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COMMUNICATION

Coalescence Extraction: A Novel, Rapid Means of Performing Solvent Extractions

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ABSTRACT

We report the development of a novel solvent extraction technique which exploits the coalescence properties exhibited by some solvent combinations at elevated temperatures. The technique allows for instantaneous mixing which approaches the theoretical extraction limit. In the extraction of Pb^{2+} from aqueous solution into either 2,4-pentanedione or glutaronitrile containing dicyclohexano-18-crown-6 (DC18C6), extraction times were reduced from 2 hours to less than 1 minute. The K_{ex} value for extracting Pb^{2+} into glutaronitrile with DC18C6 as the extractant was determined to be 260. The novel coalescence extraction technique is compared to traditional systems in terms of extraction efficiency, speed of extraction, and feasibility of practical applications.

INTRODUCTION

Cation separation systems have been a topic of intense research interest of late (1–3). Growing public sensitivity to environmental and waste disposal issues, coupled with the cost-cutting incentives associated with improved metal recovery, have moved cation separation research into a position of considerable priority. One established separation system is extractant-facilitated solvent extraction, along with the related technique of facilitated membrane transport (4).

Many attempts have been made to optimize the parameters which influence the efficiency of cation solvent extraction separations (5, 6). These

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parameters include choice of solvent, carrier hydrophobicity, volume ratios, species concentrations, and interfacial surface area, with interfacial surface area being the most significant determinant of extraction rates (7). The importance of surface area can be seen in a model proposed by Vandegrift and Horwitz (8) which describes the rate at which a number of moles, n_i, of a given species is extracted into the organic phase. This rate is given by the equation

$$dn_i/dt = A_s(k_{ao}[M^+]_{as} - k_{oa}[M^+]_o) \qquad (1)$$

where A_s is the surface area of the organic/aqueous interface, the subscripts "as" and "o" designate the aqueous source and organic phases, respectively, and k_{ao} and k_{oa} are the rate constants for the movement of ions from one phase to the other. Clearly, when cation concentration and solvent are held constant, extraction rate is directly proportional to the surface area of the liquid–liquid interface.

Limited surface area is not the only factor to limit extraction rates. Danesi (9) reports that diffusion is the predominant factor controlling extraction rates in most systems, even when efficient stirring or shaking devices are employed. Perhaps the most frequently used model for describing this phenomenon is the two-film model. It proposes that even in the most efficiently stirred system a thin aqueous film and a thin organic film along the liquid–liquid interface do not participate in mixing. These films are considered as essentially stagnant, and any extraction that occurs is restricted by diffusion across these stagnant films. Significant research (10–12) has been conducted in an attempt to describe and minimize this barrier, but it remains the rate-controlling factor in solvent extraction.

Recently, we have developed a separation technique that achieves extraction rates which approach the theoretical limit, completely eliminating the limitations of diffusion and surface area that hamper other extraction systems. At the same time, it avoids the problem of emulsion formation and eliminates the need for mechanical agitation. This technique, which we call coalescence extraction, relies on the ability of certain organic solvents to change from immiscible in water to completely miscible with a simple and moderate change in temperature. Thus, by changing the temperature, the organic phase with its extractant and the aqueous phase with its target cation are brought into intimate contact. The surface area across which cation transfer can occur reaches its theoretical limit, and equilibrium is achieved almost instantaneously. Once this has occurred, the simple act of cooling the solution results in separation of the two phases, with each species being partitioned to its appropriate phase. We here attempt to illustrate the efficiency of extraction by this mixing method

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rather than separation efficiencies. Hence, results focus on the extraction of a simple test species, Pb^{2+}.

EXPERIMENTAL

Materials and Instrumentation

In every experiment the target cation was Pb^{2+}, and solutions were prepared by dissolving the appropriate amount of $Pb(NO_3)_2$ (Aldrich) in distilled, deionized water (Millipore, Milli-Q). The organic solvents used were reagent-grade chloroform (Mallinckrodt), 2,4-pentanedione (EM Science), and glutaronitrile (Aldrich). The glutaronitrile was purified further before use by distillation. In each case the extractant was dicyclohexano-18-crown-6 (Aldrich).

