Assessing the Temperature-Dependent Tunable Polarity of \(N, N\)-Dimethylcyclohexylamine (DMCHA) and Water Mixtures

Ryan T. Berry, Elizabeth Dach, Jessica A. Melhorn, Ngai Yin Yip, and Lindsay Soh*

**ABSTRACT:** The promise of switchable solvents as green solvent alternatives lies in the ability to drastically alter their properties based on an external trigger. Switchable hydrophilicity solvent \(N, N\)-dimethylcyclohexylamine, DMCHA, is known to change properties based on both CO\(_2\) addition and variations in temperature, both in the presence of water. While the impact of temperature has been observed via changes in water solubility, the solvent properties underlying these observations have not been quantified. Kamlet–Taft solvatochromic parameters (\(\alpha\), \(\beta\), and \(\pi^*\)) and dielectric constants for DMCHA and DMCHA–water mixtures were measured across a temperature range of 25–60 °C. Temperature swing effects of DMCHA in addition to CO\(_2\)-switching capabilities were validated and quantified on the Kamlet–Taft polarity scale. Notably, binary mixtures of water in DMCHA show promising tunability in terms of its \(\beta\) and \(\pi^*\) parameters induced by moderate variations in temperature. Potential applications for this CO\(_2\)-switchable and temperature-tunable solvent are discussed.

**KEYWORDS:** switchable solvents, switchable hydrophilicity solvents, green solvents, tunable solvents, DMCHA, Kamlet–Taft parameters, dielectric constant

**INTRODUCTION**

One of the largest barriers to the implementation of green solvents is the need for distinct yet often orthogonal properties required for their applications and downstream separation.\(^1\) Thus, within a process, multiple solvents may be necessary to provide the specific physicochemical properties needed to perform single functions, each of which will require removal from the intended product.\(^2\) For example, in biomass processing, liquid extraction is used to harvest multiple products and the number of steps/solvents needed will depend on the feedstock complexity and requirements for product purity.\(^3\) Nearly, all conventional solvents used for liquid–liquid extractions are eventually separated from the product molecules through distillation. Distillation requires large amounts of energy to vaporize the solvent and for product isolation, making the requirement for multistep processing immensely wasteful both energetically and in terms of material loss.\(^1\)

Switchable solvents are a novel class of solvents that may reduce the energetic burden of downstream separations. A switchable solvent (SS) is an organic compound that can significantly change its physicochemical properties—such as polarity, hydrophilicity, ionic strength, and surfactant stability—in response to an external trigger.\(^2\) The change can be incurred by either chemical or thermodynamic manipulation such as addition of CO\(_2\) gas or changes in temperature.\(^2\) Switchable hydrophilicity solvents (SHSs)—a subclass of SS—are able to drastically change their hydrophilicity in the presence of water.\(^5\) Potential uses for SHSs include liquid–liquid extractions or reactions. For example, Boyd et al. and Samori et al. showed that \(N, N\)-dimethylcyclohexylamine (DMCHA) is a highly effective SHS for the selective extraction of triglycerides from microalgae.\(^6,7\) When DMCHA is in its unswitched form, it is hydrophobic and extracts lipid-based components while forming a separate phase from water. Sparging DMCHA with CO\(_2\) in the presence of water causes the solvent to become hydrophilic and allows for phase separation from hydrophobic products. This process can be reversed by stripping the CO\(_2\) with nitrogen or increasing the temperature. In addition to its switchable nature, DMCHA displays potential as a green solvent as it avoids high volatility, flammability, and the use of halogenation while retaining the ability to recycle the solvent without distillation.\(^6\)

In addition to its switchable hydrophilicity, DMCHA displays shifts in properties induced from changing temperature. Davidson et al. measured the solubility of water in various amine solvents and found that many, including DMCHA, displayed a sharp decline in water solubility with relatively small increases in temperature.\(^8\) Boo et al. applied this principle to illustrate the effectiveness of this temperature swing behavior for desalination of hypersaline brines.\(^9,10\) The

