it is possible to increase the volume flow rate many times over. Consequently, this type of extraction equipment is well-suited for solving the problem of kinetic separation.

Experiments on the extraction of heterocyclic nitrogenous compounds quinoline, pyridine, and indole simultaneously from n-hexane by the proposed NaDES on a centrifugal extractor were carried out. It is worth noting the fact that at the used flow rates, the system worked stably, no persistent emulsions were formed, and no penetration of one phase into the other occurred. After the establishment of a stationary hydrodynamic regime, the organic phase was taken for analysis through the appropriate drain connection. The residual concentration of components in n-hexane in each sample was determined by the spectrophotometric method. As can be seen from Figure 6, the degree of extraction of quinoline and pyridine remains unchanged at any value of the volume flow rate, while the degree of extraction of indole monotonically decreases as the organic phase flow rate increases above 0.125 L/h, indicating that at higher flow rates the system does not reach thermodynamic equilibrium. At the maximum possible organic phase flow rate of 0.8 L/h, the degree of indole extraction reached 18%, which indicates that under such extraction conditions, it is possible to achieve separation of components and extraction of 82% of indole in pure form. Further increase in the flow rate on these apparatuses led to mutual entrainment of phases, so the study stopped at this value. However, it should be considered that further scaling of the process is possible, and further studies with larger volume apparatuses may lead to even higher flow rates and separation values. The process of re-extraction of substances and regeneration of NaDES after use remains poorly understood. However, in a number of works, the authors used effective methods for re-extracting pure compounds from the NaDES phase after extraction, which can also be used for pyridine, quinoline, and indole [44].

Based on the findings from the kinetics study of nitrogen-containing NaDES CA-Xyl-H_2O heterocycles, the distribution coefficients (D = y/x, where y is the concentration in the extract and x is in the raffinate) were: indole—0.44, quinoline—approximately 300, and pyridine—418.

Using the data acquired and phase flow ratio $v_x:v_y = 0.5$, the extraction factor $f = v_x/(D \cdot v_y)$ could be calculated, resulting in the following values: indole—1.14, quinoline—0.0017, and pyridine—0.0012.
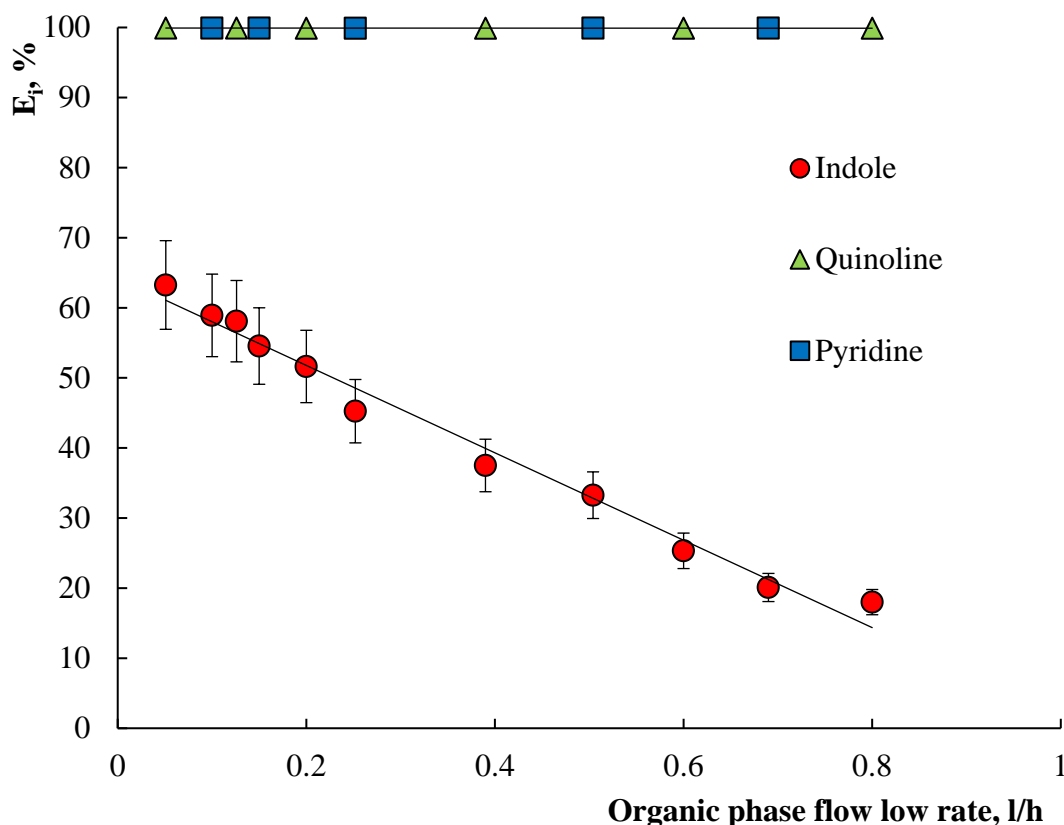
Figure 6. Dependence of the degree of extraction of indole, quinoline, and pyridine from n-hexane CA-Xyl-H_2O on a centrifugal extractor on the flow rate of the organic phase.

