Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Mahapatra, A. , Gaikar, V. G. and Sharma, M. M.(1988) 'New Strategies in Extractive Distillation: Use of Aqueous Solutions off Hydrotropes and Organic Bases as Solvent for Organic Acids', Separation Science and Technology, 23: 4, 429 — 436
To link to this Article: DOI: 10.1080/01496398808060714
URL: http://dx.doi.org/10.1080/01496398808060714

SEPARATION SCIENCE AND TECHNOLOGY, **23**(4 & 5), pp. 429-436, 1988

New Strategies in Extractive Distillation: Use of Aqueous Solutions of Hydrotropes and Organic Bases as Solvent for Organic Acids

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Abstract

Aqueous solutions of hydrotrope (*p*-toluene sulfonic acid) and organic bases (methyl diethanolamine, diethanolamine, etc.) have been successfully used as solvents in the extractive distillation of close boiling phenolic substances. This new class of solvents provides sufficiently high values of relative volatility ($\alpha \approx 3$) for such close boiling mixtures as 2,6-xylenol/*p*-cresol, *o*-chlorophenol/phenol, and 2,4-dichlorophenol/*p*-chlorophenol. Batch distillation experiments proved the efficacy of these solvents.

INTRODUCTION

The strategy of extractive distillation has been useful for the separation of close boiling substances where ordinary distillation or any other method of separation, such as crystallization and solvent extraction, fails to give adequate separation within the economic constraints. The third component, generally a high boiling solvent, modifies the relative volatility of the mixture to be separated.

The use of hydrotropes for extractive distillation has not been exploited although liquid–liquid extraction with aqueous hydrotropes has been successfully attempted by Gaikar and Sharma (*1*). Hydrotropes are the substances which, when dissolved in an aqueous phase, can increase the solubility of sparingly soluble solutes in the aqueous phase, sometimes by

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a factor of 100 to 1000. These substances include arylsulfonic acids, their potassium, sodium, calcium, and ammonium salts, sodium and potassium salts of benzoic acids and of phenols, etc. The phenomenon of hydrotropy was first reported by Neuberg (*2*) but did not receive much attention in subsequent years in fields other than drug and detergent solubilization. McKee (*3*) published a review on hydrotropy covering the literature up to 1946. Since then, very limited literature has appeared on this subject of considerable industrial potential. Recently, Janakiraman and Sharma (*4*) and Pandit and Sharma (*5*) reported the use of hydrotropes to increase the rates of heterogeneous reactions. Gaikar and Sharma (*1*) successfully separated mixtures of phenolic substances using aqueous solutions of hydrotropes in liquid-liquid extraction where it became evident that hydrotropes can selectively differentiate between the components of a mixture according to their ability to associate with the hydrotrope.

The concept of a reactive entrainer in distillation has been exploited by ANVAR (*6*), Terrill et al. (*7*), and Cleary and Doherty (*8*) for separation of *m*- and *p*-xylenes using such organometallic compounds as sodium-*p*-xylene-18-crown ether dissolved in cumene as the reactive entrainer. A similar idea was tested by Gassent et al. (*9*) for the separation of ethanol and isopropanol using different amines like pyridine, cyclohexylamine, ethylene diamine, substituted ethylene diamines, etc. in the presence of cyclohexane or toluene as a diluent. The separation of close boiling acids by reactive extractive distillation should also be amenable through the exploitation of differences in their acidities. The strategy of using a stoichiometrically deficient amount of a neutralizing agent to separate acids/bases has been exploited by several workers in dissociation extraction (*10–15*) and by Gaikar and Sharma (*16*) in dissociation extractive crystallization.

This article discusses the use of aqueous solutions of hydrotrope and of organic bases as solvents in the extractive distillation of organic acids. When an aqueous solution of hydrotrope is used as an extractive solvent, one of the components experiences higher solubility in the liquid phase and the other component is enriched in the vapor phase. In the systems investigated in this work, the second component formed an azeotrope with water and therefore the overhead product condensed into two layers (aqueous phase and the second phenolic component). The aqueous phase may be refluxed so that nowhere in the column do "dryout" conditions exist. Since the hydrotrope is nonvolatile, all of it is confined to the liquid phase, and it flows downward in the column and can be recovered from the bottom and recycled.

When an organic base is selected as an extractive solvent, it is expected to form preferentially a relatively nonvolatile complex with the stronger component and thus the vapor phase should be enriched in the weaker component. The relative volatility of the mixture must then be different from that in the absence of the base. A similar process can be envisioned for a mixture of bases using an acid as an extractive solvent.

EXPERIMENTAL AND ANALYTICAL PROCEDURE

2,6-Xylenol, *p*-cresol, *o*-chlorophenol, phenol, *p*-chlorophenol, diethanolamine, and triethanolamine were of reagent or analytical grade; 2,4-dichlorophenol, methyldiethanolamine, and *p*-toluenesulfonic acid were of Fluka grade.

