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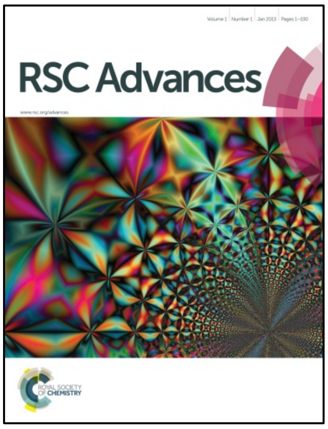

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Structure-Function Study of Tertiary Amines as Switchable Polarity Solvents

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ABSTRACT

A series of tertiary amines have been screened for their function as switchable polarity solvents (SPS). The relative ratios of tertiary amine and carbonate species as well as maximum possible concentration were determined through quantitative ^{1}H and ^{13}C NMR spectroscopy. The viscosities of the polar SPS solutions were measured and ranged from near water in dilute systems through to gel formation at high concentrations. The van't Hoff indices for SPS solutions were measured through freezing point depression studies as a proxy for osmotic pressures. A new form of SPS with an amine:carbonate ratio significantly greater than unity has been identified. Tertiary amines that function as SPS at ambient pressures appear to be limited to molecules with fewer than 12 carbons. The *N,N*-dimethyl-n-alkylamine structure has been identified as important to the function of an SPS.

INTRODUCTION

Developing safe, energy efficient, and environmentally friendly alternatives to traditional solvent systems is a primary goal of "green" and sustainable chemistry research.[1] These goals can be achieved by reducing solvent volumes, changing processes to function with more benign solvents, or developing alternative solvents with new behaviors that allow better process lifecycle performance. Advances in alternative solvents are expected to improve conventional solvent process such as oil extraction from biomass, as well as non-standard uses of solvents. Novel "solvent" materials will allow the development of new processes in areas such as CO_2 separations, water purification, and energy storage. Among the most well-known and promising alternative solvents are the various room-temperature ionic liquids, supercritical fluids, and switchable polarity solvents (SPSs) explored in this study.

SPSs can be divided into various subcategories based on composition and behavior.[2–5] This study targeted water-compatible single-component SPSs which are immiscible with water in their basic form but when they are reacted with carbonic acid, derived from exposure to ~1 atm carbon dioxide, the water miscible acid form [H^+(Base) HCO_3^-] of the SPS is produced, Reaction 1. Similar behavior can be obtained from dual component SPSs involving a nitrogen base (amidines and guanidines) and an alcohol or primary amine; but such systems require balanced stoichiometry to function correctly and tend to be water sensitive which makes them unattractive for many applications.[2,6–8] Some single component SPS, such as secondary amines, also suffer water sensitivity in the form of material precipitation at relatively low water concentrations and thus are ignored in this study.[9] Known water-compatible single-component SPSs include highly functionalized amidines and guanidines[4], tertiary amines[5], and pH sensitive ionic liquids[10]; The scope of research was further focused to tertiary amines based on their potential cost effectiveness when produced at large scale.

$$NR_{3(org)} + CO_{2(gas)} + H_2O \rightleftharpoons HNR_3{}^+{}_{(aq)} + HCO_3^- \qquad (1)$$

Our laboratory became interested in SPS for their use as thermolytic draw solutes[11] (versus more conventional non-thermolytic draw solutes[12,13]) in osmotically driven membrane processes (ODMPs). As thermolytic solutes, SPS can be used in water purification through forward osmosis (FO)[14], solution concentration through direct osmotic concentration[15], and for osmotic heat engines through pressure retarded osmosis[16]. Since its introduction in 2006, the ammonia-CO_2 system has been considered one of the more viable next generation draw solute for FO.[17] SPS draw solutes have a number of advantages over the ammonia-CO_2 system; including negating the need to handle and store gaseous ammonia, lower permeability to properly selected membranes, lower energy requirements, and facile removal of SPS from water through liquid phase separation.

Tertiary amines, such as those screened in this publication, long have been considered unlikely candidates for carbon capture or natural gas sweetening. Primary and secondary amines react chemically with carbon dioxide rapidly to form carbamates.[18] Tertiary amines, on the other hand, follow a second route in which carbon dioxide forms carbonic acid and then reacts via an acid-base reaction with the amine.[18] The carbonic acid pathway is generally slower due to the rate of carbonic acid formation. However, tertiary amines and mixtures which include tertiary amines have recently been reported for carbon capture in conjunction with phase change processes.[19–37] Amines included in our study have also been investigated by Zhang as carbon capture agents where he refers to them as biphasic or lipophilic amine solvents.[19–22] A phase change carbon capture system, DMX^{TM}, has been developed by *IFP Energies nouvelles*; however the chemical composition of their formulation was not available to us.[23,24] Heldebrant at is exploring performance of single-component CO_2-binding organic liquids (CO2BOLs).[25–28] Hu of *3H Company* has reported a two phase acid capture system involving a polarity switching amine.[29–33] Eckert has worked with a switchable polarity ionic liquid.[34–37]

There have been various publications addressing the use of SPS for processing, extraction, and separation. This includes plastic recycling,[5] extraction of oils from biomass and microbes,[38–42] activation of recalcitrant biomass,[43] and the use of SPS as a chemical synthesis solvent.[2,44] The use of SPS in these applications has similarities to distillable room temperature ionic liquids (RTIL) which are often comprised of amines and carboxylic acids.[45–48] There is also the well-established use of ammonium carbamate and carbonate salts as polyurethane polymerization catalysts.[49]

Each of the potential applications can benefit from achieving a higher concentration of the SPS polar form, $[HNR_3^+\ HCO_3^-]$; however, how the concentration is considered best depends on the application. In the case of FO, the osmotic strength of the draw solute is the thermodynamic driving force for the water transport process and is best measured by molality.[50] In solvent extraction, the osmotic pressure is less important than the volume of non-aqueous amine contained within the SPS polar form. A solution with a high weight percent (wt%) of $[HNR_3^+]$ allows the solution volumes used in the solvent extraction process to be minimized. In a carbon capture system, the SPS carbon capture agent would ideally have an extremely large capacity for carbon dioxide and the ideal unit is wt% of CO_2. The most serious drawback of high concentration solutions is increased viscosity which may be problematic for many applications.

Theoretical treatments of high concentration solutions are usually modeled through activity, a_s. Activity ($a_s = y_s x_s$) is a product of the mole fraction, (x_s, moles solute/total moles solvent and solute), and a dimensionless empirically based activity coefficient, y_s. Thus, the mole fraction, x_s, also was also considered when looking for concentration trends.

Previous to this study, the information concerning the maximum concentration of amine based SPS in their polar form was limited to *N,N*-dimethylcyclohexylamine (**5**) and *N,N,N'*-tributylpentanamidine.[4,5] Tertiary amines are among the most attractive SPS reported so far due to their simplicity and low cost. These advantages motivated the screening of tertiary amines **1-26** for a variety of physical properties similar to the study recently published by Eckert.[36] This screening has identified a new form of SPS, as well as structural features and limitations of tertiary amines that are fundamental to their performance as SPS.

RESULTS AND DISCUSSION

Due to the fact that many SPS applications would benefit from higher SPS concentrations in the polar form, the maximum concentration was characterized for a series of tertiary amines, **1-26**. This series was selected not because each amine was expected to be a top performer but rather they are representative of many small tertiary amines with features such as rings systems, different length carbon chains relative to the nitrogen, and alkyl chain branching. These representative amines were selected not only to set limits on the maximum and minimum number of carbons in a functional SPS but also to determine how structural features affect that function. The set of amines included the re-visitation of 12 tertiary amines that had been previously studied for SPS behavior, confirming that 8 amines transition from a water immiscible state to a water miscible state with the introduction of CO_2 and thus “function” as SPS.[5] In addition, 14 previously unreported amines were investigated for SPS behavior and, of these, 8 additional amines have been identified to function as SPS. The structures of the amines that functioned as SPS are illustrated in Figure 1 and those that did not measurably function as SPS under our experimental conditions are illustrated in Figure 2.

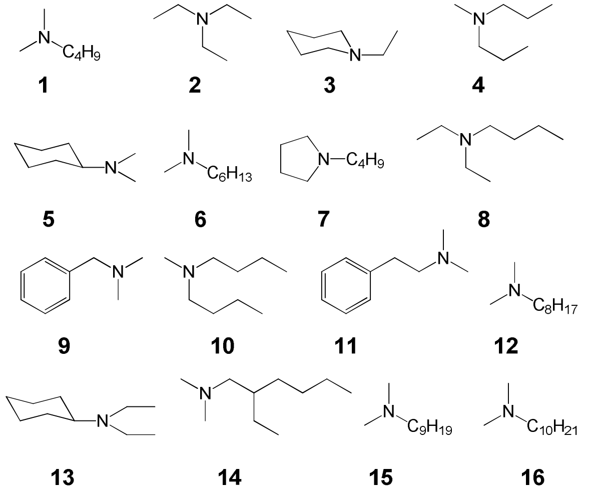

Figure 1. Structures of tertiary amines that functioned as SPS.

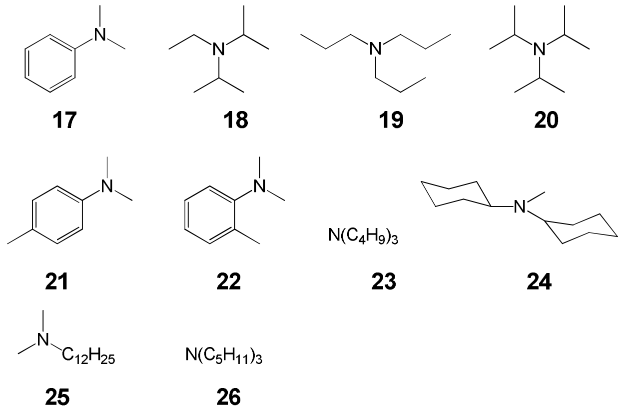

Figure 2. Structures of tertiary amines that did not function as SPS.

While a variety of properties were recorded including viscosity, density, and freezing point depression; it was the NMR spectroscopic studies that were of primary importance where it was used to measure both concentration and composition of SPS solutions. The procedure to identify the maximum concentration involved combining known quantities of water and tertiary amine and purging the solution with carbon dioxide at ambient pressure. The volume of the amine that did not react to form the polar water soluble SPS was measured and a tentative maximum solution concentration was calculated based on the initial masses and unreacted volume. This volume derived concentration measurement was used to corroborate the concentrations found through quantitative NMR studies of the polar SPS solutions.

The NMR studies also were used to identify composition characteristics of the polar SPS solutions. This compositional data indicated that the assumption featured in Equation 1 that all SPS form in a ratio of one tertiary amine to one carbonic acid is incorrect. There are two types of SPS whose primary compositional difference is in the amine:H_2CO_3 ratio.

Osmotic SPS

An SPS that can produce an osmotic driven flux across a semi-permeable membrane can be considered "osmotic". Osmotic SPS amines are characterized by a maximum concentration of their polar SPS form, after which additional amine is rejected by the aqueous phase and remains separated in a nonpolar phase, even in the presence of excess ambient pressure carbon dioxide. Osmotic SPS systems remain fully liquid under all the experimental conditions and no precipitate is observed; although clouding is common during the switching process. Osmotic SPS can be diluted with water and display predictable decreases in osmotic pressure. Correlation between osmolality and molality produces representative van't Hoff indices. To accurately measure the maximum concentration of these SPS, quantitative NMR spectroscopy was conducted.

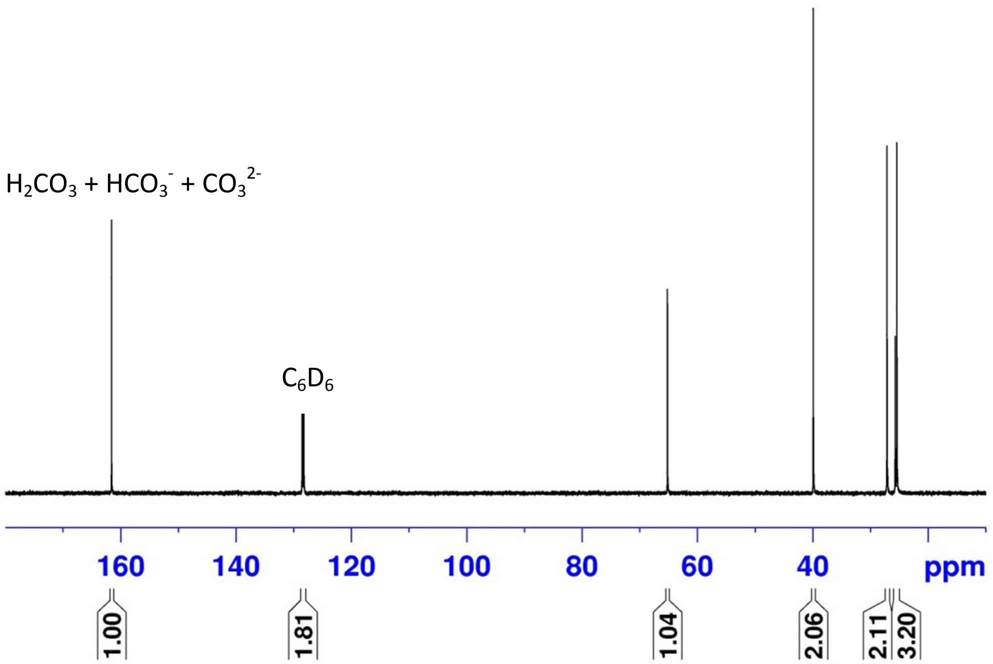

Figure 3. The quantitative ^{13}C NMR of dimethylcyclohexylamine bicarbonate solution **5'**.

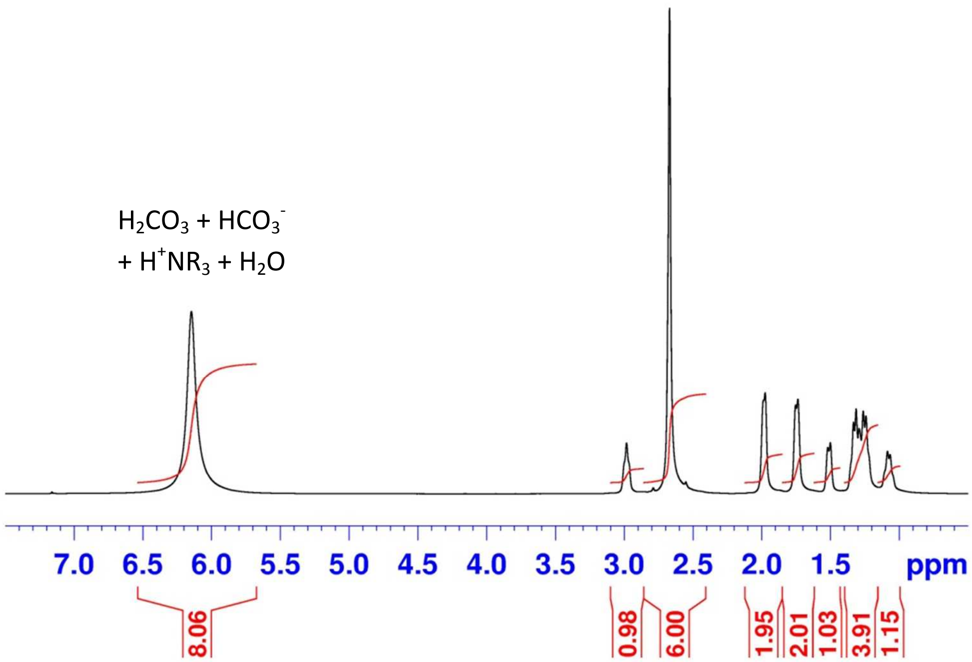

Figure 4. The quantitative ^1H NMR of dimethylcyclohexylamine bicarbonate solution **5'**.