If equilibrium is achieved in the extractor (one theoretical stage), the output concentrations in the raffinate can be determined by Equation (4):

$$X = \frac{x_{yield}}{x_0} = \frac{f}{1+f} \qquad (4)$$

The calculations yielded the following results: during indole extraction, X = 0.53, during quinoline extraction, X = 0.0017, and during pyridine extraction, X = 0.0012.

Experimental results during indole extraction at organic phase consumptions of v_x = 0.1–0.25 L/h showed X = 0.34–0.59. As the consumption of the organic phase increased (v_x = 0.39–0.8 L/h), the concentration in the raffinate also increased (X = 0.65–0.82), indicating that equilibrium was not reached in the extractor (X > 0.53). This observation aligns with the earlier graphical representation (see Figure 6).

In contrast, during the extraction of quinoline and pyridine, at all organic phase flow rates, equilibrium was achieved in the extractor. The concentrations of quinoline and pyridine in the raffinate were X = 0.0014–0.0016 and 0.0012–0.0013, respectively, consistent with the calculated results.

It is important to note that, in extractors, the ratio of phase volumes in the mixer is equal to the ratio of phase flow rates. In experiments conducted on a centrifugal extractor with a flow rate ratio of extract phases (water phase) to raffinate (organic phase) = 2:1, the ratio of phase flow rates (volumes of phases in the mixer) at 1:1 under conditions of the equilibrium distribution of components between phases resulted in the following calculated concentrations in the raffinate, using Equation (4): indole—(X = 0.7), quinoline—(X = 0.0034), pyridine—(X = 0.0024). Therefore, under equilibrium conditions, practically pure indole can be isolated by adjusting the ratio of phase flow rates, but this would lead to a more dilute solution of the product, resulting in a lower yield than with kinetic separation.

During the extraction of indole in experiments with high phase consumption (v_x = 0.39–0.8 L/h), equilibrium was not achieved in the extractor due to insufficient phase contact time. The output concentrations in the raffinate under these conditions can be determined by Equation (5):

$$X = \frac{1 + tf}{1 + t(1 + f)} \qquad (5)$$

where $t = a_c\, k_x\, V_c/v_x$—the number of transfer units, a_c—the specific contact surface of the phases in the extractor mixer, k_x—surface mass transfer coefficient, V_c—the volume of the mixer. At high mass transfer rates ($t \to \infty$), Equation (5) converges to Equation (4).

