ABSTRACT: CO₂-switchable solvents, typically neutral solvents that switch with CO₂ into ionic species, were investigated for use as entrainer in fluid separations such as extractive distillation. Their switchable nature was investigated, which may facilitate liquid–liquid extraction or extractive distillation as ionic liquid (IL), whereas during regeneration their decarboxylation into the amine form prevents temperature shoot-up. Studied elements included a property screening and detailed mechanistic and kinetic studies on the switching of 2-ethylhexylamine and N,N-benzyl methylamine. Decarboxylation of a 50 vol % switchable solvent, 25 vol % heptane, and 25 vol % toluene mixture at 1.00 × 10⁴ Pa showed a 40% CO₂ release before reaching the operational pressure, and total decarboxylation took over 2 h. An effective increase of the relative volatility of heptane/toluene was found, showing that, indeed, CO₂-switchable solvents can be applied for extractive distillation. However, low pressure in combination with elevated temperature will lead to quick decarboxylation, limiting the operational window of this class of solvents. Their use in low temperature applications such as CO₂-distillations or a liquid-liquid extraction appears more suited.

KEYWORDS: CO₂-switchable solvents, Extractive distillation, Liquid–liquid extraction, 2-Ethylhexyl amine, Benzylmethylamine, Entrainer

INTRODUCTION

Where distillation has been the work horse for separations in the chemical industry for ages and energy costs in industry amount to about 40–50% of the total costs,¹ during recent years the awareness grew that we should become more energy efficient to reduce CO₂ emissions significantly,²–⁴ and research has been focused on both replacing traditional separations with, e.g., affinity separations⁵–⁷ and on replacing traditional petrochemical production routes with biobased routes.⁵–⁷ For many separation challenges in biorefineries, distillation is not technically feasible,¹ and solvent-based approaches may provide sustainable solutions. For a solvent-based separation process to be sustainable, it is essential that a good energy efficiency can be reached and that the solvent is environmentally benign. A class of solvents that has often been claimed as a green solvent class is that of the ionic liquids (ILs).⁸ Especially the negligible volatility is mentioned often as a beneficial feature,⁸ because this eliminates losses through the air, such as with volatile organic solvents. This is indeed true, but this also limits their distillability. The boiling point of mixtures depends on their composition, and when an IL is to be regenerated to high purity, the boiling point will approach that of the IL itself. Since they have a negligible vapor pressure, this will result in a sharp temperature rise, and full regeneration through distillation is simply not possible. Alternatively, IL regeneration by stripping can be applied when the solutes are volatile, but then also large amounts of strip gas are needed for deep regeneration.

Ideally, an IL could be distillable in the solvent regeneration stage, while in the primary separation stage, this is not necessary or even undesirable. A group of solvents that is also known as distillable ILs are the CO₂-switchable solvents.¹⁰ CO₂-switchable solvents switch their behavior upon reaction with CO₂,¹¹ affecting the polarity of the solvent. Since 2005, a range of papers has appeared on the use of such solvents, mostly for the extraction of lipids from various sorts of biomass, e.g., soy bean¹² and microalgae,¹³,¹⁴ but also as a reversible protecting group¹⁵ and to switch the ionic strength in aqueous solutions.¹⁶ Using their IL character, CO₂-switched amines may potentially be applied in, e.g., the separation of aliphatics and aromatics by extractive distillation or liquid extraction. The nonvolatile character, that normally is a
drawback for thermal IL regeneration, can be lost by back-switching, enhancing their distillability. A conceptual process flow diagram of such an extractive distillation process is displayed in Figure 1. In this diagram, after the primary separation, i.e., the extractive distillation, a recovery column is placed, and the CO$_2$ escaping from both the extractive distillation column (EDC) and the recovery column (RC) is sent with the recovered solvent to the carbamate regeneration column (CRC) to regenerate the solvent in its carbamate form. The CO$_2$-switchable solvents might thus be applied in a much wider range of fluid separations than the extraction of natural products. We here report a study on the applicability of this highly interesting class of solvents for other fluid separations than the known lipid extractions, and in our studies, we have investigated the physical properties of a series of switched amines. Among the most interesting ones from the property point of view (viscosity/physical state of switched IL form and boiling point of unswitched amine form) are 2-ethylhexyl amine (2EHA), dibutylamine (DBA), and benzylmethylamine (BMA). For these amines we have studied their application in extractive distillation of heptane−toluene mixtures and for 2EHA and BMA also in detail the mechanism of switching and the rates of switching at temperatures up to 75 °C using $^1$H NMR and $^{13}$C NMR spectroscopy.