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authors used the high water solubility at low temperature (15 °C) to draw fresh water into the more hydrophobic phase from the saline feed, retaining the salt in the separate hydrophobic phase. Increasing the temperature (68 °C) on the isolated hydrophobic phase caused fresh water to phase-separate from DMCHA due to the lower water solubility. The thermoresponsive hydrophilicity of the basic amine solvents was also utilized to precipitate hydroxide minerals in high-scaling propensity brine solutions.11

While DMCHA’s CO2− and temperature-dependent properties have both been described in the literature, the collective nature of these two adjustable triggers has not been determined. In the temperature swing application, the more hydrophobic form of DMCHA has limited water solubility, which modestly increases at lower temperatures. CO2−switched DMCHA (sDMCHA), on the other hand, is hydrophilic in a water content no more than 0.05 wt % water. All samples were run in experimental triplicate (three separate samples) with error bars reflecting the experimental standard deviation.

The Kamlet−Taft solvatochromic parameters α, β, and π* were determined according to the equations modified by Lagalante et al.16 The α, β, and π* parameters were determined as a function of temperature and water concentration from the frequency maximum for 4NA, 4NAi, NND4, and RD in each solvent. The frequency maximums for the reference solvents for α, β, and π* were taken from Lagalante et al.17 The maximum frequencies for the reference solvents for α, β, and π* were fixed at the 25 °C values which is in accordance with the literature.16–19 Using a single reference temperature (i.e., 25 °C) is recommended in order to maintain the same normalized scale.16–19

The π* parameter is a measure of the solvent’s dipolarity/polarizability. Probes used to calculate π* are nonhydrogen-bonding such that their solvatochromic shift depends on the solute−solvent, dipole−dipole, and dipole-induced dipole interactions.14 In this work, both 4NA and NND4 were used to calculate two separate π* values. However, NND4 was chosen as the preferred probe due to its better solubility in DMCHA and higher resolution. The π* value of a solvent is calculated using the transition frequency maximum of the probe in the solvent (νw), relative to the frequencies of the probe in cyclohexane (νcyclohexane) and dimethyl sulfoxide (νDMSO), as shown in eq 1.20

\[
π* = \frac{ν_{\text{solvent}} - ν_{\text{cyclohexane}}}{ν_{\text{DMSO}} - ν_{\text{cyclohexane}}}
\]

While the values for cyclohexane and DMSO used in this study were taken from Lagalante et al., both cyclohexane and DMSO were cross-referenced to ensure the accuracy of the method used in this work. The π* equation for NND4 is presented in eq 2.

\[
π* = \frac{ν_{\text{solvent,NND4}} - 28.18}{-3.52}
\]

The β value is a measure of a solvent’s hydrogen bond-accepting (HBA) capabilities. The β value of a solvent is proportional to its displacement from the solvatochromic shift of its reference solvent (hexamethyolphosphoramide) for a given solvatochromic probe pair.16

The magnitude of this displacement is measured by the observed difference in the electronic transition energy.20 NND4 and 4NAi were recommended by Lagalante et al. for β calculation for N–H donor capable solvents following eq 3.16

\[
β = \frac{0.9841ν_{\text{solvent,NND4}} + 3.49 - ν_{\text{solvent,4NAi}}}{2.759}
\]

The α value of a solvent is a measure of its hydrogen bond-donating (HBD) capabilities and is also determined via its displacement from the solvatochromic shift of its reference solvent (methanol) for a solvatochromic probe pair.20 4NA and RD were chosen from common practice defined by Kamlet−Taft and α was calculated following eq 4.20

\[
α = \frac{1.873ν_{\text{solvent,4NA}} - 74.58 + ν_{\text{solvent,RD}}}{6.24}
\]

Solvants with no HBD capability will not readily solubilize RD. For these solvents (including any mixtures with DMCHA), the α was not able to be determined. In the literature, non-HBD solvents were assigned an α value of zero.20

