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Polyelectrolyte Complexes as Desiccants: Thirsty Saloplastics

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Abstract

Desiccants or drying agents are used extensively to remove water from liquids and gasses. Many organic reactions, from the lab to the industrial scale, are sensitive to even trace amounts of water. A new class of desiccant made from complexed polyelectrolytes, PECs, is described here, exploiting the affinity of charged polymer repeat units for water. The enthalpy of hydration of dry PECs was used for the first time as a quantitative measure of PEC water affinity. Several combinations of positive, Pol^+, and negative, Pol^-, polymers were used to prepare PECs. All of these displayed significant exothermic (favorable) enthalpies of hydration, measured at room temperature using solution calorimetry. A PEC made from poly(diallyldimethylammonium), PDADMA, and poly(styrene sulfonate), PSS, was extruded into convenient shapes. This PEC was used to dry three common solvents, acetonitrile, tetrahydrofuran, and toluene, representing a range of polarities. Added water was radiolabeled with tritium to provide accurate and sensitive detection of residual water after treatment. This PEC was almost as efficient as the comparison desiccants, molecular sieve 3A and calcium sulfate, after three days of static drying, but could be regenerated at a lower temperature (120 ^oC) and shed far fewer dust particles.

INTRODUCTION

Water is often a reactive or corrosive component that must be removed from liquid or gaseous reaction streams. A great deal of expense and effort is expended in attempts to dry organic solvents prior to water-sensitive reactions such as those containing organometallic catalysts, used on a large scale for commercial production.[1] Such requirements have led to a long history of desiccants which must extract water efficiently and completely, should be regenerable (commonly by heating), nontoxic, low-cost and inert to solvents. The overall efficiency of a desiccant is determined by the speed of drying action, capacity to bind water, as well as the residual solvent water content (ppm).[2,3]

Solid desiccants[4,5] may be preferred over liquid desiccants[6, 7,8] since they are non-corrosive, have lower maintenance cost, larger surface area and offer flexible applications.[9] Silica has been employed for drying in many applications.[10] Dehydration or activation is achieved by heating between 150 °C and 400 °C.[10] Alumina, activated at 175 °C, is employed in desiccators and columns. $CaCl_2$, CaH_2 and CaO have been recommended to dry solvents such as toluene, dichloromethane, methanol, and ethanol.[11] Anhydrous calcium sulfate, made by controlled dehydration of gypsum, is commercially available as Drierite™ and is activated over the range 200 - 225 °C.[2] Desiccation using Drierite has been studied in several polar aprotic solvents, toluene,[12] dioxane and moist ether extracts.[13] However, the desiccant water capacity is limited to only 6.6 wt% which makes it suitable for solvents with low water content.[11,2] Anhydrous sodium and magnesium sulfate are other salts typically employed for drying organic solvents. In comparison to calcium sulfate, sodium sulfate has a larger water absorption capacity, but the process is slower.

Activated molecular sieves are universal desiccants composed of porous crystalline sodium or calcium aluminosilicates (zeolites).[11] They possess a system of cavities and channels of defined molecular dimensions. Type 3A molecular sieve has cavities of size about 3 Å, which is ideal for trapping water molecules of size 2.8 Å.[14] It has higher affinity for water compared to other desiccants and the water capacity is high (22 wt.%) due to the mechanism of selective sorption. Thermal activation is achieved by heating at 300 °C.[3]

Polymers, including the “superabsorbent” polyelectrolyte poly(acrylic acid) and copolymers, have been used in desiccants wheels.[15,16] Polyelectrolyte complexes or coacervates (PECs) are formed by mixing solutions of oppositely-charged polyelectrolytes.[17] In the ensuing phase separation, oppositely-charged polymer repeat units, Pol^+ and Pol^- form pairs, which have an affinity for water.[18] All properties of PECs are influenced by their water content.[19] The plasticization of PECs transforming them from brittle solids to rubbery or liquid-like materials, is the best-known example of the influence of water on properties.[20] In addition, ion mobility decreases substantially as the PEC is dried.[21] Water content is an equilibrium property, which means the state of hydration of a PEC depends on the chemical potential (partial pressure, osmotic pressure[22]) of water in the surrounding medium. Because many PECs are used in aqueous solution, the water content may as high as 30% to 80% by weight. In fact, PECs that are nominally assumed to be "dry" in ambient air contain about 10 wt% water, which means most properties measured in ambient can be quite variable.

