This article was downloaded by:
On: *30 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation & Purification Reviews

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597294

Design of Solvent Extraction Systems

Ruth Blumberg[a]
[a] Miles Israel Ltd., Haifa, Israel

To cite this Article Blumberg, Ruth(1979) 'Design of Solvent Extraction Systems', Separation & Purification Reviews, 8: 1, 45 — 71

To link to this Article: DOI: 10.1080/03602547908057230

URL: http://dx.doi.org/10.1080/03602547908057230

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION AND PURIFICATION METHODS, 8(1), 45-71 (1979)

DESIGN OF SOLVENT EXTRACTION SYSTEMS

Ruth Blumberg
Miles Israel Ltd., Haifa, Israel

1. Introductory

In order to approach the design of solvent extraction systems in a logical manner, one needs to consider where such systems are being used and how these uses could be extended; also where solvent extraction is not used but could well be expected to find application.

A generalized classification of solvent extraction systems of all types would be the most likely to lead to a broad interdisciplinary approach to their design, but at this time there has been little progress towards such an all encompassing scheme. It is not possible, therefore, to come up with clearly defined guidelines for designing solvent extraction systems. Instead, at best, one can try to exemplify different cases, to indicate which parameters are general and which specific, and then to show how new problems can be handled. This presentation will of necessity be very personal, deriving from a particular scientific and technological background, but it can nevertheless serve as a general approach towards system selection and design. The main aim of the exercise is to encourage extention to separations thus far not regarded as amenable to this technique.

2. Applications and Classifications

In its most fundamental sense, solvent extraction implies one thing only, namely mass transfer across a liquid-liquid boundary. Inherent in this basic concept lies the technological definition of solvent extraction as a means of separation and purification, by combining mass transfer with phase separation.

Solvent extraction has been used for many decades as a tool for purifying pharmaceutical or organic compounds. It has also found very wide-spread use in the petrochemical industry. Its entry into the processing of inorganic materials received impetus in the 1940's as a tool for uranium recovery, rare earth separations, etc. Only since the 1960's has it found a place in the processing of more common inorganic materials.[1] In parallel with the developments in inorganic chemical processing runs the use of solvent extraction in biochemical separations, particularly for the recovery and purification of antibiotics. The concepts of solvent extraction are implied also in chromotographic separations, particularly the paper chromatography of the 1950's.

In the present context we shall be relating only to solvent extraction systems with express potential industrial application; however, the petrochemical and pharmaceutical fields will be excluded, excepting insofar as broader application of the solvent system can be postulated in specific cases. Table I lists some industrial applications in various fields.

Classification of solvent extraction systems may be end-oriented, being based upon the type of separation desired e.g. concentration, recovery, purification, or upon the type of material being transferred e.g. metal recovery, acid extraction, salt separation. It may also describe the reactions being promoted by the mass transfer, e.g. metathetic reactions, double salt decompositions, equilibrium shifting. A different type of classification would relate to the physico-chemical nature of solute/solvent interactions which form the basis of the mass transfer and hence of the separations achieved. Table II presents a sample of

TABLE I

SOME COMMERCIAL SOLVENT EXTRACTION PROCESSES

A)	Metal	Reagent
	Copper	LIX64N® in Diluent
	Rare Earths	Di Ethyl Hexyl Phosphoric Acid Tributyl Phosphate (TBP)
	Uranium	Fatty Amines in Diluent TBP in Diluent
	Boron	Polyol in Diluent
B)	Others	
	Aromatics from Aliphatics	Sulpholane Dimethyl Sulphoxide
	Mixed formic, acetic, propionic acids	Isopropyl Ether
	Phosphoric Acid via HCl Purification of Wet Process Phosphoric Acid	C_4, C_5 Aliphatic Alcohols
	Cleaning Wet Process Phosphoric Acid	Isopropyl Ether Methyl Isobutyl Ketone C_4, C_5 Alphatic Alcohols
	Potassium Nitrate	C_5 Aliphatic Alcohols

a currently accepted classification of solvents and extraction types[2].

TABLE II

A CLASSIFICATION OF SOLVENTS AND EXTRACTION TYPES

Solvent Types

Inert, graded e.g. according to polarity, hydrogen bonding ability;

Basic, graded according to basicity;

Acidic, graded according to acidity;

Chelating;

Ionic;

Extraction Types

Compound Formation e.g. with chelating agents, or acidic reagents;

Solvation e.g. with C-O or P-O containing reagents;

Ion pair formation e.g. with amines, quatenary ammonium compounds.

3. System Description

The description of solvent extraction systems has two distinct facets, the one operational, the other relating to solvent composition and quality. Both are limited by the tendency of the solute components to distribute between the two liquid phases.

Operationally, the format of the system is simple and quite general. If one of the phases is always an aqueous phase, containing the solute to be extracted, then the basic operations will consist in mass transfer from the aqueous phase into the solvent phase - extraction - and transfer back from the solvent into a second aqueous phase - stripping, washing, product recovery. According to the ratio of distribution coefficients, i.e. the separation factor between the desired product and the undesired components, additional steps may be necessary. Thus "back-washing" serves to remove contaminants from the extract by transfer to a minor aqueous stream, while "back extraction" is a secondary extraction from product for removing coextracted components; both lead to an overall higher degree of separation. In Figures 1a, 1b, 1c, schematic flow diagrams are presented for these general variations, showing also the direction of mass transfer.