The quantitative ^{13}C and ^1H NMR spectra were conducted as neat solutions with a coaxial insert containing C_6D_6 as a reference. As examples, Figures 3 and 4 feature the spectra for solution **5'**. The ^1H NMR spectrum contains chemical shifts, δ, which have been assigned to the exchangeable protons of water (H_2O), carbonates (HCO_3^- and H_2CO_3), and ammonium (H^+NR_3) ions, Figure 4. The analysis of this data can be simplified by ascribing two protons to carbonic acid and its salts. Based on ^1H NMR spectrum integration, the ratio of water and carbonic acid to amine can be calculated. This ratio combined with the amine to carbonic acid ratio derived from the quantitative ^{13}C NMR, Figure 3, allow for the calculation of the relative mole ratio of amine:carbonic acid:water. With the molecular mass and solution density it is possible to calculate mole fractions, molarities, molalities, and weight percent (Table 1), all of which were considered in looking for trends associated with physical properties (Table 2).

Table 1. The relative integration of quantitative NMR select properties and concentrations of tertiary amine bicarbonate solutions.

Amine	**number**	**molecular mass (amine)**	**density (solution)**	**amine:H_2CO_3 (^{13}C)**	**(H_2O+ H_2CO_3) :amine (^1H)**	**wt% (amine+H_2CO_3)**	**mole fraction (amine)**	**molal (amine)**	**molarity (amine)**
dimethylbutylamine	1’	101.2	1.05	1.06	5.13	67.9	0.163	13.3	4.47
triethylamine	2’	101.2	1.05	1.05	9.46	51.1	0.096	6.52	3.35
1-ethylpiperidine	3’	113.2	1.09	1.05	4.93	70.6	0.169	14.0	4.47
methyldipropylamine	4’	115.2	1.01	1.07	25.8	27.9	0.037	2.23	1.63
dimethylcyclohexylamine	5’	127.2	1.10	1.05	4.03	77.0	0.199	18.0	4.55
dimethylhexylamine	6’	129.2	0.98	1.23	6.40	64.1	0.135	9.94	3.50
1-butylpyrrolidine	7’	127.2	0.99	1.26	6.44	63.4	0.134	9.84	3.56
diethylbutylamine	8’	129.2	1.02	1.09	19.2	36.1	0.050	3.04	1.98
dimethylbenzylamine	9’	135.2	1.05	1.14	23.4	31.9	0.041	2.47	1.77
methyldibutylamine	10’	143.3	1.00	1.14	88.8	11.1	0.011	0.63	0.56
dimethylphenethylamine	11’	149.2	1.03	2.42	4.45	70.6	0.184	13.8	4.16
dimethyloctylamine	12’	157.3	0.92	1.91	5.97	65.9	0.143	10.2	3.20
diethylcyclohexylamine	13’	155.3	1.04	1.02	23.5	34.8	0.041	2.47	1.67
dimethyl-2-ethylhexylamine	14’	157.2	1.00	1.05	508	2.3	0.002	0.11	0.11
dimethylnonylamine	15’	171.3	0.88	2.70	5.73	66.8	0.149	10.4	3.03
dimethyldecylamine	16’	185.4	---	2.87	7.54	61.5	0.117	7.72	2.97

Table 2. The properties of tertiary amines bicarbonate solutions.

Amine	**number**	**carbon: nitrogen**	**density (amine)**	**wt% (amine+H_2CO_3)**	**density (solution)**	**amine:H_2CO_3 (^{13}C)**	**van‘t Hoff index (amine)**	**van‘t Hoff index (Σ ions)**	**max. osmotic pressure (atm)**	**viscosity (cP)**
dimethylbutylamine	1’	6	0.721	67.9	1.05	1.06	1.81	0.93	616	25.0
triethylamine	2’	6	0.726	51.1	1.05	1.05	1.73	0.88	288	10.6
1-ethylpiperidine	3’	7	0.824	70.6	1.09	1.05	1.72	0.88	641	71
methyldipropylamine	4’	7	0.734	27.9	1.01	1.07	1.69	0.87	92.9	2.8
dimethylcyclohexylamine	5’	8	0.849	77.0	1.10	1.05	1.73	0.88	835	108
dimethylhexylamine	6’	8	0.744	64.1	0.98	1.23	1.37	0.76	328	25.5
1-butylpyrrolidine	7’	8	0.814	63.4	0.99	1.26	1.36*	0.76*	325*	29
diethylbutylamine	8’	8	0.748	36.1	1.02	1.09	1.79	0.93	135	11.3
dimethylbenzylamine	9’	9	0.900	31.9	1.05	1.14	1.37	0.73	87.1	2.8
methyldibutylamine	10’	9	0.745	11.1	1.00	1.14	1.77	0.94	27.3	1.6
dimethylphenethylamine	11’	10	0.89	70.6	1.03	2.42	---	---	---	15.0
dimethyloctylamine	12’	10	0.765	65.9	0.92	1.91	---	---	---	58
diethylcyclohexylamine	13’	10	0.845	34.8	1.04	1.02	1.82	0.92	114	4.8
dimethyl-2-ethylhexylamine	14’	10	0.768	2.3	1.00	1.05	---	---	---	1.1
dimethylnonylamine	15’	11	0.773	66.8	0.88	2.70	---	---	---	86
dimethyldecylamine	16’	12	0.778	61.5	---	2.87	---	---	---	gel

*Based on amine concentration <1.05 mol/Kg.

The concentrations calculated from quantitative ^{13}C and ^{1}H NMR spectra studies allow the calculation of van’t Hoff indices based on either the sum of tertiary amine/ammonium molality or the total species molality, which includes tertiary amines, tertiary ammonium, and carbonate species, Table 2. The total species molality is more informative as it removes the variation in the relative carbonate concentration and is more directly related to the ion dissociation. The degree of dissociation cannot be perfectly gauged because these indices are composites of various forms of “ion pairing”, which reduce the van‘t Hoff index, and the role of “bound” waters of hydration, which raise the indices.[50,51] Freezing point depression studies were conducted to obtain experimental van’t Hoff indices which allow estimation of osmotic pressure, Table 2.[50] The van‘t Hoff indices were based on values measured generally between 0.10 and 2.0 Osm/kg, such as Figure 5.

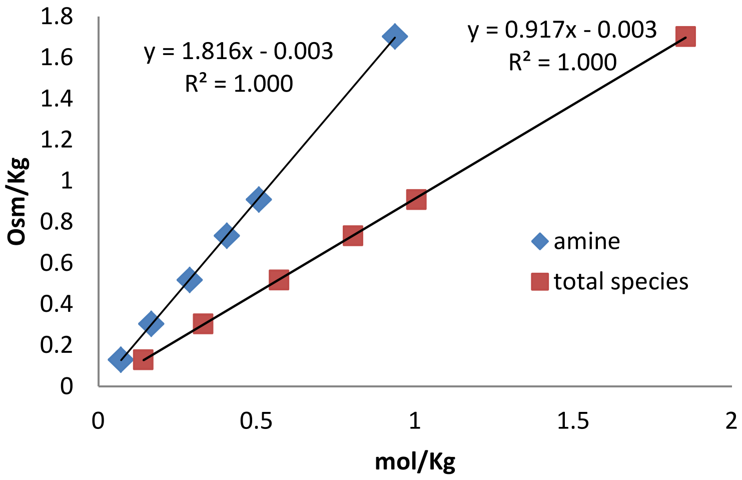

Figure 5. The van't Hoff plot for diethylcyclohexylamine, **13'**. The diamonds are based on molality of tertiary amine and tertiary ammonium ions. The squares are based on the total species molality including tertiary amines, tertiary ammonium ions, and carbonate species

The correlation over the 0.10 to 2.0 Osm/kg range, as measured by freezing point depression, was generally linear where total species van't Hoff indices ranged between 0.73 and 0.94 (Table 2) for osmotic SPS, indicating high degrees of dissociation for nearly all the solutions measured. One example that did not follow this trend is solution **7'**, which deviated negatively from linearity when the amine concentration exceeded 1 mol/Kg, Figure 6, suggesting higher order "ion pairing" equilibrium processes. No other solutions deviated from linearity, but solution **8'** would not freeze cleanly at or above 1.2 mol/Kg of amine, which may be a result solution out gassing or exceeding a eutectic point.

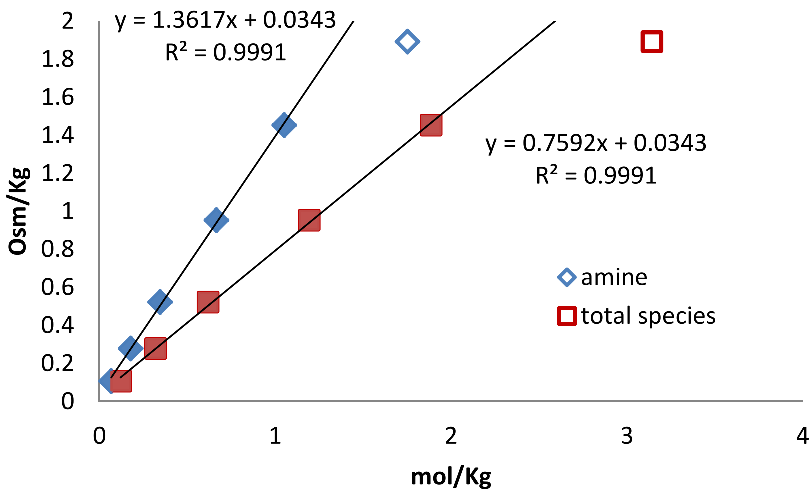

Figure 6. The van't Hoff plot for diethylcyclohexylamine, **7'**. The diamonds are based on molality of tertiary amine and tertiary ammonium ions. The squares are based on the total species molality including tertiary amines, tertiary ammonium ions, and carbonate species. Only the filled-marker data was used to calculate the trend lines. The higher concentration open-marker data feature a negative deviation from linearity.

It was previously reported that **5** forms a solution in a 1:1 (vol:vol) ratio with water which our lab reported as a viable ODMP draw solute.[11] The maximum concentration of **5'** was revisited and was found to have a maximum concentration of 77 wt%, which corresponds to 18 molal and 4.6 M by amine. This concentration is considerably higher than the value previously reported. The osmotic pressure of solution **5'** has been estimated at 836 atm based on previously described methods[50], which is considerable for an FO draw solute.

Non-osmotic SPS

Osmotic SPS were not the only SPS form encountered in this study; there were also "non-osmotic" SPS which differed in both composition and behavior. These SPS are coined "non-osmotic" because they did not produce the expected osmotic driven flux across a semi-permeable membrane when used as a FO draw solution in their “polar” form. The van ‘t Hoff indices of non-osmotic SPS could not be measured because the solutions do not dilute homogenously when water is added. All measured freezing points were much lower than expected given the concentration. For these reasons Table 2 does not contain a maximum osmotic pressure for non-osmotic SPS. This is an unexpected result for a solution made from the addition of carbon dioxide and tertiary amine to water. When water is added to a concentrated non-osmotic SPS, a portion of the solution dilutes, and is reflected in freezing point osmometry measurements, but another portion phase separates as the nonpolar tertiary amine. To understand this dilution phenomenon, the relative concentrations of the species in solution must be known. The solutions are comprised of amines species, both protonated and unprotonated, and carbonate species, which is mostly bicarbonate with equilibrium quantities of carbonate and carbonic acid. Because of the complexity involved with tracking the equilibrium concentration, it is useful to consider this acid-base system in its non-ionized form to compare the “amine” to “carbonic acid” ratios. The ratio of tertiary amine to carbonic acid for non-osmotic SPS varies between 1.82 and 2.87 based on the integration of the quantitative ^{13}C NMR spectra. These values for non-osmotic SPS are significantly higher than polar SPS with all values listed in Table 1 and 2 and plotted in Figure 7.

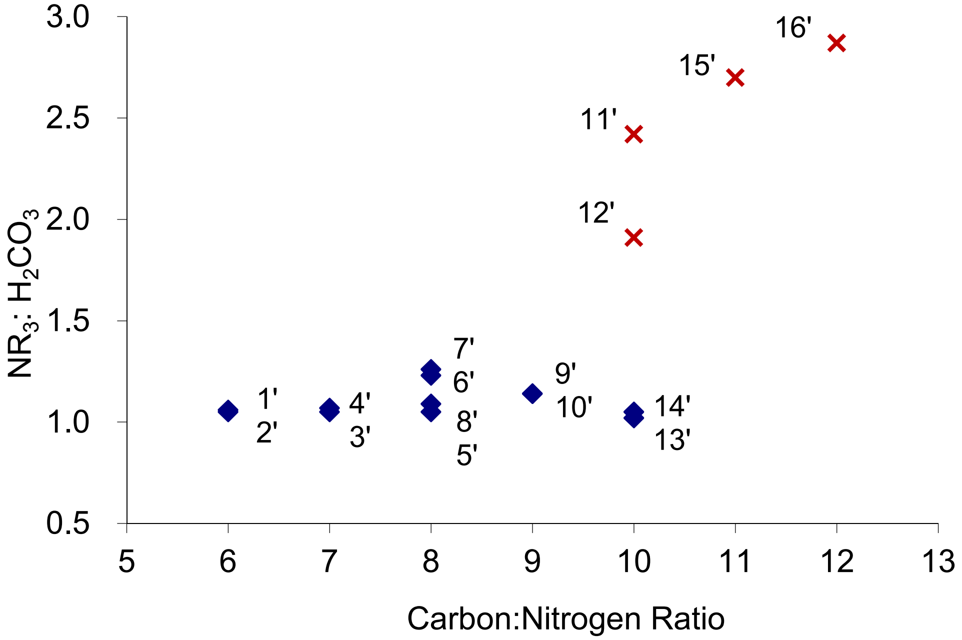

Figure 7. The NR_3:H_2CO_3 ratio represents the ratio between all forms of amine protonated and unprotonated and the sum of carbonate, bicarbonate, and carbonic acid; Diamonds represent "osmotic" SPS, crosses represent "non-osmotic" SPS.