### MATERIALS AND METHODS

**Materials.** All chemicals used were commercially obtained at Sigma-Aldrich, Cambridge Isotope laboratories (deuterated solvents), or Praxair (CO$_2$).

**Vapor–Liquid Equilibrium Measurements.** Vapor−liquid equilibria (VLE) were measured in an ebulliometer from Fischer, type VLE 602 at an operational pressure of 10$^4$ Pa. After setting the pressure, the temperature was measured, and compositional analysis of both the liquid phase and the condensed vapor was performed using GC. Prior to analyzing mixtures, the equipment was validated by measuring pure component boiling points of heptane and toluene at the operational pressure of 10$^4$ Pa. Samples of the liquid phase were also analyzed on the solvent composition using quantitative $^{13}$C NMR. In experiments with a solvent, the solvent was applied in a solvent-to-feed ratio S/F = 1 (mass based).

**Variable Temperature $^1$H NMR Studies.** Variable temperature $^1$H NMR experiments were performed on a Bruker Avance II 600 MHz provided with an external BCU-Xtreme cooling unit to study on...
the stability of the ammonium carbamates and on the mechanism of the back-switching from the ammonium carbamates to the amine forms of the solvents. Typically, an amine was bubbled extensively with CO$_2$ (up to 4 h) before mixing it with toluene-$d_8$ and starting the measurement over temperatures ranging from $-30$ to $+75$ °C for BMA and from $30$ to $75$ °C for 2-EHA.

Quantitative $^{13}$C NMR Measurements. Quantitative $^{13}$C NMR measurements were performed on the same spectrometer as the variable temperature $^{1}$H NMR studies using inverse gated decoupling mode and a d1 of 2 s. After taking the samples from the ebulliometer, they were directly dissolved in toluene-$d_8$ and the NMR tube closed so that no CO$_2$ could escape during the measurement.

RESULTS AND DISCUSSION

Solvent Prescreening. The use of CO$_2$-switchable solvents as entrainer in extractive distillation processes is conditional to several solvent properties. Key properties that have been reported for a range of solvents include the boiling point of the amine form, the technical feasibility of switching, and the physical appearance of both amine form and the switched form. Ideally, for extractive distillation, both the amine form and the ammonium carbamate form appear as liquid, and the boiling point of the amine form should still be significantly (preferably close to or more than 50 °C) above the boiling points of the mixture to separate. For the separation of heptane and toluene, this means ideally a solvent with a natural boiling temperature close to or above 160 °C is preferred. Based on the literature on CO$_2$-switchable solvents, a list of possible solvents with proven switchability is presented in Table 1. In this table, only single amines are listed, as CO$_2$-switchable solvents with two components (e.g., guanidines with alcohols$^{11}$) were regarded as too complicated. Furthermore, tertiary amines requiring water in the switching chemistry were also not considered. From Table 1, the top three solvents were selected as they appeared most appropriate with high enough boiling points of the amine form, no solidification of the ammonium carbamate form, and still reasonable viscosities (exact values were not measured). However, DBA did show gelation upon switching, which might hinder process ability. Due to the gelation, it was decided to limit extensive NMR studies to the other two promising candidates, i.e., 2EHA and BMA.

