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Liquid-Liquid Equilibrium Study of Phenol Extraction with Cyanex 923

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Abstract: Although phenol extraction with Cyanex 923 has widely been studied, liquid-liquid equilibrium between phenol and undiluted Cyanex 923 has not been thoroughly investigated. Many factors influence the phenol extraction with undiluted Cyanex 923. Increasing the phenol concentration causes a water molecule replacement in the extractant by phenol molecules. Increasing the pH value above 12 decreases the phenol distribution coefficient K_D by 99.9%. A temperature increase from 15°C to 65°C results in a K_D decrease of 70%. With increasing salt content K_D increases due to salting-out. Adding organic acids stabilizes phenol in the aqueous phase and obstructs the extraction.

Keywords: Cyanex 923, liquid-liquid equilibrium extraction, phenol

INTRODUCTION

Liquid-liquid extraction is a standard unit operation to remove phenol from aqueous streams (1). In the past, polar organics like ethers or butyl acetates were favored to phenol extractants, as it was reasoned that the polar substance phenol could be extracted more efficiently by polar extractants (2–4). However, these extractants are usually quite hydrophilic and cause significant extractant loss and contamination of the aqueous

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phase (5). This has a significant environmental impact (6). Extensive downstream processing to recover the extractant is thus necessary when using these kinds of extractants (7). Nowadays, the trend goes more and more towards hydrophobic extractants (5,8). Due to increased hydrophobicity, extractant loss and contamination of the aqueous phase can be minimized. The trioctylphosphine blend Cyanex 923 is such an extractant, which provides low water solubility and a high capacity for the solute phenol (9). The water solubility of Cyanex 923 is very low ($10\,\mathrm{mg\,L^{-1}}$ at 25°C (9)) compared to other solvents such as toluene ($526\,\mathrm{mg\,L^{-1}}$ at 25°C (10)) or propylbenzene ($52.2\,\mathrm{mg\,L^{-1}}$ at 25°C (11)). Also other phenol extractants have a higher water solubility than Cyanex 923, e.g. tributylphosphate ($280\,\mathrm{mg\,L^{-1}}$ at 25°C (12)). In previous studies, it was shown that Cyanex 923 can be applied effectively for phenol extraction in liquid-liquid extraction systems (9,13–16). Additionally, it can be used for phenol extraction by supported liquid membranes (1,8,17) as well as by solvent impregnated resins (18).

Many different factors can influence liquid-liquid extraction. These can be, e.g. the system temperature, the phase ratio, or the salt content. On the one hand, the determination of these factors can help to optimize the extraction. On the other hand, effects occurring in a potential process application can be anticipated. For phenol extraction, many studies have already been performed. However, these often deal with different extractants than Cyanex 923, e.g. trioctylamine and trioctylamine salt systems (19–25). Even when the use of Cyanex 923 is reported, it is mostly diluted with, e.g. kerosene (9,26) or isoparaffinic hydrocarbon solvents (1,13). It is stated that the use of a diluent decreases the viscosity of Cyanex 923 significantly and thus makes the extractant phase handling easier (9). Another reason, which is given as a benefit of diluting Cyanex 923, is that difficult phase separation is encountered in the settling stage, when undiluted Cyanex 923 is used. This is attributed to its high loading capacity (27). However, this phase separation problem is encountered in a different system, namely the extraction of Nb and Ta from concentrated HF-H_2SO_4 solution. Although Watson et al. have used undiluted Cyanex 923, their study only investigates a system at 50°C, with high initial phenol concentrations ($10\,\mathrm{g\,L^{-1}}$) and with $30\,\mathrm{g\,L^{-1}}$ Na_2SO_4 in the aqueous phase to simulate effluent from a phenol/bisphenol plant (16). Also, in many studies a great excess of extractant is used (5,13,26).

As yet, liquid-liquid extraction of phenol from dilute aqueous solutions with undiluted Cyanex 923 has not been intensively studied. This is relevant when considering the treatment of low phenol concentration process wastewater or contaminated groundwater. Using undiluted Cyanex 923 allows for a high solute capacity of the extractant and thus an effective contaminant reduction in the treated aqueous streams. This is why in this study a broad range of factors that can influence the extraction of dilute phenol by pure Cyanex 923 is investigated. The factors, which are considered, are temperature, the ratio between the aqueous and the organic phase, the pH value of the aqueous phase, the salt content of the aqueous phase, and the organic acid content of the aqueous phase. The latter two factors of salt content and organic acid content in the aqueous phase are of particular interest when treating wastewater from the industrial cumene oxidation process for phenol production, the so-called Hock synthesis (4). All these factors are also of interest when the phenol extractant is immobilized, e.g. in a solvent impregnated resin. The observations made during liquid-liquid equilibrium experiments can be used for solvent impregnated resin applications (18). An additional factor that can influence phenol extraction is the phenol concentration in the aqueous phase (19). With higher phenol concentration the K_D value is decreasing. However, this effect of aqueous phenol concentration on the extraction with Cyanex 923 has already been described in by Burghoff et al. for liquid-liquid equilibrium extraction as well as a solvent impregnated resin application (18).

