Salt Effects in Extraction of Ethanol, 1-Butanol and Acetone from Aqueous Solutions

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Experimental studies were performed to assess the effect of salt addition on the extraction of 1-butanol, ethanol and acetone from dilute aqueous solutions using cyclopentanol, n-valeraldehyde, tert-amyl alcohol, and Adol 85NF as extractants. The liquid-liquid partitioning was examined for a few strong electrolytes in a broad range of concentrations. Results demonstrate that the distribution coefficient and selectivity in systems with reduced water activity resulting from salt addition were markedly increased. These observations can be qualitatively explained on the basis of the hydration theory. It was also determined that strong electrolytes added to the aqueous feed reduced extractant solubility in the aqueous phase, thus contributing to lower solvent losses. The results showed that the extraction efficiency was not significantly affected by increasing salt content beyond a level that reduces the water activity to a value of 0.92.

Introduction

For the past decade there has been a renewed interest in fermentation processes based on renewable raw materials focused especially on ethanol production. Efforts have been prompted by prospects of extending existing fuel supplies by mixing the ethanol with gasoline, which also results in increased octane and oxygen content of the fuel. Another fermentation product which has potential to be an attractive fuel extender and chemical feedstock is 1-butanol obtained from the fermentation of carbohydrates by the bacterium *Clostridium acetobutylicum*. Whereas mixtures of diesel fuel and ethanol are not entirely without drawbacks since alcohol will promote phase separation at low temperature, particularly when water is present in the system, butanol is completely miscible with diesel even at low temperatures (Lenz and Moreira, 1980). Butanol has also been cited as the co-solvent of choice for methanol-gasoline blends for motor fuel (Wayman and Parekh, 1987).

Low reactor productivities and inhibition of product formation because of accumulation of end products in the broth are characteristic of many fermentation processes. The final products have to be recovered from very dilute solutions, usually under 10 wt. % product, and more generally 1-5%, often by means of very energy intensive means such as conventional distillation techniques. For example, the total concentration of solvents (butanol, acetone, and ethanol) which can typically be achieved in the acetone-butanol-ethanol (ABE) fermentation is about 2 wt. %. Therefore, various methods have been proposed for integration of appropriate *in situ* recovery operations into the production scheme with the goal of enhancing product formation and reducing downstream processing cost (Daugulis, 1988, 1991; Groot et al., 1992).

Among these alternatives, the extractive fermentation process seems to have the greatest potential. This process takes advantage of the partitioning of a product between an appropriate organic solvent (extractant) and the fermentation broth, and makes possible the continuous *in situ* removal of product before it reaches inhibitory levels in the broth. The choice of a suitable extractant is a first and basic consideration for the development of an effective extractive fermentation process. The biocompatibility of the organic solvent is one of the most important characteristics for this processing concept. Some important criteria for such solvents were given by Daugulis (1988). Extractive ethanol fermentation has been the subject of intensive research during the last ten years (Minier and Goma, 1981, 1982; Cho and Shuler, 1986; Kollerup and Daugulis, 1986; 1987; Bruce et al., 1991; Chang et al., 1992). The applicability of this processing strategy has been also examined

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for the production of butanol (Ishii et al., 1985; Wayman and Parekh, 1987; Roffler et al., 1988; Barton and Daugulis, 1992; Qureshi et al., 1992). The results of these studies suggest that extractive fermentation offers the prospects of economic benefits such as lower capital costs and energy requirement compared to conventional fermentation, the possibility of utilizing concentrated feedstocks and thus reduced cost of wastewater treatment (Roffler et al., 1987; Daugulis et al., 1991).

