ORIGINAL ARTICLE

Effects of external pressure and solvent polarity on inclusion complexations of phenothiazine dyes and *trans*-4-[4-(dimethylamino)styryl]-1-methylpyridinium with water-soluble *p*-sulfonatocalix[8]arene in alcohol–water mixtures

Yoshimi Sueishi · Kazuyuki Asano

Abstract The effects of pressure and solvent were examined for the inclusion complexation of phenothiazine dyes and *trans*-4-[4-(dimethylamino)styryl]-1-methylpyridinium (St-4Me) with water-soluble *p*-sulfonatocalix[8]arene (Calix-S8). Depending on the bulkiness of the guest dyes, external pressures and solvent polarity increase the inclusion equilibrium constants of dyes with Calix-S8. From the pressure dependence of the inclusion equilibria, the reaction volumes for inclusion by Calix-S8 in the alcohol-water mixtures were estimated to be negative values (-19.8 to -5.29 cm^3 mol^{-1} for the phenothiazine dyes and -13.1 to -9.85 cm^3 mol^{-1} for St-4Me). Analysis of the results of the high pressure indicated that the intrinsic volume change related to inclusion into the Calix-S8 cavity plays an important role in the inclusion of Calix-S8, depending on the bulkiness of the guest molecules. Based on ^{1}H NMR measurements, the structures of the inclusion complexes of Calix-S8 with phenothiazine dyes have been established and the differences in the inclusion behaviors of the phenothiazine dyes and St-4Me are discussed.

Keywords Inclusion complex · Pressure effect · p-Sulfonatocalix[8]arene · Phenothiazine dye

Introduction

Calixarenes are cyclic oligomers that possess hydrophobic cavities and can form inclusion complexes of host–guest types [1]. It is well known that calixarenes exhibit a conformational flexibility by comparing them with cyclodextrins (CDs). Water-soluble calixarenes are versatile host molecules for metal and charged species in aqueous media [1, 2]. Investigation of host–guest interaction of water-soluble calixarenes helps in the modeling of molecular recognition.

Quantitative information on volume change during the inclusion reaction can be obtained by changing external pressures, and such experiments may be useful in characterizing the inclusion reaction mechanism. Previously, using substituted phenols and radical species as guest molecules, we demonstrated that CD inclusion equilibrium was pressure dependent [3–5]. In those reports, we showed that examination of the pressure effects on inclusion complexations is informative for understanding the reaction mechanism of inclusion equilibrium. The majority of the studies that involve water-soluble calixarenes have been focused on the ionic metal species [1]. In a preliminary report, we have examined the effect of pressure on inclusion complexation of methylene blue (MB) with *p*-sulfonatocalixarenes and reported the large effects of pressure on the inclusion equilibria of calixarenes [6]. However, studies on the inclusion complexation of organic molecules with water-soluble calixarenes have not been well established.

In this study, to obtain further information concerning the inclusion complexation of water-soluble calixarenes with organic species, five kinds of phenothiazine dyes and *trans*-4-[4-(dimethylamino)styryl]-1-methylpyridinium (St-4Me) were used as guest molecules. We have examined the effects

Y. Sueishi (✉) · K. Asano
Department of Chemistry, Faculty of Science, Okayama University, 3-1-1 Tsushima-naka, Okayama 700-8530, Japan
e-mail: ysueishi@cc.okayama-u.ac.jp

of pressure and solvent on their inclusion equilibria with water-soluble *p*-sulfonatocalix[8]arene (Calix-S8) and found a peculiar pressure dependence of inclusion complexation by Calix-S8. Based on the results, we conducted a volumetric study concerning the inclusion mechanism of water-soluble calix[8]arene and assessed the differences in pressure dependence on the inclusion complexation.

Experimental

Materials

The water-soluble *p*-sulfonatocalix[8]arene (Calix-S8), five kinds of phenothiazine dyes, and *trans*-4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide (St-4Me) used in this study are shown in Fig. 1. Calix-S8 was purchased from Sugai Chemie Inc. (Wakayama, Japan). The phenothiazine dyes (thionine (Th), azure A, azure B, methylene blue (MB), and new methylene blue (NMB)) and St-4Me were obtained from Wako Pure Chemicals (Osaka, Japan). Calix-S8, phenothiazine dyes, and St-4Me were recrystallized from water–ethanol mixtures and dried under vacuum before use. Reagent-grade alcohols were obtained commercially (Wako Pure Chemicals, Osaka, Japan).

