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Physico-chemistry in distillation process of $BiCl_3$-HCl-H_2O system①

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[Abstract] The gas-liquid equilibrium and evaporation behaviors of HCl and H_2O in the distillation process of the $BiCl_3$-HCl-H_2O ternary system were investigated. With increasing content of $BiCl_3$, the quasi-azeotropic point moves toward the low acidity and high temperature. The evaporation law of HCl and H_2O in low-acidity $BiCl_3$ solution was summarized. The residue phases were studied as well. The results show that the residue phases vary with the distillation temperature, namely $BiCl_3$ and $BiCl_3 \cdot x HCl$ at low temperature and $BiCl_3$ and BiOCl exist at higher temperature. The causes for the formation of different residue phases were discussed.

[Key words] $BiCl_3$; HCl; distillation; physico-chemistry
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1 INTRODUCTION

Chlorination-dry distillation method is an effective way to purify and extract bismuth compounds from the complex bismuth mass, by which pure chlorination-bismuth products and high metal recovery ratio can be gained, environmental pollution by harmful elements can be prevented, and valuable accompanying elements can be synthetically recycled as well[1,2]. Problems in basic theories, such as thermodynamic equilibrium of the $BiCl_3$-HCl-H_2O system in wet bismuth refining have been studied[3-7], but physico-chemistry in the process of distillation is seldom reported. In this paper, the gas-liquid equilibrium and behaviors of HCl and H_2O in the distillation process of the $BiCl_3$-HCl-H_2O system are investigated and the system residue phases at different temperatures are measured as well, which means much to understand the evaporation law of low-acidity $BiCl_3$ solution in the dry distillation process. These can also be used theoretically to find the best controlling conditions for $BiCl_3$ extract to obtain high distillation ratio in the process.

2 EXPERIMENTAL

The azeotropic point and the composition of the gas and liquid phases of a certain $BiCl_3$-HCl solution were measured by Othmer method. HCl concentration of the solution was controlled in a low state considering the actual HCl content of Bi extract and insufficiency of test conditions. The solution was heated to its azeotropic point and kept for a long time enough to reach the equilibrium, then the temperature of azeotropic point was measured by a standard thermometer (precision ±0.2 ℃), and gas and liquid solution were collected respectively from the condensate ball and reactor to measure the content of $BiCl_3$, HCl and H_2O, hereby phase diagrams were drawn.

Chemical compositions of residue phases were studied in the way as follows. The $BiCl_3$ solution was laid in the reactor, the equipment was kept sealed and heated to the temperature, at which H_2O and HCl were evaporated and completely cooled by the condenser. So H_2O and HCl were collected in the condensate cup and this process was continued until HCl and H_2O were dry distilled. After it cooled down, the reactor was weighted. Residue masses in it were calculated before HNO_3 was added to dissolve the residue and the contents of Bi^{3+} and Cl^- were measured, namely, the content of residue phases could be calculated.

Reagent $BiCl_3$, HCl and HNO_3 were analytically pure, H_2O was secondary distilled water, and the content of Bi^{3+} and Cl^- were measured respectively by EDTA and $AgNO_3$-SCN^- titrations.

3 RESULTS AND DISCUSSION

3.1 Gas-liquid equilibrium of $BiCl_3$-HCl-H_2O system

3.1.1 $t-x$ phase diagram

Temperature $-x$(HCl) phase diagrams of the 1 mol/L and 2 mol/L $BiCl_3$ solution are shown in Fig. 1 (pressure 101.3 kPa). It's seen that the azeotropic point of the solution varies with mole fraction of HCl in the liquid phase. With increasing HCl (salt-free base) content in the solution, the azeotropic point increases and so does x(HCl) in the gas phase. When x(HCl) (salt-free base) in the solution grows to some extent, the liquid and gas lines are tangent and the solution reaches its azeotropic point, i. e., the

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composition of salt-free bases in the gas phase equates that in the liquid phase and the azeotropic point of the solution arrived at its maximum. In the HCl solution containing 1 mol/L $BiCl_3$, the solution reaches its azeotropic point (111.3 ℃) with $x(HCl) = 0.096$; while in 2 mol/L $BiCl_3$ the solution reaches its azeotropic point on condition that $x(HCl) = 0.091$ and the azeotropic point is 113.5 ℃. It can also be seen that, the composition and temperature of the azeotropic point change with $BiCl_3$ concentration. When $BiCl_3$ concentration increases, the composition of azeotropic point, i.e., the mole fraction of HCl (salt-free base) decreases and the temperature of the azeotropic point increases.

