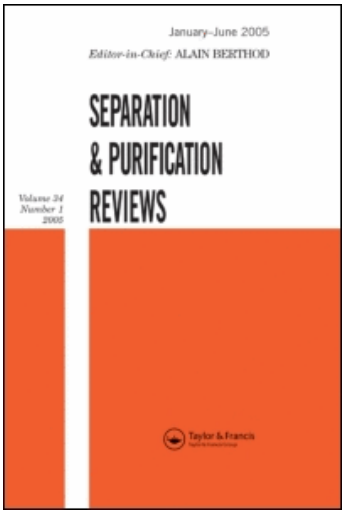

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Separations Through Reactions and other Novel Strategies

V. G. Gaikar[a]; M. M. Sharma[a]
[a] Department of Chemical Technology, University of Bombay Matunga, Bombay, INDIA

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SEPARATIONS THROUGH REACTIONS AND OTHER NOVEL STRATEGIES

V. G. GAIKAR and M. M. SHARMA
Department of Chemical Technology
University of Bombay
Matunga, Bombay - 400 019
INDIA

Contents :

I. INTRODUCTION

Separation processes are essential to virtually all manufacturing processes. Literally, thousands of products are fractionated to the desired purity by different separation techniques. These techniques play a pivotal role in industry due to high associated capital and operating costs. Frequently, the cost of the separations constitute a major part of the economics of the plant. There is an ever increasing emphasis on improving the quality of industrial products and it is not uncommon to find impurities specified at ppm level and some cases even at ppb level. There is demand on reducing capital and running costs and make separation processes safer, reliable and more selective.

Separation of close boiling substances continues to be a challenging area. Chemical reactions, complexation through hydrogen bonding, acid-base reactions, clathration and chelation offer many opportunities to make such separations economical. Reactions can enhance the extent of separation when imposed on conventional processes, such as gas absorption, solvent extraction, crystallization, extractive distillation and membrane processes.

Separations through selective reactions have played a significant role in chemical industries from early stages. Even today many separations, which otherwise are very difficult by physical methods, are carried out by exploiting the differences either in the chemical equilibria or in the reaction

rates. The alkylation of m- and p-cresols by isobutylene followed by separation of alkylated products and dealkylation is a commercial process for the separation of cresols.[1] Nitrosation of the mixture of cresols followed by separation of products by dissociation extraction/crystallization may be yet another viable route.[2]

A mixture of o-/m-/p-nitrochlorobenzenes can be separated by exploiting the reactivity of the labile -Cl group on o- and p-isomers in nucleophilic displacement reactions; m-nitrochlorobenzene hardly undergoes these reactions[3]. A similar strategy is applicable for the separation of m- and p-xylenes; p-xylene hardly reacts with acetaldehyde when m-xylene is present in the mixture. The separation of m/p-xylenes by selective complexation reaction of m-xylene with $HF-BF_3$ has been a commercial success[4]. The sulphonation and desulphonation is another method suitable for the separation of xylenes, diethylbenzenes, dichlorobenzenes and chlorotoluenes. During desulphonation, the difference in the rates of hydrolysis of o-/p-/m-substituted sulphonic acids can pssibly be exploited to achive further separations.[5].

The selective absorption of isobutylene from the mixtures with butenes into 50-60% H_2SO_4 is an example of manipu-lation of the kinetics of the reactions.[2] Recently, the selective reaction of isobutylene with methanol in presence of ion exchange resin catalyst to give methyl-tert-butyl ether (MTBE) has been exploited.[6] Pure isobutene may be obtained by cracking MTBE and methanol can be recycled. The process is equally applicable to isoamylenes. The separation of mixtures of ethylene with ethane or propylene with propane can be accomplished by selective reactions with aromatic compounds to prepare alkylated products or with isopropanol to form isoalkylethers. A similar process has been developed by EC-Erdölchemie to obtain ultrapure isoolefins, such as isoamylene and isohexene, which are gaining

increasing importance as starting materials for a wide variety of intermediate products, via corresponding isoalkylethers using ion exchange resin catalysts.[7]

The removal of H_2S or the separation of H_2S from CO_2 by absorption in chemically reacting solvents, such as alkanolamines has been practiced in the chemical industry for a long time. Even this field has witnessed a number of advances in the last few years because of creative combination of chemical and steric factors in designing new chemical solvents. The use of hindered amines, first suggested by Sharma[8], has been the centre of investigation in recent years to increase the selectivity towards H_2S and to improve the ease of regeneration[9,10], the costs of the chemical solvents and of regeneration are important factors in the overall economics of the plant.

A number of such separation techniques, based on reactions, have been reviewed by Sharma[2] and later by Gaikar and Sharma[11].

Recent reports which discuss the directions and the scope for separations include a study by the National Research Council's Committee on Separation Science and Technology[12] and an AIChE monograph by Keller[13]. Both these reports have emphasised the need for the development of new separation techniques by generating improved selectivity among solutes in separations.

This review will deal with some of the reactions based separation processes along with newer separation techniques which are useful as alternatives to the existing technologies or as the only solution to the separation problem.

Dissociation extraction, dissociation extractive crystallization, dissociation extractive distillation are some novel techniques based on relative acidities and basicities of the components of the mixture.

Clathration and chelation form a special class of complexations and may offer an efficient method of separation

based on the differences in molecular geometries of the components.

The use of micelles and hydrotropes in extractive separations forms a new class of separation processes. Hydrotropes are useful in extractive distillation also. A combination of these principles with other fields, such as membranes is opening a new area of separation for recovering chemicals from dilute aqueous solutions.

The recovery of chemicals from aqueous solutions either as a part of the waste stream or as a product obtained biochemically is very relevant both from the pollution and economic points of view. Adsorption on polymeric adsorbents, ion exchange resins and chemical gels can provide suitable energy efficient alternatives and may be more economical.

Biochemical separations give highly selective routes for separation of components which are very close in their properties. The separation of racemic mixtures is another challenging area where enzyme catalysed reactions can offer high specificity.

Membrane processes are finding widespread industrial applications, in bulk separations and in recovery/separation of chemicals from dilute streams. The imposition of chemical reactions on membrane transport can facilitate the permeation rates as well as enhance the selectivity.

II. DISSOCIATION EXTRACTION

Dissociation extraction is a two phase technique of separation of organic acids or bases. This process exploits the differences between the dissociation constants and distribution coefficients of the components[14-18]. It is specially useful when the boiling points of the components are very close or when the mixtures should not be distilled, e.g., nitrophenols, aminophenols, pharmaceutical products, such as flurbiprofen with an impurity of Dimeric acid, etc. In the latter case even

high vacuum distillation was impractical because of sublimation of the mixture[18].

A conventional dissociation extraction involves equilibrating a mixture, dissolved in a water-immiscible organic solvent, with an aqueous phase containing a neutralizing agent in stoichiometrically deficient amount. This stoichiometric deficiency of the neutralizing agent with respect to the total acids (bases) leads to a competition between the components to react with the neutralizing agent resulting in preferential reaction of the stronger component with the neutralizing agent.

The use of dissociation extraction can be traced back to 1924, when Warnes[19] separated phenolic mixtures using this technique. Later, coal tar industry saw the commercial exploitation of dissociation extraction[20] but theoretical analysis and various modifications of this process were introduced only in the last fifteen years. Hanson and co-workers[14,15,21] made valuable contributions in early seventies to this field. In the course of last ten years Sharma and co-workers[16,17,22-29] have separated different mixtures of industrial importance along with the development of regenerative processes, prediction of separation factor and development of thermodynamic guidelines to select a solvent.

The basic theory of dissociation extraction, developed by Anwar et al.[14] following the treatment of Wise and Williams[30], gives the expression for the separation factor as

$$\alpha = \frac{D_A K_B}{D_B K_A}\left[\frac{N(\delta + 1) + T\{1/D_A + (K_B/K_A)(\delta/D_B)\}}{N(\delta + 1) + T\{(K_B/K_A)(1/D_A) + \delta/D_B\}}\right] \quad ..(1)$$

where T is the total concentration of components in the organic phase and δ is the molar ratio of the components in the organic phase. D's and K's are the distribution coefficients and dissociation constants, respectively; N is the concentration of the neutralizing agent. Table I shows some typical mixtures separated by dissociation extraction.

TABLE I

DISSOCIATION EXTRACTION

Acidic Mixtures	Ref.	Basic Mixtures	Ref.
Alkylphenols		**C-Alkylanilines**	
(a) p/m-Cresols	20,31-33,41	(a) 2,6-/2,5-Xylidines	17,27
(b) 2,6-Xylenol/p-Cresol	17,27	(b) 2,6-/2,4-Xylidines	17,27
(c) Xylenols/m-Cresol	38	(c) 2,4-/2,5-Xylidines	17,27
(d) 2,4-/2,5-Xylenols	34	(d) o-/p-Cumidines	28
(e) 2,6-Xylenol/Guaiacol	17,23	**N-Alkylanilines**	
(f) p-Cresol/Guaiacol	17,23	(a) N-Ethyl aniline/ N,N-Diethylaniline	22
(g) o-Ethylphenol/ Guaiacol	17,12	(b) N-Et-o-toluidine/ N,N-Diethyl-o-toluidine	22
(h) o-Cyclohexylphenol/ o-Phenyl phenol	42	(c) m-Toluidine N-Ethyl-m-toluidine	24
Chlorophenols		(d) N-Ethyl-m-toluidine N,N-Diethyl-m-toluidine	24
(a) Phenol/o-Chlorophenol	17,22	**Nitroanilines**	
(b) p-Chlorophenol/ 2,4-Dichlorophenol	26,29	(a) o-/p-Nitroanilines	17,24
(c) 2,4-/2,5-Dichloro-phenols	26	**Chloroanilines**	
(d) 2,3-/2,6-Dichloro-phenols	35,36	(a) o-/p-Chloroanilines	17,24
(e) o-Cresol /6-Cl-o-cresol		**Heterocyclic amines**	
(f) 4-Chloro-m-xylenol/ 2,4-Dichloro-m-Xylenol	26 26	(a) 3-/4-Picolines	14, 15,21
Nitrophenols		(b) Quinoline/Iso-quinoline	40
(a) 6-Nitro-m-cresol / other Nitro-m-cresols	37	(c) Piperidine/N-Methyl-piperidine	23
(b) o-/p-Nitrophenols	39	(d) Hexamethyleneimine/ N-Methylhexamethylene-imine	23
Flurbiprofen/Dimeric Acid	18	(d) Piperazines	44
m-Chloroperoxybenzoic Acid/ m-Chlorobenzoic acid	43		

A. Regenerative Dissociation Extraction

(a) Weak extracting agents

The major cost factor deciding the economics of dissociation extraction as a separation process is the cost of the chemicals, i.e. the cost of the extracting agent and the cost of the neutralizing agent required to recover the extracted material. Attempts, therefore, were made to develop processes where the extracting agent can be recovered and reused.

