

The Vapor-Liquid Equilibrium of Bromine-Brine System at Atmospheric Pressure

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Abstract. The air blow-out method of extracting bromine from seawater or brine is widely used at home and abroad. The key parameter in this unit operation is the vapor-liquid equilibrium data (T, x, y) for bromine-brine system, which were obtained with the Bubble Equilibrium equipment at 10 and 20°C in this paper. The experimental equilibrium data were carried out by using Margules Equation for liquid phase and ideal equation for gas phase, and the nonlinear least square method was used to regress the parameters of Margules model for the system. It showed good consistency for the calculated data from Margules model and the experimental data.

key word: Bromine; air blow-out method; vapor-liquid equilibrium (VLE).

1. Introduction

Bromine is the basic chemical raw material for the production of flame retardants, fire extinguishing agents and photosensitive materials. It is widely used in the pharmaceutical, pesticide, fuel and oil industries, which is one of the important branches of the marine chemical industry. Extracting bromine by the air blow-out method from (concentrated) seawater or salt brine is the most widely used production process at home and abroad [3]. The main steps include acidification, oxidation, blowing out, absorption, distillation and condensation [4]: when the bromine ion is oxidized to bromine molecular by chlorine gas, it is blown out from the (concentrated) seawater or salt brine by air, and then reacts with sulfur dioxide or alkali to become the concentrated solution with high concentration of bromine ion. the bromine molecular is blown out by chlorine gas oxidation or acidizing from the concentrated solution with high concentration of bromine ion by steam distillation process. Finally, the bromine is separated from the liquid phase and condensed to obtain product [1,2].

The main unit operation equipment of the air blow-out method is the reaction tower, such as the blowing-out tower, absorption tower, and distillation tower. The design of the blowing tower is critical [5]. However, the design is mainly based on the previous data or empirical correlation so far, and few rigorous calculations are carried out in theory. This is mainly because the vapor-liquid equilibrium data of bromine-brine systems are very few. In the existing literature, the saturated vapor pressure of bromine at a specific temperature under atmospheric

pressure, Henry coefficient of bromine in pure water and saturated vapor pressure data of brine in certain salt fields can be found or calculated by using the Antony Formula, although the relative volatility can also be estimated, and then the phase equilibrium and mass transfer behavior in the tower can be studied. However, due to the different kinds of raw materials, the chemical compositions are also different, so not only the saturated vapor pressure data of brine cannot be generalized, resulting in a narrow application range of this method, but also the interference of other ions, resulting in the dissolution behavior of bromine often deviates from Henry's Law. Gergert V R pointed out that due to the interference of chloride ions, the dissolution behavior of bromine in dilute sodium chloride solution does not strictly follow Henry's Law. Ostapenko L F studied the distribution coefficient of bromine between vapor and liquid phases at 15 and 35 °C, and found that when the molar fraction of bromine in liquid phase is less than 2.8×10^{-6} , its phase equilibrium behavior also deviates from Henry's law. This study shows that the distribution coefficient of bromine is not only affected by the concentration of bromine in the liquid phase, but also increases with the increase of temperature and decreases with the increase of salt concentration. The above studies are earlier, and the existing data are far from meeting the needs. Therefore, it is necessary to measure the vapor-liquid equilibrium data of specific raw materials through experiments, and then design and calculate the blow-out tower in combination with the actual process operation, which plays an important guiding role in improving the bromine blowing rate and reducing the consumption of raw materials [3,4].

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Vapor-liquid equilibrium data mainly includes temperature, pressure, vapor phase and liquid phase composition of the system. The methods of vapor-liquid phase equilibrium determination are divided into direct determination and indirect determination. The former refers to the direct determination of the temperature, pressure and composition of liquid and vapor phases at equilibrium state through experiments. This method mainly includes distillation method, flow method, static method, quasi-static method and circulation method. The key of this method is the design of equilibrium kettle. However, in actual measurement, the gas phase composition is not easy to measure accurately, especially when the component contains heavy components. In most practical situations, T, P and x are measured, and then y is calculated indirectly. The relationship between P and x can be measured at constant temperature, and the relationship between T and x can also be measured at constant pressure. In addition, many studies also pointed out that the parameters of the activity coefficient equation can be directly determined by measuring the infinite dilution activity coefficient, so as to calculate the gas-liquid equilibrium data of the whole concentration range of the system. The main methods include boiling point meter method, gas chromatography, gas chromatography and inert gas saturation strip method. In addition, in special cases, thermodynamic estimation can also be carried out by looking up physical property data in the manual [5,6].

In this paper, the vapor-liquid equilibrium behavior of bromine - brine system is studied by using the bubbling entrainment equilibrium kettle method to directly determine the concentration of bromine in the liquid and vapor phases. The method has simple equipment and high accuracy. In view of practical application, the vapor-liquid equilibrium state of the actual raw material system containing dozens to hundreds of ppm of bromine at 10 and 20 °C at atmospheric pressure is mainly studied [7].

