Solvent Polarity Parameters of Supercritical Carbon Dioxide as Measured by Infrared Spectroscopy

Yutaka IKUSHIMA,* Norio SAITO, Masahiko ARAI,† and Kunio ARAI††

Government Industrial Research Institute, Tohoku,
Nigatake 4-chome, Miyagino-ku, Sendai 983
† Institute for Chemical Reaction Science, Tohoku University,
Katahira, Aoba-ku, Sendai 980
†† Department of Biochemistry and Chemical Engineering, Tohoku University,
Aramaki, Aoba-ku, Sendai 980
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The solvent polarity parameters of supercritical carbon dioxide were determined as a function of the temperature and pressure within the ranges 318—353 K and 5.85—28.5 MPa. An infrared (IR) spectroscopic technique has been employed to determine the values of π^* dipolarity/polarizability and the Lewis basicity parameter B_{MeOD} by measuring the transitions in the IR absorption wavelength of functional groups (such as C=O and O–H···BA, where BA is a hydrogen-bond acceptor), in supercritical carbon dioxide. Ultraviolet/visible (UV/vis) spectroscopy was used to determine the value of the Kamlet–Taft's solvatochromic acidity partameter, α. The B_{MeOD}-value was enhanced with density, but was very small at the temperatures and pressures examined, almost the same as that for hexane. The α-value tended to be dependent on density at lower pressures, but was remarkably smaller compared with those for alcohols. The π^*-value significantly increased with an increase in the density, becoming more negative at higher temperatures above 10 MPa. Furthermore, the $E_T(30)$-value was estimated by using the determined π^*-value. A reliable $E_T(30)$-value for supercritical carbon dioxide has been obtained.

Supercritical carbon dioxide and some other supercritical fluids have recently been attracting much attention concerning their interesting properties for extraction solvents and reaction media.[1-5] When we use cabon dioxide at supercritical conditions, the desired extractions and chemical reactions are expected to be attained at around the ambient temperatures by adjusting the pressures and/or using proper entrainers.[6] In particular, in the near-critical region, the solvent stength varies widely with both the pressure and temperature; this sensitivity in solvent strength could be applied to controling the chemical reaction processes, as well as that of extraction. It is, therefore, be very important to know the solvent strength of supercritical fluids as a function of the pressure, temperature, and/or other variables of state.

For the above-mentioned use of supercritical carbon dioxide to be well effected, its solvent strength should be quantitatively evaluated. The solvent strength has so far been represented by the dipole monent, dielectric constant, refractive index, and solubility parameter.[7-9] When one is interested in the solvent strength at molecular levels, however, these are not adequate, since in these evaluations solvents are regarded as being nonstructured types; solute/solvent interactions, such as hydrogen-bond donor (HBD)/acceptor (HBA) interactions, are not considered, even though they often play dominant roles in many chemical processes.

The variation of the absorption wavelength of a chromophore in IR, NMR, ESR, or UV/vis spectroscopy represents the intermolecular solute–solvent interaction forces,[10-14] and can be used as a good measure of the solvent strength. A few spectroscopic studies have been applied to fluids under supercritical conditions. For example, Johnston et al. measured the solvent strength with the transition energy of a phenol blue indicator in a given solvent by the UV/vis method.[15] Leffler et al. estimated the π^* dipolarity/polarizability of supercritical carbon dioxide using several indicators by the UV/vis method as well.[16] For supercritical carbon dioxide, as well as others, however, the spectroscopic solvent strength is not widely available, since either no convenient polarity parameters could be determined or the precision in measurements and evaluations of its solvent strength was low; the spectroscopic approach is therefore still very much limited at present.

The present work has been aimed at determining the HBD acidity parameter, α; the HBA basicity parameter, B_{MeOD}; and the dipolarity/polarizability parameter, π^*, of carbon dioxide within the range 5.85—28.5 MPa and 318—353 K. In order to consider two or more aspects of solvation, the following multiparameter approach has been presented and shown to be useful:[17]

$$A = A_o + s\pi^* + a\alpha + bB_{MeOD}, \quad (1)$$

where A is a solvent-dependent physicochemical property in a given solvent; A_o is a quantity corresponding to this property in an inert solvent; and the coefficients s, a, b describe the sensitivity to property A. The present study has used FTIR spectroscopy methods to determine the values of B_{MeOD} and π^* as well as UV/vis spectroscopy for the α-value. According to the literature the FTIR method has been only slightly used so far,[18] while many studies have used UV/vis methods.[19-23] In addition, we have attempted to estimate the $E_T(30)$ parameter by using the determined π^*-values. The $E_T(30)$ parameter is one of the polarity parameters

used most widely and possesses great advantages.[24-28] Little is presently known about the $E_T(30)$-values for supercritical fluids.

