Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

The Removal of Indigo Carmine from Water by Solvent Sublation

Yujuan Lu[a]; Jizhen Liu[b]; Jie Tang[c]; Bo Wei[a]; Jianhong Liu[a]
[a] Chemical and Biology Department, Normal College, Shenzhen University, Shenzhen, P.R. China [b] Organic Chemistry Department, College of Chemistry, Jilin University, Changchun, P.R. China [c] Soils & Materials Engineering Corporation Limited, Hong Kong

To cite this Article Lu, Yujuan , Liu, Jizhen , Tang, Jie , Wei, Bo and Liu, Jianhong(2005) 'The Removal of Indigo Carmine from Water by Solvent Sublation', Separation Science and Technology, 40: 5, 1115 — 1127
To link to this Article: DOI: 10.1081/SS-200048175
URL: http://dx.doi.org/10.1081/SS-200048175

Separation Science and Technology, 40: 1115–1127, 2005
Copyright © Taylor & Francis, Inc.
ISSN 0149-6395 print/1520-5754 online
DOI: 10.1081/SS-200048175

The Removal of Indigo Carmine from Water by Solvent Sublation

Yujuan Lu
Chemical and Biology Department, Normal College,
Shenzhen University, Shenzhen, P.R. China

Jizhen Liu
Organic Chemistry Department, College of Chemistry, Jilin University,
Changchun, P.R. China

Jie Tang
Soils & Materials Engineering Corporation Limited, Hong Kong

Bo Wei and Jianhong Liu
Chemical and Biology Department, Normal College,
Shenzhen University, Shenzhen, P.R. China

Abstract: Indigo Carmine (IC, $C_{16}H_8N_2Na_2O_8S_2$), an anonic dye, was removed from an aqueous solution by solvent sublation of Indigo Carmine—Cetyltrimethyl Ammonium Bromide (CAB) complex (sublate) into 2-octanol. A stoichiometric amount of surfactant (surfactant: dye = 2 : 1) was the most effective for the removal, with over 93% IC removed from the aqueous solution in 5 min by solvent sublation. The removal rate was somewhat enhanced by higher air flow rates and almost independent of the volume of the organic solvent floated on the top of the aqueous column. The effects of electrolytes (e.g., NaCl), nonhydrophobic

Received March 3, 2004, Accepted November 14, 2004

This work was supported by the Natural Science Foundation of Guangdong Province (Grant No. 04300883).

Address correspondence to Yujuan Lu, Chemical and Biology Department, Normal College, Shenzhen University, Shenzhen 518060, P.R. China. E-mail: yujuanlv@163.net

organics (e.g., ethanol), and pH of the solution upon the process were studied. The solvent sublation process followed first-order kinetics. A characteristic parameter, apparent activation energy of attachment of the sublate to bubbles, was estimated at a value of 1.3 kJ/mol.

Keywords: Solvent sublation, Indigo carmine

INTRODUCTION

Solvent sublation, originated by Sebba (1) for ionic-surfactant complexes, has shown a promise for removing hydrophobic molecular compounds and ion-pair complexes from aqueous systems. Solvent sublation is one among the several adsorptive bubble separation techniques, wherein a hydrophobic compound is levitated on a bubble surface 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 as the bubbles move through the solvent layer (2, 3).

Solvent sublation process is different from solvent extraction. When fine gas bubbles (of very small radii in the range of 0.01–0.05 cm and in laminar flow) pass through an aqueous column (with an overlaying organic layer) containing hydrophobic compounds, because of their inherent tendency to concentrate at the air-water interface, these hydrophobic materials would be collected on the bubble surface by diffusion through the thin boundary layer surrounding the air bubble. As the bubble transits the aqueous column and moves through the organic solvent layer, the adsorbed phase gets stripped into the organic phase. Thus the solvent sublation process improves the efficiency of a bubble aeration column. Moreover, the presence of the organic solvent also reduces the eventual redispersion of the material into the aqueous column upon bubble bursting which usually occurs in conventional bubble aeration columns (4, 5).