2. Experiment

2.1 Experimental principle

Considering that in practical application, the content of bromine in the raw material solution is very low, only tens to hundreds of ppm. It is a dilute solution, and its composition does not cover the full concentration range. Therefore, at this time, it is not appropriate to use the pure component standard state to describe the thermodynamic properties, but should use Henry's law based on the fugacity of the infinite dilution solution standard state. Henry's constant can be strictly defined by the following process of finding the limit

$$H_{2,1} = \lim_{x_2 \rightarrow 0} (y_2 \phi_2^V P / x_2) \quad (1)$$

Where: $H_{2,1}$: Henry constant of solute 2 in solvent 1,

ϕ_2^V : Vapor phase fugacity coefficient of solute 2 in solvent 1,

x_2, y_2 : Molar fraction of component 2 in the liquid phase and gas phase respectively,

P : Total system pressure

2.2 Experimental process

In this experiment, an improved bubble entrainment flow equilibrium kettle was used to measure the vapor-liquid equilibrium data. It mainly consists of two balance kettles: the first is a pre-saturation kettle, in which the brine which is exactly the same as the main saturation kettle but does not contain bromine, while the second balance kettle is placed with brine solution containing different concentrations of bromine. Each balance kettle has a precision thermometer to measure the temperature of the solution directly. The whole set of balance kettle device is in the thermostatic water tank, which is externally connected to the atmosphere to keep the pressure constant. When the temperature is stable, blow the air in with constant flow rate. The air bubbles continuously through the sand core filter at the bottom of the bottle. The bromine molecular is dissolved into the air bubble and blown out after a long contact time with the solution. Then it enters the washing bottle containing potassium iodide solution for absorption, and finally enters the mass air flow meter to measure the air volume. The equipment is shown in Figure 1. The same equipment was also used in our previous work.

The main function of the pre-saturation kettle is to take out the saturated steam of the solvent from it, so that the solvent in the main balance kettle will not be vaporized, which can ensure the constant composition of the solvent in the main balance kettle; The long contact time and the tiny bubbles produced by the sand core filter nozzle ensure the full contact between gas and liquid; And use a drying filter to absorb the moisture carried out in the gas; Excessive potassium iodide solution ensures that bromine carried out in the air can be completely absorbed.

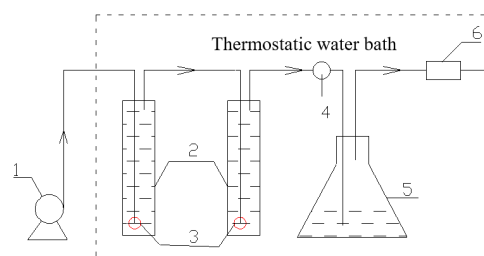


Figure 1. Equipment

1. Air pump
2. Vapor-liquid balance kettle
3. Sand core filter nozzle
4. Drying filter
5. KI conical flask
6. Gas mass flowmeter

3. Experimental data and analysis

3.1 Data results

Figure 2 (a) and (b) show the relationship between the partial pressure of bromine in the vapor phase and the molar fraction of bromine in the liquid phase in the

bromine-medium brine system at 10 and 20 °C respectively. It can be seen that in dilute solution, the relationship between the two is not linear but quadratic function, which deviates from Henry's law. This is because the liquid phase in the system is a non-ideal solution, and the sulfate radical, chloride ion and other interfering impurities in the raw liquid brine affect the phase equilibrium behavior of bromine; On the other hand, it can also be found from the fitting formula that the quadratic term has little influence. If this term can be ignored, it is a linear relationship, which conforms to Henry's law. According to the fitting formula in the figure and the above theoretical analysis, the Henry constant values of the bromine-brine system are 16.92 and 23.05 atm at 10 and 20 °C, respectively. The trend of this data just reflects the trend that the volatility of bromine in the brine increases with the increase of temperature.