Experimental

The solvatochromic indicator molecules chosen for the measurements of the π^*-values were methyl acetate (Tokyo Kasei Co., Inc.), cyclohexanone (Merck), acetone (Merck), and *N*,*N*-dimethylformamide (Tokyo Kasei Co., Inc.). As indicators, methanol-*d* CH_3OD (Merck) for Lewis basicity B_{MeOD} and 1-ethyl-4-methoxycarbonylpyridinium iodide (Tokyo Kasei Co., Inc.) and 4-nitroanisole (Tokyo Kasei Co., Inc.) for Lewis acidity α measurements were used. Commercial-grade carbon dioxide (above 99.999%) was used. All chemicals were used without further purification.

Details concerning the experimental apparatus used have been described elsewhere.[6-c] Liquid carbon dioxide was charged into a JASCO Model 880-PU syringe pump through a 1/16-in. tube (1 in.=2.54 cm) and a check valve, and then compressed to the desired pressures. Pressure control was achieved by a back-pressure regulator (Model 880-81, JASCO), which can perform a high-speed flow switching and also control the outlet pressure, irrespective of the mass flow rate of SCF. Then, a 0.2-μL of an indicator was injected using an injection valve (Pheodyne Inc.) which contained a 10-μL sample loop; this made it easy to introduce an indicator into the cell.

The infrared spectrometer used in this study was a JASCO Model FTIR-7300 instrument (Japan Spectroscopic Co., Ltd.) equipped with a narrow-bandwidth mercury cadmium telluride (MCT) detector cooled by liquid nitrogen. The low-frequency cut-off was approximately 800 cm^{-1}. Spectra were acquired at 1 cm^{-1} nominal resolution and interferrograms were accumulated at a rate of 1 scan per 1.2 s. Details concerning the high-pressure IR flow cell used (nominal volume of 16-μL, optical path length of 5 mm, and cross section area of 3 mm^2 were described previously.[6-c] The IR flow cell which was placed in a JASCO Model HC-12 cell heating unit was maintained at temperatures of 318—353±0.5 K. The UV/vis absorption spectra were measured by a Model JASCO MULTI-340 recording spectrometer. The high-pressure cell used for UV/Vis was constructed from stainless steel with quartz windows 1 mm i.d., having a 1-cm path length and a 8 μL nominal total volume. The flow cell was wrapped with heating tape and maintained at a temperature of 318±1 K.

An indicator was passed into the high-pressure flow cell, trapped there by stopping the flow, and the absorption spectrum of the indicator in supercritical carbon dioxide was recorded. Only the spectrum of supercritical carbon dioxide was measured in advance in order to provide a background spectrum. No data manipulation, such as spectral subtraction or base line corrections, was used.

Results and Discussion

Density-Dependence of the HBD Acidity, α. We examined Kamlet–Taft α-value[29] for supercritical carbon dioxide by using the wavenumber (ν_{max}) of the maximum absorbance of 4-nitroanisole in the UV/vis spectrum through the following relationship:

$$Z = 79.6(1 + S) \quad (2)$$

and

$$Z = 2.859 \times 10^{-3}\nu, \quad (3)$$

where S is Brownstein's polarity parameter,[30] Z is Kosower's Z-value,[31] and ν is the charge-transfer band in the UV/vis spectrum of 1-ethyl-4-methoxycarbonylpyridinium iodide. These relations were obtained for a number of solvents and will be applied to supercritical carbon dioxide. This S-value from Eq. 2 is here defined as S_{obs}.

