Solvent Polarities of Supercritical CO₂/Methanol Mixtures

Dmitry S. Bulgarevich, Takeshi Sako, Tsutomu Sugeta, Katsuto Otake, Masahito Sato, Masayuki Uesugi* and Masahiro Kato*

Department of Chemical Systems, National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305, Japan

*Department of Industrial Chemistry, Faculty of Engineering, Nihon University, 1 Nakagawara Tamuramachi Kooriyam, Fukushima 963, Japan

UV/VIS absorption spectroscopy was used to estimate the microscopic solvent polarities of supercritical carbon dioxide alone and its mixtures with methanol. It was found that the local composition of methanol in the cybotactic region of 4-nitroanisole was larger than the corresponding bulk concentration. With increasing pressure the methanol molecules were pressed out of the solvation shell of probe molecule by the carbon dioxide molecules. From the solubility measurements the solvation numbers of the carbon dioxide molecules around 4-nitroanisole were calculated as a function of fluid density. [polarity, solvation, methanol, carbon dioxide, supercritical fluid]

1. Introduction

The investigation of a microscopic solvent structure of supercritical fluids in the cybotactic region of solute molecules provides a general understanding concerning the supercritical fluid extraction, chromatography and solvent effects on chemical reactions. Carbon dioxide is one of the most promising supercritical fluids due to its environmental safety and accessibility, but the solubility of organic solids in this solvent decreases strongly with their rising polarity. Fortunately, a small amount (usually less than 10%) of a polar organic cosolvent can increase the solubility of organic compounds in supercritical CO₂ greatly. The cosolvents used widely for this purpose are methanol, ethanol and 2-propanol. Therefore, the investigation of the microscopic solvation structure of pure CO₂ and CO₂/methanol mixture is useful and interesting. Application of spectroscopic methods is most favorable since the information can be obtained on molecular level.

2. Experimental

The JASCO UV/VIS V-550 spectrophotometer with high pressure cell unit was used to measure the absorption spectra of 4-nitroanisole (4-NA) in the UV region from 240 to 360 nm at 45 °C. For better reproducibility the mixtures were equilibrated at least for two hours and the spectra near to the peak maximum were well fitted to the Gaussian function to get the correct peak position. The solvatochromic probe 4-nitroanisole and methanol were GC grade and were used as received from WAKO.

3. Results and Discussion

The polarities of CO₂/methanol mixtures.

The inability of solvent macroscopic dielectric constant, refractive index and dipole moment to describe the solute-solvent interaction on the molecular level (especially in supercritical fluids as it was found recently^{1,2}) has led to the introduction of various empirical solvent polarity scales such as Dimroth's E_T , Kosover's Z , Brooker's χ_A and χ_B , Dubois's Φ , and Kamlet's and Taft's π^* scales from spectroscopic measurements³. The empirical Kamlet's and Taft's π^* scale of solvent polarities can adequately describe the solvent polarity in both liquids⁴ and supercritical fluids^{5,6}. In accordance to this scale the position of absorption maximum of aromatic molecule with the lowest $\pi \rightarrow \pi^*$ or $p \rightarrow \pi^*$ transition can be represented as follows⁷:

$$\tilde{\nu}_{\max} = \tilde{\nu}_0 + s\pi^* + a\alpha + b\beta, \quad (1)$$

where π^* is dipolarity/polarizability, α is a hydrogen-bond donor acidity and β is a hydrogen-bond acceptor basicity of the solvent; coefficients s , a and b are the susceptibilities of solute corresponding to the indicated solvent property scales; and $\tilde{\nu}_0$ is the position of absorption maximum in a reference solvent (cyclohexane). Here it should be pointed out that the parameters π^* , α , β are the properties of solvent and the coefficients s , a , b are the properties of solute, accordingly, and both groups are independent each other. Furthermore, the parameters π^* , α , β are the microscopic properties of the solvent.