PECs in the bulk and ultrathin "multilayer" formats are known to absorb a variety of species in addition to water. For example, Michaels used tertiary mixtures of water, acetone and a salt to swell PECs to the point of dissolution.[20] PECs are doped to various extents using simple inorganic salts, following a Hofmeister series.[23] Hydrophobic ions such as those in ionic liquids are also sorbed by PECs,[24] as are charged dyes.[25] The range of solvents absorbed by PECs is surprisingly limited. Only small, polar solvents appear to be taken up.[26]

Given its fundamental importance to PEC properties, the disposition of water in PECs has been investigated widely. Due to the confinement arising from the micro- and nano-porous structure in PEC,[27] water shows anomalous diffusive properties.[28] Using differential scanning calorimetry,[29] the water in hydrated PECs has been classified into at least three different states based on its melting temperature T_m: non-freezable, bound water (T_m non detectable); freezable, bound water (T_m below 273 K); and freezable, free water ($T_m \sim 273$ K). [28] [29] [30] The reduction in T_m for bound water can be explained by either weaker interactions of water with polyelectrolytes (PEs) or the porous structure of the PEC.[28] While both freezable, bound water and freezable, free water are not found at low PEC hydration, tightly-bound water surrounding polyelectrolyte charge pairs is thought to be non-freezable.[28]

Solution calorimetry[31,32] provides insight into the fundamental mechanisms of polyelectrolyte complexation.[33,34, 35, 36] Using isothermal calorimetry,[37, 38] the enthalpy of complexation for poly(diallyldimethylammonium chloride) PDADMAC with sodium poly(styrene sulfonate) PSSNa was determined.[39,40] The enthalpy of complexation between sodium poly(acrylic acid) (PAANa) and poly(allylammonium) (PAH) has been measured.[41] Though much is known about PECs, their properties and potential applications, they have not been used as drying agents.[20] In addition, calorimetry has been acknowledged to provide significant insight into mechanisms of complexation, but the technique has not been used to compare "hydrophilicities" among PECs.

In this work, the enthalpies of hydration for various PEC systems, including PDADMA/PSS, were measured using solution calorimetry. Enthalpic driving forces for water uptake were compared to those for component polyelectrolytes, PEs, such as PSSNa and PDADMAC, as well as to common commercially available desiccants. A solid-like PEC with high negative enthalpy of hydration was processed into a thermally stable extruded form. These materials were applied as competitive desiccants (in comparison to molecular sieve and Drierite) for drying common organic solvents. Model organic solvents with varying polarity were dosed with tritiated water to determine the rate and extent of water sorption using sensitive radiotracer methods.

EXPERIMENTAL

Materials. Poly(diallyldimethylammonium chloride) (PDADMAC, 20 wt. % in water, molar mass 400 000 – 500 000), poly(4-styrenesulfonic acid) (PSS, 18 wt. % in water, molar mass 75 000), poly(acrylic acid) (PAA, molar mass 240 000), tris(hydroxymethyl)aminomethane (TRIS) (99.9 %), potassium chloride (99%) and sodium chloride (99.5%) were from Sigma-Aldrich. Poly(vinylbenzyltrimethylammonium chloride) (PVTAC, 27 wt. % in water, molar mass 100 000) and poly(N,N-dimethyl-3,5-dimethylene piperidinium chloride) (PDDPC, 20 wt. % water molar mass 200 000 – 300 000,) were obtained from Scientific Polymer Products. Methacrylamidopropyltrimethylammonium chloride (MAPTAC, 50 wt. % in water) and 2-acrylamido-2-methylpropanesulfonate (AMPS, 50 wt.% in water), both from Sigma-Aldrich, were polymerized via free radical polymerization to obtain polymer PMAPTAC, molar mass 320 000 and PAMPS, molar mass 420 000, respectively. Poly(allylamine) (PAH, molar mass 15 000, Polysciences, Inc.), polyvinylamine (PVA, BASF Lupamin 9095 molar mass 205 000) were used as examples of polyamines. The molecular weights of polymers were mostly provided by the manufacturer and molecular weight distributions were assumed to be broad (M_w/M_n ~2). HPLC grade solvents, toluene (99.9%, Fisher Chemical), tetrahydrofuran (THF, 99.9%, Honeywell), acetonitrile (ACN, 99.9%, Fisher) were further dried through an alumina column. 0.100 M hydrochloric acid was from VWR. Molecular sieve, type 3A (8-12 mesh, 1.5 – 2.4 mm) and Drierite, (8 mesh, about 2 mm) were obtained from J.T. Baker. Tritiated water (^3H_2O, 1 mCi in 1 mL water, half-life 12.5 years, β emitter, E_{max} = 18.6 KeV) was supplied by PerkinElmer. EcoLite(+) liquid scintillation cocktail (LSC) was used as received from MP Biomedical. All solutions were prepared using 18 MΩ cm deionized water (Barnstead, E-pure).

Polymer Complexation and Extrusion. Complexes were prepared by mixing polycations and polyanions (both in 0.5 M NaCl) in equal volumes (molar ratio 1:1) simultaneously under vigorous stirring for 30 min at 60 ^oC. The precipitate was allowed to consolidate for 1 day then rinsed with copious amounts of water to remove any salt ions. Fully hydrated complexes were chopped into chunks between 5 mm and 10 mm. For extrusion, hydrated PECs were fed into a Model LE-075 laboratory extruder (Custom Scientific Instruments). For PDADMA/PSS the extruder parameters were set as follows: rotor temperature, 90 °C; header temperature 115 °C; gap space 3.8 mm; and rotor speed 60% (110 rpm). The extruded rod-shaped complex (Figure S1) was collected on a Model CSI-194T take-up reel with a 3 cm diameter drum rotating at 10 rpm. These parameters allowed the extrusion of fiber at approximately 2 g min^{-1}.[42]

