Articles

An NMR Study on Complexation of Cesium Ion by
p-tert-Butylcalix[6]arene Ethyl Ester

Kee-Choo Chung, Hyun Namgoong,[†] and Jo Woong Lee[*]

School of Chemistry and Molecular Engineering, College of Natural Sciences, Seoul National University, Seoul 151-742, Korea
[†]E&A Center, Kolon Central Research Park, Yongin 447-797, Korea

Complexation of cesium ion by *p-tert*-butylcalix[6]arene ethyl ester was studied by NMR spectroscopy in nonpolar $CDCl_3$ and polar acetone-d_6 and the results were compared with each other. Analysis of temperature dependent ^1H spectra and titration curves reveals that both solvents result in a 1 : 1 cone-form complex with nonpolar $CDCl_3$ yielding a more tightly bound one than acetone-d_6. Unexpectedly, at very low temperature, we have found that two phenyl ring proton peaks of equal intensity appear both in $CDCl_3$ and in acetone-d_6 solution which gradually collapse and eventually coalesce into a single line as temperature is raised. This observation could be interpreted in terms of the chemical exchange through direct and/or indirect interconversion between two equivalent conformations possible the complex in both solvents over the temperature range observed. And broadening of ^{133}Cs ($I = 7/2$) nmr line with increasing temperature has also been observed, indicating the exchange of ^{133}Cs ion between the complex and the solvent. From numerical fitting of lineshape changes for one-dimensional ^1H and ^{133}Cs spectra, the exchange rate constants and other relevant parameters for this conformational interconversion and the complex-solvent exchange were deduced.

Key Words : NMR, Calix[6]arene, Cesium, Chemical exchange

Introduction

Calixarenes have attracted widespread attention because of their ability to interact with various metal ions.[1] For example, calixarene-based metalloreceptors are increasingly employed usefully in various applications such as analytical luminescent sensors[2] and highly luminescent lanthanide-containing probes[3] as well as metal extraction and separation reagents.[4] To understand the structure of metal-calixarene complex in terms of the interaction between metal ion and host calixarene can also be important because it provides a guideline for use of a conformational template of the specific calixarene skeleton[5] for synthesis of polymeric sensory materials[6] as well as new calixarene derivatives.[7,8] In addition to the topic of structure of metal-calixarene complexes, the location of metal binding site has also interested several researchers who have published some reports on this subject.[9,10] Calixarene derivatives usually show ambidentate character, binding some metal ions in the calixarene basket formed by surrounding phenyl rings while others at the lower rim oxygen sites. J. M. Harrowfield *et al.* revealed by X-ray crystallography that the binding site of cesium ion with calix[4]arene in CH_3CN solution is located within the inclusive calixarene basket instead of being around the oxygen atoms,[9] while Shinkai *et al.* demonstrated that sodium ion, on the contrary, binds at the oxygen sites in THF

solution.[10] Several factors such as metal ion size, solvent polarity, *etc.* may account, partly or fully, for these differences but the exact reason is not fully understood yet.

Recently, among alkali metals, cesium has attracted particular attentions because it is a major important component of nuclear wastes which may pollute water and soil.[11,12] This has stimulated the studies on calixarenes which can act as separation and extraction reagents for this detrimental metal. Such studies included the synthesis of calix[4]arene based benzocrowns as a cesium selective fluorescent probe,[13] molecular dynamics study about cesium binding ability of calix[4]arene based macromolecules,[14] *etc.* Also, there have been numerous reports on the structure of Cs^+ complexes with calix[4]arene derivatives. B. A. Murray *et al.* reported the synthesis of calix[4]arene derivatives of cone conformation which retain the same conformation even after complexing with cesium.[15]

In contrast to the case of calix[4]arenes, not much has been reported on the complexation of cesium ion by their hexamer counterparts, which may be due to the fact that the latter have larger and more flexible cavities than their tetramer counterparts, thus being inherently more complex both structurally and functionally, despite the advantage that more functional groups can easily be substituted into them. Such lack of information regarding calix[6]arenes has prompted us to take up the investigation we report in this paper. For the study concerning the details of complexation of cesium ion by calix[6]arenes in solution phase, liquid

NMR spectroscopy provides a suitable tool since sharp NMR resonance lines are usually observed for ^{133}Cs ($I = 7/2$), in contrast to other alkali metal ions, due to its exceptionally small quadrupole moment ($Q = -3 \times 10^{-3}$ barn[5]).[16] In our present work complexation of cesium ion by *p-tert*-butylcalix[6]arene ethyl ester has been studied by observing the changes of chemical shift and lineshape of both ^{133}C and ^{1}H nmr lines in two different solvents, polar acetone-d_6 and nonpolar $CDCl_3$, at various temperatures. The nmr chemical shifts of ^{133}Cs in Cs$^+$-calix[6]arene derivatives complexes are found to depend strongly on the solvent property and the more polar solvent leads to the nmr lines observed at the lower fields. Calixarenes tend to dissolve better in non-polar solvents than in polar ones, while most metal salts used as guest are ionic and prefer polar solvents. Metal-calix complexes are, however, usually soluble in both polar and nonpolar solvents, which made our observations possible in both polar acetone-d_6 and nonpolar $CDCl_3$ solutions. In consideration of the solubility of cesium picrate and calix[6]arene ethyl ester in various solvents, we have chosen just the two solvents, $CDCl_3$ and acetone-d_6, for comparison.

Theory of Chemical Exchange between two Uncoupled Sites

In this section we briefly outline the theory of chemical exchange between two nonequivalent uncoupled sites, although it is very well established and its description can be found in standard NMR textbooks,[17] because we frequently invoke it into our discussion for quantitative results obtained in the present paper.

