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The Thermodynamics and Kinetics on the Solvent Sublation of NiYu-juan Lü^{a*}, Wei-liang Hong^a, Yuan Gao^a, Xue-li Zhang^a, Ji-zhen Li^{b*}*a. Chemistry and Biology Department, Normal School, Shenzhen University, Shenzhen 518060, China;**b. Organic Department, College of Chemistry, Jilin University, Changchun 130012, China*

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The removal of Ni ion from an aqueous solution was carried out by solvent sublation of Ni-diacetyldioxime-sodium dodecylbenzensulphonic (sublate) into isopentanol. The ratio of surfactant to Ni-diacetyldioxime complex at 20:1 was most effective for the removal, with over 90% Ni ion removed from the aqueous solution within 1 h. The effects of electrolytes (e.g. NaCl), non-hydrophobic organics (e.g. ethanol) and pH of the solution upon the process were well studied. The removal rate was enhanced by higher airflow rates but almost independent on the volume of the organic solvent floating on the top of the aqueous column. The process of solvent sublation followed first order kinetics. A characteristic parameter, the apparent activation energy of attachment of the sublate to bubbles, was estimated to be 8.99 kJ/mol. Furthermore, the simulation of a mathematical model with the experiment data on the solvent sublation of Ni-diacetyldioxime-SDS was proved to be validated.

Key words: Solvent sublation, Ni ion, Sodium dodecylbenzensulphonic, Thermodynamics

I. INTRODUCTION

Solvent sublation, originally introduced by Sebba [1] as an improved method for the flotation of ionic-surfactant complexes, has shown promising features for removing hydrophobic compounds and ions from aqueous systems. It is one of adsorptive bubble separation techniques, in which hydrophobic compounds on bubble surface are levitated to the top of an aqueous column where they encounter a solvent layer (e.g. mineral oil, lauryl alcohol) to which the material is transferred while the bubbles move through the solvent layer. This method, with its advantages of simultaneous separation and pre-concentration, attracts a lot of attention in the field of environmental analysis and wastewater treatment [2-14].

In the present work, the removal of Ni ion by solvent sublation was studied. Physical and chemical behaviors of this process have been investigated, and kinetics and thermodynamic studies have also been carried out.

stock solution: 1.7×10^{-3} mol/L, SDS stock solution: 8.5×10^{-3} mol/L, diacetyldioxime ammonia stock solution: 2.15×10^{-2} mol/L.

B. Apparatus

The solvent sublation system was similar to what we described previously [7]. The glass column with the size of 90.0 cm \times 7.4 cm i.d was used, which contains three access ports. The bottom access acts as the outlet of the aqueous phase while the upper one is the outlet of the organic layer. The sampling of the aqueous phase was controlled by the middle access. Air bubbles were introduced into the aqueous phase from the bottom of the column with a micro porous titanium plate.

The pH meter used to prepare solutions was from Shanghai Rex Industry (Shanghai, China). UV-Visible spectra of the sample were obtained on a Unico PC2100 UV/Vis spectrophotometer (Unico Com., China).

II. EXPERIMENTAL**A. Reagents**

All chemicals other than sodium dodecylbenzensulphonic (SDS, chemical grade) were analytical grade and purchased from Shanghai Chemical Agents Factory (Shanghai, China). The solutions were diluted as necessary to prepare working standard solutions. Ni²⁺

C. Procedure

The red complex of Ni-diacetyldioxime was freshly prepared with the addition of the diacetyldioxime ammonia solution to the Ni (II) stock solution. Suitable amounts of SDS solution were added to the Ni-diacetyldioxime complex solutions and the pH value was adjusted with diluted hydrochloric acid or sodium hydroxide. When the airflow rate was stable, 250 mL of 6.8×10^{-5} mol/L Ni-diacetyldioxime with surfactant SDS complex solution was poured into the sublation column followed by the addition of 10 mL isopentanol which spread on the surface of the solution. Aqueous

*Author to whom correspondence should be addressed. E-mail: yjlv@szu.edu.cn, lijizhen11@yahoo.com

phase was taken out periodically for analysis with the UV/Vis spectrophotometer at 440 nm.