The solvent sublation techniques have been studied by some workers. Most of these studies have been focused on the removal of organic pollutants from aqueous systems, such as alkyl phthalate, volatile chlorinate organics, dichlorobenzenes, nitrophenols, polynuclear aromatics, and chlorinated pesticides (6–11) and the emission of volatile organic compounds (volatile chlorinated organics and Toluene) to atmosphere in the solvent sublation (12, 13). Other studies are the solvent sublation of dyes in the aqueous solution, such as removal of bromophenol blue from water by solvent sublation with hexadecyl-pyridiumchlorid into iso-pentanol (14, 15) the separation of Methyl orange from Rhodamine B (16) the solvent sublation of Methyl orange–Hexadecyltrimethylammonium ion pair (17), Magaenta (a cationic dye) with sodium lauryl sulfate (18) and Direct Red and Acid Red (two anionic dyes) with hexadecyltrimethylammonium ion (19, 20).

Recently both mechanism and kinetics of solvent sublation were investigated by Palagyi et al. (21, 22). They have proposed an ionic associate formation mechanism and second-order kinetics in the separation of iodide from water by solvent sublation with CPC (N-cetylpyridinium chloride) into benzene. However the studies of both kinetics and thermodynamics of the solvent sublation are few (23–25). The removal of IC, an anionic dye, from an aqueous solution by solvent sublation was studied. For IC can cause some environmental problem, the search of a simple and effective removal method is necessary. In this paper, the kinetics and thermodynamics of the solvent sublation of IC–CAB were investigated and the efficiencies of solvent sublation with some conventional separation methods were compared. The effects of parameters, such as the air flow rates and the volume ratio of aqueous to the organic solvent, were studied, and the effects of certain co-solutes were also tested. In the solvent sublation system, 2-octanol was chosen as the organic solvent, which has a high solubility of the IC–CAB, immiscible to the aqueous phase, low-aqueous-organic solvent interfacial tension, nontoxic, and nonvolatile.

EXPERIMENTAL

The solvent sublation system was similar to that described earlier (26). The glass column was 90 cm in length and 3.7 cm in inside diameter with three access ports. A titanium plate (pore size 5–10 m) was used to introduce air bubbles into the aqueous phase. Air flow rate was measured with a soap flow meter. To obtain a representative concentration of the aqueous phase, the sample solution was withdrawn from the middle access for analysis.

Reagent-grade Cetyltrimethyl ammonium bromide (Shanghai Chemical Agents Factory, China) was used as collector without further purification. Reagent–grade Indigo Carmine, 2-octanol (Shanghai Chemical Agents Factory, China), and the other agents were all analytical grade.

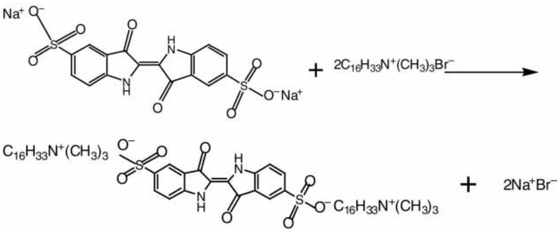
For the solvent sublation runs, firstly, CAB was added to the 2.5×10^{-5} mol/L IC solution (400 mL) to form the dye-surfactant complex, followed by co-solute, such as ethanol and NaCl. Secondly, the solution containing IC–CAB was poured into the sublation column, and 5 mL 2-octanol was added immediately, then the timer was started and the samples of aqueous solution were taken for analysis at a certain time.

The pH of the solution was measured with a pHs-3C (Shaihai Rex Industry, China). UV-visible spectra of the sample solutions were measured with a Unico PC2100 UV/Vis Spectrophotometer (Unico Com., China) at the maximum peak of 290 nm.

RESULTS AND DISCUSSION

The Effect of the Molar Ratio of CAB to IC on Solvent Sublation

The effect of CAB concentration on the solvent sublation of IC is shown in Fig.1. It was found that a 2 : 1 mole ratio of surfactant to dye gave the fastest rate of separation and the lowest residual dye concentration, with over 93% of IC being removed in 5 min. As we know that there existed an ion-pair equilibrium in the aqueous solution between the dye and surfactant molecules:



At smaller concentration of surfactant, the rate of removal was slower and the level of the residual dye was greater, presumably due to incomplete