Regarding solvent composition and quality, the options are much broader and are also much more specifically related to the nature of the mass transfer. In the simplest cases, the solvent will consist of a single component, leading to non-specific solvation of the extracted species. Solvents of this type will probably be oxygen-containing, e.g. alcohols, ketones, ethers, neutral phosphate esters, and diketones, with the lone donor electron pair of the oxygen making them weakly basic.

The next simplest system is composed of an "extractant" and a "diluent". The "extractant" may be a "cation exchanger," an "anion exchanger," or any of various specific complexing agents; the diluent is regarded as "inert" and is assumed to influence only the physical characteristics of the system, particularly viscosity, but also to help solubilize the extractant-solute complex. However, since diluents are never wholly inert, active diluents may be selected by intention. Secondary diluents or modifiers may be added as well, thus leading to less simple solvent systems, where interactions within the solvent phase provide a gradation of properties making finer separations possible. These interactions may affect the relative acidity or basicity of systems, the tendency to form a second solvent phase, and so on. Typical diluents are hydrocarbons of a range of polarity and structure, while alcohols of limited miscibility with water have been the accepted modifiers.

The single solvent case offers small room for manipulation of the system, since it alone must meet all process and operational requirements. In other words, it must satisfy all aspects that will lead to an overall viable system, i.a. specificity, capacity, solubility, mass transfer, phase separation, cost. At most, one can broaden the choice by comparing solvent types and solvent structures, e.g. alcohols can be compared with ketones, or various alcohols can be compared among themselves, and so on.

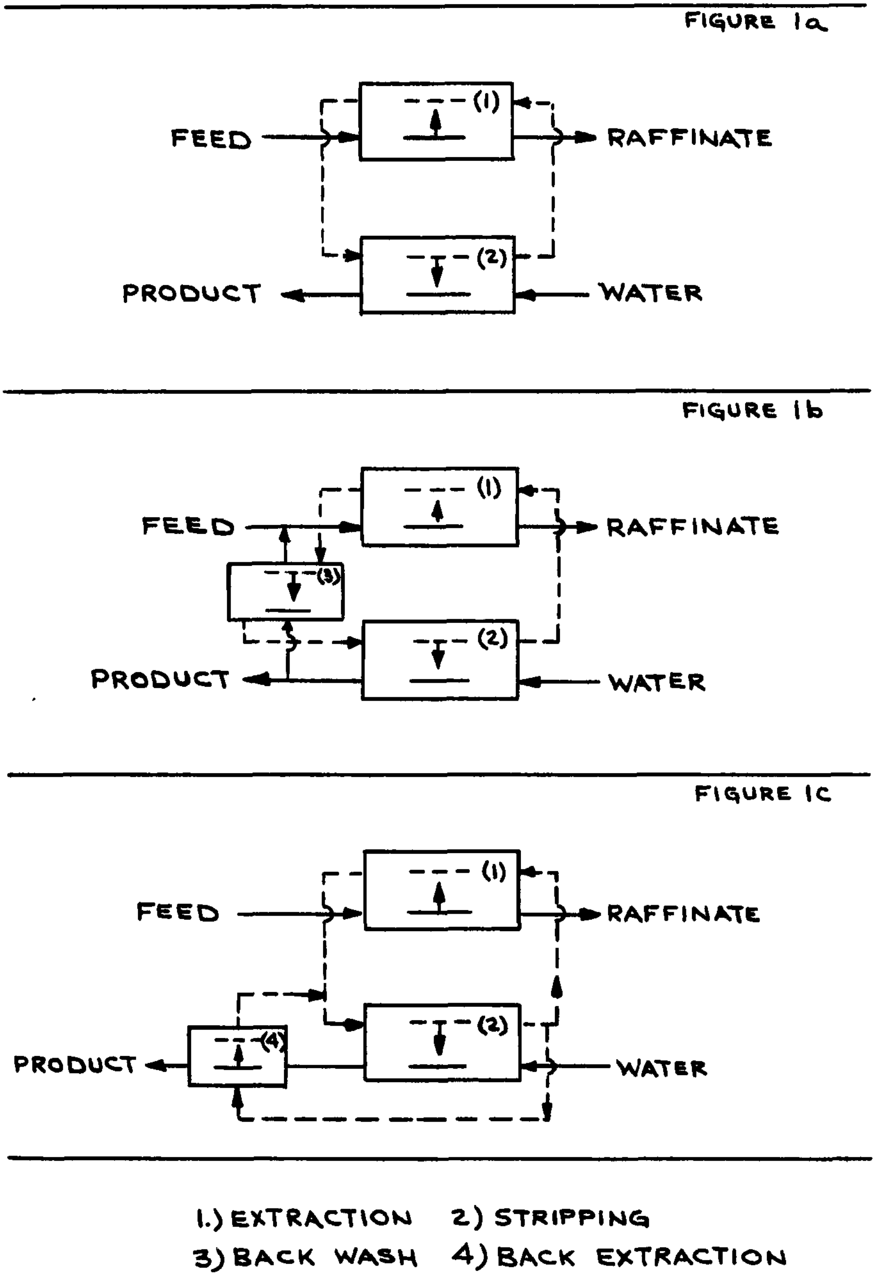
FIGURE 1a
(1)
FEED
RAFFINATE
(2)
PRODUCT
WATER
FIGURE 1b
(1)
FEED
RAFFINATE
(3)
(2)
PRODUCT
WATER
FIGURE 1c
(1)
FEED
RAFFINATE
(4)
(2)
PRODUCT
WATER
1.) EXTRACTION 2) STRIPPING
3) BACK WASH 4) BACK EXTRACTION

FIGURE 1

Systems composed of an extractant and an inert diluent immediately offer more possibilities in selection than does a single component. Thus the extractant itself can be optimized without changing the overall physical properties of the compounded solvent; synthetic organic chemistry has a large part to play in designing extractants for specific purposes. This is well exemplified by the synthetic effort made in developing cation exchangers to satisfy the constraints of the copper recovery/electrowinning process.