Consider a system hopping between two different states A and B.

$$\text{State } A \xrightleftharpoons[k_{ba}]{k_{ab}} \text{State } B \qquad (1)$$

where k_{ab} and k_{ba} are, respectively, the forward and reverse exchange rate from A to B and B to A; that is, the inverse of lifetime at the two states A and B shown in Eq. (1). The complex NMR spectrum is determined under slow passage condition by the following equations:

$$
\begin{aligned}
dM_A^+/dt &= i\gamma B_1 M_{Az} + i(\omega_A - \omega)M_A^+ - M_A^+/T_{2A} \\
&\quad - k_{ab}M_A^+ + k_{ba}M_B^+ \\
dM_B^+/dt &= i\gamma B_1 M_{Bz} + i(\omega_B - \omega)M_B^+ - M_B^+/T_{2B} \\
&\quad - k_{ba}M_B^+ + k_{ab}M_A^+
\end{aligned} \qquad (2)
$$

where M_A^+ and M_B^+ are, respectively, the transverse complex magnetization $M^+ \equiv M_x + iM_y$ developed at the state A and the state B while M_{Az} and M_{Bz} are the corresponding z-components of induced magnetization. And ω_A and ω_B denote, respectively, the Larmor frequency of the given spin at the two sates A and B and T_{2A} and T_{2B} are, respectively, the corresponding spin-spin relaxation time. Also γ and B_1 are, respectively, the magnetogyric ratio of the given spin and the

strength of irradiating *rf* field.

If steady state is reached, one may let $dM_A^+/dt = dM_B^+/dt = 0$ to have

$$
\begin{aligned}
[i(\omega_A - \omega) - 1/T_{2A} - k_{ab}]M_A^+ + k_{ba}M_B^+ &= -i\gamma B_1 M_{Az}^0 \\
k_{aa}M_A^+ + [i(\omega_B - \omega) - 1/T_{2B} - k_{ba}]M_B^+ &= -i\gamma B_1 M_{Bz}^0
\end{aligned} \qquad (3)
$$

where M_{Az}^0 and M_{Bz}^0 are, respectively, the equilibrium value of M_{Az} and M_{Bz}.

After sloving Eq. (3) with respect to M_A^+ and M_B^+ we can obtain the lineshape function from imaginary part of $M^+ \equiv M_A^+ + M_B^+$ and the result may be expressed as follows:

$$\Im m(M^+) = \gamma B_1 M_0 \frac{P[1 + \tau(p_B/T_{2A} + p_A/T_{2B})] + QR}{P^2 + Q^2} \qquad (4)$$

where p_A and p_B are, respectively, the probability of finding the given nucleus at the state A and the state B, and

$$P = \tau\left[\frac{1}{T_{2A}T_{2B}} - (\Delta\omega)^2 + \frac{1}{4}(\delta\omega)^2\right] + \frac{p_A}{T_{2A}} + \frac{p_B}{T_{2B}}, \qquad (5)$$

$$Q = \tau\left[\Delta\omega - \frac{1}{2}\delta\omega(p_A - p_B)\right], \qquad (6)$$

$$
\begin{aligned}
R &= \Delta\omega\left[1 + \tau\left(\frac{1}{T_{2A}} + \frac{1}{T_{2B}}\right)\right] + \frac{1}{2}\delta\omega\tau\left(\frac{1}{T_{2B}} - \frac{1}{T_{2A}}\right) \\
&\quad + \frac{1}{2}\delta\omega(p_A - p_B)
\end{aligned} \qquad (7)
$$

with

$$\tau = \frac{p_A}{k_{ba}} = \frac{p_B}{k_{ab}}, \quad \Delta\omega = \frac{1}{2}(\omega_A + \omega_B) - \omega, \quad \delta\omega = (\omega_A - \omega_B),$$

$$M_0 = M_{Az}^0 + M_{Bz}^0, \quad M_{Az}^0 = p_A M_0, \quad \text{and} \quad M_{Bz}^0 = p_B M_0. \quad (8)$$

By making use of Eq. (4) we can evaluate the lineshape for the exchanging system for a given set of the parameters involved. Or conversely, by least squares fitting of Eq. (4) with observed data through successive adjustment of the parameters involved we can find an adequate set of these parameters that produces the best fitting. To help this numerical fitting procedure be carried out more efficiently a mathematical routine based on the Marquadt algorithm is normally employed, as we have done in this work. The results of lineshape fitting and the thermodynamic parameters thereby deduced will be discussed in a later section.

NMR Titration Curves

The nmr titration experiments provide further insight into this problem in which the change of the chemical shift of a proton line is monitored as one gradually increases the concentration ratio of guest *vs*. host and the resultant titration curve is graphically fitted with that predicted on the basis of an assumed model of chemical exchange. If we assume the chemical exchange between free and complexed host molecules, the observed chemical shift of a proton line for

An NMR Study on Complexation of Cesium Ion

Bull. Korean Chem. Soc. **2004**, Vol. 25, No. 5   611
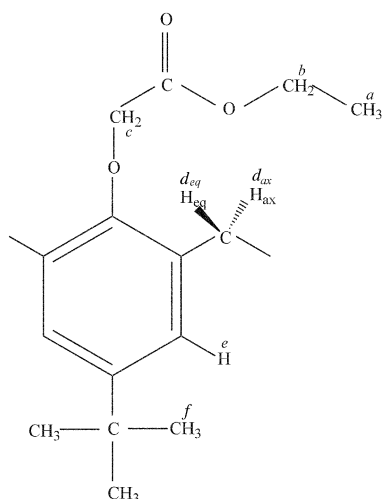
Scheme 1

this system may be expressed as

$$\delta_{obs} = \frac{1}{2}[(1 - \rho - 1/K_f[H]_t) + \{(1 - \rho - 1/K_f[H]_t)^2$$
$$+ 4/K_f[H]_t\}^{1/2}] \times (\delta_f - \delta_c) + \delta_c \qquad (9)$$

