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Critical Assessment of CO_2 Solubility in Volatile Solvents at 298.15 K

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Supporting Information

ABSTRACT: Fifteen different low molar mass compounds are assessed as CO_2 solvents based on bubble-point loci on the solvent-rich end (0.6 to 1.0 solvent wt fraction) of the CO_2-solvent pressure−composition diagram at 298.15 K. Four of the five best solvents (in descending order of solvent strength on a mass fraction CO_2 dissolved basis), acetone, methyl acetate, 1,4-dioxane, and 2-methoxyethyl acetate, are oxygen-rich, low molar mass species possessing one or more oxygen atoms in carbonyl, ether, and/or acetate groups that can interact favorably with CO_2 via Lewis acid/Lewis base interactions. Methanol, a very low molar mass solvent, is comparable to 1,4-dioxane in solvent strength. The remaining solvents, in descending order of solvent strength on a mass basis, include 2-nitropropane, *N*,*N*-dimethylacetamide, acetylacetone, 1-nitropropane, iso-octane, 2-(2-butoxyethoxy)ethyl acetate, *N*-formylmorpholine, propylene carbonate, 2-butoxyethyl acetate, and *N*-*tert*-butylformamide. When compared on a molar basis, each of the six best CO_2 solvents, 2-(2-butoxyethoxy)ethyl acetate, methyl acetate, 2-methoxyethyl acetate, 1,4-dioxane, acetone, and acetyl acetone, is rich in CO_2-philic ether or carbonyl oxygen atoms. Methanol, which possesses a CO_2-phobic hydroxyl group, is the worst CO_2 solvent. COSMOtherm accurately predicted the relative solvent strengths of eight of the solvents that contain carbonyl, acetate, ether, and carbonate groups. However, COSMOtherm was not able to predict the correct ordering of solvents possessing hydroxyl, nitro-, amide, secondary amine, and tertiary amine groups. This important failure of the COSMOtherm approach for these molecules is apparently due to problems with the COSMO-RS parametrization.

INTRODUCTION

In recent decades, concern has been growing about the release of CO_2 into the atmosphere primarily from the burning of fossil fuels. There are a few large point sources associated with public heat and power generation and the manufacturing and construction sectors that present viable opportunities to capture CO_2 from large scale production. Each of these opportunities to capture CO_2 presents its own challenges to the capture process. To meet these challenges, several strategies have been developed for the removal of CO_2 from these large point sources. Each of these capture strategies have ongoing research efforts funded through government organizations as well as the private sector. No single strategy has demonstrated a clear advantage in the capture of CO_2 from all possible sources.

One capture strategy is the physical absorption of CO_2 using a CO_2-philic solvent. This strategy is viable when the partial pressure of CO_2 present in waste streams is elevated such that the conditions lend themselves to high solubility values of CO_2 in the physical absorption solvent of choice. (The capture of CO_2 from mixed gas streams at low pressure, such as the post-combustion effluent streams from coal-fired power plants, is more amenable to chemical absorption methods employing amine-functionalized solvents, such as aqueous solutions of monoethanol amine.) Integrated gasification combined cycle (IGCC) power plants, sweetening of natural gas, ammonia synthesis, steam methane reforming for the production of H_2, and ethylene oxide production are all examples of large production scale processes that produce CO_2 in a mixed gas stream that meets this high pressure requirement for physical absorption.[1]

Currently there are several processes that are used to capture CO_2 from high pressure sources. Broadly, liquid solvents for the absorption of CO_2 can be divided into two types of solvents: high molar mass, low volatility, oligomeric or polymeric solvents and low molar mass, volatile compounds that are typically used at ambient or subambient temperatures to reduce evaporative losses. With regard to low volatility solvents, the Selexol solvent and dimethyl ether of polyethylene glycol (DEPG) employ proprietary mixtures of oligomers that include polyethyleneglycol dimethyl ethers (PEGDME).[2] Our recent work on oligomeric dimers[3] and hexamers has shown that several other low volatility solvents, including polypropyleneglycol dimethyl ether, polybutyleneglycol dimethyl ether, and polydimethylsiloxane, exhibit roughly the same ability to absorb CO_2 but are far more hydrophobic than PEGDME.[4] Having a hydrophobic solvent could be advantageous because the CO_2-contaminated streams usually contain water vapor and the absorption of water vapor leads to a more energy-intensive solvent regeneration step.