MATERIALS AND METHODS

Substances

The chemicals which are used are tri-(C6,C8)-alkylphosphine oxide (Cyanex 923) (93%, Cytec Industries Inc., Netherlands), n-hexane ($\geq$99%, Fluka AG, Switzerland), barium hydroxide ($\geq$98%, Fluka, Italy), and phenol ($\geq$99%, Merck KGaA, Germany). These substances are used without further purification.

Liquid-Liquid Equilibrium Extraction

The liquid-liquid equilibrium extraction setup consists of magnetically stirred, temperature controlled glass flasks. The ratio between the organic and the aqueous phase is 1:10 (15). The aqueous phase consists of 40 g demineralized water spiked with phenol. The initial phenol concentration in the aqueous phase is $1\,g\,kg^{-1}$ ($0.01\,mol\,L^{-1}$). This aqueous phenol solution has a pH of approximately 6. The organic extractant phase consists of 4 g of undiluted Cyanex 923. The two phases are stirred at ambient temperature (25°C) and ambient pressure for at least 12 hours to ensure that equilibrium is reached. After equilibration and complete phase separation samples are taken from the aqueous phase and filtered two times with Syringe filters (Spartan 30/0.2 RC, Schleicher & Schuell GmbH – Whatman Group, Germany). The phenol content of these samples is analyzed with a standard photometric method (28,29). Depending on the expected phenol content of the sample, which is taken from the aqeous phase after the liquid-liquid equilibrium extraction, 0.1 – 10 mL are transfered to a 100 mL volumetric flask. The flask is then filled with demineralized water to give 100 mL of solution. After this, 5 mL of buffer solution (Bernd Kraft GmbH, Germany) are added. This buffer solution consists of ammonium solution (25%), ammonium chloride, potassiumsodiumtartrate-tetrahydrate, and demineralized water, and is used to adjust the pH to a value of 10 ± 0.2. The sample solution is now shaken and then spiked with 3 mL of standard aminoantipyrene solution (Bernd Kraft GmbH, Germany). After shaking again, 3 mL of a standard potassium-hexacyanoferrate(III) solution (Bernd Kraft GmbH, Germany) are added and the sample solution is shaken for another time. This sample solution is now analyzed photometrically (Cary 300 Conc UV/VIS spectrophotometer, Varian, Netherlands) at 510 nm against a similarly prepared blind solution which does not contain phenol. The phenol content of the aqueous sample solution is determined using a calibration line. The phenol content of the organic phase in equilibrium can be determined via a simple mass balance. The systematic error of this photometric method is approximately 2%. The phenol distribution coefficient K_D is determined as the ratio between the phenol concentration in the organic phase and the phenol concentration in the aqueous phase.

The water content of the organic phase is determined with a Karl-Fischer-Titrator 795 KFT Titrino with 703 Ti Stand (Methrom Ltd., Switzerland), which is connected to a Sartorius CPA3245 balance (Sartorius AG, Germany). The density of the organic phase is determined with an Anton Paar DMA 5000 Density Meter (Anton Paar GmbH, Austria).

Temperature Dependence of Phenol Extraction with Cyanex 923

These experiments are performed with the procedure described above for liquid-liquid equilibrium extraction with an initial phenol concentration in the aqueous phase of $1\,\mathrm{g\,kg^{-1}}$ ($0.01\,\mathrm{mol\,L^{-1}}$). The only difference is that the temperature is varied between 15°C and 65°C. The analysis of the phenol content of the aqueous phase after equilibration is performed as explained above.

Influence of the Ratio between the Aqueous and the Organic Phase on Phenol Extraction with Cyanex 923

Basically, the influence of the ratio between the aqueous and organic phase should be similar to the influence of the phenol concentration in the aqueous phase as given in (18). In this study, the influence of the ratio between the aqueous and the organic phase is investigated to see whether these results for phenol concentration in the aqueous phase hold. This series of extraction experiments is performed at 30°C and ambient pressure in closed magnetically stirred glass vessels at initial phenol concentrations of $1\,\mathrm{g\,kg^{-1}}$ ($0.01\,\mathrm{mol\,L^{-1}}$) in the aqueous phase. The ratio between the organic and the aqueous phase is adjusted to 1:1, 1:2 and 1:10, respectively. The aqueous phenol solutions have a pH of approximately 6. The two phases are stirred for at least 12 hours to ensure that equilibrium is reached. The analysis of the phenol content of the aqueous phase after equilibration is performed as explained above.