Spectral measurements

We used a water–alcohol mixture (1:1 (v/v) phosphate buffer pH = 6.9 and ionic strength = 0.1) as a solvent because dimerization of phenothiazine dyes is observed in aqueous solution [7] and St-4Me forms a colorless dicationic species, formed by protonation of the amine nitrogen,

in acidic alcohol–water mixtures (pH < 5.5). The spectral change of the dyes in the presence of Calix-S8 was monitored by using a Hitachi U-3200 spectrophotometer (Tokyo, Japan); the reaction temperature was controlled at 298 ± 0.1 K by circulating thermostated water. The sample solution was loaded in a Teflon inner cell, which was set in a pressure vessel. The pressure vessel was connected to a Hitachi U-3200 spectrophotometer through an optical fiber. The procedures for spectral measurements under high pressures have been described elsewhere [3]. The ^{1}H NMR spectra in a D_2O–CD_3OD mixture at room temperature were measured with a Varian Mercury 300 (300 MHz). Chemical shifts were reported as δ values relative to CHD_2OD (δ 8.31) as an internal standard [8].

Results and discussion

Calix-S8 complexation with phenothiazine dyes and St-4Me

Figure 2 shows the typical absorption spectra of phenothiazine dyes upon consecutive additions of Calix-S8. When Calix-S8 is added to a solution of azure B in a 1-propanol–water mixture, the peak in the vicinity of 640 nm caused by the dye decreases with the isosbestic point at $\lambda = 660$ nm. The existence of the isosbestic point is related to the 1:1 inclusion equilibrium, which is in agreement with previous UV-Vis and NMR studies on inclusion complexation of methylene blue (MB) with Calix-S8 [6]. The equilibrium constant for the inclusion complexation can be expressed as:
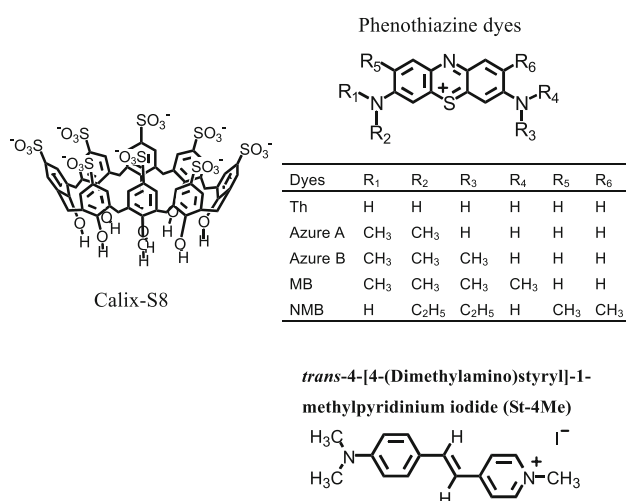
$$\text{Calix-S8} + \text{G} \rightleftarrows \text{Calix-G}$$

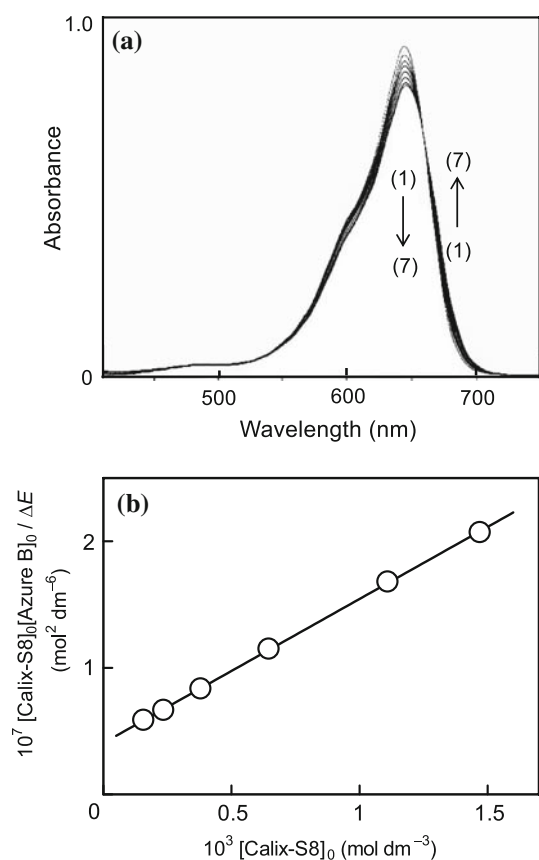$$K = \frac{[\text{Calix} - \text{G}]}{[\text{Calix-S8}][\text{G}]}. \tag{1}$$