Plots of the S-values for non-hydrogen-bonding solvents against the corresponding ν_{max}-values yielded linear relationship, as expressed by[17]

$$S = -0.0846\nu_{max} + 2.569,$$
$$r = 0.9925, \ SD = 0.0052, \text{ and } n = 8. \quad (4)$$

Here, r is the correlation coefficient, SD the standard deviation, and n the number of solvents examined. The S-value determined using Eq. 4 is here expressed as S_{cal}, and is evaluated to be

$$\Delta\Delta S = S_{obs} - S_{cal}. \quad (5)$$

The $\Delta\Delta S$-values represent the deviations of the HBD solvents from the correlation line for non-hydrogen-bonding solvents. Furthermore, the solvatochromic displacement ($\Delta\Delta\nu$) attributable to enhanced hydrogen bonding by HBD solvents to the strong HBA Dimroth' betaine dye[32] is related to $\Delta\Delta S$ as follows:

$$\Delta\Delta S = 0.0403\cdot\Delta\Delta\nu + 0.002,$$
$$r = 0.9962, \ SD = 0.0036, \text{ and } n = 8. \quad (6)$$

Using $\Delta\Delta S$, Kamlet and Taft determined the α-value using the following equation:

$$\alpha = (\Delta\Delta S - 0.002)/(0.0403\cdot 6.24). \quad (7)$$

Figure 1 shows the dependence of the α-value for supercritical carbon dioxide on the density at 318 K. The α-value ranges from the negative values at densities above 0.44 g cm^{-3} to 0.195 at 0.25 g cm^{-3}. The negative α-values at higher densities are assumed to be zero by taking into account errors in the present calculations. The α-value of 0.19 for supercritical carbon dioxide at 0.25 g cm^{-3} is larger than that for acetone (α=0.08),[29] and is comparable to that for acetonitrile (α=0.23).[17] Although the α-values at lower densities show a certain strength of acidity, the α-values are remarkably smaller than those of formamide and alcohols.

Temperature- and Pressure-Dependence of the HBA Basicity, B_{MeOD}. The large solvent-induced shifts of the IR stretching vibrations, $\nu_{X=H}$, do not occur in HBD solvents, but do in the HBA solvents of the Lewis-base type, as shown in Eq. 8:[33,34]

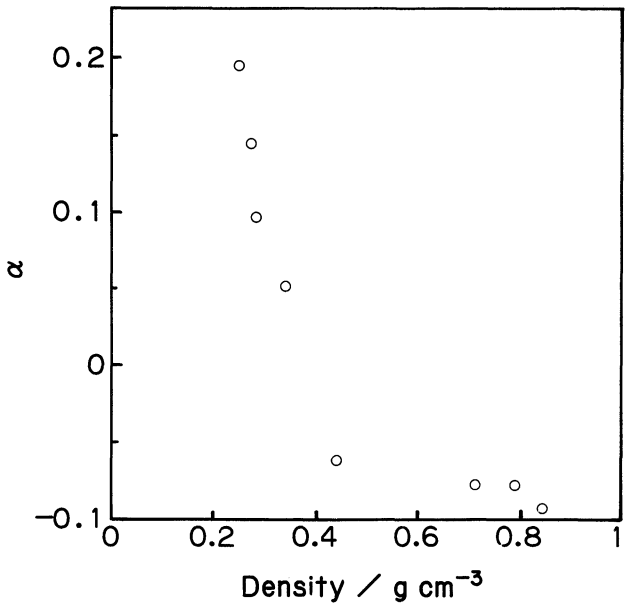

Fig. 1. Plot of α versus density of supercritical carbon dioxide at 318 K.

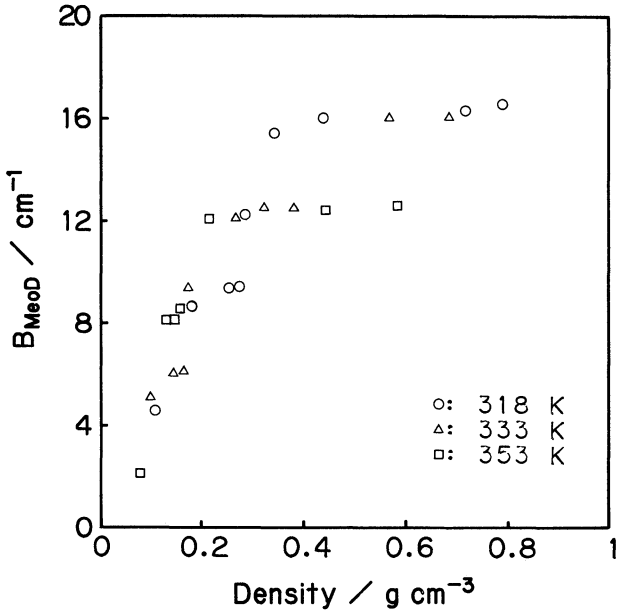

Fig. 2. Plots of B_{MeOD} versus density of supercritical carbon dioxide at (○) 318, (△) 333, and (□) 353 K.

