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Application of Molecular Connectivity Indices to the Design of Supercritical Carbon Dioxide-Soluble Metal Ion Extractants: SC-CO_2 Solubilities of Symmetrically Substituted Alkylenediphosphonic Acids[#,‡]

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ABSTRACT

Using a dynamic flow method, the supercritical carbon dioxide (SC-CO_2) solubilities of two series of symmetrically substituted alkylenediphosphonic acids, bearing 2-ethylhexyl and 3-trimethylsilyl-1-propyl ester groups, respectively, were determined as a function of the number of methylene groups separating the two phosphorus atoms. An even–odd effect, similar to that observed previously for the aggregation of these compounds in nonpolar diluents, was observed, with compounds that form more highly aggregated species in nonpolar diluents exhibiting lower solubility in SC-CO_2. Differences in the relative solubilities of analogous members of these series prompted the study of the SC-CO_2 solubilities of symmetrically substituted methylenediphosphonic acids bearing seven- and eight-carbon ester groups of various degrees of branching to determine the relative importance of steric and electronic effects in determining SC-CO_2 solubilities. When molecular connectivity indices were used to quantify the extent of branching in the ester groups, a remarkable correlation between these molecular descriptors and SC-CO_2 solubility was observed.

Key Words: SC-CO_2; Solubility; Diphosphonic acid; Seven- and eight-carbon ester; Molecular connectivity.

INTRODUCTION

The use of so-called neoteric solvents constitutes a key element in recent efforts to devise more environmentally benign (green) methods for chemical synthesis, catalysis, and separations.[1–4] Of this diverse group of solvents, supercritical carbon dioxide (SC-CO_2) has been the subject of particularly intense interest. Carbon dioxide offers numerous benefits in the context of green processing: it is nontoxic, nonflammable, and does not contribute to either photochemical smog or to ozone destruction. Moreover, in its supercritical state (i.e., above its readily accessible critical point of 31°C and 73.8 atm), its solvating power can be tuned over a wide range by relatively small changes in temperature and pressure.[5]

The use of SC-CO_2 as a medium for metal ion separations is by now well established, and numerous reports describing the extraction of any of a number of metal ions by various complexants from a wide range of matrices have appeared.[6–9] Recent work in this laboratory has concerned the possibility of coupling the unique solvent properties of SC-CO_2 with the remarkable metal ion complexing power of alkylenediphosphonic acids.[10–13] Diphosphonic acids have been extensively studied as metal ion chelating agents[14–18] and,

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upon appropriate substitution, have provided the basis for powerful metal ion extractants[19–21] and a variety of novel ion-exchange[22–28] and extraction chromatographic[29] materials. Previous work has demonstrated that these compounds form extremely stable complexes with a variety of metal ions, particularly lanthanides and actinides.[18,19] Their use in SC-CO_2 could thus provide a powerful tool for separating these ions from a variety of media. Unfortunately, neither unsubstituted diphosphonic acids nor the alkyl-substituted derivatives reported to date are sufficiently soluble in unmodified SC-CO_2 to comprise practical metal ion extractants in this medium.[30,31] Although the low solvent power of SC-CO_2 can be improved through the addition of modifiers (such as methanol) or increasing the applied pressure, these approaches are not always effective or desirable, as such measures increase operating costs or render the method less environmentally friendly. For this reason, much effort has been directed toward the development of metal ion complexants incorporating "CO_2-philic" substituents, such as fluorine atoms or silicone polymer functionalities.[32,33]

Our recent work has focused on the synthesis and characterization of alkylenediphosphonic acids possessing discrete, well-defined, silicon-containing functional groups (e.g., the 3-trimethylsilyl-1-propyl group)[34–36] for possible application in SC-CO_2. (This moiety was initially chosen to determine the feasibility of incorporating a silicon functionality into a diphosphonic acid because the corresponding alcohol was commercially available and could be used to esterify diphosphonic acids via a well-characterized method.[12,13,34]) Such compounds were targeted because they are expected to be considerably less expensive than their fluorinated analogs, increasing the likelihood of eventual large-scale application. Also, since current plans for the disposal of high-level radioactive waste include vitrification into borosilicate glass (typically consisting of 30–50% SiO_2),[37] the incorporation of silicon functionalities into alkylenediphosphonic acids could increase their compatibility with this waste form. Furthermore, while significant effort has been devoted to the examination of the effect of fluorination[30–33] on the metal ion complexation/extraction behavior and the SC-CO_2 solubility of various ligands, relatively little work has been reported on the effect of adding silicon-based functionalities. Finally, unlike the heterogeneous mixtures produced by derivatization of a molecule (e.g., a complexing agent) with silicone polymers, alkylenediphosphonic acids bearing structurally well-defined functionalities are suitable for the determination of structure–property relationships.