Extensive studies for 1:1 complex formations based on the Benesi–Hildebr and (B–H) treatment [9] have been made by many investigators. Under the condition of [Calix-S8] >> [dye], the spectral data were analyzed according to the equation:

$$\frac{[\text{Calix} - \text{S8}]_0 [\text{G}]_0}{\Delta E} = \frac{1}{K \Delta \varepsilon} + \frac{1}{\Delta \varepsilon} [\text{Calix-S8}]_0, \tag{2}$$

where $[\text{Calix-S8}]_0$ and $[\text{G}]_0$ are total concentrations of calixarene and guest molecules, respectively. $\Delta \varepsilon$ is the difference in the molar extinction coefficients for bound and unbound dye with Calix-S8, and ΔE is the change in the absorption intensity of the dye solution. As shown in Fig. 2b, a good linear relationship between $[\text{Calix-S8}]_0 [\text{G}]_0 / \Delta E$ and $[\text{Calix-S8}]_0$ can be obtained, indicating 1:1 inclusion

Phenothiazine dyes

Dyes	R_1	R_2	R_3	R_4	R_5	R_6
Th	H	H	H	H	H	H
Azure A	CH_3	CH_3	H	H	H	H
Azure B	CH_3	CH_3	CH_3	H	H	H
MB	CH_3	CH_3	CH_3	CH_3	H	H
NMB	H	C_2H_5	C_2H_5	H	CH_3	CH_3

Calix-S8

trans-4-[4-(Dimethylamino)styryl]-1-methylpyridinium iodide (St-4Me)

Fig. 1 Structures of *p*-sulfonatocalix[8]arene, phenothiazine dyes, and St-4Me

Fig. 2 (**a**) Absorption spectra of azure B (1.56×10^{-5} mol dm^{-3}) containing different concentrations of Calix-S8 in a 1-propanol–water mixture at 298 K: [Calix-S8] = (1) 0, (2) 1.57×10^{-4}, (3) 2.35×10^{-4}, (4) 3.80×10^{-4}, (5) 6.46×10^{-4}, (6) 1.11×10^{-3}, and (7) 1.47×10^{-3} mol dm^{-3}. (**b**) Determination of 1:1 inclusion equilibrium constant according to the B–H equation

complex formation. The association constants K for the inclusion complexation of Calix-S8 can be determined from the slope and intercept of Eq. 2 except azure A and B in a methanol–water mixture. The K values obtained in the alcohol–water mixtures are listed in Table 1. Analysis of the spectral data using the B–H type equation is not suitable for the inclusion complexation of azure A and B in a methanol–water mixture because their association constants are extremely large compared with the others. The concentration of Calix-S8 for azure A and B inclusion in a methanol–water mixture is not much higher than is that of the dyes, and thus we used the optimization method of Lang's treatments for determining the association constants of the 1:1 inclusion complexation [10]:

$$\frac{[\text{Calix} - \text{S8}]_0 [\text{G}]_0}{\Delta E} = \left([\text{Calix-S8}]_0 + [\text{G}]_0 - \frac{\Delta E}{\Delta \varepsilon K}\right) \frac{1}{\Delta \varepsilon} + \frac{1}{\Delta \varepsilon K}.$$
(3)

The association constants for azure A and B inclusion in a methanol–water mixture are listed in Table 1.