III. EXPERIMENTAL RESULTS

A. Effect of the molar ratio of SDS to Ni (II)

A series of experiments were carried out using solutions at pH 11 with different SDS to Ni (II) molar ratios while keeping the airflow rate at 75 mL/min. The effect of SDS concentration on the solvent sublation of Ni (II) is shown in Fig.1. It was found that the efficiency of separation improved with the increase of molar ratio of surfactant to Ni (II), and that the efficiency became highest at 20:1. At smaller concentration of surfactant, the removal rate was slower and the level of the residual Ni (II) was greater, presumably due to incomplete formation of Ni-diacetyl dioxime-surfactant complex. On the other hand, the removal rate was smaller and the removal efficiency became lower when the ratio was more than 20:1, presumably due to the competition of the bubble surface by the excess surfactant ion with the dye-surfactant complex.

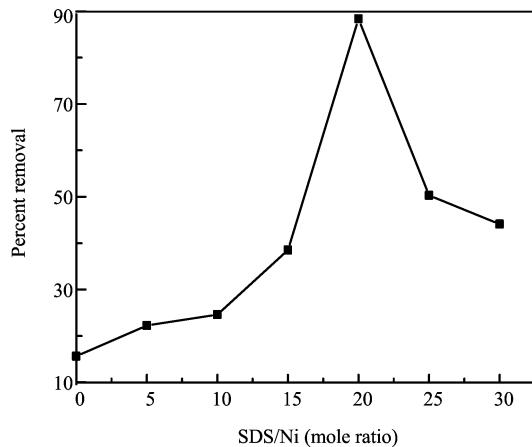


FIG. 1 Effect of SDS dose on solvent sublation, rate of air flow is 75 mL/min.

B. Effect of the volume of organic solvent

Sebba has shown that the removal efficiency is independent of the amount of the volume of 2-octanol in the case of the solvent sublation of ion-surfactant complexes from aqueous solution into 2-octanol [1]. Caballero has further draw the conclusion that the sublation efficiency is independent on the organic solvent volume only until the phase saturation by the sublate [13]. The effect of organic solvent on the solvent sublation was shown in Fig.2. It was observed that the removal efficiency went up with the increase of the solvent when the amount of the solvent was less than 6 mL. No significant improvement in removal efficiency was observed when the volume of ispentanol exceeded 6 mL in the 250 mL

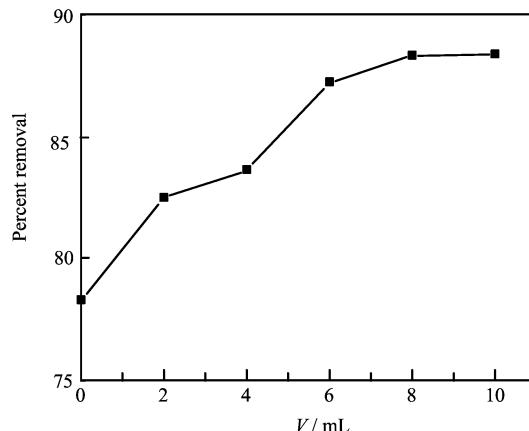


FIG. 2 Effect of solvent volume on solvent sublation, rate of air flow is 75 mL/min.

solution. The results showed that sublation was independent of the volume of organic solvent only until the saturation of the phase occurs by the sublate. Generally, mass-transfer occurs from gas bubbles crossing the aqueous-solvent interface and not from diffusion of solute across this interface. And the amount of material transferred should depend only on the amount of air crossing the interface and not on the organic volume. On the other hand, the volume ratio of the two immiscible phases is a very important parameter in liquid-liquid extraction, which is an important difference between the liquid-liquid extraction and solvent sublation. But if the organic volume used in solvent sublation is too low, the oil-water interface will be drastically disrupted at a high airflow rate and the process will lose its efficiency. The airflow rates and solvent volume should be chosen carefully in order to keep the minimal disruption of the interface.