There are several commercial CO_2 absorption processes that employ lower molar mass, volatile compounds, sometimes referred to as "small molecules". The Fluor process utilizes propylene carbonate, which has a high affinity for CO_2.[5,6] It is typically installed in natural gas sweetening processes because of

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its ability to clean streams that may contain up to 70 % CO_2.[7] Another process primarily used in natural gas sweetening is Morphysorb which is a mixture of morpholines, mostly *N*-formylmorpholine (NFM) and *N*-acetylmorpholine (NAM).[8] Methanol is also commercially used under the process name Rectisol.[9] To mitigate evaporative losses associated with methanol's high vapor pressure, the solvent is chilled to subzero temperatures (approximately (233.15 to 253.15) K), which also increases the solvent's capacity to absorb CO_2. It has been suggested that dodecane[10] and other alkanes[11,12] can serve as CO_2 solvents.

There are two main objectives to this study. The first is to identify the best commercially available, "small molecule" solvents for the absorption of CO_2 based solely on their ability to absorb CO_2 at 298.15 K (i.e., volatility, cost, health and safety, and environmental toxicity issues are not included in the ranking). The choice of candidates was based on molecules that possess functionalities that have previously demonstrated to be "CO_2-philic". In general, such compounds are rich in functional groups capable of exhibiting low cohesive energy density (*t*-butyl groups), Lewis acid/Lewis base interactions with CO_2 (carbonyls, acetates, esters), or potentially reactive interactions with CO_2 (secondary or tertiary amines).[13,14] Some of the compounds chosen for this study have been studied in the past either at different temperatures and/or on the CO_2-rich end of the *Px* diagram during various studies of the solubility of small compounds, oligomers, or polymers in CO_2. The 11 candidates for this experimental study include 1,4-dioxane,[15−17] acetone,[18−22] methyl acetate,[23−25] acetylacetone,[26] 2-butoxyethyl acetate, 2-(2-butoxyethoxy)ethyl acetate, 1-nitropropane, 2-nitropropane, *N*,*N*-dimethylacetamide, 2-methoxyethyl acetate, and *N*-*tert*-butylformamide. To the best of our knowledge, seven of these solvents, 2-butoxyethyl acetate, 2-(2-butoxyethoxy)ethyl acetate, 1-nitropropane, 2-nitropropane, *N*,*N*-dimethylacetamide, 2-methoxyethyl acetate, and *N*-*tert*-butylformamide, have never before been suggested as a potential solvent for carbon dioxide. The structures, molar masses (*M*), and normal boiling points at a pressure of 101.325 kPa (bp) of these 11 candidates, along with four other solvents, methanol, propylene carbonate, iso-octane, and NFM, whose solubility with CO_2 has been previously reported, are listed in Table 1. There are several other low molar mass oxygenated hydrocarbons with at least one carbonyl or ether oxygen atom that were considered. Formaldehyde is available only in aqueous solution, however, while both acetaldehyde (bp 294 K) and dimethyl ether (bp 248 K) are inappropriate for use as a neat, liquid, organic solvent at ambient temperature due to their near- or subambient boiling points. Diethyl ether (bp 308 K) may be a promising candidate in that it has four carbons and a CO_2-philic ether oxygen, but safety concerns associated with its flammability and stability dissuaded us from using it in this study.

