

Reactions and processes in liquid-liquid (L/L) systems

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Abstract - Chemical transformations obtainable by shifting equilibria in L/L systems can provide for efficient processes. The range of solvents applicable to aqueous systems can be extended by the introduction of reagents, held captive by virtue of solubility in one or the other phase, and which compete for a species reversibly transferred. Predetermined equilibria thus established permit processes that cannot be constructed with conventional solvents. Temperature sensitive solvents provide an additional parameter in process design. Approaches to basic inorganic transformations by novel processes are presented.

INTRODUCTION

Solvents can assist processes in a number of different ways. These range from enabling a key reaction by the provision of a medium which favors it to the straightforward recovery of a product by solvent extraction (SE). This paper deals with processes that depend on shifting equilibria by transfers between two liquid phases. This is a class of SE processes in which reaction and extraction are interdependent.

The shifting of equilibria established in a solid phase or liquid phase by the transfer of a reaction product to a vapor phase has been the subject of extensive descriptions starting about a hundred years ago. It initially centered on solid-vapor and liquid-vapor systems of which numerous examples existed in industry. Le Chatelier formulated "rules of displacement" with respect to such systems that were named after him. Typical were displacement of an acid by a less volatile acid (e.g. HCl by H₂SO₄) or a base by a less volatile base (e.g. NH₃ by Ca(OH)₂).

The recognition of equilibrium displacement in a liquid phase by extraction with a second liquid phase came much later - as did the technology of solvent extraction itself. The application of equilibrium displacement in liquid-liquid (L/L) systems to the production of acids and salts was stated by the author(ref.1) in connection with the development of manufacturing processes. Two of these have attained rapidly industrial implementation: phosphoric acid from phosphate rock and HCl(ref.2), potassium nitrate from KCl and HNO₃(ref.3).

What is the potential scope of processes that exploit SE bound with equilibrium displacements? How dependent is it on new knowledge and how accessible is such knowledge? These, as related primarily to inorganic transformations taking place in aqueous media are addressed below.

GENERAL ASPECTS OF EQUILIBRIA DISPLACEMENTS

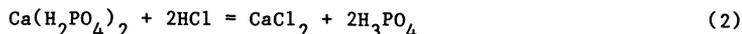
Let us consider an equilibrium



that establishes itself spontaneously in a system of two liquid phases, an aqueous phase and a solvent phase. If the ratio of a product to reactant e.g. Z to X is higher in the solvent phase than in the aqueous phase, the reaction can be shifted from left to right by extracting Z. If Z is separated and recovered while accompanying reagents and solvent are returned to reequilibration - the fundamental requirements of a process converting V and X to Y and Z are achieved.

The separation technique must be adapted to the system. It may involve the expenditure of energy only e.g. the crystallisation of a product by cooling or its recovery by solvent

evaporation; it may also be achieved by the consumption of a reagent when a derivative of a reaction product is desired e.g. the recovery of an acid in the form of its salt. There is however one particularly desirable form of separation that consists of backextraction with water so that products are recovered as aqueous solutions. What is the scope of applicability of this scheme? what are its limitations? The key to such processes is a small free energy change for the main reaction when taking place in an aqueous/solvent system. Also, distribution characteristics must ensure molar concentration levels of product in solvent that are higher or at least similar to the levels of accompanying reagents. Naturally operational requirements of viscosity, stability etc must be satisfied. To illustrate let us consider two reactions that take place in aqueous media:



The first can be shifted easily to the right by oxygenated solvents such as alcohols which extract virtually acids only (HCl and H_3PO_4) with phosphoric acid somewhat favored compared to HCl ; the reaction can thus be shifted fully to the right by means of a modest excess of HCl which is separated from product H_3PO_4 and recycled(ref.2). The second reaction (which may be considered as the basis for producing K-phosphate with HCl as a by-product) cannot be shifted to the right by solvents that are effective for the first reaction; if an excess of H_3PO_4 is applied to drive the reaction to the right the costs of its recycle become prohibitive. What is really needed is a solvent that extracts both acids with reversed performances compared to alcohols. A solvent with these preferences is apparently not available in commerce. Devising such a solvent is a challenge and of a considerable practical potential.

