Measurement of Bubble Point Pressures of Zirconium and Hafnium Tetrachloride Mixture for Zirconium Tetrachloride Purification Process

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***Abstract*—Vapor-liquid equilibrium for the binary system of zirconium tetrachloride and hafnium tetrachloride over a pressure range from 23 to 50 bars, and a temperature range from 440°C and 490°C have been measured. This method was implemented based on the bubble point determination of binary mixture. The obtained experimental data were correlated with the Peng-Robinson equation of state. It was found that the Peng-Robinson equation of state provided satisfactory prediction for the binary system. Based on the regressed values, high pressure distillation technology has been investigated to produce hafnium-free zirconium tetrachloride.**

***Index Terms*—Zirconium tetrachloride, hafnium tetrachloride, bubble point pressure, Peng-Robinson, distillation.**

I. Introduction

As tetrachlorides are the starting materials for the production of zirconium and hafnium for the Kroll process reduction to Zr and Hf metal, several commercial processes have been suggested for the separation of $ZrCl_4$ and $HfCl_4$ directly. Physical properties data has been shown in Table I. The possible temperature range for the separation of hafnium from zirconium tetrachloride is really strict. Nevertheless, technical difficulties at the required high pressure prevented the process from becoming commercially feasible.

The development of a new method to separate hafnium tetrachloride from zirconium tetrachloride by a distillation operation under high pressure is highly desirable. However, no information regarding the vapor-liquid equilibrium existed; it was therefore felt to be desirable to accumulate such data. As a first step, the vapor - liquid equilibrium data for $ZrCl_4$/$HfCl_4$ mixture has been accumulated in this study.

The objective of this work is to provide good estimates for binary interaction parameters to be used with the simplest and most widely-used equations system for the prediction of high – pressure vapor – liquid equilibrium. Thus, we estimate the values of the binary interaction parameters to be used with Peng-Robinson equation of state combined with van der Waals mixing rules. The experimentally measured bubble point data were correlated with the popular Peng-Robinson equation of state (PR-EOS) containing an adjustable binary interaction parameter [2]. The vapor phase compositions, i.e., the dew pointcomposition corresponding to the bubble points, were calculated with the optimum values of the PR-EOS binary interaction parameter. Then, the high pressure distillation column was investigated in case of hafnium-free zirconium tetrachloride separation.

TABLE I: Several Physical Properties of Zirconium and Hafnium Tetrachlorides [1]

Properties	$ZrCl_4$	$HfCl_4$
Sublimation temperature (°C)	331	317
Triple point		
Temperature (°C)	437	432
Pressure (bar)	22.36	45.01
Critical point		
Temperature (°C)	506	499
Pressure (bar)	57.66	57.76
Volume (ml/mol)	319	303

II. Experiment

A. Chemicals

$ZrCl_4$ and $HfCl_4$ was supplied by the Alfa Aesar, Johnson Matthey Catalog Company with a certified purity of 99.5wt.% and 99.9wt.%, respectively. These chemicals were used without further purification.

B. Apparatus for Vapor-Liquid Equilibria Equipment

A schematic of the experimental setup is shown in Fig. 1. The equilibrium cell was made with an inner volume of about 150cm^3. It was input in the electrical furnace with high temperature capacity. The chemicals of both phases in the equilibrium cell were mixed together, which was heated from the furnace.

Fig. 1. Experimental apparatus for determining the bubble point pressure of binary mixture.

The temperature in the cell was measured with a platinum resistance thermometer, which was directly inserted into the equilibrium cell. The pressure was measured by a Helium pressure gauge, and a pressure indicator. All the sensor was

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connected with the computer through using Labview 8.6 software.

The mass of each component introduced into the cell was determined with a digital balance having an accuracy of ±0.0001g.

III. Calculations

A. Vapor Pressure of Pure Component

The vapor pressure of $ZrCl_4$ and $HfCl_4$ in our study was investigated from 440°C to 490°C. The acentric factors of pure components have been regressed based on the experimental data. The vapor pressure data and the regressed acentric factor ($\omega_{reg.}$) of each component are given in the Table II and Table III, respectively. Virtually, the vapor pressure of $HfCl_4$ was higher than that of $ZrCl_4$.