The use of weak extracting agent was the first step towards this development by Anwar et al[15,35] In this process a weak extracting agent is used to carry out dissociation extraction which gives an aqueous phase enriched in the stronger component and an organic phase enriched in the weaker component. The aqueous phase then is contacted in a secondary extractor with an organic solvent, highly polar with respect to the organic solvent in the first column, which extracts the desired component from the aqueous phase in the undissociated form. The process was tested by Anwar et al[15] for separation of 3- and 4-picolines, dissolved in benzene, using aqueous solutions of sodium dihydrogen phosphate, which is weakly acidic in nature. The aqueous extract was then reextracted with chloroform which has high affinity for picolines in undissociated form. However, a limitation of the process using a weak extracting agent is that separation factors and the percentage extraction are low which results in considerable increase in the number of stages to achieve separation.

Anwar et al[35] later separated mixtures of 2,3-dichlorophenol and 2,6-dichlorophenol using aqueous monoethanolamine solutions with toluene as a primary solvent and ethyl acetate as a secondary solvent. However, loss of ethyl acetate in the aqueous phase would be substantial and it thus becomes necessary to add yet another step to recover the material.

Pratt[41] investigated the separation of m-cresol/p-cresol by aqueous sodium hydroxide which was regenerated by

an organic solvent having high affinity for the cresols, such as n-octanol; the reaction in the aqueous phase was partially reversed and m-cresol was extracted into the organic solvent.

(b) Thermally regenerative dissociation extraction

The use of a proper extracting agent may facilitate the regeneration by a simple thermal treatment given to the aqueous extract. Wadekar and Sharma[26] separated p-chlorophenol/2,4-dichlorophenol mixtures using aqueous ammonia solutions and 2,6-xylenol/p-cresol mixtures using aqueous monomethylamine solutions. In both the cases, the extractant was recovered by distillation from the aqueous phase and was recycled.

Jagirdar and Sharma[24], and later Gaikar and Sharma[28], used a similar thermal treatment to recover hydrogen chloride gas from the hydrochloride salts of N-alkylanilines, nitroanilines and cumidines suspended in xylene or cumene.

(c) Extraction with alkanolamines followed by carbonation as regenerative process

Gaikar and Sharma[29] used a new concept to recover weak extracting agent which is superior to the use of the secondary solvent extraction regeneration. Aqueous solutions of highly water soluble alkanolamines were used to separate p-chlorophenol/2,4-dichlorophenol. The aqueous extract which was rich in 2,4-dichlorophenol was then carbonated by passing carbon dioxide gas through it. In this case carbon dioxide, being more acidic, reacts selectively with the alkanolamine and the water insoluble chlorophenols separate as a second liquid phase. The desorption of carbon dioxide from alkanolamine solutions under boiling conditions is well known and regenerated alkanolamine solutions can be recycled; even CO_2 can be recycled. The yield of recovered chlorophenols from the carbonator was quantitative (> 99%).

B. Prediction of Separation Factor in Dissociation Extraction

Equation (1) has been used successfully to predict the separation factor for a number of acidic/basic mixtures.

The values of D_A, D_B, K_A and K_B are necessary to predict the separation factor which are usually obtained experimentally.

The dissociation constants can be predicted with a fairly good accuracy on the basis of extensive collection of available pKa data coupled with the thermodynamic considerations, using Hammett and Taft equations of the form[45].

$$PKa = pKa^{\circ} - \rho \Sigma \sigma \quad ..(2)$$

Prediction of distribution coefficients of organic acids (and bases) is, however a difficult task because of highly nonideal behaviour of these substances. However, a linear free energy approach forwarded by Hansch and his co-workers[46-48] has led to a group contribution method to predict distribution coefficients of a solute between n-octanol and water. The $\log D_{ow}$ of any solute is obtained by simply adding the contributions of each group in the molecule.[47,48] Gaikar and Sharma[17] used these correlations successfully to predict separation factors for separations of o-/p-cumidines and of phenol/o-chlorophenol.

C. Selection of Solvent for Dissociation Extraction

Dissociation extraction exploits not only the difference in the dissociation constants, but also the difference in the distribution coefficients of the components of a mixture to be separated. By changing the solvent it is often possible to change the difference in distribution coefficients. Thus a judicious selection of a solvent is important in realising better separation. It is very likely that the relative interactions between different components with solvents decide the difference in distribution coefficients.

Organic solvents can be classified according to their ability to interact with phenolic and basic substances. Aliphatic hydrocarbons, such as, n-heptane, cyclohexane, constitute the group of inert solvents with negligible tendency to interact with OH or NH_2 groups. These are followed by aromatic hydro-

carbons, halogenated hydrocarbons ethers and ketones, esters and finally alcohols, in the order of increasing tendency of interacting with the solutes. Alcohols can form strong hydrogen bonds with various hydrogen bond donors and acceptors. The knowledge of these interactions coupled with the structural information about the molecules can help in selection of a proper solvent.

Gaikar and Sharma[17] formulated the guidelines on the basis of the above thermodynamic considerations such as solute-solvent interactions, solute-solute interactions and steric hindrance to the functional group and successfully used them for a number of systems to enhance the separation factor, sometimes by an order of magnitude. The guidelines suggested by Gaikar and Sharma[17] are as follows :

(i) use an inert solvent if the stronger component has a relatively free aquophilic group and

(ii) use a polar solvent if the weaker component has a relatively free aquophilic group.

In the separation of o-cresol (b.p. 191-2°C) and 6-chloro-o-cresol (b.p. 191-3°C) mixtures if benzene is selected as a solvent practically no separation can be achieved despite a large difference in their pKa values (10.28 and 8.69 at 25°C, respectively). This is because of very high distribution coefficient difference acting in the opposite direction; 6-chloro-o-cresol has a higher distribution coefficient than that of o-cresol because of the presence of hydrophobic Cl group. However, with a polar solvent, such as di-butyl ether and n-octanol, the separation factors were 3-4 and 9, respectively. o-Cresol, having comparatively a free hydroxyl group can interact with these polar solvents while there may not be an equivalent change in the distribution coefficient of 6-chloro-o-cresol because of steric hindrance provided to OH group by bulky Cl group.

In the separation of 2,6-xylenol/p-cresol mixtures the situation is reversed. The distribution coefficient of

2,6-xylenol (pKa : 10.59) is always higher than that of p-cresol (pKa : 10.28) because of close proximity of two bulky methyl groups to the hydroxyl group. For such a mixture the use of a polar solvent will be detrimental as free OH group on p-cresol can interact with polar solvents. Thus the use of an inert solvent should be a better choice. Indeed, separation factors were about 6 in di-butyl ether, 13 in benzene and 35 in n-heptane[17].

D. Separation and Recovery of Organic Acids From Dilute Aqueous Solutions

The principle of dissociation extraction can be modified to recover/separate acids/bases from dilute aqueous streams. Jagirdar and Sharma[23] explored the possibilities of recovering formic/acetic acids, acetic/monochloroacetic acids, formic/oxalic acids, monochloroacetic/dichloroacetic acids with simultaneous separation by extraction using tri-n-octylamine dissolved in solvents like o-xylene, 2-ethyl hexanol etc. Values of separation factors in the range 2 to 38 were realised for the above mentioned acids. The purification of glyoxal solution, containing glyoxalic acid and the acetic acid as impurities was also carried out in a similar manner[49].

Aromatic sulfonic acids, such as, p-toluene sulfonic, phenol sulfonic, 4-aminobenzene sulfonic, nitrobenzene sulfonic, etc., which are encountered in aqueous streams in dyestuff, drug and pesticide industries, were effectively recovered from dilute solutions containing less than 20,000 ppm of sulfonic acid through reactive extraction using tri-n-octyl amine (TOA) or trilaurylamine taken in 2-ethylhexanol, even in the presence of a large excess of sulfuric acid.[50] Recently, Kroupa and Vrana[51] have claimed selective recovery of the aromatic monosulfonic acids from mixtures with disulfonic acids in aqueous solutions by extraction with TOA dissolved in chlorobenzene, taken in a stoichiometrically deficient amount.

To recover phenolics from aqueous alkaline streams, Krishnakumar and Sharma[52] devised a novel phase transfer catalyst based process where the phenols were recovered as their esters by reaction with benzoyl chloride or p-toluene sulfonyl chloride. This scheme can possibly be advantageously extended to mixtures of phenols by using stoichiometric deficiency of benzoyl chloride[53].

Sasson et al[54] have demonstrated a similar strategy, based on phase transfer catalyst, for the recovery/separation of carboxylic acids, as esters *via* reaction with RBr, with selectivity and recovery approaching 99%.

E. Dissociation Leaching

The separation of o-chlorobenzoic/p-chlorobenzoic acids was carried out by suspending the solid mixture in an aqueous solution containing an appropriate amount of sodium hydroxide[22]. The separation factor was as high as 26. At 65°C o-isomer was leached out completely from a mixture initially containing 40% o-isomer. Higher solubility of o-isomer compared to that of p-isomer coupled with lower pKa seems to be responsible for such excellent separation.

4-Chloro-m-xylenol/2,4-dichloro-m-xylenol mixtures have been separated by dissociation leaching with separation factor 10, against 5 obtained *via* conventional dissociation extraction[26].

Mixtures of nitrophenols and nitrocresols are often separated by steam distillation. Jagirdar and Lawson[55], however, have separated o-/p-nitrophenols and p-nitroplhenol/2,4-dinitrophenol by using solid-liquid dissociation extraction. Separation factors as high as 9.2 and 10.5, respectively, were obtained for these mixtures in a single stage extraction.

Jagirdar[39,56] exploited the difference in solubilities of the nitrocompounds in organic solvents, such as, toluene in addition to dissociation constants and distribution coefficients. Nitrophenols and nitroanilines show a very large differ-

ence in their solubilities in organic solvents; ortho-isomer being highly soluble in all cases. The first step involves, therefore, preferential solubilization of o-isomer with little extraction of p-isomer, which can be extracted in the second step from the organic solution by dissociation extraction. Both the isomers, therefore, can be isolated in 99% purity. Very large difference in the solubilities helps in the first step while the complete purification in the second step is because of very large differences in the distribution coefficients and in the dissociation constants of the nitro-isomers.

III. DISSOCIATION EXTRACTIVE CRYSTALLIZATION

The key equilibrium reaction in the dissociation extraction decides the actual extent of separation. If the equilibrium is shifted towards the desired component by simultaneous precipitation the separation should increase several fold.

$$A + B - C \underset{}{\overset{K}{\rightleftharpoons}} A - C + B$$

Separation of N-methylaniline/N,N-dimethylaniline, N-ethylaniline/N,N-diethylaniline, o-nitroaniline/p-nitroaniline and o-chloroaniline/p-chloroaniline were explored by Jagirdar and Sharma[24] by using a gaseous extractant like hydrogen chloride and the product was either a solid or liquid phase. The separation factors were as high as 40. Later Gaikar and Sharma[28] showed that 100% selectivity towards p-isomer could be obtained in the separation of o/p-cumidines using HCl gas and cumene as solvent.