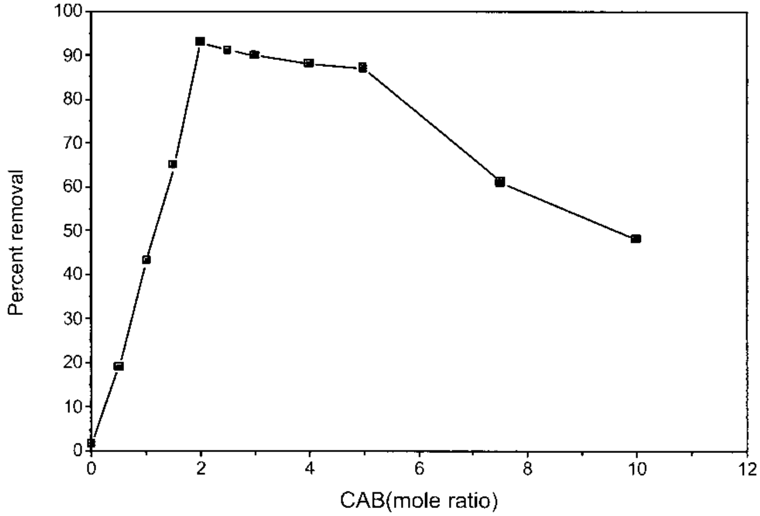


Figure 1. Effect of CAB/dye ratio dose on solvent sublation, $C = 2.5 \times 10^{-5}$ mol/L, $V_w = 400$ mL, $V_o = 5$ mL, rate of air flow = 75 mL/min, duration of air flow = 5 min.

formation of a dye–surfactant complex. But when the ratio was higher than 2 : 1, the rate of solvent sublation was smaller and the removal efficiency was slower, presumably due to the competition of the bubble surface by the excess surfactant ion with the dye-surfactant complex.

To find the effect of the surfactant itself on the solvent sublation of IC, an experiment was carried out. For the process of solvent sublation of surfactant CAB, the recovery efficiency was higher than 98%, which indicated that the surfactant was competing for the adsorbed spots of bubbles. The excess surfactant also caused the emulsification of the 2-octanol (which was observed during the solvent sublation process with a larger excess of surfactant), such that the dye-surfactant complex in the 2-octanol was constantly dispersed back into the solution and the separation efficiency decreased largely. The optimal separation efficiency with surfactant dosage at the stoichiometric amount was also observed for the solvent sublation of HTA-Acid Red (20). It was noted that this finding was quite different from the results of the solvent sublation of methylene blue and methyl orange studied by Wilson et al. and Karger et al. (15–17, 27) who found that the rate of removal of dyes increased with the increase of the surfactant concentration when it was much in excess of the stoichiometric amount. This contradiction was probably due to the difference in the formation constant of the varied complexes of surfactant-dye and may be also due to the altered molar ratio of the surfactant and dye in the complexes (20).

The Effect of Different Air Flow Rates on Solvent Sublation

The solvent sublation of IC into iso-octanol was investigated at three different air flow rates (38, 75, 150 mL/min). It was observed that the removal rates increased with the increase of air flow rates, as shown in Fig. 2. However the increase in removal rate was out of proportional to the increase of air flow rates, similar to the results by Valsaraj et al. (4). This was probably explained that with increasing air flow rates the mean bubble radius increased, thus the interfacial area per unit volume of air (which is given by 3/r) decreased, and the bubble residence time also reduced since larger bubbles had higher rise velocities. Furthermore, the axial dispersion certainly increased with the increase of the air flow rates, which would impair the performance of the sublation process.

It was observed that at higher flow rates the oil-water interface was drastically disrupted and some drops of the top layer could return to the solution. Although the increased air flow rate can improve the removal rate of solvent sublation, the removal efficiency would decrease if the air flow rate was quite high, for the air currents arise from the quite high air flow rates would disrupt the oil–aqueous interface.