Other research projects involving liquid extraction, especially of ethanol, have dealt with its separation from well defined aqueous solutions (Roddy, 1981; Roddy and Coleman, 1983; Munson and King, 1984; Ruiz et al., 1987; Arenson et al., 1990). The added constraint of solvent biocompatibility has not been addressed in these works, particularly when solvent extraction was examined as a substitute for the downstream distillation step (Roddy, 1981). Data from these investigations on liquid-liquid partitioning for different solvents and solvent mixtures provide some general recommendations on solvent selection. Solvents may be compared taking into account equilibrium distribution coefficients (capacity) and separation factors (selectivity with respect to water). Among classes of solvents, Lewis acids (alcohols, carboxylic acids) provide much better selectivity for a given capacity than do Lewis bases (ketones, esters, amines). Branching on the alcohol solvent molecule appears to be of benefit. The underlying chemistry of the extraction of low molecular weight aliphatic alcohols has recently been reviewed (Kertes and King, 1987), but the understanding of it is still far from complete.

Most recently, Dadgar and Foutch (1988) have proposed an improved design for product separation from the ABE fermentation, which combines solvent extraction with distillation. The inclusion of liquid extraction appears to offer a considerable improvement over the conventional distillation process. An economic evaluation of the process and comparison with the conventional one, shows a 15% reduction in the cost of production of butanol. This may make the fermentation scheme economically competitive with the existing petrochemical process.

Experimental observations show that the extractability of alcohol from fermentation broth which contains cells, salts, and so on tends to be better than from pure water (Kollerup and Daugulis, 1986). Murphy et al. (1982) obtained a 1.5 fold increase in distribution coefficient for ethanol by the addition of potassium chloride to the fermentation broth. In a recent investigation we also observed an improvement in extraction characteristics of ternary systems with salts (Malinowski and Daugulis, 1993). This is related to the "salting out" effect, which has been extensively studied, especially with regard to vapor-liquid equilibria (Furter, 1977). The term "salting out" is generally used to denote an increase in the activity coefficient of the nonelectrolyte in solution with increasing concentration of electrolyte. A great amount of work has been done on the influence of electrolytes on the activity coefficients of nonelectrolytes in aqueous solutions (Long and McDevit, 1952). These studies can provide considerable information of fundamental importance to the complex interactions in solutions, and to the behavior of water as a solvent. They also have a practical bearing on the separation of nonelectrolytes by the salting out processes, which should be considered in concert with distillation, solvent extraction, and so on in an overall separation strategy (Donaldson, 1984). As the salt effect is very complicated due to the large number of different types of intermolecular interactions (ion-water, ion-nonelectrolyte, nonelectrolyte-water) which come into play, no theory has been successfully developed to describe all the phenomena in various solutions. The representative theories devoted to the salt effect such as hydration theories, electrostatic theories, van der Walls concepts, and internal pressure concept have been summarized by Sekine and Hasegawa (1977). In the case of an extraction system with salt added, the problem is much more complicated because the influence of an extractant also has to be taken into account. However, recent attempts to construct a model applicable to systems with salts are encouraging. Sander et al. (1986) proposed a model for the prediction of salt effects on vapor-liquid equilibrium (VLE), which combines a term of the Debye-Hückel type with a modified UNIQUAC equation with concentration dependent parameters. A UNIFAC-based model recently developed by Dahl and Macedo (1992) can be useful for VLE and liquid-liquid equilibrium (LLE) calculations in mixtures with strong electrolytes.

The purpose of this research project was to investigate the influence of salts on the extraction of ethanol, butanol, and acetone from dilute aqueous solutions using different organic solvents as extractants. In light of the limited data on this subject, salt addition appeared to be a powerful tool in transferring alcohols from aqueous mixtures to the organic phase. The partitioning process was examined for a few electrolytes in a broad range of concentrations. This study is closely related to the problem of recovery of products from fermentation broth.

Materials and Methods

Solvent selection

Solvent selection for the present study was performed using a computer program known as the extractant screening program (ESP), originally developed by Kollerup and Daugulis (1986), and described recently for extractive biocatalysis applications (Bruce and Daugulis, 1991). The program utilizes the UNIFAC group contribution method to calculate multicomponent liquid-liquid equilibria data (Magnussen et al., 1981). ESP also contains extensive database features, allowing for a ranking of extractants on the basis of predicted distribution coefficient, selectivity, and so on, screening by solvent type and/or specific physical properties, as well as estimated biocompatibility. It is useful as a tool for semiquantitative analysis of multicomponent liquid systems, and for preliminary selection of promising solvents for liquid extraction in different applications, such as simple liquid-liquid extraction and extractive fermentation.

