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Measurement and Linear Correlation of the Solvent Polarity Parameters of Supercritical Carbon Dioxide and Its Cosolvent Systems

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Synopsis. The solvent polarity parameters, including the dipolarity/polarizability π^* parameter, hydrogen-bond donor acidity α parameter, and hydrogen-bond acceptor basicity β parameter, were measured for supercritical carbon dioxide and cosolvent systems with ethanol, 2,2,2-trifluoroethanol, and dimethyl sulfoxide at pressures of 9.81—27.95 MPa and 318 K. A linear correlation was examined for relating those parameters with each other.

Supercritical carbon dioxide (SC-CO_2) and SC-CO_2-cosolvent systems have been attracting much attention concerning their solvent strength in controlling chemical reactions and extraction processes.[1—5] The solvent strength of SC-CO_2 can be widely changed at ambient temperatures by not only adjusting the operating pressures, but by also using proper cosolvents. Recently, the solvent strength was measured based on the solvatochromic change of a certain chromophore in a given solvent for SC-CO_2 and other supercritical fluids.[6—9] This method may distinguish different solute/solvent interactions by using different solvatochromic indicators.[10,11]

The linear combination of a few parameters that are determined by the solvatochromic method is known to be useful for describing solvent effects:[12]

$$A = A_o + s\pi^* + a\alpha + b\beta, \qquad (1)$$

where A is a solvent-dependent physicochemical property in a given solvent and A_o a quantity of property A in an inert solvent; π^* is the dipolarity/polarizability parameter, α the hydrogen-bond donor (HBD) acidity parameter, and β the hydrogen-bond acceptor (HBA) basicity parameter of the solvent considered. Coefficients s, a, and b describe the sensitivity to property A. Of these parameters, α and β are due to specific solute/solvent interactions; they can be well determined by using proper solvatochromic indicators. In contrast, π^* is due to non-specific interactions; the measured values often include the specific interactions corresponding to α- and β-parameters. This is significant for SC-CO_2 at low densities, i.e., in the near-critical region.[13] At high pressures, the π^*-value can be estimated from a relationship with the $E_T(30)$-parameter that was previously obtained for many organic solvents.[14—16]

One objective of the present work was to determine the values of the π^*-, α-, and β-parameters for SC-CO_2 and cosolvent systems with ethanol, 2,2,2-trifluoroethanol, and dimethyl sulfoxide at pressures of 9.81—27.95 MPa and at a constant temperature of 318 K. The other objective was to examine the following multiparameter correlation:

$$\pi^{*\prime} = \pi^* + (a/s)\alpha + (b/s)\beta. \qquad (2)$$

Here, $\pi^{*\prime}$ is an apparent π^*-parameter which includes the contribution of the HBD and HBA interactions. Using the $\pi^{*\prime}$-, α-, and β-values that can be experimentally determined, this correlation was used to estimate the value of the π^*-parameter in the near-critical region.

Experimental

The solvatochromic indicators used in the present work are shown in Table 1. The spectroscopic measurements were performed with the same flow-type apparatus as previously described in detail.[17] An indicator was introduced into a high-pressure cell, and trapped there by stopping the flow. The absorption spectrum of this indicator in SC-CO_2or SC-CO_2 with a cosolvent was recorded. The spectrum of SC-CO_2 or SC-CO_2 with the cosolvent was measured in advance in order to provide a background spectrum. The cosolvents examined were ethanol, 2,2,2-trifluoroethanol (TFE) and dimethyl sulfoxide (DMSO), supplied by Tokyo Kasei Co., Inc. The concentration of each cosolvent in SC-CO_2 was fixed at 8.9 mol%.

Results

The values of the α-, β-, and $\pi^{*\prime}$-parameters of SC-CO_2 are nearly zero at pressures above about 10 MPa. The addition of the cosolvents was found to significantly influence these parameters. The measured values are collected in Table 2.

Table 1. Solvatochromic Indicators Used for the Determination of $\pi^{*\prime}$-, α-, and β-Values

Parameter	Indicator[a]	Note
$\pi^{*\prime}$	Cyclohexanone	Solvent strength including HBD acidity and HBA basicity (Ref. 19)
α	1-Ethyl-4-methoxycarbonyl pyridinium iodide 4-Nitroanisole	HBD acidity (Ref. 12)
β	4-Nitrophenol 4-Nitroanisole	HBA basicity (Ref. 18)

a) Cyclohexanone from Merck, the others from Tokyo Kasei Co., Inc.

