SUPERCRITICAL FLUID SOLVENT EFFECTS ON CARBOXYLIC ACID DIMER FORMATION

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The equilibrium constants for dimerization of three different carboxylic acids in near and supercritical carbon dioxide and ethane at various temperatures and densities are presented. Fourier-Transform infrared spectroscopy was used to determine the equilibrium constants by examining the C=O stretching frequencies of the monomer and dimer of the acids in solution. The equilibrium constants for formic acid, propionic acid, and trifluoroacetic acid are shown to decrease with temperature for both ethane and CO_2 solvents, but also depend strongly upon CO_2 solvent density. The modified lattice fluid hydrogen-bonding (MLFHB) model was used to interpret this density dependence of the equilibrium constants. This density dependence provides evidence for specific solvent-solute interactions between CO_2 and the carboxylic acid functional group, which is attributed to strong Lewis acid-Lewis base interactions. Since carboxylic acids contain both a Lewis acid and a Lewis base moiety, the examination of a strong acid such as trifluoroacetic acid provides insight as to whether CO_2 acts as a Lewis acid or as a Lewis base in these specific interactions.

INTRODUCTION

Existing industrial and biological processes may be optimized and new processes may be developed with a thorough understanding of how carboxylic acids interact both with themselves and with other solvents. Because of the emphasis on green engineering and chemistry and because of the wide range of conditions which may be employed, the use of supercritical solvents such as carbon dioxide (CO_2) in applications of carboxylic acids would be attractive. Researchers have investigated the self-association of carboxylic acids in a wide variety of solvents [1-8]. Although the general trend of these studies shows that the solute-solvent interactions increase as the solvent becomes more polar, no systematic description of how the acids interact with solvents has been given. Much attention has been given to the effect of solvent density on the equilibrium constants associated with hydrogen bonding [3,9-11]. The highly tunable density of CO_2 [12], which can be used to examine these effects on such acids, along with its environmentally benign nature makes CO_2 in the near- and super-critical states an attractive solvent to study. Moreover, recent research has focused on the design of molecules soluble in CO_2 [13,14], so understanding of interactions of these functional groups in carboxylic acids with CO_2 could aid in the design of new CO_2-philic compounds. Although carboxylic acids have been shown to form dimers, trimers, tetramers and even higher order oligomers, the bulk of current literature [2-8] suggest that only the monomer and the cyclic dimer of carboxylic acids exist in any appreciable quantity at low concentrations in the gas phase. This single dimerization allows a direct correlation between the density of a solvent and its stabilization of the monomer form of the acid. This provides a quantifiable interaction between the acid and the solvent. Here we investigate the self-

association of formic acid, propionic acid, and trifluoroacetic acid (TFA) in supercritical fluid (SCF) and near-critical CO_2 using Fourier-Transform infrared spectroscopy (FTIR). This allows the examination of the effects of carbon chain length on the dimerization constant as well as the adjustable physical properties of the SCF solvent. Because of the high solubility of perfluorinated compounds in CO_2 [13], the use of TFA allows a means to study the influence of this functionality on the dimerization. The non-polar solvent ethane is also employed to provide a comparison of the effects of the solvent type on the acid dimerization of formic acid and propionic acid self-association. Additionally, the modified lattice-fluid hydrogen bonding (MLFHB) model is used to predict the dimerization constants and compare to those obtained spectroscopically. MLFHB parameters are then used to quantify the solvent-solute interactions. We have previously reported on the effects of SCF ethane and CO_2 solvents on the dimerization of formic acid including the application of MLFHB modeling [3].
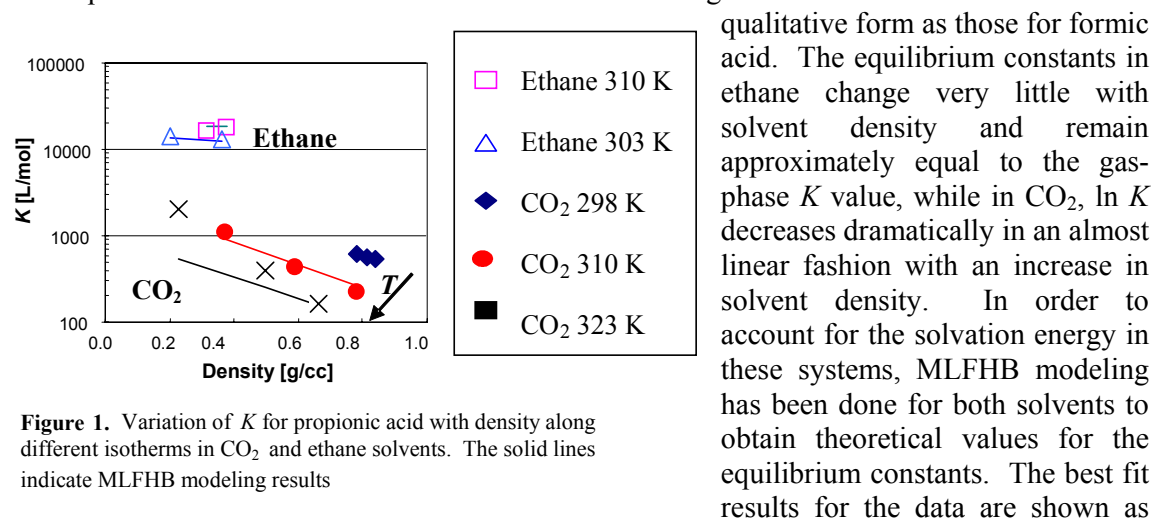
MATERIALS AND METHODS