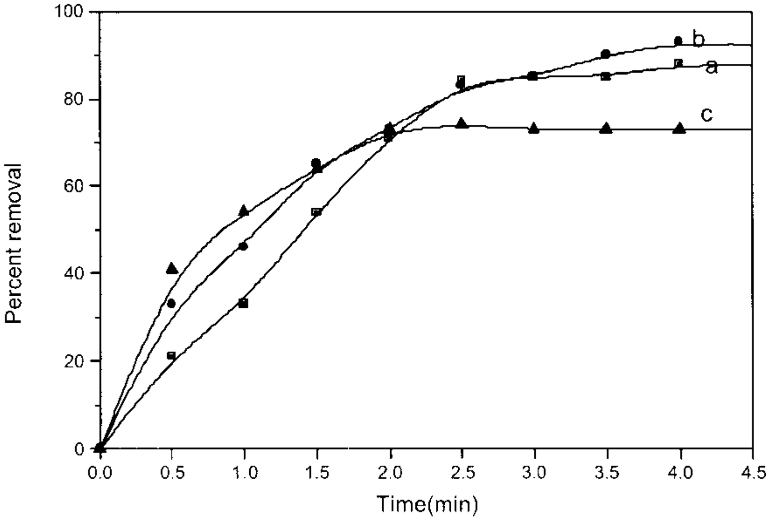


Figure 2. Effect of rate of air flow on solvent sublation, $C = 2.5 \times 10^{-5}$ mol/L, ratio of CAB to IC = 2 : 1, $V_w = 400$ mL, $V_o = 5$ mL, a: 38, b: 75, c: 150 mL/min.

The Effect of the Volume Ratio of Organic Solvent to Aqueous for Solvent Sublation

Sebba (1) has shown that in the case of the solvent sublation of ion-surfactant complexes from aqueous solution into 2-octanol, the removal efficiency is independent of the amount of the volume of 2-octanol. Caballero has made a conclusion that the sublation efficiency is independent on the organic solvent volume only until the saturation of the phase occurs by the sublate (28). We achieved the same result with these experiments, which are shown in Fig. 3. It is observed that the removal efficiency is about 77% without the organic solvent, which showed the organic solvent was not a decisive factor. No significant improvement in removal efficiency was observed when the volume of 2-octanol exceeded 5 mL in the 400 mL solution. The results showed that sublation was independent of the volume of organic solvent 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, the amount of material transferred should depend only on the amount of air crossing the interface and not on the organic volume. While in liquid-liquid extraction the volume ratio of the two immiscible phases is a very important parameter, 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 air flow

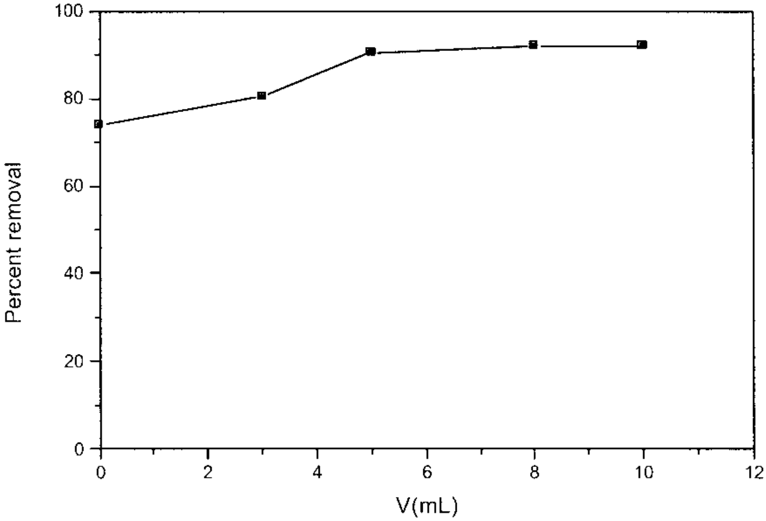


Figure 3. Effect of solvent volume on solvent sublation, $C = 2.5 \times 10^{-5}$ mol/L, ratio of CAB to IC = 2 : 1, $V_w = 400$ mL, rate of air flow = 75 mL/min.

rate and the process will lose its efficiency. Hence the air flow rates and solvent volume must be chosen to keep the minimal disruption of the interface.

The Effects of Co-solute

The influence of various mole fractions of ethanol used as co-solute upon the removal rates of IC is shown in Fig. 4. The low mole fraction of ethanol enhanced removal rates, while high mole fraction of ethanol decreased the removal rates.