The E_T values are used as a measure of solvent polarity. From the absorption spectra of Reichardt's dye, we determined the E_T values to be 244, 230, and 225 kJ mol^{-1} for methanol–water (1:1 v/v), ethanol–water (1:1 v/v), and 1-propanol–water (1:1 v/v), respectively. As can be seen in Table 1, the K values in the alcohol–water mixtures decrease with a decrease in solvent polarity, which is similar to the cyclodextrin inclusion complexation [11]. It should be noted that the K values for the inclusion of azure A and B are large compared with those of the other phenothiazine dyes. Overall, the K values tend to decrease as the bulkiness of the guest molecules increases. The stability of an inclusion complex is determined by how well a guest fits in the Calix-S8 cavity.

Structure of the inclusion complex with phenothiazine dyes

To obtain useful information concerning the inclusion complexes, we performed ^{1}H NMR measurements for the complexes of phenothiazine dyes with Calix-S8. Table 2 lists the changes ($\Delta\delta$) in the chemical shifts of the protons of the dyes in a CD$_3$OD–D$_2$O mixture (1:1 v/v). The protons of the phenothiazine dyes used in the present study were assigned with reference to the NMR spectral data of MB [6]. The upfield shifts of the guest protons indicate inclusion of the proton moiety into the Calix-S8 cavity [12, 13]. Analogous with the inclusion with MB [6], changes in the chemical shifts for the C(2,4,6)–H, N–(CH$_3$)$_2$, N–CH$_3$, and N–C–CH$_3$ of the phenothiazine dyes are large compared with those for the others. These indicate that the C(4,6)–H moieties and the amino groups of both sides are included in the Calix-S8 cavity. In the inclusion complex of Th, the relative chemical shift value of $|\Delta\delta(\text{C}(1)\text{–H})|/|\Delta\delta(\text{C}(2)\text{–H})|$ is large compared with that of the others, which is responsible for the deep inclusion into the Calix-S8 cavity. In the inclusion complexes of azure A and B, it is noted that the $|\Delta\delta|$ values of the C(1)–H and C(2)–H protons for the inclusion complex are larger than are those of the C(8)–H and C(9)–H protons, indicating that the C(1,2)–H proton moieties are included in the Calix-S8 cavity and the C(8,9)–H proton moieties may be located outside the cavity. Shinkai et al. suggested that the conformation of water-soluble calixarenes is fixed to a cone shape upon inclusion of guest molecules based on a circular dichroism study of the inclusion complexes [14]. Using the Corey-Pauling-Koltun (CPK) space-filling model, we examined the structures of the inclusion complexes of the phenothiazine dyes with Calix-S8. The CPK models show that a cone conformation is more suitable to the formation of inclusion complexes than is any other conformation, which is in agreement with the suggestion by Shinkai et al. Based on the above results, plausible

Table 1 The equilibrium constants (K) and reaction volumes for inclusion complexation of Calix-S8 in various solvents at 298 K

