Temperature and Salting out Effects on Nicotine Dissolution Kinetics in Saline Solutions

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ABSTRACT: The dissolution rate of nicotine in aqueous solutions of sodium chloride (NaCl) was investigated at room temperature and 70 °C by quantitatively visualizing the shrinkage rate of microscopic nicotine droplets. Four different salt concentrations were used: 15 wt % (3.0 M), 20 wt % (4.3 M), 25 wt % (5.7 M), and the saturation NaCl concentration of 26 wt % (6.0 M). These results, together with the Epstein–Plesset mathematical model, provided estimates of nicotine’s diffusion coefficient in the NaCl solutions. At room temperature, the dissolution rate of nicotine and diffusion coefficients decreased with increasing NaCl concentration, and below 15 wt %, the dissolution kinetics were too fast to measure accurately via optical microscopy. At the higher temperature of 70 °C, nicotine’s dissolution rate showed a decrease for 15 and 20% NaCl. However, at near-saturation 25% NaCl, nicotine’s dissolution rate did not exhibit significant change for the two temperatures, and for 26%, dissolution was higher at 70 °C than at room temperature.

INTRODUCTION

Nicotine (Figure 1) is widely present in tobacco products, and recently, a continuously increasing means of nicotine consumption has been in the form of electronic cigarettes (e-cigarettes; ECs). An extremely toxic alkaloid, nicotine, is completely soluble in water at temperatures that are lower than 60.8 °C and therefore can be easily transported from waste to groundwater, possibly compromising the environment and human health. Waste compounds from tobacco products such as nicotine and cotinine (tobacco byproduct) are found in solid-waste landfills and dumps, and these compounds have been classified as contaminants of emerging concern. Nicotine and related products can still persist in treated wastewater, and for conventional purification processes of drinking water, the removal efficiencies are 94% for cotinine and 79% for nicotine. Even with advanced purification treatments, these compounds cannot be completely eliminated from water, which means that nicotine can potentially contaminate water available for consumption. Therefore, knowledge of nicotine’s physicochemical behavior and properties will be helpful in understanding and predicting its environmental fate and transport. Related previous studies for the purification/recovery of water from nicotine have used organic solvents such as toluene, kerosene, and hexane in the widely applied liquid–liquid extraction process. To avoid the use of organic compounds, alternative methods such as adsorption, microbiological degradation, extraction by hydrophobic ionic liquids, and two-phase systems with hydrophilic ionic liquid and inorganic salts have also gained attention. Use of inorganic salts to separate/extract nicotine is a more sustainable treatment, and several related studies have dealt with the thermodynamics of nicotine dissolution. Davies and Gillard studied the solubility loop of nicotine in water, and Lopes et al. investigated the phase separation of nicotine from water—salting out effects—in nicotine aqueous solution in the presence of inorganic salts. In Lopes et al., sodium chloride was used as the inorganic salt, and liquid–liquid equilibria of the ternary solutions (nicotine + water + salts) were determined. The current paper is the first study on the kinetics of nicotine dissolution, focusing on dissolution rates of

Figure 1. Structure of nicotine.
microscopic nicotine drops in aqueous solutions of different NaCl concentrations at room temperature and 70 °C.

Different approaches to quantify dissolution rates have been discussed such as measurement of the size of individual drops.20 Chen et al. used video microscopy to measure the dissolution rate of nonionic surfactant drops in water.21 In the present paper, the dissolution rate of nicotine was visualized and quantified within cylindrical, thin-walled glass capillaries microscopically. A unique capillary-pulling technique that allows very clear imaging of microscopic objects, like different kinds of droplets such as water, ethanol, and sulfuric acid undergoing reaction, has been developed in our laboratory and has elucidated several key reaction and transport processes, especially in acid neutralization by lubricant oils.22–26 Fu et al.

introduced high-temperature capability to this technique by coating the capillary with an ITO (indium tin oxide) film that acted as a thermal jacket when electrical current passed through it,24 and in the present paper as well, we are using this technique for high-temperature experiments.

**RESULTS AND DISCUSSION**

Nicotine was injected into the capillary that was filled with NaCl solution by using a specially pulled injection micro-pipette with an inside diameter of 30–40 μm. Snapshots of the dissolving drop of nicotine in 20% NaCl solution at room temperature, taken every 10 s, are depicting nicotine’s dissolution in Figure 2.
Triplicate experiments were conducted for each salt concentration, and because the measurable horizontal and vertical dimensions of the drop are not identical, the transient characteristic drop length chosen to report is its perimeter, \( P(t) \). In Figure 2, the perimeter is shown to have shrunk from a \( P_0 = 334 \) \( \mu \)m (average diameter = 105 \( \mu \)m) to a \( P = 89 \) \( \mu \)m (average diameter = 30 \( \mu \)m) within 140 s. The time dependence of the relative drop shrinkage, \( P/P_0 \), for all four NaCl concentrations of the nicotine-drop dissolution experiments is shown in Figure 3.

