PURIFICATION OF ISOCYANATES BY SUPERCRITICAL FLUID FRACTIONATION USING CARBON DIOXIDE AND CARBON DIOXIDE-PROPANE MIXTURES

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The extraction of hydrolysable chlorinated compounds from an isocyanate formulation using supercritical carbon dioxide and mixtures of carbon dioxide and propane as solvents was investigated applying the usual methods. Information about the distribution of the components between the coexisting phases and about the mutual solubilities was obtained from phase equilibria (313 K - 353 K, 10 MPa - 30 MPa) for CO_2 and 10% to 30% C_3H_8. An approximate solution for the number of theoretical stages was determined for the assumed quasi-binary separation problem to reduce chlorinated compounds. Countercurrent extraction experiments carried out in a column with a height of 4 m and an inner diameter of 25 mm (15 MPa - 18 MPa, 333 K) reduced at an isocyanate concentration of 99.5% (GC area-percent) the concentration of hydrolysable chlorinated compounds from 2000 ppm to 800 ppm which is much higher than the objective of 100 ppm. Based on these results it was concluded that the assumption (based on the usual analytical method) that one chlorinated substance is the main source of hydrolysable chloride was not true. An extensive development of a new analytical procedure lead to an estimation of the distribution of the unknown hydrolysable chlorinated compounds. Based on this knowledge, a new two-step purification of the isocyanates was proposed.

INTRODUCTION

Polyfunctional isocyanates (PFIC) are of widespread use in polymer chemistry especially as key intermediates in formation of polyurethanes by polyaddition with polyfunctional alcohols. Due to the toxic and explosive compounds used in the phosgene-based formation the production of isocyanates is practiced by only a limited number of companies. In the phosgene-based production of isocyanates typical by-products and intermediates are chlorinated organic compounds. The possible formation of HCl by hydrolysation of those compounds forces their removal from isocyanates prior to application in formation of polyurethanes, especially when this is done at the ultimate consumer. The aim of this investigation was to remove the chlorinated compounds by supercritical fluid fractionation. Supercritical fluid fractionation overcomes the typical drawbacks of a thin film evaporation such as high temperatures, when dealing with compounds of high molecular weight.

The raw polyfunctional isocyanate used in this study had a low vapor pressure due to its relatively high molecular weight and was contaminated with hydrolysable chlorides to a content of about 2000 ppm. Since the isocyanate fraction was pretreated in different purification operations, it was assumed that the residual contamination was due to a single class of chlorinated substances.

This study examines if the purification of the isocyanate is possible by fractionation with supercritical carbon dioxide or with mixtures of carbon dioxide and propane. Propane was used in order to enhance the solubility and hence the operating efficiency.

MATERIALS AND ANALYSIS

All isocyanate charges were supplied by Bayer AG, Leverkusen, and stored in glass bottles under nitrogen headspace at 353 K. The carbon dioxide used for both the phase equilibrium measurements and the countercurrent experiments was 99.995% purity (CO_2 4.5, Linde AG, Germany) and had a guaranteed water content less than 5 ppm. The propane used for the phase equilibrium measurements was of 99.95% purity (Propane 3.5, Westfalen AG, Germany). The propane used for the countercurrent experiments was 99.5% purity (Propane 2.5, Westfalen AG, Germany). The composition of the raw isocyanate was determined with respect to the content of isocyanate (PFIC) and hydrolysable chlorides (HC).

Determination of isocyanate concentration was performed using a Hewlett Packard 5890 gas chromatograph equipped with a capillary column (DB-1, 30 m, 0.32 mm i.d., 0.25 μm film thickness, J&W scientific) and FID. The temperature program was set to 100°C-200°C with 5°C/min, 200°C-280°C with 10°C/min. The temperatures of injector and detector were set to 280°C and 320°C respectively. The gases used in this chromatographic method were, nitrogen 5.0 as carrier gas (Linde AG, Germany), synthetic air (Messer Griesheim, Germany), and hydrogen 5.0 as combustible gas (Messer Griesheim, Germany).