Influence of Salt Contents of the Aqueous Phase on Phenol Extraction with Cyanex 923

In this series of experiments sodium sulphate Na_2SO_4 is used to adjust the salt concentration of the aqueous phase. Salt loads in waste waters are a common problem. The reason why sodium sulfate is used is that it is present in waste water of the Hock process—which is the major phenol synthesis process nowadays—due to an intermediate neutralization step. In this study, experiments are performed at 25°C and ambient pressure in closed magnetically stirred glass vessels as explained above. The initial phenol concentrations are varied between 0.25, 0.5 and $1\,\mathrm{g\,kg^{-1}}$ (0.0025, 0.005, and $0.01\,\mathrm{mol\,L^{-1}}$) in the aqueous phase. The salt concentration of the aqueous phase is varied between $0\,\mathrm{g\,kg^{-1}}$ ($0\,\mathrm{mol\,L^{-1}}$), $1.57\,\mathrm{g\,kg^{-1}}$ ($0.01\,\mathrm{mol\,L^{-1}}$) and $15.7\,\mathrm{g\,kg^{-1}}$ ($0.1\,\mathrm{mol\,L^{-1}}$), respectively, prior to the extraction. The analysis of the phenol content of the aqueous phase after equilibration is performed as explained above.

pH Dependence of Phenol Extraction with Cyanex 923

This series of liquid-liquid equilibrium experiments is performed at an initial phenol concentration in the aqueous phase of $1\,\mathrm{g\,kg^{-1}}$ ($0.01\,\mathrm{mol\,L^{-1}}$) in closed magnetically stirred glass vessels at ambient temperature and pressure in the same way as explained above. The pH of the aqueous solution is adjusted prior to the extraction in a range between 2 and 12.5 with hydrochloric acid and sodium hydroxide, respectively. In a second set of experiments, barium hydroxide is used instead of sodium hydroxide to adjust the pH in the alkaline range. This is done in order to show that different bases have the same effect on the distribution coefficient for phenol extraction with Cyanex 923. The analysis of the phenol content of the aqueous phase after equilibration is performed as explained above.

Influence of Organic Acids on Phenol Extraction with Cyanex 923

This series of experiments is performed at initial phenol concentrations in the aqueous phase of 1 to 8 $g\,kg^{-1}$ (0.01 to 0.08 $mol\,L^{-1}$) in closed magnetically stirred glass vessels at ambient temperature and pressure. The relation between organic and aqueous phase is again 1:10. Four sets of experiments are performed. First, no organic acid is contained in the aqueous phase. In the second series, acetic acid with an initial concentration of approximately 3.4 $g\,kg^{-1}$ (0.056 $mol\,L^{-1}$) is contained in the aqueous phase besides phenol. In the third series, formic acid with an initial concentration of approximately 4.3 $g\,kg^{-1}$ (0.093 $mol\,L^{-1}$) is contained in the aqueous phase besides phenol. In the fourth series, formic acid with an initial concentration of approximately 4.3 $g\,kg^{-1}$ (0.093 $mol\,L^{-1}$) and acetic acid with an initial concentration of approximately 3.4 $g\,kg^{-1}$ (0.056 $mol\,L^{-1}$) are contained in the aqueous phase besides phenol. These concentrations of the organic acids are used, as they resemble the organic acid concentrations in waste water of the Hock process. Both phases are stirred with magnetic stirrers for more than 12 hours. After this, the phases are separated and the phenol content of the aqueous phase is analyzed as described above.

In order to get insight in the extraction of formic acid and acetic acid by the phenol extractant Cyanex 923 without phenol present in the system, liquid-liquid equilibrium extractions are performed as described above excluding phenol. The initial acetic acid concentration is approximately 3.4 $g\,kg^{-1}$ and the initial formic acid concentration is approximately 4.3 $g\,kg^{-1}$, respectively. This particular extraction experiment is also performed with toluene instead of Cyanex 923, in order to determine whether there is a significant physical solubility of the organic acids in the organic phase. Toluene does not have any functional group, which can provide hydrogen bonding or other complexation mechanisms. This is why toluene is selected for the determination of the physical extraction of formic acid and acetic acid. Again, in these experiments both phases are stirred with magnetic stirrers for more than 12 hours. After this, the phases are separated and the organic acid content of each aqueous phase is analyzed using a Varian ProStar high performance liquid chromatography (HPLC) system (Varian Inc., Netherlands) consisting of a Model 410 autosampler, a Model 240 pump and a Model 310 UV detector. The column used for this HPLC analysis is an Inertsil 5 ODS-3, 250 × 4.6 mm Chromsep stainless steel. The flow rate through the column is adjusted to $1\,\mathrm{mL\,min^{-1}}$ at a temperature of 40°C. The mobile phase consists of a 20 mM potassium phosphate (K_2HPO_4) buffer ($pH = 3$). The detection of formic acid and acetic acid is done with the UV detector at a wavelength of 210 nm.