From Equation (5), the number of transfer units can be determined from the experimental values X and f:

$$t = \frac{1 - X}{X(1 + f) - f} \qquad (6)$$

Knowing the number of transfer units, $t = a_c\, k_x\, V_c/v_x$, it is possible to calculate the volumetric mass transfer coefficient $a_c k_x$. To calculate the surface mass transfer coefficient k_x, it is necessary to determine the value of a_c. The specific contact surface of the phases in the extractor mixer a_c depends on the average droplet size d and the fraction of the volume of the dispersed phase in the emulsion S: $a_c = 6S/d$.

The ratio of the flow rates of the extract/raffinate phases is 2:1 S = 0.333. The average size of droplets formed in the extractor mixer can be assumed to be 0.1 mm in the first approximation: d = 0.01 cm and $a_c \approx 200$ cm^{-1}.

Table 3 shows the values of mass transfer parameters calculated from the results of experiments during indole extraction.

Table 3. Calculated values of mass transfer parameters during indole extraction in a centrifugal extractor.

v_x (L/h)	X	t	V_c/v_x (s)	$k_x\, a_c$ (1/s)	k_x (cm/s)
0.252	0.58558	3.66255	35.71429	0.10255	0.00051
0.390	0.65309	1.34664	23.07692	0.05835	0.00029
0.504	0.66744	1.15341	17.85714	0.06459	0.00032
0.600	0.74677	0.55282	15.00000	0.03685	0.00018
0.69	0.79911	0.35237	13.04348	0.02702	0.00014
0.800	0.82069	0.29095	11.25000	0.02586	0.00013

Comparing the results presented in Tables 2 and 3, it can be inferred that the mass transfer coefficient in a centrifugal extractor is two orders of magnitude higher than in experiments studying the kinetics of extraction in a Lewis cell. This discrepancy arises from variations in hydrodynamic conditions within the apparatus. Specifically, the intensity of phase movement relative to the interface in the extractor surpasses that in the Lewis cell. Additionally, in the extractor, the phase contact surface is continually refreshed due to the coalescence and redispersion of droplets. Consequently, the proportion of convective mass transfer, and hence the mass transfer rate, is notably higher in the extractor than in the Lewis cell.

In summary, the study demonstrates that the proposed extraction systems using 'green' NaDES comprised of carboxylic acids and xylitol have promise for the kinetic separation of various classes of heterocyclic compounds. The commendable performance metrics of these systems position them as being highly promising as an environmentally friendly, cost-effective, and accessible approach to producing heterocyclic nitrogenous compounds for medical and pharmaceutical purposes. Furthermore, their application contributes to a reduction in environmental impact through deep denitrification of light hydrocarbon fractions.

4. Conclusions

This study investigated the kinetics of extracting pyridine, quinoline, and indole within a system using natural deep eutectic solvents. The time required to attain equilibrium for each substance has been precisely determined, with pyridine reaching equilibrium within 4 min, quinoline within 5 to 7 min, and indole within 30 min. These disparate equilibrium times can be attributed to distinct extraction mechanisms inherent to each compound. Importantly, the study has demonstrated the potential for selective extraction of pyridine and quinoline over indole using kinetic separation.

The findings indicate a significant difference in mass transfer coefficients among the compounds studied. Specifically, the mass transfer coefficient for indole was observed to be an order of magnitude lower than that for pyridine and quinoline under identical experimental conditions. Furthermore, the experimental results have demonstrated that, during indole extraction, the mass transfer coefficient in a centrifugal extractor surpasses that in a Lewis cell by two orders of magnitude. This discovery underlines the superior efficiency of the centrifugal extraction process for indole.

This promising result opens up new possibilities for the practical application of the proposed extraction systems, which are based on carboxylic acids, xylitol, and water. The study emphasizes that these systems not only excel in equilibrium processes but also harbor the potential for efficient kinetic separation of diverse classes of heterocyclic compounds. In summary, the research contributes valuable insights into the versatile application of these extraction systems in both equilibrium and kinetic separation processes for nitrogen-containing heterocyclic compounds.

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