Polymer Stoichiometry. For PDADMA/PSS, ^1H solution NMR spectroscopy (Bruker Avance 600 MHz) was used to determine the stoichiometry i.e., the ratio of PDADMA:PSS monomer repeat units in the complex formed. A 50-100 mg piece of hydrated complex was rinsed with three sequential aliquots of 0.25 M NaCl in D_2O over 24 h to replace H_2O with D_2O. The PEC was dissolved in 2.5 M KBr in D_2O. NMR spectra are shown in Figure S2 (Supporting Information). Integration of the peaks from the four aromatic hydrogens of PSS (between 5.5 and 9 ppm) was compared against the 16 aliphatic ^1H (between 0 and 4.6 ppm). The stoichiometry or ratio was determined to be 0.99:1.00 for PDADMA:PSS. The stoichiometries of other PECs were previously determined to be close to 1:1 by radiolabeling methods.[42]

Thermal Gravimetric Analysis (TGA). To verify the thermal stability of PDADMA/PSS, 5 mg of a well hydrated PEC of PSS/PDADMAC was dabbed with a wipe to remove excess water. Analysis was performed with a TA Instruments model Q600 TGA at a heating rate of 10 °C min^{-1} from room temp to 700 °C under Ar (Figure S3). The thermal stability of other PECs has been reported.[42]

Desiccant activation. Molecular sieve was dried to constant weight in a vacuum oven at 300 °C for 15 h. Drierite (calcium sulfate) was dried at 220 °C while extruded PECs were activated at 120 °C in a drying oven. Dried desiccants were stored in an argon-filled dry box.

Solution Calorimetry. The enthalpies of hydration for the dry desiccants were determined using a Paar 6755 Solution Calorimeter charged with 100.0 g water. Dry PEC and polyelectrolyte (PE) samples were finely ground in coffee grinder then passed through a 100 µm sieve, dried at 120 ^{o}C, and loaded into a PTFE dish in a dry box. The dish was sealed and transferred to the calorimeter. After temperature equilibration, a calorimetry measurement was initiated by plunging the sample into water using the rod actuator. Temperatures in the dewar were monitored with a Parr 6772 calorimetric thermometer. Readings were taken with a thermistor sealed in a stainless-steel probe near room temperature (Figure S4 - Figure S11). The calorimeter was calibrated by neutralizing 0.500 g tris(hydroxymethyl)aminomethane, TRIS, in 100 mL 0.100 M HCl (a slight excess). All calorimetry measurements were performed at least in triplicate and the error is presented as the standard error of the mean.

Liquid Scintillation Counting. A Charm II liquid scintillation counter with two photomultiplier tubes working in coincidence was used to count the β emissions from the tritium labeled water for 3 minutes. The counting efficiency for tritium was 25 %. A coincidence resolution time of 60 ns ensured extremely low background counts (less than 1 count per minute). Samples were mixed with 2 mL of the liquid scintillation cocktail in capped 13 x 100 mm borosilicate tubes. The water concentrations (ppm) in solvents were determined by converting the counts per minute (cpm) to ppm (Figure S12 – Figure S14) using a separate calibration curve for each solvent (Figure S15). 10 μL aliquots of labeled water each containing 10 nanocurie were used to prepare an instrument response curve over the experimental range of 0 to 1000 ppm H_2O (Figure S16). Additional solvent was added after counting to verify there was no significant quenching by solvent. The counting error is $\pm\sqrt{number\ of\ counts}$. The calibration curves (Figure S15) show a response of about 60 counts per minute (cpm) per ppm. Thus, the percent counting error, for a 3- minute count, is $\pm\frac{\sqrt{180ppm}}{180ppm}\times 100\%$. For 1000 ppm this corresponds to ±0.2% and for 1 ppm it is ± 7%.

Drying Kinetics. Solvents used to monitor the drying kinetics were first dried by passing them through an activated alumina column. 1.00 g of dried desiccant was weighed into 20 mL vials in a dry box and sealed with rubber septa. 10 mL of each solvent was transferred into the vials with a syringe. 10 μL of tritiated water was added into the sealed vials and gently agitated. At each time point, a 100 μL aliquot was transferred from the vial into 2 mL of liquid scintillation cocktail for counting.

Dust Test. The potential influence of the smallest particles ("dust") that might be released by the desiccant and remain suspended in the solvent was investigated. After 3 days of drying, 100 μL aliquots were counted and then the vial was shaken to release dust particles which, having extracted radiolabeled water, would produce additional counts in the LSC. Thus, after shaking, another 100 μL aliquot was extracted and counted as an indication of the relative amount of dust produced.