**Spectroscopic Measurements.** The absorbance spectra were collected on a GENESYS 10S UV−visible spectrophotometer in conjunction with a Thermo Scientific air-cooled Peltier temperature controller, using a 10 mm quartz cuvette. The temperature was controlled within ±0.1 °C between 25 and 60 °C. Spectral data were collected over 190−1100 nm to locate the desired solvatochromic peak. Then, the range was narrowed for each solvent/probe pair. Each spectral scan was run with a step of 0.1 nm, an equilibration time at each temperature of 8 min, and fast scanning speed. The spectrophotometer and temperature controller were controlled...
RESULTS AND DISCUSSION

The IUPAC definition for solvation is “any stabilizing interaction of a solute (or solute moiety) and the solvent or a similar interaction of solvent with groups of an insoluble material.” While the qualitative mechanism behind how a solvent interacts with a solute has been well-defined and has been empirically described for over a century, it is particularly difficult to quantitatively measure and compare solute–solvent interactions across different solvents. The complex nature of solvation is derived from several related properties that, in whole, make up the solvation capacity of a solvent; therefore, a single macroscopic physical parameter cannot fully describe the ability of a solvent to solvate. Measurable properties such as relative permittivity, refractive index, and solubility parameters are commonly classified as scales of the “solvent effects” and are conventionally ascribed to a solvent’s polarity. Over the years, a number of polarity scales have been developed that employ the use of solvatochromic probes to provide a relative polarity value for various solvents (e.g., Reichardt’s $E_T$(30) scale and the Kamlet–Taft solvent solubility parameters). In this work, the Kamlet–Taft parameters are used because they comprise one of the most comprehensive polarity scales, quantifying a solvent’s hydrogen-bond donor ability, $\alpha$, the hydrogen-bond acceptor ability, $\beta$, and the dipolarity/polarizability, $\pi^*$. The Kamlet–Taft values numerically quantify solvent–solvent interactions that are representative in all types of solution equilibria by measuring a specific interaction that is local to the solvation shell around a dissolved solvatochromic probe.

Effect of Temperature on Kamlet–Taft Parameters. Kamlet–Taft parameters, $\pi^*$ and $\beta$, were measured across different temperatures for a range of solvents spanning each polarity scale (Figure 1). As DMCHA is a nonhydrogen-bond-donating (non-HBD) molecule, its $\alpha$ value is set to zero. In order to check the accuracy of the measurement technique, the wavenumbers for each probe were compared to those found in the literature at 25 °C (Table 1). The literature empirical data for Kamlet–Taft parameters across temperature are limited and thus comparison is restricted to room temperature (25 °C). Note that due to the high reproducibility of the technique, the error bars between the triplicate samples are almost imperceptible (Figure 1).

<table>
<thead>
<tr>
<th>source</th>
<th>DMSO</th>
<th>cyclohexane</th>
<th>water</th>
<th>dry DMCHA</th>
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<td>Laurence et al</td>
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<tr>
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<td>26.29</td>
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Table 1. Wavenumber (1000 cm$^{-1}$) Comparisons for N,N-Dimethyl-4-nitroaniline and 4-Nitroaniline Probes at 25 °C

![Figure 1](https://doi.org/10.1021/acssuschemeng.2c00293)
measured $\alpha$, $\beta$, and $\pi^*$ values are presented in the Supporting Information.

The $\pi^*$ parameter was determined using the NND4 probe and cyclohexane and DMSO as reference solvents (eq 1). The $\beta$ parameter inherently involves two probes, NND4 and 4NAi. Measured wavenumbers for both NND4 and 4NAi are shown to be in good agreement with the literature for all reference solvents (Table 1).14,26,27