$$R\text{-}O^{\delta\ominus}\text{-}H^{\delta\oplus} + |X\text{-}H \rightleftarrows R\text{-}O^{\delta\ominus}\text{-}H^{\delta\oplus}\cdots X\text{-}H. \quad (8)$$

Here, X=B, C, N, S, etc. In accordance with Eq. 8, the $\nu_{O\text{-}D}$ IR stretching absorption band of methanol-*d* (CH_3OD) undergoes larger bathochromic shifts in less dipolar HBA solvents, compared with those observed in dipolar non-HBA solvents.[35] Thus, a Lewis basicity parameter, B_{MeOD}, has been introduced based on measurements of the O–D IR stretching frequency of CH_3OD, as follows:[36,37]

$$B_{MeOD} = \nu^{\circ}{}_{MeOD} - \nu_{MeOD\cdots B}, \quad (9)$$

where $\nu^{\circ}{}_{MeOD}$ and $\nu_{MeOD\cdots B}$ are the O–D IR stretching frequencies of CH_3OD in the gas phase ($\nu^{\circ}{}_{MeOD}$[36]=2720 cm^{-1}) and in a given solvent, B, respectively. This Lewis basicity parameter, B_{MeOD}, can be linearly correlated well with the Kamlet–Taft parameter, β,[38] with $r>0.98$.[16,29,34] The β- and B_{MeOD}-values for supercritical carbon dioxide can bear the same linear relationship together with a number of organic solvents. Figure 2 indicates the values of B_{MeOD} for supercritical carbon dixide at 318, 333, and 353 K as a function of the density. The B_{MeOD}-value is gradually enhanced as the density increases and reaches 16 cm^{-1} in the range of higher densities above 0.4 g cm^{-3} at 318 and 333 K; the Lewis basicity of supercritical carbon dioxide is found to increase with density. In addition, the B_{MeOD}-value does not seem to show a distinct temperature dependence, except that the values at 353 K are somewhat lower than those at 318 and 333 K at higher densities. The B_{MeOD}-value of hexane is 24 cm^{-1}, the lowest among the organic solvents examined.[35] The B_{MeOD}-value of supercritical carbon dioxide is maximally 16 cm^{-1} under the above-mentioned conditions and is comparable to that of hexane; supercritical carbon dioxide can be regarded as being a non-HBA solvent. The values of β of supercritical carbon dioxide at various densities under constant temperatures of 309—315 K were determined by Leffler et al.[16] based on solvent shifts of the absorption of 4-nitroaniline and *N*,*N*-diethyl-4-nitroaniline. It was reported that since all of the values are either zero or near to zero, the Lewis basicity of supercritical carbon dioxide is negligibly small. However, the density-dependence of the Lewis basicity (as described above) could not be confirmed by the UV/vis method.

Temperature- and Pressure-Dependence of the Dipolarity/Polarizability Parameter, π^*. As shown above, the α-value of supercritical carbon dioxide is very small at densities larger than 0.3 g cm^{-3}. The B_{MeOD}-value is also small at densities lower than 0.2 g cm^{-3} and, even at higher densities, is smaller compared to that of hexane, a low HBA basic solvent.[34] In the following treatment, therefore, the contribution of the HBD acidity and HBA basicity to the solvent properties of supercritical carbon dioxide will not be taken into consideration. Strict treatment is now in progress, including those two parameters, evaluating coefficients *a* and *b* for them in Eq. 1. Eq. 1 can be thus be approximated by Eq. 10 (with $A=\nu$), reducing to

$$\nu = \nu_o + s\pi^*. \quad (10)$$

Here, ν is the frequency of a chromophore in supercritical carbon dioxide. The *s*-values for several indicators have previously been determined.[39-43] The *s*-values for

the C=O stretching frequencies of cyclohexanone, acetone, *N*,*N*-dimethylformamide, and methyl acetate chosen as indicators in the present work are −18.90±0.50, −12.15±0.38, −22.80±0.75, and −15.36±0.73, respectively. The values of ν_0 can also be quoted from the literature.[40–43] One can determine the change in the π^*-value of supercritical carbon dioxide as a function of the temperature and pressure by using Eq. 10 along with the *s*- and ν_0-values.