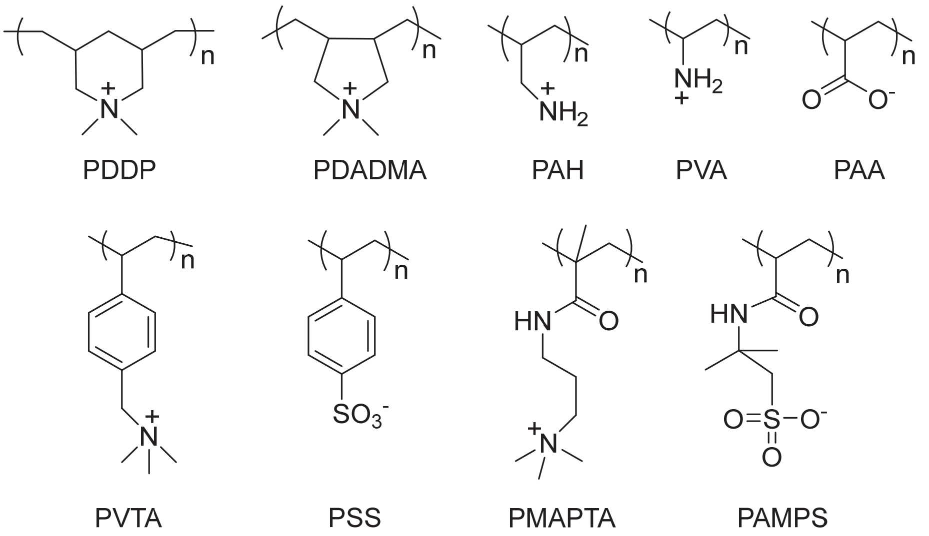
Results and Discussion

PEC Hydration Enthalpies

Water is an essential component of polyelectrolyte complexes and coacervates. Pol^+Pol^- charge pairs, whether located on synthetic or bio-polymers, have an affinity for water. With a salt-like or zwitterionic character, PECs are not swollen by most organic solvents.[26] The selectivity for water is probably a combination of the small mesh size of highly charged PECs and the strong polarity of water, driving it to the Pol^+Pol^- charge pair. This selectivity for water is a promising feature for use of PECs as drying agents.

Dry PECs are glassy and brittle, with modulii in the GPa range. For example, dry PDADMA/PSS has an elastic modulus of about 1 GPa[43] and dry PAH/PSS was reported to be somewhat stiffer (5-10 GPa).[44] When doped with water and salts,[45,46] PECs exhibit "saloplasticity" as salt breaks Pol^+Pol^- charge pairs,[47] resulting in decreased modulus and viscosity, which allows large-scale processing such as extrusion,[48] bar coating,[49] spin coating,[50] electrospinning,[51] compression,[47,52] and embossing.[53] However, the toughness of PDADMA/PSS was substantially enhanced when chains were aligned during extrusion.[43] For this reason, PDADMA/PSS PECs were extruded (using hydrated materials) without added salt. Extrusion in this way did not influence water uptake, but the PECs were less susceptible to fracture into smaller pieces, especially when completely dry, whereas unextruded PEC was very brittle. Given the desirability of separating desiccant from solvent and reducing dust (see below), toughness in PEC was considered an advantage.

Various combinations of polyelectrolytes, structures shown in Scheme 1, were used to prepare PECs. During PEC complexation, small molecule impurities are naturally excluded or washed out.[48] In addition, because the materials were nearly stoichiometric and well rinsed, counterions (that might leach out) were not incorporated into the final PECs used for drying. TGA showed that all PECs lost water above 100 °C and remained thermally stable until about 400 °C (see Figure S3).[42]



Scheme 1. Structures of Polyelectrolytes

Cations: poly(N,N-dimethyl-3,5-dimethylene piperidinium) (PDDP); poly(allylamine) (PAH); poly(vinylbenzyltrimethylammonium) (PVTA); poly(diallyldimethylammonium) (PDADMA), poly(methacrylamidopropyltrimethyl ammonium) (PMAPTA); poly(vinylamine) (PVA). Anions: poly(styrenesulfonate) (PSS); poly(acrylic acid) (PAA), poly(2-acrylamido-2-methylpropanesulfonate) (PAMPS).

General equations for hydrating dry PECs, molecular sieve and Drierite may be written as

$(Pol^{+}Pol^{-}) + nH_2O \rightarrow (Pol^{+}Pol^{-}) \bullet nH_2O$ (1)

$K_2Na_2Al_2SiO_7 + nH_2O \rightarrow K_2Na_2Al_2SiO_7 \bullet nH_2O$ (2)

$\gamma CaSO_4 + 2H_2O \rightarrow CaSO_4 \bullet 2H_2O$ (3)

The total water uptake is a function of how “activated” or dry the desiccant is at the beginning.

The ultimate (equilibrium) efficiency for extracting water from a solvent, or from a gas, depends on the free energy change of hydration $\Delta G_{hyd} = \Delta H_{hyd} - T\Delta S_{hyd}$. The more exothermic, the more efficient a potential desiccant should be in extracting water. It is assumed that entropy always favors absorption i.e., mixing of water and desiccant components. To quantitatively assess the affinity of each PEC for water, sensitive calorimetry measurements were performed to determine the enthalpy of hydration. An example of a thermogram is presented in Figure 1, where dry powdered PDADMA/PSS was exposed to water and the (exothermic) heat determined. All starting PECs were thoroughly washed with water before drying and the pH of the calorimeter water was not buffered but remained to approximately neutral (pH 5.5 - 6) before and after hydration.