Alkyl or aryl diesters of phosphoric acid have been separated from equimolar mixtures by treating the mixture with NH_3 (gas) where the ammonium salt of the monoester precipitated preferentially[57]. Gitchel et al[58] separated 3,5,6-$(MeO)_2(OH)C_6H_2CHO$ /3,4-$MeO(OH)C_6H_3CHO$ mixtures by treating it with NH_3 when the complex of the former crystallized out of aqueous methanolic solution in 99-100% purity.

Gaikar and Sharma[59] extended the principle of dissociation extraction to develop the process of Dissociation Extractive Crystallization (DEC). This selective chemical complexation process, based on acid-base reactions, has been successfully used to separate 2,6-xylenol/p-cresol[60], and guaiacol/alkylphenols[60] using anhydrous piperazine and diazabicyclooctane (DABCO) as crystallizing agents. N-alkyl substituted anilines, o-/p-chloroanilines, o-/p-cumidines, 2,4-/2,6-xylidines, piperazine/N-methylpiperazine, N-methyl piperazine/N,N'-dimethylpiperazine, 3-4-picolines were separated using p-toluene sulfonic acid and p-xylene sulfonic acid.[60] The precipitated product of neutralization increased the separation factor several times of those realised with conventional processes including dissociation extraction. The separation factors were in the range of 5-500. A complete separation was observed in the case of o-chloroaniline/p-chloroaniline[59].

In the case of m-cresol/p-cresol mixtures very encouraging results were obtained[60]. p-Cresol was separated from m-cresol with 100% selectivity and 85-90% yield as a complex with piperazine or DABCO. This system is considered as a difficult one for separation.

The solvent used for the process of DEC plays an important role, both from the point of selectivity and of yield. The selected neutralizing agent must be able to interact with the desired compound selectively and the product of neutralization must be a solid. The formation of a liquid product leads to the distribution of weaker component between the initial solvent and the newly formed liquid phase, resulting in unfavourable separations.

The crystallization can be carried out from an aqueous phase provided the product of neutralization has a limited solubility in the aqueous phase. Such a strategy has proved to be useful for the separation of 2,4,6-trichlorophenol (TCP)/

TABLE II

DISSOCIATION EXTRACTIVE CRYSTALLIZATION

System	Solvent	Extractant	Separation factor	Ref.
Phenolic systems				
(a) 2,6-Xylenol/p-Cresol	n-Heptane	Piperazine	115-532	59
(b) p-Cresol/Guaiacol	Di-iso-propyl ether	Piperazine	16- 52	60
(c) 2,6-Xylenol/ Guaiacol	Di-iso-propyl ether	Piperazine	5-109	60
(d) o-Ethylphenol/ Guaiacol	n-Heptane	Piperazine	12	60
(e) m-Cresol/p-Cresol	Di-iso-propyl ether	Piperazine DABCO	- -	60 60
Basic systems				
(a) N-Methylaniline/ Aniline	n-Heptane Toluene	p-TSA p-XSA	134 267	59 59
(b) N-Ethylaniline/ Aniline	Toluene	p-TSA p-XSA	18 78	59 59
(c) o/p-Chloroanilines	n-Heptane	p-TSA p-XSA	- -	59 59
(d) 3/4-Picolines	n-Heptane	p-TSA	38-122	60
(e) o-/p-Cumidines	Toluene	p-TSA Aq. p-TSA	9 61- 95	60 60
(f) o/p-Toluidines	Toluene	98% H_2SO_4 H_3PO_4	13.2	61
(g) m-Chloroaniline/	Toluene	Aq. p-TSA Aq. p-TSA	5- 12 6-107	60 60
o-Anisidine	Di-iso-propyl ether	Aq. p-TSA	9-100	60
(h) Piperazine/N-Methylpiperazine	Toluene	p-TSA p-XSA	- -	44 44

p-TSA : p-Toluene sulfonic acid
p-XSA : p-Xylene sulfonic acid

2,6-dichlorophenol/2,4-dichlorophenol using aqueous solutions of monoethanolamine (MEA) where 2,4,6-TCP-MEA salt being sparingly soluble in the aqueous phase precipitated as a solid crystalline product; the separation factor was as high as 100 in this case[29].

Separation of cumidines, o-anisidine/m- chloroaniline and m-/p-toluidines has been carried out by Gaikar et al[60] using concentrated aqueous solutions of p-toluene sulfonic acid. A simple theory was developed by authors to predict the separation factor when the crystallization occurs from an aqueous phase; the separation factor is given by following expression :

$$\alpha = P\,\delta_i \left[\frac{N(P+1) + [B]_{s,i}\,(1/D_B + P/D_A) - N/\delta_i}{N + [B]_{s,i}\,(1/D_B + P/D_A)} \right] \qquad ..(2)$$

where $P = \frac{K_A}{K_B}\frac{D_A}{D_B}\frac{S_A}{S_B}$ and δ_i is the ratio of initial concentrations of the components in the organic phase $(=[B]_{s,i}/[A]_{s,i})$ and S_A and S_B are the solubilities of reaction products in the aqueous phase.

Table II lists some typical systems which have been successfully handled via dissociation extractive crystallization.

Stapleton[61] used a similar process to recover linear polyamines, such as, diethylenetriamine, triethylenetetramine, etc. by crystallizing their salts with p-toluene sulfonic acid. The cyclic amines, however, showed higher solubility than linear ones and this fact can be exploited for the separation of linear polyamines from cyclic polyamines. This methodology may be useful even to recover/separate sulfonic acids from dilute aqueous solutions.

IV. EXTRACTIVE DISTILLATION WITH SIMULTANEOUS REACTION

Extractive distillation is carried out in the presence of a third component which increases the relative volatility

between the original compounds. If the two components differ in their chemical nature, imposing chemical reactions on distillation is very effective. The reactive entrainer is then expected to form a nonvolatile product preferentially with one component. It is also necessary that the reaction is reversible so the entrainer can be recovered from the bottom product.

Since 1921, when Bacchaus[62] suggested distillation column as a reactor, use of distillation column as combined reactor-separator has become widespread for equilibrium reactions of the esterification type.

Saito et al[63] proposed that p-xylene can be enriched by a transalkylation reaction in which tert-butylbenzene selectively and reversibly reacts, in presence of $AlCl_3$ as a catalyst, with m-xylene to form high boiling tert-butyl-m-xylene which can easily be separated from p-xylene. The separation of m-/p-xylenes by selective extraction of m-xylene with $HF\text{-}BF_3$ has been proved to be successful to get 99.5% m-xylene. The complex of m-xylene decomposes at high temperature into m-xylene and $HF\text{-}BF_3$.

ANVAR[64] (a French Agency), Terrill et al[65], Cleary and Doherty[66] used organometallic compounds, such as sodium p-xylene-18 crown ether or phenylsodium and tertiary amines as high boiling liquid chelating agents, dissolved in cumene as reactive entrainers. The entrainer reacts selectively with m-xylene, retaining it in the liquid phase and thus the vapor phase is enriched in p-xylene. The method is based on the difference in acidities of m-/p-xylenes; p-xylene is much less acidic than m-xylene, therefore, sodium preferentially attaches to the m-xylene, leaving p-xylene in the vapor phase to go overhead in a distillation column. The m-xylene/p-xylene transmetallation reaction is reported as :

$$\text{Na-p-xylene} + \text{m-xylene} \underset{}{\overset{K = 9.2}{\rightleftharpoons}} \text{Na-m-xylene} + \text{p-xylene}$$

Cleary and Doherty[66] have shown that p-xylene can be purified from m-xylene by using a sodium-p-xylene reactive entrainer in a column with only six theoretical trays.

The principle of dissociation extraction was extended to distillation by Mahapatra et al[67] to increase the relative volatility of 2,6-xylenol/p-cresol, phenol/o-chlorophenol and 2,4-dichlorophenol/p-chlorophenol mixtures. For 2,6-xylenol/p-cresol mixture the relative volatility was increased from unity to 3.2 in the presence of diethanolamine.

In the process of dissociation extractive distillation, a base of proper pKa and of relatively high boiling point is added to the mixture of acids in stoichiometric deficiency. The stronger component is then expected to form relatively nonvolatile compound with the base and should be retained in the liquid phase. The vapour generated from such liquid mixture will be enriched in the weaker component. An aqueous solution of monoethanolamine when was tested for the separation of 2,6-xylenol/p-cresol mixtures in a laboratory column of height about 90 cm. the distillate was pure 2,6-xylenol as an azeotrope with water[67]. It may be possible to employ similar idea to separate other close boiling acidic compounds such as m/p-cresols which differ in their acidities.

Recently Oba[68] has claimed that 2,3-dichloroaniline can be steam distilled after addition of sulfuric acid to the mixture of 2,3-/3,4-dichloroanilines. This example resembles in principle with dissociation extractive distillation.

Gassend et al[69] separated ethanol/isopropanol and ethanol/tert-butanol mixtures using different amines like pyridine, substituted cyclohexylamines, ethylenediamine and substituted ethylenediamine in the presence of cyclohexane or toluene as diluents. Although pKa's of these alcohols are close, the effect of basicity of amine and steric hindrance is prominent on the values of relative volatilities. The selec-

tivity of complexation with respect to ethanol was in the range of 2 to 7 and 3 to 22 for ethanol/isopropanol and ethanol/tert-butanol mixtures.

V. SEPARATION THROUGH CLATHRATION AND COMPLEXATION

A. Clathration

The term clathrate is generally used to define a class of molecular compounds formed from two different stable compounds without the existence of chemical interactions between them. One of these, the host, forms cavities sufficiently big to accommodate another compound, the guest, which lowers the chemical potential of the host lattice i.e. the presence of the guest stabilizes the lattice structure of the host.

Many clathrate forming compounds have been recognised : Werner compounds, gas hydrates, Dianin's compound, liquid clathrates and cyclodextrins. Of these Ni-thiocyanate based Werner complexes have been used extensively to separate a variety of organic isomers, such as xylenes, chlorotoluenes, dichlorobenzenes, etc. with selectivity about 20[70-72]. A very interesting point about these compounds is the ability of the complex $Ni(NCS)_2$(4-Methylpyridine) to retain its porosity and three dimensional structure of interconnecting pores even in the absence of guest molecules. We can visualize this structure as similar to zeolites and hence the possibility of using it as a stationary phase in a separation scheme would be well worth considering.

A large number of aromatic molecules form clathrates with diisothiocyanatotetrakis (α-arylalkylamine)nickel(II) complexes but cyclo- or linear paraffins and olefins do not form clathrates[72]. It appears, therefore, that the only condition for certain guest to be included is the presence of an aromatic moiety in the molecule. This also stresses the point that apart from the steric effects which are normally considered to be decisive in the formation of clathrates, electronic interactions decides the selectivity of the formation of a clathrate.