The symbols appearing in Eq. (9) have the following meanings:
  δ_{obs} : observed chemical shift of the monitored nucleus,
  δ_f : chemical shift of the monitored nucleus in the free host,
  δ_c : chemical shift of the monitored nucleus in the complexed host,
  $[H]_t$: total concentration of the host,
  $[G]_t$: total concentration of added guest,

  $\rho = [G]_t/[H]_t$

with K_f being the association constant for the host-guest complex under consideration.

We have obtained the titration curve by monitoring methyl proton *a* (Scheme 1) for CDCl$_3$ solution and *t*-butyl proton *f* (Scheme 1) for acetone-*d*$_6$ solution. Each titration curve was numerically fitted with Eq. (9) to obtain the formation constant K_f. The results are shown in Figure 1(a) and (b), respectively, from which it has been concluded that the calix[6]arene ethyl ester forms a 1 : 1 complex with cesium ion both in CDCl$_3$ and in acetone-*d*$_6$. The values estimated at various temperatures are also listed in Table 1. The magnitude of values was found to be of the order of to over the temperature range of experiment (see Table 1), indicating that the formation of complex between the calixarene host and Cs$^+$ ion is strongly favored in both CDCl$_3$ and acetone-*d*$_6$ solvent. The larger K_f value for CDCl$_3$ indicates that cesium ion is more tightly held by the calixarene host (and, thus, the resultant complex is more stable) in CDCl$_3$ than in acetone-*d*$_6$. This difference may qualitatively be understood on the basis of difference in polarity of the two solvents, considering that more polar acetone-*d*$_6$ molecules are expected to be more competitive in attracting Cs$^+$ ion away from the calixarene host than less polar CDCl$_3$ molecules. From
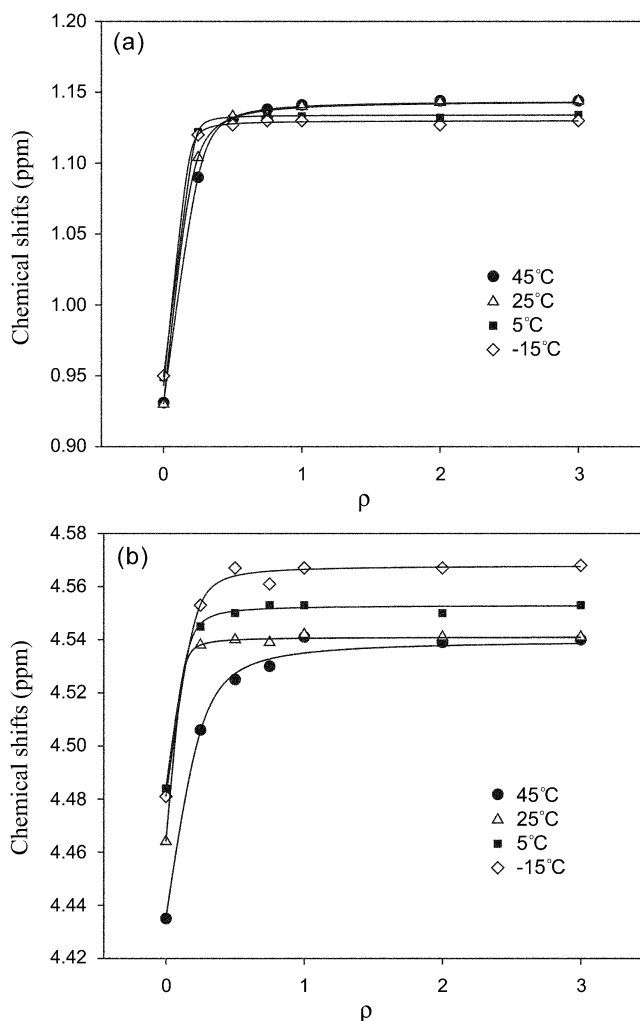

Figure 1. Plots of chemical shifts of (a) *t*-butyl proton in acetone and (b) ether proton in CDCl$_3$ as a function of guest/host ratio at several different temperatures.

Table 1. Association constants and thermodynamic parameters for complexation in acetone-*d*$_6$ and CDCl$_3$ solutions

		Acetone-*d*$_6$	CDCl$_3$
log K_f	45 °C	3.00	3.83
	25 °C	3.30	3.94
	5 °C	3.44	4.08
	-15 °C	3.70	4.20
ΔH^0 (kJ/mol)		-17.46	-9.62
ΔS^0 (J/mol K)		3.28	43.19
ΔG^0_{298} (kJ/mol)		-18.44	-22.49

measured values of we could first estimate ΔG^0, standard free energy change of complex formation, on the basis of the relation $\Delta G^0 = -RT \ln K_f$. Plot of log K_f against inverse of temperature, $1/T$, shows linear relationship for both CDCl$_3$ and acetone-*d*$_6$ solution, from which ΔH^0, standard enthalpy change of complex formation, could be estimated.[18] These, then, led us to ΔS^0, standard entropy change of complex formation at the given temperature. These are tabulated in Table 1.

