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Organic deliquescence: organic vapor-induced dissolution of molecular salts†

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This report demonstrates organic vapor-induced dissolution of several molecular salts (*i.e.*, organic deliquescence), like water vapor-induced deliquescence. Systematic experiments indicate that appropriate organic deliquescent responses to volatile organic compounds can be designed according to the principle, "like dissolves like". The phenomena will be useful for developing agents to collect various volatile organic compounds.

The importance of interactions between solid materials and gaseous molecules has recently been highlighted in the context of (i) CO_(g) adsorption or H₂ storage using metals,^{1–8} (ii) vapor molecule detection in the environment,^{9–17} and (iii) uptake and catalysis involving gaseous molecules, *e.g.*, CO₂ reduction,^{18–22} despite the limited interactions allowed by the extremely low density of gaseous molecules ($\sim 10^{-3}$ times the density of liquids).

Deliquescence is an essential phenomenon that relies on interactions between solid chemicals and water vapor;^{23–25} specifically, solid chemicals absorb enough water vapor to become dissolved in an aqueous solution. This behavior has been observed as far back as ancient times when table salt containing nigari (magnesium chloride) hardened under high humidity. To date, deliquescence has been reported for various chemicals (*e.g.*, citric acid, sodium hydroxide, potassium carbonate, magnesium chloride, calcium chloride), which capture water vapor from the atmosphere and spontaneously create aqueous solutions in humid conditions. For some water-soluble chemicals, simply increasing the environmental humidity can promote deliquescence (observed as the solid \rightarrow liquid change) without heating or adding liquid. This phenomenon can be exploited to capture atmospheric water vapor, and calcium chloride (CaCl₂) has been employed as a chemical desiccant. However, to our knowledge, deliquescence involving organic vapor has not yet been reported, despite increased efforts to remove environmental volatile organic compounds (VOCs) in recent decades.^{26–30} This may be because there are significantly lesser amounts of organic vapors in human living environments than there are water vapors in humid conditions. This report describes organic vapor-induced deliquescent phenomena involving several solid molecular salts

that undergo solid \rightarrow liquid changes in response to organic vapors. These changes were systematically investigated by varying the solid molecular salts and organic vapors in a closed system and confirmed to result from deliquescent phenomena, rather than melting (by heating) or dissolution (by adding liquid). Moreover, the organic vapor-induced deliquescence could be designed by considering the molecular structural relationship between the salt and the target organic vapor, thereby highlighting the generalizability of this behavior. Thus, deliquescent phenomena (previously believed to occur only with water vapor) were observed and designed with various organic vapors; these findings will be useful for treating environmental VOCs.

Fig. 1a shows the setup for organic vapor exposure experiments (further details in the ESI†). Briefly, ~ 0.5 mg of powdered salt on a thin glass plate was placed onto blue cobalt glass, and 1.0 mL of organic solvent was divided among two small reservoirs in a 9 cm Petri dish. After isolating the system by adding a top glass cover sealed with grease, changes to the physical state of various salt powders were monitored under exposure to various organic vapors at room temperature. In a typical control experiment (*i.e.*, water vapor-induced deliquescence of CaCl₂; Fig. S1 and Movie S1†), the CaCl₂ powder clearly changed to an aqueous solution *via* deliquescence.

First, we evaluated the deliquescence of tetrabutylammonium hexafluorophosphate ((*n*-Bu₄N)PF₆), which is a common organic salt that is soluble in organic solvents and widely used as an electrolyte in electrochemical experiments. When chloroform (CHCl₃) widely used as a solvent in chemical industry was employed as the organic solvent, the (*n*-Bu₄N)PF₆ powder gradually changed to liquid, while the amount of CHCl₃ in the Petri dish reservoirs decreased (Fig. 1b and Movie S2†). This solid \rightarrow liquid change was similar to the water vapor-induced CaCl₂ deliquescence under analogous conditions. After three hours of CHCl₃ vapor exposure, the entire area around (*n*-Bu₄N)PF₆ became liquid, and its weight increased by 1.8 times, thus confirming that the solid \rightarrow liquid change was not caused by

