Supercritical Carbon Dioxide: Behavior of π* and β Solvatochromic Indicators in Media of Different Densities

Michael E. Sigman, Susan M. Lindley, and John E. Leffler*

Contribution from the Department of Chemistry, Florida State University, Tallahassee, Florida 32306. Received October 9, 1984

Abstract: The π^*_i dipolarity–polarizability values for ten solvatochromic indicators have been measured in supercritical carbon dioxide. They are negative and decrease smoothly toward the value for vacuum[3] as the density of the supercritical CO_2 is decreased. Values for liquid CO_2 are close to those for supercritical CO_2 at the same density. The difference between the highest and lowest π^*_i values for the solvatochromic indicators is considerably greater than that reported[1,2] for ordinary solvents. This suggests that specific effects, not encompassed by the π^* parameter, will be relatively more important in CO_2. The H-bonding basicity parameters β for supercritical CO_2, liquid CO_2, and vacuum[3] are all near zero or very slightly negative and do not show a significant variation with the density.

The Kamlet–Taft π^* parameters[1,2] were designed to represent the dipolarity and polarizability of the solvent. Individual π^*_i values[1,2] are obtained from the shifts of the electronic absorption maxima of a set of solvatochromic indicators. These values were found to differ from one indicator to another, because of specific effects peculiar to the individual indicators and not relevant to the dipolarity/polarizability mechanism for the interaction of solute and solvent. The irrelevant contributions were largely removed by defining π^* as a mean value after abandoning the lowest and highest π^*_i, a procedure that seems reasonable because the dispersion of the π^*_i in the solvents studied was small compared to the difference between solvents. The π^* values determined in this way for common liquid solvents fell in a range from about 0.0 for alkanes to +1.0 for the most polar solvents. the π^* values for vacuum, from π^*_i indicators in the vapor phase at low pressure, were negative and near -1.0.[3,4]

Results and Discussion

π^*_i **Parameters.** As can be seen from Table I, each π^*_i decreases smoothly from a value near zero at high densities of the supercritical CO_2 to more negative values as the density approaches zero. Plots of the individual π^*_i values against density do not intersect one another and closely resemble Figure 1. The π^* parameter plotted in that figure is the mean from all ten indicators (**1–10**), including the extreme π^*_i values. Figure 1 includes the value obtained by Essfar et al.[3] for vacuum, i.e., for the vapor phase of the indicators at low pressure, as well as a point for liquid CO_2.

The dispersion of the individual π^*_i values about their means is considerably greater than that reported for ordinary solvents, not only in supercritical CO_2 but also in liquid CO_2 and in vacuum. For example, in supercritical CO_2 at a density of 0.68 g/mL, the π^*_i cover a range of 0.29 units, which would have been reduced only to 0.16 if the highest and lowest values had been eliminated. Since this is about 4 times the dispersion found for ordinary solvents,[2] specific effects of the solute structures are clearly more important here, at least for these typical π^* indicators. If specific effects of solute structure prove to be more important generally in CO_2, the usefulness of the π^* parameter in this solvent will be limited.

The reason for the greater dispersion of π^*_i values of the indicators in CO_2 is not clear. The sequence of values is the same at different densities, with very few inversions. There is no apparent tendency for the dispersion to become less at the higher

Table I. Values of π^* for Supercritical CO_2, Liquid CO_2, and Vacuum[h] as a Function of Density

indicator[a]	density[b]	$10^{-3}\nu$,[c] cm^{-1}	π^*_i[d]	indicator[a]	density[b]	$10^{-3}\nu$,[c] cm^{-1}	π^*_i[d]
1	0.86	34.45	-0.11	**6**	0.86	27.53	-0.01
	0.80[e]	34.62	-0.19		0.79[e]	27.52	0.00
	0.68	34.66	-0.20		0.67	27.79	-0.09
	0.46	35.34	-0.48		0.46	28.58	-0.33
	0.0[h]	36.90	-1.15		0.0[h]	30.39[f]	-0.90
2	0.86	25.73	-0.07	**7**	0.86	30.81	-0.21
	0.82[e]	25.75	-0.08		0.82[e]	30.73	-0.16
	0.68	25.98	-0.19		0.68	31.03	-0.31
	0.45	25.37	-0.36		0.43	31.50	-0.54
3	0.85	30.67	-0.29	**8**	0.86	31.39	-0.09
	0.82[e]	30.52	-0.22		0.81[e]	31.41	-0.13
	0.68	30.87	-0.38		0.68	31.68	-0.19
	0.46	31.44	-0.63		0.45	32.44	-0.43
4	0.86	37.96	-0.17		0.0[h]	34.48	-1.08
	0.80[e]	38.20	-0.28	**9**	0.86	18.43	-0.25
	0.68	38.06	-0.23		0.80[e]	18.49	-0.27
	0.46	38.65	-0.49		0.68	18.74	-0.36
5	0.86	23.84	-0.01	**10**	0.86	35.35	-0.17
	0.81[e]	23.77	+0.04		0.79[e]	35.34	-0.17
	0.68	24.07	-0.15		0.68	35.58	-0.28
	0.46	24.46	-0.39		0.46	36.05	-0.50
					0.0[h]	37.31	-1.08