However displacing the equilibrium of the second reaction to the right becomes easy if the restriction of small free energy change for the reaction occurring in a two phase system is dispensed with. In fact reaction (3) can be shifted completely to the right by means of amines provided that the amine as well as its hydrochloride are contained in a water-immiscible liquid phase. The reason is that amines bind to HCl much more strongly than to H_3PO_4 . A solvent that contains amine is an "extractant" of HCl since it provides for its transfer from the aqueous phase. However it does so by virtue of the amine being a "reagent" as measured by free energy decrease due to the formation of the amine hydrochloride: HCl cannot be recovered by backextraction with water; the considerable energy required to separate an amine hydrochloride to amine and HCl cannot be supplied by the formation of aqueous HCl . Generalising, (and enclosing in brackets species captively held in solvent), we can write



where R is a reagent carried in the solvent phase that binds to Z to form ZR and thereby imposes the desired equilibrium shift.

The introduction of chemical reactions radically broadens the field of extractable species: virtually any metal can be extracted by ion exchange or complexation; anions can be extracted by bases or as constituents of salts etc. But the recovery of the extracted species requires then the destruction of R - e.g. by pyrolysis- or its displacement by some other reagent. When reagent costs can be disregarded the achievement of a specific transformation becomes relatively simple.

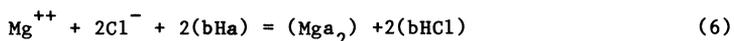
In practice reagent consumption would exclude most large scale transformations. Exceptionally the costs that attach to virtual irreversibility can be overcome by integration with other operations within an overall process. Thus when copper is extracted from a dilute solution of its sulfate by a powerful complexant, ion-exchange takes place and dilute sulfuric acid is obtained as raffinate; for backextraction a concentrated acid is needed; such acid is available as recycle from electrolytic deposition of Cu . Solvent recovery in this particular case is achieved indirectly by electrical energy used in another part of the process(ref.4).

Should liquid-liquid systems in which selective reactions obtain that involve large changes in free energies be excluded as a tool in large scale processes? Obviously one should rather aim at achieving virtual reversibilities though reagents of high selectivities are used. What are the ways open to us to achieve this desirable end?

We shall examine the possibilities inherent in the combination of two reagents for cooperative ion-exchange as well as for the balancing of competing reactions. We shall also examine temperature as a major operational parameter in processing by solvent extraction.

COOPERATIVE ION-EXCHANGE

Grinstead was probably the first to demonstrate that a couple consisting of an oil soluble base and an oil soluble acid can constitute a novel extractant capable of extracting reversibly water soluble ionic couples i.e. salts. Thus $MgCl_2$ (ref.5) can be extracted from alkali chloride brines and recovered by backextraction with water. Let us consider a "couple" that Grinstead found to be particularly effective for this purpose: an oil-soluble tertiary amine and an oil-soluble carboxylic acid. Each of these reagents by itself would act as a weak ion-exchanger. However an observer ignorant of the nature of the solvent who analysed the system for ions only would conclude that a selective extractant for $MgCl_2$ was present in the hydrocarbon phase! Reversibility is achieved by the interplay of several energies: the strong hydration of the Mg ion favors its retention in the aqueous phase; formation of amine hydrochloride favors transfer of chloride into the solvent phase; divalent Mg is strongly preferred over monovalent Na. The resultant overall small free energy change provides for great flexibility in the use of concentration gradients as the means of determining transfers between phases (and thereby reactions) just as with solvents that provide distributions through dispersion forces of similar magnitudes in both phases. Introducing the notation aH, b for oil soluble acid and base respectively we can describe Grinstead's solvent and the extraction of magnesium chloride by (5) and (6) :



Naturally one could attempt to devise an equivalent extractant by the synthesis of a molecule that is oil soluble and highly selective to Mg with binding energy so adjusted as to allow backextraction. Thus Y.Marcus (ref.6) has shown that multidentate compounds dissolved in carefully adjusted organic media can provide reversible extractants for alkali salts. This approach however is far from simple. The advantages of achieving reversibility through the coupling readily available reagents by simple mixing hardly need stressing.