RESULTS AND DISCUSSION

Effect of Phenol Extraction on Cyanex 923

Liquid-liquid equilibrium extraction experiments allow a straightforward analysis of both the aqueous and the organic phase. Tests with binary systems just containing phenol and Cyanex 923 are performed to get information on the maximum phenol solubility in Cyanex 923. However, phenol itself does not show a significant solubility in the pure extractant. It seems that phenol does only dissolve in Cyanex 923 to a greater extent, when it is dissolved in water. Water appears to be crucial as a solubility mediator for the phenol extraction in Cyanex 923. During the extraction of phenol with Cyanex 923, physical extraction of phenol with Cyanex 923 is negligible. The major part of the phenol extraction depends on chemical complexation (5). The complexation mechanism is based on the hydrogen bonding between the oxygen in the phosphine oxide group of the extractant and the hydrogen atom in the phenolic hydroxyl group. According to Cuypers et al. the hydrogen bonds between phenol molecules and the P=O moieties of the phosphine oxides show a geometry with a near-ideal linear hydrogen bond (30). In aqueous as well as ideal systems, the complexation between trialkylphosphine oxides and phenol is according to a 1:1 stoichiometry (8,30,31). It is furthermore reported that in water-saturated toluene, the binding affinities are lower due to co-complexation of water with the active site of the extractant (30).

A Karl-Fischer analysis of pure Cyanex 923 shows that Cyanex 923 has a water content of 4.28% (w/w), but when it is equilibrated with water its water content increases to 11.09% (w/w). Determination of the water content of the organic phase after phenol extraction shows that the water content decreases with increasing amount of phenol in the organic phase, see Fig. 1. A possible explanation could be that the extractant molecules are hydrated and that the water molecules are replaced by phenol molecules during the extraction. More information on the exact mechanisms can be obtained by determining the aggregation states of

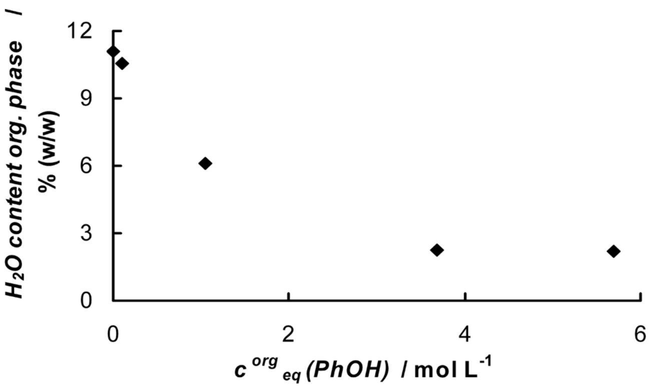

Figure 1. Dependence of organic phase water content from phenol content of organic phase.

the alkyl phosphine oxide molecules with and without water present, and comparing these aggregation states with the ones after phenol extraction. This investigation can be carried out experimentally with Fourier Transform Infrared spectroscopy (32) or in silico using quantum chemical calculations, e.g., at the B3LYP/6-311G(d,p) level of theory (30). However, the intrinsic microscopic effects are not investigated, as they are not subject of this research.

Density measurements of Cyanex 923 containing different concentrations of phenol extracted from aqueous solutions show that there is an increase in density with increasing phenol content. Figure. 2 shows that the density of the organic phase increases linearly with increasing phenol

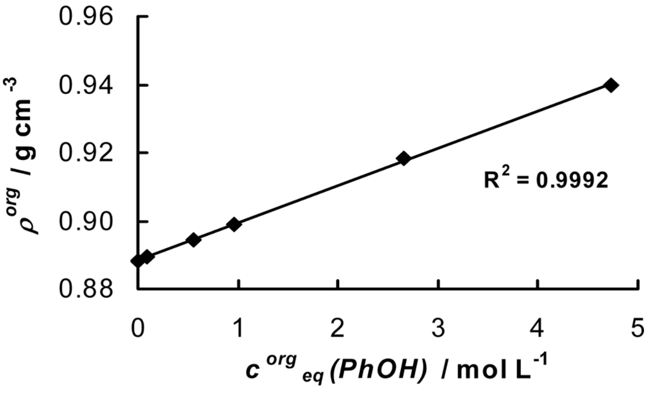

Figure 2. Dependence of organic phase density from phenol content.

content of the organic phase. Along with this increase of density, also a volume increase of the organic phase is qualitatively observed.