Experiments and Calculations

The *p*-tert-butylcalix[6]arene ethyl ester were prepared following the reported procedures. Both $CDCl_3$ and acetone-d_6 (of the nmr solvent grade) were purchased from Aldrich and Sigma Chemical Co. and used without further purification. All the NMR spectra were obtained on Varian VXR-200S and Jeol YH400 spectrometer.

For NMR titration experiment the chemical shifts of protons in host molecule were observed as a function of ρ (= [guest]/[host]) at four different temperatures [See Figure 1(a) and Figure 2(b)]. The host concentration was fixed at 0.02 M and that of guest was varied over the range of 0 to 0.06 M.

Temperature was maintained to the accuracy of ± 0.5 °C throughout the variable temperature experiments with the aid of precalibrated variable temperature controller equipped with the NMR spectrometer. All the fitting calculations determining the parameters involved in this work, such as K_f and the rate constants, were carried out on an IBM PC using a least-squares fitting program employing the Marquadt algorithm.

Results and Discussion

The nmr measurements for protons in *p*-tert-butylcalix-[6]arene ethyl ester complexed with various alkali metal ions, Li^+, Na^+, K^+, Rb^+, Cs^+, were carried out both in $CDCl_3$ and in acetone-d_6 at several temperatures. Except for acetone-d_6, the polar solvents tested were found to give only low sensitivity spectra of phenyl protons because of low solubility of calix[6]arene and metal picrates in these solvents. Hence we were forced to perform the NMR experiments in only two solvents, $CDCl_3$ and acetone-d_6, each as representative nonpolar and polar solvent. In $CDCl_3$, among alkali ions, only cesium was found to give a well resolved ^{1}H NMR spectrum of the characteristic *AB*-type pattern for methylene protons *d* (see Scheme 1) over the temperature range of 238-313 K as shown in Figure 2 and 3, indicating the presence of *p-tert*-butylcalix[6]arene ethyl ester complexed with cesium ion in the form of *cone* conformation.[1] In acetone-d_6, similar *AB* pattern for methylene protons *d* was also observed to suggest that the Cs-calix-[6]arene complex assume a *cone* conformation in this solvent as well. Furthermore, observed Cs NMR spectrum indicates that the complex assume an *endo* form since the Cs resonance signal in Cs-calix[6]arene complex, in contrast to the report by U.C. Meier and C. Detellier for Cs-calix[4]-arene complex,[15] is found at nearly 80 ppm upfield from that of the solvated Cs^+ ion due to the strong shielding effect caused by benzene ring current and the Cs-π interaction inside the calixarene cavity (Figure 7).

However, the most conspicuous feature of proton NMR spectrum for our Cs^+-calix[6] complex system was that two separate peaks of equal intensity could be observed for phenyl ring protons at low temperatures in both acetone-d_6 and $CDCl_3$, as shown in Figures 2 and 3. The authors were at
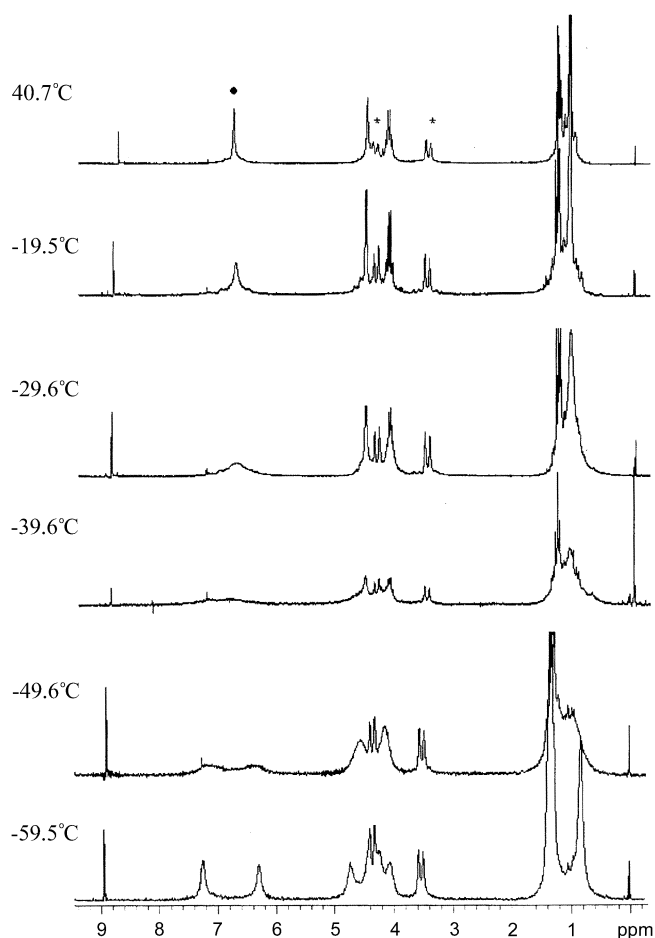

Figure 2. Proton spectra taken at various temperatures in $CDCl_3$ solution. Methylene proton *d* is marked by * and phenyl ring proton *e* by •.

