



Distribution of organic acids in a biphasic system based on hydrophobic deep eutectic solvents applied to the separation of critical metals.

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ABSTRACT

This study characterized biphasic systems formed by water and hydrophobic deep eutectic solvents (HDES), composed of decanoic acid and thymol, in the presence of organic acids with linear chains (formic acid, acetic acid, propanoic acid, or butanoic acid). The goal was to examine the distribution of these acids within the biphasic systems and evaluate the effects of carbon chain length, temperature, and HDES molar ratio on partition behavior. Distribution coefficients and their relationship with acid concentration in the phases were determined, and the potential for extraction and separation of critical metals, particularly copper and cobalt, was evaluated. The results obtained will be fundamental for improving processes to recover and valorize waste containing strategic metals.

Keywords: deep eutectic solvents, biphasic systems, recovery, critical metals.

Introduction

Biphasic systems based on hydrophobic deep eutectic solvents (HDES) show promise for selectively extracting various analytes from aqueous solutions. These systems can be obtained by mixing HDES with water, forming a biphasic system with an aqueous phase in equilibrium with a hydrophobic phase composed of HDES with minimal content of water. These systems are versatile, and the use of adjuvants can modulate their properties, expanding, for instance, their potential for use in extraction and separation methods for critical metals. In this study, biphasic systems formed by water and HDES composed of decanoic acid and thymol, in the presence of linear-chain organic acids, were investigated and tested for the separation of copper and cobalt from aqueous solutions.^{1,2,3}

Experimental

Preparation of biphasic systems

Decanoic acid and thymol were mixed at different molar ratios at 50 °C for approximately 30 minutes to prepare the HDES. Aqueous solutions of formic, acetic, propanoic, and butanoic acids were prepared at concentrations of 0.5, 1.0, 2.0, and 4.0 mol/kg. Then, the biphasic systems were obtained by mixing 1.0 g of HDES with 1.0 g of acid solution, and the mixtures were left to stand for 24 hours in a thermostatic bath at 25, 40, or 55 °C.

Determination of Distribution coefficient

After the system reached equilibrium in the thermostatic bath, the aqueous phase was partially separated using a syringe and needle. The separated phase was weighed into an Erlenmeyer flask, to which 10 mL of deionized water and two drops of phenolphthalein indicator were added. The solution was then titrated with 0.125 mol/L NaOH to determine the acid concentration in the aqueous phase. By mass balance, the acid concentration in the HDES phase was determined. The distribution coefficient (K) was calculated as the ratio of the acid concentration in the HDES phase to that in the aqueous phase.

Metal extraction

The system's ability to extract the metals copper and cobalt was analyzed. The metals were leached into an acid solution (formic acid, acetic acid, propanoic acid, or butanoic acid). The leachate was added to the biphasic systems prepared as previously described. After extraction, the metal concentrations in the HDES phase were quantified using total reflection X-ray fluorescence.

Results and Discussion

Distribution coefficient

Figure 1 presents a graph showing the distribution coefficient as a function of the initial acid concentration in the aqueous phase.

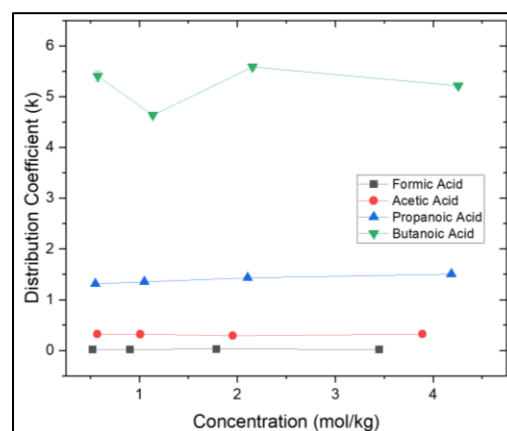


Figure 1. Distribution coefficient of different organic acids in biphasic systems based on HDES as a function of the initial acid concentration in the aqueous phase.

As observed, for all acids, the distribution coefficients change little with increasing acid concentration in the system. However, the affinity of the HDES phase for the acids increases with the length of

the acid's carbon chain. This is evident when the distribution coefficient is evaluated as a function of the number of carbon atoms in each acid, as shown in Figure 2.