Temperature Dependence of Phenol Extraction with Cyanex 923

Liquid-liquid extraction experiments are performed at different temperatures to investigate whether back extraction can be facilitated by increasing the temperature. According to different authors, the phenol distribution coefficient K_D—defined as the ratio between the phenol concentration in the organic phase and the phenol concentration in the aqueous phase—decreases with increasing temperature (1,15). This observation was made also for systems with other extractants than Cyanex 923 (3,19). However, the decrease of K_D is reported to be not significant (19).

When using undiluted Cyanex 923 for the extraction of phenol from dilute aqueous solutions, the K_D value decreases by around 70% in the temperature range between 15–65°C, see Fig. 3. This decrease is almost linear.

Obviously, this is advantageous when considering the back extraction of the solute phenol from the organic extractant phase. However, for a full regeneration of the extractant this decrease of K_D would not be sufficient.

The experiments at varying temperatures also provide data about the reaction enthalpy. The data from Fig. 3 can be depicted in a graphical representation of the van't Hoff equation (1), see Fig. 4.

$$d\ln(K_D) = \left(\frac{\Delta H}{R \cdot T^2}\right)dT \tag{1}$$

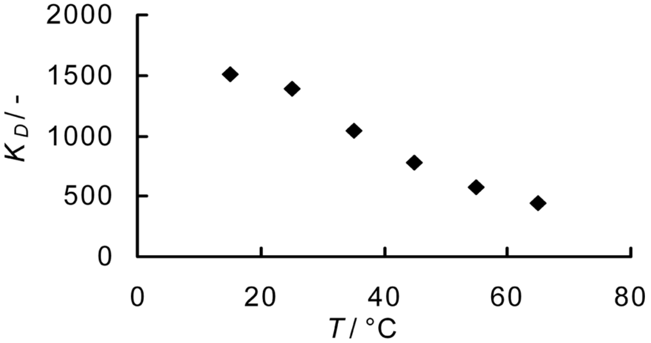

Figure 3. Temperature dependence of phenol extraction with Cyanex 923.

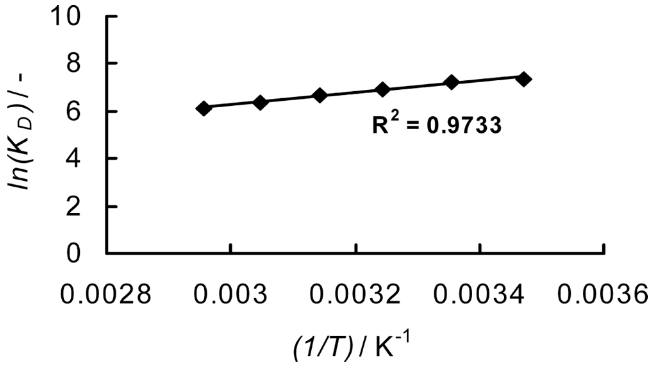

Figure 4. Determination of the apparent extraction enthalpy $\Delta_r H^0$ according to van't Hoff.

This plot of $\ln(K_D)$ versus $1/T$ results in a straight line with the slope proportional to the apparent enthalpy of reaction. The apparent enthalpy of reaction can thus be determined as $\Delta H = -20.8\,kJ\,mol^{-1}$. This value is in good agreement with the ΔH of $-24.7\,kJ\,mol^{-1}$ determined by MacGlashan et al. for phenol extraction by trioctylphosphine oxide in kerosene (15).

The apparent free energy can be calculated via $\Delta G = -RT\ln(K_D)$ (33). From this the apparent entropy can be calculated as $\Delta S = (\Delta H - \Delta G)/T$ (33). With the data at hand the apparent free energy can be determined as $\Delta G = -17.9\,kJ\,mol^{-1}$ at 298.15 K and the apparent entropy becomes thus $\Delta S = -9.74\,J\,mol^{-1}\,K^{-1}$ at 298.15 K. This value of ΔS may mostly reflect steric factors concerning molecular association in the extractant phase. The value of ΔS shown in this study is lower than the values described by Aksnes and Albriktsen for the association of phenol and different phosphoryl components diluted with carbon tetrachloride (34). They determine for example $\Delta S = -78.2\,J\,mol^{-1}\,K^{-1}$ for tributylphosphine oxide and $\Delta S = -77.4\,J\,mol^{-1}\,K^{-1}$ for dimethyl phenyl phosphine oxide. The lower value of ΔS given in this study could reflect a higher degree of disorder for the solvation of phenol and the phenol-extractant Cyanex 923 (15).