The $\pi^*$ values for all solvents are constant or slightly decrease as temperatures increases (Figure 1a). Since the $\pi^*$ trend for dry DMCHA is comparable to that of the reference solvents, temperature does not seem to uniquely impact the $\pi^*$ of dry DMCHA. The high $\pi^*$ value of CO2-switched DMCHA (1:1 v/v DMCHA/water) illustrates the switching behavior of the solvent; however, temperature increase up to 45 °C did not have a marked impact on the change in sDMCHA $\pi^*$ value. The chosen DMCHA/water ratio is sufficient to achieve a single phase, but it should be noted that varying this ratio may result in property differences of the hydrophilic mixture.29 At temperatures above 45 °C, poor bandshape of NND4 with sDMCHA confounded accurate measurement of $\pi^*$. While the literature on measuring Kamlet–Taft parameters contains a debate surrounding whether to use a single $\pi^*$ probe or to average multiple $\pi^*$ probes, in this study, a single $\pi^*$ probe was used. Laurence et al. suggested that a single $\pi^*$ probe is particularly pertinent when measuring $\pi^*$ across different temperatures.27 For single-probe measurements, 4-NA and NND4 are commonly used probes.16,25 However, due to poor solubility and bandshape of 4-NA in DMCHA, NND4 was chosen as the $\pi^*$ probe. Poor bandshape has previously been reported for NND4 with certain solvents but was not seen in this system with NND4.27 Sample spectra for each probe and $\pi^*$ values using 4-nitroanisole are reported in the Supporting Information.

Unlike $\pi^*$, the $\beta$ value of dry DMCHA shows a marked decrease with an increase in temperature (Figure 1b), the magnitude of which is far larger than any change in $\beta$ for the reference solvents. This change in $\beta$ parameter supports the experimentally observed temperature swing effect on DMCHA—water solubility established by Boo et al.16 The authors proposed that the temperature swing effect is from an increase in steric hindrance around the HBA amine site of DMCHA due to increased rotation of the alkyl group around the nitrogen atom at higher temperatures.7 The steric hindrance decreases the HBA capabilities of DMCHA, which could also decrease the interaction of dry DMCHA with the HBD moieties of the $\beta$ probes and lead to the observed decrease in $\beta$ values.30

Effect of Water Content on Temperature Swing Effect. Despite being hydrophobic in its unswitched form, DMCHA is capable of dissolving non-negligible quantities of water particularly at low temperatures. For example, Stephenson determined that water was soluble in DMCHA at 21.4 wt % at 20 °C and 5.0 wt % at 60 °C.31 It is expected that below the solubility limit, water will have significant impacts on the homogeneous system’s polarity scale. To quantify properties of the DMCHA—water system (wt DMCHA), $\pi^*$ and $\beta$ values were determined for wet DMCHA at water concentrations below the measured solubility limit at 60 °C. The $\alpha$ value was not measurable for wet DMCHA as RD was immiscible and developed no solvatochromic absorbance band.

DMCHA and wet DMCHA with increasing water content. At a given temperature, the value of $\pi^*$ increases with higher water content. This trend might be expected due to the high $\pi^*$ value of water. Notably, a small increase in water content can lead to large differences in properties of the solvent mixture. As with dry DMCHA, an increase in temperature decreases the $\pi^*$ value of the wet DMCHA, for a single water content. However, the decrease in $\pi^*$ per degree Celsius (as measured by the slope of the fitted line) is greater at higher water contents (Figure 2). This change in $\pi^*$ for wet DMCHA is greater than both of its constituents (water and dry DMCHA) and all other reference solvents as the water content increases (Figure 1a).

This change in the temperature responsiveness of wet DMCHA is evidence of a synergistic interaction between DMCHA and water.14 Interaction between the system components can be further analyzed using the wavenumber (maximum frequency) of the $\pi^*$ dye, NND4, with wet DMCHA. If there was no interaction between the water and DMCHA, then the wavenumber would be a simple weighted average of the wavenumbers for each pure component (DMCHA and water). However, the actual wavenumbers significantly deviate (with ≥95% confidence) from those predicted by the weighted average (portrayed as dashed lines in Figure 3) and the deviation is greater at higher temperatures. This deviation can be interpreted as evidence of the temperature swing effect of DMCHA—water systems, although preferential solvation of the probe must first be ruled out as a cause.

The study of mixed systems of green solvents has been of recent interest due to their unique physicochemical properties.15 It is well-known that intermolecular interactions between different species in a mixed system play a key role

Figure 2. Calculated $\pi^*$ values for dry, ~1, ~3, and ~5 wt % water in DMCHA across temperature. Equations represent the linear best fit line for each series. Water (not shown) had a slope of approximately zero. The error bars represent the standard deviation of experimental triplicates. The slopes of each series are statistically different >95% confidence.