The quantification of HC-content was performed by hydrolysation of chlorinated compounds and subsequent titration against $AgNO_3$. Approximately 3g of a sample were weighed into a round flask and dissolved in 100 mL of methanol. After 10 minutes boiling with backflow cooling, 50 mL of water were added and the mixture was again left to boil for 30 minutes. Finally the flask was placed in an ice bath to cool down for 5 minutes. Afterwards 3 mL of nitric acid (10% H_2NO_3) were added and the solution was titrated against $AgNO_3$ (0.05 M) using an automated titrating apparatus (Metrohm, Germany).

EXPERIMENTAL FACILITIES

<u>Phase equilibrium measurements:</u> A high pressure phase equilibrium apparatus applying the static-analytical method was used to determine phase equilibrium of the system CO_2-PFIC and CO_2-C_3H_8-PFIC.

<u>Countercurrent extraction experiments:</u> Countercurrent extractions were carried out using a laboratory plant of 4 m height and 25 mm inside diameter filled with regular structured packings (Sulzer, Type EX). At the top of the column an empty column of 0.7 m prevents the entrainment of small droplets. Below the extraction zone the raffinate is collected in an empty column of 1 m equipped with a sapphire window to observe falling droplets and the level of raffinate. Feed can be supplied above or in the middle of the two extraction segments to enable the operation as stripping column only, or with incorporated enriching section respectively. Leaving at the top of the column the extract phase passes an expansion valve and subsequently a heat exchanger and enters the separator at desired temperature and pressure (normally 5 to 6 MPa). The extract is withdrawn at the bottom of the separator, whereas the gaseous solvent leaves at the top, is cooled down and pumped to the extraction column again. In order to retain even high volatile organic substances, a separation column of 35 mm inner diameter and 1.5 m in length was filled with stainless steel coils of 10 mm diameter. While the extract is withdrawn from the bottom of the column, which is heated to 303 K, sub-cooled liquid solvent is pumped to the top of the separation column inducing a multistage separation of the solvent.

Considering the different solubility of propane and carbon dioxide in the liquid phase it was necessary to assure a constant concentration of propane in the supplied solvent. Since the

separation of extract is forced by decreasing the pressure and hence reducing the solvents density, the phase equilibrium of the propane – carbon dioxide system can be used to achieve the desired propane concentration in the solvent. Phase equilibrium data of the binary system carbon dioxide – propane is well documented. According to phase equilibrium, the propane concentration in the gas phase of a two phase mixture at 5 MPa can be controlled over a wide range by changing the temperature of the system. In order to use this effect the separation section of the extraction plant was modified. Instead of the column, which was formerly used as separator with liquid carbon dioxide reflux, a 5 L autoclave was used as flash separator (5 MPa, 333 K). Leaving the separator the solvent passed a cooler and entered the separating column. The column was now used as a saturator circulating the propane-rich liquid phase countercurrently to the carbon dioxide-rich gas phase. The temperature of the saturator was controlled using a profiled heat exchanging hose and a thermostat. The liquid phase was pumped by a high pressure gear pump and the liquid level was manually controlled observing the phase boundary line by means of two sapphire windows and supplying or releasing propane and propane-rich liquid phase respectively. Propane was supplied using a cooled air driven pump. Applying this setup, a constant propane concentration of 20% ($\pm$ 1%) was accomplished.
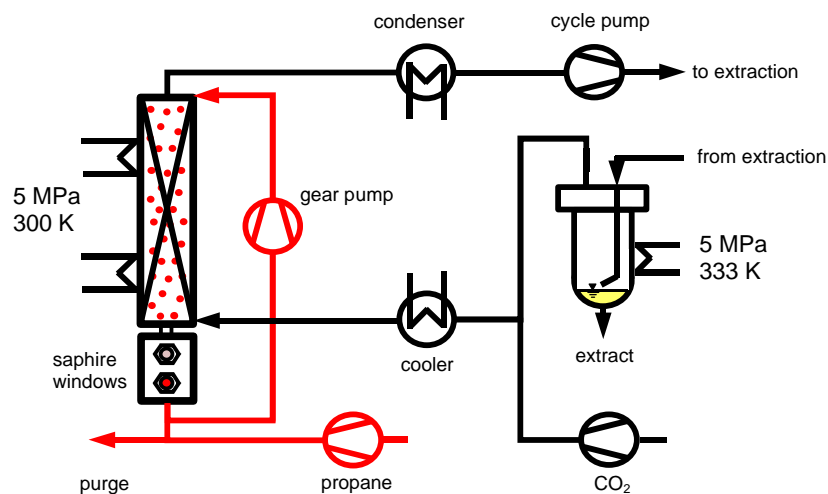

Fig. 1: Separation section incorporating a flash separator and saturation of carbon dioxide with propane.