C. Effect of pH

The study of the pH influence of the aqueous phase on the removal efficiency was carried out initially keeping a constant SDS to Ni (II) molar ratio of 20:1 and adjusting the pH by suitable addition of hydrochloric acid or sodium hydroxide solution. The effect of pH on the removal of Ni (II) complex in the process of solvent sublation is shown in Fig.3, which shows that the best yield was obtained at pH 10.7. At pH value of 7 to 8, more Ni(OH)_2 formed in the aqueous solution made against the attracted forces of SDS, which decreased the removal efficiency. At a higher pH, the more Ni-diacetyl dioxime complex produced in the aqueous solution improved the attracted forces of SDS, which increased the removal efficiency. But at the pH value of 11 to 12, more $[\text{Ni(OH)}_3]^-$ and $[\text{Ni(OH)}_4]^{2-}$ formed in the aqueous solution made against the attracted forces of SDS, which decreased the removal efficiency.

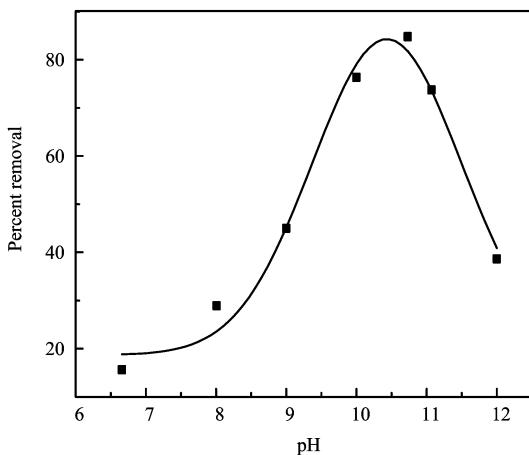


FIG. 3 Effect of pH value on solvent sublation, rate of air flow is 75 mL/min.

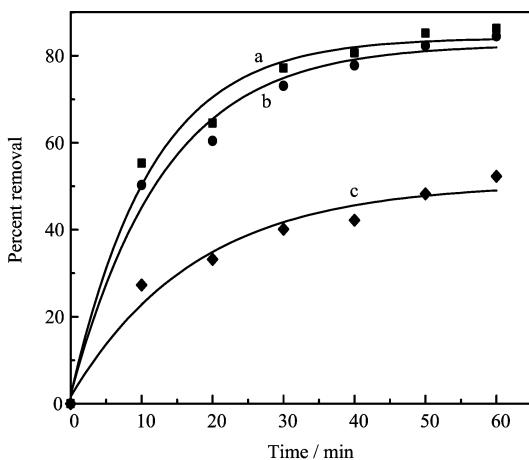


FIG. 4 Effect of mole fraction of ethanol on solvent sublation a: 0; b: 0.005; c: 0.05.

D. Effect of co-solute

The influence of various mole fractions of ethanol used as co-solute ranging from 0.005 to 0.05 upon the removal rates of Ni (II) is shown in Fig.4. The addition of ethanol decreased removal rates and the removal efficiency, which is due to the solubility of Ni (II) complex in the aqueous solution.

The effect of inorganic salt NaCl used as co-solute on the sublation of Ni (II) complex is shown in Fig.5. Increasing the NaCl concentration tended to decrease greatly the removal rate and the removal efficiency. This was attributed to an ion-pair equilibrium existed in the aqueous solution of dye-surfactant complex.



For the Ni (II) complex, A is the surfactant ion, B is Na^+ , C is the Ni (II)-diacetylidioxime complex, and D is Cl^- . Ni (II)-diacetylidioxime-surfactant complex AC and surfactant AD act as the active surface. It can

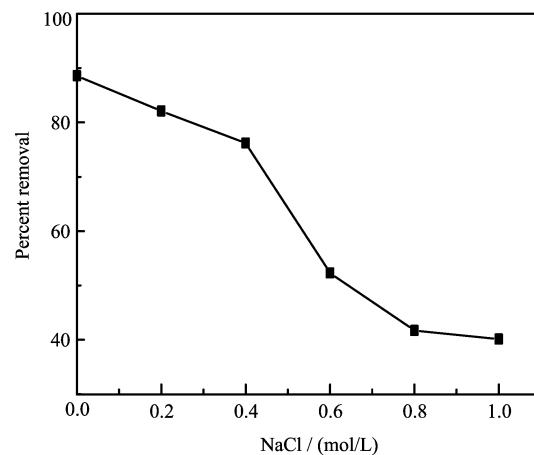


FIG. 5 Effect of NaCl concentration on solvent sublation, rate of air flow is 75 mL/min.

be seen from the equation that the increase of the salt concentration (e.g. NaCl) drove the equilibrium toward a larger concentration of BC, which was hydrophilic, and less Ni (II)-diacetylidioxime-surfactant complex (i.e. AC) existed in the aqueous phase. As a result, the rate of removal decreased.

