LIQUID–LIQUID EXTRACTION

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Liquid–Liquid Extraction

Preface

This monograph is intended for those already working in the liquid–liquid extraction (LLX) field. It is not a formal teaching manual, nor is it a review of solvent extraction processes. It is an exposé of an integrated approach to the development and design of liquid–liquid extraction processes, based on broad personal experience, and on a generalized research and development philosophy which extends to the development of any novel chemical process.

In this approach to research and development (R & D) the separate aspects which may have a bearing on the process are to be identified from the outset, as far as this is possible, and are then to be pursued in parallel, so that an outline of the whole is pictured from the beginning and becomes more clearly defined and tangible as work proceeds. It has been the aim, in writing this monograph, to show up as many as possible of the separate aspects of research which must be taken together to form the basis for the development of a liquid–liquid extraction process. The "thinking" models presented are based firmly on practice, experience and experimentation.

Liquid–liquid extraction with its unique flexibility is a powerful separation tool; the successful choice of the second liquid phase for an entirely new application of liquid–liquid extraction is an exciting, satisfying experience; not less so is the development of a workable process scheme based on this choice.

The skill of process development (PD), in its broadest sense, can be extended only "on the job", by working with others who have expertise and experience. The writing of this monograph is a welcome opportunity to place broad personal expertise and experience at the service of the wide spectrum of researchers who aim to put liquid–liquid extraction to use for novel purposes by developing new, viable processes.

Two central themes have been stressed—one is the great variety of two-phase systems that potentially exist, the other is the integrated approach in selecting and using LLX systems for practical purposes. Overall the integrated approach aims at asking relevant questions so that correct answers may be sought and found.

The text is divided into three parts—Part I exposes problems and questions relating to the scope of, and the approach to, the LLX procedure,

Part II concentrates on the LLX separation, Part III deals with the separation process itself. The overall approach is process oriented since the process is the ultimate aim and is the measure of R & D success. Examples and procedures are given in so far as these make the approach clearer; the examples are all drawn from personal experience. However, it is not the main purpose of the book to teach how "to do" LLX, but how "to think" LLX, so as to develop and expand its application and use.

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Dedication

This book is in memory of those young members of our family who were eliminated from this life in the 1940's and were thus ever prevented from encountering life's challenges and triumphs.

Introductory

One can assume that LLX for its own sake has no justification, since it is only a separation procedure, which, for success, requires that it be incorporated into a separation process. This means that the overriding aspect of an integrated LLX program will be the interactions and interconnections that enable the procedure to become the process. The presentation here aims to indicate how to make these interconnections.

The development of any process must be an inter-disciplinary activity, and so indeed the development of a LLX process depends on the interaction of many participants. The primary aims here have been to show how one approaches LLX, what are its scope and versatility, and what constrains its application. The broadness of the scope and the versatility of LLX mean that an appreciation of its potential and an awareness of the basic aspects will indicate its applicability for each specific case. LLX is not a natural property of systems, hence it is important first to examine the possibility of devising a LLX system to achieve a desired separation, and then to proceed to the construction of the process based on this separation.

The novelty in this approach to LLX lies in the awareness that the construction of the two-liquid phase system is the prerogative of whosoever wishes to utilize LLX for a specific separation. No one such system is unique, hence a variety of selections are feasible for the same purpose; since each selection will be different, its integration into an overall LLX process will result in one of a variety of possible process schemes. However, all these schemes will have certain basic concepts in common; furthermore, comparison between schemes requires that fixed terms of reference be defined in order to validate the comparison.

The generalized approach presented here has not required concentrating on details or specifics, even though such have been utilized occasionally to exemplify a concept or to illustrate a point. Here the logic of the analysis and the logical build-up towards the separation process have been considered of paramount importance, and this has determined the format of the presentation. In the main, therefore, only concepts have been considered significant, since data and details will follow naturally once basic aspects are defined and

understood. For this reason too, multiple references have not been given since in every specific case such references will have to be sought positively, as and when required.

In process development, as in any other "master-craft" the success of the final work may be judged against its simplicity and its elegance, in conjunction with achievement of goals. LLX has a natural simplicity and elegance which should not be lost when the LLX separation is integrated into a process.

Since this is not a teaching manual nor a handbook, the author's advice to the reader is first to read it right through, as one would in any other area dealing with ideas and concepts, so as to place the presentation in correct context.

Scope and Approach

This monograph is intended for R & D personnel who aim at devising and developing novel chemical processes. (Note, chemical is used here in the most general sense.)