RESULTS: PHASE EQUILIBRIUM

The PFIC showed a moderate solubility in carbon dioxide depending on density of the carbon dioxide and temperature of investigation. The composition of gas phase was found to be dependent only on gas phase solubility in the investigated range of temperatures and pressures. The results of the analysis are represented in Fig. 2. At low gas phase solubilities (< 2 wt.-%) a complete separation of HC from the isocyanate seems possible. At higher solubilities the composition of the solvent-free gas phase approaches the composition of the solvent-free liquid phase. At gas phase solubilities >8% the HC concentration is lower than the corresponding concentration in the liquid phase rendering an extraction of HC impossible.

It was tried to enhance gas phase solubility by adding propane as a co-solvent without reducing selectivity. There is an increase of gas phase solubility of about 1% at propane concentrations of 20% and 30% with a simultaneous increase in selectivity (Fig. 3).
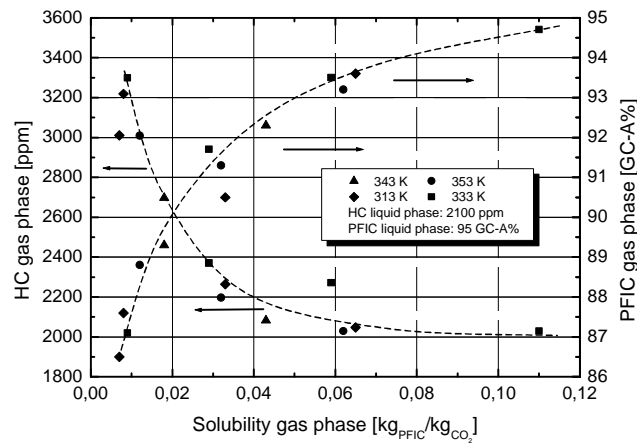
Fig. 2: Results of the analysis of the solvent-free fractions of gas phase samples at different temperatures and pressures versus the gas phase solubility.
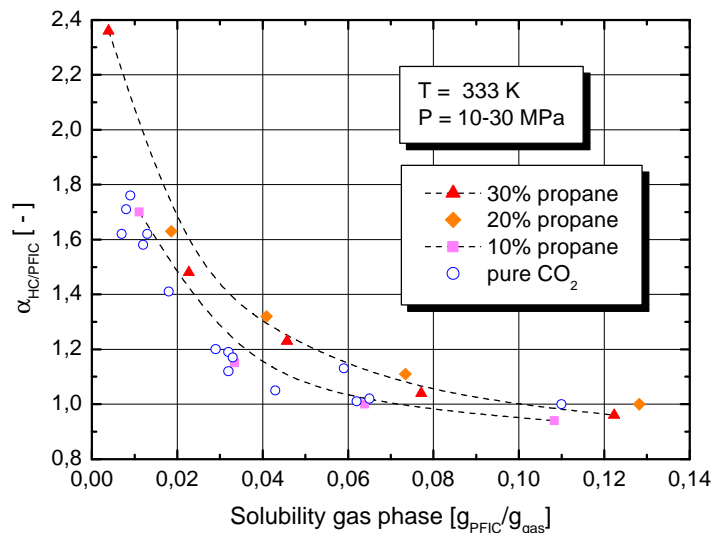

Fig. 3: Separation factor $\alpha_{HC/PFIC}$ versus gas phase solubility.

Separational analysis: For a first estimate on a separation of HC by countercurrent extraction, the McCabe-Thiele method was applied, assuming the feed mixture to be represented by a pseudo-binary system. Minimum solvent to feed ratios and necessary equilibrium stages were calculated for a HC-concentration of 100 ppm in the extract and a yield of 80% raffinate. Results of those calculations are shown in Table 1.