For the present investigation we are interested in the solvent polarity π^* alone. At the same time, since our solvent is CO₂/methanol mixture, the parameters α and β are not negligible. This complicated situation can be simplified by choosing an appropriate probe solute molecule for which the coefficients a and b are zero. It has been reported that $a=0$ and $b=0$ for 4-NA⁷. Precisely speaking, Kamlet's and Taft's π^* , α and β scales are based on this statement since 4-NA is one of primary indicators used to construct these scales^{7,8,9}. As a result, the eq.(1) for 4-NA is reduced to

$$\tilde{\nu}_{\max} = \tilde{\nu}_0 + s\pi^*, \quad (2)$$

where $s = -2.343$ kK and $\tilde{\nu}_0 = 34.12$ kK for 4-NA⁷.

The plot of π^* as a function of pressure for different mole fractions of methanol is given in Fig. 1.

Fig. 1. Change of microscopic solvent polarity of CO₂/methanol mixtures with pressure for different bulk mole fractions of methanol.

Here it should be mentioned that all our mixtures are in supercritical state at $t = 45^\circ\text{C}$ and $P > 85\text{ bar}$ ¹⁰. The plots in this figure consist of two distinct regions displaying gas-phase solute-solvent clustering at low pressure (low density) region and liquid-like solvation at high pressure region, respectively. Primarily due to the dispersive interactions¹¹ the initial growing of cluster size with pressure causes a large incremental effect on solvatochromism in the low density region. The present results were compared with published data for the supercritical CO_2 and CO_2 /2-propanol mixtures, where 2-nitroanisole was used as a probe molecule^{5,6}. The absolute values of π^* for the pure supercritical carbon dioxide in the present work were lower by approximately 0.15 than these in literature⁶. This was originated from experimental errors primarily due to: 1) experimental apparatus ($\pm 20\%$); 2) the different procedure in estimation of the absorption peak maximum ($\pm 15\%$); 3) values of coefficient s ($\pm 10\%$). Thus, the total error in the value of π^* may be around 45–50%, which is really observed. At the same time the $d\pi^*/dP$ for the pure CO_2 and the corresponding differential for CO_2 /cosolvent mixtures in this work are quite similar with literature data. It is also evident that the polarities of CO_2 /2-propanol and CO_2 /methanol mixtures were not so different from each other. The $\Delta\pi^*$ in pure CO_2 and CO_2 /cosolvent at 170 bar were approximately 0.11 for CO_2 /2-propanol and 0.15 for CO_2 /methanol mixtures at $x_2 = 0.05$.

Local composition of methanol in the cybotactic region of 4-NA in CO_2 /methanol mixture:

The local mole fraction of cosolvent x_2^* in the cybotactic region of the solute probe molecule can be calculated with the following equation⁶:

$$x_2^* = (\pi_m^* - \pi_1^*) / (\pi_2^* - \pi_1^*), \quad (3)$$

where π_m^* , π_1^* and π_2^* are the polarities for the binary mixture of supercritical fluid and cosolvent, pure supercritical fluid and pure organic cosolvent, and measured at specified pressure and temperature conditions, respectively.

Fig. 2 shows the behavior of the local mole fraction of methanol vs. pressure for different initial bulk mole fractions of methanol.

Fig. 2. Plot of the local mole fractions of methanol in cybotactic region of 4-NA vs. pressure for different bulk mole fractions.

The general tendency is that the local mole fraction of methanol is much higher than the corresponding bulk value at low pressure region and it decreases with pressure. The present results are in agreement with literature^{6,12} and Monte Carlo computer simulations¹³. Thus, the attractive interactions between the solute and organic cosolvent are predominant at the low density condition. At higher density region the packing effect plays a major role in the local composition effect. The local composition in the cybotactic region should

asymptotically approaches the limiting value of the bulk composition as the pressure increases. In addition the ratio of x_2^*/x_2 at around 120 bar, 45°C and 0.05 of x_2 is almost 4 for both CO_2 /2-propanol⁶ and CO_2 /methanol systems. Therefore, the local composition of 2-propanol is almost same as that of methanol in cybotactic regions of 4-NA. In the case of phenol blue the similar x_2^*/x_2 ratios were reported in the CO_2 /methanol mixture and we also observed the maximum in the local composition of methanol around 4-NA at low pressure^{12,14}.