Table 2. Measured Values of α-, β-, and π*′-Parameters and Estimated Values [a] of π*-Parameter for SC-CO_2–Cosolvent Systems at 318 K

Pressure	Cosolvent[b]									
	TFE			DMSO			Ethanol			
MPa	α	$\pi^{*\prime}$	π^*	β	$\pi^{*\prime}$	π^*	α	β	$\pi^{*\prime}$	π^*
9.81	0.590	0.83	0.60	0.474	0.16	0.10	0.420	0.000	−0.032	−0.008
11.77	0.590	0.83	0.60	0.504	0.19	0.12	0.410	0.015	−0.016	0.016
14.71	—	—	—	0.518	0.21	0.12	0.513	0.036	0.198	0.033
19.12	0.595	0.90	0.60	0.520	0.21	0.13	0.532	0.079	0.343	0.119
25.00	0.617	0.90	0.60	0.521	0.22	0.13	0.567	0.405	0.396	0.150
27.95	0.675	0.90	0.62	—	—	—	0.680	0.430	0.604	0.261

a) From $E_T(30)$-values (see text). b) The concentration of each cosolvent is 8.9 mol%.

SC-CO_2–TFE System. TFE increases both the α- and π*′-values, which increase slightly with increasing pressure, ranging over 0.59—0.68 and 0.83—0.90, respectively. This system is free from the contribution of the HBA basicity, since the β-value of TFE as well as SC-CO_2 is negligibly small.[13,18)]

SC-CO_2–DMSO System. Both the β- and π*′-values are increased by the DMSO. These depend weakly on the pressure, being in the range of 0.47—0.52 and 0.16—0.22, respectively. The latter is smaller compared to the SC-CO_2–TFE system. The SC-CO_2–DMSO system does not indicate the HBD acidity, since the α-value is negligibly small for DMSO as well.[13,18)]

SC-CO_2–Ethanol System. Ethanol indicates both HBD acidity and HBA basicity;[18)] it therefore affects the three parameters, increasing their values. It is noteworthy that they are more strongly dependent on the pressure, compared with the abovementioned two systems; in particular, the β- and π*′-values change widely over 0—0.43 and 0—0.60, respectively. This shows that the solvent properties of this cosolvent system may be widely and precisely controlled by only adjusting the pressure.

Discussion

Multiparameter Correlation. As described above, it is desirable to know the values of α, β, and π* (rather than π*′) for considering the various solvent effects. However, it is difficult to experimentally determine the π*-value for a wide range of operating conditions. The estimation of the π*-value is possible under a limited condition, i.e., at high pressures. Under this limited condition we examined the relationship between the four parameters (α, β, π*′, and π*), the former three which can be measured and the latter which can be estimated using a multiparameter correlation of Eq. 2. We can determine the values of the three coefficients of *a*, *b*, and *s* in Eq. 2 from the results of SC-CO_2–TFE and SC-CO_2–DMSO systems, and can apply this correlation to SC-CO_2–ethanol and pure SC-CO_2 systems.

Of the three coefficients, the value of *s* is found in the literature.[19)] The values of *a* and *b* were obtained from the results of SC-CO_2–TFE and SC-CO_2–DMSO systems, respectively, provided that β is 0 in the former and that α is 0 in the latter. The π*-value can be estimated through $E_T(30)$-value by the method given in Appendix. From a set of the measured α- (or β-) and π*′-values and the estimated π*-value at a given pressure (see Table 2), the coefficients *a* (or *b*) was calculated. The mean value determined is −8.22 (±0.9) for *a* and −2.91 (±0.33) for *b*, giving the following correlation:

$$\pi^{*\prime} = \pi^* + (-8.22/-18.90)\alpha + (-2.91/-18.90)\beta. \quad (3)$$

Figure 1 shows the relationship between the π*-value obtained from the method using the $E_T(30)$-value and the π*-value calculated from the multiparameter correlation (MPC). We obtained a good correlation between the π*(MPC)- and π*($E_T(30)$)-values, and an estimation of the π*-value by the MPC may be reasonable. At low pressures for the SC-CO_2–ethanol sys-

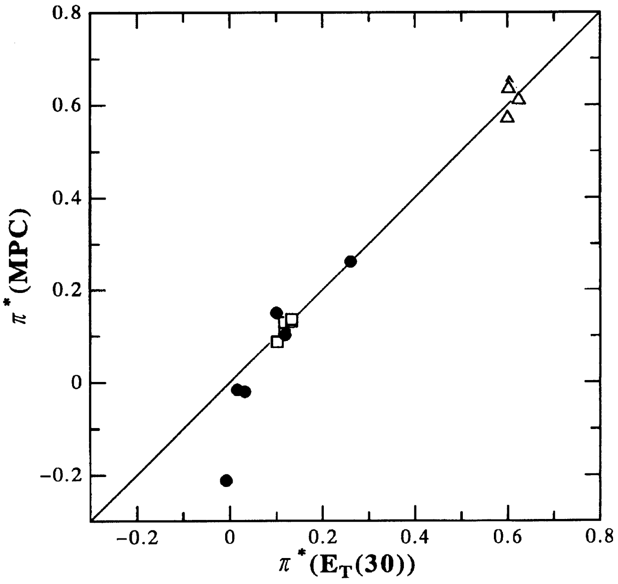

Fig. 1. Plot of π*(MPC) against π*($E_T(30)$) for SC-CO_2–cosolvent systems with DMSO(□), TFE(△), and ethanol(●).