Guest	Solvent[a]	10^{-3} K (mol^{-1} dm^3)				ΔV (cm^3 mol^{-1})	ΔV_{inclu} (cm^3 mol^{-1})	ΔV_{solv} (cm^3 mol^{-1})
		1 bar[b]	196 bar	491 bar	785 bar			
Th	Methanol–H_2O	14.5 ± 0.7	14.9	15.8	16.9	-6.09 ± 0.21	-6.15 ± 0.48	0.06
Th	Ethanol–H_2O	3.65 ± 0.11	3.78	3.93	4.16	-5.29 ± 0.13	-6.15 ± 0.48	0.86
Th	1-Propanol–H_2O	2.74 ± 0.14	2.88	3.02	3.10	-5.43 ± 0.39	-6.15 ± 0.48	0.72
Azure A	Methanol–H_2O	21.8 ± 0.9	23.9	25.5	27.9	-8.60 ± 0.49	-8.95 ± 0.24	0.34
Azure A	Ethanol–H_2O	7.92 ± 0.44	8.53	9.23	10.1	-8.78 ± 0.28	-8.95 ± 0.24	0.17
Azure A	1-Propanol–H_2O	3.86 ± 0.03	4.06	4.23	4.82	-8.27 ± 0.74	-8.95 ± 0.24	0.68
Azure B	Methanol–H_2O	19.1 ± 0.6	20.8	23.9	27.3	-12.5 ± 0.1	-14.2 ± 0.1	1.7
Azure B	Ethanol–H_2O	5.41 ± 0.17	5.79	6.62	7.32	-10.9 ± 0.3	-14.2 ± 0.1	3.3
Azure B	1-Propanol–H_2O	2.83 ± 0.13	3.00	3.23	3.60	-9.02 ± 0.29	-14.2 ± 0.1	5.2
MB	Methanol–H_2O	7.54 ± 0.37	8.52	9.78	11.3	-13.8 ± 0.3	-14.6 ± 0.3	0.8
MB	Ethanol–H_2O	3.33 ± 0.12	3.63	4.20	4.77	-12.8 ± 0.1	-14.6 ± 0.3	1.8
MB	1-Propanol–H_2O	2.57 ± 0.08	2.80	3.22	3.54	-12.0 ± 0.3	-14.6 ± 0.3	2.6
NMB	Methanol–H_2O	6.30 ± 0.15	6.82	8.66	11.2	-19.8 ± 1.1	-20.8 ± 0.4	1.0
NMB	Ethanol–H_2O	2.59 ± 0.09	3.21	3.93	4.61	-19.1 ± 1.3	-20.8 ± 0.4	1.7
NMB	1-Propanol–H_2O	1.59 ± 0.06	1.99	2.31	2.80	-18.6 ± 1.3	-20.8 ± 0.4	2.2
St-4Me	Methanol–H_2O	3.84 ± 0.18	4.38	4.56	5.19	-9.85 ± 1.02	-8.35 ± 0.42	-1.5
St-4Me	Ethanol–H_2O	2.19 ± 0.08	2.49	2.68	3.09	-11.5 ± 0.8	-8.35 ± 0.42	-3.2
St-4Me	1-Propanol–H_2O	1.56 ± 0.03	1.54	1.95	2.16	-13.1 ± 1.7	-8.35 ± 0.42	-4.8

[a] Alcohol/H_2O = 1 (v/v). [b] 1 bar = 1 × 10^5 Pa

Table 2 Chemical shift changes ($\Delta\delta$/ppm)[a] of phenothiazine dyes in the presence of Calix-S8

Guest[b]	C(1)–H	C(2)–H	C(2)–CH$_3$	C(4)–H	C(6)–H	C(8)–H	C(9)–H	N–(CH$_3$)$_2$	N–CH$_3$	N–CH$_2$	N–C–CH$_3$
Th[c]	−0.45	−0.61	–	−0.53	(−0.53)	(−0.61)	(−0.45)	–	–	–	–
Azure A[d]	−0.43	−0.81	–	−0.48	−0.53	−0.29	−0.13	−0.35	–	–	–
Azure B[e]	−0.15	−0.30	–	−0.49	−0.60	−0.01	−0.04	−0.36	−0.31	–	–
MB[f]	−0.18	−0.39	–	−0.54	(−0.54)	(−0.39)	(−0.18)	−0.61	–	–	–
NMB[g]	−0.16	–	−0.17	−0.37	(−0.37)	–	(−0.16)	–	–	−0.39	−0.24

[a] $\Delta\delta = \delta$ (complex with Calix-S8) − δ (dye unbounded with Calix-S8). Negative values indicate upfield shifts

[b]
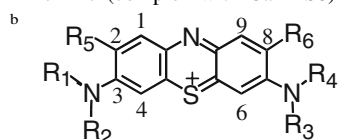
[c] [Calix-S8]$_0$/[Th]$_0$ = 1.0

[d] [Calix-S8]$_0$/[Azure A]$_0$ = 1.0

[e] [Calix-S8]$_0$/[Azure B]$_0$ = 0.50

[f] [Calix-S8]$_0$/[MB]$_0$ = 7.6 (cited from Ref. 6)

[g] [Calix-S8]$_0$/[NMB]$_0$ = 1.0

structures of the inclusion complexes of dyes with Calix-S8 are depicted in Fig. 3, together with the structure of the St-4Me inclusion complex, which was suggested by Nishida et al. [15].