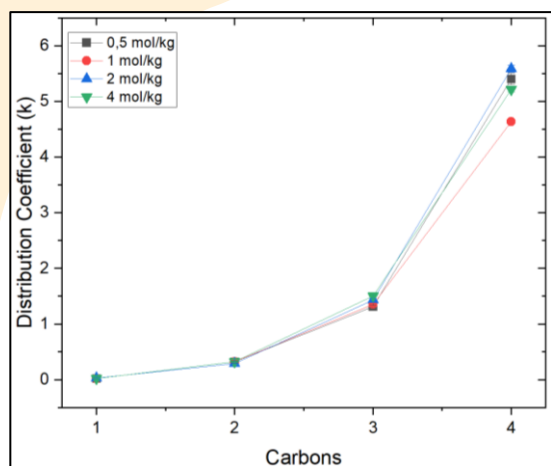


Figure 2. Distribution coefficient as a function of the number of carbon atoms in the organic acid.

As can be seen, the distribution coefficient increases exponentially with an increase in the length of the acid's carbon chain, suggesting that hydrophobic interactions between the HDES and the organic acids may drive the distribution process.

Additionally, a study was conducted to investigate the effect of temperature on the behavior of the distribution of the acids. In this study, the acid concentration was 1 mol/kg, and the evaluated temperatures were 25, 40, and 55 °C. The effect of HDES molar ratio was also evaluated, with three ratios selected: 1:2, 1:1, and 2:1 of decanoic acid to thymol. These results are presented in Figure 3. Overall, the HDES molar ratio appears to have no significant effect on the distribution coefficient. Similarly, temperature had no observable effect for any of the four acids studied.

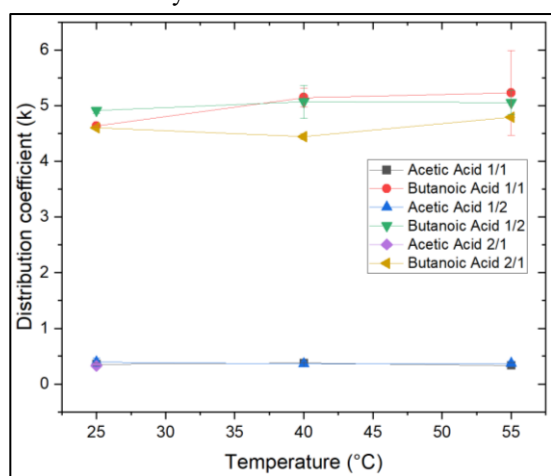


Figure 3. Distribution coefficient of the acids in the biphasic system as a function of the equilibrium temperature, at different HDES molar ratio.

The independence of K values from temperature suggests that hydrogen bonds do not define the distribution coefficient. If that were the case, an increase in temperature would reduce the distribution.

Having determined some of the physical and chemical properties of the developed system, we also assessed the capacity of the two-phase system to extract copper and cobalt. Figure 4 shows the extraction data obtained using different acids at a concentration of 1 mol/kg for comparison purposes. The acids used are formic acid (AF), acetic acid (AA), propanoic acid (AP), and butanoic acid (AB)

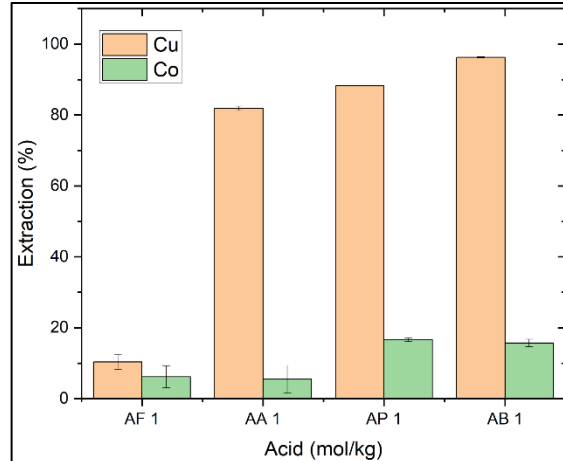


Figure 4. The percentage of Cu and Co extraction as a function of the acid used in the biphasic system. Acid concentration is 1 mol/kg.

Copper exhibits high extraction rates with all acids, ranging from around 80% (AF 1) to almost 100% (AB 1). Cobalt, on the other hand, has a considerably lower extraction rate, ranging from around 5% (AF 1) to approximately 20% (AP 1). All acids are more efficient at extracting copper than cobalt, with AB 1 and AP 1 being the most effective at extracting both metals.

Conclusions

Biphasic systems based on HDES have recently gained recognition for their applicability in the extraction and separation of compounds. While the literature has demonstrated the use of these systems for polar and organic compounds, there is still significant potential for metal extraction. One example of a HDES with potential metal extraction applications is a mixture of decanoic acid and thymol. Thymol is responsible for complexing and extracting metals. Combining this type of HDES with organic compounds in a two-phase system creates a new system with the potential to extract and separate critical metals.

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