Solvation numbers of CO_2 molecules in the cybotactic region of 4-NA:

In order to estimate the solvation number of solvent molecules around the solute for pure supercritical fluid, we followed the method proposed by Kajimoto¹⁵. As the first step, the plot of $\ln(c/c_0)$ vs. reciprocal of the molar volume $1/V_m$ at low density regions is constructed from the solubility measurement and the second virial coefficient for mixture B_{12} is estimated:

$$\ln(c/c_0) = (V_s - B_{12})/V_m + C/V_m^2, \dots, \quad (4)$$

where c , c_0 and V_s are the equilibrium concentration of solute at a given pressure, that at a vapor pressure and the molar volume of the solid phase. The second virial coefficient is related to the intermolecular potential $V(r)$ by eq. (6), where $V(r)$ can be represented, for example, by the Sutherland type given in eq. (6):

$$B_{12} = -2\pi N_A \int_0^\infty (\exp(-V(r)/kT) - 1) r^2 dr, \quad (5)$$

$$V(r) = \begin{cases} +\infty, & r \leq r_1 \\ -C_6/r^6, & r \geq r_1 \end{cases}, \quad (6)$$

where N_A , k and r_1 are the Avogadro number, the Boltzmann constant and the radius of the core potential, respectively. Thus, the parameter C_6 can be calculated from eqs. (5) and (6). On the next step, eq. (7) enables us to calculate the particular density of supercritical fluid ρ_1 at which just one solvent molecule is in the solvation shell of solute:

$$4\pi \int_{r_1}^R \exp(V(r)/kT) r^2 dr = 1, \quad (7)$$

where ρ_1 is in molecules/ $\text{\AA}^3$ and R is the outer radius of the solvation shell, respectively. Finally, since the solvation shell can accommodate only a limited number of solvent molecules, the Langmuir adsorption equilibria was applied to calculating the densities of supercritical fluid molecules ρ which correspond to the density at different number of solvent molecules in the solvation shell of the solute.

$$\rho = \rho_1 (n-1)/(n-m). \quad (8)$$

In eq. (8) symbols n is the maximum number of the solvent molecules which can be accommodated and m is the number of the solvent molecules which are accommodated at a certain density ρ . Eq. (8) can be used to estimate the degree of the aggregation of the supercritical fluid around the solute at the

given density by comparing the calculated and experimentally measured absorption peak shifts.

Fig. 3. Bathochromic shifts of the absorption maximum of 4-NA against the density of supercritical CO_2 , where $\blacksquare$ and $\circ$ are the observed and calculated shifts, respectively.

Fig. 3 shows the plot of the experimental and calculated absorption peak shifts as a function of the fluid density. As seen in this figure, the best simulation of the experimental data was obtained when the maximum solvation number is 8 and the bathochromic peak shift per one solvating CO_2 molecule $\Delta\tilde{\nu}_1$ is 46 cm^{-1} .

Table 1. Parameters for intermolecular interaction between solute and solvent molecules.

Parameter	4-NA in CO_2	DMABN in CF_3H , ref. 15
T/T_c	1.046	1.080
$V_S, \text{cm}^3/\text{mol}$	100	100
$-B_{12}, \text{cm}^3/\text{mol}$	296	1400
$r_1, \text{\AA}$	3.5^a	4
$R, \text{\AA}$	7.9^b	6
$C_6, 10^6 \text{\AA}^6 \text{cm}^{-1}$	1.3	4.1
$\rho_1, \text{g/cm}^3$	0.066	0.025
n	8	7
$\Delta\tilde{\nu}_1, \text{cm}^{-1}$	46	225

^a)calculated from the sum of the unit volumes of atomic elements by additivity method of Immirzi and Perini (ref. 17).

^b)this value is not very critical, but the contribution far from $7.9 \text{\AA}$ is very small due to the rapid decrease of potential energy in this region.