The following solvents were selected for experimental tests: cyclopentanol, *n*-valeraldehyde (pentanal), *tert*-amyl alcohol (2-methyl-2-butanol), and Adol 85NF. The first three were ranked on a mass distribution basis as being among the best extractants for butanol, and they also have a good capacity for ethanol. Adol 85NF (comprised largely of oleyl alcohol) is a biocompatible solvent with potential application in the large-scale extractive ethanol fermentation process (Kollerup and Daugulis, 1989). Pure oleyl alcohol has also previously been used as a solvent for extractive butanol fermentation by Ishii et al. (1985). Selected properties of these extractants are shown in Table 1.

Table 1. Selected Properties of Investigated Solvents

Solvent	Molec. wt.	Density kg/m^3	Boiling Point °C	Source
Adol 85NF	≈267.00	840	282-349	Sherex
n-valeraldehyde	86.13	815	103	Aldrich
tert-amyl alcohol	88.15	810	102	BDH
cyclopentanol	86.13	949	139-140	Aldrich

Partition Experiments

The aqueous feed in these experiments contained 6 wt. % of ethanol, or 1.5 wt. % of butanol, and 0.5 wt. % of acetone. These concentrations were selected to correspond to typical conditions of fermentation broths for ethanol and acetone-butanol fermentations, respectively. In experiments with salts, strong electrolytes such as calcium chloride ($CaCl_2$), potassium chloride (KCl), sodium chloride (NaCl), potassium acetate (CH_3COOK), and sodium acetate (CH_3COONa) were used with the aqueous feed being prepared by addition of salts to the aqueous solutions of composition given above. Salts were obtained from the following suppliers: $CaCl_2$, NaCl, and CH_3COOK from BDH, KCl from Fisher Scientific, and CH_3COONa from Matheson, Coleman and Bell.

Partition experiments with ethanol solutions and Adol 85NF were performed as previously described (Malinowski and Daugulis, 1993). In the case of the remaining extractants and experiments with aqueous solutions of butanol and acetone, equal volumes (100 mL) of solvent and aqueous feed were equilibrated in a glass separatory funnel at room temperature (≈25°C). The contents were allowed to settle under isothermal conditions until the phases separated. The volume of each phase was measured after phase separation. The aqueous phase was then analyzed using a gas chromatograph (GC) equipped with a flame ionization detector (FID), and the organic phase composition was inferred from a mass balance. The distribution coefficient D was calculated as the ratio of the solute concentration (g/L) in the organic phase to that in the aqueous phase.

Analysis

Analysis for ethanol in experiments with Adol 85NF was performed as previously described (Malinowski and Daugulis, 1993). Samples of aqueous phase from the remaining experiments were analyzed using a Perkin Elmer Sigma 1B gas chromatograph with FID and a 30 m DB FFAP Megabore column (0.53 mm dia., 1 μm film thickness) from J & W Scientific (Folson, CA). Helium was used as a carrier gas, at a flow rate of 10 mL/min. The temperatures of oven, injector, and detector were set at 80°C, 150°C, and 250°C, respectively. All chromatographic data were processed using the chromatography workstation, Maxima 820 (Dynamic Solution, Div. Millipore, Ventura, CA). At least three consecutive injections were made from each sample to ensure that the results were representative. The results for each sample were then averaged. The injection volume was 1 μL. 1-Propanol was employed as the internal standard to determine the amount of ethanol in samples from experiments with cyclopentanol, while 1-butanol proved to be appropriate as an internal standard to quantify an extractant and ethanol in samples from experiments with *n*-valeraldehyde and *tert*-amyl alcohol. 2-Methyl-1-propanol was applied as an internal standard in analysis for 1-butanol and acetone. At the same time, the amount of extractant in the aqueous phase was also determined, except in the case of samples from experiments with Adol.

The amount of salt in the aqueous phase was determined gravimetrically after drying the samples in an oven at 80°C.

