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Local Polarity in CO_2-Expanded Acetonitrile: A Nucleophilic Substitution Reaction and Solvatochromic Probes

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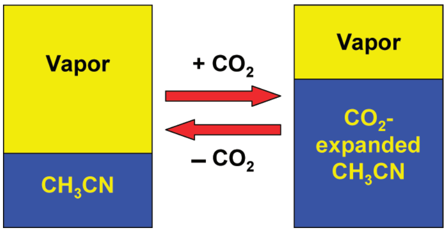

Many processes that use highly tunable gas-expanded liquids (GXLs) rely on the fact that CO_2 addition can greatly affect the polarity of the solvent. We have examined several measures of bulk and local polarity in CO_2-expanded acetonitrile to enable more effective exploitation of these polarity changes. The rate of the nucleophilic substitution reaction of tributylamine with methyl *p*-nitrobenzenesulfonate has been analyzed as a function of solvent composition by using in situ high-pressure UV/vis spectroscopy. We have also measured solvatochromic properties including the Kamlet–Taft π^* parameter and Kosower's *Z*-value. We correlate these local polarity-based kinetic and solvatochromic measures to develop a better understanding of these property changes as a function of bulk and local solvent composition. The data suggest that local composition enhancement in CO_2-expanded acetonitrile has a significant impact on the reaction kinetics.

Introduction

Gas-expanded liquids (GXLs) are an important class of alternative solvents that have received a great deal of attention in the last 20 years, as evidenced by a recent review by Jessop and Subramaniam.[1] Several techniques for particle and nanoparticle formation have been developed that exploit the tunable nature of GXLs to control the particle quality and size distribution.[2–7] GXLs have also been used for photoresist removal in microelectronics processing.[8] Another significant application of GXLs is as a reaction solvent for homogeneous and heterogeneous catalysis.[9–14] Characteristic to many of these processes is the utilization of CO_2 to alter the polarity of the solvent and facilitate a change in the phase behavior of the system.

Previous work with cosolvent-modified supercritical CO_2, as well as gas-expanded liquids, has suggested an important phenomenon in these solvents: differences between the local and bulk properties of the solvent. Preferential solvation of solute

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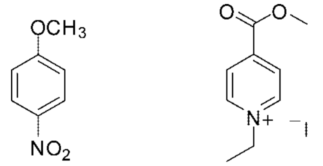

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FIGURE 1. Solvatochromic probes: *p*-nitroanisole (**1**) and 1-ethyl-4-carbomethoxypyridinium iodide (**2**).

molecules by one of the components in a mixed solvent can result in behavior not adequately described in terms of bulk solvent properties. The differences between bulk and local properties have been demonstrated by spectroscopic, solubility, and kinetic measurements in supercritical fluids and GXLs.[15–18]

Knowledge of how these properties change for various solvents as a function of CO_2 concentration can lead to opportunities in design of reactions and separation process development. In this work, we examine and compare several measures of solvent polarity in CO_2-expanded acetonitrile. Our purpose in this work is to determine how both the bulk and local polarity change as a function of solvent composition to enable more effective industrial implementation of these unique tunable solvents.

We have examined several probes as indicators of either local or bulk polarity in CO_2-expanded acetonitrile. As in our previous study, polar aprotic acetonitrile was chosen as the organic solvent to provide a wide property range for the resulting CO_2-expanded liquid.[19]

Solvatochromic Probes. Solvatochromic probes are often used to quantify solvent properties for pure fluids and fluid mixtures.[20–28] We focus in this work on two well-established solvatochromic probes of polarity and/or polarizability: the Kamlet−Taft π^* parameter and Kosower's Z (see Figure 1).[21,29]

The Kamlet−Taft dipolarity/polarizablity parameter, π^*, provides a comprehensive measure of a solvent's ability to stabilize a solute molecule based on dielectric effects.[30–32] Because it is a measure of a probe molecule's response to its surroundings upon excitation, π^* is a quantitative index of the solvent's dipolarity/polarizability in the cybotactic region of the ground state of the probe molecule.[31] The technique has been used extensively for measuring the polarity of pure solvents, ambient liquid mixtures. and CO_2-expanded solvents.[28,30,33,34] The experimental determination of individual π^* values is typically obtained from the shifts of the electronic absorption maxima of designated spectroscopic indicators.[30,32] We applied previously measured π^* values based on *p*-nitroanisole as the probe molecule to correlate the kinetic behavior of the S_N2 reaction.