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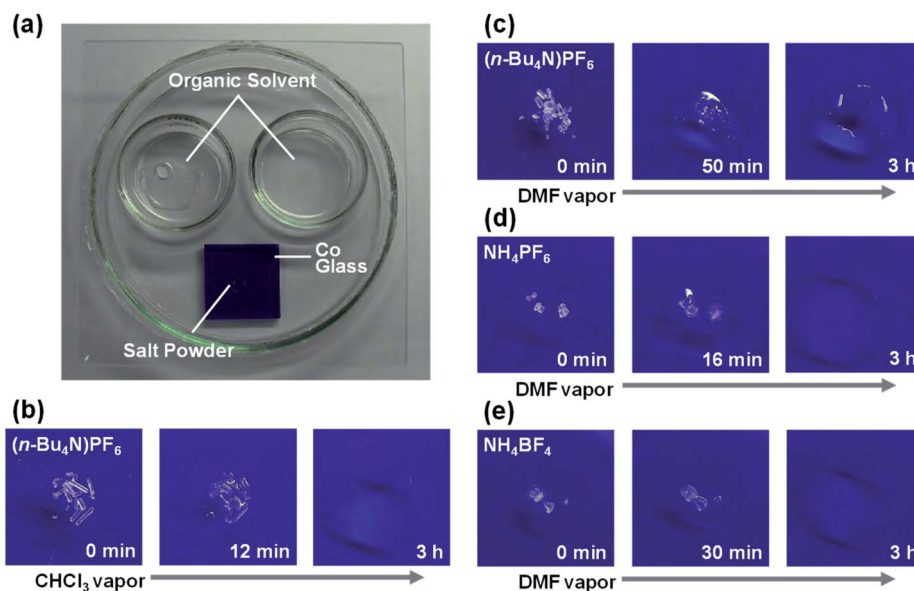


Fig. 1 Organic deliquescence. (a) Experimental setup for organic vapor exposure in a sealed system. Organic deliquescent behaviors of (*n*-Bu₄N)PF₆ (b and c), NH₄PF₆ (d), and NH₄BF₄ (e) exposed to CHCl₃ (b) or DMF (c–e) (Movies S2–S5,† respectively).

melting. These results were highly reproducible ($p < 0.05$), although the phase-change initiation depended on the experimental conditions (*e.g.*, crystal size, organic solvent surface area). Thus, CHCl₃ was transferred from the reservoirs to the (*n*-Bu₄N)PF₆ powder, allowing (*n*-Bu₄N)PF₆ to dissolve in CHCl₃ owing to its high solubility (0.64 g (*n*-Bu₄N)PF₆ can be dissolved in 1.0 g CHCl₃ at 20 °C). These results confirmed that deliquescent phenomena could be induced by an organic solvent (organic deliquescence). However, such organic deliquescence was not observed for inorganic salts that were insoluble in CHCl₃ (*e.g.*, ammonium hexafluorophosphate (NH₄PF₆), ammonium tetrafluoroborate (NH₄BF₄), sodium chloride (NaCl)).

Next, analogous experiments were performed using *N,N*-dimethylformamide (DMF), which is used in large quantity for wet spinning and is a common polar organic solvent that can dissolve various types of salts. With DMF (Fig. 1c–e and Movies S3–S5†), solid → liquid changes were observed for organic ((*n*-Bu₄N)PF₆) and some inorganic salts (NH₄PF₆ and NH₄BF₄), but not for NaCl and not for any salts without DMF (example control experiments with NH₄PF₆ shown in Fig. S2†). After three hours of DMF vapor exposure, the weights of the salt components increased by 3.1, 6.9, and 7.2 times for (*n*-Bu₄N)PF₆, NH₄PF₆, and NH₄BF₄, respectively. Repeated experiments showed that $p < 0.05$ for the solid → liquid change of (*n*-Bu₄N)PF₆, and the sample weight of (*n*-Bu₄N)PF₆ under DMF vapor exposure was monitored over time by constructing a closed system in an analytical balance. The DMF vapor concentration was also monitored with a VOC monitor connected to the closed system. When the DMF vapor concentration exceeded $\sim 4 \times 10^3$ ppm (~ 0.4 kPa), the solid → liquid change was initiated (Movie S6†). Then, the sample weight clearly increased after the DMF vapor concentration reached $\sim 5 \times 10^3$ ppm (~ 0.5 kPa) corresponding to the saturation vapor pressure.^{31–33} Therefore, the observed