A recirculating modified Othmer still was used to study the vapor–liquid equilibrium. The desired mixtures of phenols were added along with an aqueous solution of the hydrotrope (*p*-toluene sulfonic acid) or a stoichiometric deficient amount of a base corresponding to the stronger component according to pK_a values of phenols. The mixture was refluxed for 2 h to ensure equilibrium. Analysis was then carried out either on a Perkin-Elmer high performance liquid chromatograph (HPLC) or on a Perkin-Elmer Sigma 3B Gas Chromatograph (GLC). A C_{18}-3μ reversed phase column was used with 40% MeOH and 60% H_2O eluent for HPLC analysis and an SS column, 3 mm × 2 m, packed with 10% carbowax 20 M and 2% orthophosphoric acid supported on Chromosorb WAW (80/100 mesh) was used with nitrogen as a carrier gas and flame ionization detector (FID) for GLC analysis.

RESULTS AND DISCUSSION

In extractive distillation an added substance modifies the vapor–liquid equilibrium relationship by selective association with one of the key components in the liquid phase. Since the extractive solvent interacts with both the components, the volatilities of both components are likely to be lowered but by differing amounts.

The relative volatility is defined as the ratio of concentrations of components in the vapor phase divided by the ratio of concentrations of components in the liquid phase; the concentration of the component, which is affected more by extractive solvent, forms the denominator of the ratio.

Aqueous Solutions of Hydrotropes as Extractive Solvents

2,6-Xylenol/p-Cresol

Figure 1 illustrates the large effect of a hydrotrope, *p*-toluene sulfonic acid (*p*-TSA), on the vapor–liquid equilibrium. The compositions of both the liquid and the vapor phases are based on the phenolic contents only. The relative volatility of 2,6-xylenol/*p*-cresol mixtures increased from ~1 to 3.0 in the presence of the above hydrotrope.

o-Chlorophenol/Phenol

Figure 2 gives the relative volatilities for the *o*-chlorophenol/phenol system in the presence of aqueous solutions of *p*-toluene sulfonic acid. The relative volatility increased from ~1.5 to 3.91 when *p*-TSA/phenol (mol/mol) in the liquid phase was 2.0.

In the above cases it was found that the compound having a relatively

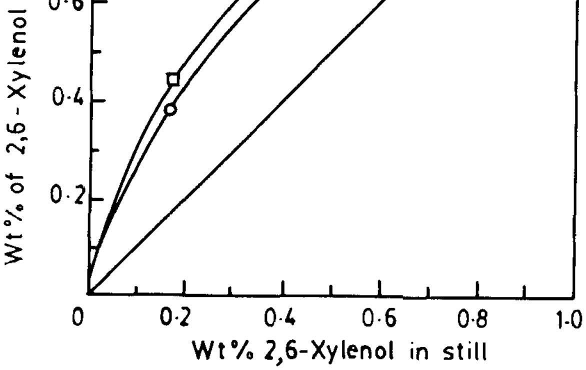

FIG. 1. Vapor/liquid equilibrium studies for 2,6-xylenol-*p*-cresol in the presence of a hydrotrope (*p*-TSA): (total phenol)/(*p* – TSA) = 1.

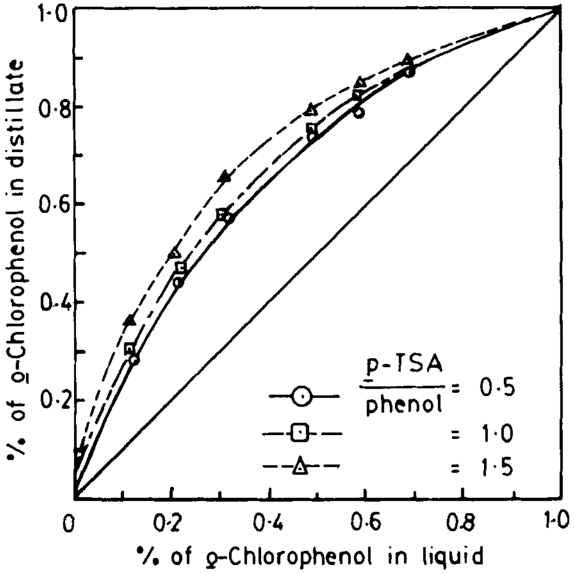

FIG. 2. Vapor/liquid equilibrium studies of *o*-chlorophenol/phenol in the presence of a hydrotrope (*p*-TSA) (50%).

free hydroxyl group was affected most while the other component was enriched in the vapor phase, i.e., *p*-cresol and phenol were found to have more affinity for the liquid phase containing hydrotrope while the vapor phase was enriched in 2,6-xylenol and *o*-chlorophenol, respectively.