Alkylenediphosphonic acids contain two sites that can be functionalized to modify their solubility properties: the alkylene bridge separating the phosphorus atoms (site a in Fig. 1) and the acidic POH groups (site b). In principle, the presence of two sites for derivatization, the ability to adjust the

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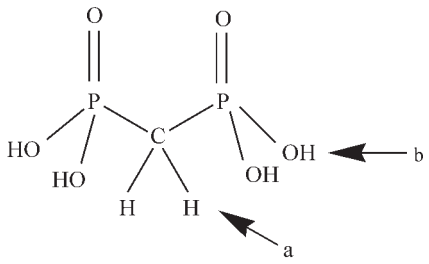

Figure 1. Functionalization sites of alkylenediphosphonic acids.

bridge length, and the many structural variations possible in the appended functional groups offer numerous opportunities to enhance the SC-CO_2 solubility of diphosphonic acids. At the same time, however, this flexibility poses a significant challenge, namely, the identification of those compounds most likely to exhibit satisfactory solubility in SC-CO_2 from among the multitude of possible candidates for synthesis. Obviously, the challenge of relating SC-CO_2 solubility to molecular structure is not unique to alkylenediphosphonic acids, and, in fact, considerable effort has been devoted to the development of means by which to predict the SC-CO_2 solubility of a variety of organic compounds. Among the approaches that have been employed are the application of equations of state,[38–42] neural networks,[43] linear free energy relationships,[44] and any of a variety of molecular descriptors encoding the geometric, topological, or electronic properties of the compounds of interest.[45–47]

Our interests lie not in making predictions of SC-CO_2 solubility from first principles, but rather once the solubility in SC-CO_2 of a particular "parent" ligand (the general structure of which is dictated by the coordination requirements and charge of the metal ion of interest) has been established, in simply correlating changes in this solubility with various structural modifications in the ligand framework. To this end, we have examined the SC-CO_2 solubility properties of a series of alkylenediphosphonic acids of varying bridge length, symmetrically-substituted at two of the acidic hydrogens with either a 2-ethylhexyl or 3-trimethylsilyl-1-propyl functionality (Fig. 2, with $n = 1–6$ and R = 2-ethylhexyl or 3-trimethylsilyl-1-propyl). Also, for a series of symmetrically disubstituted methylenediphosphonic acids (Fig. 2, with $n = 1$), we have determined the effect of the extent of branching of the ester groups on the aggregation and SC-CO_2 solubility of these compounds and have demonstrated the utility of molecular connectivity indices in quantifying the influence of branching on solubility.

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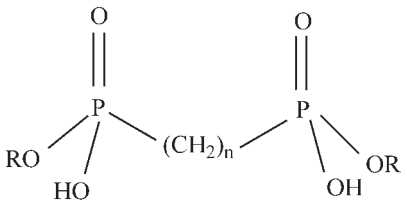

Figure 2. Symmetrically diesterified alkylenediphosphonic acid.

EXPERIMENTAL

Materials

The silyl-substituted alkylenediphosphonic acids and their di(2-ethylhexyl) analogs were synthesized via the dicyclohexylcarbodiimide-facilitated esterification of one molar equivalent of the appropriate alkylenediphosphonic acid with two molar equivalents of 3-trimethylsilyl-1-propanol or 2-ethylhexanol in anhydrous tetrahydrofuran. The resultant products were purified and characterized as previously described.[34] The symmetrically-substituted methylenediphosphonic acids containing seven- and eight-carbon ester groups were synthesized by the 1*H*-tetrazole-catalyzed coupling of one equivalent of methylenebis(phosphonic dichloride) with two equivalents of the appropriate alcohol as described previously.[12,13] Note that in this article, an abbreviated naming system (Fig. 3) is used to represent the diphosphonic acid extractants. This system emphasizes (a) the number of acidic protons ($H_2 \rightarrow 2$); (b) the ester group (D = di); and (c) the number of methylene groups bridging the two phosphorus atoms.