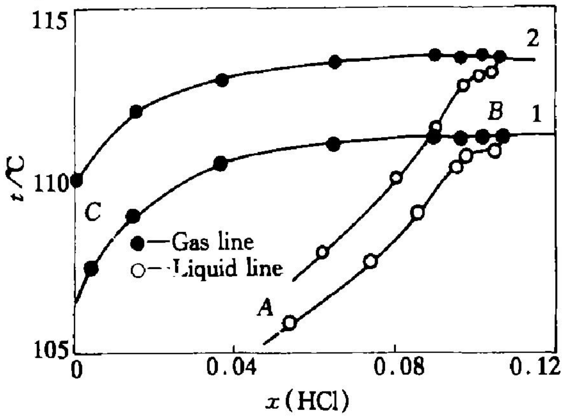

Fig. 1 Temperature—$x(HCl)$ curves of different solutions (pressure 101.3 kPa)
1—1 mol/L $BiCl_3$; 2—2 mol/L $BiCl_3$

3.1.2 Y_1—X_1 diagram

Y_1—X_1 diagram of the solution under 101.3 kPa is shown in Fig. 2 (Y_1—$x(HCl)$ in the gas phase, X_1—$x(HCl)$ (salt-free base) in the liquid phase). It can be seen that with a very low content of HCl in the solution, the content of HCl in the gas phase is close to 0. When $x(HCl)$ (salt-free base) in the solution approximates to the composition of azeotropic point, the content of HCl in the gas phase increases rapidly. Meanwhile, with increasing concentration of $BiCl_3$ in the solution, the composition of azeotropic point decreases, as shown in Fig. 2, where the azeotropic point moves down towards left($a \rightarrow b \rightarrow c$), and that's why the azeotropic point is named the quasi-azeotropic one.

3.1.3 Quasi-azeotropic curve

Temperature curve of the quasi-azeotropic point with different $BiCl_3$ concentrations is shown in Fig. 3. It can be seen that with increasing $[Bi^{3+}]_T$ in the solution, the temperature of the quasi-azeotropic point increases. This may be explained as follows. With low concentration of $[Bi^{3+}]_T$, the quasi-azeotropic mass comprises mostly of HCl and H_2O and the change of $[Bi^{3+}]_T$ influences little on the quasi-azeotropic temperature; while with high-concentration of $[Bi^{3+}]_T$, the phenomena mentioned above is just the reverse.

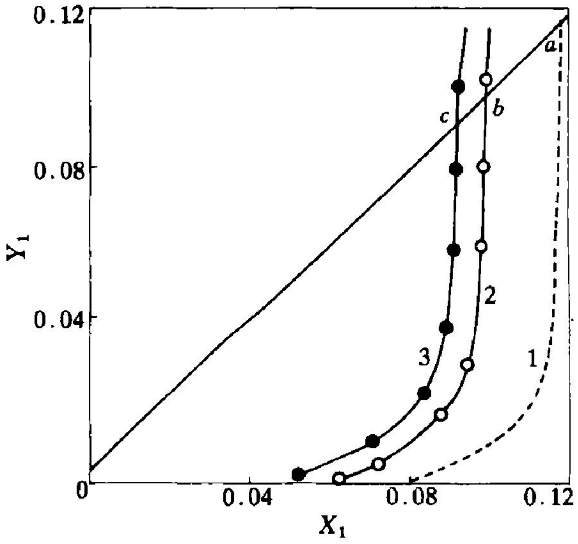

Fig. 2 Y_1-X_1 curves of different solutions
(Y_1—$x(HCl)$ in gas phase;
X_1—$x(HCl)$ in liquid phase)
1—0 mol/L $BiCl_3$; 2—1 mol/L $BiCl_3$;
3—2 mol/L $BiCl_3$