Results and Discussion

In Table 2, experimental and calculated distribution coefficients together with selectivities (the ratio of the distribution coefficient of the solute to that of water) for investigated systems without salt additions are presented. It can be seen that distribution coefficients predicted by the UNIFAC LLE method are, in some cases (especially for 1-butanol), reasonably close to experimental values. A possible reason for the larger discrepancy between the experimental and calculated distribution ratios for acetone in the system with Adol is that UNIFAC calculations could be performed only for pure oleyl alcohol, which is different from Adol. The distribution coefficient for acetone in oleyl alcohol as an extractant is reported to be 0.45 at 37°C (Ishii et al., 1985). The distribution ratio for 1-butanol in Adol observed experimentally was very close to those obtained in partition experiments with pure oleyl alcohol (Ishii et al., 1985; Barton and Daugulis, 1992). The UNIFAC-based predictions for selectivity of solvents in examined extraction systems are not accurate in most cases, although the *ranking* of the extractants on the basis of selectivity (a usual application of ESP) was consistent with the experimental data. Selectivities calculated by ESP were always overestimated compared to experimental data. In spite of these shortcomings and incorporating the UNIFAC LLE model, ESP can provide a preliminary assessment of extractants prior to selection for experimental evaluation. From the standpoint of extraction capability, all studied solvents appeared to be very good extractants for 1-butanol, with *n*-valeraldehyde being the best.

Table 2. Experimental (Exp.) and UNIFAC LLE (ESP) Data for Distribution Coefficients (D_o) and Selectives (S_o) without Salts

	Ethanol		1-Butanol D_o		Acetone	
Extractant	Exp.	ESP	Exp.	ESP	Exp.	ESP
Adol 85NF	0.22	0.34	3.97	3.24	0.07	0.75
n-Valeraldehyde	0.93	2.37	15.80	25.47	1.26	1.44
tert-Amyl alcohol	1.04	1.54	9.85	10.63	0.41	2.29
Cyclopentanol	1.28	1.72	6.59	11.26	0.75	2.37
			S_o			
	Exp.	ESP	Exp.	ESP	Exp.	ESP
Adol 85NF	25	35	n.a.*	339	n.a.*	66
n-Valeraldehyde	87	126	720	2,573	58	118
tert-Amyl alcohol	4	12	38	93	2	16
Cyclopentanol	n.a.*	11	32	80	4	16

*Not available.

Adol 85NF is additionally biocompatible, so it can be used as an *in situ* extractant for fermentation broths. All solvents tended to extract 1-butanol preferentially over acetone from aqueous solutions containing these two solutes.

In partition experiments with systems containing salts, considerable alteration of extraction equilibria was observed. The addition of an electrolyte to the aqueous feed causes a change in the water activity. The water activity can be calculated by the equation:

$$-\ln A_w = m\nu\phi/55.51$$

where m is the molality, ν is the number of moles of ions formed from one mole of the electrolyte, and ϕ is the molal osmotic coefficient. Since the osmotic coefficients are available for many electrolyte solutions (Robinson and Stokes, 1959), the water activity may be calculated from this equation if complete dissociation of the electrolyte can be assumed. This assumption was found to be valid for many strong electrolytes, even when the electrolyte concentration was very high (Hasegawa, 1969). It is true that the water activity is also affected by the presence of nonelectrolyte; ethanol, 1-butanol, or acetone in this study. That contribution can be estimated from osmolality data (Jones and Greenfield, 1986). For a 6 wt. % aqueous ethanol solution, reduction in the water activity is about 2.5%, and for the more dilute aqueous solution of 1-butanol and acetone that decrease will be substantially lower. Therefore, the water activity reported in this article was estimated using the equation given above and neglected the contribution of nonelectrolyte to final water activity. As a first approximation, this seems to give good estimates.