B. Bubble Point Calculation of Binary Mixture

The bubble point calculations estimate the pressure at which the first bubble of vapor is formed when reducing the pressure of a liquid mixture and they also estimate the composition of the first bubble formed [3] .

TABLE II: Vapor Pressure Data and The Regressed Acentric Factor of ZrCl4.

$ZrCl_4$		
T(°C)	P(bar)	$\omega_{reg.}$
440	23.32	1.012
450	26.83	
460	30.94	
470	35.34	
480	40.63	
490	46.52	

TABLE III: Vapor Pressure Data and The Regressed Acentric Factor of HfCl4.

$HfCl_4$		
T(°C)	P(bar)	$\omega_{reg.}$
440	45.92	-0.4844
450	48.06	
460	49.12	
470	51.94	
480	53.78	
490	55.34	

A suitable equation of state when applied to both phases and combined with appropriate mixing rules provides good results in the prediction of vapor-liquid equilibrium. Binary interaction parameter is generally incorporated in the mixing rules of an equation of state in order to obtain the best predictions [4]. The availability of experimental bubble point pressure data enables the determination of the interaction parameter k_{ij} to be used in the calculations with equation of state. The optimal values of binary interaction parameters were determined from binary vapor-liquid equilibrium data by minimizing the deviation in predicted bubble point pressures. In this study, the well-known Peng- Robinson equation of state (PR-EOS) has been used for the prediction [5].

IV. Results and Discussion

Experimental vapor pressures for the binary $ZrCl_4$/$HfCl_4$mixture are shown in Table IV at various $ZrCl_4$ compositions and temperatures.

Fig. 2 shows the Px diagram calculated by the PR-EOS at several temperatures for the $HfCl_4$/$ZrCl_4$ system along with the experimental points. Correlation of the experimental data with the PR- EOS gives the optimum value of binary interaction parameter k_{ij} at 0.0181. The relatively small value of this parameter suggests a minor deviation from ideal behavior in the liquid phase. The bubble points calculated by the PR-EOS gave a good agreement with those measured experimentally for all temperatures.

Virtually, as the higher temperature, the relative volatility tends to be smaller through two adjacent lines of gas and liquid phase. The separation of binary mixture becomes more strictly due to the limited range of temperature. However, although the results of the bubble calculated by the PR-EOS showed good agreement with their experimental values, the dew points estimated by the PR-EOS are not guaranteed to be accurate values. Thus, there may exist a difference between the calculated and actual values of the mixture dew points.

TABLE IV: Experimental Bubble Point Pressure Data for ZrCl4/HfCl4 Mixture

T(°C)	P(bar)	T(°C)	P(bar)	T(°C)	P(bar)
x_{ZrCl4} = 0.124		x_{ZrCl4} = 0.188		x_{ZrCl4} = 0.249	
440	43.92	440	42.82	440	41.12
450	45.93	450	44.86	450	43.71
460	48.11	460	47.35	460	46.47
470	51.33	470	50.42	470	49.33
480	53.03	480	52.5	480	51.84
490	54.92	490	54.65	490	54.41
T(°C)	P(bar)	T(°C)	P(bar)	T(°C)	P(bar)
x_{ZrCl4} = 0.376		x_{ZrCl4} = 0.502		x_{ZrCl4} = 0.625	
440	39.02	440	35.32	440	32.24
450	41.41	450	37.93	450	34.89
460	44.2	460	41.21	460	38.32
470	47.33	470	44.42	470	42.1
480	50.42	480	48.53	480	46.68
490	53.43	490	52.1	490	50.82
T(°C)	P(bar)	T(°C)	P(bar)	T(°C)	P(bar)
x_{ZrCl4} = 0.748		x_{ZrCl4} = 0.812		x_{ZrCl4} = 0.874	
440	28.57	440	27.08	440	25.81
450	31.82	450	30.11	450	28.71
460	35.73	460	34.06	460	32.92
470	40.02	470	38.56	470	37.36
480	44.54	480	43.4	480	42.29
490	49.72	490	48.68	490	47.8