The drawback of low loading, 15-25% in case of solid clathrates, is overcome in liquid clathration which can give as high as 67-88% loading of aromatic substrates[72]. Most facile separations achievable using liquid clathrates are for aromatic-nonaromatic mixtures. Aromatics are selectively included with separation factors in the range of 12-24[72]. The selectivity of Ni(SCN) compounds towards geometric isomers can be tailored by selecting a suitable amine which in fact governs the shape and size of the cavities of Werner complexes. There seems to be a wide scope to modify or synthesize new Werner compounds so as to apply them to separate a desired component.

Dianin's compound (4-p-hydroxyphenyl-2,2,4-trimethylchroman) has a very remarkable ability to form inclusion compounds due to very interesting crystal structure with 'hourglass' shaped cavities which can differentiate even linear paraffin of different chain lengths i.e. $n\text{-}C_7$ from $n\text{-}C_8$ depending on the length of the cavity[73].

B. Cyclodextrins

Amongst the clathrate forming substances, cyclodextrins have been most widely used for not only in physical separations but also to carry selective reactions. Such selective reactions can facilitate separation of closely similar molecules especially the isomers. Cyclodextrins are macrocyclic, non-reducing D + (-) glucopyranose polymers containing six or more residues bonded by α-(1,4)-linkages and have doughnut shapes with all the glucose units in substantially undistorted conformations. The specific structure of a cyclodextrin molecule provides an apolar cavity which can differentiate a chiral guest and thus does not necessarily need the crystal lattice to form inclusion compounds. The guest molecule can range from polar reagents, such as acids, amines, small ions, to highly apolar aliphatic and aromatic hydrocarbons. The high selectivity in cyclodextrin assisted reactions can be attributed to different sizes of

cyclodextrin cavities, the molecular dispositions of guest molecules inside the cavities and the conformational effects[74-76].

The most intriguing facet of these compounds is the ability to identify and separate optical isomers. The optical enrichment of halothan, $CF_3CHBrCl$, using α-cyclodextrin is the only strategy for racemate resolution of this compound[77]. Similarly separation of cymenes using β-cyclodextrin gave 97.5% p-cymene[72].

The use of 5% aqueous solutions of β-cyclodextrin has been reported to purify air by selective absorption of benzene, 1,2-dichloroethane and n-hexane vapors. The removal of these organic solutes is because of the ability of β-cyclodextrin to form the inclusion compounds with organic compounds.[78]

C. Inclusion compounds

Recently Vögtle et al[79] have claimed a complexation process, akin to clathration, based on hexamine hydrochloride to separate isomeric and partially hydrogenated arenes in the form of liquid-liquid extraction. The following mixtures were separated : phenanthrene/anthracene; phenanthrene/dihydrophenanthrene; pyrene/hexahydrophrene; acenaphthylene/acenaphthene etc. The selectivity towards unsaturated compounds was attributed to specific cavity volume and complexation of arenes with hexamine hydrochloride.

Separation of p-xylene from m-xylene and ethylbenzene by formation of inclusion compound with metacyclophane[80] and separation of p-cresol from m-cresol using fluorene[81] are some interesting examples of clathrations which have potential for industrial exploitation. Another recent example has been reported by Toda[82] where he separated m-cresol from its isomers via its inclusion complex with 1,4-bis(4-hydroxyphenyl)cyclohexane.

D. Complexation

The selective complexation of one of the components of mixture has been followed for a very long time with emphasis

on the recovery of complexing agent for recycle. For example, 2,6-lutidine is separated from picolines as an insoluble adduct with urea[83]; bisphenol A is purified by formation of an adduct with phenol[84], cuprous chloride complexes of different organic bases precipitate from their mixtures. High selectivity associated with such complexation reactions has attracted several workers for the separation of isomeric/nonisomeric compounds. However, the problem of solid handling and low loading hinders the application of these methods on industrial scale; some of these are, however, being used on industrial scale[83,84].

Leston[85-87], in the recent past, has developed a separation process for phenolic as well as for basic mixtures which is based on preferential complexation of one of the isomers by calcium or lithium bromide in hexane or toluene. This method may become important in separation of isomeric cresols from each other, resorcinol from byproducts during production, or in separations of isomers formed in chlorination or alkylation of phenols. The complexed material can be recovered from the precipitated product either by hydrolysis or thermal treatment. Leston[88] has claimed almost complete separations of p-cresol/2-t-butyl-p-cresol, 3-thymol/4-thymol, hydroquinone/4-methyl pyrocatechol, m/p-cresols, 3-/4-picolines and 2,3,6-collidine/2,4,6-collidine.

VI. MICELLES IN SEPARATION

Micelles, which are aggregates of the surfactant molecules in the aqueous solution, have attracted attention of many researchers for the separations in the mid to late 1970 mainly in micellar liquid chromatography, capillary electrokinetic separations and membrane techniques. An excellent overview of the structure and properties of micelles has been published by Armstrong[89].

The association of solutes with micelles is responsible for most of the useful applications of these aggregates. Solute

can interact electrostatically or hydrophobically or more likely by a combination of these effects with a micelle. The micelle in fact is supposed to have at least two types of interaction sites; one which is analogous to the dissolution in the organic solvent i.e. in the core of the micelle and another which is a more polar absorbed state near the micellar surface. The varying extents of interaction of different solutes with a micelle is decided by the hydrophobicity and polarity of the solutes. These relative interactions are the decisive factors in determining the selectivity.

The first deliberate use of micelles in a separation was probably in the gel permeation chromatography of the transfer-RNAs where t-RNA-micelle complex was excluded from the gel; the fractionation of RNAs was due to differential binding of RNAs to the cationic micelles of hexadecyltrimethylammonium chloride[90]. The binding of the solute on a micelle of size larger than the pore size of gel facilitate the separation as the micelle bound solute can be eluted faster than the small molecules existing in the intersticial pores. Separation of amino acids from neutral compounds was later reported by Maley and Guarino[91] using aqueous solutions of sodium lauryl sulphate-formic acid as a mobile phase.

Micellar solutions have been used to separate a wide variety of compounds in thin layer chromatography; amino acids[92], fatty acids[93], mycotoxins[94], nucleosides[95], quinones[89], substituted phenols, anilines and benzoic acids[96] are some of the mixtures separated on TLC.

The micelle mediated separations are more common in liquid chromatography than in any other technique. An effective resolution of nine phenols and two polynuclear aromatic hydrocarbons on a C_{18} reversed phase column has been obtained in a modern liquid chromatography separation. In addition to the separation of a wide range of compounds, the three phase

model was proposed to represent the partitioning of solute between a solid adsorbent, water and micellar pseudophase and supported by experiments in 1981 by Armstrong and Nome[97]. One of the most important aspects of this work was that it allowed partition coefficients and/or binding constants of solute with the micelles to be evaluated.

The values of the binding constants are helpful in predicting selective solubilization of solutes from their mixtures. These values are supplemented by other spectroscopic investigations of probable sites of solutes on the micelle. In aqueous solutions it is generally accepted that non-polar solubilizates, such as aliphatic hydrocarbons, are dissolved in the hydrocarbon core of the micelle. Semi-polar and polar solubilizates like fatty acids and alcohols lie in the palisade layer, a layer near the surface of the micelle, oriented with their hydrophobic moieties towards the centre of the micelle and their polar groups in its surface. The type of penetration is further subdivided into 'deep penetration' as exhibited by such compounds as naphthalene and azobenzene and 'short penetration' as exhibited by such compounds as benzoic acid and phenols[99,98].

While it is obvious that the charge on an ionic micelle will have a substantial effect on charged or ionizable solutes it also appears that micelle charge can have a profound effect on uncharged solutes. It is now known that any molecule with a dipole moment can be bound to micelle profoundly by electrostatic interactions. Even benzene has been shown to prefer interaction with the charged Stern layer of cationic micelles[100].

The choice of surfactant can play a significant role in altering the partitioning behaviour to a considerable extent as a result of the combined effects of hydrophobic, electrostatic and interfacial interactions. The separation can be made more versatile by changing the ionic strength, pH, buffer capacity etc.

Micelles have been used in extraction techniques which are similar to liquid-liquid extractions or solid-liquid extractions. Janini and Attari[101] studied the partitioning of hydroxybenzenes between n-octanol and micellar solutions of SDS.

In the recent past, Nagarajan and Ruckenstein[102] have reported separation of different binary mixtures of hydrocarbons e.g. benzene-cyclohexane, benzene-hexane and hexane-cyclohexane mixtures in aqueous solutions of common anionic and cationic surfactants. The selectivity was 7 when solutions of dodecyltrimethylammonium chloride (DTAC) were contacted with hexane rich phases, and the selectivity decreased with an increase in the benzene content of the mixture. It was also shown that other surfactants e.g. cetyl pyridinium chloride (CPC) and sodium lauryl sulfate (SDS) in aqueous solutions exhibit significant selectivity for benzene when the organic phase was hexane rich.

Nagarajan et al[103] designed block copolymers to achieve highly selective solubilization of aromatic components from a mixture of aromatics with nonaromatics. A substantial improvement in the selectivity was observed for aromatics; the ratio of solubilized benzene to hexane in conventional surfactant solutions was 4-7 whereas the same ratio was 20-50 using ethylene oxide-propylene oxide and styrene-N-vinyl pyrrolidone copolymer solutions. The molar solubilization ratio, maximum number of solubilizate molecules to the number of surfactant molecules in a micelle, of a single component solubilizate was found to depend on molecular volume and the polarity of the solute. The experimental data on the amounts of hydrocarbon solubilized were correlated with a molecular volume - polarity parameter characterising the solubilizate as well as with the Flory-Huggins interaction parameter between the solubilizate and the polymer block constituting the micellar core.

Recently, Ramesh and Labes[104] have demonstrated that concentrated surfactant solutions form rod and disk like aggre-

gates which in turn constitute lyotropic nematic phases. These phases offer solubility 100 fold higher than the corresponding micellar solutions for p-nitrophenyl-isopropyl phenyl phosphine. The characteristic structure of such phases may be useful in separation as well.

From practical point of view, it is necessary to recognise the emulsion formation and the aggregate formation in the organic phase while dealing with liquid-liquid systems using surfactant solutions. In fact the emulsion formation may mask the advantages of better separation using micelles.

Mahapatra and Sharma[105,106] have recently reported the separations of close boiling isomeric/nonisomeric solid substances like o-nitrochlorobenzene/p-nitrochlorobenzene, o-nitrotoluene/p-nitrotoluene, 2,6-xylenol/p-cresol, 2,4-dichlorophenol/2,4,6-trichlorophenol, o-isopropylphenol/p-isopropylphenol, etc. Exceptionally high values of separation factors in the range of 30 to 850 were obtained using aqueous solutions of lauryl alcohol-7-ethoxylate (LA7EO), cetylpyridinium chloride (CPC) and cetyltrimethylammonium bromide (CTABr). The selectivity towards ortho-substituted isomers was much higher than the corresponding para-isomer; a 5% impurity of o-nitrochlorobenzene could be removed completely from p-nitrochlorobenzene without any significant loss of para-isomer. The higher values of separation factor were due to higher solubility enhancement factor of o-NCB than p-NCB at the same concentration of surfactant. The preferential extraction of o-NCB may be due to favourable interaction of the benzene ring of o-NCB with palisade layer of micelles.