Solutions used in the vapor pressure osmometry experiments were prepared by dissolving a known mass of the alkylenediphosphonic acid in toluene (Fisher Scientific, Pittsburgh, PA) to achieve the desired molality. All other reagents were ACS grade and used without further purification.

Measurements

Vapor Pressure Osmometry

Vapor pressure osmometry (VPO) measurements were performed on a Jupiter Model 833 vapor-pressure osmometer (Jupiter Instrument Co., Jupiter, FL) thermostated to 25.0°C $\pm$ 0.1°C using a Neslab (Neslab Instruments, Inc., Newington, NH) constant-temperature bath using previously described methods.[35,36] The instrument was calibrated using standard solutions of

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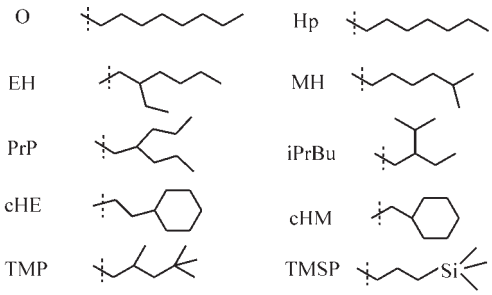

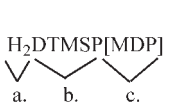

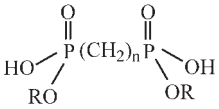

n		
1	[MDP]	methylenediphosphonic acid
2	[EDP]	ethylenediphosphonic acid
3	[PrDP]	propylenediphosphonic acid
4	[BuDP]	butylenediphosphonic acid
5	[PDP]	pentylenediphosphonic acid
6	[HDP]	hexylenediphosphonic acid

Figure 3. Naming system for alkylenediphosphonic acids.

sucrose octaacetate in toluene. A plot of measured voltage vs. monomeric sucrose octaacetate molality (m) yielded a slope of 1788 mV/m for the instrument calibration constant.

Supercritical Carbon Dioxide Solubility

The solubilities of the diphosphonic acids in SC-CO_2 were determined using an Isco, Inc. (Lincoln, NE) SFX System 2130 equipped with two Model 260D syringe pumps and an SFX 220 extractor with a coaxially heated (60°C) adjustable restrictor. The CO_2 syringe pump was cooled to 5°C by a water jacket connected to a Neslab recirculating water bath. A known mass (~400 mg) of extractant was placed in a 9-mL, high-temperature crystalline-polymer sample cartridge with 2-μm frits containing glass beads (60–100 mesh, Fisher Scientific) to reduce the dead volume. The sample cartridge was charged with CO_2, and a 15-min static extraction step was carried out. While the pressure and temperature were maintained at a predetermined value (e.g.,

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200–250 bar and 60°C), the restrictor was opened to achieve a flow rate of 2.30 ± 0.20 mL/min, and the eluent collected as a series of 3.00-mL aliquots into preweighed, dried borosilicate glass sample vials containing hexane (Fisher Scientific Co.). The hexane was removed under reduced pressure at 40°C on a rotary evaporator and the sample vials placed in a vacuum oven at 60°C for 18 hr. The vials were then allowed to cool to room temperature in a desiccator, and the mass of recovered extractant determined gravimetrically. The solubility was calculated as the number of moles of solute collected divided by the number of moles of CO_2 required for transfer.

Prior to use, the sample cartridges were dried in vacuo at 60°C for 18 hr, then weighed to allow the determination of mass balance. In all cases, a satisfactory mass balance (±5%) was obtained. Duplicate experiments showed that the reproducibility was generally within 5%, unless experimental conditions (e.g., dead volume, flow rate, or equilibration time) varied dramatically. Care was therefore taken to keep these conditions uniform over the entire series of experiments.

The validity of the method for making SC-CO_2 solubility measurements was confirmed by the determination of the solubility of several solid compounds (i.e., stearyl alcohol, stearic acid, and biphenyl) for which literature values[48,49] are available. The results of these test determinations, summarized in Table 1, generally reproduced the literature data to within 10% of the reported value.