While the inert diluent has been considered mainly for operational reasons, the use of a diluent does immediately provide the system with an additional degree of freedom, by permitting the extractant concentration to be varied at will.

The multicomponent, interactive solvent system has been mentioned in recent years, but its usage is not wide spread; even when it is utilized, the significance of the interactions is not necessarily appreciated. This can be seen in systems where a modifier is added specifically for the purpose of preventing "third" phase formation, even though such a modifier may have a real effect on the transfer system itself[3].

4. Case Histories as System Models

Technologically, solvent extraction is a separation tool, hence the measure of its success in a particular application is the degree of separation attained. However, the quality of the separation cannot be the only yardstick; obviously, quantitative aspects of recovery and efficiency, as well as economic considerations of cost must be satisfied.

When one considers extending the accepted types of operation to encompass other analogous cases, the line of thought and the criteria for evaluating success are fairly clear. Thus as an example of the utilization of a liquid-liquid cation exchange system one can take the recovery of copper, can develop a case history by reviewing the progress in this field, and can use this as a model for continuing studies, either to recover other metals by analogy, or to circumvent existing constraints and deficiencies in the copper case itself. Another case history, extensive enough to be used as an example for analogy, is the extraction of phosphoric acid. This started out as a production procedure and became in time an upgrading, purification operation. The purification and recovery of phosphoric acid[4] is probably one of the most studied cases outside that of metal extraction. It is a typical case of extraction by a non-specific solvating solvent.

Both these case histories and one other, relating to metathetic reactions, will be described as a basis for analogies.

4.1. Cation Exchange for Metal Recovery - Cu^{2+}

The classic cation exchangers are acidic, solid, polymeric resins of the type $(HR)_n$ which permit the following reversible reaction to take place:

$$HR_{(solid)} + M^{+}{}_{(aq)} \leftarrow\rightarrow MR_{(solid)} + H^{+}{}_{(aq)}$$

When the monomeric acid is dissolved in an organic liquid diluent, the same reaction may take place, provided that MR too is soluble in the diluent. Therefore, the reaction becomes:

$$HR_{(solvent)} + M^{+}{}_{aq} \leftarrow\rightarrow MR_{(solvent)} + H^{+}{}_{(aq)}$$

Among the first liquid ion exchange systems to be considered were carboxylic acids, mono or diesters of phosphoric acid, and sulphonic acid esters, with increasing pKa's, in that order. However, since the exchange reaction is equilibrium controlled, free $H^{+}{}_{(aq)}$ limits the conversion. The weaker the acid, the more the H^{+} level is limiting, but even in the case of the strongest of these acids, neutralization of H^{+} is necessary if the reaction is to proceed. Such neutralization is usually uneconomic and inconvenient, especially if an external base must be used, leading to wasted chemicals. It became clear, therefore, that reagents were required with equilibrium constants favoring the forward reaction. In analytical chemistry, oximes have been used as complexants for metal cations under acidic conditions. It was natural, therefore, that oximes were the first practical large scale extractants proposed for obviating the necessity for neutralization.

A typical flowsheet for Cu^{2+} extraction as an integrated operation is shown in Figure 2.

The first practical reagent proposed for extraction from basic media was LIX63®. In 1970, the LIX64N® was proposed for extraction from acidic media. In 1971, LIX70® became available for higher loadings of Cu^{2+} and sulphuric acid, and other reagents have subsequently been added to the LIX® list[5]. All these reagents are hydroxy oximes, and this has continued to be the route followed by others, aiming at improving operation or at bypassing reagent patents.

The copper case leans heavily upon synthesis, and upon adaptation of the complexing reagent to process needs, hence it is natural that new claims relate in the main to new reagents, but that no change in basic flowsheet has been suggested. This is, perhaps, because the success of the copper case is entirely dependent upon a viable acid balance, requiring integration of all the steps of the operating copper recovery facility, from ore leaching, through the ion exchange, to electro-winning.

4.2. Phosphoric Acid Recovery

In order to be able to extract an acid and to strip the acid from the solvent, the solvent must be weakly basic, showing reversible binding of the acid and thus competing with water. The solvents considered for extraction of acids in general were alcohols, ketones, esters, and triesters of phosphoric acid. These are all weakly basic solvating agents. In Table III distributions of phosphoric acid in water/alcohol systems is presented. The interesting point is the similarity in the coefficients for the various

