**ENVIRONMENTAL AND WASTE MANAGEMENT: ADVANCEMENTS THROUGH THE ENVIRONMENTAL MANAGEMENT SCIENCE PROGRAM**

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# COMBINED UTILIZATION OF CATION EXCHANGER AND NEUTRAL RECEPTOR TO VOLUME REDUCTION OF ALKALINE TANK WASTE BY SEPARATION OF SODIUM SALTS

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Toward the reduction of the volume of the low-activity waste salt stream that will result from treatment of tank wastes stored at Hanford, novel approaches to the selective liquid-liquid extraction of sodium hydroxide and sodium nitrate are being investigated[1]. Removal of these bulk sodium constituents is expected to obviate the building of expensive new waste tanks and to reduce the costs of vitrification. Sodium hydroxide is one of the primary salts present in the waste and has the most value for recycle. Approaches to NaOH separation based on a sodium cation-exchange principle are especially suited for the hydroxide ion, because they avoid thermodynamically unfavorable partitioning of $OH^-$ ion into an organic phase by resorting to Brönsted acid-base chemistry[2–4]. In the simplest process, referred to as *pseudo*-hydroxide extraction (PHE), a weakly acidic lipophilic organic hydroxy compound HA (*e.g.*, alkylated phenol or fluorinated alcohol) is dissolved in a water-immiscible diluent to extract a hydroxide equivalent by exchange of its ionizable proton for an alkali metal cation at elevated pH. On contact with water, the organic-phase sodium salt releases its cation *via* hydrolysis, thereby producing an aqueous solution of the alkali metal hydroxide and regenerating the organic acid. In the present work, we describe a variant of PHE using a crown ether (CE) to assist in the extraction process by binding the $Na^+$ ion. The system is then called *synergistic* PHE or SPHE, as the combination of the ionizable lipophilic alcohol and CE results in the synergistic enhancement of sodium extraction from alkaline solutions[5,6]. The question being addressed in the present work concerns whether one

can extend this concept to a simultaneous removal of sodium hydroxide and sodium nitrate by a single SPHE solvent system.

The concept of an extraction of sodium as both hydroxide and nitrate relies on the CE promoting two types of processes, cation-exchange and ion-pair extraction. In general, the poor solvation ability of water-immiscible organic solvents toward alkali metal cations relative to water renders extraction of such cations thermodynamically unfavorable. An effective host for $Na^+$ ion can be employed to lower the net barrier to its partitioning *via* complexation. The literature abounds with examples of the use of CEs for this purpose[7]. For example, we recently showed how this effect operates in a model SPHE system employing nitrobenzene as a diluent, where *cis-syn-cis*-dicyclohexano-18-crown-6 (DC18C6) complexes $Na^+$ ion in the organic diluent with a binding constant of $5 \times 10^6$ [6]. In the absence of DC18C6, the cation-exchange of sodium by the weakly acidic alcohol HA is hindered by the poor cation solvation ability of the diluent and requires a high aqueous hydroxide concentration to drive an effective separation. The addition of CE effectively lowers the effective pH at which extraction by HA will occur, or equivalently, at a given alkalinity, the sodium distribution ratio increases. The binding of $Na^+$ ion by the CE will also drive extraction of sodium nitrate by ion-pair extraction. Consider the step-wise extraction of aqueous sodium hydroxide and sodium nitrate by a solvent consisting of HA and CE. We may ask what happens qualitatively as the aqueous phase is contacted multiple times by small volumes of fresh solvent. Initially, during the first contacts, the aqueous hydroxide concentration is high and the cation-exchange mechanism dominates. As the hydroxide ion in the aqueous phase becomes gradually depleted, the cation-exchange process can be expected to give way to ion-pair extraction of sodium nitrate. Overall, the efficiency of the sodium extraction is expected to be greatly enhanced, as it is not limited by hydroxide content in the waste solution. To this end, the high concentration of nitrate ion in the aqueous waste is desirable. Moreover, the nitrate anion has a moderately large radius relative to other aqueous inorganic anions of the same charge which, in accord with Hofmeister series, makes nitrate to be the most extractable bulk anion in the waste stream.

The concept of synergistic PHE has been reported in the literature[5,6] and the extraction mechanism can be described by the following equilibrium reaction:

$$Na^+_{(aq)} + OH^-_{(aq)} + Crown_{(org)} + HA_{(org)} \rightleftharpoons H_2O + NaCrownA_{(org)} \quad (1)$$

Analogous to the simple PHE process, the reverse hydrolysis reaction regenerates the neutral hydroxy compound in the organic phase and recovers sodium hydroxide in the stripping phase:

$$NaCrownA_{(org)} + H_2O \rightleftharpoons Na^+_{(aq)} + OH^-_{(aq)} + Crown_{(org)} + HA_{(org)} \quad (2)$$

SPHE is much more efficient than simple PHE as has been demonstrated in our previous investigations[5,6] where the degree of synergism (synergistic factor) depends on the acidity of the organic acid and the structure of an organic phase sodium ion

complex with the crown ether. The crown ether also controls the sodium selectivity of the separation process.