[a] The solvatochromic indicators are (**1**) 4-nitroanisole, (**2**) *N,N*-diethyl-3-nitroaniline, (**3**) 4-methoxy-β-nitrostyrene, (**4**) 1-ethyl-4-nitrobenzene, (**5**) *N*-methyl-2-nitro-*p*-toluidine, (**6**) *N,N*-diethyl-4-nitroaniline, (**7**) 4-(dimethylamino)benzophenone, (**8**) 4-nitroaniline, (**9**) Brooker's merocyanine,[2] and (**10**) 4-nitrophenol. [b] Densities were interpolated from the tables in ref 4. [c] Each density and frequency in this table is the mean value from experiments at several densities close to the tabulated one. The range in the densities for which the entry is the mean is equivalent to a range of about 0.03×10^3 cm^{-1} or less in frequency. The temperatures ranged from 36 to 42 °C for supercritical carbon dioxide and from 26.5 to 28 °C for liquid carbon dioxide. The frequencies from experiments at the extremes of these temperature ranges, after correction for any differences in density, were found to differ very little. The π^*_i from experiments at the upper end of the 36–42 °C temperature range were on the average only 0.02 units more negative than those for the lower end. The gas-phase results[3] are also reported to be insensitive to temperature. [d] Calculated from $\pi^*_i = (\nu_{obsd} - \nu_0)/(-s)$ by using ν_0 and s values from ref 2. [e] In liquid CO_2 at temperatures between 26.5 and 28 °C. [f] Center of a doublet. [g] Calculated from $\pi^*_i = (\nu_{obsd} - \nu_0)/(-s)$ by using ν_0 and s values from ref 3. [h] For the low-pressure gas phase of the indicator, from ref 3.

densities, i.e., as densities comparable to those of ordinary solvents are approached. There is no apparent correlation of the dispersion with the s value of the indicator. The absorption curves of the indicators with extreme π^*_i values are not very different in shape from those in cyclohexane and have about the same oscillator strength. We are left only with the observation that the CO_2 molecule is unique in its small size relative to the size of the solute

(1) Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *98*, 6027.

(2) Kamlet, M. J.; Hall, T. N.; Boykin, J.; Taft, R. W. *J. Org. Chem.* **1979**, *44*, 2599.

(3) Essfar, M.; Guiheneuf, G.; Abboud, J.-L. M. *J. Am. Chem. Soc.* **1982**, *104*, 6786.

(4) Angus, S., Armstrong, B., de Reuck, K. M., Eds. "International Thermodynamic Tables of the Fluid State: Carbon Dioxide"; Pergamon Press: New York, 1976; Vol. 3.

Table II.[d] Observed Frequencies and β_1 and β_2 Values for Supercritical CO_2,[a] Liquid CO_2,[b] and Gas Phase[c]

density	ν_8	ν_6	β_1	ν_{10}	ν_1	β_2	β_{av}
0.86	31.39	27.53	−0.09	35.35	34.45	−0.07	−0.08
0.80[b]	31.41	27.52	−0.10	35.34	34.62	0.00	−0.05
0.68	31.68	27.79	−0.10	35.58	34.66	−0.08	−0.09
0.46	32.44	28.58	−0.08	36.05	35.34	−0.02	−0.05
0.00[c]	34.48	30.39	−0.14	37.31	36.90	+0.04	−0.10

[a] Unless otherwise noted, all entries are for supercritical CO_2 at 36–42 °C. [b] Liquid CO_2 at 26.5–28.0 °C. [c] Gas-phase, dilute vapor of the indicator, ref 3. [d] Indicator numbers are the same as in Table I.
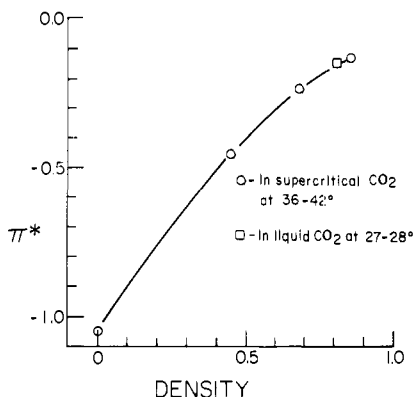
Figure 1. Dependence of CO_2 π^* parameters on density.

molecules. It may be significant that the three indicators with the most negative π^*_i values are also the largest molecules and the molecules with the most extended conjugation, p-methoxy-β-nitrostyrene, Brooker's merocyanine, and p-(dimethylamino)-benzophenone.