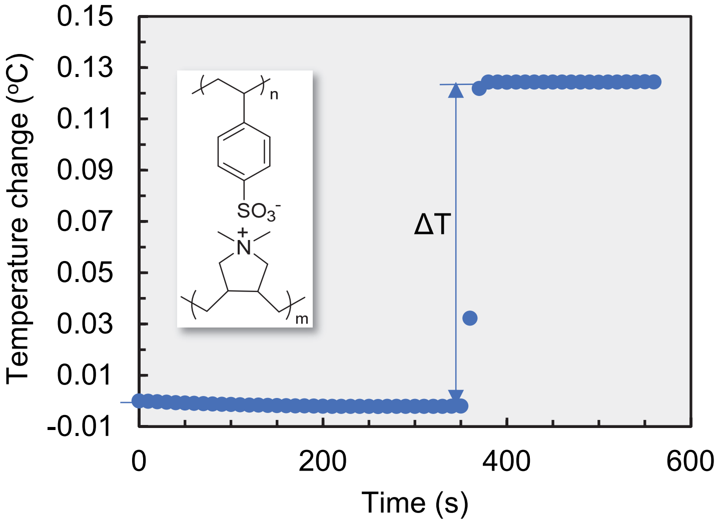


Figure 1. Thermogram showing the exothermic hydration of 0.5003 g dry PDADMA/PSS PEC in 100 mL of water. After room temperature equilibration, the sample was introduced to water at 350 s. ΔT was determined as shown. The heat capacity of the calorimeter with contents was 539.2 J K^{-1}.

Similar measurements were performed on other PECs and the results tabulated in Table 1 (see Supporting Information Figures S4 - S11 for the individual thermograms). In addition, hydration enthalpies, ΔH_{hyd}, of a couple of individual polyelectrolytes (PSSNa and PDADMAC), KCl (as a reference) and two classical desiccants, molecular sieve 3A and $CaSO_4$, were determined. Because water is known to occupy different environments within a PEC,[28] [29] the first water molecules taken up probably generate the most enthalpy per gram. The enthalpy of hydration was thus normalized by the number of grams or moles of Pol^+Pol^-.

The ΔH_{hyd} values for PECs, the first determined for such materials, display an interesting and unpredicted range. Enthalpies were exothermic, as expected for a material that is full of charge. The number of water molecules per pair of Pol^+Pol^- charges, n_{H2O}, taken from earlier work, also listed in Table 1, reflects the equilibrium water content of PECs when immersed in water at room temperature. Interestingly, there is little correlation between ΔH_{hyd} and n_{H2O}. It is probable that the first few water molecules taken up by the PEC hydrate the Pol^+Pol^- pair and the balance of water sits outside the hydration shell in a different environment.

Table 1. Molar mass (repeat unit), enthalpy per mol, enthalpy per gram and number of water molecule per mole of Pol^+Pol^- hydrating the PEC in water at equilibrium. Room temperature. Values in parenthesis are the standard error of the mean.

	MW[a]	ΔH_{hyd} mol^{-1} (kJ mol^{-1})	ΔH_{hyd} g^{-1} (J g^{-1})	n_{H_2O}
PDADMA/PSS	309	-42.4 (±0.8)[b]	-137.4 (±3)	~ 10[c]
PAH/PAA	129	-29.8 (±0.4)	-226.7 (±0.6)	2.4[c]
PDDP/PSS	323	-40.7 (±2)	-126 (±6)	25.5[c]
Molecular Sieve	303	-53.4 (±1)	-172.9 (±4)	-
Calcium Sulfate	136	-4.3 (±0.1)	-31.9 (±0.2)	~ 2[d]
KCl[f]	75	+16.5 (±0.7)[e]	+222 (±9)	-
PSSNa[f]	207	-16.3 (±1)	-78.9 (±5)	-
PDADMAC[f]	162	-14.4 (±0.5)	-88.9 (±3)	-
PVTA/PSS	360	-30.2 (±0.1)	-84.2 (±0.2)	8.8[c]
PVA/PSS	227	-4.4 (±0.2)	-20.1 (±0.9)	7.1[c]
PMAPTA/PAMPS	392	-57.2 (±0.3)	-145.8 (±0.8)	-

[a] molecular weight of the repeat unit

[b] standard error of the mean

[c] from Chen et al.[54]

[d] from Burfield et al.[2]

[e] similar to value reported by Kilday.[55]

[f] enthalpies of solution

Hydration enthalpies did not correlate well to charge densities. The ΔH_{hyd} for PMAPTA/PAMPS was the most exothermic in terms of J mol^{-1} while PAA/PAH boasted the most negative ΔH_{hyd} in terms of J g^{-1}. Enthalpies of salts and homopolyelectrolytes include hydration of the small counterion(s). If enthalpy were used as a measure of hydrophobicity, PSS with Na^+ as a counterion and PDADMA with Cl^- have about the same hydrophobicity.