phenomena were also attributed to organic deliquescence. To clarify the differences between the tested molecular salts, their solubilities in DMF were determined: 1.27 g (*n*-Bu₄N)PF₆, 1.07 g NH₄PF₆, or 0.29 g NH₄BF₄ could be dissolved in 1.0 g DMF at 20 °C, whereas NaCl was insoluble in DMF. In general, organic deliquescent phenomena were observed with organic and inorganic ammonium salts that were soluble in the target organic solvent. When using a polar organic solvent (DMF), the amount of transferred (*i.e.*, collected) solvent was much greater than the amount of salt. This is an important feature of organic deliquescence, compared with conventional adsorption phenomena. To evaluate organic deliquescence by non-ammonium salts, similar experiments were performed using tetraphenylphosphonium bromide ((Ph₄P)Br) with CHCl₃ (solubility = 0.29 g g^{−1}) or DMF (solubility = 0.25 g g^{−1}) at 20 °C; solid → liquid changes were observed in both cases (Fig. 2a, b and Movies S7, S8†). After three hours of vapor exposure, the weight of the (Ph₄P)Br component increased by 2.0 or 1.7 times in the presence of CHCl₃ or DMF, respectively. Thus, organic deliquescent phenomena can occur with non-ammonium salts (*e.g.*, (Ph₄P)Br) that are soluble in organic solvents.

The observed organic deliquescence involved three processes (Fig. 3): (i) the evaporation of pure organic solvent generates organic vapor, which adsorbs onto the surface of the salt powder; (ii) some salt dissolves, thereby creating a small amount of saturated organic solution on the powder surface; (iii) because the vapor pressure is depressed in the saturated organic solution, the continuous supply of organic vapor (from evaporation) is condensed into the organic solution, thus allowing further dissolution of the salt. This condensation cycle continues until the vapor pressure of the highly-concentrated organic solution becomes comparable to that of the atmosphere. Meanwhile, evaporation reduces the amount of organic solvent in the reservoirs, and the organic vapor is transferred



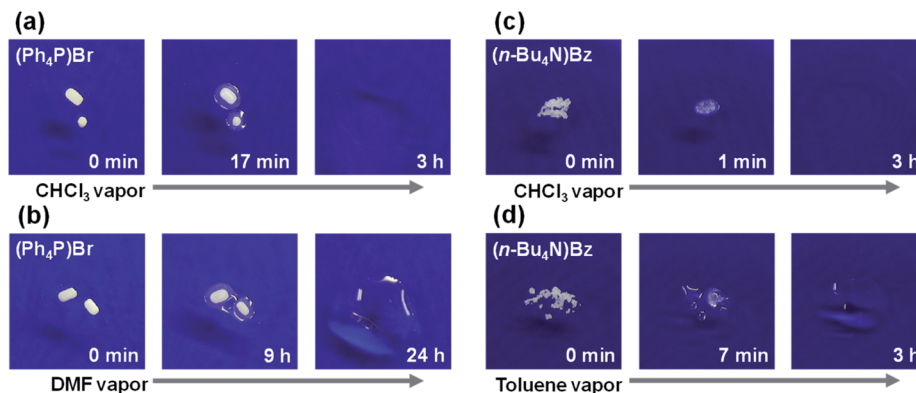


Fig. 2 Organic deliquescent behaviors of (Ph₄P)Br (a and b) and (*n*-Bu₄N)Bz (c and d) exposed to CHCl₃ (a and c), DMF (b), or toluene (d) (Movies S7–S9†).

and condensed, thus increasing the amount of liquid around the salt component. The choice of molecular salt and its solubility in organic solvents are crucial factors for promoting organic deliquescence because the vapor pressure depression of the highly-concentrated solution is proportional to the molar concentration (*i.e.*, each salt molecule splits into a cation and an anion in solution, which increases ion molar concentrations and facilitates vapor pressure depression). Thus, organic deliquescence can occur with salts exhibiting high solubility in organic solvents.

Toluene used as a paint solvent is an important VOC whose emissions should be reduced; however, none of the aforementioned salts (*i.e.*, (*n*-Bu₄N)PF₆, NH₄PF₆, NH₄BF₄, (Ph₄P)Br, NaCl) exhibited organic deliquescence or solubility in non-polar toluene. Instead, based on the general rule that “like dissolves like”, tetrabutylammonium benzoic acid ((*n*-Bu₄N)Bz) was used, owing to its superior solubility in toluene (2.42 g (*n*-Bu₄N)Bz in 1.0 g toluene at 20 °C). A solid → liquid change was observed

when using (*n*-Bu₄N)Bz and toluene as the salt and organic solvent, respectively (Fig. 2d and Movie S9†), and no change was noted in the absence of toluene (Fig. S3†). After three hours of toluene vapor exposure, the weight of the (*n*-Bu₄N)Bz component increased by 1.1 times, which indicated organic deliquescence. These results confirm that (*n*-Bu₄N)Bz is suitable for organic deliquescence of toluene. The (*n*-Bu₄N)Bz salt also exhibited high solubility in CHCl₃ (2.06 g g^{−1}) and DMF (1.64 g g^{−1}), which enabled organic deliquescence in the presence of CHCl₃ (Fig. 2c and Movie S10†) and DMF vapors (Fig. S3†). After three hours of vapor exposure, the weight of the (*n*-Bu₄N)Bz component increased by 1.1 or 3.9 times when using CHCl₃ or DMF solvents, respectively.