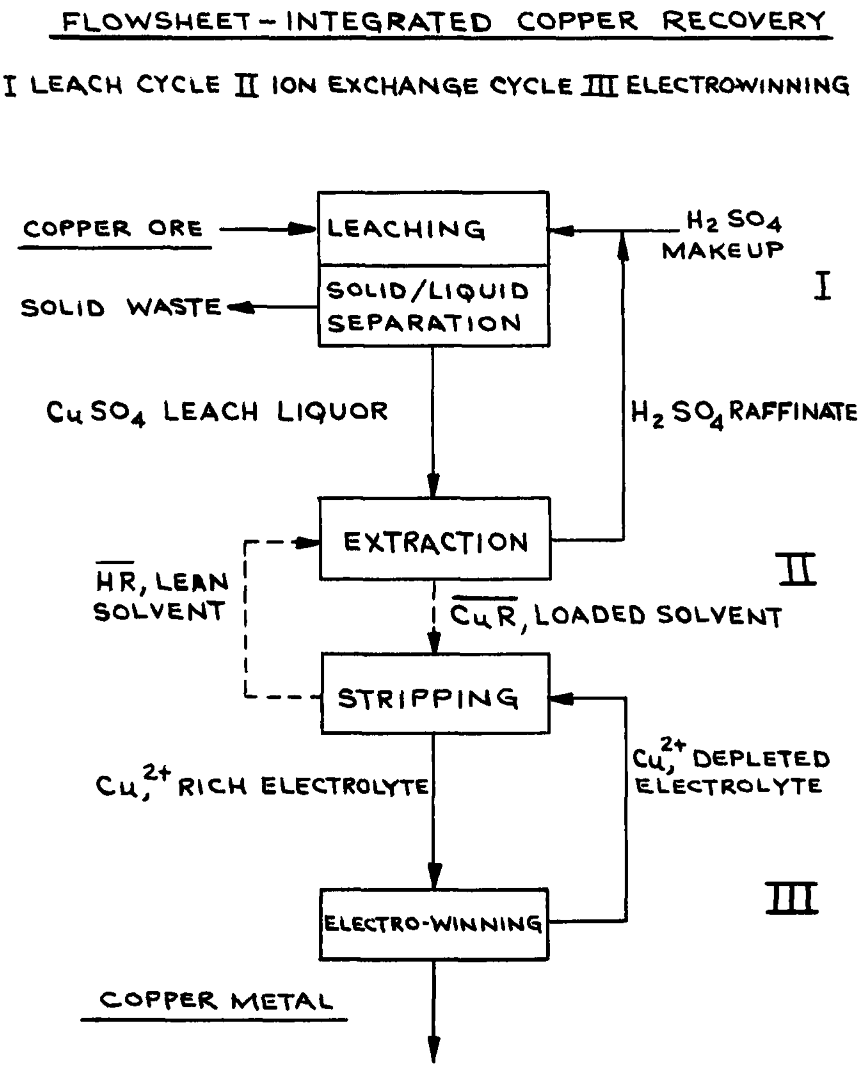

FIGURE 2

alcohols, irrespective of carbon chain length. In the course of time, many other solvents have been checked, among these the N.N. disubstituted amides showed a very good distribution coefficient for phosphoric acid[6].

TABLE III

DISTRIBUTION COEFFICIENTS IN PHOSPHORIC ACID - WATER - ALCOHOL SYSTEMS

Alcohol	Aqueous Phase H_3PO_4, wt %	K $\frac{\text{alc.}}{\text{aq.}}$
n Butanol	4.6	0.15
	21.3	0.32
	32.7	0.48
	41.0	0.73
	50.0	Full Miscibility
i Pentanol	29.0	0.14
	40.8	0.26
	51.7	0.52
	67.5	0.79
	74.0	Full Miscibility
n Hexanol	46.3	0.27
	55.6	0.40
	68.2	0.59
	78.0	0.87
	82.0	Full Miscibility
n Octanol	50.6	0.21
	61.4	0.41
	79.8	0.83
	82.0	0.90
	84.0	Full Miscibility
n Decanol	53.5	0.21
	65.6	0.41
	76.5	0.75
	85.0	0.97
	86.0	Full Miscibility

The first approach to phosphoric acid extraction dealt with the separation of the acid from a soluble aqueous system, obtained by utilizing a mineral acid for decomposing phosphate rock, but without separating the Ca^{2+} constituent of the rock by precipitation. Both nitric and hydrochloric acid belong to the non-precipitating category, since their calcium salts are highly water soluble, whereas sulphuric acid permits separation by virtue of the relative insolubility of calcium sulphate in aqueous medium. With hydrochloric and nitric acids, it would be desirable, therefore, to extract H_3PO_4 preferentially over $CaCl_2$ or $Ca(NO_3)_2$, as the case may be. Such extraction processes, utilizing C_4 or C_5 alcohols, have been described at length in the literature[7,8]. The key to success is the high rejection of cations compared to H^+, therefore not only is Ca^{2+} not extracted, but the rejection of contaminating cations like Fe, Al, Mg, commonly present in phosphate rocks, is equally great, leading to a high quality product acid.

The effect of the presence of $CaCl_2$ in the aqueous phase on the distribution of H_3PO_4 into the solvent was clearly to be seen[9a]. As a result, the next step in phosphoric acid solvent extraction technology was the development of a system based on addition of calcium chloride to "wet process" phosphoric acid produced via sulfuric acid[9b]. Here advantage was taken of the effect of $CaCl_2$ on H_3PO_4 distribution, while at the same time benefitting from the rejection by the solvent of other cations deriving from the phosphate rock[10].

As acid quality became a more stringent requirement, a completely different approach to phosphoric acid recovery and purification was proposed, based on the disproportionation of acid and impurities.[10] Solvents were evaluated in a different way now, not only by looking at capacity, i.e. the distribution of acid as a function of concentration, but also at selectivity, as a function of phosphate concentration and temperature. The latest development in this case history has led to the use of mixed solvents, aimed at obviating specific prior process constraints[11].