first baffled by this finding because no previous encounter with such observation had ever been known or reported. One may easily be tempted to interpret these two peaks as arising from phenyl ring protons, respectively, in free calixarene and complexed one. However, this possibility could immediately be ruled out because the spectral feature did not change even in the presence of excessive Cs^+ concentration (See Figure 4). As reported in this work, the association constant for this system is fairly large and, therefore, in the presence of excess guest the concentration of free calixarene must be very low. Furthermore, when excess host was added, a separate peak corresponding to free calixarene was found to appear between these two peaks (see Figure 5). Therefore, it could be concluded that these two proton peaks originate from two different kinds of phenyl ring protons in the Cs^+-calix complex itself. In order to gain further insight into the nature of these proton peaks we also observed the lineshape change of the two phenyl ring proton peaks as a function of temperature, which showed a typical coalescence pattern of absorption lines for chemical exchange between two uncoupled sites of equal population (Figures 2 and 3). This suggests that the complex itself interconverts between two equivalent forms in which six phenyl rings are tilted alternately toward and away from the calixaene cavity as
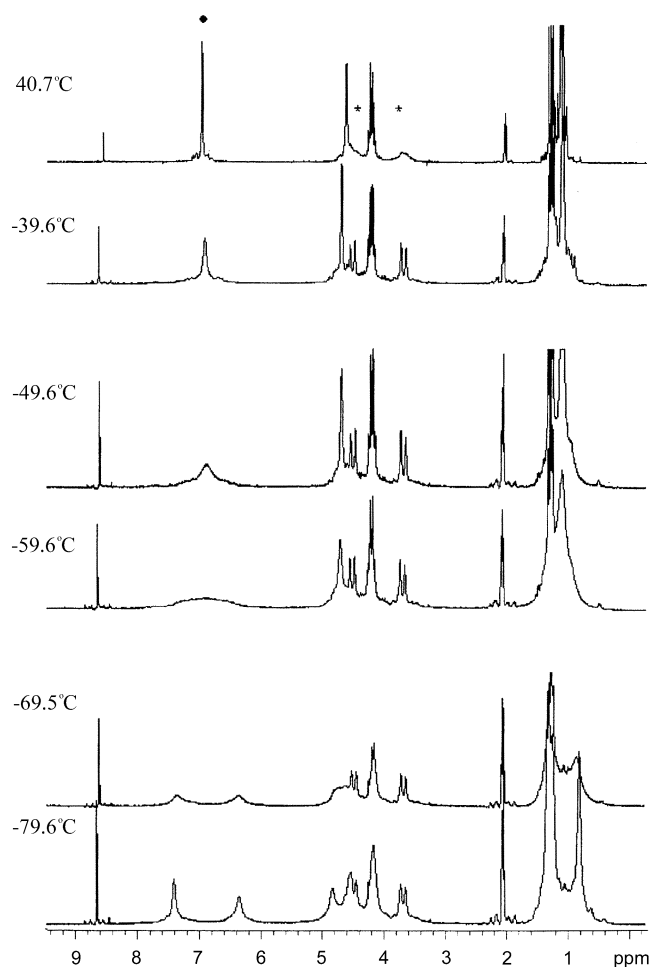
Figure 3. Proton spectra taken at various temperatures in acetone-d_6 solution. Methylene proton **d** is marked by ∗ and phenyl ring proton **e** is ●.
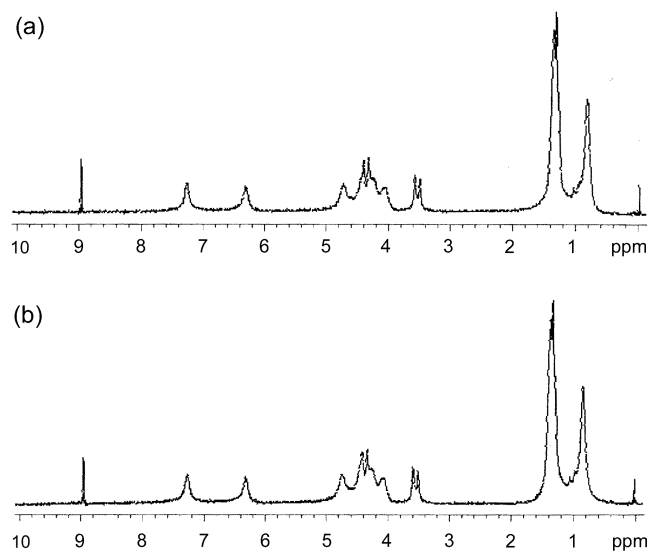

Figure 4. Proton spectra taken at the mixing ratio of (a) Calix[6] : Cs = 1 : 1 and (b) Calix[6] : Cs = 1 : 2 at -60 °C in CDCl₃ solution.

Figure 5. Proton spectra taken at the mixing ratio of (a) Calix[6] : Cs = 4 : 1 at 25 °C and (b) Calix[6] : Cs = 1 : 1 at -60 °C both in CDCl₃. Phenyl ring proton of complexed calixarene is marked by ● and those of free calixarene by ○ .