In summary, this report elucidates the solid → liquid changes of molecular salts in response to organic vapors and provides the first experimental demonstration of organic vapor-induced deliquescence by systematically investigating various salts and organic solvents. In contrast to water vapor-induced

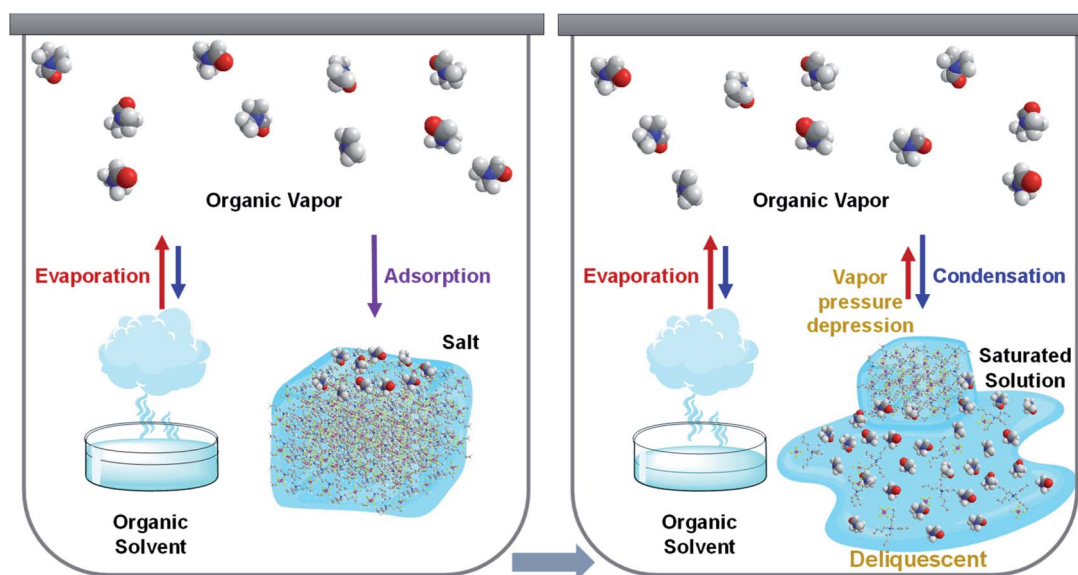


Fig. 3 Proposed mechanism of organic deliquescence.

deliquescence by common chemicals under humid conditions, organic deliquescence had not been observed because of the low concentrations of atmospheric VOCs in human living environments. The results presented herein indicate that organic deliquescence is not unusual, but rather, organic deliquescent systems can be designed to target specific solvents based on the general rule that “like dissolves like”. Considering the success of CaCl_2 as a chemical desiccant to capture atmospheric water vapor and the urgent need to remove large volumes of VOCs from facilities using organic solvents,^{26–30} organic deliquescence represents a promising approach for developing agents to collect VOCs.

Conflicts of interest

There are no conflicts to declare.

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- 31 The saturation vapor pressure of DMF is 0.49 kPa at 25 °C based on International Chemical Safety Cards.
- 32 Time dependence of powder X-ray diffraction was measured during the powder of $(n\text{-Bu}_4\text{N})\text{PF}_6$ was exposed to DMF (Fig. S4†). After the organic deliquescence was initiated, the intensity in the small angle region ($2\theta \sim 8\text{--}11$ degree) decreased in contrast to the unchanged intensity in the wide angle region. This suggests that in organic deliquescence, the disorder in nm- μm order initially occurs before the dissolution.
- 33 Even when using unsaturated DMF vapor ($\sim 80\%$), the organic deliquescence of $(n\text{-Bu}_4\text{N})\text{PF}_6$ was confirmed to occur within 30 min. In this experiment, N_2 gas containing unsaturated DMF vapor was flowed to the powder of $(n\text{-Bu}_4\text{N})\text{PF}_6$ in a box.