The second objective is to determine whether the solubility of CO_2 in each of these solvents can be accurately predicted using the combined quantum and statistical mechanical modeling of the COSMOtherm formalism.[27,28] The Conductor-like Screening Model for Real Solvents (COSMO-RS), developed by Klamt et al.,[27,28] is based on unimolecular quantum chemical calculations of individual species and is widely used to predict thermodynamic properties of fluids.[29−31] COSMOtherm was chosen because it is capable of qualitatively, and to some degree, quantitatively capturing intermolecular interactions such as hydrogen bonding and Lewis acid/base interactions.[32−35] Also, COSMOtherm has been successfully used before in a prior study of the solubility of CO_2 in dimers of CO_2-philic compounds.[3]

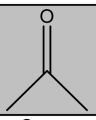
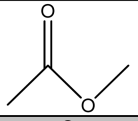
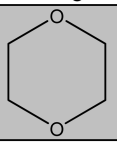
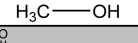
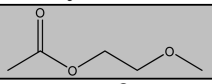
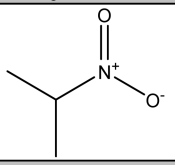
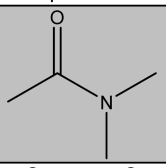
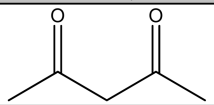
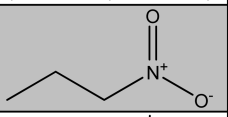
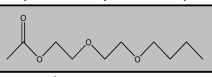
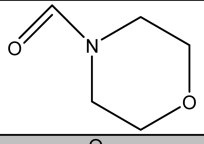
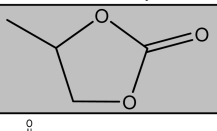
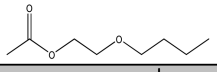
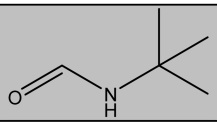
METHODS AND MATERIALS

Materials. The compounds 1,4-dioxane (anhydrous, mass purity of 0.998), 2-(2-butoxyethoxy)ethyl acetate (mass purity of 0.99), 1-nitropropane (mass purity of ≥ 0.985), 2-nitropropane (mass purity of 0.96), *N*,*N*-dimethylacetamide (mass purity of ≥ 0.995), acetylacetone (mass purity of ≥ 0.99), 2-methoxyethyl acetate (mass purity of 0.98), and *N*-*tert*-butylformamide (mass purity of 0.98) were purchased from Sigma Aldrich and used as received. The other compounds methyl acetate (mass purity of 0.99 and mass purity of water < 0.00005), 2-butoxyethyl acetate (mass purity of 0.98), and acetone (mass purity of 0.996) were purchased from Acros Organics through Fisher Scientific and were used as received. CO_2 was purchased from Penn Oxygen and Supply Company with a mass purity of 0.9999 and used without further purification.

Experimental Procedures. Solubilities of CO_2 in each solvent were obtained from bubble-point pressure measurements using a high-pressure, agitated, windowed, variable-volume, view cell from Schlumberger Ltd. Phase behavior diagrams are constructed for each small compound and CO_2 mixture using a high pressure stainless steel vessel with 1 1/2 in. thick borosilicate windows on opposing sides. Each experiment uses standard nonsampling techniques also known as the synthetic method, described in detail elsewhere.[3,4,36,37] The inside of this cell is a thick-walled, hollow quartz tube (1.25 in. ID, 1.75 in. OD) which contains a floating piston. The tube has a maximum capacity of 100 mL, but the sample volume (specified amounts of CO_2 and solvent) of the mixture that resides above this floating piston is lower than this (approximately (30 to 90) mL) during a given experiment. The floating piston contains an O-ring, which is used to separate the sample volume above the floating piston from the overburden fluid. The silicone oil overburden fluid resides below the floating piston inside of the hollow Pyrex tube and also surrounds the Pyrex tube that resides within the high pressure windowed vessel, so that there was no pressure drop across the walls of the hollow quartz tube.