The ΔH_{hyd} values for PSSNa, PDADMAC and NaCl, which are really enthalpies of solution, permitted the construction of the enthalpy cycle in Figure 2. The complexation enthalpy $PDADMA^+Cl^- + PSS^-Na^+ \rightarrow PDADMA/PSS + Na^+ + Cl^-$ was taken from the literature,[33,39] as was the hydration enthalpy of NaCl.[56] From this result, the water-free “complexation” of PDADAMC and PSSNa was calculated to be 4.7 kJ mol^{-1}. In other words, complexation in an aqueous environment is about 8 kJ more favorable than in a “dry” environment (representing exchange of $PDADMA^+Cl^-$ and PSS^-Na^+ pairing to $PDADMA^+PSS^-$ and NaCl in the solid state).

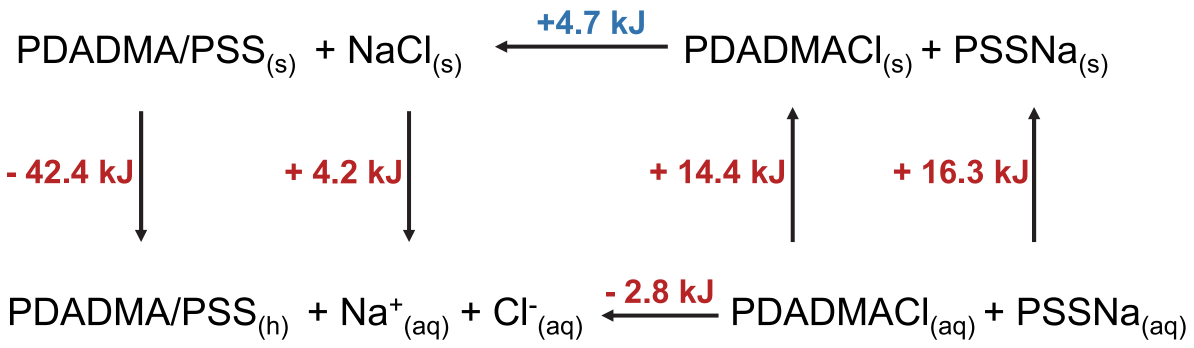


Figure 2. Hess’s cycle showing the molar enthalpies of various processes at room temperature. Subscripts “s”, “h”, and “aq” denote (dry) solid, hydrated solid, and aqueous solution, respectively. All enthalpies are experimental except +4.7 kJ.

PEC as Desiccant

The PDADMA/PSS complex, with a strongly exothermic ΔH_{hyd} and high-water capacity (Table 1), was selected for further investigation as a desiccant. This choice was based on additional factors: the starting materials were low cost (unlike PAH and PDDP) and the hydrated material remained in the glassy state at room temperature.[54] In contrast, PMAPTA/PAMPS, the most exothermic (in terms of kJ mol^{-1}), was a liquid-like coacervate in water at room temperature (i.e. considerably above T_g). When they are above T_g, hydrated PECs tend to clump or flow together. In addition, a comprehensive assessment of swelling of PDADMA/PSS in various solvents has been made and very few were found to swell this PEC when dry.[26]

Three common organic solvents were selected to illustrate and compare the drying efficiency of PECs: acetonitrile, tetrahydrofuran (THF), and acetonitrile. Table 2 shows these solvents cover a range of polarities. The relative polarities of each solvent is given by either the dielectric constant, Snyder's polarity index,[57] or Reicharts solvatochromic[58] index, E^N_T.

Table 2. A comparison of polarities at room temperature for solvents and water.

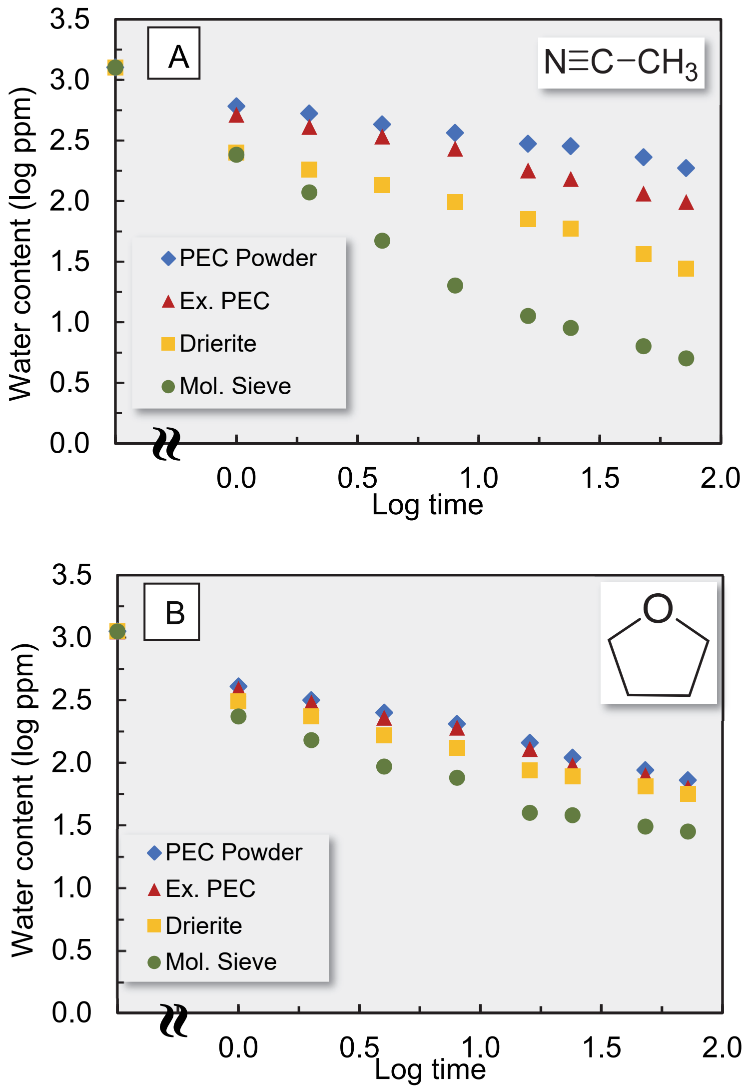
	Dielectric const.	[a]Polarity index	[b]E^N_T
Water	80	9.0	1.000
Acetonitrile	37	6.2	0.460
THF	7.6	4.2	0.207
Toluene	2.4	2.3	0.099