Modeling the maximum concentration equilibrium

Due to the discovery of non-osmotic SPS, the model SPS maximum concentration must be revisited. Since the organic amine is an immiscible material, its concentration does not change with the equilibria and thus can be taken as unity. Likewise the solvent, in this case water, is usually in a large excess such that its effective concentration does not change with the equilibrium and usually can also be treated as unity. Assuming the solvent as unity is not strictly proper for the SPS equilibria where the water concentration drops below 0.8 mole fraction and may also be involved in ionic hydration. Thus, the water concentration is included in this equilibrium. Because these are non-aqueous solutions of variable consistency, there are no known Henry's law constants for these systems. Thus, the CO_2 concentration is not calculated based on the partial pressure. In addition, because CO_2 partial pressure is the independent variable, it is preferred for the calculation of an equilibrium constant.[52] These assumptions yield the equilibrium expression, Equation 2, from the reaction described by Equation 1.

$$NR_{3(org)} + CO_{2(pressure)} + H_2O \rightleftharpoons HNR_3^+{}_{(aq)} + HCO_3^- \qquad (1)$$

$$K_1 = \frac{[HNR_3^+]_{aq}[HCO_3^-]}{pCO_2[H_2O]} \qquad (2)$$

$$NR_{3(org)} \rightleftharpoons NR_{3(aq)} \qquad (3)$$

$$NR_{3(aq)} + CO_{2(pressure)} + H_2O \rightleftharpoons HNR_3^+{}_{(aq)} + HCO_3^- \qquad (4)$$

$$a\cdot[HNR_3^+{}_{(aq)} + NR_{3(aq)}] + NR_{3(org)} \rightleftharpoons NR_{3(aq)} + b\cdot H_2O \qquad (5)$$

$$K_{(Equation\ 3-5)} = \frac{[HNR_3^+]_{aq}[HCO_3^-][NR_3]_{aq}[H_2O]^b}{pCO_2[H_2O][HNR_3^+ + NR_3]_{aq}^a} \qquad (6)$$

Non-osmotic SPS concentrations are not as simple as they can be modeled multiple ways. Because there are appreciable amounts of aqueous tertiary amine in non-osmotic SPS, the model needs to consider the conversion of organic tertiary amine to aqueous tertiary amine (Equation 3). When aqueous tertiary amine is considered directly, Equation 1 is converted into Equation 4. As the aqueous tertiary amine and aqueous tertiary ammonium bicarbonate concentrations increase, the concentration of dissolved organic materials increases. This results in a solution polarity decrease, which shifts the solution towards something more like a water immiscible organic solvent. This shift in polarity allows the solution to accept more tertiary amine (Equation 5). In this model, we assume HNR_3^+ and NR_3 contribute equally to the polarity shift for the sake of simplicity. Presumably, the increase in aqueous amine when the products are favored in Equation 3 allows the further conversion of carbon dioxide into bicarbonate and protonated tertiary amine (Equation 4) in a positive feedback loop. This feedback loop does two things: 1) increases the carbonate concentration relative to the osmotic SPS and 2) increases the absolute concentration of $HNR_3^+{}_{(aq)}$ and HCO_3^-. The relative concentration of $NR_{3(aq)}$ also increases and the solution moves further away from a composition that is strictly aqueous. If water is added to a concentrated non-osmotic SPS solution, a portion of the $NR_{3(aq)}$ phase separates as the SPS solution polarity is driven to a more polar form. The ability of water to shift the polarity of the solution is featured in its role as a product dependent on the value “b” in Equation 5. The role of water is complex and it may be necessary to identify portions as “free” or “bound” in the SPS solution, but the treatment in Equation 4 and 5 is sufficient to model the current information yielding an equilibrium expression, Equation 6.

Limits of SPS function at ambient pressure and concerns with measurements

The number of carbons or the carbon: nitrogen (C:N) ratio of a tertiary amine is a useful proxy for both the mass and polarity of the tertiary amine; More carbons in the amine result in higher molecular mass, and thus lower overall polarity. Hansen solubility parameters and its components were explored to describe tertiary amine polarity without success; the calculated parameters varied little and were less intuitive than the simple C:N ratio.

In this study, no tertiary amines with a C:N ratio of less than 6 were explored. Tertiary amines with low C:N ratio have many undesirable characteristics including low boiling points, high vapor pressures, higher water solubility, and a more difficult switch between the nonpolar and polar phases. Release of CO_2 for these amines generally requires substantially higher temperatures or greater volumes of purge gas, followed by cryogenic amine capture, which complicates their utility. These factors serve to limit the use of these amines as SPS and motivates the efforts to define the proper upper thresholds of the C:N ratio for tertiary amines that function as SPS.

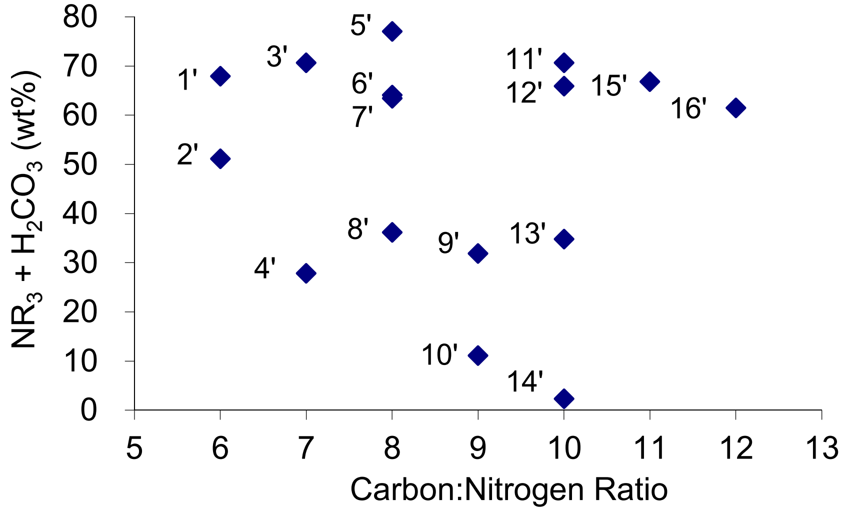

Figure 8. Maximum acquired concentration as a function of the C:N ratio.

When the total weight percent of both osmotic SPS (C:N 6-10) and non-osmotic SPS (C:N 10-12) are plotted against C:N their ratio, high weight percentages are found until C:N 12 after which no tertiary amines were found to form SPS, Figure 8. The loss of SPS formation above C:N =12 may be explained when the concentration is broken into the tertiary amine and the carbonate concentration. For example, focusing on the *N,N*-dimethyl-n-alkylamine series, Figure 9, it is clear that the carbonate concentration steadily decreases from C:N 6 to 11. Solution **16’** is excluded from this analysis because it forms a gel distinct from the other liquid solutions. A trend line can be fitted to the carbonate concentrations of the *N,N*-dimethyl-n-alkylamine series, which includes osmotic SPS (**1’** and **6’**) and non-osmotic SPS (**12’** and **15’**) that indicates increasing the C:N ratio results in a decline in the carbonate concentration. Because osmotic and non-osmotic systems are linear when the C:N ratio is plotted against carbonate molarity, this is convenient trend for comparing all SPS systems. The linearity of the trend also could be taken to suggest that concentration phenomena influence the maximum concentrations of both osmotic and non-osmotic SPS in a similar way, rendering the previous equilibrium analysis (Equations 3-6) unnecessary. Such a conclusion does acknowledge that while the C:N ratio is a useful proxy for polarity and molecular mass, it is not a fundamental physical property commonly used to compare equilibrium states and thus, in many ways, an arbitrary unit, making the resulting trend similarly arbitrary.

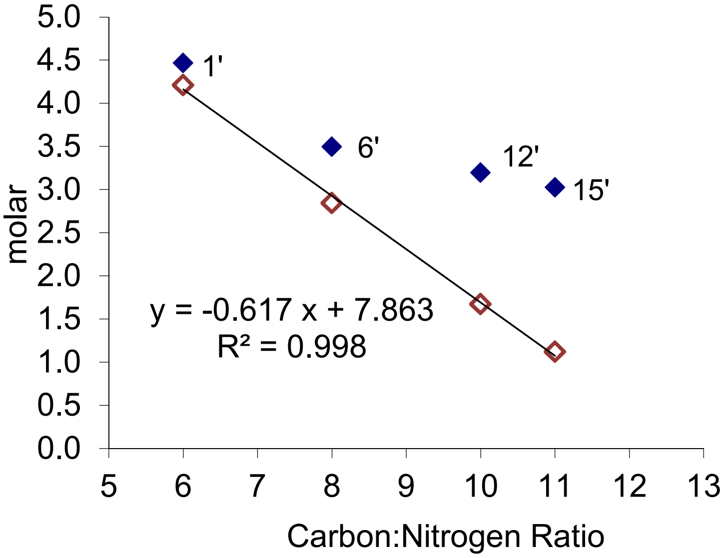

Figure 9. Maximum acquired concentration as a function of the C:N at 1 atm CO_2 for SPSs featuring the *N,N*-dimethyl-n-alkylamine structure plotted in molarity for both the amine (solid diamond) and carbonate components (open diamond).

The observed trend in Figure 9 is product of known theoretical and experimental influences. The slope of the regression might be steeper or fit a different mathematical/concentration model if not for three phenomena. First, as discussed earlier, there is a positive feedback loop associated with non-osmotic SPS and their elevated concentration of aqueous amine. This raises the concentration of carbonate in solution for **12’** and **15’** (and **16’**) which define the low end of the trend. The second feature is the home-built experimental apparatus for this study pushed carbon dioxide through a column of solution which was then exhausted through a condenser open to the atmosphere through a needle, as shown in the experimental section. For lower viscosity amines, the CO_2 pressure rapidly equilibrated with ambient pressure; however, the amines with viscosities greater than 50 cP (Table 2), namely **3’**, **5’**, **12’**, and **15’** (and **16'**) provide back pressure on the carbon dioxide flow slightly elevating the CO_2 pressures directed at the solution.

The third phenomenon that affects the trend observed in Figure 9 is the stability of the solutions. Not all solutions are stable for significant periods of time. Solutions **11'** and **15'** (and **16'**) are prone to venting carbon dioxide when mild pressure or vacuum is applied or even mixing in the absence of a saturated carbon dioxide atmosphere. When conducting NMR experiments, approximately 20% of solutions **11'** and **15'** (and **16'**) phase separated into the nonpolar amine form, suggesting they may be metastable supersaturated states.

Each of these three phenomena tend to inflate the observed concentration at high C:N ratios. Because two of these phenomena are related to the experimental process and design, the conclusions and performance trends regarding high C:N ratios and the upper threshold for tertiary amine function as SPS may be generous.

Structural Features of SPS

Within the range of C:N ratios between 6 and 12 there are structural features that influences SPS performance. Better performing SPS are those that can reach the highest concentrations. Of the better performing SPS, it was noted that every example featured the core structure of *N,N*-dimethyl-R-amine (**1'**, **5'**, **9'**, **11'**, and **15'**), or 1-alkylpiperidine (**3'**). The *N,N*-dimethyl-R-amine grouping can be broken down into *N,N*-dimethyl-n-alkylamines (**1'** and **15'**), *N,N*-dimethylcyclohexylamine (**5'**), and *N,N*-dimethylphenealkylamines (**9'** and **11'**). Because the pK_as of the studied tertiary amines are largely equivalent, it is assumed that an aspect of either or both polarity and intramolecular steric interaction are dictating the differences in the observed SPS performance.

There are many methods to model steric and polar interactions. Tolman cone angles have been used extensively to model the sterics influences of tertiary phosphines on their interactions with Lewis acid metal centers.[53–55] While Tolman cone angles have not been used to describe amines, the phosphine values were used to conduct an evaluation that, while internally consistent, was ultimately unsuccessful. A functional group contribution model similar to the Hansen system, but dedicated to the tertiary amine SPS concentration model, is proposed below.

At the core of the functional group contribution treatment is the linear relationship between C:N ratio and the maximum molarity of the HCO_3^- & HNR_3^+ concentrations in the *N,N*-dimethyl-n-alkylamine series, which holds for the alkyl = butyl (**1’**), hexyl (**6’**), octyl (**12’**), nonyl (**15’**) series. Amines which deviate from the *N,N*-dimethyl-n-alkylamine skeletal structure can be grouped into two overlapping groups. The first group of amine structures all contain carbons extending the core *N,N*-dimethyl-n-alkylamine structure but with no ring systems. For example, these carbons would include both carbons of dimethyl-2-ethylhexylamine’s, **14’**, ethyl group or 1 carbon from each of the ethyl groups in diethylbutylamine, **8’**, Figure 10. The structures of these are amines and their pertinent carbons are labeled as (<) in Figure 10 because their concentration are lower than predicted by the *N,N*-dimethyl-n-alkylamine trend.

The concentrations of ring free systems in relation to *N,N*-dimethyl-n-alkylamine trend line are also plotted in Figure 11. The second group is tertiary amines whose structures include a ring system such as a cyclohexyl group (**5’** and **13’**), phenyl group (**9’** and **11’**), piperidine (**3’**), and pyrrolidine (**7’**). The structure of ring containing systems are also included in Figure 10 and are labeled as (<, =, and >) because their concentrations vary compared to what is predicted by the *N,N*-dimethyl-n-alkylamine trend. The maximum concentrations of ring containing systems in relation to *N,N*-dimethyl-n-alkylamine trend line are plotted in Figure 12.

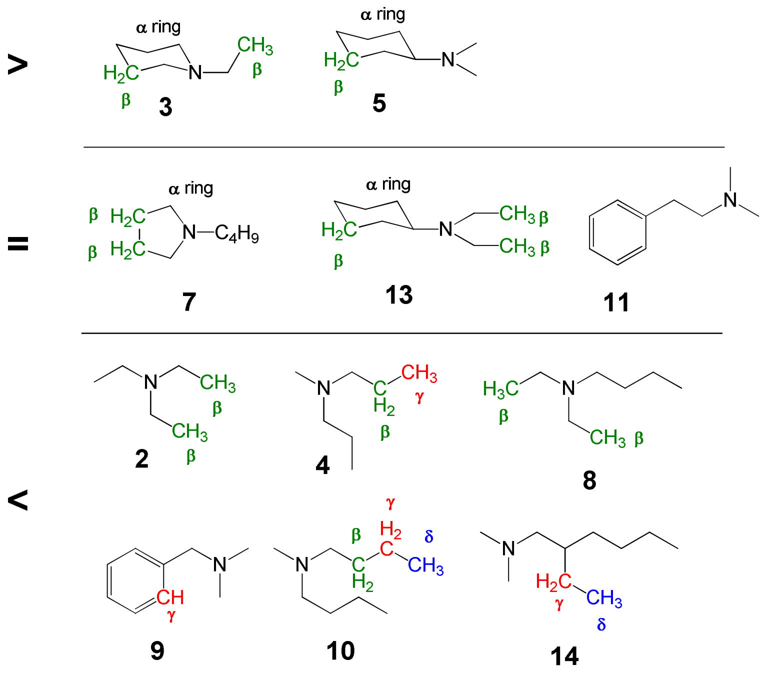

Figure 10. The amines which deviate from the *N,N*-dimethyl-n-alkylamine core structure with β, γ, and δ carbons as well as α rings systems labeled and separated into groups according to whether their carbonate concentration are greater than (>), equal to (=), or less than (<) the trend line formed from the carbonate concentration of the *N,N*-dimethyl-n-alkylamine solutions (Figure 9).