RESULTS AND DISCUSSION

Silyl- and 2-Ethylhexyl-Substituted Compounds

Solubility data obtained from dynamic transfer experiments for symmetrically-disubstituted 2-ethylhexyl and 3-trimethylsilyl-1-propylalkylenediphosphonic acids at 60°C and 250 bar (Fig. 4) suggest that the SC-CO_2 solubility of these ligands at a given temperature and pressure is determined by

Table 1. The SC-CO_2 solubilities of selected solids.

Compound	Conditions		Reported solubility[a]	Experimental solubility[a]	Reference
	°C	bar			
Biphenyl	35.8	201.7	1.43×10^{-2}	1.5×10^{-2}	48
Stearyl alcohol	35.0	218.0	8.28×10^{-4}	8.6×10^{-4}	49
Stearic acid	35.0	208.0	1.21×10^{-4}	1.1×10^{-4}	49

[a]Mole fraction solute.

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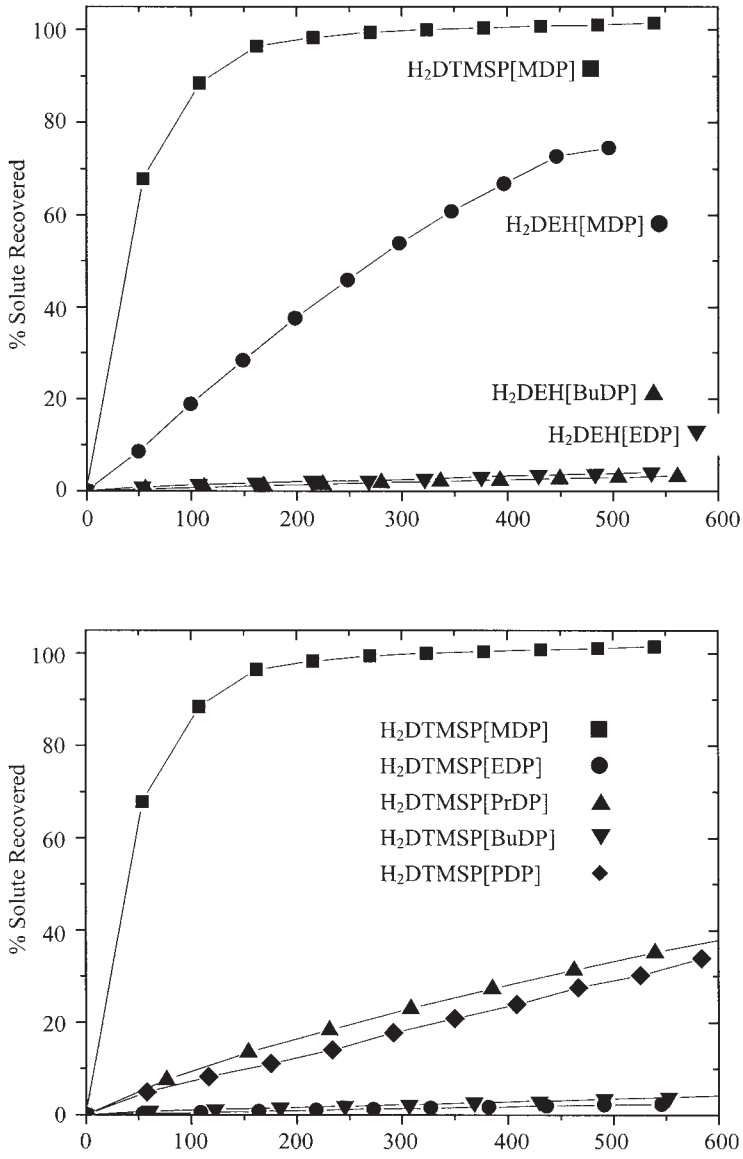

Figure 4. Percent recovery of 3-(trimethylsilyl)-1-propyl- and 2-ethylhexyl-substituted alkylenediphosphonic acids from glass beads at 250 bar, 60°C.