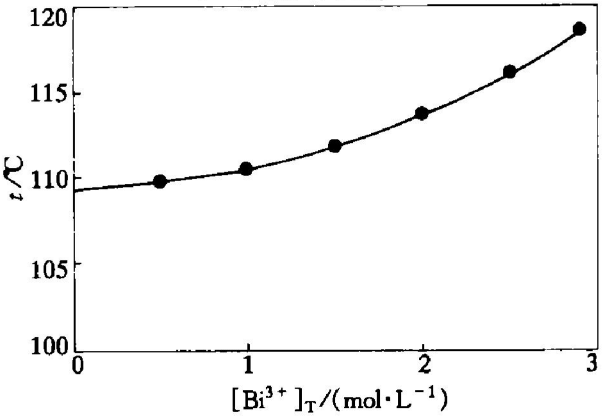

Fig. 3 Change of azeotropic point with concentration of $BiCl_3$ solution

HCl concentration curve of the azeotropic mass with different $BiCl_3$ concentrations are shown in Fig. 4. It's found that more Bi^{3+} in the quasi-azeotropic mass will cause the decline of $[H^+]$ in the azeotropic mass and it decreases more slowly with increasing $[Bi^{3+}]_T$. Moreover, hydrolytic reaction of $BiCl_3$ will happen in the distillation process if $[Bi^{3+}]_T$ continues increasing and $[H^+]$ decreases to some extent.

3.2 Evaporation behavior of HCl and H_2O in distillation process

Fig. 5 shows HCl contents in gas and liquid phases in the distillation process as a function of distillation time. It can be seen that at the beginning(45 min), nearly no HCl is found in the gas phase and its content changes slowly due to the evaporation of H_2O in the liquid phase. Then, some HCl evaporates but the H_2O evaporation amount in the gas phase is

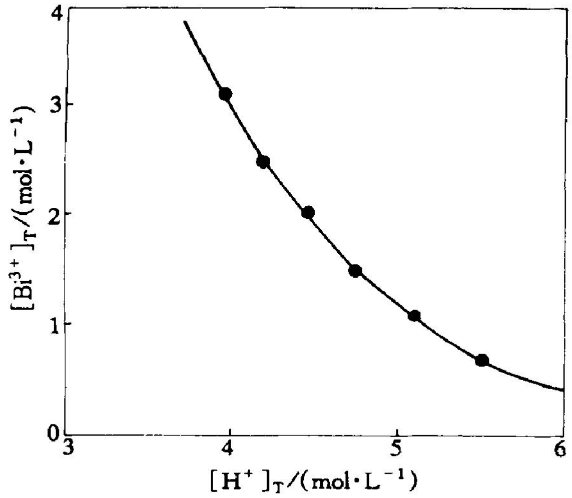

Fig. 4 Change of HCl content of azeotropic mass with different $BiCl_3$ concentrations

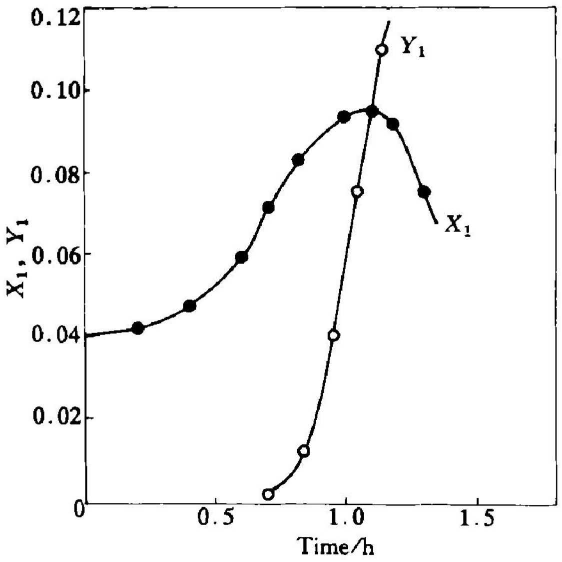

Fig. 5 Relationship between HCl content and evaporation time

(X_1 —mole fraction of HCl(salt-free base) in liquid phase;
Y_1 —mole fraction of HCl in liquid phase)

relatively higher, which results in the fast changes of HCl content in the gas phase. HCl content in the liquid phase reaches its maximum when it equals that in the gas phase. After this, it falls down. When the low-acidity $BiCl_3$-HCl solution is heated to evaporate, HCl content in the liquid phase along the liquid line ($A \rightarrow B$) in Fig. 1, and HCl content in the gas phase varies along the flat gas line ($C \rightarrow B$) and it changes much even at a small variation of temperature so that at certain temperature, the gas and liquid line will be tangent at the quasi-azeotropic point. In the distillation process, HCl and H_2O are evaporated, $BiCl_3$ concentration in the solution increases and quasi-azeotropic point B moves towards the low acidity and high temperature, which can be seen in Fig. 3 and 4.

Fig. 6 shows H_2O content in the gas and liquid phases as a function of the distillation time. It can be seen that, the H_2O content in the gas phase is 100% at the beginning of evaporation and becomes much lower after heated for 50 min. As for the H_2O content in the liquid phase, it decreases slowly firstly, intersects the content curve of H_2O in the gas phase when it falls down to the lowest, and then it increases gradually. Because H_2O content isn't calculated as part of $BiCl_3$, its variation law is opposite to that of HCl.