The results of calculation indicate that most equilibrium stages are needed in the stripping section of the extraction column. The addition of 20% propane results in much lower solvent to feed ratio at similar separation efficiency.

COUNTERCURRENT EXPERIMENTS

Countercurrent experiments were carried out according to the results of the preliminary calculations. The full length of the column was used as stripping section. First experiments showed next to no separation concerning the hydrolysable chlorides. The color of the raw isocyanate was changed from brown to yellowish in the extract, whereas the raffinate became darker.

Subsequent extractions (15 MPa, 333 K) showed different behavior. There was no remarkable difference between the extractions with pure carbon dioxide and those with 20% propane concerning the separation efficiency. However, due to the higher solubility, higher PFIC flow rates could be realized.

Table 1: Calculated numbers of equilibrium stages (n_{th}) and solvent to feed ratios.

15 MPa 333 K		carbon dioxide	
SFR	[kg$_S$/kg$_F$]	140	224
SFR/SFR$_{min}$	[-]	1,25	2
n_{th} stripping section	[-]	20	11
n_{th} enriching section	[-]	4	2

15 MPa 333 K		20% propane in carbon dioxide	
SFR	[kg$_S$/kg$_F$]	80	128
SFR/SFR$_{min}$	[-]	1,25	2
n_{th} stripping section	[-]	22	12
n_{th} enriching section	[-]	5	3

The results of the countercurrent extractions led to the assumption that there were three different classes of HC. The existence of low volatile HC was indicated by high HC values in very dark raffinate samples taken during the start up of extractions when the feed supply was started while the solvent was already circulated in the extraction plant. The relatively low separation efficiency at already lower HC concentrations in the third extraction indicated a chlorinated substance with similar behavior as the PFIC in the separation. Following this theory a third class of chlorinated substances must have existed providing higher separation factors than those determined during the phase equilibrium measurements. The three assumed classes were designated as low volatile, PFIC volatile, and high volatile HC.

According to a more detailed analysis (Fig. 4), the distribution of HC in the three stated subclasses can be estimated as follows. Based on a concentration in the feed (PFIC) of 2100 ppm HC, high volatile HC content is about 760 ppm, about 705 ppm are PFIC volatile HC, and about 635 ppm are low volatile HC. GC-MS analysis of extract and raffinate samples with high HC concentrations obtained from the countercurrent extractions support the assumption. Extract fractions showed only signals of chlorinated compounds of low molecular weight, such as chloro-benzene, whereas in the raffinate fractions only chlorinated compounds of higher molecular weight could be detected.
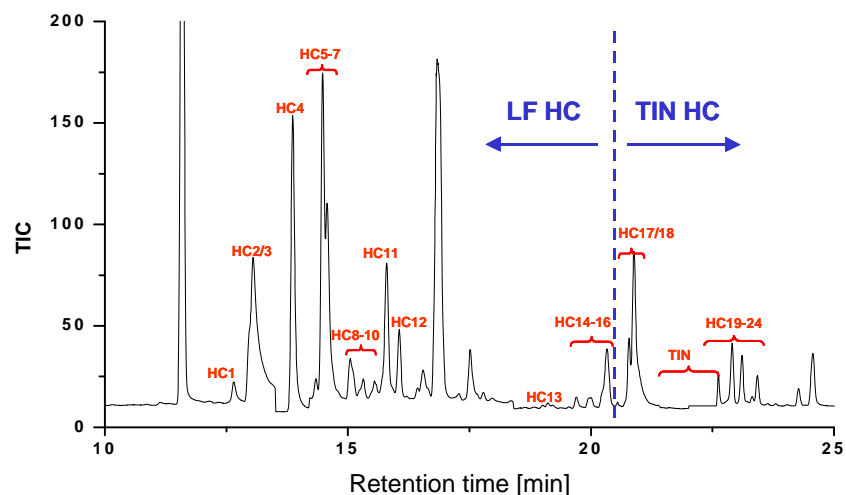

Fig. 4: SIM chromatogram.