Solvent Switching Characteristics. When the switchable solvents are applied in extraction,$^{12,13}$ typically the difference in behavior of the systems between the neutral state and the switched state is studied,$^{13}$ and the polarity before and after switching is measured, e.g., using the shift in wavelength of a light absorbance maximum of a photochromic dye.$^{13}$ Also the conditions for switching have been reported, and switching from the ammonium carbamate form back to the amine form is preferred at elevated temperature,$^{13}$ which is consistent with CO$_2$ capture and release by amine solvents and sorbents that also require an elevated temperature for release.$^{19,20}$ For potential application in extractive distillations, this might not be ideal, and in order to evaluate the applicability in such separation processes, it is essential to obtain a good insight in both the rate of switching and the mechanism of switching in an environment that is representative for extractive distillation conditions. Therefore, mixtures containing ammonium carbamates of 2EHA and of BMA and deuterated toluene were analyzed by $^{1}$H NMR in variable temperature conditions. The measurement results for the CO$_2$-switched 2EHA are displayed in Figure 2. At 30 °C, characteristic signals appear at 9.1, 5.2, 3.2, and 2.8 ppm. The signals around 7 and 2.1 ppm belong to toluene. The signals below 2 ppm belong to the hydrocarbon tails of 2EHA and its CO$_2$-switched form and are not displayed here because they are not relevant for studying the mechanism. $^{1}$H NMR, $^{13}$C NMR, and 2D heteronuclear single quantum coherence (HSQC) NMR spectra of the amine form are presented in the Supporting Information, as well as superimposed $^{1}$H NMR spectra before and after CO$_2$ bubbling. Upon increasing the temperature, different $^{1}$H NMR spectra were recorded in the range of 30−70 °C. Afterward the sample was allowed to cool to 30 °C. Both spectra recorded at 30 °C, initial and after variable temperature experiments, were identical, indicating that the process in the NMR tube during variable temperature experiments was perfectly reversible. The reversibility was possible due to the use of a sealed NMR tube, keeping all CO$_2$ that may have liberated from the liquid phase in the tube. Furthermore, it can be seen that the signals at 2.8, 3.2, and 5.2 ppm maintain their position in the spectrum but do broaden at increasing temperature. The signal at 9.1 ppm shifts down to 5.3 ppm. Similar signal changes were observed for the $^{1}$H NMR spectra of 2-ethoxyethylamine by Kortunov et al.$^{21}$ who studied in situ $^{1}$H NMR while CO$_2$-switching the amine. In analogy to the mechanism that Kortunov et al. proposed for 2-ethoxyethylamine, we propose the switching mechanism for 2EHA as displayed in Scheme 1.

Figure 2. Stacked $^{1}$H NMR spectra of 125 mg of CO$_2$-switched 2EHA in 0.55 mL of toluene-$d_8$ at varying temperature.

Scheme 1. Proposed Mechanism of Switching for 2EHA

\[ \text{RNH}_2 + \text{CO}_2 \leftrightarrow \text{RN} = \text{O} \quad \text{carbamic acid} \]

primary amine 

zwitterionic intermediate 

ammonium carbamate
tively, the carbamate can be formed by proton transfer from the zwitterionic intermediate.

The 5.2 ppm signal, assigned to the RNH-COOH and RNH-COOH± is relatively sharp at 30 °C, indicating that the equilibrium at that temperature favors the ammonium carbamate form, whereas the broadening at higher temperature is so strong that the signal is not visible any more above 65 °C, indicating fast exchange between multiple species, i.e., the zwitterionic intermediate, the carbamic acid, and the ammonium carbamate. A second indication for this fast proton exchange at higher temperatures is the broadening of the 3.2 ppm signal for the protons on C1. The signal shifting from 9.1 to 5.3 ppm is an averaged contribution of the RNH3+, RNH2+, and RNHCOOH protons. The signal starts relatively sharp at 9.1 ppm, then broadens up to 65 °C, and then sharpens again. Sharpening of the signal is explained by less exchange, i.e., one of the forms is becoming the more stable form, and equilibrium shifts strongly toward that form. From Figure S2 in the Supporting Information, it can be seen that the free amine RNH3 protons show a signal at 0.53 ppm, indicating that this species alone is in the closed environment of the NMR tube not the stable species. In Figure S2 it can be seen as well that CO2-switched 2EHA does not show a signal at 0.53 ppm. Most likely, due to the increasing partial pressure of CO2, a total shift toward the free amine is not happening, but an equilibrium has established between the carbamic acid and the amine with fast proton exchange compared to the NMR time scale.

In order to validate that indeed a relatively high partial pressure of CO2 is the cause of the limited decarboxylation toward the amine form, two types of experiments were done. In the first type, the total concentration of CO2-switched 2EHA was reduced to 75 and 25 mg, respectively, in 0.55 mL of toluene, and the same temperature program was run. These results are displayed in Figure 3. Second, a set of two experiments were done at 70 °C and in which the characteristic signal for the RNH3+, RNH2+ and RNHCOOH protons was followed in time. In the first experiment, the NMR tube remained sealed, but in the second experiment the tube was taken out of the NMR spectrometer every 20 min to flush with N2 for 1 min. These results are displayed in Figure 4.