Scheme 2

Scheme 3

Scheme 4

shown in Scheme 2. This structure looks somewhat similar to 1,3,5-alternate form of free calixarene, but unlike the latter it has a C_3 symmetry element but no inversion center;
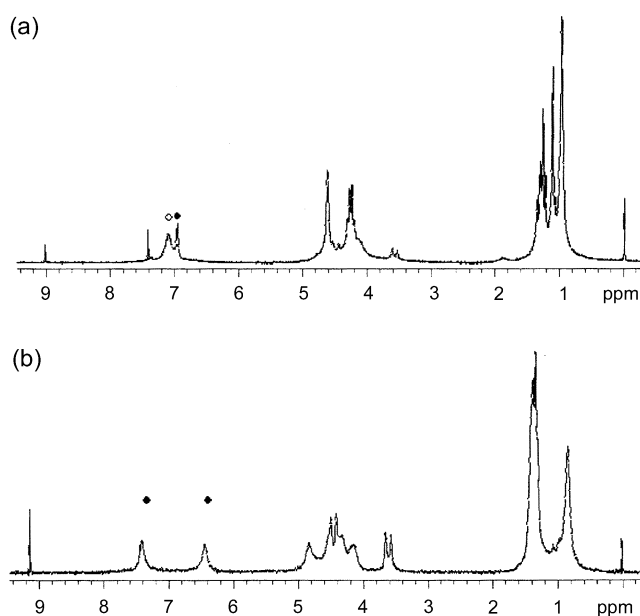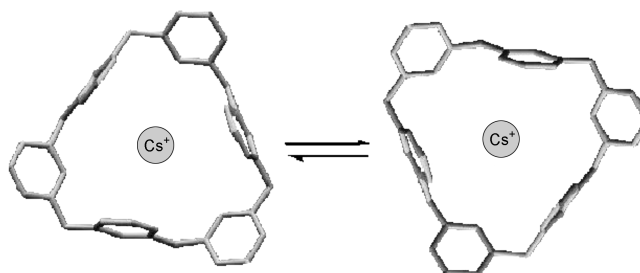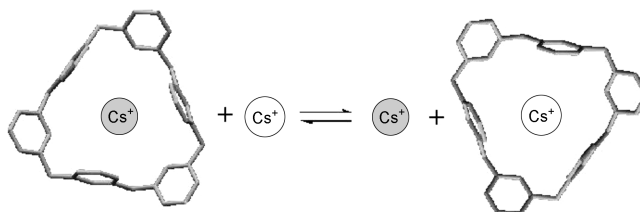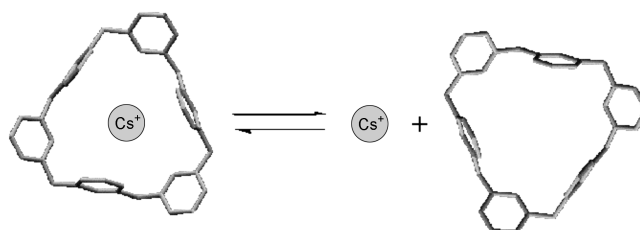
that is, it has no S_6 symmetry element. In accordance with this the *AB* pattern of metyl protons **d** could also be seen to collapse as the complex undergoes interconversion (Figure
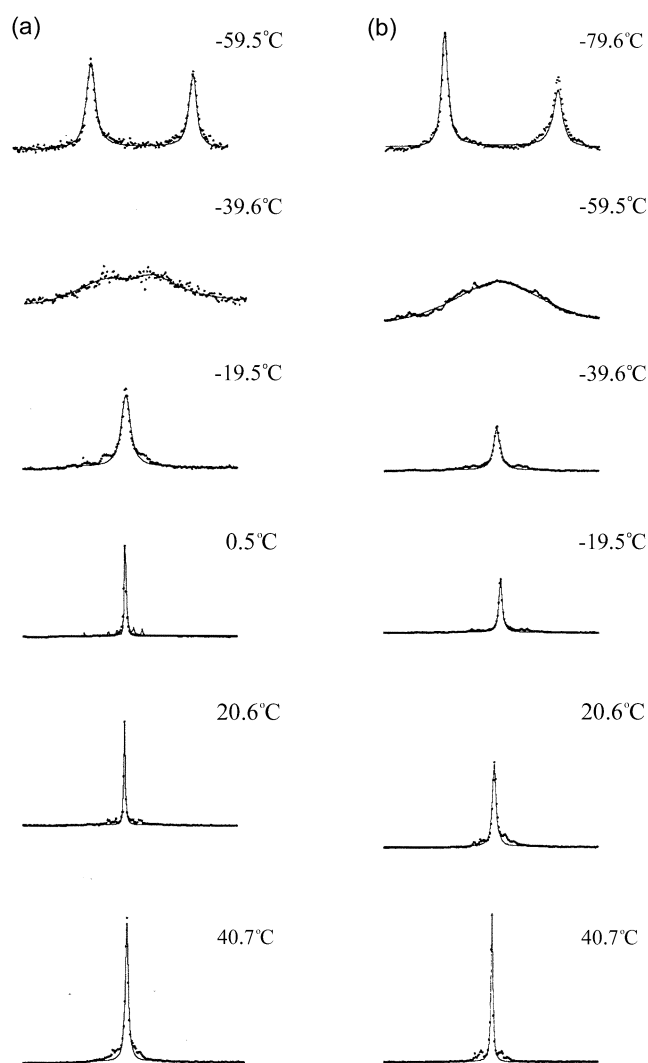
Figure 6. Change of line shape of phenyl protons in (a) CDCl$_3$ and (b) acetone solution (● experimental, ‐ calculated).

Figure 7. Change of line shape of cesium in acetone solution (● experimental, ‐ calculated).

3). Of the two phenyl ring proton peaks the one at upper field looks slightly more broadened than the other, indicating that the former protons are located at a closer distance to Cs ion than the latter. This observation bolsters that our proposed model is quite reasonable. The fact that the cesium NMR spectrum shows only a somewhat broadened single peak for the complexed cesium also supports that the two forms involved in chemical exchange are indeed equivalent. (Figure 7).