E. The kinetics and thermodynamics of the solvent sublation

In the chemical reaction, the rate is followed by:

$$-\frac{dc}{dt} = kc^n \quad (2)$$

where c is the reactant concentration, k is the apparent rate constant, n is the order of chemical reaction. Upon the analysis of the experiment results, we found that the kinetics of solvent sublation process was obedient to the equation:

$$-\frac{dc}{dt} = kc \quad (3)$$

For the concentration of Ni-diacetylidioxime was examined by the UV, the absorbance A can represent the c . From the Eq.(3), after the integration,

$$\ln c - \ln c_0 = kt \quad (4)$$

where c_0 was the intial concentration of Ni(II), $\ln A$ was used to represent the $\ln c$. The relationship of $-\ln A$ vs. t is linear, which shows that the kinetics mechanism of solvent sublation process was consistent with the first order kinetics equation.

In the solvent sublation process, firstly the Ni (II) complex molecules and the bubbles attracted, and then the pulse forces increased, which would result in that the boundary layer is compressed and become thinner and then eclipse finally. The change of energy of this process was similar to that of the chemical reaction process [4]. Therefore we could use the Arrhenius equation

to describe the process:

$$\ln k = -E_s/RT + B \quad (5)$$

where k is the apparent rate constant, R is the common gas constant, B is the integrate constant, E_s is the solvent sublation apparent activation energy. The relationship of $\ln k$ and $1/T$ is linear, and the value of the apparent active energy can be calculated from the slope of the line. With the same concentration of Ni-diacetyldioxime-sodium dodecylbenzensulphonic solution, the experiment temperature was set at 283, 298, and 333 K. The kinetics of Ni-diacetyldioxime-sodium dodecylbenzensulphonic at different temperature is shown in Fig.6. It was observed that the rate of solvent sublation was increased with the increase of temperature. The relationship of $\ln k$ vs. $1/T$ is linear, which was shown in Fig.7. The value of apparent active energy was calculated as 8.99 kJ/mol from the slope of Fig.7.

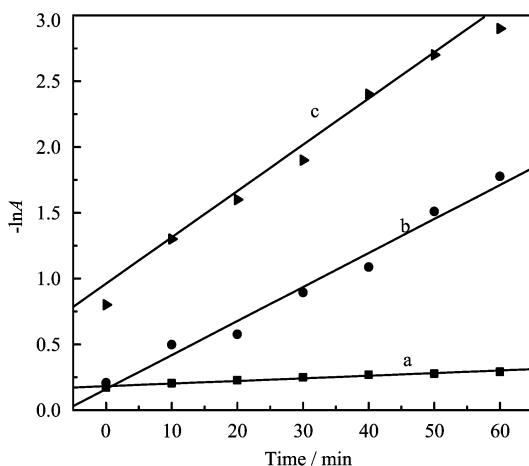


FIG. 6 Kinetics of solvent sublation at different temperatures, rate of air flow is 75 mL/min. a: 283 K; b: 298 K; c: 333 K.

IV. COMPARISON BETWEEN THEORY AND EXPERIMENT

The mathematical model of metal complex-surfactant for the solvent sublation has been described in our earlier reports [15]. In the experiment condition, the Ni-diacetyldioxime was anionic style in the solution. So the mathematical model can be applied to the Ni-diacetyldioxime-surfactant complex system. The experimental parameters such as column radius, air flow rate, concentration of Ni-diacetyldioxime complex and SDS, organic volume, and aqueous phase volume are as the real experimental data in the model. By adjusting the value of other micro parameters, the simulation results can be obtained. The simulation of experimental results for the solvent sublation of the Ni-diacetyldioxime-surfactant complex system was shown