In a given experiment (25 to 60) g of solvent is placed in the Pyrex tube, and the sample volume is then reduced by pumping in overburden fluid which raises the piston. Then CO_2 is passed through the leftover space to vent out all air. After that, known amounts of CO_2 are isothermally and isobarically injected into the sample volume using the dual pump by pumping in CO_2 while simultaneously extracting overburden fluid. Once a desired concentration is reached, the sample volume is repeatedly and slowly compressed and then allowed to equilibrate until the single phase solution is attained. The bubble-point pressure during compression corresponds to the point at which the last tiny bubble of gas remains in equilibrium with the liquid; further compression will yield a single phase solution. The raw bubble-point data corresponds to the pressure of the overburden fluid at this point. All of the raw bubble-point data were then corrected by subtracting the small pressure drop required to overcome the frictional resistance of the O-ring around the floating piston as it maintains the seal between the sample volume and the overburden fluid as it slides along the inner surface of the hollow Pyrex tube. Therefore, the raw bubble-point pressure data of the overburden fluid obtained during compression corresponds to the sum of the bubble-point pressure of the sample and the

Table 1. Solvent Structures, Molar Mass, Normal Boiling Point, Given by Supplier, and Relative CO_2 Solubility Rankings on a Weight and Molar Basis According to Experimental Results and COSMOtherm Predictions

Solvent * This work # Literature reference	Structure	*M*/ g·mol^{-1}	*T*(P=101.325 kPa)/K	Solvent strength on weight basis (exp)	(calc)	Solvent strength on molar basis (exp)	(calc)
acetone*[51]		58.08	329	1	1	5	7
methyl acetate*		74.08	330	2	3	2	9
1,4-dioxane*[16]		88.11	373	3	4	4	6
methanol[52]		32.04	338	4	8	15	15
2-methoxy ethyl acetate*		118.13	418	5	6	3	5
2-nitro propane*		89.09	393	6	10	7	12
N,N-dimethyl acetamide*		87.12	439	7	2	8	2
acetyl acetone*		100.12	414	8	7	6	8
1-nitro propane*		89.09	404	9	9	10	11
isooctane[53]		114.23	371	10	15	9	13
2-(2-butoxy ethoxy) ethyl acetate*		204.26	518	11	12	1	1
N-formyl morpholine[54]		115.13	509	12	5	12	4
propylene carbonate[55]		102.09	513	13	13	13	14
2-butoxyethyl acetate*		160.21	465	14	14	11	3
N-tert-butyl formamide*		101.15	475	15	11	14	10

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pressure drop required to displace the piston. This pressure drop was determined to be 0.20 MPa by comparing our experimental bubble-point pressures for pure CO_2 with the CO_2 bubble point values listed in the National Institute of Standards and Technology (NIST) webbook. All experiments were performed at 298.15 K and solvent mass fractions of at least 0.60. The apparatus used has an experimental pressure limitation of (0.21 to 68.95) MPa (accuracy is ± 0.07 MPa) and therefore is not used to measure the pure solvent vapor pressures.

Computational Methods. The standard procedure for COSMO-RS calculations used in this paper is the same as that previously published by our group.[3] It consists of two steps. Quantum chemical calculations are performed in the first step for all molecules in the system. We employ the density functional theory (DFT) based functional, B88-PW86,[38,39] together with a triple-ζ valence polarized basis set (TZVP[40]) and the RI approximation[41] to perform the calculations. The continuum solvation model COSMO is used in these calculations to simulate a virtual conductor environment for the molecules. The configuration of the solute molecules is optimized and converged to its energetically optimal state in a conductor. The output of these calculations is the so-called σ-profile or polarization charge density.[42,43] All DFT/COSMO calculations were performed using the quantum chemical program TURBOMOLE.[44] The σ-profiles are used in the second step of the COSMO-RS calculations to quantify the interaction energy of pairwise interacting surface segments with regards to the most important molecular interaction modes. All COSMO-RS calculations were carried out as implemented in the COSMOtherm program.[45] The BP_TZVP_C21_0107 parameterization[45] was adopted in this work. The CO_2 experimental vapor pressure value of 6.43 MPa[46] at 298.15 K was the only experimental input parameter in the COSMOtherm calculations. In that the objective of this study was to determine if COSMOtherm could be used to accurately predict the solvent strength of these liquids, the model was not adjusted nor optimized in any manner to fit the bubble-point results for the binary mixtures.