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several factors, most notably, the length of the alkylene chain bridging the phosphorus atoms. Specifically, those ligands with an odd number of bridging methylene groups, which have been shown to be dimeric in nonpolar diluents (e.g., toluene), are significantly more soluble in SC-CO_2 under a given set of conditions than those with an even number of bridging methylene groups, which tend to form more highly aggregated species in these diluents.[36] Although no data are yet available on the aggregation of these compounds in SC-CO_2, prior reports comparing the self-association of various carboxylic acids in toluene and SC-CO_2 suggest that the diphosphonic acids may be somewhat less aggregated in SC-CO_2 than in a conventional nonpolar solvent.[50] It should be noted, however, that the aggregation constants for these ligands in such solvents (e.g., toluene), which range from ca. 10^5 to more than 10^{12}, are such that even a significant decrease in their magnitude in SC-CO_2 vs. toluene will nonetheless correspond to essentially complete aggregation. The lower solubility observed for the most highly aggregated compounds is not entirely unexpected, given the reported greater solubility of the monomeric form of carboxylic acids relative to the corresponding dimers in SC-CO_2.[50]

The results presented in Fig. 4 also demonstrate that among the compounds with an odd number of bridging methylene groups, the SC-CO_2 solubility decreases as the length of the bridge increases. Thus, H_2DTMSP[MDP] is significantly more soluble in SC-CO_2 than either H_2DTMSP[PrDP] or H_2DTMSP[PDP]. Given that all of these ligands are primarily dimeric in toluene (and are expected to remain so in SC-CO_2), a factor other than aggregation clearly plays a role in determining this difference in solubility. Increases in solute molecular weight are known to lead to decreases in SC-CO_2 solubility.[51] Thus, the lower solubility observed for H_2DTMSP[PrDP] and H_2DTMSP[PDP] is certainly due, at least in part, to their higher (by 28 and 56 g/mol, respectively) molecular weights vs. H_2DTMSP[MDP]. Previous reports[51] for *n*-alkanes and primary alcohols suggest that a given increase in solute molecular weight will be accompanied by a similar decrease in SC-CO_2 solubility, with each additional methylene group leading to a decline of roughly a third. That the decrease in SC-CO_2 solubility for the two diphosphonic acids exceeds this value suggests that some other, as yet unidentified, factor also influences the solubility in this case.

It is also evident from Fig. 4 that the nature of the ester groups present has a significant effect on the solubility of the diphosphonic acid. Specifically, TMSP-substituted extractants are generally more soluble than the analogous EH-substituted extractants. To determine if the greater solubility of the TMSP compounds arises from the presence of the silicon atom in the TMSP group or from differences in branching between the TMSP and EH groups (variations in branching having been shown previously to lead to significant differences in the SC-CO_2 solubility of isomeric alkanes and alcohols[51]), the SC-CO_2

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solubilities of methylenediphosphonic acids esterified with a number of C_7 and C_8 groups with various degrees of branching were determined.

C_7- and C_8-Esterified Methylenediphosphonic Acids: Aggregation Properties

Since the aggregation of alkylenediphosphonic acids likely has considerable influence on their SC-CO_2 solubility, the degree of aggregation in toluene of members in the series of methylenediphosphonic acids containing seven- or eight-carbon ester groups (Fig. 3) was first determined. The results of these experiments (Table 2) show that, as anticipated, the ester group has no effect on the aggregation of methylenediphosphonic acids, with all of the compounds existing as dimeric aggregates.

C_7- and C_8-Esterified Methylenediphosphonic Acids: Supercritical Carbon Dioxide Solubility

The results of measurements of the SC-CO_2 solubility at 60°C and 200 bar of the series of methylenediphosphonic acids containing seven- or eight-carbon ester groups are shown in Figs. 5 and 6. It is readily apparent from

Table 2. Aggregation of methylenediphosphonates with C_7 and C_8 ester groups.

Compound	Analytical concentration[a]	Apparent concentration[b]	Aggregation number[c]
H_2DO[MDP]	0.05335	0.02665	2.00
H_2DEH[MDP]	0.05043	0.02537	1.99
H_2DPrP[MDP]	0.05237	0.02650	1.98
H_2DTMP[MDP]	0.04947	0.02508	1.97
H_2DcHE[MDP]	0.05421	0.02681	2.02
H_2DHp[MDP]	0.07060	0.03561	1.98
H_2DMH[MDP]	0.05884	0.02833	2.08
H_2DTMSP[MDP]	0.05035	0.02561	1.97
H_2DiPrBu[MDP]	0.06828	0.03377	2.02
H_2DcHM[MDP]	0.05963	0.02940	2.03

[a]Moles solute/kg toluene determined from a known mass of solute dissolved in a known mass of toluene.
[b]Moles solute/kg toluene determined experimentally using vapor pressure osmometry.[35,36]
[c]Analytical concentration/apparent concentration ($\pm$0.07).