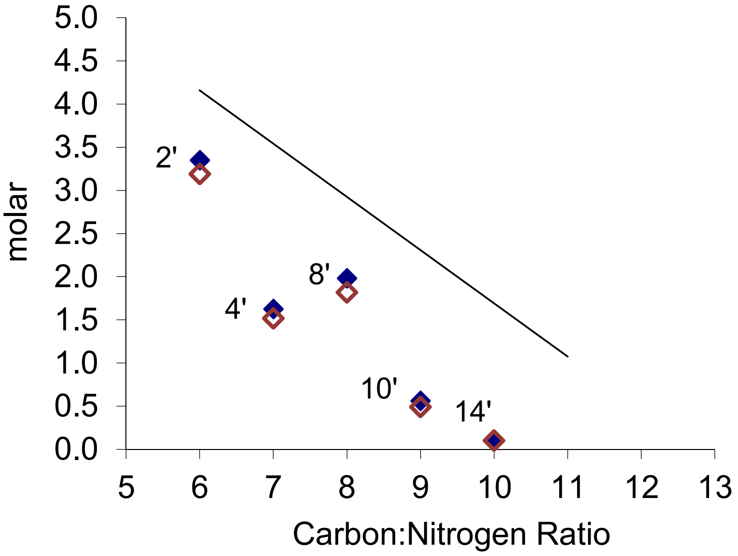

Figure 11. Maximum acquired concentration for SPSs featuring additional carbons functionality in addition to the *N,N*-dimethyl-n-alkylamine core structure. Trend line based on the *N,N*-dimethyl-n-alkylamine series from Figure 9 included here for a reference. The conditions and labeling are the same as Figure 9.

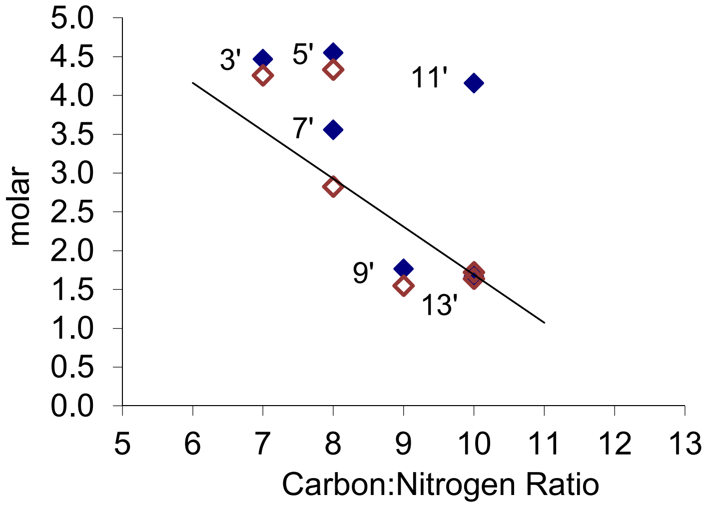

Figure 12. Maximum acquired concentration for SPSs featuring ring systems. Trend line based on the *N,N*-dimethyl-n-alkylamine series from Figure 9 included here for a reference. The conditions and labeling are the same as Figure 9.

Alkyl substituents in the absence of a ring system reduce a tertiary amine's effectiveness as an SPS. These carbons can be described as β, γ, and δ carbons, each with a different ability to influence steric crowding at nitrogen, Figure 13. The β, γ, and δ carbons have the potential to sterically disrupt the space around the nitrogen's lone pair to differing degrees. Such steric hindrance does not inherently prevent the coordination of a proton, due to its small size. Most of the amines in this study readily form highly concentrated protic ionic liquids with strong acids. Carbonic acid, derived form carbon dioxide, is neither a strong acid nor a concentrated acid under ambient conditions. The steric hindrance around the nitrogen lone pair likely prevents formation of extended solvent and counter ion (bicarbonate) network necessary to stabilize the polar form of the SPS in the aqueous phase.

The potential for maximum steric interaction increases with the carbon's proximity from the nitrogen, δ>γ>β. In contrast rotational degrees of freedom have the opposite effect based on as the carbon's potential to relax away from the amine which also increases according to the carbon's proximity from the nitrogen, δ>γ>β.

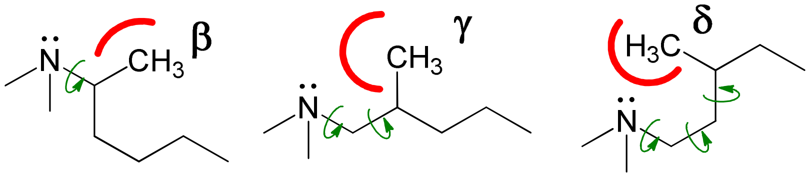

Figure 13. Position of β, γ, and δ carbons with respect to the nitrogen.

The coefficients used in Equation 7 were produced by empirically adjusting the values to produce a one to one linear relationship between the experimental and calculated molar concentrations, Table 3 and Figure 14. Based on the structures and concentrations observed in this study, the steric effect on the carbonate concentration of a γ (1.1) carbon is approximately double the effect of a β (0.55) or δ (0.5) carbon. It is expected that more distant carbons would have little effect on the nitrogen.

$$SPS\ (H_2CO_3\ (M)) = 7.86 - 0.62(\Sigma\ \text{Carbon}) - 0.55\beta - 1.1\gamma - 0.5\delta + 1.2(\alpha\ ring) \qquad (7)$$

The effects of a ring system on tertiary amines SPS function is more ambiguous than the argument presented above. All of the systems containing *carbons* beyond *N,N*-dimethyl-n-alkylamine skeleton but *no ring system* performed more poorly than the *N,N*-dimethyl-n-alkylamine series. Of the systems that *contained ring systems and additional carbons* some performed better than the *N,N*-dimethyl-n-alkylamine series, including **3'** and **5'**, but not all ring containing systems performed better. Solutions **7'** and **13'** have concentrations that are much higher than expected, lying on the line for the *N,N*-dimethyl-n-alkylamine series despite each containing two additional β carbons. Solution **11'** essentially lies on *N,N*-dimethyl-n-alkylamine trend line which suggests that the steric cost and benefit of ring system carbon γ to the nitrogen are roughly equal or are negligible. As for **9'**, definitively resolving the subtle steric and electronic effects associated with the benzyl ring system is beyond the current scope of this paper but it models well as γ carbon sterics with no ring benefit. Based on these systems, an "α ring system" which includes the cyclohexyl groups (**5'** and **13'**), piperidine (**3'**), and pyrrolidine (**7'**) provides an enhancement to an amine's SPS function, which is not observed for more distant ring systems (**9'** and **11'**). The benefit of an α ring system (1.2) was incorporated into Equation 7, Table 3, and Figure 14.

Table 3. Properties of tertiary amines that functioned as SPS.

Amine	number	number of total carbon	β carbons	γ carbons	δ carbons	α ring systems	Molar (exp.)	Molar (calc.)	Absolute Difference
dimethylbutylamine	1’	6					4.21	4.15	0.06
triethylamine	2’	6	2				3.19	3.05	0.14
1-ethylpiperidine	3’	7	2			1	4.26	3.63	0.63
methyldipropylamine	4’	7	1	1			1.52	1.88	0.36
dimethylcyclohexylamine	5’’	8	1			1	3.33	3.56	0.23
dimethylhexylamine	6’	8					2.84	2.91	0.07
1-butylpyrrolidine	7’	8	2			1	2.83	3.01	0.18
diethylbutylamine	8’	8	2				1.82	1.81	0.01
dimethylbenzylamine	9’	9		1			1.55	1.19	0.36
methyldibutylamine	10’	9	1	1	1		0.49	0.14	0.35
dimethylphenethylamine	11’	10					1.72	1.67	0.05
dimethyloctylamine	12’	10					1.67	1.67	0.00
diethylcyclohexylamine	13’	10	3			1	1.64	1.22	0.42
dimethyl-2-ethylhexylamine	14’	10		1	1		0.10	0.07	0.03
dimethylnonylamine	15’	11					1.12	1.05	0.07

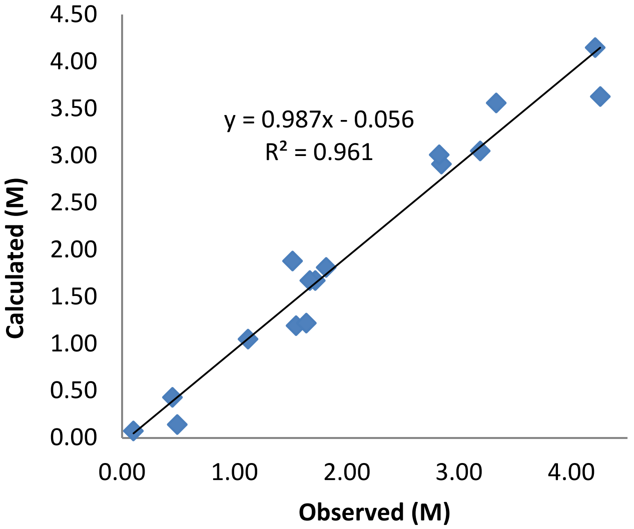

Figure 14. The correlation between the observed maximum molarity of SPS and those calculated from equation (7).

Aniline derivatives were not observed to function as SPS. The nonfunctionality of the aromatic aniline derivatives is not predicted by Equation 7, and is attributed to the pK_a of 5-6 resulting from an amine directly bonded to an aromatic ring which is significantly lower than the alkyl substituted tertiary amines with pK_a of 8-11.

CONCLUSION

In this study, a functional group contribution model has been developed for tertiary amine SPS. Also, structural limits for tertiary amines that function as SPS were identified, which suggested that a C:N ratio between 6 and 12 is necessary. Furthermore, a new form of non-osmotic SPS with an elevated amine to carbonate ratio in its polar form has been identified and characterized. This structure-function analysis and identification of a new form of SPS has implications on the design of SPS systems based on untested amine systems, as well as the selection of SPS for a variety of applications including solvent extraction systems, plastic recycling, synthetic media, acid gas capture, and osmotically driven membrane processes (ODMPs).

EXPERIMENTAL METHODS

General

Deionized water was used for these experiments. *N,N*-dimethylbutylamine, triethylamine, 1-ethylpiperidine, *N*-methyldipropylamine *N,N*-dimethylcyclohexylamine 99% ($N(Me)_2Cy$), 1-Butylpyrrolidine, *N,N*-diethylbutylamine, *N,N*-dimethylbenzylamine, *N*-methyldibutylamine, *N,N*-dimethylphenethylamine, *N,N*-dimethyloctylamine, *N,N*-dimethylcyclohexylamine, 2-ethylhexylamine, *N,N*-dimethylnonylamine, *N,N*-dimethyldecylamine, *N,N*-dimethyaniline, *N*-ethyldiisopropylamine, tripropylamine, triisopropylamine, 4,*N,N*-Trimethylaniline, *N,N*-dimethyl-o-toluidine, tributylamine, *N,N*-dicyclohexylmethylamine, *N,N*-dimethyldodecylamine, tripentylamine were obtained from Aldrich and used as received. All equipment was used in accordance with manufacturer specification unless stated otherwise. Freezing point depression osmometry was performed using an Advanced Instruments Inc. Model 3250 Osmometer. Viscosity measurements were made using the falling bob method with a Cambridge Applied systems VL4100 viscometer.

Nuclear magnetic resonance (NMR) spectra were acquired on a Bruker Avance III 600 MHz spectrometer with a magnetic field strength of 14.093 Tesla, corresponding to operating frequencies of 600.13 MHz (^{1}H), and 150.90 MHz (^{13}C). All NMR were captured with a co-axial insert containing C_6D_6 (Cambridge Isotopes Laboratories). ^{1}H NMR spectra were collected with a 30 degree pulse and 10 sec delays between scans, the T1 of every integrated shift was verified, most T1 relaxations well under 1 sec and none above 2 sec. The integration was set to a known peak in of the tertiary amine providing the relative concentration of (H_2O+H_2CO_3) : tertiary amine. ^{13}C NMR spectra with quantifiable integration were obtained with inverse gated decoupling spectra with a 30 degree pulse and 60 second delays between scans. The ^{13}C T1 values were verified and found to range between 2.5 sec and 10.5 sec for the carbonate peak, all other peaks had shorter relaxation times. The integration of the carbonate peaks was set to unity providing the relative concentration of tertiary amine:carbonate.

Conversion of 1-16 to 1'-16'

As an example, deionized water (3.884 g) and dimethylhexylamine (**6**, 5.468 g, 7.35 ml, 0.0423 mol) are placed in home-built carbon dioxide addition cell, Figure 15. The carbon dioxide addition cell was designed to measure the volume of nonpolar amine which remained phase separated from the aqueous volume. Knowing the original volume of the amine, it was possible to calculate the volume which had reacted with the known volume of water. The addition cell from bottom to top features a fine frit base with a ~2.5 cm diameter, 5 ml reservoir bulb, 10 ml graduated cylinder (1.5 cm diameter 8 cm tall), 25 ml reservoir bulb, 30 cm condenser. A small stir bar is added and stirred rapidly, the condenser is operated at 2 °C, and CO_2 is flowed through the cell at a steady rate of < 3 ml sec. After a 50 min purge, 1.0 ml of the amine is unreacted, after 2 hrs 0.9 ml of the amine unreacted. The solution was purged with carbon dioxide for a total of 5 hrs with 0.9 ml of the amine unreacted. The product, **6'** approximately [$HN(Me)_2Cy\ HCO_3$], and unreacted amine are removed with a syringe and long needle.

Figure 15. Carbon dioxide additional cell used to convert two phases of amine and water to a single phase polar SPS, **1’** through **16’**.

Synthesis of *N,N*-dimethyl-2-ethylhexylamine (14)

2-ethyl-1-hexylamine (304.55 g 2.36 mol) was slowly added to a solution of formaldehyde 37wt% (575.17 g, 7.09 mol) and formic acid (328.53 g, 7.14 mol) and allowed to stir overnight. Slow addition of NaOH (162 g, 4.1 mol) caused the solution to split into organic and aqueous layers. The organic layer was isolated, washed with water (4x350 ml), and dried with sodium sulfate. The product (315.5 g) was then distilled at 150 mTorr and 25-30 °C giving a slightly yellow liquid (235.9 g, MW 157.4, 1.5 mol) with a density of 0.768 g/ml for a final yield of 64%. The product was confirmed as *N,N*-dimethyl-2-ethylhexylamine with a water content <1wt% using ^{1}H-NMR, ^{13}C-NMR, COSY, HSQC, and HMBC.