Nicotine drop dissolution rate in deionized water was instantaneous, the reason being that, in the absence of salt, nicotine is completely soluble in water at room temperature.3 Salt concentrations lower than 15% were also tested and were found to be very fast, almost instantaneous, and therefore are not reported in Figure 3. NaCl (26.5%) is the saturation salt concentration at room temperature and thus was chosen as the highest NaCl concentration in the experiments. It should be noted that as nicotine diffused into the surrounding NaCl solution, water also diffused into the nicotine drop, much more so at the beginning of the experiment when the drop was totally devoid of water. This may explain the drop shrinkage rate being lower at the beginning and higher at later times, especially for concentration of 25 and 26.5% NaCl, when nicotine dissolution was slower. This is seen to a lesser extent for concentrations 15 and 20% in Figure 3, with slightly curved lines. In Figure 3, for nicotine drop shrinkage to \( P/P_0 = 0.2 \), it took approximately 39 s in 15% saline, 145 s in 20% saline, 800 s in 25% saline, and 1000 s in 26.5%. With increasing NaCl concentration, the nicotine droplet shrinkage rate decreased, which is because of increase in interfacial tension27 and to salting out effects.28 Salting out effects play an important role in decreasing the dissolution rate and solubility of nicotine.19 Previous Fourier transform infrared studies and ab initio calculations29 have shown that when nicotine interacts with water, hydrogen bonding to the pyrrolidine nitrogen occurs, with an approximate 10:1 ratio of pyridine/pyrrolidine complex of nicotine. In the presence of NaCl, the nicotine–water hydrogen bonding is weaker than the ionic bonding of the salt ions with water, therefore when salt concentration increases, the water available to interact with and dissolve nicotine will decrease.

Dissolution rates of nicotine droplets showed a decrease at the higher temperature of 70 °C for most salt concentrations. For 20% NaCl, it took 330 s for the nicotine droplet of Figure 4 to shrink from \( P_0 = 325 \) \( \mu \)m (average diameter = 107 \( \mu \)m) to \( P = 40 \) \( \mu \)m (average diameter = 23 \( \mu \)m). This was likely caused by two factors that accompany raises in temperature, one of them being decreased hydrogen bonding30 and the other a raise in interfacial tension.57

The solubility diagram of nicotine is a loop,18 which contains lower and upper critical temperatures of miscibility; Donahue and Bartell indicated that the interfacial tension of the water–nicotine system increased with increasing temperature in the region where miscibility decreased with increasing temperature.14 However, as the temperature approaches the upper critical solution temperature, the interfacial tension decreases and naturally becomes zero at the upper critical temperature.31 This explains the fact that at 70 °C, with accompanying increased interfacial tension,32 there was reduced dissolution of nicotine into the bulk aqueous solution. The results of Figure 5 show that the dissolution rate of nicotine was slower at 70 °C for NaCl concentrations of 15 and 20% than at room temperature; however, there was no sizeable difference for nicotine’s dissolution in 25% NaCl between the two temperatures. The dissolution rate in 26% NaCl was slower at the lower temperature, probably due to the fact that addition of NaCl shifts the critical temperatures,19 reinforced by ref 27 that states: “1 g mol/L of NaCl shifts critical temperature of miscibility to 22.5 °C.” A shift in the solubility loop at 26% NaCl may cause the temperature of 70 °C to be in the positive temperature coefficient region where interfacial tension decreased with increasing temperature and the dissolution rate of nicotine increased.

**Nicotine’s Diffusion Coefficients.** The kinetics of nicotine dissolution can lead to estimates of diffusion coefficients of nicotine in different NaCl-concentration aqueous solutions. This can be achieved based on the Epstein–Plesset diffusion model of a liquid droplet dissolving in a secondary liquid phase.33,34

\[
dR \over dt = -DC \frac{1}{\rho} \left( \frac{1}{R} + \frac{1}{\sqrt{\pi Dt}} \right)
\]  

where \( R = R(t) \) is the droplet radius at time \( t \), \( D \) is the diffusion coefficient, \( C_0 \) is the initial concentration in the bulk \( ( r > R ) \), \( C_c \) is the saturation concentration, and \( \rho \) is the density of the droplet. Because in our experiment \( t = 0 \) when the droplet is formed in an aqueous bulk devoid of nicotine, the initial concentration \( C_0 \) is zero, and the equation can be simplified and rearranged to

\[
\sqrt{\pi} \frac{dR}{dt} = -DC \left[ \frac{\sqrt{t}}{R} + \frac{1}{\sqrt{\pi D}} \right]
\]  

which may be written in terms of the perimeter \( P = P(t) \) as

\[
\sqrt{\pi} \frac{dP}{dt} = -DC \left[ 4\pi^2 \frac{\sqrt{t}}{P} + \frac{2\pi}{\sqrt{\pi D}} \right]
\]  

Based on eq 3, a plot of \( \sqrt{\pi} P^2 \) vs \( \sqrt{\pi} \frac{dP}{dt} \) (Figures 6 and 7) with slope \( -4\pi^2 DC_0 / \rho \) and intercept \( -2\sqrt{\pi} C_0 / \rho \) will reveal values for \( D \).

Diffusion coefficients were obtained by taking average of three independent experiments, as shown in Table 1.