Figure 3 shows the dependence of the π^*-values on the density of supercritical carbon dioxide at temperatures of 318, 333, and 353 K. The mean values of the π^*-values measured for the four indicators are plotted in those figures. Figure 3 includes the value obtained by Essfar et al.[44] for a vacuum at temperatures between 278 and 345 K. The π^* vs. density plot at each temperature is extrapolated to the intercept with the vacuum system. The intercept at 318, 333, and 353 K calculated by a first-order least-squares method give values of −1.03, −0.95, and −1.17, respectively; the mean is −1.05 and agrees closely with a π^*-value of −1.06±0.10 for a vacuum, obtained by Essfar et al.[44] Furthermore, the extrapolated π^*-values determined at different temperatures are the same within the experimental errors, indicating the insensitivity of π^* to the temperature. The π^*-values for supercritical carbon dioxide from shifts of the absorption maxima of several kinds of indicators in the UV/vis spectra have been reported in the literature; the π^*-values for carbon dioxide at 6.89 MPa and 315 K estimated by Hyatt[45] using dyes as indicators are −0.52 to −0.60, and are close to our π^*-value of −0.40 at 6.86 MPa and 318 K. With regard to the effect of the temperature on π^*, the values at 317 and 335 K and 10 MPa measured by Yonker and Smith[46] using 2-nitroanisole are −0.18 and −0.42, respectively; our values at 318 and 333 K and at 9.81 MPa are −0.15 and −0.38, respectively, in good agreement with their results within experimental errors. These show a high reliability in the measurements of the π^*-values for supercritical carbon dioxide by our IR method. The average π^*-values for carbon dioxide at different pressures, and around 313 K using ten indicators, were reported by Leffler;[16] these are also plotted with error ranges in Fig. 3. It has been found that the discrepancy in π^* due to the indicators in this UV/vis method is remarkably larger compared with that in our IR method. This might be because, in this work, the shifts for the C=O stretching vibrations of indicators are used for determining the π^*-values, and the diffence in the degree of C=O dipolarity among the indicators (which reflects the relative contribution of the two mesomeric forms) is less than that in the UV/vis method using entirely different types of indicator molecules.

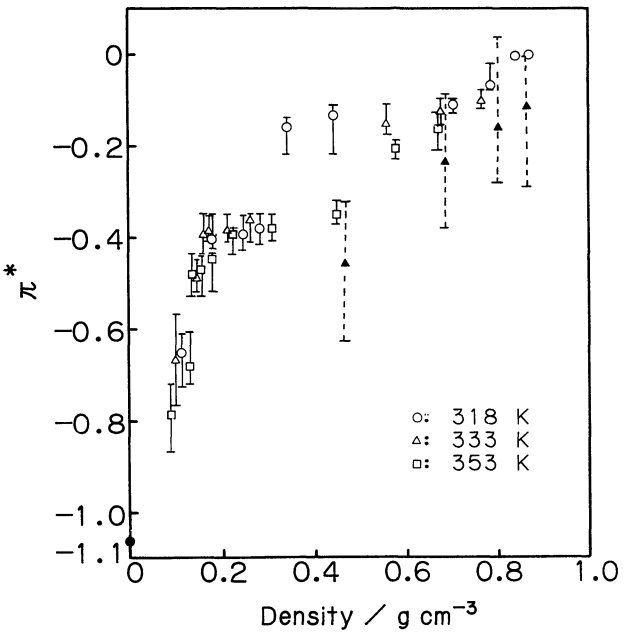

Fig. 3. Plots of π^* versus density for supercritical carbon dioxide at (○) 318, (△) 333, and (□) 353 K. The mean values of the data are plotted by the symbols ○, △, □ and the bars given are the data ranges: ●, π^* for vacuum at temperatures between 298 and 345 K determined by Essfar.[44] ⊢–▲–⊣, the mean π^*-values with error ranges measured at 309—315 K by Leffler.[16]

As shown in Fig. 3, the π^*-value decreases from a value near to zero (or zero) to a more negative value as the density decreases; it becomes more negative at higher temperatures in the range above about 10 MPa. From Fig. 3, irrespective of the temperature, the π^*-value decreases with a decrease in the density. The π^*-values of supercritical fulids have previously been reported to be dependent on the density, but not on temperature;[47] this agrees with the present result given in Fig. 3.