The various chlorinated isocyanates distribute differently in the countercurrent separation. An illustration is presented in Fig. 5.
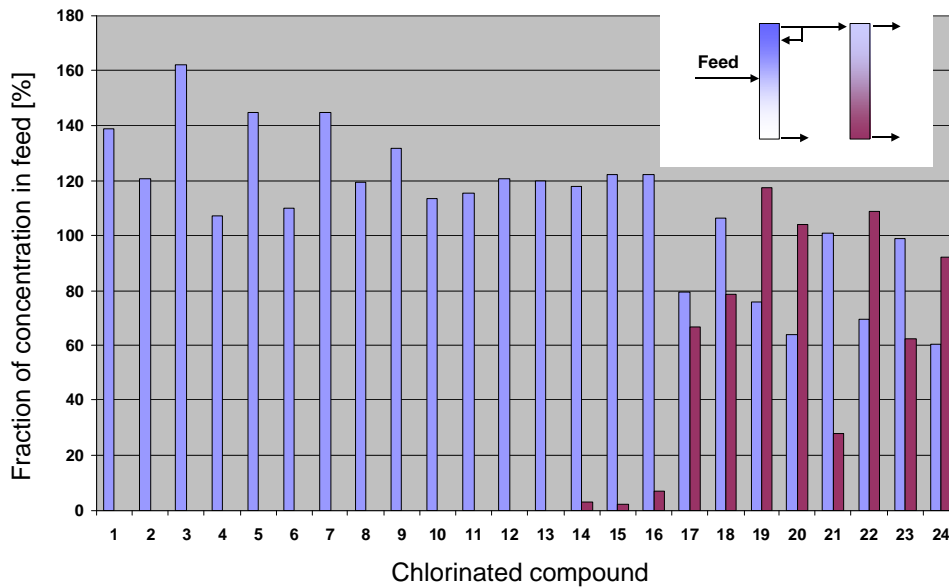

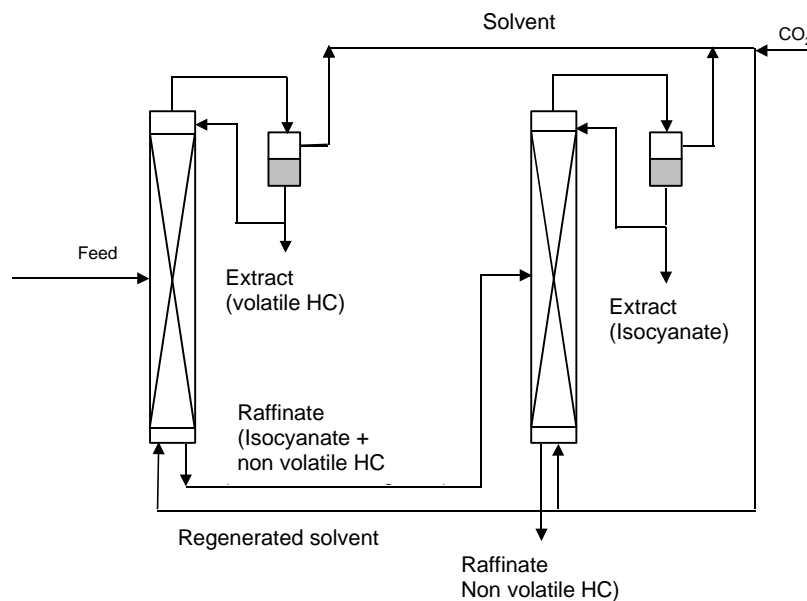**Fig. 5:** Chlorinated substances (HC) during countercurrent separation.

Fig. 6: TIN-product as extract

CONCLUSION

The extraction of chlorinated compounds with supercritical carbon dioxide and supercritical carbon dioxide-propane mixtures is possible. The addition of propane was shown to be profitable mainly due to the increase of solubility, which severely affects the economic efficiency. With a simple modification of the separation section a constant propane concentration was obtained, thus avoiding the need for complex feedback control. However, the removal of chlorinated substances (HC) is not possible in a single operation unit, since their different molecular weights obviously influence their distribution in the coexisting phases. The assumption of three different classes of chlorinated substances according to their volatility was shown to be valid. Two of these substance classes, the high volatile and low volatile HCs could be removed successfully. The third class of chlorinated substances, which is of similar volatility to the PFIC, is a more challenging separation problem.