In the azure A and B molecules, the positive partial charge on the nitrogen atom of the dimethylamino group could be caused by resonance contribution. Lhotak and Shinkai suggested that cation–π interaction is an important factor in forming stable inclusion complexes with calixarenes [16, 17]. In azure-calixarene inclusion, the cation–π interaction as well as van der Waals and/or hydrophobic interactions could be cooperative, resulting in the enhanced stability of the azure inclusion complex (Table 1).
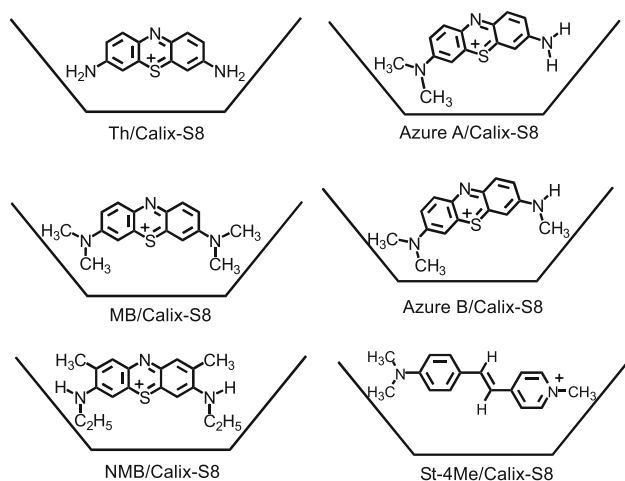
Fig. 3 Plausible structures of inclusion complexes of phenothiazine dyes and St-4Me with Calix-S8

Pressure effects

The pressure effects on the inclusion complexation of dyes with Calix-S8 are listed in Table 1. The K values increase with increasing external pressure. By utilizing these numbers, the reaction volumes (ΔV) for the inclusion complexation by Calix-S8 can be estimated according to the following equations:

$$\ln K = aP + b \tag{4}$$

$$\Delta V = -RT\left(\frac{\partial \ln K}{\partial P}\right)_T - \kappa_T RT, \tag{5}$$

where κ_T is the isothermal compressibility of the solvent mixture. The $\kappa_T RT$ values were estimated to be 1.10, 1.22, and 1.58 $cm^3 \ mol^{-1}$ for methanol–water, ethanol–water, and 1-propanol–water, respectively. The estimated reaction volumes (ΔV's) have negative values, and the absolute values of ΔV ($|\Delta V|$) increase with an increase in the bulkiness of the phenothiazine guest molecules. $|\Delta V|$ for the St-4Me inclusion is comparable to that for azure A. In the solvent effects on inclusion complexation with Calix-S8, we made an interesting observation: The $|\Delta V|$ values for phenothiazine dye inclusion become smaller with decreasing solvent polarity; conversely, those for St-4Me increase with decreasing solvent polarity.

In the previous high-pressure study on calixarene complexation, we demonstrated that the reaction volume for the inclusion which is not the change in total volume (the guest plus calixarene) consists of two discrete volume changes [6]:

$$\Delta V = \Delta V_{\text{inclu}} + \Delta V_{\text{solv}}, \tag{6}$$

where ΔV_{inclu} is the volume change related to the inclusion of guest molecules in the cavity and ΔV_{solv} denotes the volume change accompanying solvation or desolvation

around the guest and host molecules. Based on Laidler's treatments for the equilibrium reaction between ion molecules, ΔV can be expressed as:

$$\Delta V = \Delta V_{\text{inclu}} - \frac{1}{2}N_A e^2 \left(\frac{z^2}{r} - \sum_i \frac{z_i}{r_i}\right)q_P \tag{7}$$

$$q_P = \frac{1}{\varepsilon^2}\left(\frac{\partial \varepsilon}{\partial P}\right)_T, \tag{8}$$

where the notations have their usual meanings. By using the available $\varepsilon - P$ data, the q_P values were estimated to be 0.00829, 0.0136, and 0.0235 GPa^{-1} for methanol–water, ethanol–water, and 1-propanol–water, respectively [18, 19]. Equation 7 predicts a linear relationship between ΔV and q_P with an intercept of the ΔV_{inclu} value. In Fig. 4, ΔV is plotted against q_P. A linear relationship between them is maintained, and the ΔV_{inclu} values estimated from the plots are listed together with the ΔV_{solv} values evaluated from the ΔV_{inclu} values and Eq. 6. The ΔV_{inclu} values are largely negative. Compared to the $|\Delta V_{\text{solv}}|$ values, their absolute values are large and increase with an increase in the bulkiness of the guest molecules. The contribution of the guest molecule to the partial molar volume of the inclusion complex becomes small and the negative volume change is expected because the guest molecule occupies the void space of Calix-S8. It is reasonable that the larger the guest molecule, the larger the decrease in the reaction volume is caused. The ΔV_{inclu} values play an important role in volume change accompanied by Calix-S8 inclusion.