Estimation of the $E_T(30)$-Value. The $E_T(30)$ parameter has been shown to be related to the polarization of solvent molecules through linear relationships using the Kirkwood function and the Onsager reaction field function,[48] while the transition energy for the dissolved betaine dye has been demonstrated to have a linear dependence on the Kamlet-Taft's parameters.[29] According to Bekárek,[48] the $E_T(30)$-values for a set of 24 solvents including nonpolar liquids can be correlated with the π^* parameter, the Kirkwood function $[f(\varepsilon)=(\varepsilon-1)/(2\varepsilon+1)]$, and the Onsager reaction field function $[f(n^2)=(n^2-1)/(2n^2+1)]$ by Eq. 11:

$$E_T(30) = 31.84 + 10.61\pi^* f(\varepsilon)/f(n^2) - 10.85\pi^*,$$
$$r = 0.984, \text{ and } SD = 0.86. \quad (11)$$

Using the π^*-values determined in the present work in the above relationship, one can calculate the value of $E_T(30)$ of supercritical carbon dioxide as a function of the temperature and pressure. The refractive index and the dielectric constant for supercritical carbon dioxide as a function of the temperature and pressure can be determined from the Lorents–Lorenz equation and a virial expansion of the Clausius–Mossotti function with

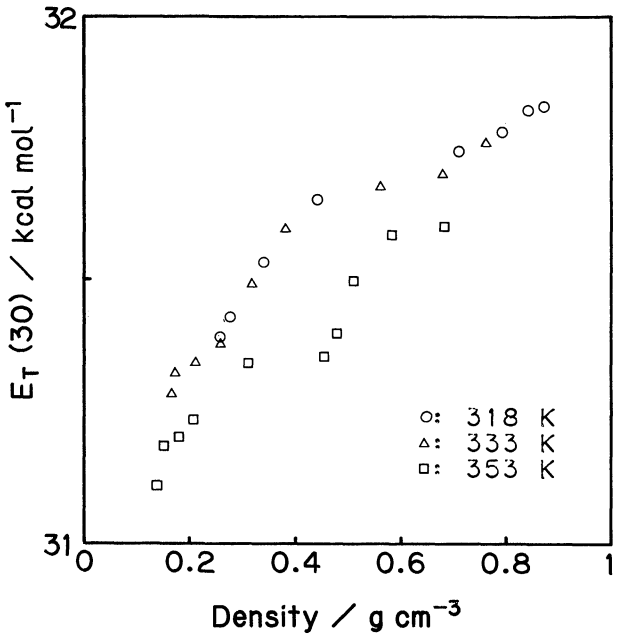

Fig. 4. Relationship between $E_T(30)$-values estimated by Eq. 11 and density of supercritical carbon dioxide at (○) 318, (△) 333, and (□) 353 K.