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these results that the extent of branching of the ester group has a pronounced effect on the SC-CO_2 solubility of these compounds, with the straight-chain and cyclic esters exhibiting far poorer solubility than the highly branched esters. It was anticipated that an increase in ester group branching would be accompanied by greater solubility, given prior reports of the influence of branching on solubility of hydrocarbons and alcohols[51] in SC-CO_2, although the magnitude of the effect (most evident from Fig. 7) is somewhat surprising.

Figure 7 summarizes the results of efforts to correlate the solubility of the C_7 and C_8 esters of methylenediphosphonic acid with a topological molecular descriptor, the molecular connectivity. This descriptor can be calculated at a number of different levels to take into account various properties of a molecule,[52,53] and it has been successfully employed in the development of structure–function relationships to predict such properties as boiling points,[54] gas chromatographic retention times,[52] and toxicity.[55] For a given ester group, the molecular connectivity index of order n, ${}^{n}\chi$, is calculated by assigning to each nonhydrogen atom in the group a number (σ_i) equal to the number of other nonhydrogen atoms to which it is bound, then

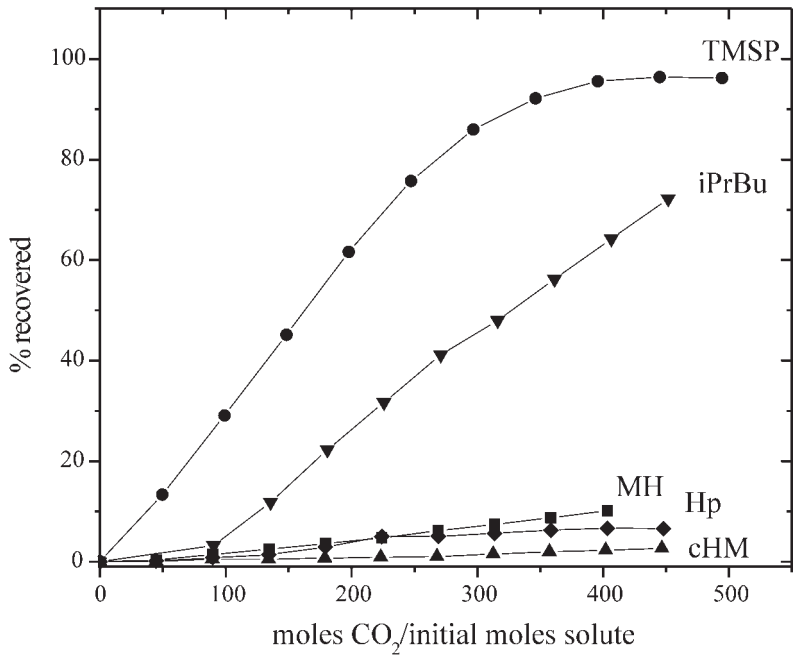

Figure 5. Percent recovery of C_7-methylenediphosphonates from glass beads at 200 bar, 60°C.

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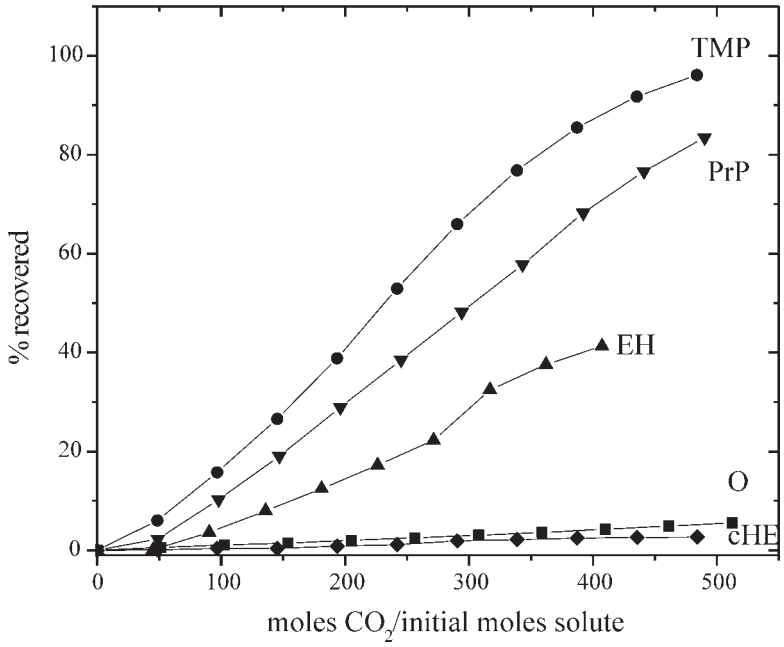