$\pi^*$ Is a Function of Temperature and Water Content. Figure 2 illustrates the temperature dependence of $\pi^*$ for dry DMCHA and wet DMCHA with increasing water content. Equations represent the linear best fit line for each series. Water (not shown) had a slope of approximately zero. The error bars represent the standard deviation of experimental triplicates. The slopes of each series are statistically different >95% confidence.
in the solvation and dissolution processes of a solute. However, studying the properties of binary, or otherwise mixed, systems is potentially problematic using the solvatochromic effect due to potential preferential solvation effects of mixture components with the probes. Single-component solvent systems can be easily and well-characterized using solvatochromic probes as the solvation shell surrounding the probe is entirely composed of the solvent under study. However, in a homogeneous solvent mixture, the probe molecule can interact differently toward one species over the other. This is caused by solvent–solvent and solute–solvent intermolecular interactions in the solution system. If preferential solvation is occurring, the question becomes: is the measured parameter representative of the bulk solution or only of a solvation shell around the probe?

According to Toma and Takasugi, one of the easiest ways to determine if preferential solvation is occurring in a solute–solvent system is to assess if the wavenumbers are deviating from predicted values as in Figure 3. The authors indicate that if no preferential solvation is occurring, the measured wavenumbers would fall on the linear trend between each pure solvent. As noted previously, some deviation from the predicted line was found, although this deviation is not necessarily indicative of a nonrepresentative solvent shell; here, the binary solution containing a temperature swing solvent is expected to exhibit intrinsically nonideal properties. In Figure 3, the trend of wavenumber over water content is linear \( R^2 > 0.99 \) and, at 25 °C, is reasonably well-represented by the predicted line determined by the weighted average of each pure component species. At higher temperatures, however, deviation from the predicted line increases with an increasing mole fraction of water, although the trend of wavenumber across water content remains linear with \( R^2 > 0.99 \). To better understand these relationships, the dielectric constant is used as a nonprobe based (i.e., noninvasive) technique to assess bulk solvent properties.

**Dielectric Constant Measurements Validate Bulk Properties.** Dielectric constants are a common measurement to quantify the polarity of a solvent or solvent mixture. Unlike the Kamlet–Taft parameters which measure the cybotactic environment around the solute, that is, solvatochromic probe, dielectric constants measure the polarity of the bulk solution. Dielectric constants cannot distinguish between the effects of hydrogen bonding, dipolarity, and polarizability but rather represent the combined effects of these specific contributions to polarity. Figure 4a summarizes the measured dielectric constants for DMCHA as a function of temperature and mole fraction of water. For reference, the dielectric constant of water was calculated as a function of temperature (°C) using eq 5 presented by Malmberg and Maryott

\[
\varepsilon = 87.740 - 0.40008T + 9.398(10^{-4})T^2 \\
- 1.410(10^{-6})T^3
\]  

The dielectric constant increases nonlinearly as water content increases toward the solubility limit. Specifically, once the mole fraction of water in DMCHA increased to above...
~0.20, the measured dielectric constants deviated from linearity by beginning to increase at temperatures above 35 °C. These findings agree with the literature observations that the dielectric constant in a mixture is rarely linear with changing composition.36 This nonlinear trend is indicative of solvent–solvent interactions in the solution. Note that the dielectric constant was measured at water contents up to 8.13 wt % (38.5 mol %), which is higher than the range for the Kamlet–Taft parameters (27.1 mol %). At the higher temperatures measured (55 and 60 °C), solubility issues arose and thus those data points are not provided in Figure 4. We originally postulated that the upward trend in the dielectric constant at elevated temperatures was due to localized demixing of the solutions with higher water contents. However, repeated experiments in which the sample vessel was periodically mixed during the experiment still exhibited the same behavior. Additionally, Figure S2 shows the behavior of the dielectric constant in a sample that is known to demix (within the immiscible region) for the temperature range studied, and the upward trend in the dielectric constant prior to the demixing temperature was still observed, with erratic measurements as the temperature increased beyond that point.37