All parameters used and obtained in the present calculation are summarized in Table 1 and compared with the reported data for (N,N-dimethylamino)benzonitrile (DMABN) in supercritical fluoroform (CF_3H)¹⁵. The B_{12} , C_6 and $\Delta\tilde{\nu}_1$ parameters are smaller for 4-NA in CO_2 than for DMABN in CF_3H . This is quite reasonable because the polarizability/volume¹⁶ of CO_2 and molar refraction¹⁷ of 4-NA are less than the corresponding values of CF_3H and DMABN. Thus the interactions between DMABN and CF_3H are expected to be stronger than those between 4-NA and CO_2 .

Another interesting fact is that the inner volume of the solvation shell of 4-NA can accommodate up to 22 CO_2 molecules from the molecular size, but the best simulation was obtained in the case of $n=8$. This result means that the solvent molecules exist in a preferable position around 4-NA. For example, the cylindrically symmetric form of potential was used to reproduce the experimental data in the case of DMABN in

supercritical ethane². So, a more accurate form of the solvation shell may be a torus rather than a sphere.

Conclusions

1. The microscopic solvent polarities of pure supercritical CO_2 and a supercritical CO_2 /methanol mixture were measured with Kamlet's and Taft's π^* scale by using 4-nitroanisole as a probe molecule.
2. The local composition of methanol in the cybotactic region of the probe molecule was much higher than the corresponding bulk value and decreased with pressure.
3. The local composition and solvation effects in supercritical fluid mixtures, even slightly above the critical point, were originated from the short-range solute-solvent interactions.
4. The best representation of experimental data for the supercritical solvatochromism was obtained when 4-nitroanisole accommodated up to eight CO_2 molecules in its first solvation shell. There were 3 to 5 CO_2 molecules in the cybotactic region of 4-nitroanisole at 45°C and a density range of $0.3\text{--}0.9\text{ g/cm}^3$.

References

- [1] S. Kim and K. P. Johnston, *Ind. Eng. Chem. Res.* **26**, 1206 (1987).
- [2] A. Morita and O. Kajimoto, *J. Phys. Chem.* **94**, 6420 (1990).
- [3] C. Reichardt, in *Solvent Effects in Organic Chemistry*, edited by E. Wenstrup-Byrne (Verlag Chemie: Weinheim, New York, 1979), and references therein.
- [4] M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.* **48**, 2877 (1983).
- [5] C. R. Yonker, S. L. Frye, D. R. Kalkwarf and R. D. Smith, *J. Phys. Chem.* **90**, 3022 (1986).
- [6] C. R. Yonker and R. D. Smith, *J. Phys. Chem.* **92**, 2374 (1988).
- [7] M. J. Kamlet, J.-L. M. Abboud and R. W. Taft, *J. Am. Chem. Soc.* **99**, 6027 (1977).
- [8] M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.* **98**, 377 (1976).
- [9] R. W. Taft and M. J. Kamlet, *J. Am. Chem. Soc.* **98**, 2886 (1976).
- [10] G. S. Gurdial, N. R. Foster, S. L. J. Yun and K. D. Tilly in *Supercritical Fluid Engineering Science: fundamentals and applications*, edited by Kiran, E. and Brennecke, J. F. (American Chemical Society, Washington, 1993), chapter 3.
- [11] J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, in *Molecular Theory of Gases and Liquids*, edited by M. G. Mayer (Wiley, New York, 1954), p. 988.
- [12] S. Kim, K. P. Johnston, *AIChE J.* **33**, 1603 (1987).
- [13] K.-H. Lee, S. I. Sandler, N. C. Patel, *Fluid Phase Equilib.* **25**, 31 (1986).
- [14] J. B. Ellington, K. M. Park, J. F. Brennecke, *Ind. Eng. Chem. Res.* **33**, 965 (1994).
- [15] O. Kajimoto, M. Futakami, T. Kobayashi and K. Yamasaki, *J. Phys. Chem.* **92**, 1347 (1988).
- [16] K. P. Johnston, S. Kim and J. Combes in *Supercritical Fluid Science and Technology*, edited by K. P. Johnston and J. M. L. Penninger, (American Chemical Society, Washington, 1989), chapter 5, and references therein.
- [17] Can be roughly estimated by additivity methods given in *Handbook of Chemical Property Estimation Methods*; (American Chemical Society, Washington, 1990), chapters 19 and 26.