Influence of the Ratio between Aqueous and Organic Phase on Phenol Extraction with Cyanex 923

In an extraction process, the ratio between the aqueous and the organic phase is an important process parameter. Yang et al. (35) and Wang and

Liu (19) show that the concentration of phenol in the aqueous phase decreases with increasing amount of organic phase. The respective initial phenol concentrations of these studies were 5.4 g kg^{-1} (0.054 mol L^{-1}) and 10 g kg^{-1} (0.1 mol L^{-1}), which is significantly higher than in this investigation. The ratio between the aqueous and the organic phase can also be important, when the high amounts of solute must be removed from the aqueous phase. In such a case, the extractant could become saturated with the solute if a low phase ratio is selected.

Basically, changing the ratio between the aqueous and the organic phase has the same effect as changing the solute concentration in the aqueous phase. It changes the final equilibrium concentration of the solute. The influence of the phenol concentration of the aqueous phase on the K_D value has already been described in (18). In the present study, different aqueous to organic phase ratios are investigated in order to determine whether the previously determined results hold. As can be seen in Fig. 5, the variation of the relation between the aqueous and the organic phase does not cause a significant difference in the overall distribution coefficient K_D. While the equilibrium concentration of phenol in the aqueous phase increases with a higher water-extractant ratio, the actual distribution coefficient remains basically unchanged. This is a different observation than the ones referred to above.

This can be explained by the relatively low initial phenol concentration of 1 g kg^{-1} (0.01 mol L^{-1}). The amount of phenol in the system is not sufficient to cause saturation effects. This is why this result is not comparable with the result of the influence of phenol concentration in the aqueous phase as given in (18). Nonetheless, at higher initial phenol concentration than the investigated 1 g kg^{-1} (0.01 mol L^{-1}) there might be an influence, when the organic phase becomes saturated with the

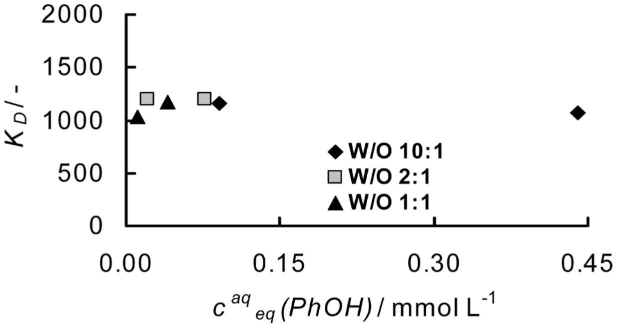

Figure 5. Phenol extraction with Cyanex 923 at different ratios of aqueous and organic phase (T = 30°C).

solute. However, this concentration range is not a subject of this investigation.

Influence of Salt Contents of the Aqueous Phase on Phenol Extraction with Cyanex 923

Addition of a defined quantity of salts to the aqueous phase can be an effective and simple way to increase the distribution coefficient of a solute. This was shown for the removal of cresols from aqueous solutions (36) and for the removal of phenol with mixtures of hexane and 2-propanol (37). When very high salt concentrations are added to a phenolic aqueous solution, even the formation of a second highly concentrated phenol layer can be enforced (38). These phenomena are caused by the so called salting-out effect. During salting-out inorganic salts are introduced in the aqueous phase. Phenol molecules are then dehydrated and thus more easily soluble in the organic phase (40), which facilitates the phenol extraction. When phenol is produced by the Hock process, a salt load in the waste stream appears. This is due to the use of sulphuric acid as a catalyst in one of the production steps and subsequent neutralization with sodium hydroxide (4). Thus, sodium sulphate Na_2SO_4 is formed. This is why Na_2SO_4 is used in this study to investigate the salting-out effect on low concentration aqueous phenol solutions. The effect of different Na_2SO_4 concentrations on the extraction of phenol from an aqueous solution with Cyanex 923 can be seen in Fig. 6.