In ion-pair extraction processes, the aqueous cation ($Na^+$) and anion ($NO_3^-$) are transferred to a solvent phase, where the cation is then complexed with the crown ether:

$$Na^+_{(aq)} + NO_3^-{}_{(aq)} + Crown_{(org)} \rightleftharpoons NaCrownNO_{3(org)} \quad (3)$$

It may be expected from eq. 3 that high salt concentration drives ion-pair extraction and extraction may be subsequently reversed by contacting the solvent with a low-salt aqueous solution, ideally water:

$$NaCrownNO_{3(org)} \rightleftharpoons Na^+_{(aq)} + NO_3^-{}_{(aq)} + Crown_{(org)} \quad (4)$$

Ion-pair extraction is one of the most adopted and well-studied methodologies in the separation science of metal ions and has proven suitable for several proposed processes for the treatment of high-salt wastes, such as alkaline high-level tank waste. One of the challenges of making this type of system practical, however, results from the engineering desirability of employing an aliphatic hydrocarbon diluent. Although the fluid properties of solvent systems employing such a diluent are excellent, the extraction power of crown ethers in the extraction of salts according to an ion-pair extraction mechanism are weakened, as it is well known[7] that ion-pair extraction is favored by polar diluents. Accordingly, a strategy for boosting the strength of the extraction given by eq. 3 entails employing polar additives, called modifiers, to the hydrocarbon diluent. Under neutral conditions, our results with DC18C6 show that selected weakly acidic lipophilic alcohols may act as effective modifiers, though further enhancement of sodium nitrate is desirable. To further enhance sodium nitrate extraction, diluent modifiers with electron-pair donor (EPD) groups can also be used. Such modifiers effectively increase the solvation power of the solvent and further lower the sodium ion partitioning energy into the organic phase. Extensive experiments were conducted involving application of extraction phases containing an EPD modifier, DC18C6, and 3,5-di-*tert*-butyl phenol. The latter two serve as model sodium extractants. A series of EPD modifiers with strong hydrogen-bond acceptance abilities was investigated, including tri-*n*-butyl- and tri-phenylphosphate, tri-*n*-butyl- and tri-phenylphosphine oxide, *N,N*-di-*n*-butyl- and *N,N*-di-phenyl acetamide and 1-octanol. Distribution results for the crown ether used alone or with the solvating agents were successfully fit using the SXLSQI modeling program, whereupon the obtained extraction constants were shown to correlate linearly with the electron-pair donicity of the added modifiers (Kamlet-Taft $\beta$ solvatochrmic parameter). In the presence of the phenol, the solvating agents slightly lowered $NaNO_3$ extraction by DC18C6 and phenol, which, however, remained higher than $NaNO_3$ extraction by DC18C6 alone.

Finally, combined solution of an organic acid and a neutral sodium extractant exhibits the added benefits of their mutually increased solubility even in a nonpolar organic solvent and of improved phase behavior. These benefits may allow flexibility in diluent selection, and application of Isopar® L, a kerosene-like aliphatic diluent, becomes

feasible. Further investigations involve examination of such bifunctional extraction phases for sodium extraction from simulated and actual salt cake waste solutions and regeneration of the sodium salts.

**REFERENCES**


1. Moyer, B. A.; Lumetta, G. J.; Marchand, A. P.; Bonnesen, P. V.; Bryan, J. C.; Delmau, L. H.; Engle, N. L.; Gadthula, S.; Gore, V. K.; Haverlock, T. J.; Huang, Z.; Kang, H.-A.; Levitskaia, T. G.; Maya, L.; Sivappa, R.; Tirunahari, P. K. Environmental Management Science Program Annual Report; Oak Ridge National Laboratory: Oak Ridge, Tennessee, June 19, 2003; available on the World Wide Web site of the USDOE Office of Environmental Management, URL http://emsp.em.doe.gov/ .
2. Moyer, B. A.; Bonnesen, P. V.; Chambliss, C. K.; Haverlock, T. J.; Marchand, A. P.; Chong, H.-S.; McKim, A. S.; Krishnudu, K.; Ravikumar, K. S.; Kumar, V. S.; Takhi, M. In *Nuclear Site Remediation: First Accomplishments of the Environmental Science Program*; Eller, P. G. and Heineman, W. R., Eds.; ACS Symposium Series, Vol. 778; American Chemical Society: Washington, DC, 2001; pp 114-132.
3. (a) Chambliss, C. K.; Haverlock, T. J.; Bonnesen, P. V.; Engle, N. L.; Moyer, B. A. *Environ. Sci. Technol*. 2002, **36**, 1861–1867. (b) Moyer, B. A.; Chambliss, C. K.; Bonnesen, P. V.; Keever, T. J. "Solvent and Process for Recovery of Hydroxide from Aqueous Mixtures," U. S. Patent 6,322,702, Nov. 27, 2001. (c) Haverlock, T. J.; Bonnesen, P. V.; Moyer, B. A. *Solvent Extr. Ion Exch.* 2003, **21**(4), 483-504.
4. Kang, H.-A.; Engle, N.L.; Bonnesen, P.V.; Delmau, L.H.; Haverlock, T.J.; Moyer, B.A. *Sep. Sci. Technol*., submitted for publication.
5. Levitskaia, T. G.; Moyer, B. A.; Bonnesen, P. V.; Marchand, A. P.; Krishnudu, K.; Chen, Z.; Huang, Z.; Kruger, H. G.; McKim, A. S., *J. Am. Chem. Soc.* 2001, **123**, 12099–12100.
6. Levitskaia, T. G.; Bonnesen, P. V.; Chambliss, C. K.; Moyer, B. A., *Anal. Chem.* 2003, **75**(3), 405–412.
7. Moyer, B. A. In *Molecular Recognition: Receptors for Cationic Guests*, Gokel, G. W., Ed.; Vol. 1, *Comprehensive Supramolecular Chemistry*, Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D.; Vögtle, F.; Lehn, J.-M., Eds.; Pergamon, Elsevier, Oxford, 1996; Chap. 10, pp. 377-416.