Formic acid (98 – 100% purity, Sigma), propionic acid (99.5+% purity, Aldrich), trifluoroacetic acid (99% purity, Acros) and SFC grade carbon dioxide (99.999% purity, BOC) were used as received. Research grade ethane was purchased from BOC and dried using a gas drier (Alltech) to completely remove the water before use.

The experimental apparatus and procedure used are described elsewhere [3]. Equilibrium constants were determined for all three carboxylic acids using the method presented by Fujii and co-workers [2], which was originally developed for acetic acid in dilute concentrations. The dependence of equilibrium constants on solvent density was modeled using the modified lattice-fluid hydrogen bonding (MLFHB) theory [15-17]. The values needed for the acids and solvents were obtained from the literature [4,10,18-22].

RESULTS AND DISCUSSION

Propionic Acid The spectral data for propionic acid consisted of two distinct peaks: one for the monomer located at 1764 cm^{-1} and the other for the cyclic dimer located at 1724 cm^{-1}. There was no spectral evidence for the presence of a linear dimer or of any higher oligomers which would have resulted in peaks at lower wavenumber. The absence of water contamination was confirmed spectroscopically by observing no peak near 1640 cm^{-1} [23]. The equilibrium constants obtained are summarized in Figure 1. These results have the same qualitative form as those for formic acid. The equilibrium constants in ethane change very little with solvent density and remain approximately equal to the gas-phase K value, while in CO_2, ln K decreases dramatically in an almost linear fashion with an increase in solvent density. In order to account for the solvation energy in these systems, MLFHB modeling has been done for both solvents to obtain theoretical values for the equilibrium constants. The best fit results for the data are shown as

Figure 1. Variation of K for propionic acid with density along different isotherms in CO_2 and ethane solvents. The solid lines indicate MLFHB modeling results

the solid lines in Figure 1. For the most part, the model agrees well with the experimental data, as the average error between the experimental data and the modeling is less than one percent. The largest deviation from the experimental results comes at the low-density data at the highest temperature. Although these deviations appear to be quite large, the experimental error associated with these points is substantial, where the variation between experimental measurements was as large as 37 percent. Because the equilibrium constants are so large, the monomer peaks are quite small, so the error associated with these peaks is large. Since this area is then squared in the equilibrium constant calculation, this error is magnified. Because of the uncertainty in these points, the modeling was optimized to fit the high density data. This gives the best overall fit to the data with an average error of less than 4%, largely due to the low density data. MLFHB parameters from the literature [10,19,22] were used which were applicable to the experimental temperatures and modeled each system best. The optimized values of F' for both systems as shown in Table 1.

Hydrogen-Bonding Molecules	Solvent	F' (kJ/mol)
Formic acid / Formic Acid	CO_2	11.5
Formic acid / Formic Acid	C_2H_6	0.5
Propionic acid / Propionic Acid	CO_2	11.7
Propionic acid / Propionic Acid	C_2H_6	1.1
TFA / TFA	CO_2	6.9
PFTB / DME	SF_6[a]	3.0

Table 1. Comparison of estimated free energy change upon hydrogen-bonding in different systems.

[a] From Kazarian et. al. [11]

The free energy change upon hydrogen bonding in CO_2 for formic and propionic acids is almost identical. This suggests that the increased carbon number has little effect on the strength of the specific interactions of CO_2 with the functional group. This implies that there is no steric effect of the carbon backbone with its increase from formic acid to propionic acid on solvent-solute interactions and that the CO_2 interacts with the functional group. As mentioned previously, these interactions could be the result of Lewis acid-base type interactions between the CO_2 and the carboxylic acid functionality. The optimized value of F' for propionic acid in ethane is higher than for that of formic acid in ethane, but is an order of magnitude smaller than that for the propionic acid in CO_2. This confirms the assertion that ethane does not have specific interactions with the carboxylic acid functional group.