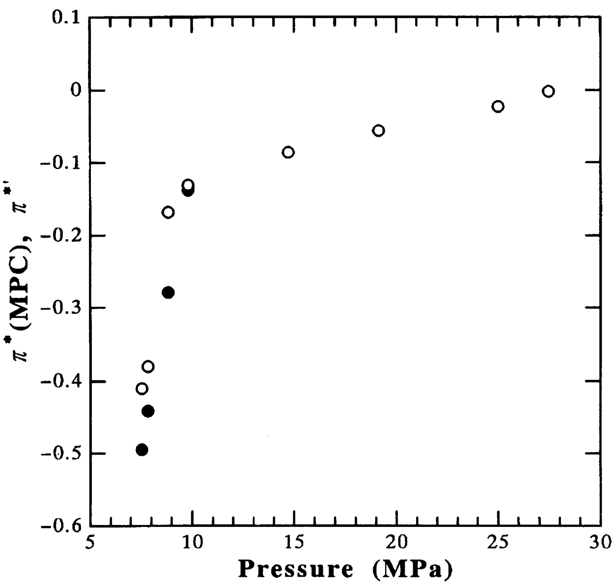

Fig. 2. Comparison of π^*(MPC) (●) and $\pi^{*\prime}$(○) values for pure SC-CO_2 at pressures from the near-critical region up to 30 MPa. Above 9.8 MPa, π^*(MPC)= $\pi^{*\prime}$ as α-value=0.

tem, however, the π^*(MPC)-value is smaller than the $\pi^*(E_T(30))$-value. This is relevant to a fact that the π^*(MPC)-value at 9.81 MPa is almost the same between pure SC-CO_2 and SC-CO_2–ethanol systems.[13] This suggests a selective aggregation of carbon dioxide molecules around indicator molecules at low pressures.

It was recently proved that the α-value of pure SC-CO_2 in the near-critical region is comparable to that for acetonitrile (α=0.23).[13] Thus, the measured π^*-value at low desities includes the specific interaction corresponding to the α-parameter. Using the $\pi^{*\prime}$-, α-, and β (β for SC-CO_2=0,[7,13])-values for SC-CO_2 that can be experimentally be determined, Eq. 3 was used to estimate the values of the π^*-parameter free from the contribution of the HBD interacton at low pressures. Figure 2 shows the pressure dependence of the measured $\pi^{*\prime}$-value and π^*-value estimated from the MPC at pressures of 7.55—27.45 MPa. The π^*-value becomes smaller compared to the measured $\pi^{*\prime}$-value as the pressure decreases. This difference is significant in the near-critical region due to the contribution of the HBD interaction.

Appendix

Estimation of π^*-Value through $E_T(30)$-Value. Kosower's polarity parameter (Z) is expressed as the longest-wavelength intermolecular charge-transfer (CT) transition of l-ethyl-4-methoxycarbonylpyridinium iodide in appropriate solvents as[14)]

$$Z = 2.859 \times 10^{-3}\tilde{\nu}/\mathrm{cm}^{-1}, \qquad \text{(A1)}$$

where $\tilde{\nu}$ is the longest-wavelength CT band. Furthermore, there is a satisfactory linear correlation between the Z- and $E_T(30)$-values as (n=54 solvents; correlation coefficient, r= 0.989)[15)]

$$Z/\left(\mathrm{kcal\,mol^{-1}}\right) = 1.337E_T(30)/\left(\mathrm{kcal\,mol^{-1}}\right) + 9.80. \quad \text{(A2)}$$

The multiparameter correlation equation between $E_T(30)$- and Kamlet–Taft's solvatochromic-parameters is obtained as (n=44 solvents; r=0.987)[16)]

$$E_T(30)/\left(\mathrm{kcal\,mol^{-1}}\right) = 14.6\,(\pi^* - 0.23\delta) + 16.5\alpha + 30.31, \qquad \text{(A3)}$$

where δ, a polarizability correction term, is 0.0 for nonchlorinated aliphatic solvents. From Eq. A1 to Eq. A3, π^*-value can be estimated.

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