Since liquid–liquid extraction (LLX) is a separation tool, it is clear that the processes referred to will entail a separation operation. This separation may be the crux of the process itself, or it may be a step interposed among other steps of equal or greater impact on the process. The use of LLX may be uniquely the way in which the separation can be attained, or it may be a unit operation competitive with other separation operations. The aspect of the approach that is common to all the applications, and which perhaps distinguishes this monograph, is the author's integrated view of a "process" and its development. Here, specifically, LLX is the central point which must be fully integrated into the whole, but the approach is quite general, and the philosophy applies equally to the development of any novel process.

This monograph is not a teaching manual, nor is it a review of LLX processes. It is meant to be an exposé of the integrated research approach involved in devising and designing the LLX process. In such an approach, the separate aspects which may have a bearing on the development of the process are identified from the outset, and these are then pursued in parallel, so that the whole is pictured from the beginning and becomes more clearly defined and tangible as work proceeds. This monograph aims at showing as many as possible of the separate aspects of research which must be taken together to form the basis for the development of a LLX process.

In PD work, apart from the constraints imposed by the nature of a system and its behavior, there is also the constraint of time. In LLX, as in other disciplines, it is possible to devise limiting tests which will give definitive information delineating the area, without necessitating the scanning of the whole area. This approach is invaluable when time is important and also when a broad coverage of possibilities is best likely to pay off in the long run.

The monograph is divided into three main sections. The first section encompasses the integrated approach to developing a process (here, of course, a liquid–liquid extraction process). The second section relates to

modes of studying LLX systems and presents specific approaches; however, it does not cover aspects commonly found in standard texts. The third section relates to the testing of any proposed separation scheme, to attain an acceptable degree of certainty for implementation considerations.

In Part I, the scope and types of LLX separations are discussed; where these can be applied, what yardsticks can be used, etc. Generalized identification and specification of the particular separation to be achieved—separation of what, from what, to what degree? What analogous separations are known? What alternative procedures are practised for the same separation? How will the LLX separation, if practised, be interposed in the process? What constraints are imposed by contiguous operations? How will these reflect on the choice of LLX system? What are the constraints inside the system? How do these reflect on flowsheet and equipment?

In Part II, the intimate aspects of LLX are discussed. Part II is subsidiary to Part I; this means that after having identified the separation required and decided how it is likely to be attained, the study of the system begins. For this it is necessary to select the type of two-liquid system which is expected to permit the separation to be attained by the mode of transfer anticipated. Distribution coefficients, separation factors, equilibrium curves, practical equilibrium constants, contact patterns, i.e. those aspects that relate to defining the flow diagram for a specific separation, are considered here.

Part I defines the scope and approach, Part II aims to show chemical feasibility, Part III is concerned with attaining the required degree of certainty of technological feasibility. Part III, therefore, relates to the success with which the relevant aspects of technological significance have been identified and the required extent of certainty defined, and leads then to assessment of the nature and scale of testing required for the degree of certainty demanded.

Contents

I. The Liquid–Liquid Extraction (LLX) Procedure—An Integrated Approach

Definition of the Separation

This section presents the integrated approach to developing a process which, here, entails separation by liquid–liquid extraction.

Liquid–liquid extraction is a separation/transfer procedure; if it is to be applied it is necessary first to identify the separation(s) desired, the main separation as well as the secondary ones. If a component has the tendency to transfer from one liquid to another across the liquid–liquid boundary by whatever mechanism, then separation of the liquid phases will constitute also a separation of the component that has transferred.

If A is to be separated from B, one must evaluate, conceptually, whether A should be transferred away from B or vice versa. Secondly one must define the differences in properties between A and B which can be exploited in order to achieve the desired separation. Clearly the more A differs from B the more likely will it be that a high degree of separation can be attained. Next, it is necessary to identify the property which is to be exploited for attaining the separation(s). Thus if an acid is to be separated from other acids, one needs to have some scale of comparison of the acids, so as to see whether separation can be anticipated directly from this scale, e.g. strong acids *vs* weak acids, or the tendency to complexation, hydrogen-bonding, etc.

Once one knows what is to be separated from what, and how one hopes to promote the separation, one can look at solvent selection. The characteristics of the solvent, which must interlock with the selected characteristics of the solute being separated, need to be identified. Once the characteristics of the solvent have been specified, it is possible to decide what the components of the solvent will be. Thus there are certain degrees of freedom, according to the type and number of solvent components, and the extent of interaction between them. It is possible to distinguish between the active extractant (reagent, complexing agent), the diluent (with various degrees of interaction and activity) and the modifier. The extractant is the central component and to a considerable extent determines the specificity or selectivity of the