A similar selectivity was observed in the case of o-nitrophenol/p-nitrophenol. The separation factors were in the range of 40-190. Although p-NP is having higher polarity than o-NP, it was o-NP which was preferentially solubilized in the micellar solutions : the solubility enhancement for

p-NP was small as compared to the o-NP. This indicates that apart from the polarity and molecular volume, as suggested by Ruckenstein and Nagarajan[102], the orientation of polar/aquophilic groups and their relative positioning may be critical factor in deciding the selectivity. Table III shows some of typical values of separation factor obtained using micellar solutions for solid mixtures.

Microemulsions, which are optically isotropic and thermodynamically stable dispersions of two immiscible liquids containing appropriate amounts of surfactant and cosurfactants, have size of the microdroplets in the range of 100-1000 Å as against 40-100 Å for a micelle. Microemulsions are, therefore, expected to have more capacity than micelles for solubilization. Mahapatra and Sharma[105,106] have used microemulsions, formulated from LA7EO or SDS and butanol, to separate solid mixtures of close boiling substances.

Borgerding and Hinze[108] extracted vanillin and ethylvanillin from tobacco leaves using aqueous solutions of Brij-35 while Watanabe and coworkers[89] used a micellar technique to concentrate a variety of metal chelates, nonpolar compounds and ion pairs.

An interesting application of surfactant solution exists for separation of oleic and stearic acids[109].The 'Henkel' or 'Hydrophilization' process involves the centrifugal separation of lighter oleic acid layer from a heavier loosely emulsified aqueous stearic acid layer. A similar process has been developed for fatty alcohols of differing melting points and for triglycerides[109].

Recently Bhat et al[110] and Dunn et al[111] have combined solubilization of organic solutes in micelles with membrane techniques to develop micellar-enhanced ultrafiltration (MEUF) which could be an efficient method of removal of dissolved, low molecular weight organic compounds from water. The equi-

TABLE III

MICELLES IN SEPARATION

System		Surfactant	Separation factor	Ref.
Liquid-Liquid Extraction				
(a)	Dihydroxybenzenes	SDS	-	101
(b)	Alcohols	TMDABr	-	107
(c)	Hexane/Benzene	Octyl glucoside	7	102
		SDS	10	
		CPC	-	
		Poly(ethylene oxide-propylene oxide)	17	103
		Poly(N-vinyl pyrrolidene-styrene)	40	103
(d)	Metal chelates and polycyclic arenes	Triton-x-100 Polyoxyethylene nonyl phenyl ether	-	89
Solid-Liquid Extraction				
(a)	o-Nitrochlorobenzene/ p-nitrochlorobenzene	LA7EO NP-9-EO	>1000	105
(b)	o-Nitrotoluene/ p-Nitrotoluene	LA7EO	181	105
(c)	p-Cresol/ 2,6-Xylenol	LA7EO	35	105
(d)	2,4-Dichlorophenol/ 2,4,6-Trichlorophenol	CPC	70	105
		LA7EO	>1000	
		CTAB	27	
(e)	o-/p-Isopropylphenols	LA7EO	100-500	106
		NP-9-EO	67-205	
(f)	o-Nitrophenol/p-Nitrophenol	LA7EO	>1000	106
		NP-9-EO		
(g)	o-/p-Nitrobenzoic acids	LA7EO NP-9-EO	>1000	106
(h)	Guaiacol/2,6-Xylenol	NP-9-EO	65	106
		SDS	25	

SDS = Sodium dodecyl sulfate; TMDABr = Trimethyldodecylammonium bromide; CPC = Cetyl pyridinium chloride; LA7EO = Lauryl alcohol-7-ethoxylate; CTAB = Cetyl trimethyl ammonium bromide; NP-9-EO = Nonyl phenol-9-ethoxylate.

librium solubilization of the solute dictates in this case the permeate purity or rejection of the solute by the membrane. It may be also possible to separate various solutes by exploiting the difference in their binding constants with the micelles.

Another separation process based on the micelles has been proposed recently by Fitzgerald and Harwell[112] known as 'Admicellar Chromatography' which is based on the phenomenon of adsolubilization i.e. the incorporation of the compounds into surfactant aggregates adsorbed on surfaces (admicelles). Adsolubilization can be considered a surface phenomena analogous to micellar solubilization. A change in the pH of the solution passing over the adsorbed molecules can cause the desorption of admicelles as well as adsolubilized solutes.

A further modification of admicellar chromatography has been suggested by Okada[113] to combine it with ion exchange to form micelle exclusion chromatography. The micelle is excluded from a part of the stationary phase because of its size, while the solute ions partition between the micellar pseudophase, water and the surfactant monomers adsorbed on non-polar stationary phase forming ion exchange sites. The retention of ions is controlled by surfactant, its concentration, the micellar size and counterions of micelles. Micelle exclusion chromatography also provide information on the partition of ions to ionic micelles and the aqueous phase. It should be applicable to separations of inorganic compounds.

VII. REVERSE MICELLES IN SEPARATIONS

A reverse micelle can be envisaged as a nanometer scale droplet of an aqueous solution, stabilized in an apolar solvent by a surfactant at the interface. Although much of the work published on the reverse micelles is related to extraction of a single enzyme, manipulation of various parameters affecting the performance of reverse micelles can allow separation of a desired protein from other protein impurities. To achieve

selective solubilization and the desired separation the following points need to be considered :

(a) Isoelectric point and pH of the solution directly affect the protein charge which dictates the binding of a protein to the polar head of a surfactant.

(b) Surfactant charge/structure, ionic strength and type of cation affect the interaction between the protein and the surfactant; the degree of separation can be manipulated by changing any of these parameters.

(c) The change of the solvent may also have significant effect on the separation factor.

Goklen and Hatton[114] have successfully employed the AOT-isooctane reverse micellar system to separate individual proteins from mixtures of Bovine serum albumin (BSA) and cytochrome C; cytochrome C transferred with ease in and out of the reverse micelle while BSA was too large to be solubilized. Ribonuclease A did not solubilize from ribonuclease A/cytochrome C/lysozyme mixture at pH 9 since it was negatively charged and was repelled by the anionic surfactant. Cytochrome C transferred to the aqueous phase when organic solution containing other two proteins was contacted with a high ionic strength aqueous solution.

Reverse micelles have shown a promising success with proteins and peptides[115,116]. By an inductive reasoning other bimolecules, including nucleic acids, can possibly be separated using reverse micelles.

Reverse micelles on the other hand show potential advantages over alternative means for the separations of isomeric compounds by exploiting enzyme catalysed reactions. Oxidation of aromatic aldehydes to carboxylic acids by xanthine oxidase preferentially gives products of m- and p-isomers; ortho substituted isomers react much slowly[117].

VIII HYDROTROPES IN SEPARATION

Hydrodropes, when present in an aqueous phase at sufficient concentration, can increase the solubility of sparingly soluble solutes in the aqueous phase. This unusual property of hydrotropes was reported for the first time by Neuberg[118] in 1916. He had also given a list of substances which can be used as hydrotropes; aromatic sulfonic acids, water soluble salts of aryl sulfonic acids, salts of benzoic and substituted benzoic acids, glycols, urea, are some of the commonly used hydrotropes. In this treatise and in subsequent papers on hydrotropy, almost for four to five decades, the capacity of hydrotropes to solubilize hydrophobic compounds, mainly drugs and detergents, was the focus of the investigations[119-123]. Precisely this high solubilization capacity has made the application of hydrotropes potentially useful in new fields. Heterogeneous reactions involving solid-liquid or liquid-liquid phases, such as alkaline hydrolysis of esters, oximation of cyclododecanone and Cannizarro reactions were speeded up, sometimes, by a factor of 1000[124-126].

The first deliberate use of hydrotropes in separations was reported by McKee[123] for separation of aniline and dimethylaniline mixtures. Aniline was found to be preferentially solubilized in aqueous solution of calcium cymene sulfonate.

Solubility differences of close boiling substances in hydrotropic solutions can be thus exploited to achieve separations. Dichlorobenzenes and chlorotoluenes show considerable differences in the solubilities of isomers in 40% aqueous solutions of sodium xylene sulfonate sufficient for the separation.

Liquid-liquid extraction using aqueous solutions of hydrotropes to separate close boiling point mixtures has been reported for the first time by Gaikar and Sharma[127]. Very high values of separation factors, in the range of 10 to 66 were realised for 2,6-xylenol/*p*-cresol, phenol/*o*-chlorophenol,

p-chlorophenol/2,4-dichlorophenol and o-cresol/6-chloro-o-cresol mixtures. Sodium xylene sulfonate, sodium toluene sulfonate, potassium toluene sulfonate, potassium xylene sulfonate. and sodium benzoate were used for these separations. Mahapatra[106] has tested sodium salt of dicarboxylic Westvaco acid (DIACID) for phenolic mixtures with better separation than that obtained with other hydrotropes. These extractive separations are based on differential effects of hydrotropes on the distribution coefficients of the components of a mixture. The nature of an organic solvent used in liquid-liquid extraction can also play an important role in these separations. Inert solvents such as n-heptane and cyclohexane were used by Gaikar and Sharma[127] as well as by Mahapatra[106] in order to have sufficient extraction into the hydrotropic solutions (Table IV). A change to polar solvent, even to aromatic solvents, can reduce the percentage extraction but may increase the separation factor. In the case of 6-chloro-o-cresol and o-cresol the highest separation factor was 32 which may be compared with the highest value 9 realized with dissociation extraction.

An interesting application of aqueous solutions of hydrotropes has recently been reported by Mahapatra et al[67] in distillation. Aqueous solutions of p-toluene sulfonic acid were used as an extractive solvent for the separation of 2,6-xylenol/p-cresol mixtures. The relative volatility of the system was increased to 3 from unity. A similar improvement was observed for the separation of phenol/o-chlorophenol mixtures; the relative volatility increased to 3.9 from 1.3 when phenol to hydrotrope ratio was 3. A laboratory column having four theoretical stages was sufficient to give pure 2,6-xylenol and o-chlorophenol as top products for the separation of 2,6-xylenol/p-cresol and o-chlorophenol/phenol mixtures, respectively. In both cases the solute retained in the liquid phase had free hydroxyl group; a similar observation was made in the extractive separations.