■ RESULTS

Experimental Results. The phase behavior at 298.15 K for the binary systems of CO_2 and all 15 solvents has been presented in the form of bubble-point measurements at the solvent-rich end of the phase behavior diagram on a weight basis in Figure 1. Also illustrated in Figure 1 are the bubble-point loci of acetone and 1,4-dioxane generated in this work compared to literature data which shows good agreement falling within the experimental error. All bubble-point measurements represent the average of six individual measurements with an uncertainty of ± 0.07 MPa, as reflected by the size of the data markers in each *Px* diagram. Table 1 presents the relative rank of the ability to absorb CO_2 on a mass and molar basis according to experimentally determined phase behavior. All data generated in this work can be viewed in Table 2.

On a weight basis, as shown in Figure 1, acetone exhibits the greatest ability to absorb CO_2 due to its low molar mass (58.08 $g \cdot mol^{-1}$) and inclusion of a CO_2-philic carbonyl group. The volatility of acetone (bp 329.15 K), which could result in significant evaporative losses and flammability concerns, is the likely reason that acetone has not been used as a commercial CO_2 solvent. Methyl acetate (bp 330 K) requires only slightly higher pressures than acetone to dissolve a specified amount of CO_2.

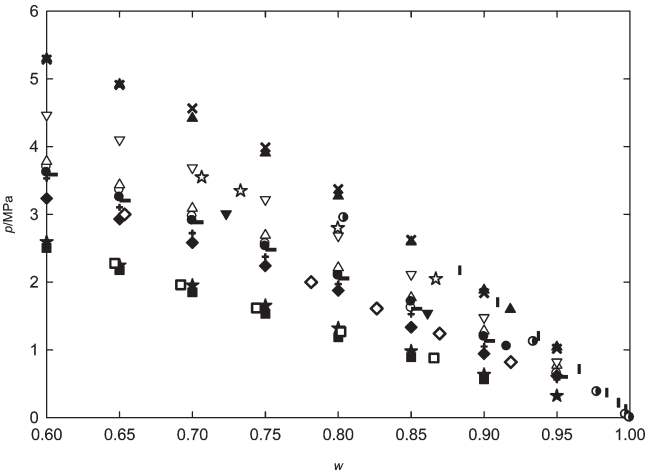

Figure 1. Solubility of CO_2 in all volatile solvents presented in mass fraction of solvents, *w*, listed in order of solvent strength from best to worst: ■, acetone (this work); □, acetone;[51] ★, methyl acetate; ♦, 1,4-dioxane (this work); ◇, 1,4-dioxane;[16] ▼, methanol;[52] +, 2-methoxyethyl acetate; −, 2-nitropropane; ○, *N*,*N*-dimethylacetamide; ● acetylacetone; △, 1-nitropropane; ☆, iso-octane;[53] ▽, 2-(2-butoxyethoxy)ethyl acetate; ◑, NFM;[54] |, propylene carbonate;[55] ▲, 2-butoxyethyl acetate; ×, *N*-*tert*-butylformamide.

Although its molar mass (74.08 $g \cdot mol^{-1}$) is greater than that of acetone, methyl acetate contains two CO_2-philic oxygen atoms in the ether and carbonyl functionalities that enhance its solvent strength. The next best solvent, 1,4-dioxane (bp 373 K) has a slightly greater molar mass (88.11 $g \cdot mol^{-1}$) and also contains two CO_2-philic ether oxygen atoms in its six-membered ring structure. The bubble-point data for methanol (bp 337.85 K) and 1,4-dioxane are comparable. Although the hydroxyl group is a CO_2-phobic moiety, methanol's very low molar mass (32.04 $g \cdot mol^{-1}$) favors high solubility values on a weight basis. The next best solvent, 2-methoxyethyl acetate (118 $g \cdot mol^{-1}$, bp 418 K), has a significantly higher molar mass and is substantially less volatile than acetone, methyl acetate, 1,4-dioxane, and methanol. The presence of two ether oxygens and a carbonyl oxygen in 2-methoxyethyl acetate accounts for its ability to be a relatively good solvent.