The experimental results of partition experiments with different organic solvents and aqueous ethanol solutions containing salts are presented in Figure 1, in which the influence of a few strong electrolytes (as described in the materials and methods section) on the distribution of ethanol between the aqueous and organic phase is plotted against the water activity. It may be seen that an increase in the ethanol distribution coefficient with decreasing water activity from 1 to about 0.7 follows essentially a linear relationship for all investigated extractants. This enhancement compared to systems without salts is almost fourfold at low water activity. A simple explanation of this experimental observation can be obtained on the basis of so-called hydration theory: when the salt is added into the aqueous solution, it will prefer to associate with water molecules. This process leads to the formation of compact clusters of water molecules around the ions. The effective removal of water molecules from their solvent role due to hydration of the ions results in an increase in the activity of nonelectrolyte present in the solution. In this way, it is salted out and an increase of distribution ratio is observed experimentally. It is interesting to note that the effect of the change in the water activity on the extractability of ethanol was independent of the extractants examined. Therefore, the salt effect for these solvents can be predicted for a given composition of the aqueous phase using data from Figure 1.

The results of experimental observations of the salt effect on the extraction of 1-butanol and acetone are plotted in Figures 2 and 3, respectively. The results are substantially different from that reported for ethanol. It can be seen that two distinct relations between the water activity and the normalized dis-

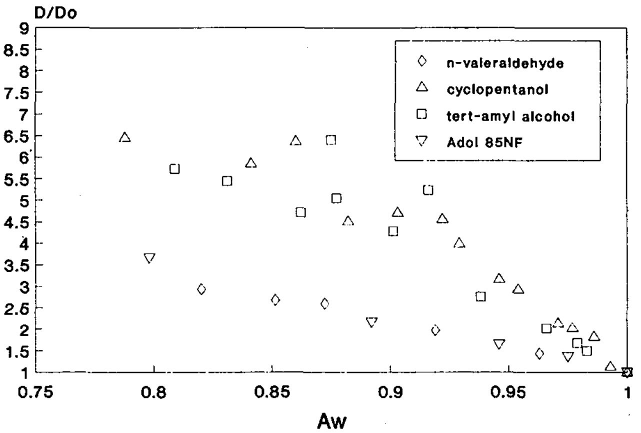

Figure 2. Normalized distribution coefficient of 1-butanol in ternary systems with different extractants vs. the water activity of an aqueous feed.

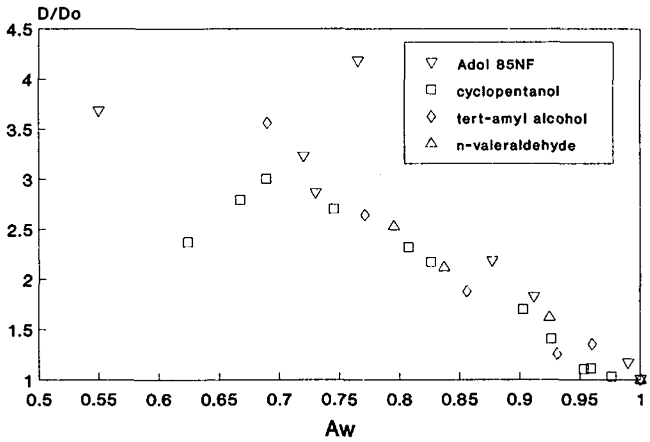

Figure 1. Normalized distribution coefficient of ethanol in ternary systems with different extractants vs. the water activity of an aqueous feed.

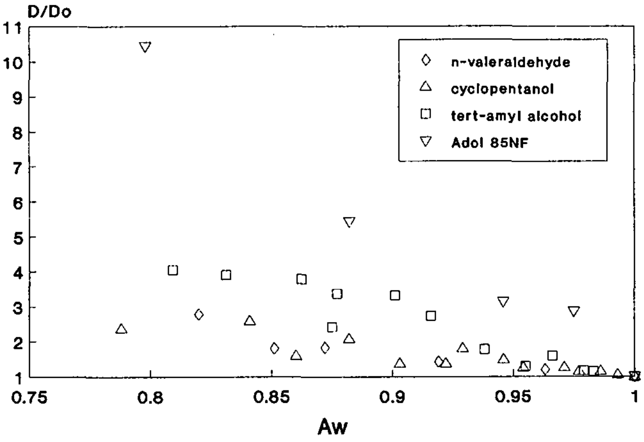

Figure 3. Normalized distribution coefficient of acetone in ternary systems with different extractants vs. the water activity of an aqueous feed.