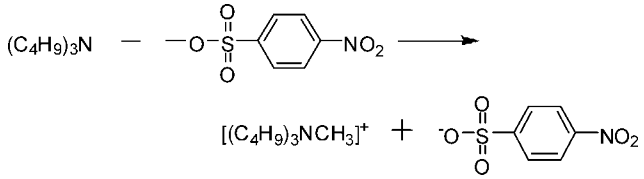

FIGURE 2. S_N2 reaction of TBA and MNBS.

Kosower developed a polarity parameter called the Z-value based on his findings that the charge-transfer light absorption band of 1-alkylpyridinium iodides is very sensitive to the polarity of a solvent.[29,35] The Z-value is defined as the transition energy (E_T in kcal/mol) for the longest wavelength absorption band observed for 1-ethyl-4-carbomethoxypyridinium iodide in that solvent, similar to solvatochromic scales such as $E_T(30)$, Nile Red, Crystal Violet, etc.[35,36] Governing equations are found in the Experimental Section under the subsection Procedure. As with π^*, a higher Z indicates a higher polarity.[29,35]

Menschutkin Reaction. The Menschutkin reaction is a nucleophilic substitution reaction proceeding by an S_N2 mechanism between a nitrogen base, typically a tertiary amine, and an organic electrophile such as an alkyl halide or sulfonate to form a quaternary ammonium salt. In this process, the hybridization of the nitrogen changes from sp^2 to sp^3.[37,38] This class of reactions is a good probe of polarity because its transition state is much more polar than the reactants, thus making the reaction kinetics strongly depend on the polarity of the surrounding medium. The Menschutkin reactions of a wide variety of substrates have been studied in a variety of media including organic solvents, ionic liquids, and gases.[39–41]

In this study we have chosen the reaction of tributylamine (TBA) with methyl *p*-nitrobenzenesulfonate (MNBS), as illustrated in Figure 2. This reaction is well-characterized and has been used to study the polarity of ionic liquids.[39,40] Importantly, MNBS has a λ_{max} at 253 nm while the product, the *p*-nitrobenzenesulfonate ion, has a λ_{max} at 275 nm. Because the two peaks are sufficiently separated, the reaction can be monitored in situ via UV–vis spectroscopy. The corresponding polar transition state, which plays a key role in probing the

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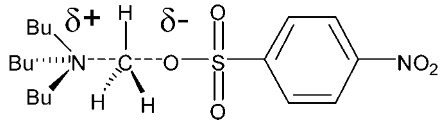

FIGURE 3. Charge-separated transition state of the reaction of TBA and MNBS.

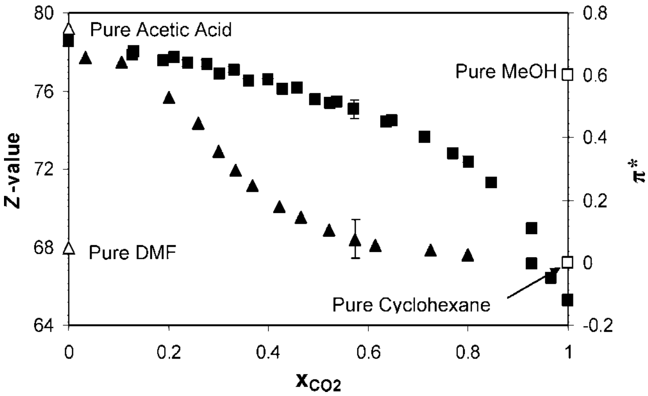

FIGURE 4. π^* and *Z*-value for CO_2-expanded acetonitrile as a function of composition: (■) π^* values plotted on the right axis (previously reported)[19] and (▲) *Z*-values plotted on the left axis. Literature values for pure solvents are plotted for comparison: (□) π^* values plotted on the right axis and (△) *Z*-values plotted on the left axis.[24,29]

polarity in the cybotactic region, is shown in Figure 3. For each reaction it was possible to record absorbance values at 253 and 275 nm at known time intervals and use them to determine the rate of the reaction. An isosbestic point is always observed.