The remaining solvents, in order of descending solvent strength on a mass basis, are 2-nitropropane, *N*,*N*-dimethylacetamide, acetylacetone, 1-nitropropane, iso-octane, 2-(2-butoxyethoxy)-ethyl acetate, NFM, propylene carbonate, 2-butoxyethyl acetate, and *N*-*tert*-butylformamide. The nitro-, secondary amine, and tertiary amine groups associated with the nitrogen atoms in 2-nitropropane, *N*,*N*-dimethylacetamide, 1-nitropropane, NFM, and *N*-*tert*-butylformamide apparently are not as CO_2-philic as the ether and carbonyl oxygen atoms associated with the best solvents. Although iso-octane has a comparable molar mass (114.23·$g \cdot mol^{-1}$) and boiling point ((371 to 372) K) to 1,4-dioxane, it does not contain any CO_2-philic oxygen atoms and is therefore a poorer solvent. Propylene carbonate is a low molar mass solvent that contains three oxygen atoms; however, the carbonate functionality has been previously shown to be less CO_2-philic than oxygens found in ether, carbonyl, and acetate groups.[47,48] Finally, the terminal butyl group of 2-(2-butoxyethoxy)ethyl acetate and 2-butoxyethyl acetate diminish the solvent strength of these compounds relative to their methyl-terminated lower molar mass analogue, 2-methoxyethyl acetate.

Table 2. Phase Behavior Bubble-Point Loci of All Volatile Solvents Determined in This Work at 298.15 K, Where *w* Is the Mass Fraction of the Solvent and *p* Is the Bubble-Point Pressure

	acetone	methyl acetate	1,4-dioxane	2-methoxyethyl acetate
w	*p*/MPa	*p*/MPa	*p*/MPa	*p*/MPa
0.95		0.320	0.617	0.562
0.90	0.566	0.635	0.943	1.049
0.85	0.893	0.980	1.334	1.527
0.80	1.196	1.320	1.877	1.971
0.75	1.532	1.653	2.239	2.375
0.70	1.848	1.952	2.582	2.722
0.65	2.178	2.247	2.930	3.104
0.60	2.504	2.593	3.235	3.531

	2-nitropropane	*N*,*N*-dimethyl acetamide	acetylacetone	1-nitropropane
w	*p*/MPa	*p*/MPa	*p*/MPa	*p*/MPa
0.95	0.601	0.651		0.773
0.916			1.051	
0.90	1.132	1.201	1.194	1.281
0.85	1.605	1.621	1.711	1.771
0.80	2.053	2.115	2.095	2.214
0.75	2.481	2.568	2.529	2.692
0.70	2.883	2.971	2.908	3.090
0.65	3.202	3.361	3.253	3.437
0.60	3.586	3.701	3.618	3.782

	2-(2-butoxyethoxy)ethyl acetate	2-butoxyethyl acetate	*N*-*tert*-butylformamide
w	*p*/MPa	*p*/MPa	*p*/MPa
0.95	0.822	1.042	1.014
0.90	1.476	1.882	1.837
0.85	2.113	2.595	2.626
0.80	2.681	3.270	3.375
0.75	3.218	3.907	3.988
0.70	3.687	4.417	4.563
0.65	4.102	4.918	4.910
0.60	4.462	5.301	5.285

The relative rank of each compound's solvent strength on a molar basis is presented in Table 1. When compared on a molar basis, the six best solvents, in descending order of solvent strength, are 2-(2-butoxyethoxy)ethyl acetate, methyl acetate, 2-methoxyethyl acetate, 1,4-dioxane, acetone, and acetylacetone. Five of these six possess multiple ether and/or carbonyl oxygen atoms, with the only exception being acetone, which has only one carbonyl group. The worst solvent when measured on a molar basis is methanol, a very low molar mass solvent (which favors its ranking on a mass basis) which possesses a CO_2-phobic hydroxyl group.

COSMOtherm Predictions. We have computed the bubble-point curves from COSMOtherm for all compounds listed in Table 1 at 298.15 K, which can be accessed in the Supporting Information. The computed data were used to determine the relative rank of each solvent near the 0.80 solvent mass fraction range. Table 1 presents the relative rank of each solvent on a weight and molar basis based on the bubble-point loci generated by COSMOtherm predictions. A numerical analysis of the predicted bubble-point loci was performed by calculating the average absolute deviation (AAD) and average absolute percent deviation (AAPD) and can be accessed in the Supporting Information.