The nonlinear behavior of dielectric constant across water content can be explained using the excess dielectric function, which has been shown to be useful in interpreting data on the dielectric constants of hydro-organic mixtures.38 Analogous to thermodynamic excess functions, if two solvents demonstrate ideal behavior upon mixing, the dielectric constant of the mixture, \( \varepsilon_{\text{mix}} \), should follow eq 6 (mole fraction-weighted mean)

\[
\varepsilon_{\text{mix}}^{\text{ideal}} = x_1 \varepsilon_1 + x_2 \varepsilon_2
\]  

where \( x_i \) denotes the mole fraction of solvent \( i \) and \( \varepsilon_i \) denotes the dielectric constant of pure solvent \( i \). The excess dielectric constant, \( \Delta \varepsilon \), is thus defined as36,39

\[
\Delta \varepsilon = \varepsilon_{\text{mix}}^{\text{expt}} - \varepsilon_{\text{mix}}^{\text{ideal}}
\]  

In Figure 4b, \( \Delta \varepsilon \) is plotted against the mole fraction of water in wet DMCHA, showing consistent negative and linear deviations. Payne and Theodorou37 postulated that significant negative deviations from ideal mixing behavior could be explained by the break-up of bulk water structure upon mixing or by the fact that the low-dielectric component may promote the association of the high-dielectric component into dimers or larger aggregates with a low overall dipole moment. More generally, Ramana et al.30 postulated that negative deviations from ideal mixing behavior are due to mixture components interacting in such a way as to reduce the total number of effective dipoles in the solution which, in this study, would include the formation of water dimers/aggregates between both solvent species in solution and water–DMCHA, hydrogen-bonding, and dipole–dipole interactions. These interactions are indicative of the bulk solution and illustrate that the trends of water–DMCHA mixtures have unique solution properties in the absence of a probe. Furthermore, the magnitude of the excess dielectric constant is a measure of the strength of the interactions between unlike molecules. As the temperature increases, the magnitude of \( \Delta \varepsilon \) decreases indicating that associations between water and DMCHA are weakening.

According to Kolling, the deviation of \( \varepsilon \) from ideal (i.e. the magnitude of \( \Delta \varepsilon \)) can be ascribed to the major perturbing influences of the mixture.36 This deviation can be described by the sum of individual contributions from the solvent interaction parameters. For aprotic, nonaromatic, nonpolyhalide solvents, the magnitude of \( \Delta \varepsilon \) is shown to trend closely with \( \pi^* \).36,37 In Figure 4b, the linearity of \( \Delta \varepsilon \) correlates well with the linear variation of \( \pi^* \) across DMCHA–water concentrations, further supporting that the deviations seen from ideality are not a result of preferential solvation but rather are a representation of the bulk solution.

Given the evidence using both the probe-based measurement and determination of the excess function for the dielectric constant, the variation in \( \pi^* \) is believed to be largely due to changes in the bulk solution, meaning that the Kamlet–Taft parameters are broadly applicable to describe the bulk properties of homogeneous DMCHA–water mixtures within the miscible region. These findings further support the role of DMCHA–water mixtures to have temperature swing properties which are enhanced by increased water content up to at least 5 wt % (27 mol %) water.
β Values Further Indicate Synergism between DMCHA and Water. The Kamlet–Taft solvent basicity parameter, β, was determined for DMCHA–water mixtures (Figure 5a), showing a positive nonmonotonic deviation of the β values compared to the pure component species values. Notably, the β values for the mixed DMCHA–water samples were higher than for either of the pure component species. Adding water to DMCHA therefore seems to increase the solution HBA capability of the solution despite water being a much weaker hydrogen-bond acceptor (β < 0.2). This phenomenon further indicates that there is a synergistic effect between water and DMCHA.14 Pasham et al. indicated that this synergistic effect may occur due to strong hydrogen-bond interactions between the two solution components.14