The inspection of the solvation-term (ΔV_{solv}) also gives useful insight into inclusion behavior. The ΔV_{solv} values for phenothiazine dye inclusion are positive and tend to increase with decreasing solvent polarity. The positive ΔV_{solv} values are responsible for the desolvation around the phenothiazine guest molecules and/or polar sulfonato groups in Calix-S8 upon formation of host–guest ion-pairs. In contrast, the ΔV_{solv} values for St-4Me inclusion are negative and its absolute value increases with decreasing
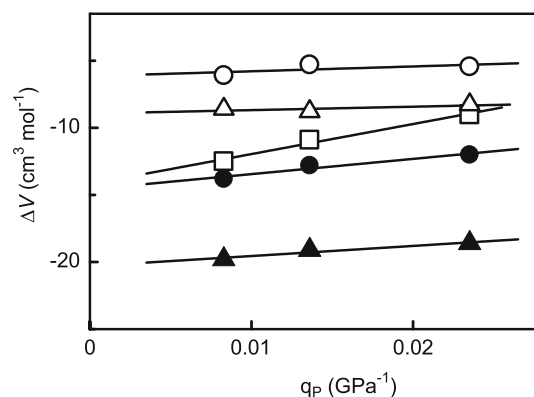
Fig. 4 Plots of ΔV against q_P according to Eq. 7

solvent polarity, which is taken as evidence for the contribution of electrostatic interaction upon inclusion. It is generally known that ionization is enhanced by pressure, and the observation of volume decrease has been interpreted in terms of electrostriction [20]. Nishimura et al. reported that the reaction volume for charge-transfer complex formation through hydrogen bonding is largely negative due to electrostriction [21]. There is a possibility that St-4Me forms the inclusion complex involving hydrogen bonding between the St-4Me guest molecule and the sulfonato group of Calix-S8. We speculate that the St-4Me inclusion complex is similar to the tight complex involving hydrogen bonding, and an additional interaction (electrostatic interaction) may be operative upon inclusion with Calix-S8, which is indicated by the high-pressure results.

In conclusion, we demonstrated that the inclusion equilibria of phenothiazine dyes with Calix-S8 are dependent on the bulkiness of the guest molecules, and the external pressure and solvent polarity increase the association constant for inclusion equilibrium. Although the present analysis of the high-pressure results utilized a simplified model, an important factor for the change in volume accompanied by the Calix-S8 inclusion is discussed.