tribution coefficient of butanol are obtained; one for *n*-valeraldehyde and Adol as extractants, and second for *tert*-amyl alcohol and cyclopentanol. The salt effect on the extraction of 1-butanol by all investigated extractants is more pronounced than that observed for ethanol. Therefore, it is apparent that the addition of electrolyte affects the activity of 1-butanol much more than the activity of ethanol in the aqueous solution. In the case of acetone (Figure 3) it is not possible to find a single specific relationship between the data obtained, beyond noting the general trend of increased distribution coefficient as water activity decreases. However, the results for individual extractants may be correlated. The relative increase of distribution ratio for acetone due to electrolyte addition was intermediate between that observed for ethanol and 1-butanol, except in the case of extraction with Adol. Acetone was found to have a very small distribution coefficient in Adol (Table 2), but in relative terms the influence of the salt addition was the highest among all reported data.

Selectivity, which is the measure of the ability of the extractant to remove solute preferentially over water, was found to be significantly affected by salt present in the system. Typical experimental results of the effect of salt addition on the effect on selectivity of investigated solvents in the extraction of 1-butanol and acetone are presented in Figures 4 and 5, respectively. It can be seen that there is a marked improvement of selectivity for 1-butanol and acetone with increasing concentration of potassium acetate in the aqueous feed. Similar behavior was observed for the extraction of ethanol, and for systems containing different salts. Obviously, the selectivity (the ratio of the distribution coefficient of product to that of water) is changed much more by the salt addition than is the distribution coefficient of the product alone. A decrease in the distribution coefficient of water, together with an enhancement of the partitioning of the product, result in higher selectivity in extraction systems with salt. The lower distribution coefficient of water can be attributed to the association of the water molecules with unextracted salt in the aqueous phase, which impedes a transfer of water to the organic phase. From a practical point of view, the resulting higher selectivities mean fewer extraction stages will be required for good separation.

The effect of the addition of two different salts on the selectivity of extracting 1-butanol with tert-amyl alcohol is shown in Figure 6. It seems clear that the proper choice of electrolyte for a specific separation application can be very important. In this case the less soluble salt (sodium chloride) would be a better choice since a smaller quantity of salt would be required to enhance the selectivity to the same extent. Therefore, the cost of recovery and reuse of the salt could be reduced. In light of the above it appears as though experimental studies will be necessary to identify the most appropriate salt for each specific extraction application.

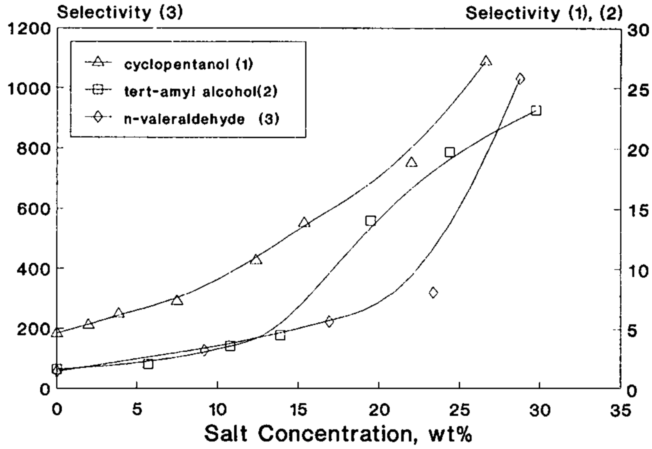

Figure 5. Effect of potassium acetate concentration on the selectivity of acetone in different extraction systems.