The case history of phosphoric acid exemplifies many interesting aspects in design of solvent extraction systems, not the least being the utilization of the effect of changes in temperature on mass transfer in specific solvent systems. This concept had been studied in the 1960's in the limited framework of the water desalination program where energy expenditure was to be kept to a minimum[12]. Now, for purifying phosphoric acid it was found that the same concept of a minor energy change causing a major compositional change can be applied, provided appropriate solvents are selected. Lastly, positive utilization of the tendency of this system towards separation of a third phase, provides a self controlling invariant system, in its "phase rule" context[13]; this is *an unusual approach to control of the extraction operation.*

4.3. Metathetic Salt-Acid Reactions

In 1954, Crittenden & Hixson[14] published a paper related to distribution of HCl between aqueous and solvent phases, and also pointed out that the addition of a salt, whether or not with a common anion, enhances the acid transfer to the solvent. The critical aspect that Crittenden & Hixson did not show was that all anions, whether deriving from acid or salt, would transfer to the solvent to a greater or lesser degree. Nevertheless, it was on the basis of this paper that A. Baniel, searching for low energy methods for converting alkali chlorides to more costly or desirable alkali salts, postulated using the extraction of HCl as a means for shifting equilibria of metathetic salt-acid reactions[15], as follows:

$$\begin{aligned} 2KCl + H_2SO_4 &\rightleftarrows K_2SO_4 + 2HCl \\ KCl + HNO_3 &\rightleftarrows KNO_3 + HCl \\ KCl + H_3PO_4 &\rightleftarrows KH_2PO_4 + KCl \end{aligned}$$

At the beginnings of the salt-acid metathetic reaction development program, it was not obvious that the phase rule must be strictly applied, nor that the aqueous phase can accordingly be regarded as determining. Indeed, even much later, solvent extraction scientists still tended to say that the phase rule gives little information on solvent extraction systems, and to place the accent of study on the solvent phase alone. Nevertheless, in two of the above cases selection of the aqueous system must be regarded as controlling, since according to its composition different solid phases will exist, e.g. K_2SO_4, $K_2SO_4 \cdot KHSO_4$, $KHSO_4$ in the one case, or K_2HPO_4, KH_2PO_4, $KH_2PO_4 \cdot H_3PO_4$ in the other, depending upon acidity level. Proper selection of an aqueous phase composition, particularly at invariant points, therefore, predetermines the whole complex multiphase, multicomponent system. This realization brought about a step-change in the approach to data collection for process development in solvent extraction systems, since it cut out the need to cover a very broad range of levels of variables for flowsheet delineation. In design of solvent extraction systems this is certainly a new departure, laying stress as it does on selecting the aqueous phase composition as fundamental to the system design and fitting the solvent accordingly[16].

Since the solvents used for this study of metathetic reactions are not specific, but extract acids by solvation, it was important to be able to utilize effectively the differences in distribution coefficients for separation of the coextracted acids. This entailed exploiting the interplay of mass balance and distribution coefficients for transfer back and forth between the aqueous and solvent phases, much in the same way that separations can be achieved in distillations by stripping and rectification with reflux, provided only that the relative volatilities make separation at all possible.

The structure of the flowsheet for the industrial coproduction of potassium nitrate and hydrochloric acid, by the metathetic reaction between potassium chloride and nitric acid, is a classic of its kind in applied solvent extraction. The process encompasses the use of a weakly basic solvent to separate acids from salts, an invariant aqueous composition at selected acidity and temperature for predetermining the fundamental mass transfer step, and finally liquid-liquid extraction with reflux and recycle for separating HCl from HNO_3[17].

5. System Selection

5.1. By Analogy or Modification

System modification or adaptation will usually be motivated by process or economic advantage. Process advantage will derive from better separations, specific separations, or easier separations. Economic advantage will relate to less solvent per unit separated, less costly solvent, reduced losses, better phase separation, faster kinetics, less hazard, lower investment, etc.

For single component solvent systems, the only modification possible is to select a different solvent. Thus, for example, for acid extraction one would make one's choice by comparing different molecular weights and structures of solvents from the same group, say alcohols, or similar molecular weights from different groups, say alcohols, ketones and ethers.

For reagent-diluent combinations, the diluent may have to be selected for reasons not directly connected with the reagent-solute interaction. Thus, for example, in liquid cation exchange systems, the solubility of the reagent-metal complex in the solvent phase may influence the diluent choice, apart from obvious aspects such as viscosity and interfacial tension.

In designing a solvent extraction system, an important consideration is the generality of the case. Thus, if one were interested only in extracting a specific metal value, say copper, one would set up a framework of criteria rather different from that for a system of broad usefulness for recovering or separating a variety of metals. Specific or highly selective extractants over a wide range of process conditions will be ideal in the former case, while the latter purpose will be better served by using a general type reagent which displays selectivity as a function of process parameters.

It is noteworthy that the earlier approach to cation exchange, which attained separations in the order of the equilibrium constants of the cation exchange reaction, i.e., by pH control[18], is again receiving attention for separations among metal values other than copper[19]. This is of particular interest when the oxide of the metal being recovered can itself be used for neutralizing the acid produced by cation exchange. A pyrometallurgical operation in conjunction with a hydrometallurgical process encompassing solvent extraction may be ideal for such cases. Thus, in a zinc winning operation, if zinc oxide from pyrometallurgy or flue dust recovery can be utilized in conjunction with the processing of zinc sulphate or chloride from a leaching operation, the inclusion of liquid cation exchange can be considered even without electro-winning.

In Table IV, the "half-binding pH" for various metal cations is given for two cation exchangers, showing the order in which the separation of metals will be attained by pH control.

Recovery of metal values in a framework without the possibility of balancing the acid, would have to be evaluated differently. Such evaluation might show that cation exchange is not the best procedure for the case in point. If so, a different view of separation may have to be taken e.g. by considering the coproduction of a second product to act as acid acceptor, or by ion pair extraction instead of ion exchange.