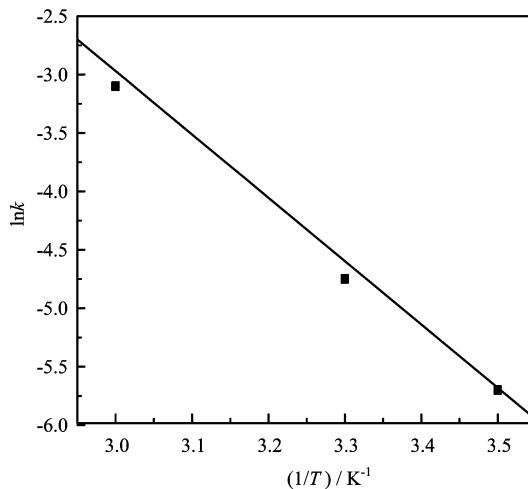


FIG. 7 Arrhenius plot of $\ln k$ vs. $1/T$, the data is obtained from Fig.6.

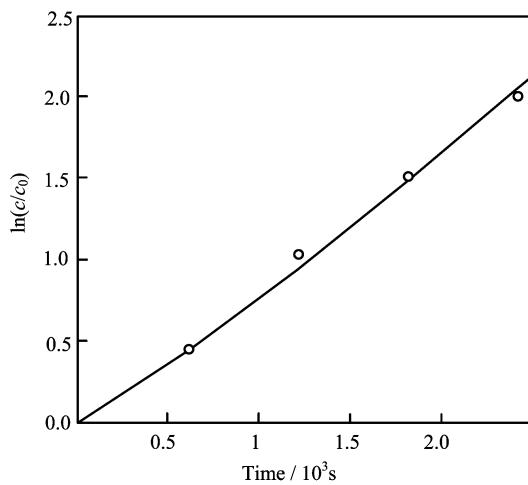


FIG. 8 Simulation of experimental results for the solvent sublation of Ni-diacetyldioxime-SDS, the line represents for the theoretical result; the circle represents the experimental result. The symbols can be referred in the literature [15]. $C_{Ni}=6.8\times 10^{-5}$ mol/L; $C_{SDS}=1.16\times 10^{-3}$ mol/L; $K_e=1000$; $K_{a1}=0.007$, $K_{a2}=0.005$ s $^{-1}$; $Q_a=75$ mL/min; $K_{l1}=0.001$, $K_{l2}=0.0025$ cm/s; $K_{ow}=800$; $V_w=250$ mL; $V_o=10$ mL; $r_c=3.7$ cm; $d_i=0.0001$ cm; $r_0=0.1$ cm.

in Fig.8. The results showed that the mathematical could be used to describe well the solvent sublation of the Ni-diacetyldioxime-surfactant complex system.

V. CONCLUSIONS

Ni (II) was removed effectively from the aqueous solution by solvent sublation of Ni-diacetyldioxime-SDS which was affected by many physical and chemical parameters, such as airflow rate, surfactant molar ratio, organic volume, pH, and co-solute. The best yield of the process is about 90%, achieved under the conditions: SDS to Ni (II) molar ratio of 20:1 at pH 10.7 in

1 h.

The solvent sublation was somewhat independent on the organic volume, provided that the organic volume is larger than a critical value, that is, disruption of organic-aqueous interface was minimal.

The co-solute ethanol impairs the solvent sublation, due to the solubility of Ni (II) complex in the aqueous. The increase of the NaCl concentration would greatly decrease the removal rate of sublation because it made the ion-equation move towards the hydrophilic product direction.

The kinetics of the solvent sublation followed first-order kinetics. The apparent activation energy of the solvent sublation process was found to be 8.99 kJ/mol.

The result of mathematical simulating experimental data of Ni-diacetylldioxime-SDS is quite satisfactory. Therefore the mathematical model can correctly describe the real solvent sublation of the Ni-diacetylldioxime-SDS. Through the investigation of the experiment and mathematical model, the adsorption process on the bubbles is the key step in the solvent sublation, and the sublation process of Ni-diacetylldioxime-surfactant ion complex obeys first order kinetic equation.

VI. ACKNOWLEDGMENTS

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