Results and Discussion

Solvatochromic Probes. Our experimental results for the Kamlet–Taft π^* in CO_2-expanded acetonitrile shown in Figure 4 were previously reported.[19] The key feature of the curve is that the π^* value decreases gradually below $x_{CO_2} = 0.85$, then drops dramatically toward the pure CO_2 value. The shape of the curve suggests preferential solvation of the probe by acetonitrile, as is often observed with mixed solvents.[20,25,28] This figure also illustrates the ability to tune the polarity of GXLs over a wide range: acetonitrile ($\pi^* = 0.75$) is slightly more polar than methanol ($\pi^* = 0.6$), but the resulting GXL can be tuned to a polarity as low as that of cyclohexane ($\pi^* = 0$).

The *Z*-value of CO_2-expanded acetonitrile decreases monotonically as a function of CO_2 composition (see Figure 4). The addition of CO_2 continuously tunes the polarity of acetonitrile ($Z \approx 78$, cf. $Z \approx 79$ for acetic acid) in pure form to *Z*-values similar to *N*,*N*-dimethylformamide ($Z \approx 68$) at a CO_2 mole fraction of ~0.8; the overall change in *Z*-value is modest. The results remain consistent with the presence of an acetonitrile-rich solvation shell within the cybotactic region surrounding the probe molecule. However, due to insolubility of the probe molecule at high CO_2 loadings, we were only able to measure *Z*-values for $x_{CO_2} < 0.80$.

The modest change in *Z*-values compared to the relatively larger changes in π^*-values can be attributed to the fact that the solvatochromic probe for the *Z* measurements is a ground-state salt while the probe for the π^* measurements is a ground-state dipolar molecule. It is conjectured that there would be greater acetonitrile–probe interaction with the salt compared to the dipolar molecule and, as such, the influence of greater quantities of CO_2 would be more dramatic with the π^* measurements than with the *Z* measurements.

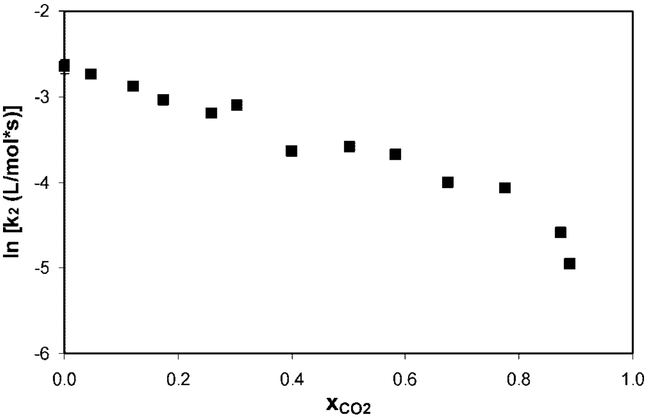

FIGURE 5. S_N2 rate constant for CO_2-expanded acetonitrile at 40 °C as a function of composition.

Menschutkin Reaction. Figure 5 shows the kinetic results for the S_N2 reaction of TBA and MNBS in CO_2-expanded acetonitrile at 40 °C. The trend in the rate constants is remarkably similar to that of π^*, with a gradual decrease at low CO_2 loadings followed by a sharper descent at higher CO_2 compositions. As with the solvatochromic measurements, these data suggest preferential solvation of the probe (in this case, the reactants) by acetonitrile. Attempts to gather kinetic data at $x_{CO_2} > 0.90$ failed due to limited solubility of the reactants in the CO_2-rich GXL. The better correlation of the kinetic data with π^* measurements makes sense since the π^* value reflects a process going from "neutral" molecules to a "dipolar" excited state. This same type of process occurs when going from the ground state to the transition state during the reaction.

Local Composition Enhancement. To further understand the kinetic and solvatochromic behavior observed in CO_2-expanded acetonitrile, we investigated the local composition enhancement of acetonitrile around the probes used in the GXL. We calculated the local mole fraction of acetonitrile ($x_{ACN,local}$) based on our π^* measurements using procedures detailed in the literature.[16,17,31,42,43] To determine $x_{ACN,local}$, we first calculated the deviation in π^* ($\Delta\pi^*$) from a mole-fraction-weighted "bulk" prediction based on the values in pure acetonitrile (π^*_{ACN}) and pure CO_2 ($\pi^*_{CO_2}$) over the entire solvent composition range:[31]

$$\Delta\pi^* = \pi^* - \left(x_{ACN,bulk}\pi^*_{ACN} + x_{CO_2,bulk}\pi^*_{CO_2}\right) \qquad (1)$$

We then assume that $\Delta\pi^* = 0$ and the bulk concentrations of the acetonitrile and CO_2 sum to 1 to calculate $x_{ACN,local}$.