3.3 Residue phases

The analysis results of residue phases at different distillation temperatures are listed in Table 1. It can be seen that the value of $x(Cl)/x(Bi)$ decreases with increasing temperature. At 140 ℃, the residue phases are composed of $BiCl_3$ and $BiCl_3 \cdot xHCl$, and the molar ratio of HCl to $BiCl_3$ is 0.12, which indicates that most of the residue phases are in the form of $BiCl_3$. When the temperature is above 160 ℃, the $x(Cl)/x(Bi)$ ratio in the solution is smaller

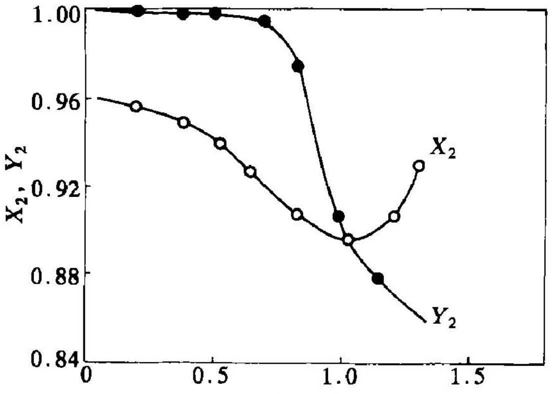

Fig. 6 Relationship between H_2O content and evaporation time

(X_2 —mole fraction of H_2O(salt-free base) in liquid phase;
Y_2 —mole fraction of H_2O in liquid phase)

Table 1 Phase composition of residue at various temperatures of distillation

Temperature/ ℃	Mass of residue/ g	Volume of solution/ mL	[Cr]/ $(mol \cdot L^{-1})$	$x(Cl)/x(Bi)$	Phase composition
140	16.662 5	125.0	1.360	3.125 0:1	98.63% $BiCl_3$+ 1.37% HCl
160	16.250 8	116.0	1.310	2.931 6:1	97.16% $BiCl_3$+ 2.84% HCl
180	16.125 9	112.0	1.295	2.764 2:1	90.92% $BiCl_3$+ 9.08% HCl
200	15.956 6	104.4	1.480	2.657 0:1	83.71% $BiCl_3$+ 16.29% HCl

than 3∶1, which indicates that no $BiCl_3 \cdot xHCl$ exists and neither can single $BiCl_3$ form, so the residue phases may be composed of $BiCl_3$ and BiOCl. The mass fraction of BiOCl rises with increasing temperature, which implies that the decomposition of $BiCl_3 \cdot xHCl$ has finished at 160 ℃.

The relationship between temperature and acidity of the solution with certain $BiCl_3$ concentration is shown in Fig. 7. For the solution with its acidity $[H]_1 < [H]_0$, the evaporation behavior isn't equilibrium at the temperature $T_1 < T_0$. However, when the solution is heated from the room temperature to T_1, its liquid composition varies along the liquid line *CD* to the point *D* and its gas phase comprises completely H_2O. Such evaporation is equilibrium. Due to the high temperature of the distillation system, H_2O evaporates, which results in the decline of its volume, increase of $BiCl_3$ concentration in the solution and the movement of the quasi-azeotropic point toward its left upper. Meanwhile, the gas line *AB* and liquid line *CDB* move with it to the same direction and the point *D* shifts to *D′*. With proceeding distillation process, much of H_2O volatilizes and point *D′* moves right. When H_2O evaporates completely, $BiCl_3 \cdot xHCl$ or $BiCl_3 \cdot xHCl \cdot yH_2O$ is left as the final residue. As for the distillation at higher temperature ($T_2 > T_0$), the composition of the gas phase becomes that of the quasi-azeotropic point *B*. Because HCl content is high in the evaporated gas phase, the large evaporation capacity of HCl makes the acidity in the solution decrease relatively and the liquid composition shift to the left. On the other hand, the evaporation of H_2O and HCl will cause the decline of the solution volume and increase of $BiCl_3$ concentration in the distillation process. When $[Bi^{3+}]/[H^+]^2$ reaches a given value, the hydrolytic reaction will occur:

$$BiCl_3 + H_2O = BiOCl(S) + 2HCl \qquad (1)$$

Thus, at a high temperature $T_2 > T_0$, BiOCl will be found as a residue phase and its content will increase with the temperature, which can be inferred from Table 1 and can be interpreted as follows. Evaporation rate increases at higher temperature and so does the evaporation capacity of H_2O and HCl, while the content of HCl in the liquid phase reduces quickly so that the hydrolytic degree is deepened and more BiOCl exists in the residue.