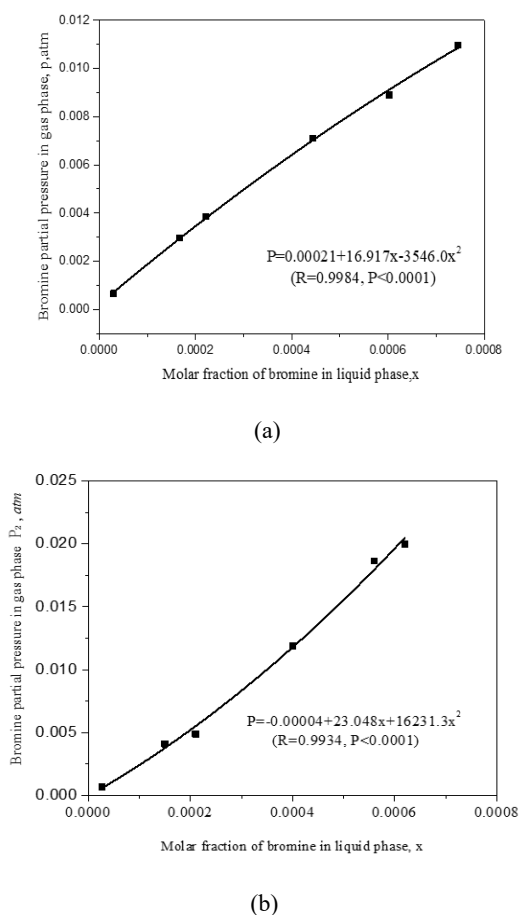


Figure 2. The Vapor-Liquid Equilibrium of bromine-brine (a) 10°C; (b) 20°C

3.2 Activity coefficient equation correlation

The thermodynamic treatment methods of vapor-liquid equilibrium include activity coefficient method and equation of state method, both of which have advantages and disadvantages, and should be selected according to different situations. Generally, the equation of state method is particularly beneficial in the calculation of high-pressure vapor-liquid equilibrium, and the activity coefficient method is often used in the low and medium pressure range. The commonly used activity coefficient

equations include Whole-type equation based on normal solution, Margules equation, Van Laar equation, Wilson equation based on local composition, NRTL equation and UNIQUAC equation model. Generally speaking, for engineering applications, the first three equations can also meet the accuracy requirements, and the calculation is simple. In this paper, we use the cubic Margles equation to correlate the relationship between the activity coefficient equation and the composition. The general formula of the equation model in the binary system is as follows:

$$\ln \gamma_1 = (A + 3B)x_2^2 - 4Bx_2^3 \quad (2)$$

$$\ln \gamma_2 = (A - 3B)x_1^2 + 4Bx_1^3 \quad (3)$$

Among the above equation, 1 and 2 represent two substances respectively, A and B are binary parameters, which need to be solved by nonlinear least square method according to the experimental data. Considering that the experimental system is a dilute solution system and bromine is a solute, it is only necessary to correlate the activity coefficient of the solute.

The correlation results of the Margules equation at 10 °C can be seen in Table 1. The Margules equation is as follows:

$$\ln \gamma_1 = -424.065 \times (1 - x_1)^2 + 424.162 \times (1 - x_1)^3 \quad (4)$$

where: γ_1 is the activity coefficient of bromine in the liquid phase, and x_1 is the mole fraction of bromine in the liquid phase.

Table 1. Correlation Results of Margules Equation at 10°C

$x_{1,exp}$	$P_{1,exp}, at$	γ_1, ca	$P_{1,cal}, at$	$\Delta P, at$	$ \Delta P / P_{1,e} $
3.0049E-5	0.00066	1.2997	0.0007	0.00004	0.0606
1.6720E-4	0.00297	1.0511	0.0029	-	0.0236
2.2165E-4	0.00386	1.0305	0.0038	-	0.0155
4.4451E-4	0.00710	0.9451	0.0070	-	0.0140
6.0234E-4	0.00891	0.8743	0.0091	0.00019	0.0213
7.4531E-4	0.01096	0.8701	0.0108	-	0.0146

From the table 1, we can see that except for the first data, the error of other data is between 1.46-2.36%, which has a very good correlation.

Similarly, at 20 °C, the correlation results of Margules equation are shown in Table 2, and its equation is as follows

$$\ln \gamma_1 = 572.421 \times (1 - x_1)^2 - 572.435 \times (1 - x_1)^3 \quad (5)$$

Table 2. Correlation Results of Margules Equation at 20°C

$x_{1,exp}$	$P_{1,exp}, ai$	γ_1, ca	$P_{1,cal}, ai$	$\Delta P, at.$	$ \Delta P / P_{1,c}$
2.743 2E-5	0.0006 7	1.06 91	0.0006	- 0.000 07	0.1058
1.521 0E-4	0.0041 0	1.16 95	0.0038	- 0.000 26	0.0631
2.103 6E-4	0.0048 8	1.06 83	0.0055	0.000 35	0.0669
4.037 6E-4	0.0118 6	1.27 44	0.0119	0.000 05	0.0043
5.602 0E-4	0.0186 4	1.44 36	0.0180	- 0.000 67	0.0362
6.201 1E-4	0.0199 4	1.39 50	0.0205	0.000 55	0.0277

From the table 2, we can see that except for the first data, the error of other data is between 0.43-6.69%.

4. Conclusion

In this paper, the vapor-liquid equilibrium data of bromine-brine system at 10 °C and 20 °C were measured by bubble entrainment equilibrium kettle, and their Henry constants were 16.92 and 23.05 atm, respectively. In this paper, the Margules activity coefficient equation model is used to correlate the experimental data. The results are satisfactory, which fully meets the requirements of engineering design. The experimental data can be applied to the design and calculation of chemical separation process.

Acknowledgments

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