References

1. Ikeda, A., Shinkai, S.: Novel cavity design using calix[n]arene skeletons: toward molecular recognition and metal binding. Chem. Rev. **97**, 1713–1734 (1997). doi:10.1021/cr960385x
2. Gutsche, C.D.: Calixarenes. In: Stoddart, J.F. (ed.) Monograph in Supramolecular Chemistry. The Royal Society of Chemistry, Cambridge, UK (1989)
3. Sueishi, Y., Itami, S.: Investigation of the pressure effects on inclusion equilibria of substituted phenols with β- and γ-cyclodextrins. Z. Phys. Chem. **217**, 677–688 (2003). doi:10.1524/zpch.217.6.677.20440
4. Sueishi, Y., Tobisako, H., Kotake, Y.: Distinctive pressure effects on the association equilibrium in cyclodextrin group-inclusion complex as studied with electron paramagnetic resonance. J. Phys. Chem. B **108**, 12623–12627 (2004). doi:10.1021/jp040326k
5. Sueishi, Y., Ide, T.: A characteristic effect of pressure on the inclusion complexation of modified β-cyclodextrins with 4-substituted phenols. Z. Phys. Chem. **219**, 498–500 (2005). doi:10.1524/zpch.219.4.489.61667
6. Sueishi, Y., Inazumi, N., Hanaya, T.: Effects of pressure on inclusion complexation of methylene blue with water-soluble p-sulfonatocalix[n]arenes. J. Phys. Org. Chem. **18**, 448–455 (2005). doi:10.1002/poc.888
7. Lee, C., Sung, Y.W., Park, J.W.: Multiple equilibria of phenothiazine dyes in aqueous cyclodextrin solutions. J. Phys. Chem. B **103**, 893–898 (1999). doi:10.1021/jp983767a
8. Gottieb, H.E., Kotlyar, V., Nudelman, A.: NMR chemical shifts of common laboratory solvents as trace impurities. J. Org. Chem. **62**, 7512–7515 (1997). doi:10.1021/jo971176v
9. Scott, R.L.: Some comments on the Benesi-Hildebrand equation. Recl. Trav. Chim. Pays-Bas Belg. **75**, 787–789 (1956)
10. Lang, R.P.: Molecular complexes and their spectra. XIV. Iodine complexes with thiourea and thioacetamide. J. Am. Chem. Soc. **84**, 1185–1192 (1962). doi:10.1021/ja00866a025
11. Sueishi, Y., Kasahara, M., Inoue, M., Matsueda, K.: Effects of substituent and solvent on inclusion complexation of β-cyclodextrins with azobenzene derivatives. J. Incl. Phenom. Macrocycl. Chem. **46**, 71–75 (2003). doi:10.1023/A:1025686605714
12. Shinkai, S., Araki, K., Manabe, O.: Does the calixarene cavity recognize the size of guest molecules? On the hole-size selectivity in water-soluble calixarenes. J. Chem. Soc. Chem. Commun. 187–189 (1988). doi:10.1039/c39880000187
13. Goto, K., Yano, Y., Okada, E., Liu, C.W., Yamamoto, K., Ueoka, R.: Catalytic specificity exhibited by p-sulfonatocalix[n]arenes in the methanolysis of N-acetyl-L-amino acids. J. Org. Chem. **68**, 865–870 (2003). doi:10.1021/jo026580v
14. Shinkai, S., Arimura, T., Sato, H., Manabe, O.: Chiral calixarene. J. Chem. Soc. Chem. Commun. 1495–1496 (1987). doi:10.1039/c39870001495
15. Nishida, M., Ishii, D., Yoshida, I., Shinkai, S.: Molecular association of water-soluble calixarenes with several stilbene dyes and its application to the facile determination of cationic surfactant concentrations. Bull. Chem. Soc. Jpn **70**, 2131–2140 (1997). doi:10.1246/bcsj.70.2131
16. Lhotak, P., Shinkai, S.: Cation-π interactions in calyx[n]arene and related systems. J. Phys. Org. Chem. **10**, 273–285 (1997). doi:10.1002/(SICI)1099-1395(199705)10:5<273::AID-POC877>3.0.CO;2-Z
17. Aoki, K., Nagae, T., Yamaguchi, S., Fujiwara, I.: Tetramethylated resorcin[4]arene- based molecular capsules incorporating a tetraethylammonium ion through cation-π interactions. Bull. Chem. Soc. Jpn **78**, 2066–2068 (2005). doi:10.1246/bcsj.78.2066
18. Marcus, Y., Hefter, G.: On the pressure and electric field dependencies of the relative permittivity of liquids. J. Solut. Chem. **28**, 575–592 (1999). doi:10.1023/A:1022687016721
19. Mashimo, S., Kuwabara, S., Yagihara, S., Higasi, K.: The dielectric-relaxation of mixtures of water and primary alcohol. J. Chem. Phys. **90**, 3292–3294 (1989). doi:10.1063/1.455883
20. Drljaca, A., Hubbard, C.D., van Eldik, R., Asano, T., Basilevsky, M.V., le Noble, W.J.: Activation and reaction volumes in solution. 3. Chem. Rev. **98**, 2167–2289 (1998). doi:10.1021/cr970461b
21. Nishimura, N., Osawa, Y., Kuramoto, K., Sukemichi, K.: Effects of temperature and pressure on the charge-transfer complex formation through hydrogen bonding and ionization reactions between 2, 6-dibromo-4-[(3, 5-dibromo-4-hydroxyphenyl)(2-ethoxy- carbonylphenyl)-methylene]-2, 5-cyclohexadien-1-one and amines. Bull. Chem. Soc. Jpn **64**, 2438–2443 (1991). doi:10.1246/bcsj.64.2438