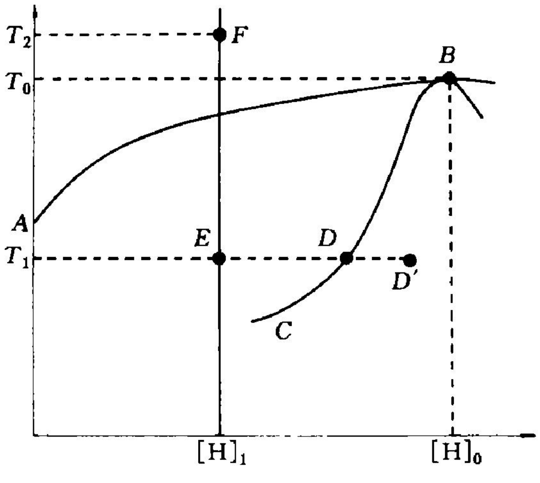

Fig. 7 Relationship between temperature and acidity of $BiCl_3$ solution

As for the equilibrium vaporization process, in which the heat input can just satisfy the need for the system evaporation (including heat to increase the temperature of the liquid phase, evaporate the gas phase and so on), compositions of the liquid and gas phases will vary with the curves shown in Fig. 7. In a solution with the acidity $[H]_1 < [H]_0$ and a given $BiCl_3$ concentration, the liquid composition changes along the *CDB* curve and the mole fraction of HCl (salt-free base) increases at a higher temperature; meanwhile, the gas composition changes along the *AB* curve. When the temperature rises to T_0, the gas and liquid lines are tangent at the point *B* and the mole fraction of HCl (salt-free base) in the liquid phase reaches its maximum. Then, the quasi-azeotropic point *B* moves towards the left upper side (i. e. low temperature and high acidity), and the mole fraction of HCl (salt-free base) in the solution decreases gradually in the distillation process. With the evaporation of H_2O and HCl, the $BiCl_3$ concentration increases in the liquid phase and BiOCl begins to be generated by the hydrolytic reaction.

To determine the point at which $BiCl_3$ starts hydrolyzing, the curves in Fig. 3 and 4 are treated by cubic regression function, which can be expressed as

$$T = 0.117\,284[Bi^{3+}]_T^3 - 0.416\,337[Bi^{3+}]_T^2 + 3.160\,036[Bi^{3+}]_T + 381.092\,8 \qquad (2)$$

$$[H^+] = 0.089\,137[Bi^{3+}]_T^3 + 0.629\,113[Bi^{3+}]_T^2 - 1.926\,83[Bi^{3+}]_T + 6.588\,91 \qquad (3)$$

In the hydrolytic equilibrium, the relationship among $[BiCl_3]$, [HCl] and temperature *T* can be calculated by the system hydrolytic Eqn. (1) and expressed as Eqn. (4):

$$T\ln([HCl]^2/[BiCl_3]) = 4479.20 - 9.598T + 8.722\ln T \qquad (4)$$

If Eqns. (2) ~ (4) are combined, the temperature, at which the hydrolytic reaction occurs in the evaporated $BiCl_3$-HCl solution, can be obtained as $T = 401.144$ K (about 128 ℃).

4 CONCLUSIONS

1) In the gas-liquid equilibrium of the $BiCl_3$-HCl-H_2O ternary system, with increasing content of $BiCl_3$, the quasi-azeotropic point moves toward the low acidity and high temperature.

2) In the distillation process of the low-acidity $BiCl_3$ solution, the HCl content in the liquid phase increases gradually at the beginning and decreases after it reaches the maximum; while the variation of H_2O

content is opposite. The composition law in the gas phase is that firstly H_2O is almost the only phase and then HCl content increase rapidly.

3) In the distillation process of the low-acidity $BiCl_3$ solution, the residue phases vary with the evaporation temperature. At low temperature, the residue phases are $BiCl_3$ and $BiCl_3 \cdot x HCl$; at high temperature, the residue phases are $BiCl_3$ and BiOCl.

4) In the equilibrium evaporation process, the liquid phase is hydrolyzed at certain high temperature and BiOCl exists as a residue phase. The formation of BiOCl phase can be prevented by controlling the evaporation temperature.

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