Shaking experiments were performed with a Burrell Wrist Action Shaker. Analysis of Pb^{2+} content in both source and receiving phases was accomplished by inductively coupled plasma (ICP) spectrophotometry (Perkin-Elmer Plasma 2000).

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Procedure

Coalescence extraction experiments were carried out in two ways. Both involved filling a glass vessel with equal volumes of aqueous lead nitrate solution and organic solvent containing dicyclohexano-18-crown-6 (DC18C6). The vessel was then heated on a hot plate to the temperature of mutual miscibility. For 2,4-pentanedione this temperature is 87.7°C, and for glutaronitrile it is 68.3°C. The attainment of these temperatures is accompanied by a sudden, visible change in the mixture from cloudy to clear. These temperatures were typically reached after less than 20 seconds of heating.

Once complete miscibility was achieved, the solutions were immediately cooled to room temperature by placing the vessel in a bath of cool water. The solutions were then centrifuged for 2 minutes to eliminate entrainment, and a 100-μL sample of the organic phase was removed. This sample was dissolved in 4900 μL of distilled, deionized water in preparation for analysis by ICP. A second set of experiments involved the removal of a sample of the aqueous phase, followed by dilution and analysis by ICP.

The coalescence technique described above was compared to traditional solvent extraction techniques which employ shaking as a means of achieving extraction. In these experiments, 4.0 mL of both the aqueous and organic solutions were placed in test tubes. The mixtures were then shaken in a Burrell Wrist Action Shaker at its maximum shaking amplitude. At 10 minute intervals, 50 μL samples of the organic phase were removed, dissolved in 2450 μL of distilled, deionized water, and analyzed for Pb^{2+} content by ICP. Glutaronitrile experiments were performed at least in triplicate, and 2,4-pentanedione experiments at least in duplicate.

RESULTS AND DISCUSSION

Brown and Bartsch (13) report that the choice of solvent in solvent extraction and membrane separations is crucial. They name chloroform as the most effective of the traditional solvents for their system involving extraction of metal cations using crown ether extractants. Table 1 compares the Pb^{2+} extraction effectiveness of our two coalescence solvents, 2,4-pentanedione and glutaronitrile, to that of chloroform. The effectiveness of chloroform was investigated using shaking while the other solvents were investigated using both shaking and coalescence. In every case the original aqueous solution contained 31.0 mM $Pb(NO_3)_2$ and the organic solutions contained 10.0 mM DC18C6. The 2,4-pentanedione system was able to extract slightly less lead than the chloroform system, while the glutaronitrile system extracted slightly more lead. For glutaronitrile and 2,4-pentanedione no difference was found between the amount of Pb^{2+} extracted using shaking versus using the coalescence technique. All three systems were much more efficient at extracting Pb^{2+} than hexane. Chloroform, 2,4-pentanedione, and glutaronitrile are all more polar than hexane and are more effective in the solvation of the macrocycle/cation complex. Figure 1 makes it clear that both 2,4-pentanedione and glutaronitrile, at least in terms of extraction efficiency, are valid alternatives to chloroform, the current solvent of choice.

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TABLE 1
The Effect of Solvent Type on Extraction of Pb^{2+} Using 10.0 mM DC18C6

Solvent	Concentration (mM)[a]
Hexane	0.0
Chloroform	6.1
2,4-Pentanedione	5.7
Glutaronitrile	7.8

[a] Aqueous source phase contained 31.0 mM $Pb(NO_3)_2$. Extractions were performed in triplicate, and reported values are accurate to within ±0.5 mM.

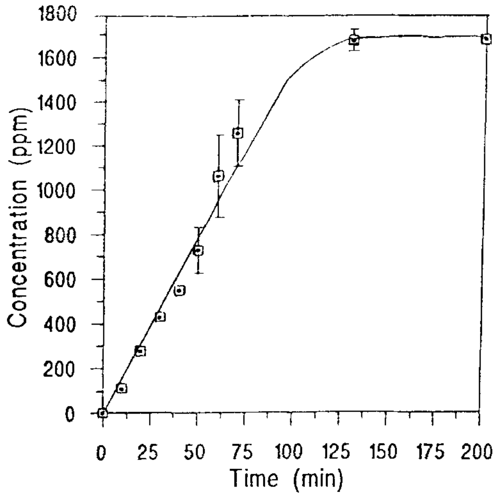

FIG. 1 The time required to reach equilibrium during solvent extraction of Pb^{2+} into glutaronitrile by shaking. The concentration of Pb^{2+} in the organic phase is plotted versus time. The organic solution contained 10.0 mM DC18C6 and the aqueous solution contained 31.0 mM $Pb(NO_3)_2$. The experiment was conducted in triplicate (error bars show standard deviation from mean).