An unfortunate aspect of specific reagents is that they teach little of a general nature; thus the broad background in synthetic modification of copper reagents teaches perhaps only the obvious, that once one has a suitable reagent, it can be improved by modifying it in certain directions. On the other hand, a general approach to solvent systems, where separation is controlled by selection of process parameters or where the reagent can be se-

TABLE IV
HALF BINDING pH

Metal Cations	α Bromo - Lauric Acid + Kerosene	Di 2 Ethyl Hexyl Phosphoric Acid
Fe^{3+}	1.5	1.4
Al^{3+}	2.3	
Cu^{2+}	3.1	3.0
Ni^{2+}	4.0	4.4
Zn^{2+}	4.8	2.0
Co^{2+}	5.2	4.2
Ca^{2+}	5.7	6.4
Mn^{2+}		5.0
Mg^{2+}		5.8

lected from a graded family, has much to be said for it. In the first case, sensitivity of distribution coefficients to a physical parameter such as temperature, or to a physico-chemical parameter like pH, can be utilized for sequential separations. Similarly, a family of extractants, like the amines which vary in base strength, can form the starting point for fitting an extractant to a specific purpose, while keeping the concepts general.

Another approach to solvent systems of broader applicability is by interplay of reagent and diluent-modifier. Thus, for example, a series of basic reagents can be generated by compounding amines with diluents. For the same amine, the system basicity will depend upon the diluent selected, alcohols leading to basicities greater than with aromatic hydrocarbons which again are greater than with aliphatic hydrocarbons[3,20]. In Table V several amine/diluent systems are compared, utilizing the half-titration pH with hydrochloric acid as the yardstick. Even from these limited examples, the importance of both components of the solvent system is clearly seen.

A similar sequence is followed with acidic reagents which become more acidic as the diluent is changed from alcohol to aromatic hydrocarbon through to aliphatic hydrocarbon[3]. In Table VI the reagent-diluent interaction is exemplified for an acidic reagent, by choosing the reagent LIX64N® and showing how the diluent and acidity level are highly interactive. Thus, for example, the addition of an alcohol as modifier favors Stripping, but is detrimental for Extraction.

5.2. By Design

It is clear that analogy with existing solvent extraction processes can hardly be expected to be the basis for designing new systems for widely different separations, hence it is necessary to explore other areas. A first approach would be to consider which other separation procedures are applicable and can teach by analogy.

TABLE V

AMINE - DILUENT SYSTEMS
HALF TITRATION pH WITH HYDROCHLORIC ACID

Amines		No Diluent	Pentanol	Xylene
Tertiary,	C_{12} Branched	2.5	3.8	2.2
	C_{12} Normal	Precipitate	5.0	2.5
	C_8 - C_{10} Normal	3.0	4.5	2.8
Primary*,	C_{18} - C_{22} Branched	6.8	6.0	6.4
	C_{12} - C_{14} Branched	7.7	7.8	7.0

- - - - - - -

*Some solubility in aqueous phase confounds pH values.

Distillation is almost the first one that comes to mind - this operation has in fact been used as a model for many of the concepts relating to solvent extraction. In distillation, we have relative volatilities, in extraction we have relative distributions, both being based on the concept of equilibrium stage, both depending directly upon the thermodynamic activities of the components in the system at equilibrium.

Selective precipitation by means of a complexing agent can be considered as a source of knowhow, even though the solubility product and not the distribution coefficient is determining; in such a case, we would need the solvent phase for dissolving the

TABLE VI

Reference Composition	{ 20% LIX64N® 80% Kerosene	} 20% Modifier added in each case

Modifier	Dielectric Constant	Aqueous Composition at Zero Extraction g/l Cu:	g/l H_2SO_4
No modifier	-	9.5	87
Amylactate	5	10.0	86
Chloroform	4.8	10.0	85
Isopropyl Ether	3.9	10.6	79
Methyl Isobutyl Ketone		11.5	77
n Hexanol	13.3	15.9	56
n Butanol	17	18.4	37
Cyclohexanone	18	8.7	94
Nitrobenzene	34.8	8.0	93

complex, thus preventing its precipitation, while still promoting removal from the aqueous phase. In either case, precipitation or solubilization, the formation constant of the complex is the deciding factor.

All the highly developed, analytical separation procedures based on partition, whether these be kinetic or equilibrium controlled, are undoubtedly very fertile sources of information and analogy.

When one comes to interactive solvent systems, the situation is more complex; the only way of arriving at systems for testing is probably by looking to other areas for sources of information[16]. Fundamental to this approach is a good understanding of solution chemistry, both aqueous and non-aqueous, and an appreciation of similarities and differences. The great attraction of interactive, multicomponent solvent systems lies in the possibility of setting up a continuous solution scale, stretching from water on the one hand through to a nonpolar, unordered organic system on the other, with all the variations and grades in between. All thermodynamic properties relating to activities, formation constants, stability constants, donor-acceptor systems, heats of solvation, acid-base scales, etc. can be drawn on and pieced together. In this way, one may come to see which property is best exploited for attaining separation, how materials to be separated differ among themselves, what type of environment is likely to lead to separations, and so on.

6. Overall Design Constraints

Clearly, the requirement to extract preferentially is by no means necessarily the overriding consideration. Energy requirements in the present time are important, thus at first glance a separation procedure which entails phase transformation with high enthalpy changes should be avoided. This, in fact, is a basic point in favor of solvent extraction, compared for example to distillation. However, this is not always so; thus it has been shown that for recovery of low concentration solutes from waste waters, a solvent of high selectivity and capacity can be used, even if distillation is required subsequently for separation of solute from extract, or for recovery of solvent components.