V. Rigorous Simulation for Conventional Distillation Column

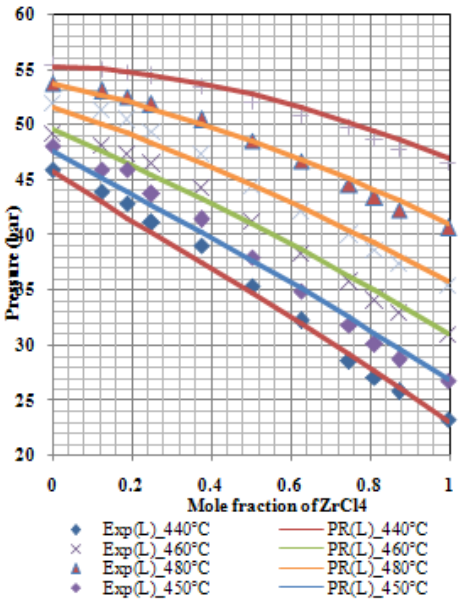

Fig. 2. Px diagram at different temperature for $ZrCl_4$/$HfCl_4$ system.

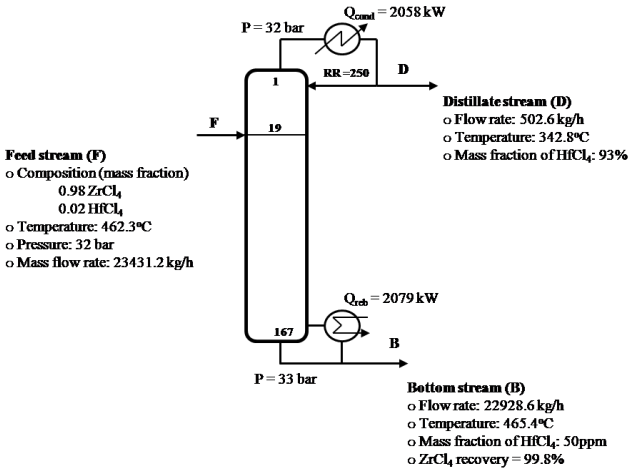

Fig. 3. High pressure distillation column configuration for $ZrCl_4$/$HfCl_4$ separation.

Once shortcut estimates were completed, the structure has been simulated rigorously using ASPEN HYSYS 7.3 to get accurate results. In this study, $ZrCl_4$ is the main product with 50ppm $HfCl_4$ content requirements. The feed stream containing $ZrCl_4$ and $HfCl_4$ mixture was introduced to the distillation column. The overhead stream with more than 90 wt% $HfCl_4$ was collected in the liquid phase. The purified $ZrCl_4$ stream with 50ppm $HfCl_4$ content was recovered in the bottom stream of the column. Since the design obtained by the shortcut method might not be the optimum, an optimizing step is essential. After the initial structure of the distillation column was fixed by the shortcut method, the number of stages and the feed stage location were investigated to establish the optimal distillation structure. The optimization was carried out by varying the number of stages or feed stage location systematically and sequentially.

The effect of the optimization steps on reboiler duty was investigated. It can be concluded that the reboiler duty get the minimum value at 167 number of stages with the 17th feed tray location.

In summary, the optimized structure of binary distillation column has been shown in Fig. 3.

VI. Conclusions

The bubble point pressures measurement for $ZrCl_4$ and $HfCl_4$ mixture was carried out in the temperature range 440 – 490°C by using a high-pressure experimental apparatus via changing $ZrCl_4$ composition in the range of temperature above the melting point. In addition, the vapor-liquid phase behavior of the mixture has been analyzed with using Peng Robinson equation of state. With an optimised value of k_{ij} = 0.0181 for PR equation of state, the experimental data at different temperatures were correlated to obtain the dew point pressures and composition in equilibrium with the bubble points. However, as the higher temperature, the relative volatility tends to be smaller through two adjacent lines of gas and liquid phase. It leads to the separation more difficultly.

In addition, the simulation of a binary distillation process employing the regression results was investigated. A process for the separation of zirconium tetrachloride from a mixture comprising tetrachlorides of zirconium and hafnium has been proposed in compatible with the Kroll process for winning pure zirconium; leads to the possible commercial process of zirconium production.

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