The enhancement in removal rates might be due to two factors. Firstly, we noticed that addition of ethanol changed the bubble properties considerably, the number of very small bubbles was much larger than when ethanol was absent. This is a well-known effect arising from the lowering of surface tension of water, which prevents the bubbles from growing to large sizes. So these smaller bubbles provide a very large surface area per unit volume of air, which contributes to enhance mass transfer from the liquid phase to the bubbles. At the same time, smaller bubbles also have slower rise velocities (29). However, higher mole fraction of ethanol decrease the removal rate is due to the increase of the solubility of sublate.

The effect of inorganic salt NaCl used as co-solute on the sublation of IC–CAB complex is shown in Fig. 5. Increasing the NaCl concentration tended to decrease the removal rate and the removal efficiency. This was

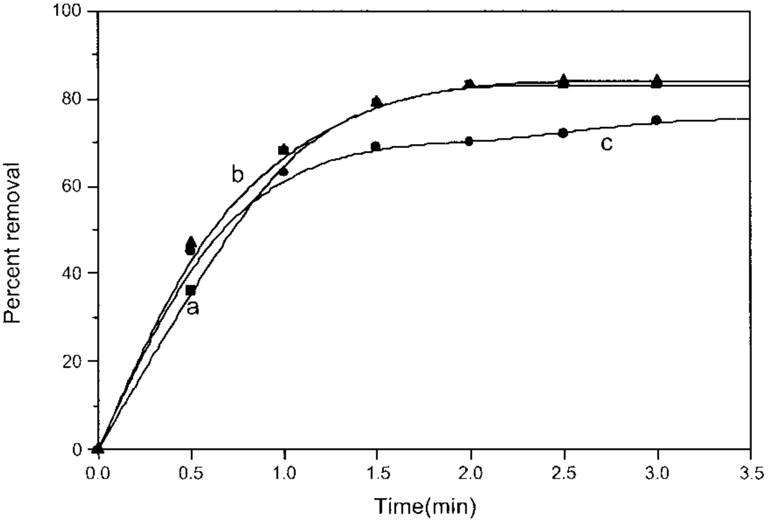


Figure 4. Effect of mole fraction of ethanol on solvent sublation, $C = 2.5 \times 10^{-5}$ mol/L, ratio of CAB to IC = 2 : 1, $V_w = 400$ mL, $V_o = 5$ mL, rate of air flow = 75 mL/min, a: 0; b: 0.005; c: 0.05.

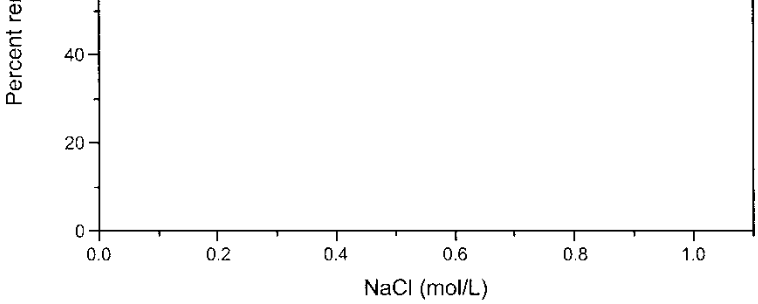


Figure 5. Effect of NaCl concentration on solvent sublation, $C = 2.5 \times 10^{-5}$ mol/L, ratio of CAB to IC = 2 : 1, $V_w = 400$ mL, $V_o = 5$ mL, rate of air flow = 75 mL/min, duration of air flow = 5 min.

attributed to an ion-pair equilibrium that existed in the aqueous solution between the dye and surfactant molecules. In aqueous solution, there existed the equilibrium:

$$CA^{+}IC^{-} + Na^{+}Cl^{-} \quad CA^{+}Cl^{-} + Na^{+}IC^{-}$$

where IC^{-} represents $C_{16}H_8N_2O_8S_2^{2-}$ (dye anionic ion), CA^{+} represents Cetyltrimethyl ammonium cationic ion. It can be seen that from the equation that the increase of the salt concentration (e.g., NaCl) drove the equilibrium toward a larger concentration of $Na^{+}IC^{-}$, which was hydrophilic, and less mole IC–CAB complex (i.e., CA^{+} IC^{-}) existed in the aqueous phase. As a result, the rate of removal decreased. The result is the same as to that of the literature (14, 15, 25).