In the meantime the cesium spectrum shows that chemical exchange can also take place between bound (or complexed) cesium and free(or solvated) one (Figure 7). This exchange is considered to take place *via* an exchange mechanism shown in Scheme 3. Another exchange process shown in Scheme 4 may also be considered; however, this is considered to play only a minor role since the concentration of free calixarene would be very low in the presence of excess cesium concentration as thevalues indicate. In order to enhance the accuracy of lineshape fittings we had to increase the intensity of the free (or solvated) Cs$^+$ peak by adding
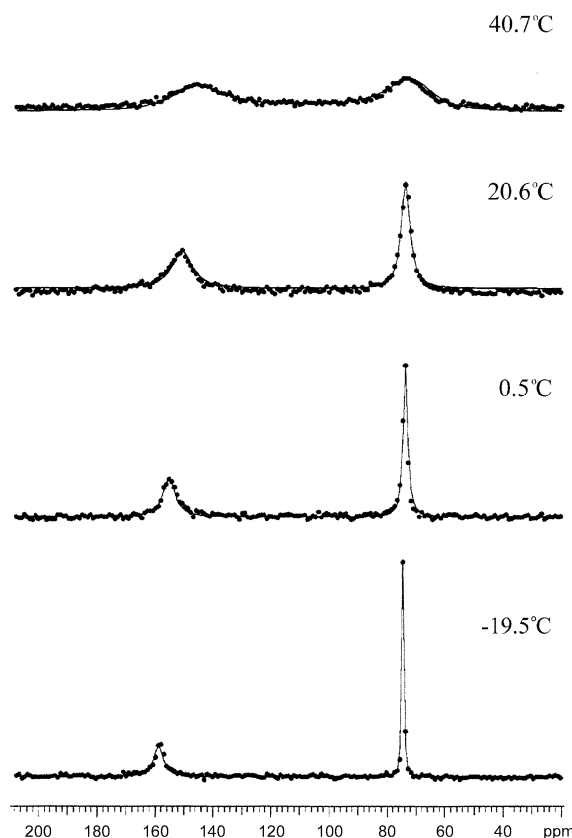
excess amount of cesium picrate since for the host/guest ratio of 1 : 1 this peak was not strong enough for precise numerical analysis. In our experiment in an acetone solution we added an excess amount of the guest. This certainly enhanced the weak intensity of the solvated Cs$^+$ peak to enable better numerical lineshape fitting for acetone solution; however, this strategy has failed to improve the situation in CDCl$_3$, where addition of the salt beyond the ratio of 1 : 1 caused the precipitation of the added cesium picrate, making the precise measurement of exchange rate of Cs in CDCl$_3$ solution impractical.

For actual lineshape fittings we have treated our system as if it undergoes two separate independent two-site exchange processes, rather than undergoing a simultaneous three-site exchange process, because these two processes were found to have much different exchange rate.

The exchange process in Scheme 2 could directly be dealt with for both CDCl$_3$ and acetone-d_6 solution on the basis of two-site exchange theory described in the previous section. However, the lineshape fitting for Cs exchange according to Scheme 3 was applied only to the acetone-d_6 solution data because for CDCl$_3$ solution the intensity of free (or solvated) Cs ions could not be made strong enough for adequate fitting. The results of the lineshape fitting are graphically presented in Figures 6 and 7, and the dynamical parameters thereby deduced are also presented in Table 2. Plots of lnk_1, lnk_2 and lnk_{-2} against inverse temperature yielded the straight lines, from which we could estimate the apparent
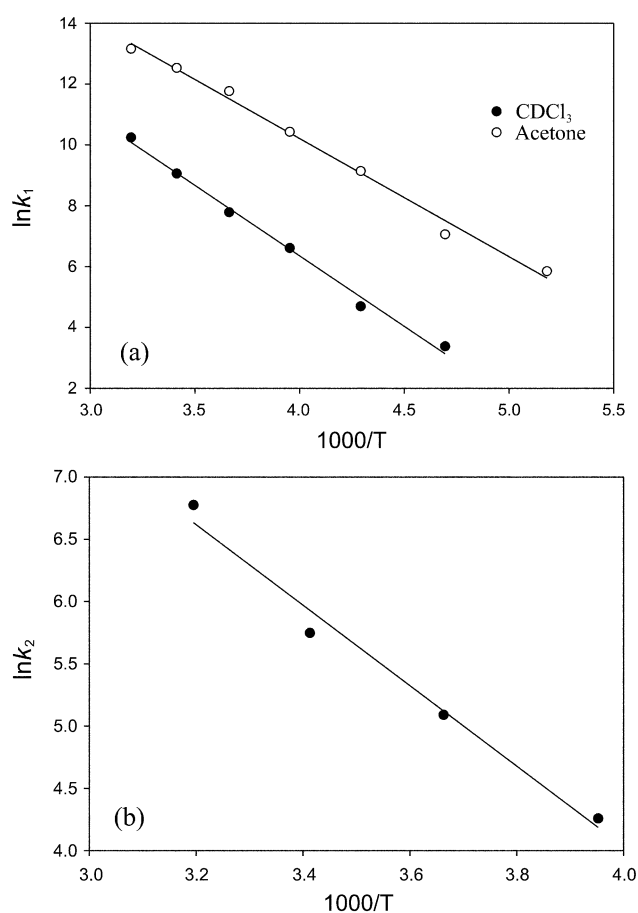
Figure 8. (a) The Arrhenius type plot for phenyl proton data in CDCl₃ and acetone-d_6 solution; (b) The Arrhenius type plot for cesium spectral data in acetone solution.

activation energies for the process represented by Scheme 2 and 3, respectively (Figure 8).