In Figure 3 it can be seen that at lower CO2-switched 2EHA concentration the change in the chemical shift is much larger, even approaching the chemical shift of the unswitched 2EHA. This is because at the lower concentration of CO2-switched 2EHA also less CO2 is liberated upon fully back-switching to the neutral amine, and the partial pressure of CO2 in the gas phase in the tube will be less limiting for the back-switching. The second type of experiment, in which N2 sparging was applied with regular intervals to a tube containing the higher 125 mg of CO2-switched 2EHA in 0.55 mL of toluene-d8, confirms that the partial pressure of CO2 in the tube is important for the back-switching, because in the experiment without N2 sparging the chemical shift is dropping gradually, while in the experiment in which N2 sparging was applied there are stepwise changes visible for the chemical shift. In this N2-sparged tube, the partial pressure of CO2 reached much lower values directly after several purges, allowing the stepwise further back-switching toward the neutral amine.

Next to the behavior of the CO2-switched primary amine 2EHA, also the switching behavior of the CO2-switched secondary amine BMA was investigated using 1H NMR variable temperature experiments. Similar to the trend seen for 2EHA, also for BMA upon increasing the temperature from 30–75 °C, there is a strong shift of the signal that at 30 °C can be found at 8.5 ppm toward 4.0 ppm at 75 °C. For this sample, to further elucidate on the operational window, spectra were recorded as low as −30 °C. The stacked 1H NMR spectra from −30 to +75 °C are displayed in Figure 5 and the proposed reaction scheme in Scheme 2.
Scheme 2. Proposed Switching Mechanism for BMA

At 30 °C the characteristic switching signal representing protons from $R_1NCOOHR_2$, $R_1NH_2R_2$, and $R_1NHR_2$ can be found at 8.6 ppm, and it is a relatively sharp signal. Upon cooling to −30 °C, this signal shifts to 10.8 ppm and becomes much less pronounced, and this is typical for acidic proton signals. When going up in temperature to 75 °C, an opposite shift is observed to 4.0 ppm, and also here the signal is broadening. The broadening of the signal at higher temperatures is due to faster reactions and species exchange between carbamic acid and the secondary amine.

The characteristic signals for the benzylic protons adjacent to N and the CH$_3$ protons appear at 4.5 and 3.5 ppm, respectively, as well as at 3.0 and 2.0 ppm, respectively. Also these signals broaden at higher temperature, indicating the fast species exchange.

Based on the NMR studies, it is clear that at higher temperature carbamic acid (nonionic form) is present in significant amounts, but when the CO$_2$ is not actively removed from the gas phase, reverting back to the amine form is a slow process hindered by thermodynamic equilibrium. It may be interesting to study these CO$_2$-switchable solvents in extractive distillation applications, and therefore we have executed vapor−liquid equilibrium measurements in which CO$_2$-switched 2EHA and CO$_2$-switched BMA were applied as entrainer.

Vapor−Liquid Equilibrium Measurements. In order to measure whether the selected solvents have an effect on the VLE behavior of binary mixtures, the VLE of n-heptane−toluene mixtures were measured in an ebulliometer. Both 2EHA and BMA were applied in their amine form, i.e., without being pretreated with CO$_2$, as well as in their ammonium carbamate form after bubbling extensively with CO$_2$. In a typical experiment done with 2EHA, samples were analyzed with quantitative $^{13}$C NMR to follow the rate of back-switching in the ebulliometer. To minimize errors due to slow relaxation of carbon spins, the quantification was done for carbons 1, 2, and 8 (see Figure S4 in the Supporting Information for the numbering). The results are shown in Figure 6. Because of the time between sampling and finalization of the $^{13}$C NMR experiments, these results have to be interpreted with caution, as the percentage of switched amines at the moment of sampling was likely higher than displayed. Nevertheless, the graph shows that, while reducing the pressure from 10$^6$ Pa down to 10$^4$ Pa, already a significant percentage of the solvent switched back to the amine state. These results indicate that, in order to maintain the switched form longer, a significant partial CO$_2$ pressure is desired.

To compare the relative volatility in the ternary systems with the binary mixture VLE, compositions of n-heptane and toluene were expressed as a pseudobinary mixture in which the solvent was disregarded. The VLE results are depicted in Figure 7, the estimated error in the composition of $\Delta x = \Delta y = 0.02$ is due to analysis error (0.017), as determined over 196 analyses, and the error in weighing.