Figure 6. Percent recovery of C_8-methylenediphosphonates from glass beads at 200 bar, 60°C.

solving the following equations for each possible combination of connected atoms of size $n + 1$:

$$^0\chi = \sum (\sigma_i)^{-0.5}$$

$$^1\chi = \sum (\sigma_i \cdot \sigma_j)^{-0.5}$$

$$^2\chi = \sum (\sigma_i \cdot \sigma_j \cdot \sigma_k)^{-0.5}$$

$$^3\chi = \sum (\sigma_i \cdot \sigma_j \cdot \sigma_k \cdot \sigma_l)^{-0.5}$$

$$^4\chi = \sum (\sigma_i \cdot \sigma_j \cdot \sigma_k \cdot \sigma_l \cdot \sigma_m)^{-0.5}$$

For example, $^0\chi$ is calculated from the sum of the individual σ values raised to the -0.5 power, while $^1\chi$ is calculated from the sum of the products of the σ values of all combinations of two adjacent atoms. Results of these calculations are given in Table 3.

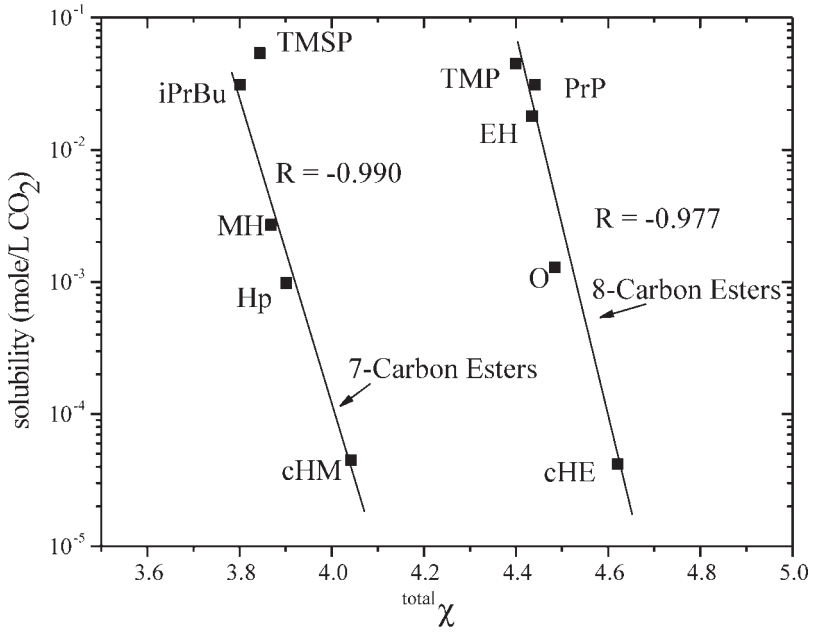

Figure 7. Supercritical carbon dioxide solubility vs. ${}^{\text{total}}\chi$ for methylenediphosphonic acids with seven and eight-carbon ester groups.

To obtain the best fit of the data using the fewest molecular connectivity indices, numerous combinations of the indices were investigated. Although the fit of the data generally improved as more indices were used, a satisfactory fit was obtained when the base-ten logarithms of the extractant solubilities were plotted vs. a simple linear combination (${}^{\text{total}}\chi$) of ${}^{1}\chi$ and ${}^{2}\chi$, as per the following equation:

$$ {}^{\text{total}}\chi = a \cdot {}^{1}\chi + b \cdot {}^{2}\chi $$

Through the use of the iterative solving feature of Corel Quattro Pro (v.8.0, Corel Corporation, Ottawa, Ontario, Canada), the coefficients (i.e., a and b) were optimized (to $a = 1.00$ and $b = 0.23$) to provide the best straight-line correlation for a plot of the negative base-ten logarithm of the extractant solubility vs. ${}^{\text{total}}\chi$. Figure 7 shows the results obtained when the coefficients were optimized using the data for the C_8-esterified methylenediphosphonates.