As we see from these results, the rate of the process shown in Scheme 2 is much faster than that of Scheme 3 in acetone solution, indicating that our treatment of these two processes as nearly independent is valid. It goes without saying that the same will also hold for the case of CDCl₃ as well. One thing

Table 2. (a) Rate constants k_1 and k_{-1} for the two site exchange in (i) CDCl₃ and (ii) acetone-d_6 calculated from phenyl proton line shape in unit of sec⁻¹, (b) Site exchange rate constants k_2 and k_{-2} for the two site exchange in acetone-d_6 calculated from cesium line shape in unit of sec⁻¹

(a)

	-79.5 °C	-59.5 °C	-39.6 °C	-19.5 °C	0.5 °C	20.6 °C	40.7 °C
(i)	*	30	110	746	2417	8625	28185
(ii)	348	1169	9365	33906	129145	277914	520710

(b)

	-19.5 °C	0.5 °C	20.6 °C	40.7 °C
k_2	72	168	320	1449
k_{-2}	122	262	481	1460

Table 3. (a) Activation parameters for complexation in CDCl₃ and acetone-d_6 calculated from Eyring equation using k_1. (b) Activation parameters for complexation in acetone-d_6 calculated from Eyring equation for k_2 (I) and k_{-2} (II)

(a)

Activation Parameters	CDCl₃	Acetone-d_6
E_a (kJ/mol)	38.5	32.3
$\Delta H^{\ddagger}$ (kJ/mol)	36.4	30.2
$\Delta S^{\ddagger}$ (J/mol·K)	-45.2	-37.7
$\Delta G^{\ddagger}_{298}$ (kJ/mol)	49.9	41.4

(b)

Activation Parameters	**I**	**II**
E_a (kJ/mol)	31.4	26.3
$\Delta H^{\ddagger}$ (kJ/mol)	29.0	23.9
$\Delta S^{\ddagger}$ (J/mol·K)	-94.5	-109.8
$\Delta G^{\ddagger}_{298}$ (kJ/mol)	57.2	56.6

we have to note here is that k_1, the site exchange rate constant for Scheme 2, a first-order reaction, may be regarded as the reaction rate constant itself, but this is not the case for k_2 and k_{-2}, the site exchange rates for the process shown in Scheme 3, because the exchange process expressed by Scheme 3 is at least a second-order reaction and depends on the concentration of Cs⁺ and the host present at equilibrium. If the process in Scheme 3 is a truly bimolecular elementary process, its reaction rate constants k_2' and k_{-2}' would be related to the site exchange rates k_2 and k_{-2}, respectively, as follows:

$$k_2 = k_2' \, [\text{Cs}^+] \text{ and } k_{-2} = k_{-2}' \, [\text{Complex}] \tag{10}$$

where [Cs⁺] and [Complex] are, respectively, the concentrations of free (or solvated) cesium ion and the Cs-calix complex present in the solution.

Since the forward and the reverse reaction rate constants k_2' and k_{-2}' are equal in magnitude, we have

$$\frac{k_{-2}}{k_2} = \frac{[\text{Complex}]}{[\text{Cs}^+]} \tag{11}$$

As temperature rises, the complex will dissociate more readily, increasing [Cs⁺] while decreasing [Complex] and the ratio expressed by Eq. (11) will decrease. This prediction was deduced in the approximation that Scheme 3 is a dominant process for the site exchange for Cs⁺ ion but correctly explains the trend shown by data in Table 2(b) and by Figure 7, at least qualitatively. This makes us well convinced that CDCl₃ solution would show a similar trend, although we were not successful in measuring precise data for lineshape change in the latter solution.

References

1. (a) Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: Cambridge, 1989. (b) Vicense, J.; Böhmer, V. *Calixarenes, A Versatile Class of Macrocyclic Compounds*; Kluwer: Dordrecht, 1990.
2. Valeur, B.; Leray, I. *Coord. Chem. Rev.* **1991**, *205*, 3.
3. Casnati, A.; Fischer, C.; Guardigli, M.; Isernia, A.; Manet, I.; Sabbatini, N.; Ungaro, R. *J. Chem. Soc., Perkin Trans. 2* **1996**, 395.
4. Ludwig, R. *Fresenius J. Anal. Chemt.* **2000**, *367*, 103.
5. Shinkai, S. *Tetrahedron* **1993**, *49*, 8933.
6. Marsella, M. J.; Newland, R. J.; Caroll, P. J.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 9842.
7. Consoli, G. M. L.; Cunsolo, F.; Geraci, C.; Gavuzzo, En.; Neri, P. *Tetrahedron Letters* **2002**, *43*, 1209.
8. Kang, S. O.; Nam, K. C. *Bull. Korean Chem. Soc.* **2002**, *23*, 640.
9. Harrowfield, J. M.; Ogden, M. I.; Richmond, W. R.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1991**, 115.
10. Yamada, A.; Murase, T.; Kikukawa, K.; Arimura, T.; Shinkai, S. *J. Chem. Soc. Perkin Trans. 2* **1991**, 77.
11. Beasley, T. M.; Jennings, D. *Environ. Sci. Technol.* **1984**, *18*, 207.
12. Alberts, J. J.; Wahlgren, M. A. *Environ. Sci. Technol.* **1981**, *15*, 94.
13. Talanova, G. G.; Elkarim, N. S. A.; Talanov, V. S.; Bartsch, R. A. *Anal. Chem.* **1999**, *71*, 3106.
14. Lamare, V.; Dozol, J. F.; Fuangswasdi, S.; Arnaud-Neu, F.; Thuery, P.; Nierlich, M.; Asfari, Z.; Vicens, J. *J. Chem. Soc., Perkin Trans. 2* **1999**, 271.
15. Creaven, B. S.; Deasy, M.; Gallagher, J. F.; McGinley, J.; Murray, B. A. *Tetrahedron* **2001**, *57*, 8883.
16. Brevard, C.; Granger, P. *Handbook of High Regolution Multinuclear NMR*; John Wiley & Sons: New York, 1981.
17. Sandström, J. *Dynamic NMR Spectroscopy*; Acedemic Press: London, 1981.
18. de Boer, J. A. A.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1985**, *107*, 5347.