Some batch distillation experiments were carried out with a distillation flask, fitted with a glass column of 2.5 cm diameter and 70 cm height, packed with multifilament wire-mesh packings (analogous to Goodloe packings; HETP ~ 15 cm). An aqueous solution of *p*-TSA (50 wt%) was fed at the top of the column. The overhead product was an azeotrope of one of the phenols with water which, on condensation, separated into two layers. The phenolic layer was substantially enriched in or entirely composed of the compound having less interaction with the hydrotrope. In the separation of *o*-chlorophenol/phenol and 2,4-dichlorophenol/*p*-chlorophenol, the top product consisted of pure *o*-chlorophenol and 2,4-dichlorophenol, respectively (Table 1).

TABLE 1
Batch Distillation with Aqueous Solution of Hydrotrope as an Extractive Solvent[a]

System	Temperature of HT solution (°C)	Composition of distillate	% Recovery
1. 2,6-Xylenol *p*-Cresol	30	97.2% 2,6-Xylenol	21
	90	99% 2,6-Xylenol	49
2. *o*-Chlorophenol Phenol	30	100% *o*-Chlorophenol	59
	90	100% *o*-Chlorophenol	74
3. 2,4-Dichlorophenol *p*-Chlorophenol	90	100% 2,4-Dichlorophenol	35

[a] Hydrotrope: *p*-Toluene sulfonic acid (50%). Pressure: 101.3 kN/m^2. Time: 1.5 h.

Organic Bases as Extractive Solvents

The values of relative volatility averaged over the composition range covered in this work are reported in Table 2 for different systems. For all the experiments, the molar ratio of amine to the stronger component was 1.

2,6-Xylenol/p-Cresol

The relative volatility of this mixture increased from ~1 to 3 in the presence of amines like diethanolamine and methyl diethanolamine.

TABLE 2
Dissociation Extractive Distillation

System[a]	Extractive solvent	Average relative volatility (α)
1. 2,6-Xylenol	Methyldiethanolamine	3.2
p-Cresol	Diethanolamine	2.9
2. 2,4-Dichlorophenol	Diethanolamine	1.6
p-Chlorophenol	Triethanolamine	1.9
	Methyldiethanolamine	1.75
3. *o*-Chlorophenol	Diethanolamine	1.7
Phenol		

[a] The vapor phase was enriched in the first component. Pressure: 33 kN/m^2.

2,4-Dichlorophenol (DCP)/p-Chlorophenol (p-CP)

In the conventional sense, as given by pK_a values in aqueous solutions of 2,4-DCP (7.75) and *p*-CP (9.18), the former is the stronger component. However, it was observed that the vapor phase experienced enrichment in 2,4-DCP rather than *p*-CP. This indicates that the acidity of a compound in the nonaqueous phase must be considered as its ability to form a hydrogen-bonded complex with a base.

o-Chlorophenol/Phenol

A reversal of acidity was observed in this system as well. The vapor phase enriched in *o*-chlorophenol (pK_a = 9.48) instead of phenol (pK_a = 10.0).

From the foregoing it is clear that if a sufficient number of theoretical stages are provided, it may be possible to accomplish complete separation of close boiling compounds by exploiting the difference either in their abilities to interact with hydrotropes or in their acidities/basicities by employing a proper acid or base as an extracting solvent.

When an organic base is employed as an extractive solvent, the acid-base interaction between a phenolic substance and an amine in a nonaqueous phase is a hydrogen bond, and thus its strength is affected by steric hindrance of the two reactants and the basicity of the selected amine.

Aqueous solutions of the amines can also be tried as an extractive solvent, in which case the weaker component can be collected as an azeotrope with water at the top of the column. Preliminary batch distillation experiments were carried out with a distillation column, similar to the one used for hydrotropes, for the separation of 2,6-xylenol/*p*-cresol using aqueous solutions of diethanolamine (1.0 mol/L) as a solvent. The distillate was pure 2,6-xylenol.

CONCLUSIONS

Aqueous solutions of the hydrotrope, *p*-toluene sulfonic acid, have been successfully applied as an extractive solvent to separate mixtures of such close boiling phenols as 2,6-xylenol/*p*-cresol, *o*-chlorophenol/phenol, 2,4-dichlorophenol/*p*-chlorophenol, etc. In the case of 2,6-xylenol/*p*-cresol and *o*-chlorophenol/phenol, the relative volatility was more than 3 in the presence of the hydrotrope.

The use of a suitable organic base as an extractive solvent allows separation of 2,6-xylenol/*p*-cresol and other phenolic mixtures using a distillation column provided with 3 to 4 theoretical stages.

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Received by editor June 15, 1987