TABLE IV

SEPARATIONS WITH HYDROTROPES

System	Solvent	Hydrotrope	Separation Factor	Ref.
Liquid-liquid systems				
(a) 2,6-Xylenol/ p-Cresol	n-Heptane	Na-p-XS	68	127
(b) o-Chlorophenol/ Phenol	Cyclohexane	Na-Sal	57	127
		Na-p-XS	25	127
(c) 2,4-Dichloro-phenol/p-Chloro-phenol	Cyclohexane	K-p-TS	38	127
		K-p-S	34	127
(d) 6-Cl-o-cresol/ o-Cresol	Cyclohexane	Na-p-XS	32	127
(e) Acetophenone/ Phenol	Toluene	K-p-XS	23	44
(f) N-Ethylaniline/ Aniline	Cyclohexane	K-OBz	13	44
(g) N-Ethylaniline/ Aniline	Cyclohexane	K-OBz	11	44
(h) o-/p-Isopropyl-phenols	Toluene	Na-p-XS	3	106
(i) 2,4-Dichloro-phenol/2,4,6-trichlorophenol	n-Heptane	Na-CS	12.5	106
Solid-liquid systems				
(a) o/p-Chloro-benzoic acids	-	K-BMGS	2000	44
		K-p-TS	404	44

Na-p-XS = Sodium-p-xylene sulfonate; Na-sal = Sodium salicylate; K-p-TS = Potassium-p-toluene sulfonate, K-OBz = Potassium benzoate; Na-CS = Sodium cumene sulfonate; K-BMGS = Potassium butyl monoglycol sulfate.

The use of hydrotropes in separations and other chemical engineering applications is particularly attractive because of various advantages, such as easy recovery of products and very high selectivity. In addition to this the problem of emulsification, which is normally encountered in micellar separations, is not faced with hydrotrope solutions. The only limiting factor in the industrial applications of hydrotropes seems to be very high concentrations of hydrotropes, normally over 1 mol/litre, required for hydrotropic effect.

There have been very few attempts in the past to characterize the hydrotrope solutions and to understand the mechanism of hydrotropy. The reported literature has no consensus on the mode of solubilization by hydrotropes. Salting-in or heteroassociation of solute with hydrotrope[123] because of cohesive forces were considered in the early attempts while stacking type aggregation was suggested recently by Saleh and coworkers.[128,129] In order for the hydrotrope molecules to stack on the top of each other the presence of an aromatic or planer structure was considered to be necessary. But this cannot be visualised with aliphatic hydrotropes, such as sodium or potassium butyl monoglycol sulphate and Westvaco diacid.

Recently Balasubramanian et al[130] and Kartha and Gaikar[131] have identified the aggregation behaviour of hydrotropes in the aqueous phase which appears to be responsible for the solubilization of the solute in the hydrotropic solutions. Although it appears to be similar to micellar solubilization, it differs in magnitude and perhaps qualitatively as well i.e. unlike micellar solutions hydrotrope solutions show unusually high selectivity for aromatics over aliphatics. There is a considerable scope for further work in characterizing these substances and predicting the selectivity in separations.

There also exists a possibility of using hydrotropes as a carrier in aqueous liquid membranes, especially for the

separation of aromatics from nonaromatics as hydrotropes show high selectivity towards aromatics. It can also increase the permeation rates of the solutes.

IX. PREDISPERSED SOLVENT EXTRACTION

It is a new method of separating solutes from aqueous solutions by solvent extraction where the solvent is converted into a polyaphron. A polyaphron is an aggregate of aphrons which themselves are globules, usually of micron or submicron size, of an oil phase encapsulated in a soapy film. A large surface area is created by converting the solvent into a polyaphron which helps in rapid rate of extraction. The rise of aphrons, which otherwise can be very slow because of very small size, can be augmented by buoying the aphrons to the surface by a flotation process using colloidal gas aphrons which essentially is a dispersion of fine bubbles.

This novel technique has been studied extensively by Sebba and coworkers[132-136] for removal of organic substances such as dichlorobenzenes, phenol as well as inorganic ions such as copper, uranyl and chromate ions. The use of aphrons in separations has been reviewed recently by Sebba[135]. Various examples including dissolved gas stripping from water, removal of dispersed oil, removal of finely divided solids, coal deashing etc. are reported[136].

There are several unique advantages of predispersed solvent extraction. In conventional solvent extraction in each stage the extraction coefficient has to be satisfied. With aphrons, each aphron leaves behind a solution poorer in the solute. It seems that the high extraction efficiency of aphrons is because of their large surface area and the ability to maintain the identity in the aqueous phase. In fact polyaphrons are also characterized by their stability which is strongly decided by the nature and concentration of the surfactants used in the preparation of aphrons. Because of very high rates of

extraction there is no need of mixing-settling stage in the main extraction unit and very low values of solvent to feed ratio can be used.

One potential problem that could be troublesome using aphrons is the amount of foam produced by rising gas aphrons. An oil phase in the foam lamella often stabilizes a foam whereas ideally it should break on the surface. This aspect of aphrons has not received sufficient attention as well as the breakage of the polyaphrons which may hinder the commercial exploitation of polyaphrons in extraction. If these practical difficulties of polyaphrons are removed this process can prove to be an economically efficient method for extraction of hazardous organic/inorganic solutes even at parts per billion level from aqueous solutions.

X. SEPARATIONS PERTAINING TO BIOTECHNOLOGY

The success of biochemical transformations brings in its wake the importance of an effective separation method for the recovery of chemicals from dilute aqueous solutions. Aqueous two phase extraction, electrophoretic techniques, extraction with reverse micelles, and membrane processes are some of the techniques developed to meet the requirements of biotechnology.

A. Extraction using two-aqueous phase systems

The incompatibility of polymers manifests into formation of two immiscible aqueous phases. The most popular system has been one containing dextran and polyethylene glycol (PEG)[137]. Because of the presence of water in both the phases this liquid-liquid system is suitable for extractive separations of proteins and enzymes which cannot withstand an organic solvent in extraction and get denatured. The interfacial tension between two aqueous phases approaches very low values and thus very large surface area can be easily generated. This helps in setting up a rapid equilibrium but it can also create problems in separating two phases in subsequent stage.

Partition of enzymes or other proteins between two aqueous phases can be strongly influenced by specific or group specific ligands bound to a water soluble polymer included in the system. An enzyme can then be extracted between the phases because of specific interaction between the enzyme and the ligand. This process of "affinity chromatography" has been employed for extraction of dehydrogenases and kinases using polymer derivatives of reactive triazine dyes such as Cibacron Blue F3GA[138-140]. Purification of cholinergic membranes[141], $\Delta_{5,4}$-3-oxo-steroid Isomerase[142], trypsin[143] and S-23 myeloma protein[144] using a specific ligand, an inhibitor, or the determinant group of an antigen, respectively, bound to PEG was carried out for biospecific interaction.

Submicron sized polymeric adsorbents (SSPP) can be utilized to enhance the separation efficiency of aqueous biphasic systems[145]. The selective adsorption of biologicals on SSPP offer various advantages including rapid separation. The partition yield of protein in PEG/dextran system can be increased by using SSPP. For example, the addition of positively charged SSPP allows complete recovery of bovine serum albumin (100%) in the dextran rich phase[145]

With negatively charged SSPP, a concentration of lysozyme can be directed to the interface or the bottom of the biphasic system and thus increases the yield of lysozyme from 65% to 97%. β-Galactosidase was purified from E. coli cell by electrostatic adsorption on positively charged SSPP. The yield was 93% as against 77% in standard liquid-liquid extraction[145].

B. Electrophoretic separations

Differences in mobilities of ions, molecules especially macromolecules and/or particles in an electric field can be exploited to perform separations. In an electrolyte solutions countercharges may build up near the charged interface. The

thermal motion prevents this countercharge lying immediately adjacent to the interface and the result is a diffuse charge layer. The relation between the gradient of applied electric field (∇E) and velocity (v) of the bulk solution is given as :

$$v = - \frac{\epsilon \nabla E \xi}{\mu}$$

(where ξ is zeta potential of particle, μ is the viscosity and ϵ is the dielectric constant of the medium)

which forms the basis for electrophoresis[146,147]. For a spherical particle of radius r which is large compared with the thickness of diffuse charge layer, an electric field uniform at a distance from the particle will produce a tangential electric field which varies with the position on the particle.

In continuous flow zone electrophoresis, the solute mixture is injected continuously in a body of carrier fluid flowing between two electrodes. As the mixture passes through the transverse field, individual components migrate sideways to produce zones depending upon the mobilities of the components[147]. This process resembles in operation the sedimentation of particles in a sedimentation pond. Because of absence of other bodies electrophoresis provides a clean method of separation of macromolecules such as monosaccharides, disaccharides and proteins. It can also be used to separate neutral compounds which can form electrically charged complexes with sodium borate, arsenate or molybdate.[148]

Membrane electrophoresis utilizes the difference in the ion mobilities and the exclusion of coions by charged membranes. The use of membranes leads to large differences in the ion mobilities but it demands very high voltage which may increase the cost of the operation. The main factor deciding the cost of electrophoresis is the cost of electricity. The generation of thermal energy which further induces the thermal motion of molecules seems to be the main drawback in the deve-

lopment of very large scale electrophoresis units and thus has confined electrophoresis to laboratory and clinical applications.[146].

The operation of electrophoresis when carried out in the presence of gel structure has certain advantages. Polyacrylamide gel electrophoresis, popularly known as PAGE, has better resolving power but may be subjected to longer time for separation. Polyacrylamide gels are most versatile and are most popular because of optical clarity, electrical neutrality and availability in a wide range of pore sizes. These hydrophilic gels are considered to be network of flexible polymer chains into whose interstices macromolecules, such as proteins are forced to diffuse under the influence of the applied electrical field according a partition governed by the steric factors. Despite of the better resolution PAGE has remained useful only in the laboratory preparative applications.[146,148].

An interesting modification of zone electrophoresis resolves mixture of ampholytes on the basis of differing isoelectric points rather than different mobilities. Isoelectric focusing is an electrophoretic method which utilizes the migration behaviour of ampholyte molecules in a pH gradient to achieve their condensation into narrow isoelectric zones.[147] Such isoelectric spectra develop when a pH gradient is established parallel to electric field. Each species then migrates until it arrives at the region of pH where it possess no net surface charge. Thus the final steady state zone distribution depends on the isoelectric points of involved molecules.

There is a distinct difference in the electrophoretic separation and isoelectric focusing. In electrophoresis the mixture of proteins is applied at a very thin starting zone in proximity of cathodic compartment and forced to migrate into an inert zonal support such as polyacrylamide buffered throughout at a constant pH. So the proteins migrate away from

the application point towards anode and the applied potential difference has to be discontinued before the migrating species are eluted in the anodic compartment. Conversely in isoelectric focusing a stable pH gradient increasing progressively from anode to cathode is established by electrophoretic sorting out of carrier ampholytes in a suitable anticonvective liquid medium. When introduced in the system a protein migrates according to its surface charge which itself changes depending on the pH of the location. The velocity of migration, therefore, diminishes to a minimum value until it comes to a full stop. Should the molecule migrate or diffuse away from its pI it develops a net charge and get repelled to its pI. The final distribution of proteins according to the pH gradient is stationary and is known as 'isoelectric spectrum'; a term coined by Kolin as early as 1954[149].