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As discussed in the Introduction, the time required to perform an extraction or membrane separation is a critical parameter. Figure 1 shows the amount of lead extracted into glutaronitrile by shaking as a function of time. About 2 hours of shaking at the maximum shaking amplitude are required to bring the system to equilibrium and achieve maximum extraction. Figure 2 shows a similar plot for the 2,4-pentanedione system. After several hours the concentration of lead in the organic phases were those given for 2,4-pentanedione and glutaronitrile in Table 1. The extraction time of over 2 hours in the glutaronitrile system was reduced to less than 1 minute by coalescence extraction, while the amount of lead extracted remained the same. Coalescence extraction by the 2,4-pentanedione system can also be performed in less than 1 minute without a decrease in the degree of extraction. Thus, the use of coalescence extraction affects the time required to reach equilibrium but does not compromise equilibrium extraction constants (K_{ex}).

A third set of experiments measured the reduction of Pb^{2+} concentration in aqueous solutions of varying initial concentrations and determination of equilibrium constants. Pb^{2+} concentration in the feed solution was varied from 10 to 1000 ppm while the amount of DC18C6 in the glutaroni-

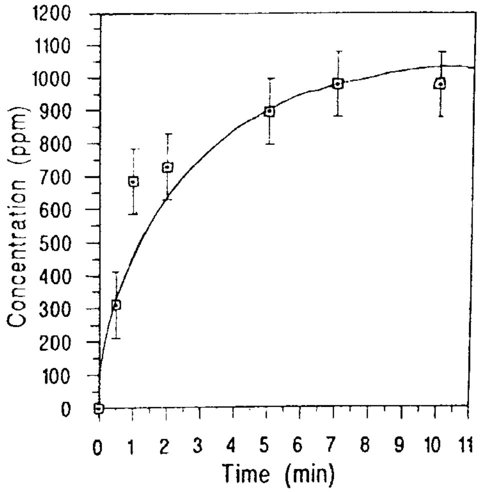

FIG. 2 The time required to reach equilibrium during solvent extraction of Pb^{2+} into 2,4-pentanedione by shaking. The concentration of Pb^{2+} in the organic phase is plotted versus time. The organic solution contained 10.0 mM DC18C6 and the aqueous solution contained 31.0 mM $Pb(NO_3)_2$. The experiment was conducted in duplicate.

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trile remained constant at 31.0 mM. In every case, 89% of the lead was removed by coalescence extraction. This corresponds to a K_{ex} value of 260, determined by a method similar to that used by Ouchi et al (14).

While this study has been restricted to the examination of coalescence in simple solvent extraction systems, coalescence extraction phenomena have obvious potential for application to more complex separation systems. Continuously flowing systems can readily be envisioned in which organic and aqueous phases merge and pass through a heat exchanger where extraction quickly takes place. As the solution leaves the heated region, the phases separate and the organic phase is removed with a continuous cyclone centrifuge. The organic phase is then stripped of its cations in another continuous step, and the solvent and extractant are returned to the beginning of the process to perform their function again. A variety of other separation systems using these principles can also be envisioned. Furthermore, coalescence makes extraction possible in remote places, such as in a pipe, down a well, or in any other situation where heating is possible, but mechanical agitation is not.

A benefit of these particular coalescence solvents is their high boiling points. Glutaronitrile and 2,4-pentanedione boil at 286 and 140.5°C, respectively. This characteristic reduces the danger of losing the organic solvent to evaporation or the accumulation of toxic and flammable fumes during industrial or laboratory use.

CONCLUSION

Coalescence extraction makes it possible to perform extractions in greatly reduced times by substantially improving mixing rates to near their theoretical maxima. It also offers higher than normal extraction efficiencies, low solvent vapor pressures, and the elimination of the need for mechanical agitation. The coalescence solvent extraction system studied has potential for future application of these principles to more complex separation systems.

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