A comparison of the COSMOtherm ranking of the solvent strength to the ranking based on experimental results, seen in Table 1, indicates that COSMOtherm is not able to correctly rank all of the solvents. If the focus is shifted solely to oxygenated hydrocarbons with oxygen atoms in CO_2-philic functionalities (e.g., carbonyl, acetate, ether, carbonate), however, COSMOtherm performs very well, correctly predicting the order of solvent strength as acetone, methyl acetate, 1,4-dioxane, 2-methoxyethyl acetate, acetylacetone, 2-(2-butoxyethoxy)ethyl acetate, propylene carbonate, and 2-butoxyethyl acetate. The only oxygenated hydrocarbon whose relative solvent strength was incorrect was methanol, which contains a CO_2-phobic hydroxyl group. Figure 2 gives comparison on a weight basis of each of the oxygenated hydrocarbons bubble-point loci determined experimentally and predicted by COSMOtherm. Overall, COSMOtherm under predicts the bubble-point pressures, or alternatively, it overpredicts the CO_2 solubility in each solvent but is still able to accurately predict the relative solvent strength.

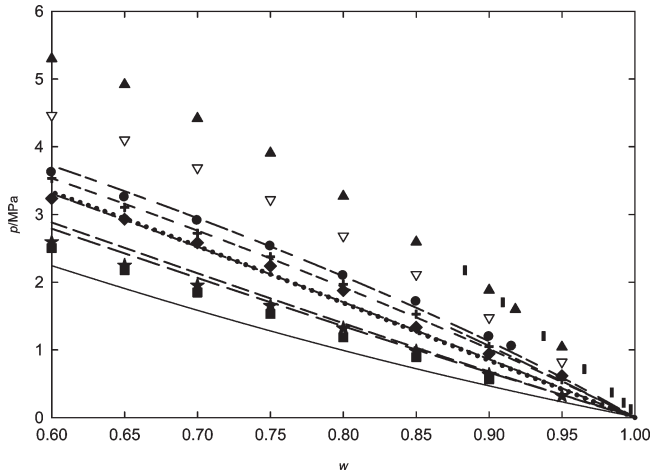

Figure 2. Comparison of the solubility of CO_2 in the eight oxygenated hydrocarbons, presented in mass fraction of solvents, *w*, COSMOtherm (lines) and experimental (symbols) listed in descending solvent strength order according to experimental results: ■, —, acetone; ★, — — —, methyl acetate; ♦, — — —, 1,4-dioxane; +, - - -, 2-methoxyethyl acetate; ●, · · ·, acetylacetone; ▽, —— ——, 2-(2-butoxyethoxy)ethyl acetate; |, —- —-, propylene carbonate;[55] ▲, -— -—, 2-butoxyethyl acetate.

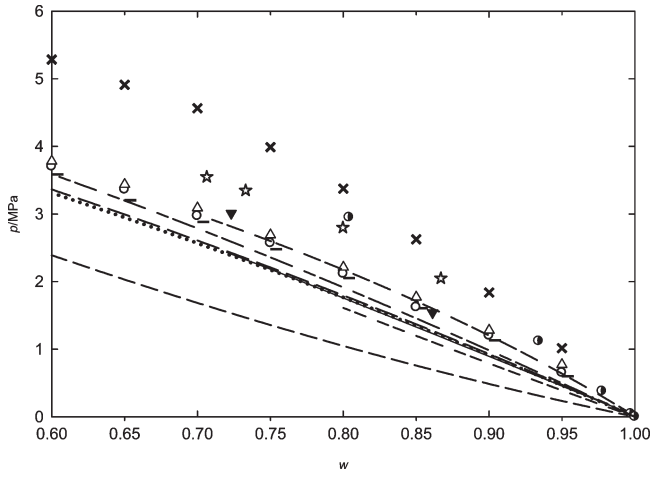

Figure 3. Comparison of solubility of CO_2 in the seven remaining solvents, presented in mass fraction of solvents, *w*, COSMOtherm (lines) and experimental (symbols) listed in descending solvent strength order according to experimental results: ▼, —, methanol;[52] —, — — —, 2-nitropropane; ○, - - -, *N*,*N*-dimethylacetamide; △, · · ·, 1-nitropropane; ☆, —— ——, iso-octane;[53] ◑, -- --, NFM;[54] ×, —- —-, *N*-*tert*-butylformamide.