The main application of isoelectric focusing has been in the field of protein and peptide separations. Proteins from various sources having different functions, such as enzyme, hormones, immunoglobins and toxins have been isolated in homogeneous form by isoelectric focusing. A monograph by Righetti[147] has been published very recently which covers the principles, methodologies and the practical applications of isoelectric focusing. The high resolving power of the technique is able to separate proteins differing only a few hundredth of a pKa unit in their isoelectric points.

Furusaki and Kikuchi[150] have recently demonstrated the possibility of continuous separation of proteins by isoelectric focusing. By the driving force originated by the electric potential field, proteins migrate towards the cells at their isoelectric points. Thus a mixture of a number of proteins can be separated by electrophoresis combined with porous membranes separating the cells having solutions at different pH. L-Alanine (pI = 6.10) and L-asparaginic acid (pI = 2.98) can

be separated by placing the mixture in a compartment with pH 4. L-Alanine will be positively charged and thus migrates towards cathode while negatively charged L-asparaginic acid migrates towards anode[151].

Studies of purification of amino acids, such as L-leucine (pI = 6.04), DL-valine (pI = 6.0) and L-α-alanine (pI = 6.11) by electrolysis in a multicompartmental electrodialyser have been reported by Zabolotskii et al[152] and by Sootome and Kawamoto[153].

The isoelectric focusing have a potential to become a common method for large scale protein purification. However, it would demand a detailed economic analysis including both the electrical energy required and the cost of maintaining the buffered solutions.

XI. EXTRACTION WITH GELS

Cussler and co-workers[154-156], in the recent past, have used cross linked partially hydrolysed polyacrylamide gels to concentrate dilute aqueous solutions. The method, first employed by Cussler et al[154] is based on size exclusion principle and has a potential of applications in the field of biotechnology where the recovery of product from dilute solutions is a common problem. Examples in this field include removal of water from starch and cheese whey, the concentration of antibiotics in fermentation products, and the recovery of protein products.

The gel absorbs a low molecular weight solvent like water, as high as twenty to fifty times of its own weight in water, but does not absorb macromolecules. The concentration efficiency of macromolecules like haemoglobin, polyethylene glycol and Bovine Serum Albumin was 80% with polyacrylamide gels[154].

The selectivity of concentrating nonelectrolyte solutes can be adjusted by changes in gel cross linking while the selectivity of separating electrolytes is governed by Donnan equilibria[156].

A divalent congo red was efficiently separated than monovalent bromocresol green. The regeneration of the gel can be accomplished either by a pH change or by a temperature change. For Vitamin B_{12} the efficiency of concentration process increases rapidly to more than 40% for highly cross linked gel (20% cross linking)[155]

Cross linked poly(N-isopropyl acrylamide) gel and cross linked co-polymers of 97% N,N-diethyl acrylamide and 3% sodium methacrylate collapse at 33°C and 55°C respectively. Thus the regeneration of gel after extraction of water can be accomplished by warming the gel to release the absorbed water. The gel efficiency was almost 95-98% for macromolecules such as sov-albumin (MW : 45,000), polyethylene oxide (MW : 6,00,000) and blue dextran (MW : 2,00,000) etc.[156]

A polyelectrolyte gel is effective because of electrostatic forces. For example, the uncharged polyisopropylacrylamide could not separate sodium pentachlorophenolate but the copolymer containing only 3% potentially ionic sodium methacrylate was more effective, with an efficiency of 51% as against only 18% in the former case.

XII. A. ION EXCHANGE RESINS AND REACTIVE POLYMERS

With the number of advances in the ion exchange materials and structures, ion exchange resins are increasingly being considered in new fields of the separations and recovery of ions and biochemicals[157]. The improvements in the morphology of the resins have made them more useful for treating aqueous solutions containing 10,000 ppm of dissolved solutes such as nitrates and ammonia.[158-160]

Separation of rare earths and radioactive metals, and most recently the separation of glucose and fructose are some of the successful applications of ion exchange resins[159,160] A most notable feature of new developments in ion exchange resins is the thermally sensitive resins. These are weak amphoteric

resins which become regenerated to H^+ and OH^- ions at about 90°C due to much higher dissociation of water at higher temperatures. At ambient temperatures the resin shifts to the salt form. The regeneration of spent resin is thus possible simply by the temperature change. This could help in reducing the cost of regeneration which otherwise has to be done with acid/alkali.

Ion exchange resins have, however, seen limited success for the recovery and separation of organic chemicals, even acidic and/or basic compounds, when these substances are present with a large percentage of inorganic ions. A judicious selection of ion exchange resins of appropriate strength may solve the problem but polymeric macroporous adsorbents can give a better alternative. For clean systems, free from polymer forming impurities, macroporous resins may prove to be attractive.

A stream containing a mixture of organic chemicals and electrolytes can be efficiently handled by polymeric adsorbents as ions do not generally interfere in the adsorption of organic chemicals on the surface of the adsorbent. Instead the adsorption capacity increases with the concentration of the electrolyte mainly because of salting out effect. A recent publication "Adsorption Technology" covers the principle and methodologies of adsorption with numerous industrially successful applications in detail.[161]

Cross linked poly(4-vinyl pyridine) has been exploited by Kawabata et al[162] for the separation/recovery of carboxylic acids such as acetic acid/formic acid, acrylic acid/propionic acid mixtures. The larger capacity of these adsorbents for the preferential adsorption of formic acid over acetic acid can be explained only on the basis of acid-base interaction between the pyridyl group of the polymer and the carboxyl group of the acid. The large capacity of adsorbent for acrylic acid over propionic acid could also be attributed to the difference in the acidities of these acids. A particular advantage in

using these reactive polymers is the strength of the chemical interaction between the solute and the adsorbent. These interactions are reversible and sufficiently strong to take large quantity of adsorbate and sufficiently weak so that the adsorbent can be solvent regenerated.

Chanda et al[163] indicated the possibility of using cross linked poly(vinyl pyridine) for the separation/recovery of a number of phenolic species, such as p-cresol, p-chlorophenol, p-nitrophenol, m-aminophenol, polyphenol and lignin. The separation was mainly influenced by pH of the solution and the molecular size of the solute. Another study of the selectivities of multiple organic solutes from aqueous solutions showed that they are strong functions of surface acidity.[164]

Adsorbents containing basic groups can provide selective uptake of carboxylic acids which are obtained as either intermediates or as products from fermentation of biomass. These also provide advantages of minimum contamination of the biomass as well as avoids the heating of the medium. Weak bases, such as Amberlite IR-4B, Amberlite XAD-12, Amberlite XE series, AG-2X8, Bio-gel P-4 etc. have been investigated very recently and the sorption equilibria have been interpreted through chemical complexation model.[165]

The sorption mechanism for acetic acid was rationalized as 1:1 complex formation with basic functional groups in the sorbent. The sorption capacity was related to Gutmann number and apparent pKa of polymer[165]. Solvent leaching of sorbates from weakly basic ion exchange resins/polymers was also found to be possible by Garcia and King.[165] Solvent leaching presents a useful alternative to leaching with a base since it is necessary to consume (and release) chemicals in the latter case if the acid is the desired product.

B. Foam Fractionation

Foam fractionation is based primarily on the tendency of certain component of a solution to preferentially concentrate

at the gas/liquid interface and the tendency of other organic compounds to associate with these organic compounds. The substance which is surface active forms monomolecular layer at the gas-liquid interface and can pick up non-surface active substances from the aqueous solution depending on the hydrophobicity of the solute. The mechanism of solubilization is analogous to adsolubilization. The principles of adsorption of surfactants at the gas-liquid interface are understood well and utilized ingeniously in foam fractionation process[166]. Foam separation techniques have been used for the purification of minerals, removal of surfactants, such as alkylbenzene surfactants from aqueous solutions, separation of oleic acid from stearic acid and palmitic acid, purification of proteins, enzymes and microorganisms[167]. For ionizable substances, such as phenols and 1-/2-naphthoic acids, cationic surfactants, such as ethylhexadecyldimethyl ammonium bromide, cetyltrimethyl ammonium bromide were found to be very effective[168].

By adjusting the pH of the solution and selecting a suitable surfactant it should be possible to separate mixtures of phenols, carboxylic acids and organic bases since the electrostatic interactions between charged surfactant and organic ions are responsible for adsorption on the foam bubble.

XIII. MEMBRANE SEPARATIONS

In the recent past membrane processes, such as, ultrafiltration , reverse osmosis, gas separations etc., have evolved from simple laboratory techniques to utilization in important industrial operations and have significant technical and commercial impact. These processes are competing with various conventional separation processes and are particularly attractive because of lower energy requirements.

A. Gas Separations Enhanced by Reactions

Membranes have found widespread industrial applications in the recovery of hydrogen from refinery gases, recovery of

carbon dioxide from natural gas, air separation to get oxygen enriched air or pure nitrogen for inert gas blanketing[169-172]. The introduction of hollow fibers modules in the gas separation field has promoted extensively the use of membranes in gas separation systems.

Freon gases, notably, carbon tetrafluoride (CTF) used in semiconductor industry, can be recovered from its mixtures with air, using silicone rubber membranes[173]. It is remarkable that permeability of CTF is only 7% of that of oxygen. Thus 99.9+% purity of CTF can be recovered and recycled.

Low concentrations of organic solvents, such as, acetone, octane, toluene can be recovered using hydrophobic membranes[174]. Permeabilities of neoprene for organic solvents was 100 to 10,000 times higher than that of air.

Polymeric membranes can find applications in petrochemical fields as well e.g. the solvent used in solvent deasphalting can be recovered through membranes instead of costly distillation[175].

In recent years there has been a growing interest in inorganic membranes made from metals, inorganic polymers, and ceramics for liquid and gaseous separations[176]. These membranes can be used at significantly higher temperatures, have better structural stability and withstand harsh chemical environment. Currently microporous stainless steel and ceramics membranes such as alumina, zirconia and glass are available commercially.

Separation of gases by inorganic membranes is mainly because of condensation of one of the components in the pores which are blocked and are, therefore, inaccessible to other component. Thus in the separation of H_2S from H_2 or in the separation of SO_2 from mixtures with H_2 the condensation of H_2S or of SO_2 in the pores blocks the transfer of H_2 due to very low solubility of H_2 in these liquids. Some alumina mem-

branes can effectively separate water vapours from ethanol with separation factor 7 to 460, possibly by the capillary condensation[176].

Despite growing interest in the use of membranes in the separation of gases and the economic incentives involved in low energy intensive operation the use of membranes is not widespread. The research, too, is concentrated on development of new configurations of membrane modules and separation of new systems. There is a very little attention given to the chemical interaction between the polymer molecules and the permeating gases. The information of this kind is useful in modifying the chemical nature of the existing polymers to make them suitable to achieve higher selectivity at negligible loss of permeability of desired gas. Very few reports are available on the selection of material for the membranes for the separation of carbon dioxide and methane. The area of selection of membrane materials is still a fertile area for research .

B. Supported Liquid Membranes

An effective method for increasing the selectivity and throughput capacity of a membrane is through chemical complexation. A substance is incorporated in the membrane which reacts chemically with the compounds to be transferred. Supported liquid membrane, which is the liquid with reacting component impregnated in porous support, is a common mode of using liquid membrane for gas separations. Such immobilized facilitated-transport membranes hold excellent promise for industrial applications.