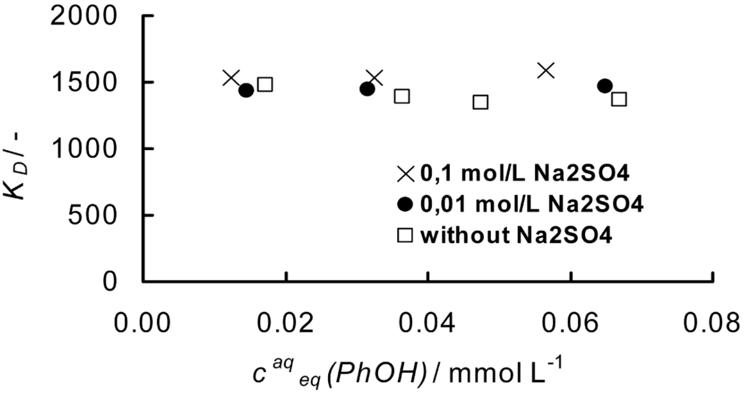

Figure 6. Phenol extraction with Cyanex 923 at different Na_2SO_4 concentrations of aqueous phase (T = 25°C).

For the different Na_2SO_4 concentrations the K_D values are almost constant over the investigated phenol concentration range up to $1\,g\,kg^{-1}$ ($0.01\,mol\,L^{-1}$). Furthermore, an increase of the sodium sulphate concentration from 0 to $0.1\,mol\,L^{-1}$ only causes a very slight increase in K_D. Nonetheless, this effect can be expected to increase with higher salt concentrations due to salting-out (38).

pH Dependence of Phenol Extraction with Cyanex 923

Based on literature a significant influence of the pH value on phenol extraction can be expected at $pH > 10$, as the pK_a value of phenol is approximately 10 (28). As a matter of fact, the recovery of phenol from organic extractants via back extraction can be achieved by using alkaline solutions at a pH above 10 (8,24,28,40–42).

As can be seen in Fig. 7, the K_D values are constant in the low pH region.

At pH values above 10 a sharp decrease of K_D can be observed, which is in good agreement with the observations by Cichy et al. (5). At a pH of above 12 the K_D value is decreased by around 99.9% compared to pH values below 10. This is caused by the formation of barium phenolate. During barium phenolate formation the barium cation Ba^{2+} complexes two phenolate ions PhO^- resulting in a salt ($Ba^{2+}(PhO^-)_2$). The barium phenolate salt has a high solubility in the aqueous phase and thus extraction is not successful. Unfortunately, using sodium hydroxide as basic compound causes persistent emulsification during the extraction (8,13,15). The reason for this could be that small amounts of dialkylphosphinic acids contained in Cyanex 923 cause an atypical

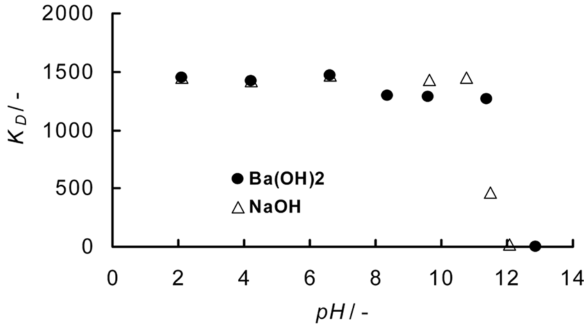

Figure 7. Phenol extraction with Cyanex 923 at different pH of aqueous phase, comparison of NaOH and $Ba(OH)_2$ ($T = 25°C$).

alteration of the interfacial tension. However, MacGlashan et al. suggest that this problem can be avoided by using solutions with high pH and high ionic strength (15). This proposes that the reason for this persistent emulsification could also be that the sodium cations and/or sodium phenolate accesses the oxygen of the extractant's phosphine oxide group. This could result in a polarized complex, which resembles a surfactant and emulsifies with the aqueous phase. Thus, a clean phase separation cannot take place. In a solvent impregnated resin application for example, this effect causes the extractant to be rinsed from the solid support (18). Using a base with a more voluminous cation can solve this problem. While the sodium ion has an ionic radius of 1.1 Å, the barium ion has an ionic radius of 1.49 Å (43). For that reason, also barium hydroxide is used for this experiment to determine the extraction's dependence on the pH value of the aqueous phase. The comparison of the extraction of phenol in the presence of NaOH and $Ba(OH)_2$ in Fig. 7 shows that both alkaline solutions cause a similar decrease of the K_D value at high pH values. In addition to that, no irreversible emulsification as with NaOH is encountered. This means that when $Ba(OH)_2$ is used, a fast and clear phase separation occurs after the extraction. This prevention of persistent emulsification and the low K_D values at a pH of approximately 12 make the pH shift with $Ba(OH)_2$ appear as a good regeneration procedure.