ACKNOWLEDGEMENTS

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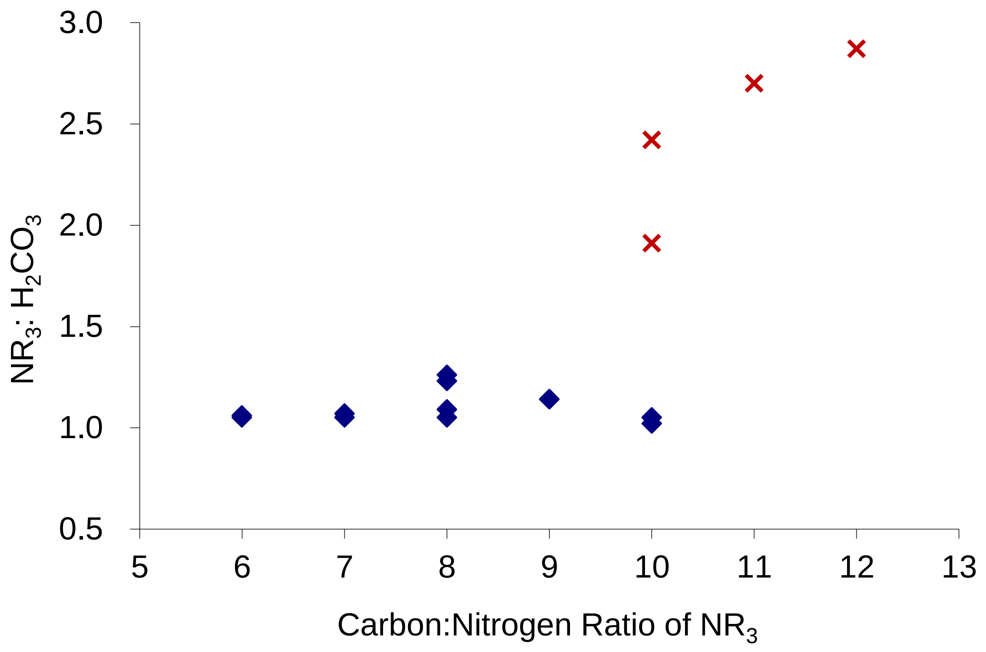
Graphical Abstract



Text Abstract

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Structure-Function Study of Tertiary Amines as Switchable Polarity Solvents

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ABSTRACT

A series of tertiary amines have been screened for their function as switchable polarity solvents (SPS). The relative ratios of tertiary amine and carbonate species as well as maximum possible concentration were determined through quantitative ^{1}H and ^{13}C NMR spectroscopy. The viscosities of the polar SPS solutions were measured and ranged from near water in dilute systems through to gel formation at high concentrations. The van't Hoff indices for SPS solutions were measured through freezing point depression studies as a proxy for osmotic pressures. A new form of SPS with an amine:carbonate ratio significantly greater than unity has been identified. Tertiary amines that function as SPS at ambient pressures appear to be limited to molecules with fewer than 12 carbons. The *N,N*-dimethyl-n-alkylamine structure has been identified as important to the function of an SPS.

INTRODUCTION

Developing safe, energy efficient, and environmentally friendly alternatives to traditional solvent systems is a primary goal of "green" and sustainable chemistry research.[1] These goals can be achieved by reducing solvent volumes, changing processes to function with more benign solvents, or developing alternative solvents with new behaviors that allow better process lifecycle performance. Advances in alternative solvents are expected to improve conventional solvent process such as oil extraction from biomass, as well as non-standard uses of solvents. Novel "solvent" materials will allow the development of new processes in areas such as CO_2 separations, water purification, and energy storage. Among the most well-known and promising alternative solvents are the various room-temperature ionic liquids, supercritical fluids, and switchable polarity solvents (SPSs) explored in this study.

SPSs can be divided into various subcategories based on composition and behavior.[2–5] This study targeted water-compatible single-component SPSs which are immiscible with water in their basic form but when they are reacted with carbonic acid, derived from exposure to ~1 atm carbon dioxide, the water miscible acid form $[H^+(Base)\ HCO_3^-]$ of the SPS is produced, Reaction 1. Similar behavior can be obtained from dual component SPSs involving a nitrogen base (amidines and guanidines) and an alcohol or primary amine; but such systems require balanced stoichiometry to function correctly and tend to be water sensitive which makes them unattractive for many applications.[2,6–8] Some single component SPS, such as secondary amines, also suffer water sensitivity in the form of material precipitation at relatively low water concentrations and thus are ignored in this study.[9] Known water-compatible single-component SPSs include highly functionalized amidines and guanidines[4], tertiary amines[5], and pH sensitive ionic liquids[10]; The scope of research was further focused to tertiary amines based on their potential cost effectiveness when produced at large scale.

$$NR_{3(org)} + CO_{2(gas)} + H_2O \rightleftharpoons HNR_3{}^+{}_{(aq)} + HCO_3^- \qquad (1)$$

Our laboratory became interested in SPS for their use as thermolytic draw solutes[11] (versus more conventional non-thermolytic draw solutes[12,13]) in osmotically driven membrane processes (ODMPs). As thermolytic solutes, SPS can be used in water purification through forward osmosis (FO)[14], solution concentration through direct osmotic concentration[15], and for osmotic heat engines through pressure retarded osmosis[16]. Since its introduction in 2006, the ammonia-CO_2 system has been considered one of the more viable next generation draw solute for FO.[17] SPS draw solutes have a number of advantages over the ammonia-CO_2 system; including negating the need to handle and store gaseous ammonia, lower permeability to properly selected membranes, lower energy requirements, and facile removal of SPS from water through liquid phase separation.

Tertiary amines, such as those screened in this publication, long have been considered unlikely candidates for carbon capture or natural gas sweetening. Primary and secondary amines react chemically with carbon dioxide rapidly to form carbamates.[18] Tertiary amines, on the other hand, follow a second route in which carbon dioxide forms carbonic acid and then reacts via an acid-base reaction with the amine.[18] The carbonic acid pathway is generally slower due to the rate of carbonic acid formation. However, tertiary amines and mixtures which include tertiary amines have recently been reported for carbon capture in conjunction with phase change processes.[19–37] Amines included in our study have also been investigated by Zhang as carbon capture agents where he refers to them as biphasic or lipophilic amine solvents.[19–22] A phase change carbon capture system, DMX^{TM}, has been developed by *IFP Energies nouvelles*; however the chemical composition of their formulation was not available to us.[23,24] Heldebrant at is exploring performance of single-component CO_2-binding organic liquids (CO2BOLs).[25–28] Hu of *3H Company* has reported a two phase acid capture system involving a polarity switching amine.[29–33] Eckert has worked with a switchable polarity ionic liquid.[34–37]

There have been various publications addressing the use of SPS for processing, extraction, and separation. This includes plastic recycling,[5] extraction of oils from biomass and microbes,[38–42] activation of recalcitrant biomass,[43] and the use of SPS as a chemical synthesis solvent.[2,44] The use of SPS in these applications has similarities to distillable room temperature ionic liquids (RTIL) which are often comprised of amines and carboxylic acids.[45–48] There is also the well-established use of ammonium carbamate and carbonate salts as polyurethane polymerization catalysts.[49]

Each of the potential applications can benefit from achieving a higher concentration of the SPS polar form, $[HNR_3^+\ HCO_3^-]$; however, how the concentration is considered best depends on the application. In the case of FO, the osmotic strength of the draw solute is the thermodynamic driving force for the water transport process and is best measured by molality.[50] In solvent extraction, the osmotic pressure is less important than the volume of non-aqueous amine contained within the SPS polar form. A solution with a high weight percent (wt%) of $[HNR_3^+]$ allows the solution volumes used in the solvent extraction process to be minimized. In a carbon capture system, the SPS carbon capture agent would ideally have an extremely large capacity for carbon dioxide and the ideal unit is wt% of CO_2. The most serious drawback of high concentration solutions is increased viscosity which may be problematic for many applications.

Theoretical treatments of high concentration solutions are usually modeled through activity, a_s. Activity ($a_s = y_s x_s$) is a product of the mole fraction, (x_s, moles solute/total moles solvent and solute), and a dimensionless empirically based activity coefficient, y_s. Thus, the mole fraction, x_s, also was also considered when looking for concentration trends.

Previous to this study, the information concerning the maximum concentration of amine based SPS in their polar form was limited to *N,N*-dimethylcyclohexylamine (**5**) and *N,N,N'*-tributylpentanamidine.[4,5] Tertiary amines are among the most attractive SPS reported so far due to their simplicity and low cost. These advantages motivated the screening of tertiary amines **1-26** for a variety of physical properties similar to the study recently published by Eckert.[36] This screening has identified a new form of SPS, as well as structural features and limitations of tertiary amines that are fundamental to their performance as SPS.

RESULTS AND DISCUSSION

Due to the fact that many SPS applications would benefit from higher SPS concentrations in the polar form, the maximum concentration was characterized for a series of tertiary amines, **1-26**. This series was selected not because each amine was expected to be a top performer but rather they are representative of many small tertiary amines with features such as rings systems, different length carbon chains relative to the nitrogen, and alkyl chain branching. These representative amines were selected not only to set limits on the maximum and minimum number of carbons in a functional SPS but also to determine how structural features affect that function. The set of amines included the re-visitation of 12 tertiary amines that had been previously studied for SPS behavior, confirming that 8 amines transition from a water immiscible state to a water miscible state with the introduction of CO_2 and thus "function" as SPS.[5] In addition, 14 previously unreported amines were investigated for SPS behavior and, of these, 8 additional amines have been identified to function as SPS. The structures of the amines that functioned as SPS are illustrated in Figure 1 and those that did not measurably function as SPS under our experimental conditions are illustrated in Figure 2.

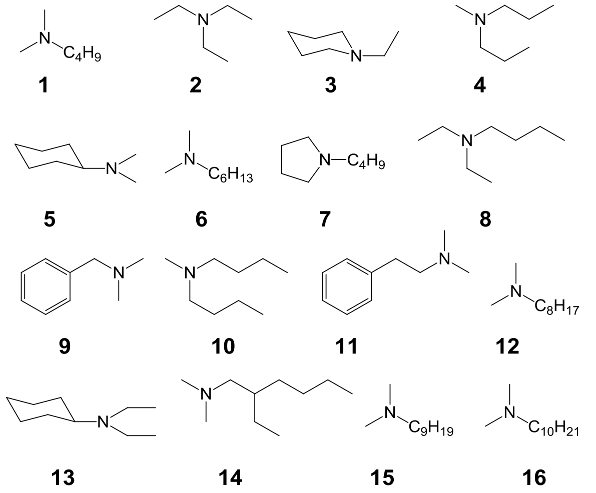

Figure 1. Structures of tertiary amines that functioned as SPS.

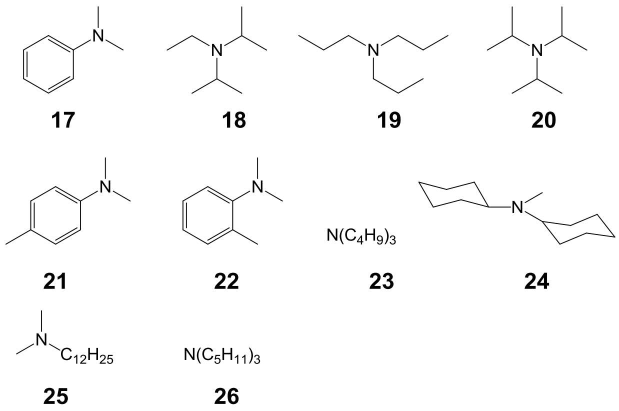

Figure 2. Structures of tertiary amines that did not function as SPS.

While a variety of properties were recorded including viscosity, density, and freezing point depression; it was the NMR spectroscopic studies that were of primary importance where it was used to measure both concentration and composition of SPS solutions. The procedure to identify the maximum concentration involved combining known quantities of water and tertiary amine and purging the solution with carbon dioxide at ambient pressure. The volume of the amine that did not react to form the polar water soluble SPS was measured and a tentative maximum solution concentration was calculated based on the initial masses and unreacted volume. This volume derived concentration measurement was used to corroborate the concentrations found through quantitative NMR studies of the polar SPS solutions.

The NMR studies also were used to identify composition characteristics of the polar SPS solutions. This compositional data indicated that the assumption featured in Equation 1 that all SPS form in a ratio of one tertiary amine to one carbonic acid is incorrect. There are two types of SPS whose primary compositional difference is in the amine:H_2CO_3 ratio.

Osmotic SPS

An SPS that can produce an osmotic driven flux across a semi-permeable membrane can be considered “osmotic”. Osmotic SPS amines are characterized by a maximum concentration of their polar SPS form, after which additional amine is rejected by the aqueous phase and remains separated in a nonpolar phase, even in the presence of excess ambient pressure carbon dioxide. Osmotic SPS systems remain fully liquid under all the experimental conditions and no precipitate is observed; although clouding is common during the switching process. Osmotic SPS can be diluted with water and display predictable decreases in osmotic pressure. Correlation between osmolality and molality produces representative van‘t Hoff indices. To accurately measure the maximum concentration of these SPS, quantitative NMR spectroscopy was conducted.

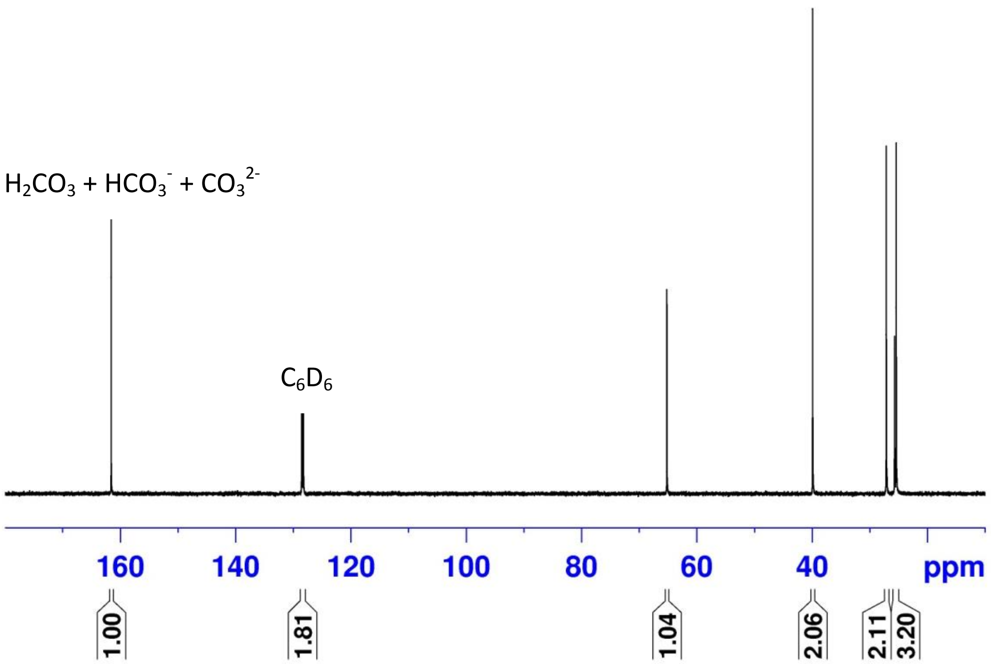

Figure 3. The quantitative ^{13}C NMR of dimethylcyclohexylamine bicarbonate solution **5’**.