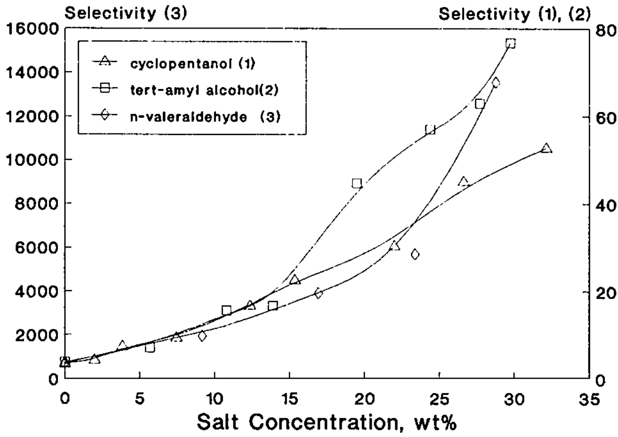

Figure 4. Effect of potassium acetate concentration on the selectivity of 1-butanol in different extraction systems.

In liquid-liquid extraction processes the solubility of the extractant in water is often great enough to make it necessary to remove and/or recover residual solvent from the aqueous stream leaving the extractor. This is important to prevent contamination of the products and to permit reuse of the extractant. Solvent recovery costs are generally less with greater insolubility of the extractant in water. All analyzed organic solvents, except Adol 85NF are characterized by some solubility in water. The effect of potassium acetate addition to the aqueous feed on extractant solubility in the aqueous phase is

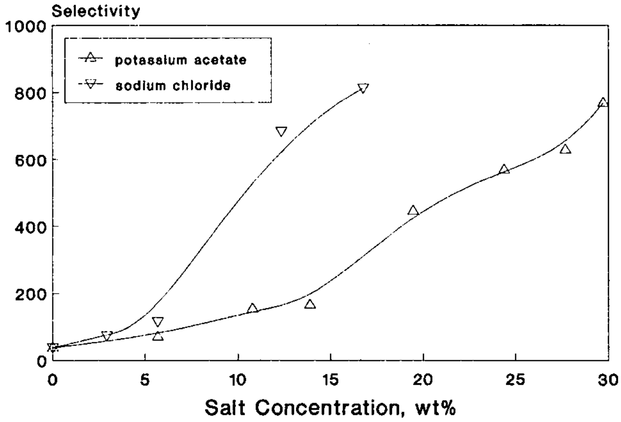

Figure 6. Effect of potassium acetate or sodium chloride concentration on the selectivity of 1-butanol in extraction systems with *tert*-amyl alcohol as an extractant.

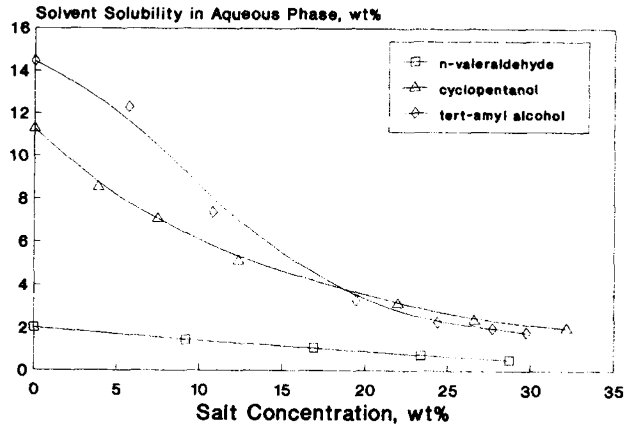

Figure 7. Effect of potassium acetate concentration in the aqueous feed on extractant solubility in the aqueous phase.

Results are for ternary systems containing 1-butanol and acetone.