In Figure 6, we plot $x_{ACN,local}$ and $x_{ACN,bulk}$ (bulk acetonitrile mole fraction) as functions of the bulk CO_2 mole fraction (x_{CO_2},bulk). Since $x_{ACN,local}$ was calculated based on π^*, we observe similar trends for these values. Our results for $x_{ACN,local}$ in CO_2-expanded acetonitrile are similar to those reported by Striolo et al. using a phenol blue spectroscopic probe.[18] We then define the composition enhancement factor (CEF) as:

$$CEF = \frac{x_{ACN,local}}{x_{ACN,bulk}} \qquad (2)$$

A plot of CEF versus x_{CO_2} is shown in Figure 7. This curve shows only a modest change for $x_{CO_2} < 0.60$ with CEF ≤ 2. At

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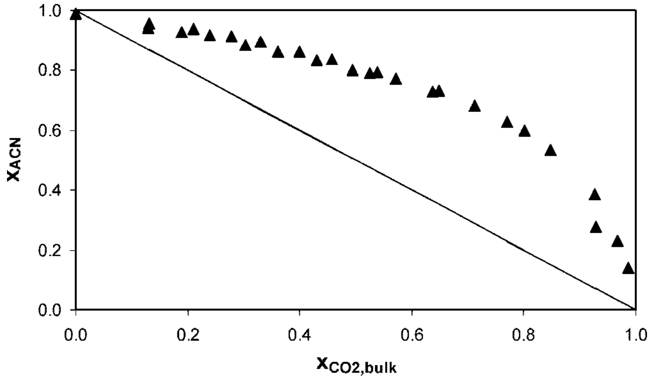

FIGURE 6. Local (▲) and bulk (—) mole fractions of acetonitrile in CO_2-expanded acetonitrile.

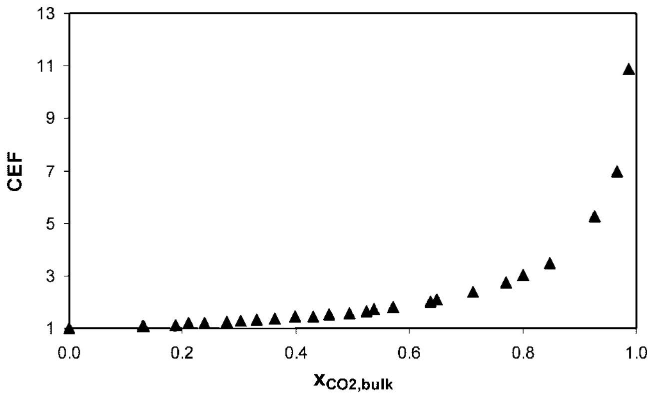

FIGURE 7. Composition enhancement factor for CO_2-expanded acetonitrile.

higher CO_2 loadings, the CEF increases noticeably to CEF > 10. The point of the transition between these two regions of the curve was chosen somewhat arbitrarily as $x_{CO_2} = 0.60$ based on the transition from a fairly linear region of the curve to a region of the curve where the slope changes more dramatically, but the transition clearly occurs in the range $0.50 < x_{CO_2} < 0.70$. The choice of a different transition point within this range would have a limited effect on the results of our subsequent analyses.

With this transition point in mind, we have plotted the rate of our S_N2 reaction of TBA and MNBS versus π^* for CO_2-expanded acetonitrile in Figure 8. If we divide the kinetic data on either side of the transition point and linearly correlate the data at $x_{CO_2} < 0.60$, we see that the points for $x_{CO_2} > 0.60$ diverge from the linear regression.

To further illustrate the solvation effects on the kinetics due to the local composition heterogeneity, we calculated a predicted ln k_2 value based on the linear regression in Figure 8. In Figure 9, we show the experimental kinetic data and the curve for the predicted ln k_2, both as functions of x_{CO_2}. Here we see that at $x_{CO_2} > 0.60$, the value of the rate constant is significantly higher than what we would predict based on our kinetic and solvatochromic data for $x_{CO_2} < 0.60$.