Before one decides on a system which lends itself to a solvent extraction separation from the chemical point of view, it is important to define the technological constraints in the particular case. Thus, for example, comparison with a technology based upon precipitation, solid/liquid separation and redissolution, may show that solvent extraction will be a viable competitor in a specific case, provided that technologically it does not introduce detrimental aspects, either economically or from the point of view of the environment.

Solvent extraction by definition requires bringing two liquids into contact to promote mass transfer, and then to separate them. An important consideration then is the residues of each phase left in the conjugate phase. Thus, in metal recovery by liquid-liquid extraction, this aspect has received considerable attention, both economically, from the point of view of losses of costly reagents, and ecologically, from the point of view of contamination of waters or air.

Similarly, aspects of solvent stability, from economic, environmental and technological points of view, may be determining. The importance of solvent losses from the economic point of view is fairly obvious, but less appreciated, perhaps, is the need to distinguish between chemical process losses and physical, technological losses since these have a different bearing upon system selection.

Another aspect may depend upon the end use of the separated or purified material, related to the seriousness of the presence of residual solvent components in the product. Even in the well established case of copper recovery, the detriment of carry-over of minute quantities of organic compounds to the electro-winning operation cannot be over-emphasized.

Auxiliary operations may sometimes be very significant, particularly where the solvent extraction operation is interposed between other steps; these operations may even make it preferable to choose a solvent system which by itself is not the optimum choice but which can be integrated with advantage into the whole. The importance of auxiliary operations has been discussed in the case of phosphoric acid[21], and is well illustrated in the cases of copper extraction, and of uranium recovery in conjunction with gold mining.

7. Process Development of a Separation Concept

At the risk of over-simplification, an attempt will be made now to indicate approaches to new separations so as to bring some concrete paths into what may otherwise seem to be an unchartered wilderness.

There are various ways in which one may come to be considering solvent extraction for a particular separation. In some cases the current separation procedures may be inconvenient, inefficient, energy intensive, or generally costly. In other cases, one may have considerable technological knowhow in the area and be seeking new applications. In any event the cardinal question is "how does one begin"?

As an exercise, we shall consider the path followed for the separation of bromide from chloride brines. This case came up for both the reasons listed above, namely apparent deficiencies in current technology for recovery of bromide values, and considerable experience in developing solvent extraction processes. The problem was very challenging, requiring the recovery of the minor component, bromide, from a high concentration chloride ambient, under stringent purity specifications.

In the primary analysis the first question asked was whether the salts have some solubility in solvents. With very little effort one can verify that bromide salts dissolve in solvents more readily than do chloride salts. The next step, therefore, was to examine distributions of the individual simple salts using various solvents[13,22]. On the basis of separation factors calculated from individual distribution coefficients in pure systems, and the capacities for bromide per unit of the various solvents tested, a simple alcohol was selected as an appropriate solvent and a separation flowsheet derived. An interesting practical finding was that this solvent, which preferred Br^- over Cl^-, also selected Mg^{2+} over Ca^{2+} and that there was strong interaction between Cl^- and Br^-, so that the final bromide concentration in product was not dependent upon the initial aqueous bromide concentration but rather upon the accompanying chloride concentration[23]. Subsequently, for a better understanding of the basics of this system, and as background for approaching other systems, measurements were made of enthalpy effects in the extraction of magnesium halides by aliphatic alcohols[24]. Also the interactive step in the process was modelled to see whether the bromide peak could be reproduced and thus provide a better understanding of the process and its control[25]. Lastly, other solvents were examined from the point of view of Mg^{2+} and Ca^{2+} separation and possible reversal of the order of preference[16], thus broadening the understanding of the mode of transfer.

Although the separation of bromide from chloride referred to here is quite particular, the concepts that were exploited are general enough to serve as an approach model for other cases. Almost invariably one must start from the separation itself and then come to the solvent system. Indeed, practical results will rarely be attained by developing a reagent, or by synthesizing or compounding a solvent and then looking for likely applications. The chemical literature is full of examples of studies of special solvent systems which have been tested with a variety of solutes, but which are never usefully applied. The reason for this may well be that all these cases remain separate without being generalized by identifying and classifying their mode of transfer, the degree of hydration and solvation, their donor-acceptor relationship, so that each isolated case will fall into an ordered pattern with others and thus become conceptually available for useful consideration.

8. Concluding Comments

If now we can define a solvent for solvent extraction, as a liquid which is only partially miscible with water, and which is chemically acceptably stable towards water, the choice of solvent would appear to be very broad. Nevertheless, solvent extraction in industrial application has been limited to a small number of defined types. It is not these applications, therefore, that will promote the development of new approaches for selection and design of solvent extraction systems; but it is all those other cases, where separations are required but solvent extraction has not been applied, that offer the challenge.

In our context a solvent is any liquid phase which does not mix completely with the aqueous phase with which it is to be contacted, thus permitting a liquid-liquid interface for mass transfer to exist. Apart from this, the solvent may be as simple or as complex as is desirable for best attainment of the purpose in hand.

If we assume that we are dealing almost always with reversible equilibria, it is clear that the distribution coefficient, which is the measure of transfer, represents the product of a whole range of equilibrium constants which may be defined with more or less certainty but which usually cannot be quantified. However, one can often indicate the relative direction in which each equilibrium should be moved in order to favor the transfer desired, even though one may not be able to say intuitively how this can be attained.