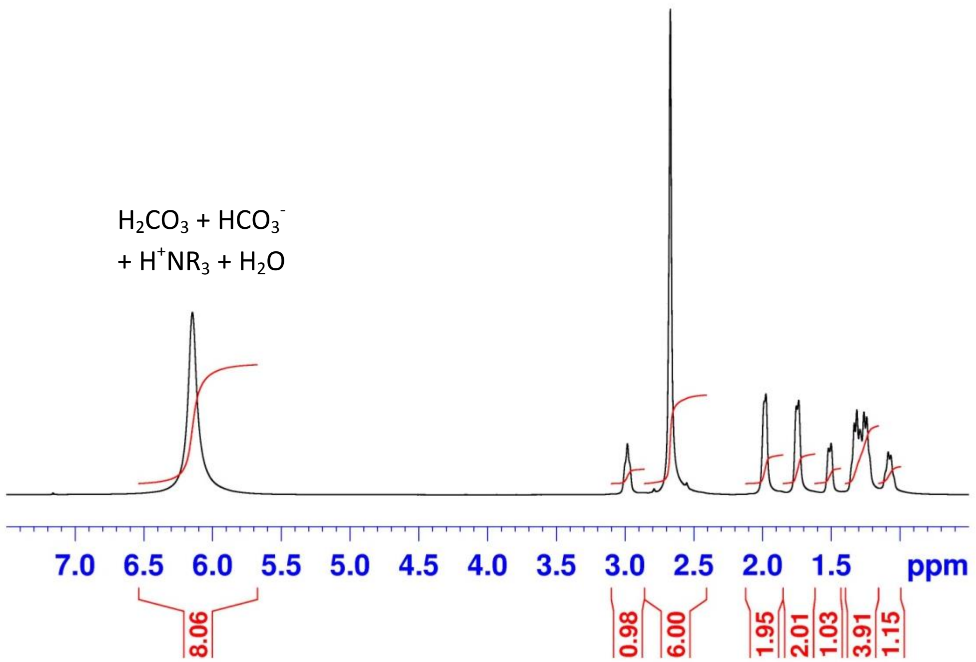

Figure 4. The quantitative ^{1}H NMR of dimethylcyclohexylamine bicarbonate solution **5'**.

The quantitative ^{13}C and ^{1}H NMR spectra were conducted as neat solutions with a coaxial insert containing C_6D_6 as a reference. As examples, Figures 3 and 4 feature the spectra for solution **5'**. The ^{1}H NMR spectrum contains chemical shifts, δ, which have been assigned to the exchangeable protons of water (H_2O), carbonates (HCO_3^- and H_2CO_3), and ammonium (H^+NR_3) ions, Figure 4. The analysis of this data can be simplified by ascribing two protons to carbonic acid and its salts. Based on ^{1}H NMR spectrum integration, the ratio of water and carbonic acid to amine can be calculated. This ratio combined with the amine to carbonic acid ratio derived from the quantitative ^{13}C NMR, Figure 3, allow for the calculation of the relative mole ratio of amine:carbonic acid:water. With the molecular mass and solution density it is possible to calculate mole fractions, molarities, molalities, and weight percent (Table 1), all of which were considered in looking for trends associated with physical properties (Table 2).

Table 1. The relative integration of quantitative NMR select properties and concentrations of tertiary amine bicarbonate solutions.

Amine	**number**	**molecular mass (amine)**	**density (solution)**	**amine:H_2CO_3 (^{13}C)**	**(H_2O+ H_2CO_3) :amine (^1H)**	**wt% (amine+H_2CO_3)**	**mole fraction (amine)**	**molal (amine)**	**molarity (amine)**
dimethylbutylamine	1’	101.2	1.05	1.06	5.13	67.9	0.163	13.3	4.47
triethylamine	2’	101.2	1.05	1.05	9.46	51.1	0.096	6.52	3.35
1-ethylpiperidine	3’	113.2	1.09	1.05	4.93	70.6	0.169	14.0	4.47
methyldipropylamine	4’	115.2	1.01	1.07	25.8	27.9	0.037	2.23	1.63
dimethylcyclohexylamine	5’	127.2	1.10	1.05	4.03	77.0	0.199	18.0	4.55
dimethylhexylamine	6’	129.2	0.98	1.23	6.40	64.1	0.135	9.94	3.50
1-butylpyrrolidine	7’	127.2	0.99	1.26	6.44	63.4	0.134	9.84	3.56
diethylbutylamine	8’	129.2	1.02	1.09	19.2	36.1	0.050	3.04	1.98
dimethylbenzylamine	9’	135.2	1.05	1.14	23.4	31.9	0.041	2.47	1.77
methyldibutylamine	10’	143.3	1.00	1.14	88.8	11.1	0.011	0.63	0.56
dimethylphenethylamine	11’	149.2	1.03	2.42	4.45	70.6	0.184	13.8	4.16
dimethyloctylamine	12’	157.3	0.92	1.91	5.97	65.9	0.143	10.2	3.20
diethylcyclohexylamine	13’	155.3	1.04	1.02	23.5	34.8	0.041	2.47	1.67
dimethyl-2-ethylhexylamine	14’	157.2	1.00	1.05	508	2.3	0.002	0.11	0.11
dimethylnonylamine	15’	171.3	0.88	2.70	5.73	66.8	0.149	10.4	3.03
dimethyldecylamine	16’	185.4	---	2.87	7.54	61.5	0.117	7.72	2.97

Table 2. The properties of tertiary amines bicarbonate solutions.

Amine	number	carbon: nitrogen	density (amine)	wt% (amine+H_2CO_3)	density (solution)	amine:H_2CO_3 (^{13}C)	van‘t Hoff index (amine)	van‘t Hoff index (Σ ions)	max. osmotic pressure (atm)	viscosity (cP)
dimethylbutylamine	1’	6	0.721	67.9	1.05	1.06	1.81	0.93	616	25.0
triethylamine	2’	6	0.726	51.1	1.05	1.05	1.73	0.88	288	10.6
1-ethylpiperidine	3’	7	0.824	70.6	1.09	1.05	1.72	0.88	641	71
methyldipropylamine	4’	7	0.734	27.9	1.01	1.07	1.69	0.87	92.9	2.8
dimethylcyclohexylamine	5’	8	0.849	77.0	1.10	1.05	1.73	0.88	835	108
dimethylhexylamine	6’	8	0.744	64.1	0.98	1.23	1.37	0.76	328	25.5
1-butylpyrrolidine	7’	8	0.814	63.4	0.99	1.26	1.36*	0.76*	325*	29
diethylbutylamine	8’	8	0.748	36.1	1.02	1.09	1.79	0.93	135	11.3
dimethylbenzylamine	9’	9	0.900	31.9	1.05	1.14	1.37	0.73	87.1	2.8
methyldibutylamine	10’	9	0.745	11.1	1.00	1.14	1.77	0.94	27.3	1.6
dimethylphenethylamine	11’	10	0.89	70.6	1.03	2.42	---	---	---	15.0
dimethyloctylamine	12’	10	0.765	65.9	0.92	1.91	---	---	---	58
diethylcyclohexylamine	13’	10	0.845	34.8	1.04	1.02	1.82	0.92	114	4.8
dimethyl-2-ethylhexylamine	14’	10	0.768	2.3	1.00	1.05	---	---	---	1.1
dimethylnonylamine	15’	11	0.773	66.8	0.88	2.70	---	---	---	86
dimethyldecylamine	16’	12	0.778	61.5	---	2.87	---	---	---	gel

*Based on amine concentration <1.05 mol/Kg.

The concentrations calculated from quantitative ^{13}C and ^{1}H NMR spectra studies allow the calculation of van’t Hoff indices based on either the sum of tertiary amine/ammonium molality or the total species molality, which includes tertiary amines, tertiary ammonium, and carbonate species, Table 2. The total species molality is more informative as it removes the variation in the relative carbonate concentration and is more directly related to the ion dissociation. The degree of dissociation cannot be perfectly gauged because these indices are composites of various forms of “ion pairing”, which reduce the van‘t Hoff index, and the role of “bound” waters of hydration, which raise the indices.[50,51] Freezing point depression studies were conducted to obtain experimental van’t Hoff indices which allow estimation of osmotic pressure, Table 2.[50] The van‘t Hoff indices were based on values measured generally between 0.10 and 2.0 Osm/kg, such as Figure 5.

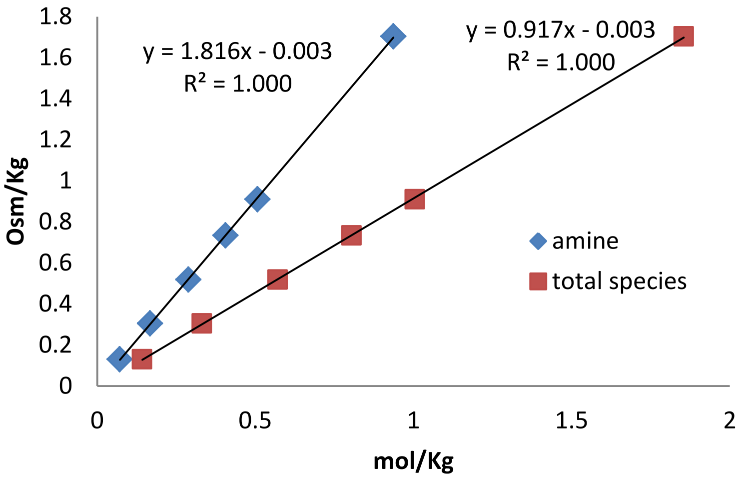

Figure 5. The van't Hoff plot for diethylcyclohexylamine, **13'**. The diamonds are based on molality of tertiary amine and tertiary ammonium ions. The squares are based on the total species molality including tertiary amines, tertiary ammonium ions, and carbonate species

The correlation over the 0.10 to 2.0 Osm/kg range, as measured by freezing point depression, was generally linear where total species van't Hoff indices ranged between 0.73 and 0.94 (Table 2) for osmotic SPS, indicating high degrees of dissociation for nearly all the solutions measured. One example that did not follow this trend is solution **7'**, which deviated negatively from linearity when the amine concentration exceeded 1 mol/Kg, Figure 6, suggesting higher order "ion pairing" equilibrium processes. No other solutions deviated from linearity, but solution **8'** would not freeze cleanly at or above 1.2 mol/Kg of amine, which may be a result solution out gassing or exceeding a eutectic point.

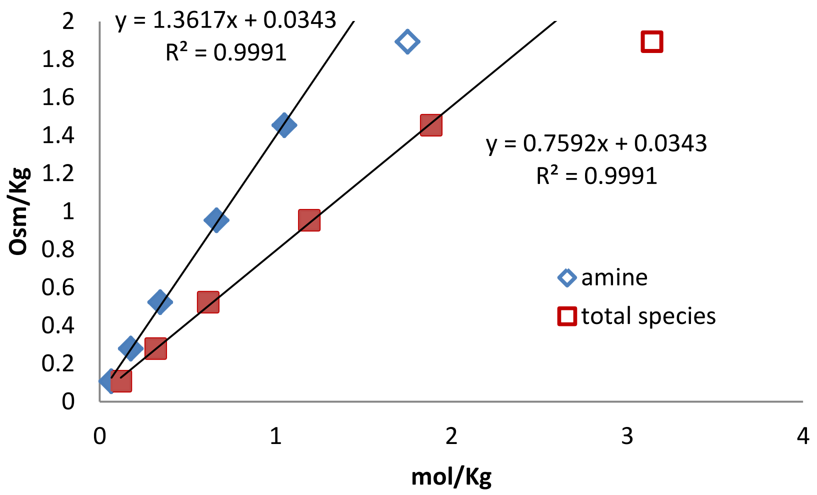

Figure 6. The van't Hoff plot for diethylcyclohexylamine, **7'**. The diamonds are based on molality of tertiary amine and tertiary ammonium ions. The squares are based on the total species molality including tertiary amines, tertiary ammonium ions, and carbonate species. Only the filled-marker data was used to calculate the trend lines. The higher concentration open-marker data feature a negative deviation from linearity.

It was previously reported that **5** forms a solution in a 1:1 (vol:vol) ratio with water which our lab reported as a viable ODMP draw solute.[11] The maximum concentration of **5'** was revisited and was found to have a maximum concentration of 77 wt%, which corresponds to 18 molal and 4.6 M by amine. This concentration is considerably higher than the value previously reported. The osmotic pressure of solution **5'** has been estimated at 836 atm based on previously described methods[50], which is considerable for an FO draw solute.

Non-osmotic SPS

Osmotic SPS were not the only SPS form encountered in this study; there were also "non-osmotic" SPS which differed in both composition and behavior. These SPS are coined "non-osmotic" because they did not produce the expected osmotic driven flux across a semi-permeable membrane when used as a FO draw solution in their “polar” form. The van ‘t Hoff indices of non-osmotic SPS could not be measured because the solutions do not dilute homogenously when water is added. All measured freezing points were much lower than expected given the concentration. For these reasons Table 2 does not contain a maximum osmotic pressure for non-osmotic SPS. This is an unexpected result for a solution made from the addition of carbon dioxide and tertiary amine to water. When water is added to a concentrated non-osmotic SPS, a portion of the solution dilutes, and is reflected in freezing point osmometry measurements, but another portion phase separates as the nonpolar tertiary amine. To understand this dilution phenomenon, the relative concentrations of the species in solution must be known. The solutions are comprised of amines species, both protonated and unprotonated, and carbonate species, which is mostly bicarbonate with equilibrium quantities of carbonate and carbonic acid. Because of the complexity involved with tracking the equilibrium concentration, it is useful to consider this acid-base system in its non-ionized form to compare the “amine” to “carbonic acid” ratios. The ratio of tertiary amine to carbonic acid for non-osmotic SPS varies between 1.82 and 2.87 based on the integration of the quantitative ^{13}C NMR spectra. These values for non-osmotic SPS are significantly higher than polar SPS with all values listed in Table 1 and 2 and plotted in Figure 7.

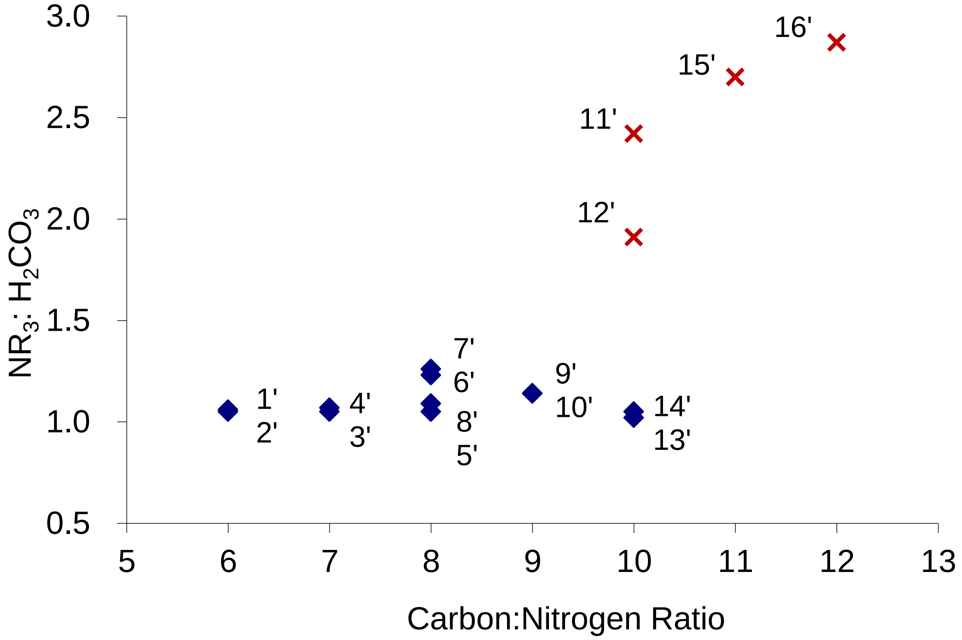

Figure 7. The NR_3:H_2CO_3 ratio represents the ratio between all forms of amine protonated and unprotonated and the sum of carbonate, bicarbonate, and carbonic acid; Diamonds represent “osmotic” SPS, crosses represent “non-osmotic” SPS.