The β value is determined from the wavenumbers for two probes, NND4 (which is also used for determination of π*) and 4NAi. While NND4 wavenumbers show linear trends over water content (Figure 3), the trends for 4NAi are not linear (Figure 5b). The deviations from the weighted-average predicted line are not large in magnitude, however, the deviation starts negative (possibly indicating a slight preference of the probe to water) and becomes positive at larger water compositions (potentially indicating a slight preference of the probe to DMCHA). This difference means that there is a change in solvent–solvent and/or solvent–probe interactions as water content increases. At lower water content, DMCHA will fully solvate water meaning that DMCHA–water interactions are likely causing the negative deviations in this range. At higher water content, water–water interactions will increase and eventually exceed DMCHA–water interactions. Laurence et al. indicated that 4NAi probe shifts are dependent on the type of solvent, where NH shifts are better represented than OH shifts.26 Despite these interactions, the deviation of β is likely not solely due to preferential solvation since the β values do not deviate toward a single component. Rather, the large positive deviation illustrates a combined effect of DMCHA and water that points to changes in the bulk solvent properties.

Similar to dry DMCHA, temperature has a significant impact on the β values of the mixed system, particularly at low water concentrations (Figure 5a). Under the 1 wt % (6.7 mol %) condition, β values drop from 0.99 at 25 °C to 0.79 at 60 °C. At higher water concentrations (5 wt %, 27.1 mol %), the values are 0.89 at 25 °C and 0.88 at 60 °C, although a slight increase of β, to 0.90, at 30 °C is observed. This difference in temperature sensitivity reflects a difference in the complexion of DMCHA and water and its impact on the interaction with the probe, 4NAi.

**CONCLUSIONS**

In this work, the variation in properties that allow DMCHA to perform as both a temperature swing and CO2-switchable solvent, was measured using Kamlet–Taft parameters. The data provide a large repository of solvent parameters for DMCHA–water mixtures, which is important for the development of SHS applications. Furthermore, this work illustrates how a combination of parameters (Kamlet–Taft and dielectric constants) can be used to determine bulk solvent property changes. The combination of the probe-based method to determine solvent bulk properties and the dielectric constant to validate those properties provides a good foundation for future characterization of other similar solvent systems.

It was found that the β parameter of dry DMCHA decreases substantially as the temperature increases. For DMCHA–water mixtures, as water content increases, the π* parameter becomes more sensitive to a change in temperature, while at lower water contents, the β parameter is more sensitive to a change in temperature. The sensitivity of the π* and β parameters as a function of water content suggests a synergistic effect between water and DMCHA. The combined effect of both parameters describes the tunability of the mixed solvent system across solvent space (Figure 6). At low water content, β values vary significantly, spanning a greater range than for t-butanol compared to octanol (Figure 6, right). As water content increases, the tunability shifts to the π* scale. Notably, the range of the exhibited properties for wet DMCHA is in a relatively unique portion of the solubility space and may offer distinct advantages for applications requiring high basicity and low polarity.
One important application of the tunability of this system is for tailored solvent extraction. The flexibility in properties of DMCHA–water mixtures can be used to gain selectivity for extraction processes. For example, in biomass processing, wet DMCHA can be applied to the feedstock to extract out hydrophobic components. Increasing the temperature on this system would cause the solvent to become less polar and potentially phase-separate more hydrophilic components. Recovery of the hydrophobic components would then easily be achieved by the addition of CO₂ to switch DMCHA to its hydrophilic form. The Kamlet–β parameters measured in this work can aid in the design of these carefully tailored extractions. Subsequent work will seek to determine the effectiveness of this tunability in applications where selectivity of extraction from a complex matrix will allow for overall process improvements.

DMCHA’s inclusion as a green solvent stems mainly from its switchability and subsequent potential for lower energy solvent recycling. A full life cycle consideration of process energy demands for DMCHA production, CO₂ isolation and switching, and other separation requirements is necessary to better understand the energy trade-offs associated with the use and application of this SHS. Furthermore, DMCHA does have some environmental and health-related concerns. To be holistically green, other SHS alternatives may be evaluated for their tunability and applicability for specific applications. However, when considering the potential for energy and material savings along with the ease of recyclability, DMCHA could be a viable greener alternative to conventional solvent-based separation processes.

ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c00293.

**α, β, and π* values for all solvents measured in this work, sample UV–vis spectra for dry and wet DMCHA, and dielectric constants for dry and wet DMCHA (PDF)**

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Notes

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