Not less important for an appreciation of solvent systems, is the definition of the behavior of water in the aqueous/solvent two phase system and in particular its distribution. This distribution may have considerable bearing also upon solute transfer, particularly in hydrogen-bonding systems. It is essential to take this into account if one hopes to deal successfully, even if only pragmatically, with new separations in unexplored systems[16]. In Table VII a range of water solubilities is shown for a random selection of solvents.

The important point, here, is the realization that one can compound a solvent system so as to be as nearly similar to water as is deemed necessary for successful extraction, while keeping it sufficiently different to maintain the liquid-liquid phase boundary, and thus to exploit selective transfer due to solute differences.

From all that has been presented above, it seems that the design of solvent extraction systems can be handled only on an inter-disciplinary basis, combining together, for example, the

TABLE VII

SOLUBILITY OF WATER IN A SELECTION OF SOLVENTS

Solvent	wt % H_2O; 23°C
Butyl Lactate	11.9
Hexyl Carbitol	40.5
n Pentanol	9.4
t Pentanol	22.3
2-Methyl 5-Ethyl Pyridine	19.3
2-Ethyl Hexyl Amine	23.3

approaches of non-aqueous solution chemistry, of complexation, solvation, acid-base relations, solvent polarity, the phase rule, thermodynamics, synthetic organic chemistry, and so on.

The past two decades have seen major advances in solvent extraction technology, but the next decade will be the era of solvent extraction science, drawing from various sources and combining many skills. There are only two questions to be asked in approaching a problem, firstly, what is the nature of the material requiring separation, and secondly, which of its characteristics can be exploited to facilitate this separation. The rest will follow naturally if one is "skilled in the art".

Acknowledgements

While the views expressed in this paper are peculiarly my own, it was only by interaction and discussion with my colleagues at IMI over a period of years that I was able to arrive at the integrated picture of solvent extraction systems that I now hold.

I am grateful to the Editors of this Journal for their invitation to present this paper.

Dr. J. E. Alter of Miles Laboratories, Inc., Elkhart, Indiana kindly read and criticized this text in the writing.

References

1. R. Blumberg, D. Gonen and D. Meyer, in "Recent Advances in Liquid-Liquid Extraction", C. Hanson, ed., Pergamon Press, Oxford, 1971, p. 93.
2. Y. Marcus and A. S. Kertes, "Ion Exchange and Solvent Extraction of Metal Complexes," Wiley-Interscience, New York, 1969.
3. R. Blumberg and J. E. Gai, in Proceedings, International Solvent Extraction Conference, Toronto, Canada, 1977 (in print).
4. R. Blumberg, Solvent Extraction Revs., 1 (1), 93 (1971).
5. LIX® - Proprietary Reagents of Henkel Corp. (previously General Mills).
6. A. Baniel and R. Blumberg, U.S. Patent, 3,304,157 (1967).
7. A. Baniel and R. Blumberg in "Phosphoric Acid" Vol. I, Pt. II, A. V. Slack, ed., Marcel Dekker, Inc., New York, 1968, p. 889.
8. R. J. Piepers, in "Phosphoric Acid", Vol. I, Pt. II, A. V. Slack, ed., Marcel Dekker, Inc., New York, 1968, p. 913.

9a. A. Baniel and R. Blumberg, Dechema Monographien, Band 33 Nr477-502, 57 (1959).

9b. A. Alon, paper presented at ISMA, Edinburgh, Scotland, 1965.

10. A. Baniel and R. Blumberg in "Phosphoric Acid" Vol. I, Pt. II, A. V. Slack, ed., Marcel Dekker, Inc., New York, 1968, p. 709.
11. R. Blumberg, Proceedings No. 151, The Fertilizer Society, London, 1975.
12. R. R. Davison, W. H. Smith, Jnr. and D. W. Hood, J. Chem. Eng. Data, 11 No. 3, 304 (1966).
13. R. Blumberg, Israel Chem. Eng., 2, 23 (1973).
14. E. D. Crittenden, Jr. and A. N. Hixson, Ind. & Eng. Chem., 46, 268 (1954).

15. A. Baniel and R. Blumberg, Chimie et Industrie, 78 No. 4, 327 (1957).

16. R. Blumberg in Proceedings, International Solvent Extraction Conference, Toronto, Canada, 1977 (in print).

17. Y. Araten, A. Baniel and R. Blumberg, Proceedings No. 99, The Fertilizer Society, London, 1967.

18. R. Blumberg and P. Melzer in Proceedings, 7th Int. Mineral Processing Congr. 1964, Gordon and Breach, New York, 1966, p. 139.

19. V. A. Ettel, J. Babjak and A. J. Oliver in Proceedings, International Solvent Extraction Conference, Toronto, Canada, 1977 (in print).

20. R. Blumberg, J. E. Gai and K. Hajdu in Proceedings, International Solvent Extraction Conference, Lyon, France, 1974, Society of Chemical Industry, London 1974, p. 2563.

21. IMI Staff Report in Proceedings, International Solvent Extraction Conference, The Hague, Holland 1971, Society of Chemical Industry, London 1971, p. 1386.

22. H. Aharon, A. Baniel and R. Blumberg, Bull. Res. Council of Israel 6C No. 1, 69, (1957).

23. A. Baniel and R. Blumberg, Israel Patents 23760 (1965), 41225 (1973).

24. R. Blumberg, J. E. Gai, and J. Moscovici, in Abstracts 43rd Annual Meeting, Israel Chemical Society 1975, p. 139.

25. J. E. Gai, in Proceedings, International Solvent Extraction Conference, Toronto, Canada, 1977 (in print).