It should be noted that diffusion coefficients decreased with increasing temperature, which appears contrary to the usual
behavior of diffusion coefficients increasing with temperature, according to an Arrhenius behavior. However, temperature changes may also give rise to other factors that will have the opposite effect, for example, Guo et al. have reported that ferrocene molecules could diffuse faster in ionic liquids mixed with CO₂ at lower temperatures but higher pressures because of the higher solubility of CO₂.35 Based on our earlier discussion of interfacial tension effects, decreasing diffusion coefficients of nicotine may cause by increasing interfacial tension with temperature increase.31 In previous research,
Bagalkot and Hamouda indicated that for CO₂ diffusing into a hydrocarbon drop in a high-density CO₂ system, diffusion coefficient increased with pressure because of lower interfacial tension, which assisted mass transfer of CO₂. For the first three concentrations, the lower diffusion coefficients as temperature decreased may be explained via decreases in interfacial tension increased.

It should be noted that the above analysis assumes that only the droplet dissolves into the surrounding liquid, without taking into account the diffusion of the surrounding liquid (water) into the drop (nicotine). Furthermore, the Epstein–Plesset diffusion model does not consider any phenomena other than diffusion, for example, the roles played by Laplace pressure and other components present, like NaCl in the case of our experiments. Besides, two variables (D and C) are unknown and affected by each other during calculation. Therefore, the extracted diffusion coefficients in this work may not be accurate. To narrow down and compare the errors, we can use the only C values from literature that correspond to some of our experiments: at room temperature, C is about 0.59 M for 15% NaCl, and at 70 °C, C is about 0.353 M for 15% NaCl and 0.239 M for 20% NaCl. Using these C values, diffusion coefficients can be obtained by directly solving eq 3 as: 260 \× 10^{-12} m^2/s (room temperature and 15% NaCl), 139 \times 10^{-12} m^2/s (70 °C and 15% NaCl), and 99 \times 10^{-12} m^2/s (70 °C and 20% NaCl). Comparing these diffusion coefficients with those in Table 1, differences can be seen, leading to the need for developing a more sophisticated mathematical model that will account for factors other than simple dissolution and diffusion of one phase into another.

**CONCLUSIONS**

Addition of inorganic salts and temperature raises being methods to separate nicotine from water, this paper has shown that nicotine’s dissolution rates decrease with increasing concentration of NaCl or temperature in the region where the temperature coefficient of miscibility is negative. However, increases in both NaCl concentration and temperature may also lead to a negative effect of separation because nicotine in a 26.5% NaCl solution had the slowest dissolution rate at room temperature but had a higher dissolution rate at 70 °C. At lower salt concentrations (15 and 20%), a slower dissolution rate was exhibited at 70 °C than at room temperature, and 25% NaCl produced similar dissolution rates at room temperature and 70 °C. Even though estimates of nicotine diffusion coefficients in different NaCl concentrations may be obtained via the Epstein–Plesset model, the latter may need to be improved upon for furnishing reliable values.

**EXPERIMENTAL SECTION**

**Material.** Nicotine (≥99%) and sodium chloride (≥98%) were purchased from Sigma-Aldrich. Deionized water was obtained from a Barnstead E-pure purifier, and the resistivity of the water was 18.2 MΩ cm. ITO, one of the most widely used transparent and conductive material, was purchased from Chemat technology. Microcapsillaries and micropipettes were pulled from Microcaps (Drummond Scientific) using a Narashige PB-7 puller. Software XCAP was used to measure the droplet diameter.

**Methods.** To prepare a cylindrical, thin-walled capillary for microscopically viewing the nicotine drop inside it, a glass tube was pulled with a micropipette puller so as to achieve a middle-part diameter of ~200 μm. For high-temperature experiments, sol–gel process was used to coat an electrically conductive film that acted as a thermal jacket for the capillary. For the experiments presented in this paper, the high-temperature capillaries were made by dipping them into the ITO precursor solution and pulling them back into the air at a rate of 7 cm/min. The coated substrate was heated at 530 °C for 30 min after each dipping. By repeating the above procedure until electrical resistance was below 100 kΩ, the final resistance of capillaries was reduced to 30–50 kΩ after allowing the coated capillaries to sit at room temperature overnight.

A photograph of the assembled high-temperature capillary microreactor is shown in Figure 8, with the lubricant-filled capillary fixed on a plastic holder. The two copper foils attached to the capillary served for supplying ac electrical current to the capillary-coated ITO film, which increased the temperature inside the capillary to a desired value almost instantly.

**Figure 8.** Photograph of a high-temperature capillary microreactor. (Photograph courtesy of Chia-yu Chen).

**Figure 9.** Temperature–voltage working curve (for 30–40 kΩ resistance).
A K-type fine-wire thermocouple was used to measure the temperature inside the capillary. To obtain calibration of temperature versus applied voltage, capillaries were filled with substances of very different boiling points, and voltages were recorded when boiling took place for ethanol (BP = 78 °C), water (BP = 100 °C), and n-hexadecane (BP = 287 °C). Once the thermocouple had been calibrated, the complete relationship between temperature and voltage was obtained and is shown in Figure 9.

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