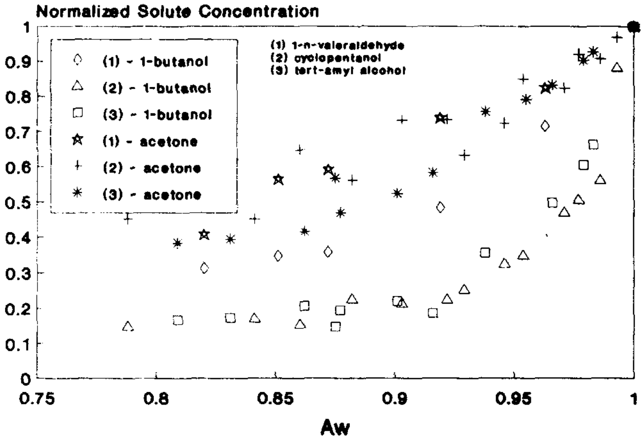

Figure 8. Normalized 1-butanol and acetone concentrations in the aqueous phase vs. the water activity of the aqueous feed.

shown in Figure 7. These results demonstrate that considerable reduction in solvent loss, up to 50% in systems with 10 wt. % of potassium acetate added to the feed, can be achieved.

The normalized 1-butanol and acetone concentrations in the aqueous phase, after single stage extraction, as a function of the water activity are presented in Figure 8. This figure provides information about the efficiency of the extraction process in systems with salt compared to ones without salt added. A decrease in the water activity as a result of electrolyte addition leads to a decrease in solute (1-butanol or acetone) content in the aqueous phase after extraction. As liquid extraction is an equilibrium process, some limitation to this trend obviously exists. As can be seen from Figure 8, the 1-butanol content is almost unchanged when A_w drops below ≈ 0.92. The same is true in the case of acetone extraction although the water activity threshold is not so distinct. Obviously, it would not be possible to transfer all of the solute into the organic phase despite the significant enhancements in extraction characteristics of systems in which electrolytes are present. In fact the extraction efficiency was not significantly affected by increasing the salt content in the feed beyond a certain point. A typical value for the single stage extraction efficiency for 1-butanol was about 90% in systems without salt. Salt addition made it possible to achieve efficiencies of 95-98%. In light of the results presented above, it seems that it is not necessary to utilize electrolyte addition to excessively high levels (and accordingly decrease the water activity too much) in order to enhance markedly the process efficiency. This is an important observation when considering the potential problems associated with salt recovery when high electrolyte concentrations are applied.

Conclusions

Partition experiments have shown that cyclopentanol, *n*-valeraldehyde, *tert*-amyl alcohol, and Adol 85NF function well as solvents for extraction of ethanol, 1-butanol, and acetone from dilute aqueous solutions. The ESP program based on the UNIFAC group contribution method facilitated preliminary solvent selection prior to experimental analysis. The effect of strong electrolyte addition to investigated ternary systems on extraction characteristics was assessed. In systems in which the water activity was reduced as a result of salt addition to the aqueous feed, the distribution coefficient and the selectivity were markedly improved. A simple qualitative explanation of this behavior can be obtained on the basis of the hydration theory.

Salt addition leads to a decrease of the solvent solubility in the aqueous phase. This is an important observation when considering the need for solvent reuse. Although extraction performance as measured by distribution coefficient, selectivity, and aqueous solubility of the extractant continue to improve as salt concentration is increased, it can be concluded that it is not necessary to reduce the water activity excessively in order to still gain significant improvements in the efficiency of the extraction process.

In spite of the advantages that salt addition offers to the extraction of ethanol, 1-butanol, and acetone from dilute aqueous solutions typically found in fermentation processes, the practical implementation of such a process configuration is presently limited. As an *in situ* recovery strategy (extractive fermentation) the relatively high salts concentrations which may be required could have severely deleterious effects on cells arising from osmotic shock. As an aid to downstream fermentation product recovery, a key economic tradeoff would need to balance the enhanced extraction resulting from salt addition against the cost of salt recovery from the aqueous stream leaving the extractor.

Future work will concentrate on more detailed characterization of such systems through the use of solubility data, activity coefficients measurements, and so on. An analysis of the influence of different salts with common anion or cation components may also provide additional insights into the problem. With such data, one may be able to draw more general conclusions about the behavior of extraction systems in the presence of strong electrolytes.

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Notation

A_w = water activity
D = distribution coefficient
D_o = distribution coefficient for system without salt
m = molality
S = selectivity
S_o = selectivity for system without salt

Greek letters

ν = number of moles of ions from one mole of electrolyte
ϕ = molal osmotic coefficient

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