Trifluoroacetic Acid (TFA) Unlike the other acid systems studied which only had two distinct peaks associated with the monomer and cyclic dimer forms, TFA was observed to have three distinct peaks under certain conditions. An example of this is shown in Figure 2. This third peak only exists at the lowest temperature and densities studied. As either the pressure, and consequently density, or temperature of the system is raised, the third spectral band essentially disappears as shown in Figure 3. This example is given at higher density, though spectra at a higher temperature look very similar as well. *Ab initio* simulations were performed on several geometrical configurations to determine which species could be responsible for this absorbance [24]. These led to the assignment of the peak near 1760 cm^{-1} to the linear dimer. It is well known that CO_2 can act as a Lewis acid [25-27]. We previously suggested that acid-base type interactions could occur with the free electrons on the carbonyl oxygen or with the hydroxyl oxygen, thus stabilizing the monomer. Studies of compounds containing carbonyl groups using *ab initio* computations [28], experimental observations [29,30], and FTIR spectroscopy [26] all supported this idea. In each case, the enhanced solubility of compounds containing carbonyl groups in carbon dioxide was attributed to the free electrons on the carbonyl oxygen interacting with the slightly acidic carbon of CO_2 in a
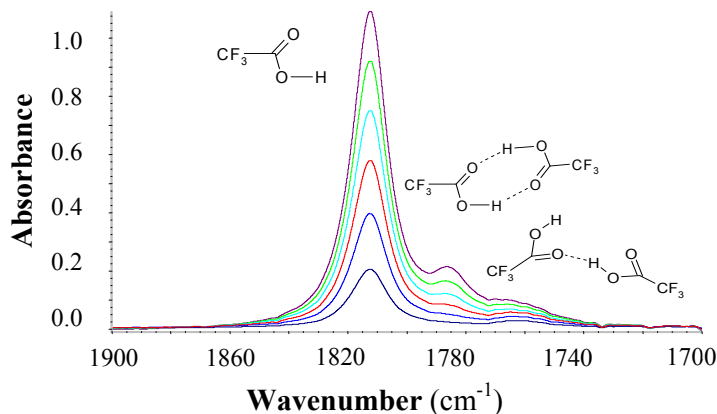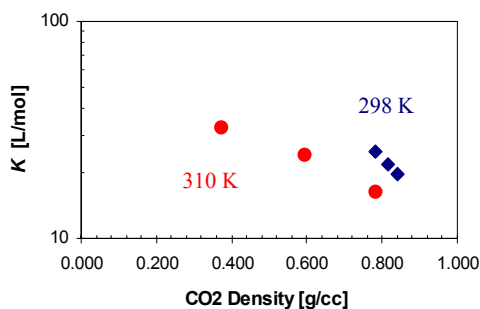
Figure 2. TFA spectra taken at 25 °C and 82.7 bar in CO_2. The three peaks shown correspond to the monomer, cyclic dimer, and linear dimer of TFA in that order as the wavenumber decreases
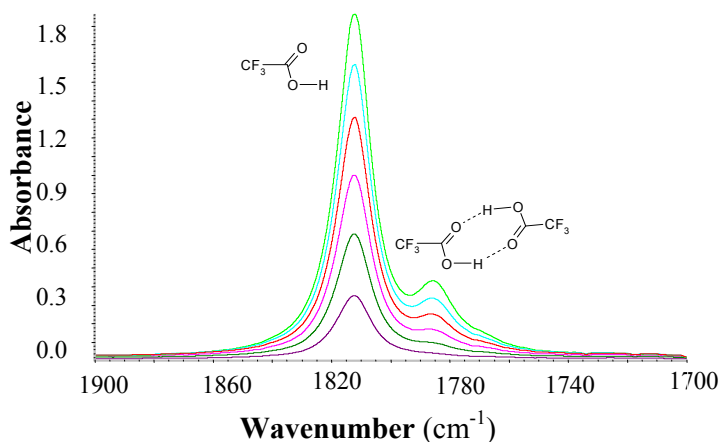
Figure 3. TFA spectra taken at 25 °C and 11 bar in CO_2. At this density (0.841 g/cm^3), only two distinct peaks, corresponding to the monomer and the cyclic dimer of TFA, are observed. The third peak corresponding to the linear dimer