[a]Snyder 1974[57]

[b]Reichardt 1994[58]

Dry solvents were added to dry PEC, then dosed with tritium labeled water. Radiocounting *versus* time provided highly sensitive and accurate measurements of water content, with a detection limit of 0.02 ppm H_2O. For each solvent, the drying efficiencies of PEC in powder form and extruded PEC (Ex-PEC) were compared with two classical desiccants, $CaSO_4$ (Drierite^{TM})

and molecular sieve 3A. Figures 3 compares drying efficiencies in acetonitrile, THF and toluene. In each case, solvents were left unstirred and water contents, starting at values close to 1000 ppm, were determined for up to three days at room temperature.



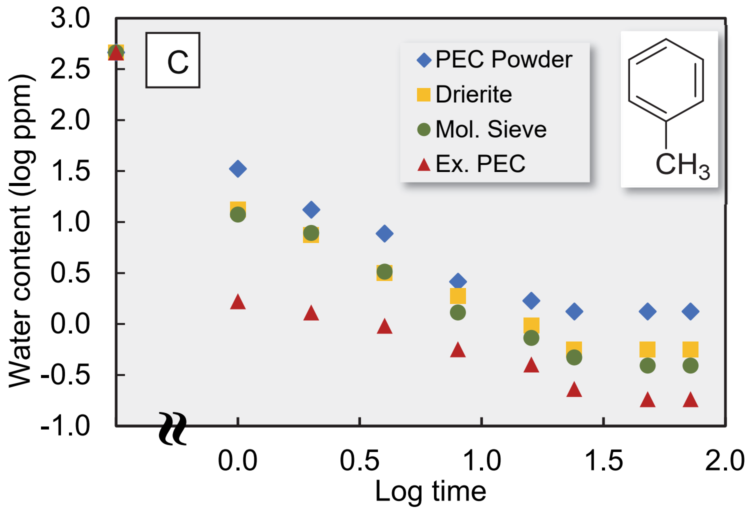


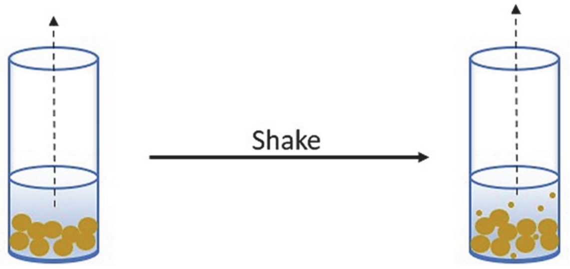
Figure 3. Drying kinetics of three desiccants in **A**) Acetonitrile; starting water concentration 1265 ppm. **B**) THF; starting water concentration is 1125 ppm. **C**) Toluene; starting water concentration 460 ppm. All loadings were 1.0 g desiccant in 10 mL solvent. 100 µL aliquots were removed at each time point (time in hours), mixed with 2 mL liquid scintillation cocktail, and counted. Error is less than the size of the points down to 1 ppm.

Table 3 summarizes the findings that the amount of residual water depends on the solvent and the desiccant. Acetonitrile is highly miscibile with water and forms an azeotrope which can be challenging to completely dry. For comparison to Table 3, at 5 % desiccant loading of molecular sieve 3A, it was reported that ACN was dried from 2500 ppm to 52 ppm after 3 days under static conditions.[2] The water content using $CaSO_4$ powder was only reduced to 180 ppm after 3 days.[2] Williams and Lawton showed that ACN could be dried to a water content of 0.5 ppm after 48 h,[12] while the water content in THF was reduced from above 100 ppm to 4 ppm after 3 days using molecular sieve 3A, and natural alumina could dry these to as low as 6 ppm water. They also reported that with molecular sieve 3A wet toluene was dried to as low as 0.9 ppm water after 24 h.[12] These findings are comparable to those in Table 3.