BALANCED COMPETING REACTIONS

Let HA represent a water soluble strong mineral acid; b a water-immiscible oil-soluble base that forms with the acid an oil-soluble salt bHA which makes b an irreversible extractant of the acid; assume now that the oil phase contains an oil-bound acid Ha that binds to b with a free energy decrease similar to the decrease due to bHA formation; the mineral acid will then distribute reversibly:



The extractant bHA is formally similar to a Grinstead extractant but the mechanism is completely different: reversibility is provided by two opposing reactions.

Solvents consisting of amine-acid couples retain selectivities characteristic of amines while providing for reversibilities essential for large scale chemical conversions. Obtained by simple mixing of available chemicals they make possible the processing of reaction systems at acidity levels which are not accessible to more conventional solvents (ref.7). Thus, for instance, ammonium bisulfate NH_4HSO_4 can be disproportionated in an aqueous medium to sulfuric acid and ammonium sulfate (ref.8); HCl and HNO_3 can be separated in making KNO_3 at acidity levels of 10 normal in H (ref.9).

Generalising, one can imagine that any species X could be made to distribute between an aqueous phase and a hydrocarbon phase by means of reagents R and r held captively in these phases respectively:



The reagents R and r could themselves be reaction systems rather than single reagents if this be required to secure a satisfactorily equilibrated distribution for the species in question.

In practice, availability of reagents restricts the scope of solvents that can be readily constructed. Important processes, however, could justify the synthesis of novel reagents, in particular oil-soluble complexants. Several potentially important processes are considered further below.

REVERSING DISTRIBUTIONS BY TEMPERATURE CHANGE

Temperature is rarely used as a major parameter in establishing solute distribution in L/L systems. This contrasts sharply with solid/solid and solid/liquid systems where equilibria displacements by temperature are a major process tool. What are the reasons for this apparently astonishing fact? The net change in free energy due to distribution varies little with temperature; add to it that the range over which temperature may be varied is limited as a rule by considerations of viscosity and of phase and chemical stability. Endowing L/L systems with temperature sensitivity could broaden their usefulness. Are there practical approaches to this end?

There is not much that can be done to increase temperature sensitivity of the enthalpy term of free energies that characterise the interaction of a class of extractants with a given solute molecule. However the contribution of the entropy term can have considerable influence. Thus an oil-soluble amine acetate cannot be hydrolysed by water effectively to obtain free amine concurrently with aqueous acetic acid in a practical concentration range. In other words though acetic acid can be effectively extracted by amines it cannot be effectively backextracted into water even at a higher temperature. With citric acid, however, this is perfectly feasible and is in fact industrially applied (ref.10). Citric acid is attached to the amine by one carboxy group; the acid moiety carries the strongly hydrophilic two unattached carboxyls and one hydroxyl which can assume numerous configurations thus contributing to the entropy term of free energy and the consequent reversal of distribution at higher temperatures. A similar though considerably weaker effect was observed for amines with a sterically hindered amino group with respect to mineral acids (ref.11).

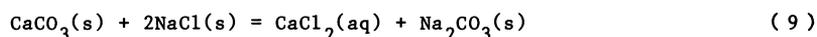
The foregoing would indicate a fairly general approach to devising amine solvents that could extract acids efficiently and selectively, as is characteristic of this class, and subsequently release them to water at a higher temperature. Several possible applications are discussed further below.

Free energies with which chelating agents and other strong complexants bind ions and molecules are similarly subject to change with temperature. Thus the dissolution of calcium phosphate in aqueous EDTA and similar chelating compounds can be reversed at the relatively high temperatures of 100°C and was proposed for recoveries of phosphate values from phosphate rock by-passing the usual attack by acids (ref.12). Imagine chelating agents characterised by very high stability constants and therefore high selectivities with respect to certain ions and also by high entropy factors that impose a steep decrease of stability constants with temperature; imagine further that for each cation we could have a reagent that is either water-soluble or oil-soluble - the scope of reversible solvents and of processes based on reversible transformations would be remarkably widened.