Influence of Organic Acids on Phenol Extraction with Cyanex 923

As can be seen in Fig. 8, an increasing amount of organic acid in the aqueous phase causes a decrease of the K_D value of phenol. Two major

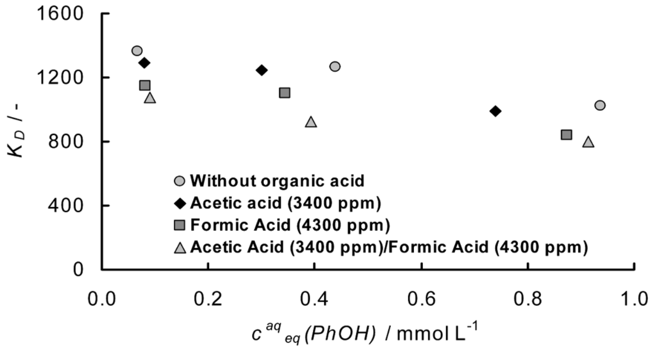

Figure 8. Effect of organic acids on the extraction of phenol (T = 25°C).

effects could be causing this decrease. On the one hand, co-extraction of the organic acids could decrease the phenol capacity of the organic phase. On the other hand, the so-called salting-in effect could be the reason for the decrease of K_D. During salting-in undissociated organic acid molecules form intermolecular hydrogen bonds with the phenol molecules in the aqueous phase (39). These complexes are stabilized in the aqueous phase. The salting-in is the opposite process of the so called salting-out, which is explained in the section on the influence of salt contents of the aqeous phase.

In order to investigate, whether co-extraction is occurring, formic acid and acetic acid, respectively, are extracted from an aqueous solution without phenol being present. This results in $K_D = 10$ for formic acid and $K_D = 6$ for acetic acid. These K_D values of these two organic acids are very low compared to the K_D values of phenol. Such low K_D values for organic acid extraction with Cyanex 923 were also observed by Wisniewski and Pierzchalska (44), Cai et al. (45) and Watson et al. (46). In order to achieve additional information about the extraction mechanism of formic acid and acetic acid, i.e. whether the extraction is dominated by physical solubility or by chemical complexation, each of the two organic acids is extracted from water with the solvent toluene. Toluene is selected as a reference solvent for this purpose, as it does not have functional groups which could provide a complexation mechanism. The extraction of formic acid and acetic acid with toluene results in very low distribution coefficients. The distribution coefficients are $K_D = 0.01$ for formic acid and $K_D = 0.04$ for acetic acid. This means that there is no significant physical solubility of the organic acids in the solvent toluene. The amount of organic acid which is extracted by Cyanex 923 is thus probably chemically bound. However, the affinity of the organic acids towards the phosphine oxide group of Cyanex 923 is significantly lower than the affinity of phenol for this extractant. Thus, it can be concluded that the decrease of K_D, as observed in Fig. 8, is not caused by competing extraction of organic acids but more likely by the salting-in effect.

CONCLUSIONS

During phenol extraction the water content of Cyanex 923 is decreasing by replacement of the water molecules by phenol molecules. The density of the organic phase increases linearly. Changing the ratio between the aqueous and the organic phase in the range of 10:1 to 1:1 does not have an effect during extraction of low concentration phenol with undiluted Cyanex 923. Nonetheless, temperature and pH have a significant influence on the liquid-liquid equilibrium extraction of low concentration phenol with undiluted Cyanex 923. This is important when considering regeneration procedures of the extractant. Apparently, a pH above 12 and an increase of the temperature can facilitate regeneration. From the data determining the influence of temperature on the phenol extraction the apparent enthalpy is determined as $\Delta H = -20.8\,\mathrm{kJ\,mol^{-1}}$, the apparent free energy as $\Delta G = -17.9\,\mathrm{kJ\,mol^{-1}}$ and the apparent entropy as $\Delta S = -9.74\,\mathrm{J\,mol^{-1}\,K^{-1}}$. While salting-out with inorganic salts enhances the extraction, salting-in by addition of organic acids inhibits phenol extraction.

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NOTATION

c^0_{PhOH}	initial phenol concentration of aqueous phase $\mathrm{g\,L^{-1}}$
c^{aq}_{salt}	salt concentration in aqueous phase $\mathrm{mol\,L^{-1}}$
ΔG	apparent free extraction energy $\mathrm{kJ\,mol^{-1}}$
ΔH	apparent extraction enthalpy $\mathrm{kJ\,mol^{-1}}$
K_D	overall distribution coefficient $\mathrm{mol\,L^{-1}\,(mol\,L^{-1})^{-1}}$
K_D^{salt}	overall distribution coefficient in presence of salt $\mathrm{mol\,L^{-1}\,(mol\,L^{-1})^{-1}}$
K_S	salting out constant $\mathrm{L\,mol^{-1}}$
R	gas constant $\mathrm{J\,(mol\,K)^{-1}}$
ΔS	apparent extraction entropy $\mathrm{J\,(mol\,K)^{-1}}$
T	temperature K

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