Parameters β_1 and β_2. The various Kamlet–Taft β parameters were designed to separate, at least approximately, the H-bond accepting property of the solvent from other properties such as the general dipolarity–polarizability represented by π^*.[5-7] Values for β_1 and β_2 for liquid and supercritical CO_2, at various densities and for vacuum,[3] are given in Table II. The parameter β_1 is based on the solvent shifts of the absorptions of 4-nitroaniline (**8**) and N,N-diethyl-4-nitroaniline (**6**). In the absence of H-bonding, the frequencies in a series of solvents are linearly related. The presence of H-bonding as an additional interaction mechanism[8-10] causes deviation from the simple linear free energy relationship, and the extent of the deviation is used to define β_1. The parameter β_2 is defined similarly by using the absorption maxima of 4-nitrophenol (**10**) and 4-nitroanisole (**1**).[5,6]

Although the β values for the CO_2 media and for vacuum seem to be consistently negative,[11] they are all about the same regardless

(5) Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 377.

(6) Taft, R. W.; Gramstad, T.; Kamlet, M. J. *J. Org. Chem.* **1982**, *47*, 4557.

(7) Nguyen, M. T.; Ha, T.-K. *J. Am. Chem. Soc.* **1984**, *106*, 599.

(8) Leffler, J. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions"; Wiley: New York, 1963.

(9) Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.

(10) Lindley, S. M.; Flowers, G. C.; Leffler, J. E. *J. Org. Chem.*, in press.

(11) It is worth noting that a negative value of β for the gas phase is not excluded in principle. If separation of the variables is incomplete, so that β values represent a mix of more than one intrinsic property, then an absolute scale would assign zero to the vacuum and solvents such as hexane would have small positive β values.

of density, and the differences among them are not experimentally significant. The range from zero on the β scale to the most negative value in the table is about the same as the standard deviations of points for non-hydrogen bonding solvents from the linear free energy relationships used to define β_1 and β_2. Since all the values are essentially zero, β, unlike π^*, does not show any correlation with the density of the CO_2.

It is to be expected that β for CO_2 should be small, if not zero, on several grounds. Electronegative substituents lower β. For example, β for acetone is 0.48, compared to 0.14 for trichloroacetone.[9] Actually, the substituted-carbonyl group model is not a good one for CO_2, since the nominally unshared electrons on oxygen are in an orbital that overlaps with the π orbitals of the bond between carbon and the other oxygen. An ab initio SCF calculation for complexes of CO_2 and one water molecule shows a lower energy for structures in which the closest approach of the two molecules is between the carbon and the oxygen of the H_2O rather than between an oxygen of the CO_2 and hydrogen.[7]

Experimental Section

The UV and visible absorption spectra of the indicators were measured on a Model 14 Cary recording spectrophotometer. The high-pressure optical cell, constructed of magnetic stainless steel, had a 4-cm path length and sapphire windows 10 mm in diameter and 8 mm thick, resting on Teflon gaskets. The cell was connected to a valve block assembly and Bourdon gage by coned fittings. The CO_2 was pumped as a liquid with a Milton-Roy reciprocating minipump. It was necessary to cool the head of the pump with ice.

The indicators were the same as those used in a previous publication.[10] The CO_2 was grade 4, supplied by Airco Industrial Gas Corp. and reported to have a minimum purity of 99.99% and the following maximum impurities (in parts per million): Ar 5, He 4, H_2 4, O_2 50, N_2O 4, CO 5, H_2O 10, and total hydrocarbons 10.

General Procedure. A known amount of the indicator was dissolved in freshly distilled dry ether or acetone, an amount sufficient to give a concentration of from 10^{-6} to 10^{-4} M pipeted into the cell and the solvent blown off in a stream of dry nitrogen. The cell was connected to the valve block and gage and the pump flushed with CO_2. The cell was then evacuated to a pressure of 0.250 torr and filled with CO_2 to a pressure at room temperature that would result in the desired pressure when the temperature was raised. The apparatus was then covered with a rubber glove, heated in a constant temperature bath to 56.7 °C, and transferred to the spectrometer. The temperature was measured by a thermocouple-operated linear temperature probe. The pressure and the temperature were noted at the time that the spectrum was run. For runs at lower temperatures and/or lower pressures, the system was allowed to cool or was partly vented.