Modeling the maximum concentration equilibrium

Due to the discovery of non-osmotic SPS, the model SPS maximum concentration must be revisited. Since the organic amine is an immiscible material, its concentration does not change with the equilibria and thus can be taken as unity. Likewise the solvent, in this case water, is usually in a large excess such that its effective concentration does not change with the equilibrium and usually can also be treated as unity. Assuming the solvent as unity is not strictly proper for the SPS equilibria where the water concentration drops below 0.8 mole fraction and may also be involved in ionic hydration. Thus, the water concentration is included in this equilibrium. Because these are non-aqueous solutions of variable consistency, there are no known Henry’s law constants for these systems. Thus, the CO_2 concentration is not calculated based on the partial pressure. In addition, because CO_2 partial pressure is the independent variable, it is preferred for the calculation of an equilibrium constant.[52] These assumptions yield the equilibrium expression, Equation 2, from the reaction described by Equation 1.

$$NR_{3(org)} + CO_{2(pressure)} + H_2O \rightleftharpoons HNR_3{}^{+}{}_{(aq)} + HCO_3^{-} \qquad (1)$$

$$K_1 = \frac{[HNR_3^{+}]_{aq}[HCO_3^{-}]}{pCO_2[H_2O]} \qquad (2)$$

$$NR_{3(org)} \rightleftharpoons NR_{3(aq)} \qquad (3)$$

$$NR_{3(aq)} + CO_{2(pressure)} + H_2O \rightleftharpoons HNR_3{}^{+}{}_{(aq)} + HCO_3^{-} \qquad (4)$$

$$a\cdot[HNR_3{}^{+}{}_{(aq)} + NR_{3(aq)}] + NR_{3(org)} \rightleftharpoons NR_{3(aq)} + b\cdot H_2O \qquad (5)$$

$$K_{(Equation\ 3-5)} = \frac{[HNR_3^{+}]_{aq}[HCO_3^{-}][NR_3]_{aq}[H_2O]^{b}}{pCO_2[H_2O][HNR_3^{+} + NR_3]_{aq}^{a}} \qquad (6)$$

Non-osmotic SPS concentrations are not as simple as they can be modeled multiple ways. Because there are appreciable amounts of aqueous tertiary amine in non-osmotic SPS, the model needs to consider the conversion of organic tertiary amine to aqueous tertiary amine (Equation 3). When aqueous tertiary amine is considered directly, Equation 1 is converted into Equation 4. As the aqueous tertiary amine and aqueous tertiary ammonium bicarbonate concentrations increase, the concentration of dissolved organic materials increases. This results in a solution polarity decrease, which shifts the solution towards something more like a water immiscible organic solvent. This shift in polarity allows the solution to accept more tertiary amine (Equation 5). In this model, we assume HNR_3^{+} and NR_3 contribute equally to the polarity shift for the sake of simplicity. Presumably, the increase in aqueous amine when the products are favored in Equation 3 allows the further conversion of carbon dioxide into bicarbonate and protonated tertiary amine (Equation 4) in a positive feedback loop. This feedback loop does two things: 1) increases the carbonate concentration relative to the osmotic SPS and 2) increases the absolute concentration of $HNR_3{}^{+}{}_{(aq)}$ and HCO_3^{-}. The relative concentration of $NR_{3(aq)}$ also increases and the solution moves further away from a composition that is strictly aqueous. If water is added to a concentrated non-osmotic SPS solution, a portion of the $NR_{3(aq)}$ phase separates as the SPS solution polarity is driven to a more polar form. The ability of water to shift the polarity of the solution is featured in its role as a product dependent on the value “b” in Equation 5. The role of water is complex and it may be necessary to identify portions as “free” or “bound” in the SPS solution, but the treatment in Equation 4 and 5 is sufficient to model the current information yielding an equilibrium expression, Equation 6.

Limits of SPS function at ambient pressure and concerns with measurements

The number of carbons or the carbon: nitrogen (C:N) ratio of a tertiary amine is a useful proxy for both the mass and polarity of the tertiary amine; More carbons in the amine result in higher molecular mass, and thus lower overall polarity. Hansen solubility parameters and its components were explored to describe tertiary amine polarity without success; the calculated parameters varied little and were less intuitive than the simple C:N ratio.

In this study, no tertiary amines with a C:N ratio of less than 6 were explored. Tertiary amines with low C:N ratio have many undesirable characteristics including low boiling points, high vapor pressures, higher water solubility, and a more difficult switch between the nonpolar and polar phases. Release of CO_2 for these amines generally requires substantially higher temperatures or greater volumes of purge gas, followed by cryogenic amine capture, which complicates their utility. These factors serve to limit the use of these amines as SPS and motivates the efforts to define the proper upper thresholds of the C:N ratio for tertiary amines that function as SPS.

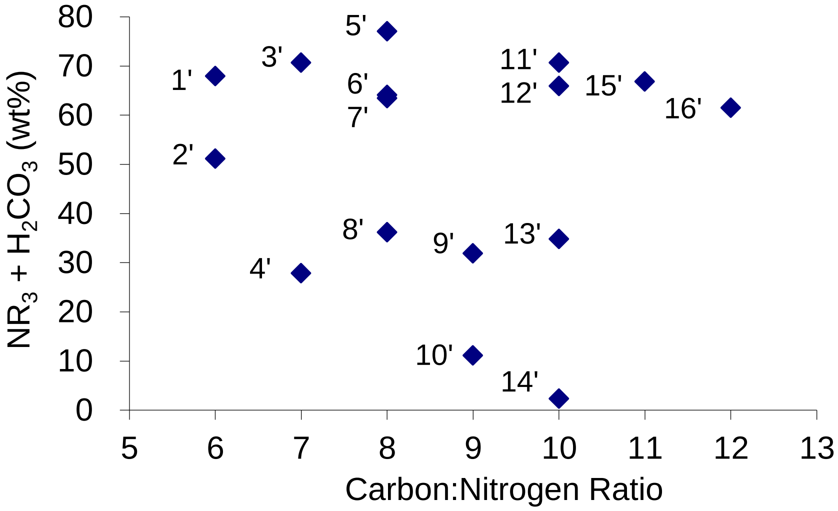

Figure 8. Maximum acquired concentration as a function of the C:N ratio.

When the total weight percent of both osmotic SPS (C:N 6-10) and non-osmotic SPS (C:N 10-12) are plotted against C:N their ratio, high weight percentages are found until C:N 12 after which no tertiary amines were found to form SPS, Figure 8. The loss of SPS formation above C:N =12 may be explained when the concentration is broken into the tertiary amine and the carbonate concentration. For example, focusing on the *N*,*N*-dimethyl-n-alkylamine series, Figure 9, it is clear that the carbonate concentration steadily decreases from C:N 6 to 11. Solution **16'** is excluded from this analysis because it forms a gel distinct from the other liquid solutions. A trend line can be fitted to the carbonate concentrations of the *N*,*N*-dimethyl-n-alkylamine series, which includes osmotic SPS (**1'** and **6'**) and non-osmotic SPS (**12'** and **15'**) that indicates increasing the C:N ratio results in a decline in the carbonate concentration. Because osmotic and non-osmotic systems are linear when the C:N ratio is plotted against carbonate molarity, this is convenient trend for comparing all SPS systems. The linearity of the trend also could be taken to suggest that concentration phenomena influence the maximum concentrations of both osmotic and non-osmotic SPS in a similar way, rendering the previous equilibrium analysis (Equations 3-6) unnecessary. Such a conclusion does acknowledge that while the C:N ratio is a useful proxy for polarity and molecular mass, it is not a fundamental physical property commonly used to compare equilibrium states and thus, in many ways, an arbitrary unit, making the resulting trend similarly arbitrary.

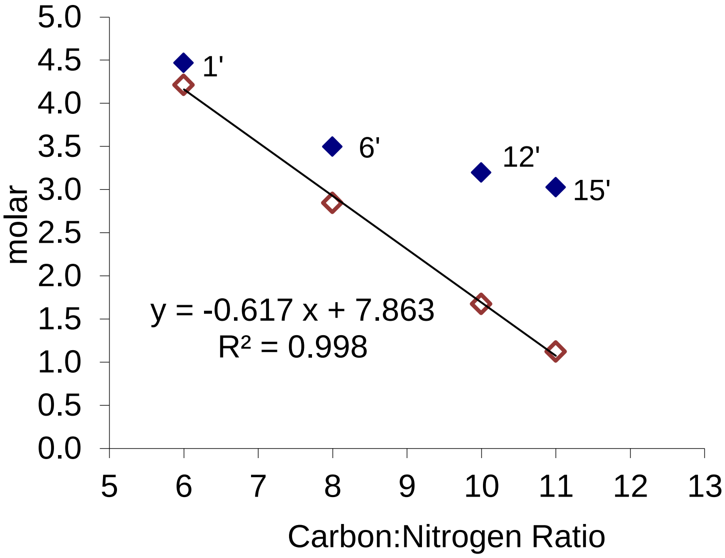

Figure 9. Maximum acquired concentration as a function of the C:N at 1 atm CO_2 for SPSs featuring the *N*,*N*-dimethyl-n-alkylamine structure plotted in molarity for both the amine (solid diamond) and carbonate components (open diamond).

The observed trend in Figure 9 is product of known theoretical and experimental influences. The slope of the regression might be steeper or fit a different mathematical/concentration model if not for three phenomena. First, as discussed earlier, there is a positive feedback loop associated with non-osmotic SPS and their elevated concentration of aqueous amine. This raises the concentration of carbonate in solution for **12’** and **15’** (and **16’**) which define the low end of the trend. The second feature is the home-built experimental apparatus for this study pushed carbon dioxide through a column of solution which was then exhausted through a condenser open to the atmosphere through a needle, as shown in the experimental section. For lower viscosity amines, the CO_2 pressure rapidly equilibrated with ambient pressure; however, the amines with viscosities greater than 50 cP (Table 2), namely **3’**, **5’**, **12’**, and **15’** (and **16’**) provide back pressure on the carbon dioxide flow slightly elevating the CO_2 pressures directed at the solution.

The third phenomenon that affects the trend observed in Figure 9 is the stability of the solutions. Not all solutions are stable for significant periods of time. Solutions **11’** and **15’** (and **16’**) are prone to venting carbon dioxide when mild pressure or vacuum is applied or even mixing in the absence of a saturated carbon dioxide atmosphere. When conducting NMR experiments, approximately 20% of solutions **11’** and **15’** (and **16’**) phase separated into the nonpolar amine form, suggesting they may be metastable supersaturated states.

Each of these three phenomena tend to inflate the observed concentration at high C:N ratios. Because two of these phenomena are related to the experimental process and design, the conclusions and performance trends regarding high C:N ratios and the upper threshold for tertiary amine function as SPS may be generous.

Structural Features of SPS

Within the range of C:N ratios between 6 and 12 there are structural features that influences SPS performance. Better performing SPS are those that can reach the highest concentrations. Of the better performing SPS, it was noted that every example featured the core structure of *N*,*N*-dimethyl-R-amine (**1’**, **5’**, **9’**, **11’**, and **15’**), or 1-alkylpiperidine (**3’**). The *N*,*N*-dimethyl-R-amine grouping can be broken down into *N*,*N*-dimethyl-n-alkylamines (**1’** and **15’**), *N*,*N*-dimethylcyclohexylamine (**5’**), and *N*,*N*-dimethylphenealkylamines (**9’** and **11’**). Because the pK_as of the studied tertiary amines are largely equivalent, it is assumed that an aspect of either or both polarity and intramolecular steric interaction are dictating the differences in the observed SPS performance.

There are many methods to model steric and polar interactions. Tolman cone angles have been used extensively to model the sterics influences of tertiary phosphines on their interactions with Lewis acid metal centers.[53–55] While Tolman cone angles have not been used to describe amines, the phosphine values were used to conduct an evaluation that, while internally consistent, was ultimately unsuccessful. A functional group contribution model similar to the Hansen system, but dedicated to the tertiary amine SPS concentration model, is proposed below.

At the core of the functional group contribution treatment is the linear relationship between C:N ratio and the maximum molarity of the HCO_3^- & HNR_3^+ concentrations in the *N*,*N*-dimethyl-n-alkylamine series, which holds for the alkyl = butyl (**1’**), hexyl (**6’**), octyl (**12’**), nonyl (**15’**) series. Amines which deviate from the *N*,*N*-dimethyl-n-alkylamine skeletal structure can be grouped into two overlapping groups. The first group of amine structures all contain carbons extending the core *N*,*N*-dimethyl-n-alkylamine structure but with no ring systems. For example, these carbons would include both carbons of dimethyl-2-ethylhexylamine’s, **14’**, ethyl group or 1 carbon from each of the ethyl groups in diethylbutylamine, **8’**, Figure 10. The structures of these are amines and their pertinent carbons are labeled as (<) in Figure 10 because their concentration are lower than predicted by the *N*,*N*-dimethyl-n-alkylamine trend.

The concentrations of ring free systems in relation to *N*,*N*-dimethyl-n-alkylamine trend line are also plotted in Figure 11. The second group is tertiary amines whose structures include a ring system such as a cyclohexyl group (**5’** and **13’**), phenyl group (**9’** and **11’**), piperidine (**3’**), and pyrrolidine (**7’**). The structure of ring containing systems are also included in Figure 10 and are labeled as (<, =, and >) because their concentrations vary compared to what is predicted by the *N*,*N*-dimethyl-n-alkylamine trend. The maximum concentrations of ring containing systems in relation to *N*,*N*-dimethyl-n-alkylamine trend line are plotted in Figure 12.

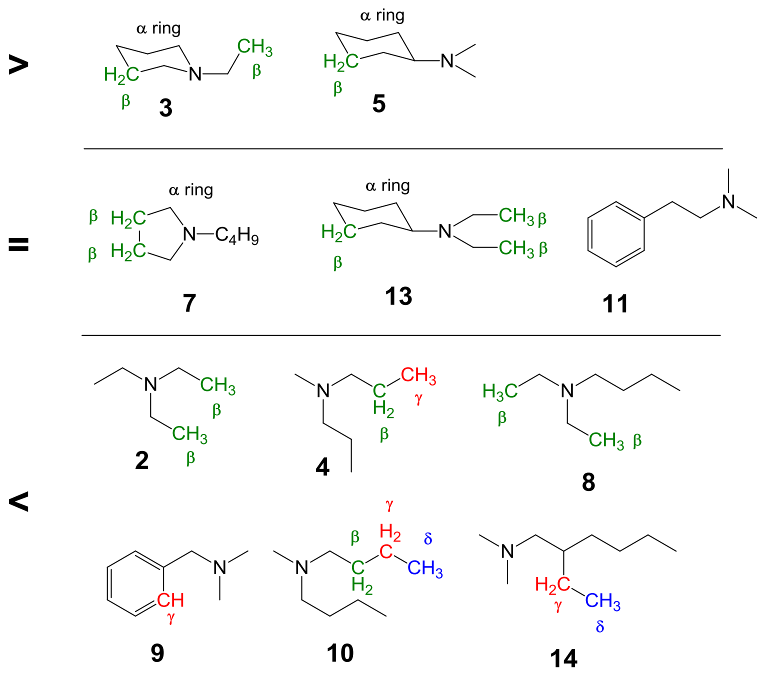

Figure 10. The amines which deviate from the *N*,*N*-dimethyl-n-alkylamine core structure with β, γ, and δ carbons as well as α rings systems labeled and separated into groups according to whether their carbonate concentration are greater than (>), equal to (=), or less than (<) the trend line formed from the carbonate concentration of the *N*,*N*-dimethyl-n-alkylamine solutions (Figure 9).