The Effect of pH

The effect of pH on the removal of IC–CAB in the process of solvent sublation is shown in Fig. 6. The removal rate and removal efficiency of IC increased with the increase of the value of pH, and reached the most high removal efficiency at the natural pH value, then decreased with the increase of the value of pH. At the natural pH value, over 90% of IC was removed

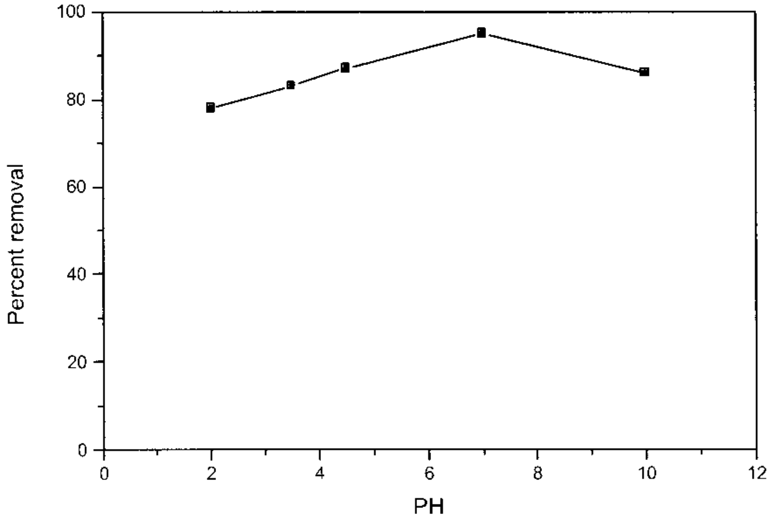


Figure 6. Effect of pH on solvent sublation, C = 2.5 × 10^{-5} mol/L, ratio of CAB to IC = 2 : 1, V_w = 400 mL, V_o = 5 mL, rate of air flow = 75 mL/min, duration of air flow = 5 min.

from the solution by solvent sublation in 5 min at the natural pH value. But at lower pH value, the removal rate and efficiency decreased.

The Kinetics and Thermodynamics of the Solvent Sublation

In the chemical reaction, the rate is followed by:

$$-\mathrm{d}c/\mathrm{d}t = kc^n \tag{1}$$

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

$$-\mathrm{d}c/\mathrm{d}t = kc \tag{2}$$

It showed that the kinetics mechanism of solvent sublation process was consistent with the first-order kinetics equation.

In the solvent sublation process, firstly the IC–CAB molecules and the bubbles attracted, and then the repulsive forces increased, which would result in the boundary layer 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). So we could use the Arrhenius equation to describe the process:

$$\ln k = -E_s/RT + B \tag{3}$$

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 IC–CAB solution, the experiment temperature was set at 278 K, 283 K, 298 K, 308 K, and 323 K. The kinetics of IC at different temperature is shown in Fig. 7. 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. 8. The value of apparent active energy was calculated as 1.3 kJ/mol by the slope of Fig. 8, which was so small that the solvent sublation process was very rapid.

CONCLUSIONS

IC was removed effectively from the aqueous solution by solvent sublation with a cationic surfactant, CAB. A stoichiometric amount of surfactant (dye: surfactant = 2 : 1) was found to be the most effective where over 93% of IC was removed in 5 min. The increased air flow rates enhance the