APPLICATIONS

New or better processes based on transformations that are not at present attainable constitute a challenge to organic chemists and process engineers that could combine efforts to attain them. Comparisons with existing processes will clarify this statement.

The venerable Solvay process still in use after more than a century since its invention achieves a global transformation summarised by



through energy demanding operations: thermal decomposition of limestone, boiling-off of ammonia, calcining sodium bicarbonate to sodium carbonate. In sharp contrast the enthalpy of (9) is only +5KCal and the free energy approximates +9KCal. Cannot this double decomposition be directly achieved? Referring to (8), let R be a complexant of Ca that dissolves CaCO₃ in its aqueous solution; r a complexant retained in the solvent phase competing for the Ca; if, further, the solvent is adjusted to solvate preferentially Cl⁻ over CO₃²⁻, the main requirements for (9) to exist as an equilibrium reaction in a two phase system will be satisfied. These are also the main requirements for an energy efficient process replacing Solvay.

In the foregoing example the complexant R acted as solubiliser for calcium carbonate in addition to its function of satisfying a condition for the reversible distribution of Ca between two liquid phases. Following this approach one can conceive of a variety of transformations that could be achieved in L/L systems though one or more of the feeds to the imagined process are insoluble in water as well as in non-aqueous solvents. Thus for instance one could think of converting directly insoluble phosphate rock (the primary source of calcium phosphate) to soluble alkali phosphates by means of alkali chlorides.

Two major manufacturing operations would be replaced by one. At present phosphoric acid manufactured from phosphate rock is reacted with alkali hydroxide or carbonate manufactured from alkali chloride. Equilibria can be shifted by small energies provided by reagents that have, as a rule, little reactivity. Carbonic acid (in practice carbon dioxide and water) is typical. To illustrate, consider (10) which is easy to establish (ref.13):



One can conceive of a b that has a structure such as to make bHCl hydrolysable at higher temperatures to b and concentrated aqueous HCl. A process summarised by



is conceptually a novel approach to providing alkali and acid from NaCl.

Processes using carbon dioxide as a primary source of acidity could have far reaching effects on major industries. Thus if phosphoric acid and phosphates were to be made by means of CO₂ rather than by H₂SO₄ world needs of elemental sulfur would be reduced by more than 50%!

In summary, equilibrium reactions in L/L systems provide routes to chemical processes that can be efficient operationally and energy-wise. Their scope can be greatly extended by the use of reagents captively held in one or another phase to secure the desired equilibrium and by the use of temperature effects. Reagents tailored to specific primary feeds: metal oxides, silicates, phosphates....could lead to novel basic processes of considerable economic potential.

REFERENCES

1. A. Baniel and R. Blumberg Chimie et Industrie, 78 (1957), 327-335.
2. A. Baniel and R. Blumberg, A.V. Slack, Fertiliser Science & Technology II, 889-911.
3. Y. Araten, A. Baniel, R. Blumberg Proceedings No.99, The Fertiliser Society, London.
4. J.F.C. Fisher & al., B. Hanson, Handbook of Solvent Extraction, Wiley 1983, 649.
5. R.R. Grinstead, I&EC, Prod. R&D 1970, 9(1), 66-72.
6. Y. Marcus and L.E. Asher, J. Phys. Chem. 82, (1978), 1246.
7. A. Eyal and A. Baniel, I&EC, Process Design & Dev., 21, 1982 334-337.
8. A. Eyal, C. Appelbaum and A. Baniel, Solvent Extraction and Ion Exchange, in print.
9. A. Eyal, J. Mizrahi and A. Baniel, I&EC, Process Design & Dev., 24, 1985, 387-390.
10. A. Baniel & al, United States Patent 4,275,234.
11. A. Baniel and A. Eyal, unpublished results.
12. M. Fava and A. Baniel, demande de brevet 81 18584.
- 13A. Baniel & al, Israeli Patents 33,551; 33,552.