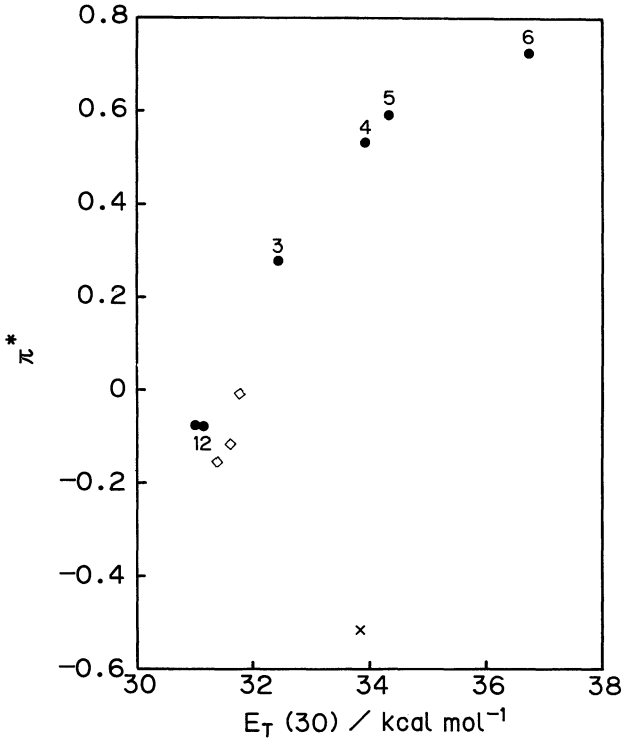

Fig. 5. Relationship between $E_T(30)$- and π^*-values[29] for 1, hexane; 2, heptane; 3, tetrachloromethane; 4, toluene; 5, benzene; 6, chlorobenzene; ◇, supercritical carbon dioxide at 318 K estimated in this work; ×, supercritical carbon dioxide at 297 K and 6.9 MPa reported by Hyatt.[45]

respect to density, respectively:

$$(n^2 - 1)/(n^2 + 2) = A_R\rho_m + B_R\rho_m^2 + \cdots \quad (12)$$

and

$$(\varepsilon - 1)/(\varepsilon + 2) = A_E\rho_m + B_E\rho_m^2 + \cdots, \quad (13)$$

where ρ_m is the molar density; A_R and B_R the first and second refractivity virial coefficients, respectively; and A_E and B_E the first and second dielectric virial coefficients, respectively.[49,50] The refractivity (A_R, B_R) and dielectric virial coefficients (A_E, B_E) for carbon dioxide have been reported by Bose and St-Arnaud[49] and Johnston and Cole.[50] The refractive index and the dielectric constant determined by substituting the corresponding virial coefficients into Eqs. 12 and 13 are used for calculating $f(n^2)$ and $f(\varepsilon)$ for supercritical carbon dioxide.

Figure 4 shows the $E_T(30)$-values for supercritical carbon dioxide at 313, 333, and 353 K as a function of the density. The $E_T(30)$-value increases with an increase in the density, and seems to be not much dependent on the temperature, although in the range of about 0.4—0.6 g cm^{-3} the $E_T(30)$-values at 353 K are only slightly lower, compared with those at 318 and 333 K.

Figure 5 shows the relationship between the π^*- and $E_T(30)$-values for solvents that have very low HBD acidities and HBA basicities (α, $\beta<0.1$), including supercritical carbon dioxide. The $E_T(30)$-values for supercritical carbon dioxide are linked to the relationship for the other solvents, as shown in Fig. 5; the $E_T(30)$-values for supercritical carbon dioxide estimated by the present method are believed to be both reasonable and reliable results. Although the $E_T(30)$-value for supercritical carbon dioxide at 6.9 MPa and 297 K (estimated by Hyatt[45]) is 33.8 kcal mol^{-1}, supercritical carbon dioxide scarcely contains a hydrogen-bonding contribution; in Figure 5 the $E_T(30)$-value (given as symbol (×)) seems to be only slightly greater than that expected from the π^*-values of −0.07[46]—−0.20[16] of supercritical carbon dioxide determined at around 6.9 MPa and 297 K. The reason for this discrepancy is unknown.

Conclusions

Although the B_{MeOD}-value increases with density, the value is very small and almost the same as that for hexane. The α-value is also relatively small, although it tends to increase with a decrease in the density in the range below 0.44 g cm^{-3}. The π^*-values of supercritical carbon dioxide at 5.85—28.5 MPa and 318—353 K are determined using the displacements of the IR stretching frequencies of the same chromophore of the four indicators based on the assumption that the B_{MeOD}- and α^*-values are negligibly small. The π^*-value become more negative as the pressure decreases. The π^*-value decreases with temperature above 10 MPa, but is scarcely dependent on the temperature at lower pressures. The

π^*-value deterrmined by the IR method is found to be highly reliable and the discrepancy in the π^*-values due to the indicators in this IR method have the advantage of being smaller than that in the UV/vis method. The $E_T(30)$-values for supercritical carbon dioxide have been estimated by using the π^*-values determined in this study as well as the $f(\varepsilon)$ and the $f(n^2)$ functions. The $E_T(30)$-value increases with an increase in density. The $E_T(30)$-value can be well-correlated with the π^*-value together with other nonpolar organic solvents, and the estimated $E_T(30)$-values are believed to be reliable.

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