Table 3. Residual water content in acetonitrile, THF and toluene after 1, 3 and 14 days of drying. Desiccants were first dried/activated. All solvents were dried under static (unstirred) conditions. Starting water content in ACN and THF was about 1000 ppm. Due to low the solubility of water in toluene, the initial amount of added water was 460 ppm.

	Residual Water (ppm)								
	After 1 day			After 3 days			After 14 days		
	ACN	**THF**	**Toluene**	**ACN**	**THF**	**Toluene**	**ACN**	**THF**	**Toluene**
Mol.Sieve 3A	7	31	0.4	4	23	0.3	ND	ND	ND
Ex-PEC	112	79	0.3	79	47	0.1	8	9	0.06
Drierite	47	63	0.5	22	46	0.5	ND	ND	ND
PEC Powder	206	90	1.4	155	60	1.2	61	40	0.6

When using a column or a slurry of desiccant to dry a solvent, the release of any contaminating particles is an important practical consideration. Inorganic desiccants produce dust when they are handled in the dry and the wet state. These dust particles may influence the eventual lab- or production-scale process which uses the solvent, perhaps requiring a final filtration step. In order to assess the extent of particle release, the drying solvents were manually shaken after the 3-day measurement point and a second sample/aliquot was collected and counted (Scheme 2). These counts contain particles that have sorbed water and thus contribute additional counts. Table 3 shows the additional counts resulting from this “dust test.” It is clear from this semi-quantitative comparison that the extruded PEC produced far less dust than any of the other desiccants. It was originally assumed that, because of a higher surface area, PEC powder might dry solvents faster to lower residual water contents than Ex-PEC. As seen in the graphs and tables, this was not the case. It was observed that PEC powder formed a packed bed at the bottom of the vial, which likely resulted in slower water diffusion to the desiccant underneath. A sample of Ex-PEC in toluene was put through three desiccation and regeneration (drying at 120 °C for 2 h) cycles as above and the residual water content was 1.7 ppm after the last cycle.



Scheme 2. Dust Test. Aliquots for counting were taken after 3 days. The vials were shaken to allow release of dust particles and second batch of aliquots was taken. A subtraction of counts was translated to a ppm water value as a relative indicator of the dust produced.

Desiccant	Dust (ppm)		
	ACN	**THF**	**Toluene**
Mol. Sieve3A	2	6	0.1
Ex-PEC	0.4	0.2	0.03
Drierite	21	19	0.7
PEC Powder	107	88	1.6

Table 4. Dust released into ACN, THF and toluene. The lowest amount of dust was recovered from Ex-PEC while PEC powder produced the greatest amount of dust.

In addition to efficient water uptake (Table 3) and low production of particulates (Table 4), PECs offer a number of practical advantages for use in various applications. For example, in heat and humidity management using desiccant wheels[5,9, 15] the balance between water uptake and humidity depends on the ΔH_{hyd} of the material and PECs clearly offer a range of hydration enthalpies depending on composition (Table 1). PECs rely on bulk water absorption,[59] rather than adsorption to materials with high specific surface areas such as silica and alumina, which means there is less surface area to foul with microbes. PECs are generally nonreactive whereas molecular sieve 3A reacts with some solvents, such as methanol.[60] PECs may be washed with aqueous cleaning agents without dissolving or degrading the materials. PDADMA/PSS is stable in strongly acidic or basic solutions.[61] PECs based on quaternary ammonium even show excellent stability against bleach.[62] As polymers, PECs may be molded, extruded, or stamped into specific structures. Finally, traditional desiccants may be combined with PECs as composites in order to combine the optimal drying qualities of both media.

CONCLUSIONS

Complexes of synthetic polyelectrolytes were introduced many decades ago. Michaels envisioned several possible uses of solid-like PECs, including membranes for dialysis and ultrafiltration, separators for batteries and fuel cells, in medical implants, contact lenses, low oxygen transmission coatings, and in sensors.[20] Most potential applications involve hydrated PECs because they tend to be brittle when dry. The use of PECs as drying agents is a promising new application, supported by fundamental insight provided by a new class of calorimetry experiments on PECs to measure their enthalpies of hydration. A full picture of whether PECs as desiccants may be adapted for large-scale use, something which has not yet occurred for other applications of these interesting materials, will come with engineering studies that track energy efficiency, cost and recyclability on a systems basis. However, because PECs are generally inexpensive, stable and of low toxicity, there is good reason to believe they may be adapted as desiccants. PECs may be recycled by softening them in hot, salty water (saloplasticity[47, 63]) which allows them to be re-extruded in a materials- and energy-efficient “saloplastic cycle.”

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Notes

The authors declare no competing financial interests.

Data and materials availability

All data are available in the manuscript or supplementary materials.

Supplementary Materials

Image of desiccants; NMR of PDADMA/PSS PEC; example of thermal gravimetric analysis to show thermal stability; calibration procedure for calorimetry; examples of individual thermograms for all materials measured; solvent drying kinetics on linear scales; calibration curves for determining water by radiolabeling methods.

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