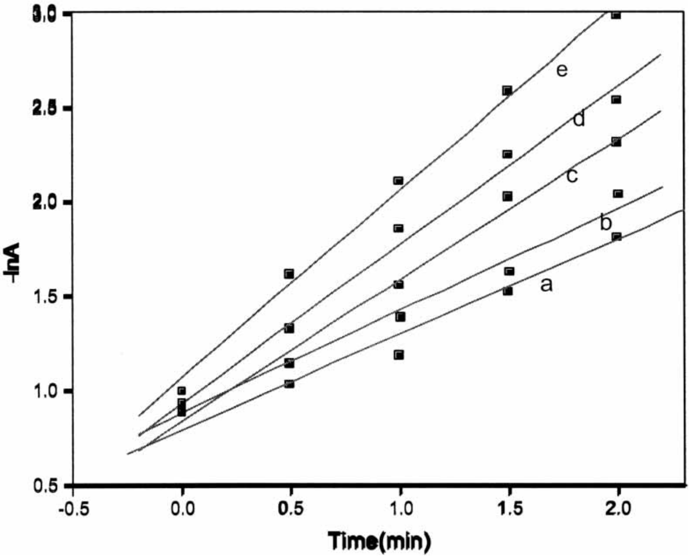


Figure 7. Kinetics of solvent sublation with different temperature, $C = 2.5 \times 10^{-5}\,mol/L$, ratio of CAB to $IC = 2:1$, $V_w = 400\,mL$, $V_o = 5\,mL$, rate of air flow = 75 mL/min, duration of air flow = 5 min, a: 278, b: 283, c: 298, d: 308, e: 323 K

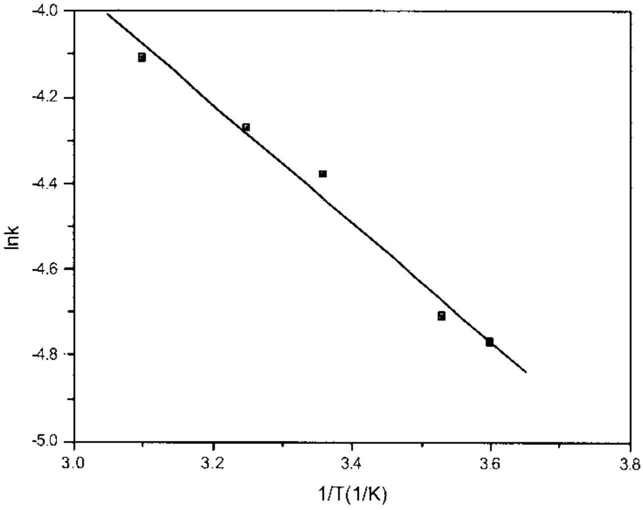


Figure 8. Curve of $\ln k$ vs. $1/T$, the data from the Fig. 7.

process of solvent sublation, provided that the bubbles size is kept small. However, at higher air flow rates, the generation of axial dispersion would compromise the efficiency of the solvent sublation.

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

Smaller fraction of ethanol (0.005) enhanced the efficiency of the solvent sublation; by contrast, larger fraction of ethanol (0.05) decreased the efficiency of removal. The increase of the NaCl concentration would greatly decrease the removal rate of sublation for it made the ion-equation move toward the hydrophilic product direction. The natural pH value is the optimal to the higher removal efficiency, but the lower pH value decreased the removal efficiency.

The kinetics of the solvent sublation was followed by first-order kinetics. The apparent active energy was put forward as a parameter of the solvent sublation and was calculated as 1.3 kJ/mol.

REFERENCES

1. Sebba, F. (1962) *Ion Flotation*; Elsevier: New York, p112–123.
2. Lemlich, R. (1972) *Adsorptive Bubble Separation Techniques*; Academic: New York.
3. Carleson, T.F. (1989) *Adsorptive Bubble Separation Process, in Surfactant–Based Separation Process*; Scamehorn, J.T. and Harwell, J.H., Eds.; Dekker: New York.
4. Valsaraj, K.T., Portor, J.L., Liljenfeldt, E.K., and Springer, C. (1986) Solvent sublation for the removal of hydrophobic chlorinated compounds from aqueous solutions. *Wat. Res.*, 20 (9): 1161–1175.
5. Lu, Y.J. and Zhu, X.H. (2001) Solvent sublation, theory and application. *Separation and Purification Method*, 13 (2): 157–189.
6. Wilson, D.J. and Pearson, D.E. (1984) *Solvent Sublation of Organic Contaminants for Water Reclamation*; Bureau of Reclamation, U.S., Department of Interior: Washington, DC, Report RU-83/6.
7. Tamamushi, K. and Wilson, D.J. (1984) Removal of refractory organics by aeration. Solvent sublation of alkyl phthalates. *Sep. Sci. Technol.*, 19 (13): 1013–1023.
8. Lionel, T., Wilson, D.J., and Pearson, D.E. (1981) Removal of refractory organics by aeration. Methyl chloroform. *Sep. Sci. Technol.*, 16 (8): 907–935.
9. Wilson, D.J. and Valsaraj, K.T. (1983) Removal of refractory organics by aeration. A fast algorithm for modeling solvent sublation columns. *Sep. Sci. Technol.*, 17 (12): 1387–1396.
10. Huang, S.D., Valsaraj, K.T., and Wilson, D.J. (1983) Removal of refractory organics by aeration. Solvent sublation of naphthalene and phenanthrene. *Sep. Sci. Technol.*, 18 (10): 941–968.
11. Valsaraj, K.T. and Wilson, D.J. (1983) Removal of refractory organics by aeration. Solvent sublation of chlorinated organics and nitrophenols. *J. Colloid Surf.*, 8 (2): 203–224.