Several possible causes may be attributed to the observed rate enhancement at higher CO_2 loadings. Transition state stabilization by acetonitrile is one potential source of this enhancement. Since the charge-separated transition state should be stabilized in acetonitrile relative to CO_2, and we observe much more dramatic composition enhancement of acetonitrile at high CO_2 loadings than we would predict based on lower CO_2 loadings (e.g., Figure 7), this hypothesis seems to be supported by the data.

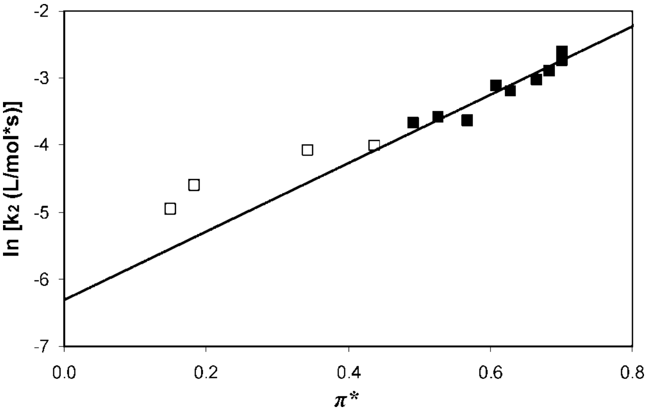

FIGURE 8. S_N2 rate constant versus π^* for CO_2-expanded acetonitrile at 40 °C: the trendline (—) is the linear regression of the data based on $x_{CO_2} < 0.60$; (■) kinetic data for $x_{CO_2} < 0.60$ included in the linear regression; and (□) kinetic data for $x_{CO_2} > 0.60$.

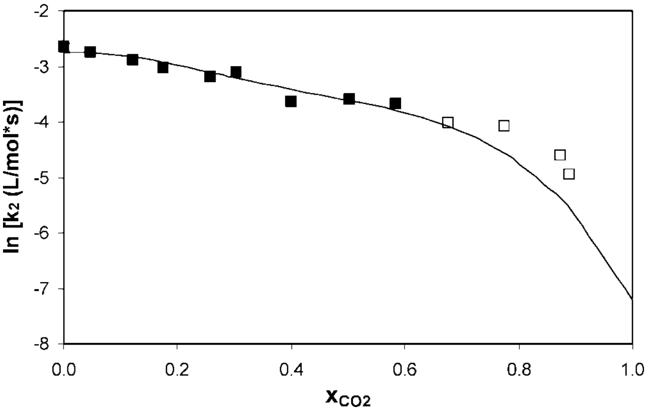

FIGURE 9. Experimental and predicted values of the S_N2 rate constant for CO_2-expanded acetonitrile at 40 °C as a function of composition: (■) kinetic data for $x_{CO_2} < 0.60$; (□) kinetic data for $x_{CO_2} > 0.60$; and (—) the trendline for ln k_2 vs π^* data from Figure 8, on a mole fraction basis.

Another source of this deviation from bulk behavior could be clustering and/or aggregation of polar solutes (i.e., reactants) in the increasingly nonpolar GXL. Experimental evidence of enhanced kinetics by solute–solute clustering has been previously reported in the literature.[44] This aggregation can lead to an increased number of collisions of the reacting species, accelerating the reaction beyond what would be expected based on bulk compositions.

Conclusions

We have examined the kinetics of a nucleophilic reaction as well as solvatochromic probes to gain insights into local solvent polarity in CO_2-expanded acetonitrile as a function of CO_2 composition. We calculated the local composition enhanced factor and correlated the rate constants based on the solvatochromic parameters. Both the kinetic and solvatochromic behaviors support our hypothesis of the enhanced local solvent structure in the cybotactic region: that polar molecules such as acetonitrile tend to associate with the solvatochromic probes

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and the reactants to enhance their local compositions in the GXL. In addition to the solute–solvent clustering, we have also demonstrated the possible occurrence of enhanced solute–solute interaction at high CO_2 composition range. These local composition enhancement phenomena can have a significant impact on reactions, as observed in this work, as well as separations such as gas-antisolvent crystallization.

While this work has focused on local composition in CO_2-expanded acetonitrile, other GXLs may prove interesting as well. A similar study with another polar aprotic solvent such as tetrahydrofuran, or a different expansion gas such as ethane, may help to determine the role of specific molecular interactions on the behavior observed in this study.