Lewis acid – Lewis Base type interaction. However, our current studies have led us to believe that CO_2 can act as a Lewis base and interact with the acidic proton. It is therefore possible that either one or a combination of both of these factors is responsible for the solvent-solute interactions in CO_2. Recently, Raveendran and Wallen have used *ab initio* computations to study interactions of compounds containing Lewis base groups with CO_2 suggesting that a ring like structure can be formed between the sugar and a CO_2 solvent molecule with two hydrogen bonds: one between the carbonyl oxygen and the carbon of CO_2 and the other between an oxygen on the CO_2 and an aliphatic hydrogen on the compound [31]. This study shows that CO_2 can act both as an electron donor and as an electron acceptor. However, the interaction with carbon dioxide acting as the Lewis acid is stronger. In our studies, the stabilization of the linear dimer of TFA is consistent with the fact that CO_2 is capable of acting as a Lewis base. As observed by Murty et. al. [8,9] basic solvents, such as benzene, can stabilize the linear dimer form of the TFA self-association. This existence of the linear form is possible because the free electrons on a Lewis base solvent, such as CO_2 can interact favorably with the highly acidic proton on the acid. The fact that this dimeric form does not exist for the other acids in CO_2 is explained by observing that the proton on TFA is much more acidic, a pKa of 0.23 [32], than those of the non-fluorinated carboxylic acids, a pKa of 3.77 for formic acid and a pKa of 4.88 for propionic acid[33]. The presence of the highly electronegative fluorine atoms on the perfluorinated acetic acid results in the electron density shifting toward the fluorines and away from the hydrogen. This effect results in the high acidity which strengthens the solute-solvent interactions, thereby acting to stabilize the linear dimer relative to the cyclic form. As the temperature is increased, the hydrogen-bond will be broken due to thermal energy. This accounts for the essential disappearance of the peak with temperature. As the pressure is increased, the linear dimer will convert to the cyclic dimer. For TFA dimerization in CO_2, there is an enormous decrease in the values of

Figure 4. Variation of K for trifluoroacetic acid with density along different isotherms in carbon dioxide

the equilibrium constant going from gas phase to carbon dioxide solvent shown in Figure 4. For instance, at 298 K, the equilibrium constant is approximately 5000 L/mol in gas phase, while all values in CO_2 are less than 50 L/mol. This is a two order of magnitude decrease and is much more significant than the decreases of formic acid or propionic acid. This very large decline indicates a much stronger interaction than those for the weaker acids. This result along with the stabilization of the linear dimer of TFA leads us to believe that it is the interaction of the highly acidic proton of TFA with an oxygen of CO_2 that is the dominant stabilizing interaction. This means that CO_2 in the role of a Lewis base is more significant in this case than the role of CO_2 as a Lewis acid.

CONCLUSIONS

Both formic acid and propionic acid hydrogen-bonding studies showed that the monomer form was much more stabilized in CO_2 than in ethane relative to the dimer. As the density of the CO_2 solvent increased, the equilibrium constant decreased strongly, due to the existence of a specific interaction between the acids and the CO_2 solvent. Whereas, the equilibrium constant remained relatively constant as ethane density was increased. The density dependence for hydrogen-bonding was modeled using MLFHB theory, which suggested that both the acid monomers were stabilized by roughly the same amount relative to the acid dimers as the CO_2 density is increased. Therefore, the carbon number seems to have little effect on the specific interactions of CO_2 with the acid functional group, suggesting no difference in steric hindrance. TFA did not exist purely as a monomer / cyclic dimer equilibrium in all conditions. Studies showed the existence of a third peak in CO_2 at a low temperature (298 K) and low densities (0.781 – 0.816 g/cm^3) which corresponded to the linear dimer of TFA. All of these results suggest that a combination of Lewis acid-Lewis base interactions between the carbon on CO_2 and the carbonyl oxygen on the acids and between an oxygen on CO_2 and the acidic proton on the acids act to stabilize the monomer. However, the interaction of the CO_2, acting as a Lewis base, with the acidic proton seems to be the dominant solvent-solute interaction. As a result, the ability of CO_2 to act both as a Lewis base (this study) and as a Lewis base [25] and to have significant interactions should be taken into account when designing CO_2-soluble molecules.