Figure 6. Percentage of the switched solvent that is still in CO$_2$-switched state during the $^{13}$C NMR measurement. At $t = 0$ there are two data points: one for the initial mixture and one after the operational temperature and pressure of 10$^5$ Pa had been achieved. Symbols: squares = C$_1$, circles = C$_8$, and triangles = C$_6$.

Figure 7. Vapor liquid equilibrium diagram for n-heptane−toluene at 100 mbar. The line has been simulated in ASPEN Plus using NRTL-LIT property package. The experimental data points are all pseudobinary points (heptane + toluene = 1, solvent not taken into account) and have all been obtained using a S/F ratio of 1. Symbols correspond to experiments with 2EHA (open squares), CO$_2$-switched 2EHA (closed squares), BMA (open triangle), and CO$_2$-switched BMA (closed triangles). The results for the CO$_2$-switched solvents are operational vapor liquid correspondence data, because due to escaping CO$_2$, the composition and temperature changed slowly in time and the system was not completely at thermodynamic equilibrium.

It can be seen in Figure 7 that the line representing the VLE of binary n-heptane−toluene mixtures at 100 mbar shows a tangent pinch at high molar fractions of heptane, i.e., the relative volatility $\alpha$ approaches unity at compositions approaching $x = y = 1$. When using 2EHA (open squares) and the CO$_2$-switched 2EHA (closed squares) as solvent in S/F = 1, there is an improvement visible of the relative volatility, and at high molar fractions of heptane the improvement is best visible. However, the improvement in the relative volatility is with these solvents only marginal. Samples from heptane/toluene mixtures with CO$_2$-switched 2EHA appeared hazy, indicating that there is no perfect miscibility under the
operational conditions. This likely affects the effectiveness of the solvent. The use of BMA (open triangle) improves the relative volatility of n-heptane over toluene more significantly, and this improvement is even more pronounced for the CO2-switched BMA (closed triangles). Samples from these mixtures were always clear, showing perfect miscibility of this system. Because of the labor intensity of VLE measurements and the results with 2EHA indicating that the region \( x > 0.7 \) is the most important region, with BMA and CO2-switched BMA only measurements were done starting at \( x = 0.8 \). The relative volatility reaches \( \alpha = 2.3 \) with BMA and \( \alpha = 2.7 \) with CO2-switched BMA.

Although these values for the relative volatility are promising and show that indeed, CO2-switchable solvents can be applied as entrainer in extractive distillation, the data series for CO2-switched BMA represents only one experiment, and the reported relative volatility is an operational relative volatility and not a full thermodynamic equilibrium, because the temperature and composition kept changing with time. This is due to the mode of operation of the ebulliometer, in which the pressure is set and the temperature monitored. Because of back-switching of CO2-switched BMA during the experiment, CO2 was released resulting in an increasing pressure in the system. This increasing pressure then triggered the pressure control to activate the pump. As a result, over time the solvent was changing from (almost) pure CO2-switched BMA toward BMA. At the same time, upon activation of the pump, also vapors of n-heptane and toluene were pumped out of the system, and because n-heptane is more volatile, the fraction of n-heptane reduced during the experiment. A similar effect was observed for the three experiments with CO2-switched 2EHA, starting with \( x = 0.8, 0.5, \) and \( 0.2, \) respectively.

From these results it appears that CO2-switching of BMA can increase the relative volatility in the n-heptane–toluene system as compared to nonswitched BMA, and application of such switchable solvents in affinity separations such as extractive distillation and liquid–liquid extraction can open new windows of opportunities for sustainable separations. To longer maintain the switched form and to push the equilibrium toward the carbamate, however, lower temperature is desired, and for application as entrainer in extractive distillation, fractionations of lower boiling \( C_2 \)-fractions appear more beneficial. Also for liquid–liquid extraction the lower temperature may be applied, which means that yes, CO2-switchable solvents have applicability in fluid separations wider than thus reported, but back-switching rates narrow the operational window to low temperature applications. Follow-up studies should focus on further optimizing the molecular structure of the CO2-switchable solvents in relation to the eventual application to reach higher relative volatilities and become competitive with current solvents that are less benign such as NMP and sulfolane.

**ASSOCIATED CONTENT**

- Supporting Information
  The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b01771.

  2D-HSQC analysis and NMR spectra of pure compounds (PDF)

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