The relative ranking for the compounds that contain nitrogen groups such as nitro, amide, and secondary or tertiary amines was unsuccessfully predicted with the COSMO-RS approach. This was seen especially in predictions for *N*,*N*-dimethylacetamide and NFM with each of these solvents containing a tertiary amine. Shown in Figure 3 is a comparison on a weight basis of the remaining solvents whose relative solvent strength was not accurately predicted by COSMOtherm. Kholod et al.[49] predicted the water solubility for nitrogen containing compounds using the COSMO-RS approach and found significant disagreement between calculated and experimental values for some of the compounds. Accordingly, Kholod made an ad-hoc modification to the COSMO-RS approach to improve the agreement between predicted and experimental solubility values. It appears that properties of molecules with nitrogen-containing groups are not always accurately modeled within the COSMOtherm formalism and that the error can be ascribed to problems with the COSMO-RS part of the calculation. At present we have no adequate explanation for this. The failure to predict the correct ordering for the methanol/CO_2 system may be due to specific hydrogen bonding interactions not adequately described in COSMOtherm, although previous studies have been able to accurately predict properties of systems containing hydrogen bonding liquids.[32,33]

■ CONCLUSION

The solubility of CO_2 in various "small molecule" solvents has been determined at 298.15 K. To the best of our knowledge, these results have not been previously reported for 2-butoxyethyl acetate, 2-(2-butoxyethoxy)ethyl acetate, 1-nitropropane, 2-nitropropane, *N*,*N*-dimethylacetamide, 2-methoxyethyl acetate, and *N*-*tert*-butylformamide.

When compared on a weight basis, acetone exhibits the greatest capacity for the absorption of CO_2 solubility. Three of the next four best solvents, methyl acetate, 1,4-dioxane, and 2-methoxyethyl acetate, are rich in carbonyl and/or ether groups that favor Lewis acid/Lewis base interactions with CO_2, and the solvent strength decreases with increasing molar mass and increasing boiling point. Although methanol possesses a CO_2-phobic hydroxyl group, the very low molar mass of this alcohol enables it to exhibit a solvent strength comparable to that of 1,4-dioxane when measured on a weight basis.

When the solvents were compared on a molar basis, the six best solvents, 2-(2-butoxyethoxy)ethyl acetate, methyl acetate, 2-methoxyethyl acetate, 1,4-dioxane, acetone, and acetylacetone, were rich in highly CO_2-philic carbonyl and/or ether oxygen atoms. The poorest solvent on a molar basis was methanol.

In general, when compared on either basis, solvents containing butyl, *t*-butyl, nitro, and secondary or tertiary amines exhibited poorer solvent strength than the carbonyl and ether-rich solvents.

Despite its ability to accurately predict carbon dioxide gas solubility in oligomeric solvents[3] and ionic liquid membranes,[50] the COSMOtherm formalism did not accurately predict the relative solubility of CO_2 in all of the volatile, small molecule solvents. However, a closer evaluation of the data revealed that COSMOtherm was able to correctly predict the relative solvent strengths of those compounds containing only C, H, and O, except for methanol. It appears that COSMOtherm is not able to correctly account for the interactions in the systems with nitrogen-containing molecules and for methanol. Similar problems have been noted previously,[49] with the failure linked to the COSMO-RS part of the formalism. A modification of COSMO-RS is apparently needed to correctly account for nitrogen-containing systems.

■ ASSOCIATED CONTENT

Supporting Information. Phase behavior of each binary system as predicted by COSMOtherm on a weight and molar basis (Figures 1 and 2) and the AAD and AAPD of the solubility pressures (Table 1). This material is available free of charge via the Internet at http://pubs.acs.org.

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