ACKNOWLEDGEMENTS

REFERENCES

[1] ALLEN, G., CALDIN, E. F., Q. Rev. Chem. Soc., Vol. 7, **1953,** 255
[2] FUJII, Y., YAMADA, H., MIZUTA, M., J. Phys. Chem., Vol. 92**, 1988**, 6768

[3] PARK, Y., GUPTA, R. B., CURTIS, C. C., ROBERTS, C. B., J. Phys. Chem. B, Vol. 106, **2002**, 9696

[4] CHRISTIAN, S. D., STEVENS, T. L., J. Phys. Chem., Vol. 76, **1972**, 2039

[5] YAMAMOTO, M., IWAI, Y., NAKAJIMA, T., ARAI, Y., J. Phys. Chem. A, Vol. 103**, 1999**, 3525

[6] HIZAGY, W. S., TAHA, A. A., J. Phys. Chem., Vol. 74, **1970**, 1982

[7] MURTY, T. S. S. R., J. Phys. Chem., Vol. 75, **1971**, 1330

[8] MURTY, T. S. S. R., PITZER, K. S., J. Phys. Chem., Vol. 73, **1969**, 1426

[9] FULTON, J. L., YEE, G. G., SMITH, R. D., J. Am. Chem. Soc., Vol. 113, **1991**, 8327

[10] GUPTA, R. B., COMBES, J. R., JOHNSTON, K. P., J. Phys. Chem., Vol. 97, **1993**, 707

[11] KAZARIAN, S. G., GUPTA, R. B., CLARKE, M. J., JOHNSTON, K. P., POLIAKOV, M., J. Am. Chem. Soc., Vol. 115, **1993**, 11099

[12] MCHUGH, M. A., KRUKONIS, V. J., <u>Supercritical Fluid Extraction: Principles and Practice</u>, Butterworths, Boston, **1994**

[13] HOEFLING, T. A., BEITLE, R. R., ENICK, R. M., BECKMAN, E. J., Fluid Phase Equilibria, Vol. 83, **1993**, 203

[14] SARBU, T., STYRANEC, T. J., BECKMAN, E. J., I&EC Res., Vol. 39, **2000**, 4678

[15] GUPTA, R. B., PANAYIOTOU, C. G., SANCHEZ, I. C., JOHNSTON, K. P., AIChE J., Vol. 38, **1992**, 1243

[16] GUPTA, R. B., BRINKLEY, R. L., AIChE J., Vol. 44, **1998** 207

[17] PANAYIOTOU, C., SANCHEZ, I. C., J. Phys. Chem., Vol. 95, **1991**, 10090

[18] JENTSCHURA, U., LIPPERT, E., Ber. Bunsenges. Phys. Chem., Vol. 75, **1971**, 782

[19] MIYAMOTO, S., NAKAMURA, S., IWAI, Y., ARAI, Y., J. Chem. Eng. Data, **44, 1999**, 48

[20] WINKLER, A., HESS, P., J. Am. Chem. Soc., Vol. 116, **1994**, 9233

[21] COOLIDGE, A., J. Am. Chem. Soc., Vol. 50, **1928**, 2166

[22] MIKHAILOVA, O. K., SOLOMENTSEVA, T. V., MARKUZIN, N. P., Deposited Doc.**, 1981**, 9

[23] SCHULTZ, C. P., EYSEL, H. H., MANTSCH, H. H., JACKSON, M., J. Phys. Chem., Vol. 100, **1996**, 6845

[24] BELL, P., THOTE, A. J., PARK, Y., GUPTA, R. B., AND ROBERTS, C. B., I&EC Res. (submitted), **2003**

[25] MERIDITH, C. J., JOHNSTON, K. P., SEMINARIO, J. M., KAZARIAN, S. G., ECKERT, C. A., J. Phys. Chem., Vol. 100, **1996**, 10837

[26] KAZARIAN, S. G., VINCENT, M. F., BRIGHT, F. V., LIOTTA, C. L., ECKERT, C. A., J. Am. Chem. Soc., Vol. 118, **1996**, 1729

[27] REILLY, J. T., BOKIS, C. P., DONOHUE, M. D., Int. J. Thermophys., Vol. 16, 1995, 599

[28] NELSON, M., BORKMAN, R., J. Phys. Chem. A, Vol. 102, 1998, 7860

[29] FINK, R., HANCU, D., VALENTINE, R., BECKMAN, E. J., J. Phys. Chem. B, Vol. 103, 1999, 6444

[30] RINDFLEISCH, F., DINOIA, T., MCHUGH, M. J., J. Phys. Chem., Vol. 100, 1996, 15581

[31] RAVEENDRAN, P., WALLEN, S., J. Am. Chem. Soc., Vol. 124, 2002, 7274

[32] CAI, B., LI, J., Analytica Chimica Acta, Vol. 399, **1999**, 249

[33] SCHUURMANN, G., COSSI, M., BARONE, V., TOMASI, J., J. Phys. Chem. A, Vol. 102, **1998**, 6706