As can be seen, the data for the C_8 compounds are highly correlated ($R = -0.977$) to ${}^{\text{total}}\chi$. Interestingly, the same coefficients yield a straight-line relationship ($R = -0.990$) between the solubility and ${}^{\text{total}}\chi$ for the C_7-

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Table 3. Molecular connectivity indices and solubility data for methylenediphosphonates.

Group	$^{0}\chi$	$^{1}\chi$	$^{2}\chi$	$^{3}\chi$	$^{4}\chi$	$^{\text{total}}\chi$	Solubility[a]
n-Octyl	6.243	3.914	2.414	1.458	0.854	4.485	$1.3(\pm 0.3) \times 10^{-3}$
2-Propylpentyl	6.405	3.807	2.683	1.564	1.130	4.441	$3.1(\pm 0.3) \times 10^{-2}$
2-Ethylhexyl	6.405	3.807	2.656	1.748	0.756	4.435	$1.8(\pm 0.8) \times 10^{-2}$
2,4,4-Trimethylpentyl	6.784	3.416	4.159	1.020	1.225	4.399	$4.5(\pm 0.6) \times 10^{-2}$
2-Cyclohexylethyl	5.819	3.931	2.915	2.302	1.593	4.620	$4.2(\pm 1.7) \times 10^{-5}$
Cyclohexylmethyl	5.112	3.393	2.745	1.894	1.307	4.042	$4.5(\pm 1.9) \times 10^{-5}$
n-Heptyl	5.535	3.414	2.062	1.208	0.677	3.901	$9.8(+0.5) \times 10^{-4}$
2-Methylhexyl	5.698	3.269	2.536	1.136	0.612	3.868	$2.7(+0.5) \times 10^{-3}$
Isopropylbutyl	5.861	3.179	2.629	1.782	0.472	3.801	$3.1(\pm 0.4) \times 10^{-2}$
3-Trimethylsilyl-1-propyl	5.914	3.061	3.312	1.000	0.750	3.844	$5.4(\pm 0.5) \times 10^{-2}$

[a]Moles solute/L CO_2.

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esterified methylenediphosphonates, suggesting that the relative SC-CO_2 solubility of methylenediphosphonates bearing different alkyl ester groups can be predicted through the calculation of molecular connectivity indices.

It is important to note (Fig. 7) that H_2DTMSP[MDP] is roughly an order of magnitude more soluble in SC-CO_2 than would be expected from its molecular connectivity index alone. Thus, the greater solubilizing effect of the TMSP group vs. the EH group arises not merely from the introduction of greater branching into the extractant but also from the presence of the silicon atoms. That a silicon-containing functionality should increase the solubility of the extractant in SC-CO_2 is not surprising given previous reports of "CO_2-philic" silicon-based polymers and amphiphiles.[56,57] The magnitude of the effect observed was unanticipated, however, given that each TMSP group contains only a single silicon atom. Interestingly, the observed solubility (ca. 0.054 M at 60°C and 200 bar) of H_2DTMSP[MDP], while not as great as that of tri-*n*-butyl phosphate (1.2 M under the same conditions of temperature and pressure),[58] is comparable to that of diisodecylphosphoric acid (0.041 M)[58] and octyl(phenyl)(*N*,*N*-diisobutylcarbamoyl)-methylphosphine oxide (0.089 M),[58] two organophosphorus extractants regarded as having sufficient SC-CO_2 solubility to render them applicable in the supercritical fluid extraction (SFE) of metal ions.[58]

CONCLUSIONS

The results presented here, in addition to elucidating the factors governing the solubility of alkylenediphosphonic acids in SC-CO_2, represent the first demonstration of the utility of simple branching indices in the design of carbon dioxide-soluble metal ion extractants. In addition, the results provide the first indication that metal ion extractants having SC-CO_2 solubility adequate for application in SFE can be prepared by incorporation into the extractant of simple, structurally well-defined, silicon-bearing substituents. Work addressing the opportunities for improved CO_2-based systems for metal ion separations suggested by these results is currently underway in this laboratory.

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