Experimental Section

Materials. Carbon dioxide was filtered before use. Tributylamine (ReagentPlus, ≥98.5%), 1-ethyl-4-carbomethoxypyridinium iodide (97%), acetonitrile (HPLC, ≥99.9%), and methyl *p*-nitrobenzenesulfonate (99%) were used as received. All solvents were used as received. No assays for water content were performed.

Apparatus. A stainless steel vessel with two sapphire windows (6.4-mm thick) was constructed for in situ high-pressure UV–vis spectroscopy. The windows were sealed with Teflon gaskets capable of withstanding pressures over 250 bar. The cell has a path length of 2.2 cm and an internal volume of 13 mL. Temperature was controlled with a refrigerated constant temperature flow bath (Thermo Electron Corporation, Neslab RTE7) with a mixture of ethylene glycol and water as the heat transfer fluid and monitored with a thermocouple and readout (Omega). The temperature variation was maintained within ±0.1 °C of the set point. Pressure was monitored by a pressure transducer and readout (Druck) with an uncertainty of ±1 psi. A magnetic spin bar and motor (H+P Labortechnik, Variomag Telemodul 20C) constantly agitated the cell contents to facilitate equilibrium. Temperature and pressure gauges were calibrated to ensure their accuracy in these experiments. CO_2 was metered into the vessel with a syringe pump (ISCO, 260D). All measurements were performed on a Hewlett-Packard 8453 UV/vis spectrophotometer (1 nm resolution and ±0.2 nm wavelength accuracy). Both kinetic and solvatochromic experiments were performed in the same apparatus.

Procedure. For kinetic experiments, we prepared stock solutions of TBA and MNBS in acetonitrile. We loaded the cell with 5 mL of a 6×10^{-4} mol/L solution of TBA in acetonitrile and heated the cell to 40 °C. Then we added 50 μL of a 6×10^{-3} mol/L solution of MNBS in acetonitrile, sealed the cell, and added CO_2 to the desired pressure (i.e., x_{CO_2}). We maintained at least a 10:1 excess of TBA to MNBS in all experiments to allow pseudo-first-order kinetic analysis. We corrected the concentrations of the reactants for solvent volume expansion using phase behavior data from the literature for CO_2-expanded acetonitrile.[45] We monitored the reaction at given time intervals until both product and reactant peaks remained constant for at least 1 half-life. The experiment durations range from 6 h to more than 2 weeks, depending on the solvent composition.

Peak intensities at 253 and 275 nm were recorded and plotted as a function of time. Data were treated by a least-squares fitting procedure, using a user-defined function in OriginLab Software Package (Version 7.5).[46] Equations 3 and 4 are fit to the data simultaneously to determine the pseudo-first-order rate constant, k_{obs}. The model is based on a typical "A to B" reaction where A_0 is the initial amount of substrate and B_∞ is the final amount of product. A and B denote the amounts of reactant and product, respectively, at a given time, t. The constants C_1 and C_2 are required to correct for the fact that the UV absorbance is not zero when the concentration of A or B is equal to zero. The resulting k_{obs} value is divided by the initial concentration of TBA to calculate a second-order rate constant, k_2.

$$A = A_0 e^{-k_{obs}t} + C_1 \tag{3}$$

$$B = B_\infty(1 - e^{-k_{obs}t}) + C_2 \tag{4}$$

In our solvatochromic measurements, we prepared concentrated stock solutions of the solvatochromic probes in acetonitrile. We then diluted a known volume of the stock solution into acetonitrile to attain a UV–vis response within the range of the detector. After sealing the cell, we added CO_2 to the desired pressure (i.e., the desired x_{CO_2}) and waited until the contents reached equilibrium before spectral acquisition. Multiple cell loadings with different initial liquid volumes were used to present the entire solvent composition range, and the data show a consistent trend. The sample error bars in Figure 4 indicate the uncertainty of these measurements, which is fairly satisfactory.

Kosower's Z-value for a given solvent is obtained by eq 5, where λ (in nm) is the wavelength of maximum absorbance of 1-ethyl-4-carbomethoxypyridinium:

$$Z = \frac{2.859 \times 10^4}{\lambda} \text{ kcal/mol} \tag{5}$$

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