12. Ososkov, V., Kebbekus, B., and Chou, C.C. (1996) Emission of volatile organic compounds to the atmosphere in the solvent sublation process. Toluene. *Sep. Sci. Technol.*, 31 (2): 213–227.
13. Ososkov, V., Kebbekus, B., and Chen, M. (1996) Emission of volatile organic compounds to the atmosphere in the solvent sublation process. Volatile chlorinated organic compounds. *Sep. Sci. Technol.*, 31 (10): 1377–1391.
14. Lu, Y.J. and Zhu, X.H. (2001) Removal of bromophenol blue from water by solvent sublation. *Sep. Sci. Technol.*, 36 (16): 3763–3776.
15. Lu, Y.J., Zhu, X.H., and Peng, Y.F. (2003) The removal of methyl violet from water by solvent sublation. *Separation Science and Technology*, 38 (6): 1385–1398.
16. Carger, A.B. and Karger, B.L. (1966) Use of rate phenomena in solvent sublation separation of methyl orange and rhodamine B. *Anal. Chem.*, 38 (4): 652–654.
17. Karger, B.L. and Pinfold, T.A. (1970) Studies in the mechanism of sublate removal by solvent sublation. *Sep. Sci.*, 5 (5): 603–617.
18. Sheu, G.L. and Huang, S.D. (1987) Solvent sublation and adsorbing colloid flotation of magenta. *Sep. Sci. Technol.*, 22 (11): 2253–2262.
19. Huang, J.Y. and Huang, S.D. (1991) Solvent sublation and adsorbing colloid flotation of acid red. *Sep. Sci. Technol.*, 26 (1): 59–71.
20. Cheng, M.H. and Huang, S.D. (1988) Solvent sublation and adsorbing colloid flotation of direct red. *J. Colloid Interface Sci.*, 126 (1): 346–354.
21. Palagyi, S. (1999) Kinetics of transport extraction based on solvent sublation. *Czech. J. Phys.*, 49 (2): 739–745.
22. Palagyi, S. (1998) Separation and preconcentration of ionic solutes by transport extraction based on solvent sublation. *Chem. Pap-Chem. Zvesti.*, 52 (5): 671–681.
23. Lu, Y.J., Liu, J.H., Xiong, Y., and Zhu, X.H. (2003) Study of a mathematical model of metal ion complexes in solvent sublation. *Journal of Colloid and Interface Science*, 263: 261–269.
24. Lu, Y.J. and Zhu, X.H. (2002) A mathematical model and mechanism of sublation of some surfactants. *Talanta*, 57 (5): 891–898.
25. Lu, Y.J. and Zhu, X.H. (2002) A mathematical model and mechanism of sublation of dye-surfactant ion complexes. *Analytical and Bioanalytical Chemistry*, 374 (5): 906–914.
26. Lu, Y.J., Wang, Y.S., Xiong, Y., and Zhu, X.H. (2001) Study on the kinetics and thermodynamics of surfactants in solvent sublation. *Fresen. J. Anal.Chem.*, 370 (8): 1071–1076.
27. Womack, J.L., Lichter, L.C., and Wilson, D.J. (1982) Removal of refractory organics by aeration. Solvent sublation of methylene blue and methyl orange. *Sep. Sci. Technol.*, 17 (7): 897–924.
28. Caballero, M., Cela, R., and Perez-Bustamante, J.A. (1990) Analytical applications of some flotation techniques–a review. *Talanta.*, 37 (2): 275–300.
29. Levich, V.G. (1962) *Physicochemical Hydrodynamics*; Prentice Hall: Englewood Cliffs, NJ, p.434.