Scholander[177] was the first to report the facilitated transport of O_2 through the cellulose acetate filter impregnated with aqueous haemoglobin solutions.

Ward[178] investigated the flux of nitric oxide, facilitated by reaction of NO with ferrous ion; flux of NO against its concentration gradient was also reported by him later by applying a voltage difference across the film[179].

Separation of CO_2, through liquid membrane can be handled very effectively. Ward and Robb[180] employed arsenite ion to design the system for the removal of CO_2 from O_2/CO_2 mixtures with a separation factor of 4100.

Matson et al[181] reported removal of H_2S from gasified coal using carbonate solution immobilized in porous polymer support. This system was complicated by the fact that CO_2 in the mixture also competes for the carbonate with H_2S molecule.

LeBlanc et al[182] noted that ion exchange membranes have the advantage over polymeric porous support where the reactant is a counterion of ion exchange membrane.

Two applications of ion exchange membranes are for CO_2 and ethylene transport. Silver ions were the counterions for ethylene[183] and monopositive cation of ethylenediamine was the counterion for CO_2[184].

Steigelman and Hughes[185] and later Smith and Quinn[186] have studied the facilitated transport of CO by cuprous chloride; the flux of CO was increased two orders of magnitude over the non-facilitated flux.

C. Emulsion Liquid Membranes (ELM)

The first work performed by Li[187,188] on emulsion liquid membrane dealt with the separation of a binary mixture of aromatic and paraffinic hydrocarbons. The aromatics preferentially permeated through the aqueous liquid membrane phase due to solubility difference. As mentioned earlier the incorporation of carrier in membrane, like hydrotrope, may open up a new area of hydrocarbon separation.

The use of emulsion liquid membrane for the hydrometallurgical recovery of ions has aroused considerable interest. Much of the published work deals with Cu^{+2} recovery and to some extent with recovery of uranium and strategic metals from lean ores[189-191].

The use of macrocyclic polyether of suitable size to facilitate the transport of metal ions was extensively studied

by Christensen, Izatt and others[192-194]. These authors also studied selectivity for a competitive cation transport through liquid membranes. The selectivity can be adjusted by proper selection of a cavity size corresponding to the diameter of the ion being transported, the steric and conformational properties of the macromolecules and the electron density of the oxygen coordination atoms[195]. The separation of Sr(II) from Ba(II) and the separation of Ag(I) from Pb(II) using pyridone and triazole type macromolecules were reported by Izatt et al[196].

The receiving phase has a profound effect on the selectivity. Transport of Ag^{+} to the exclusion of Pb^{2+} was found, when $S_2O_3^{2-}$ was present in the receiving phase. On the other hand Pb^{2+} was transported preferentially when $P_2O_7^{2-}$ was present in the receiving phase[197,198]

Emulsion liquid membranes may be particularly advantageous in recovering organics from dilute aqueous streams. For example, citric acid, obtained in a dilute form, can be extracted from fermentation broths, using liquid membranes containing Alanine 336 as an extractant and sodium carbonate in the receiving phase[199].

D. Membranes as Reactor/Separator

Simultaneous reaction and separation of products is possible with ELM technique e.g., oxidation of ethylene to vinyl acetate by means of an acetic acid - palladium chloride - copper chloride membrane phase[200].

In the production of adiponitrile by hydrodimerization of acrylonitrile, the oxidation of adiponitrile can possibly be avoided by separating it by ion exchange membrane from the oxygen generated in the catholyte[201].

The possibility of application of membrane catalysis in industrial organic syntheses is determined by formation of pure and energetically uniform hydrogen in hydrogenation.

Some palladium rich alloys are only permeable to hydrogen and thus hydrogen transfer through such membranes provides a new method of selective hydrogen addition or removal. The hydrogenation of acetylenic alcohols, such as, butynediol, into ethylenic alcohols takes place in palladium-ruthenium membrane catalyst with 99% selectivity[202].

The products of oxidation of cyclohexane, cyclohexanone/-ol were separated by permeation through a flurocarbon membrane with sulfonic acid groups into an aqueous HNO_3 solution for further oxidation to adipic acid[203].

XIV. SEPARATION USING SUPERCRITICAL FLUIDS

Extraction with supercritical fluids (SCF) is a new process of separation in the developing stage and presently is an active area of research. One of the first processes that has led to a commercial operation is the removal of caffeine from coffee using supercritical CO_2[204]. There is a growing interest in using SCF to extract liquid fuel from heavy crude and residue.

Separation of liquid hydrocarbons was one of the earliest applications of SCF[205]. Extraction of lanolin from wool-grease using liquefied propane[206], extraction of lemon oil[207], separation of mixtures of 2,3-butadiene and 1-butene using mixtures of NH_3 and ethylene[208], are some of the recent applications of SCF technology.

Separation of mixtures of aluminium trialkyls having alkyl groups of different chain lengths[209], removal/fractionation of free fatty acids[210], selective extraction of coumarins and fragrance compounds from mixtures with polysaccharides, acids and flavenoids[211], separation of mono-, di- and tri-glycerides with CO_2 and hexane[212,213], are some other promising applications of SCF. It may be mentioned that in the case of glycerides the conventional processes such as distillation are not applicable.

Reactions in supercritical fluids may lead to new separation techniques. Shimshick[214] suggested supercritical CO_2 with dimethyl ether for extraction of carboxylic acids from alkaline fermentation broths. CO_2 is an extractant as well as a reactant for carboxylic ions in the solutions.

Separations of isomers of hydroxybenzoic acids[213], bisphenol isomers[215] and dimethylnaphthalenes[216] have been tried with supercritical CO_2. The possibility of using supercritical bases, such as, methylamines exists for the separation of acidic isomeric/nonisomeric compounds.

XV. MISCELLANEOUS SEPARATIONS

Selective reduction of nitroisomers

Nickson[217] has reported a selective sulfide reduction of nitration isomers to obtain pure isomeric compound. Sulfide salts are sensitive to the steric environment of the nitro group and thus sterically hindered nitro compound does not undergo reduction.

Separation of primary/secondary amines

A mixture of primary and secondary amines when contacted with mesityl oxides (MO) results in formation of an adduct of MO with primary amine. The secondary amine can be separated from the mixture by distillation as the adduct has high boiling point. Piperidine and n-amylamine were separated by Smith[218] using this reaction.

Separation of olefins

Cuprous aluminium complexes show high selectivity towards olefinic compounds. Allene and methylacetylene were separated by chemisorption in toluene containing $CuAlCl_4$[219]. Similarly ethylene could be separated from gas mixtures by absorption in methanolic solution of CuCl and tetraethylenediamine; ethylene could be desorbed by heat treatment at 90°C with 90% recovery[220].

Winston et al[221] have recently reported separations of C_2-C_5 olefins from paraffins and of α-olefins from internal

or branched olefins via reversible complexation with a solution of cuprous diketonate in α-methylstyrene. The complexation is greatly influenced by the steric hindrance to the double bond.

Separation of primary/secondary alcohols

Primary and secondary fatty alcohol mixtures could be separated by selective esterification by exploiting differences in the rates of the reaction using phthalic anhydride monoester. Thus 1-octanol/2-octanol could be separated by selective esterification using monohexyl phthalate[222].

Isolation of Decosahexenoic acid and Ecosapentenoic acid

These acids, obtained from cod liver oil, are important because of beneficial effect on cardiovascular health. Thus, only unsaturated fatty acids can be isolated from saturated fatty acids by precipitating latter as barium salts from acetone[223].

Pure isobutylene from C_4 mixture

In the Adib process, the absorption of isobutylene corresponds to alkylation with phenol, using an acidic catalyst in the liquid phase giving tert-butylated phenols. The reactions are selective to isobutylene so that other butenes do not react[224]. Heating the alkylated phenol in the presence of acid catalyst yields the isobutylene product. The process is also applicable to separation of isoamylene from C_5 mixture.

Separation of di(2-ethylhexyl)phosphoric acid from mono(2-ethylhexyl)phosphoric acid

D2EHPA and M2EHPA were separated using selective precipitation of M2EHPA as its barium salt from the mixture, followed by regeneration of the acid by contacting with other mineral acids[225]. This mixture is amenable to separation by dissociation extraction.

Selective solubilization of PNA

2,4,7-Trinitrofluoren-9-one or its derivatives could selectively solubilize carcinogenic polynuclear aromatics (PNA)

in aqueous phase and therefore they may be found useful as an extractant for the removal of PNA's from lubricating oils. The polyethylene glycol monomethyl ether diester of 4,5-dinitrofluoren-9-one,2,7-dicarboxylic acid showed more selectivity towards PNA having larger size of the hydrophobic moiety[226]. The complexing ability reduced at higher temperatures and from a practical point of view temperature cycling can be used to facilitate the regeneration of acceptor solutions.

Reactive sublimation

1,5-Diaminonaphthalene was purified from its mixture with 1-amino-5-hydroxynaphthalene by sublimation at 180°C[227]. The mixture was treated with aqueous NaOH initially and then vacuum dried. The treatment converts hydroxy derivative into a nonvolatile salt and therefore the sublimed product was pure diamine. This principle can possibly be extended to even two isomeric bases or acids, such as the mixture of o-phenylenediamine with p-phenylenediamine.

XVI. CONCLUSIONS

Separations through reactions are attractive in many cases of close boiling mixtures and may possibly provide alternative to conventional energy intensive separation processes. If the reactions are reversible, the cost of the chemical separations can be reduced considerably which otherwise can hamper their use on commercial scale.

Dissociation extraction, dissociation extractive crystallization and dissociation extractive distillation offer elegant processes for the separations of acidic and basic mixtures. There exists a potential to investigate the behaviour of acid/bases in the nonaqueous phases as it is relevant in crystallization from nonaqueous phases as well as for distillation.

Clathration and complexation are useful for separating closely related substances. A considerable scope exists to

design clathrate forming hosts to increase the selectivity and to increase their capacity.

Micelles have been used in a wide variety of separation processes : chromatography being the most studied. The use of hydrotropes is attractive because of very high values of separation factor. Hydrotropes have a potential for industrial exploitation and deserve attention for investigation of the actual mechanism of solubilization.

Reverse micelles have proved to be advantageous in biotechnology for separating proteins and other biomolecules. The advances in separation science to handle fragile and heat sensitive bio-substances have been supplemented by selective biotransformations and selective reactions. A combination of established electrophoretic techniques with recent developments in membranes can be beneficial to carry separations efficiently.

Membrane processes have been considered to be alternatives to the existing separation methods. Advances in membrane materials and the incorporation of chemical reactions in membranes will speed up the rates of separations and will enhance the selectivity.

The use of supercritical fluids in the separations can be advantageous in certain cases.

Separation through reactions demand imaginative combination of physical and chemical factors to improve the selectivity and thus there is a considerable scope for further work in this field.

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