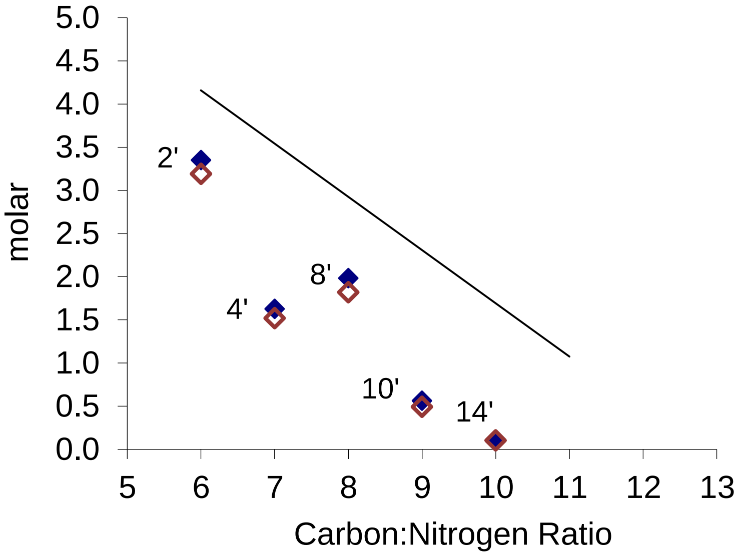

Figure 11. Maximum acquired concentration for SPSs featuring additional carbons functionality in addition to the *N*,*N*-dimethyl-n-alkylamine core structure. Trend line based on the *N*,*N*-dimethyl-n-alkylamine series from Figure 9 included here for a reference. The conditions and labeling are the same as Figure 9.

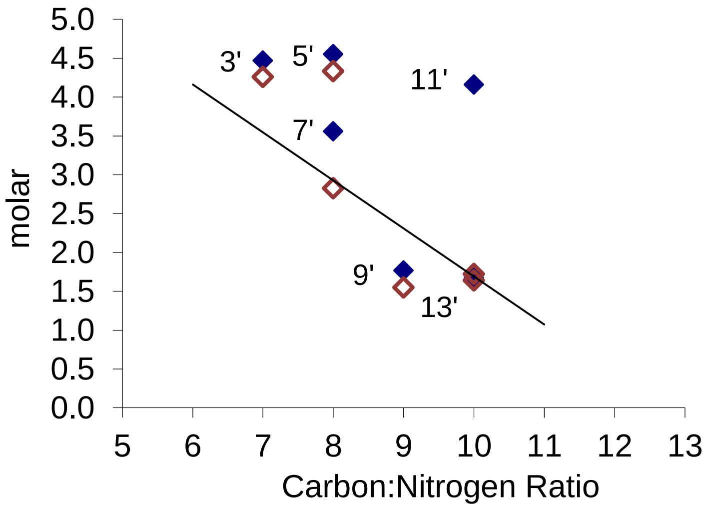

Figure 12. Maximum acquired concentration for SPSs featuring ring systems. Trend line based on the *N*,*N*-dimethyl-n-alkylamine series from Figure 9 included here for a reference. The conditions and labeling are the same as Figure 9.

Alkyl substituents in the absence of a ring system reduce a tertiary amine's effectiveness as an SPS. These carbons can be described as β, γ, and δ carbons, each with a different ability to influence steric crowding at nitrogen, Figure 13. The β, γ, and δ carbons have the potential to sterically disrupt the space around the nitrogen's lone pair to differing degrees. Such steric hindrance does not inherently prevent the coordination of a proton, due to its small size. Most of the amines in this study readily form highly concentrated protic ionic liquids with strong acids. Carbonic acid, derived form carbon dioxide, is neither a strong acid nor a concentrated acid under ambient conditions. The steric hindrance around the nitrogen lone pair likely prevents formation of extended solvent and counter ion (bicarbonate) network necessary to stabilize the polar form of the SPS in the aqueous phase.

The potential for maximum steric interaction increases with the carbon's proximity from the nitrogen, δ>γ>β. In contrast rotational degrees of freedom have the opposite effect based on as the carbon's potential to relax away from the amine which also increases according to the carbon's proximity from the nitrogen, δ>γ>β.

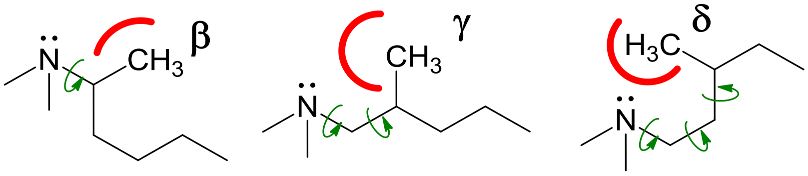

Figure 13. Position of β, γ, and δ carbons with respect to the nitrogen.

The coefficients used in Equation 7 were produced by empirically adjusting the values to produce a one to one linear relationship between the experimental and calculated molar concentrations, Table 3 and Figure 14. Based on the structures and concentrations observed in this study, the steric effect on the carbonate concentration of a γ (1.1) carbon is approximately double the effect of a β (0.55) or δ (0.5) carbon. It is expected that more distant carbons would have little effect on the nitrogen.

$$SPS\ (H_2CO_3\ (M)) = 7.86 - 0.62(\Sigma\ \text{Carbon}) - 0.55\beta - 1.1\gamma - 0.5\delta + 1.2(\alpha\ ring) \qquad (7)$$

The effects of a ring system on tertiary amines SPS function is more ambiguous than the argument presented above. All of the systems containing *carbons* beyond *N*,*N*-dimethyl-n-alkylamine skeleton but *no ring system* performed more poorly than the *N*,*N*-dimethyl-n-alkylamine series. Of the systems that *contained ring systems and additional carbons* some performed better than the *N*,*N*-dimethyl-n-alkylamine series, including **3'** and **5'**, but not all ring containing systems performed better. Solutions **7'** and **13'** have concentrations that are much higher than expected, lying on the line for the *N*,*N*-dimethyl-n-alkylamine series despite each containing two additional β carbons. Solution **11'** essentially lies on *N*,*N*-dimethyl-n-alkylamine trend line which suggests that the steric cost and benefit of ring system carbon γ to the nitrogen are roughly equal or are negligible. As for **9'**, definitively resolving the subtle steric and electronic effects associated with the benzyl ring system is beyond the current scope of this paper but it models well as γ carbon sterics with no ring benefit. Based on these systems, an "α ring system" which includes the cyclohexyl groups (**5'** and **13'**), piperidine (**3'**), and pyrrolidine (**7'**) provides an enhancement to an amine's SPS function, which is not observed for more distant ring systems (**9'** and **11'**). The benefit of an α ring system (1.2) was incorporated into Equation 7, Table 3, and Figure 14.

Table 3. Properties of tertiary amines that functioned as SPS.

Amine	number	number of total carbon	β carbons	γ carbons	δ carbons	α ring systems	Molar (exp.)	Molar (calc.)	Absolute Difference
dimethylbutylamine	1’	6					4.21	4.15	0.06
triethylamine	2’	6	2				3.19	3.05	0.14
1-ethylpiperidine	3’	7	2			1	4.26	3.63	0.63
methyldipropylamine	4’	7	1	1			1.52	1.88	0.36
dimethylcyclohexylamine	5’’	8	1			1	3.33	3.56	0.23
dimethylhexylamine	6’	8					2.84	2.91	0.07
1-butylpyrrolidine	7’	8	2			1	2.83	3.01	0.18
diethylbutylamine	8’	8	2				1.82	1.81	0.01
dimethylbenzylamine	9’	9		1			1.55	1.19	0.36
methyldibutylamine	10’	9	1	1	1		0.49	0.14	0.35
dimethylphenethylamine	11’	10					1.72	1.67	0.05
dimethyloctylamine	12’	10					1.67	1.67	0.00
diethylcyclohexylamine	13’	10	3			1	1.64	1.22	0.42
dimethyl-2-ethylhexylamine	14’	10		1	1		0.10	0.07	0.03
dimethylnonylamine	15’	11					1.12	1.05	0.07

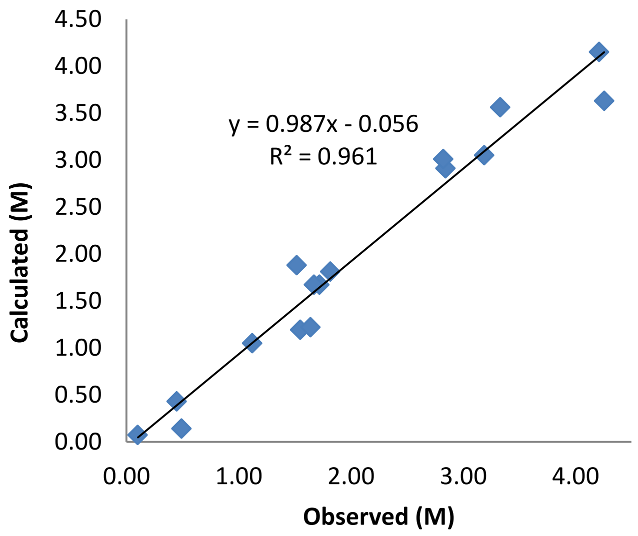

Figure 14. The correlation between the observed maximum molarity of SPS and those calculated from equation (7).

Aniline derivatives were not observed to function as SPS. The nonfunctionality of the aromatic aniline derivatives is not predicted by Equation 7, and is attributed to the pK_a of 5-6 resulting from an amine directly bonded to an aromatic ring which is significantly lower than the alkyl substituted tertiary amines with pK_a of 8-11.

CONCLUSION

In this study, a functional group contribution model has been developed for tertiary amine SPS. Also, structural limits for tertiary amines that function as SPS were identified, which suggested that a C:N ratio between 6 and 12 is necessary. Furthermore, a new form of non-osmotic SPS with an elevated amine to carbonate ratio in its polar form has been identified and characterized. This structure-function analysis and identification of a new form of SPS has implications on the design of SPS systems based on untested amine systems, as well as the selection of SPS for a variety of applications including solvent extraction systems, plastic recycling, synthetic media, acid gas capture, and osmotically driven membrane processes (ODMPs).

EXPERIMENTAL METHODS

General

Deionized water was used for these experiments. *N*,*N*-dimethylbutylamine, triethylamine, 1-ethylpiperidine, *N*-methyldipropylamine *N*,*N*-dimethylcyclohexylamine 99% ($N(Me)_2Cy$), 1-Butylpyrrolidine, *N*,*N*-diethylbutylamine, *N*,*N*-dimethylbenzylamine, *N*-methyldibutylamine, *N*,*N*-dimethylphenethylamine, *N*,*N*-dimethyloctylamine, *N*,*N*-dimethylcyclohexylamine, 2-ethylhexylamine, *N*,*N*-dimethylnonylamine, *N*,*N*-dimethyldecylamine, *N*,*N*-dimethyaniline, *N*-ethyldiisopropylamine, tripropylamine, triisopropylamine, 4,*N*,*N*-Trimethylaniline, *N*,*N*-dimethyl-o-toluidine, tributylamine, *N*,*N*-dicyclohexylmethylamine, *N*,*N*-dimethyldodecylamine, tripentylamine were obtained from Aldrich and used as received. All equipment was used in accordance with manufacturer specification unless stated otherwise. Freezing point depression osmometry was performed using an Advanced Instruments Inc. Model 3250 Osmometer. Viscosity measurements were made using the falling bob method with a Cambridge Applied systems VL4100 viscometer.

Nuclear magnetic resonance (NMR) spectra were acquired on a Bruker Avance III 600 MHz spectrometer with a magnetic field strength of 14.093 Tesla, corresponding to operating frequencies of 600.13 MHz (^{1}H), and 150.90 MHz (^{13}C). All NMR were captured with a co-axial insert containing C_6D_6 (Cambridge Isotopes Laboratories). ^{1}H NMR spectra were collected with a 30 degree pulse and 10 sec delays between scans, the T1 of every integrated shift was verified, most T1 relaxations well under 1 sec and none above 2 sec. The integration was set to a known peak in of the tertiary amine providing the relative concentration of (H_2O+H_2CO_3) : tertiary amine. ^{13}C NMR spectra with quantifiable integration were obtained with inverse gated decoupling spectra with a 30 degree pulse and 60 second delays between scans. The ^{13}C T1 values were verified and found to range between 2.5 sec and 10.5 sec for the carbonate peak, all other peaks had shorter relaxation times. The integration of the carbonate peaks was set to unity providing the relative concentration of tertiary amine:carbonate.

Conversion of 1-16 to 1'-16'

As an example, deionized water (3.884 g) and dimethylhexylamine (**6**, 5.468 g, 7.35 ml, 0.0423 mol) are placed in home-built carbon dioxide addition cell, Figure 15. The carbon dioxide addition cell was designed to measure the volume of nonpolar amine which remained phase separated from the aqueous volume. Knowing the original volume of the amine, it was possible to calculate the volume which had reacted with the known volume of water. The addition cell from bottom to top features a fine frit base with a ~2.5 cm diameter, 5 ml reservoir bulb, 10 ml graduated cylinder (1.5 cm diameter 8 cm tall), 25 ml reservoir bulb, 30 cm condenser. A small stir bar is added and stirred rapidly, the condenser is operated at 2 °C, and CO_2 is flowed through the cell at a steady rate of < 3 ml sec. After a 50 min purge, 1.0 ml of the amine is unreacted, after 2 hrs 0.9 ml of the amine unreacted. The solution was purged with carbon dioxide for a total of 5 hrs with 0.9 ml of the amine unreacted. The product, **6'** approximately [$HN(Me)_2Cy\ HCO_3$], and unreacted amine are removed with a syringe and long needle.

Figure 15. Carbon dioxide additional cell used to convert two phases of amine and water to a single phase polar SPS, **1’** through **16’**.

Synthesis of *N,N*-dimethyl-2-ethylhexylamine (14)

2-ethyl-1-hexylamine (304.55 g 2.36 mol) was slowly added to a solution of formaldehyde 37wt% (575.17 g, 7.09 mol) and formic acid (328.53 g, 7.14 mol) and allowed to stir overnight. Slow addition of NaOH (162 g, 4.1 mol) caused the solution to split into organic and aqueous layers. The organic layer was isolated, washed with water (4x350 ml), and dried with sodium sulfate. The product (315.5 g) was then distilled at 150 mTorr and 25-30 ⁰C giving a slightly yellow liquid (235.9 g, MW 157.4, 1.5 mol) with a density of 0.768 g/ml for a final yield of 64%. The product was confirmed as *N,N*-dimethyl-2-ethylhexylamine with a water content <1wt% using ^{1}H-NMR, ^{13}C-NMR, COSY, HSQC, and HMBC.

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