

Conductance Study of the Complexation of Substituted and Lariat 16-Crown-5 Derivatives with Alkali Metal Ions in Nonaqueous Solvents

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Abstract. Formation constants (K_{ML}) of 1:1 complexes of 15-(2,5-dioxaheptyl)-15-methyl-16-crown-5 (L16C5) and 15,15-dimethyl-16-crown-5 (DM16C5) with alkali metal ions were determined in acetonitrile (AN) and propylene carbonate (PC) by conductometry at 25°C. Except for the case of Li^+ – and K^+ –16C5 complexes in PC, the selectivity sequences of L16C5 and DM16C5 are identical with those of the parent crown ether 16-crown-5 (16C5) regardless of the solvent (AN, PC, methanol) ($\text{Na}^+ > \text{Li}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$), which show the size-fit correlation. The selectivities of L16C5 and DM16C5 for the alkali metal ions are governed not by the sidearms but by the cavity size. The stability of the crown ether complex is dependent not on the dielectric constant but largely on the donor number of the solvent. The $K_{ML}(\text{M}_1^+)/K_{ML}(\text{M}_2^+)$ ratio of L16C5 or 16C5 varies very much with the solvent in the cases of $\text{M}_1 = \text{Na}$, $\text{M}_2 = \text{K}$ and $\text{M}_1 = \text{Na}$, $\text{M}_2 = \text{Li}$, but that of DM16C5 is almost constant regardless of the solvent.

Key words. Solvent and lariat effect, 16-crown-5 derivatives, alkali metal ions, complex stability, conductometry.

1. Introduction

Lariat crown ethers contain a crown ring to which cation-ligating sidearms are introduced. In general, their complexes show additional stability compared with those of the reference crown ethers [1]. It was reported in a previous paper [2] that slightly reduced complex stabilities and selectivities of 15-(2,5-dioxaheptyl)-15-methyl-16-crown-5 (L16C5) (Figure 1) were observed from a conductance study in methanol, which conflicts with the basic concept of the lariat effect and may require further verification of its applicability to the other ligand and solvent systems. In this work, in order to study solvent effects on the role of the cation-ligating sidearm of L16C5 in the complexing ability and the selectivity, complex-formation constants

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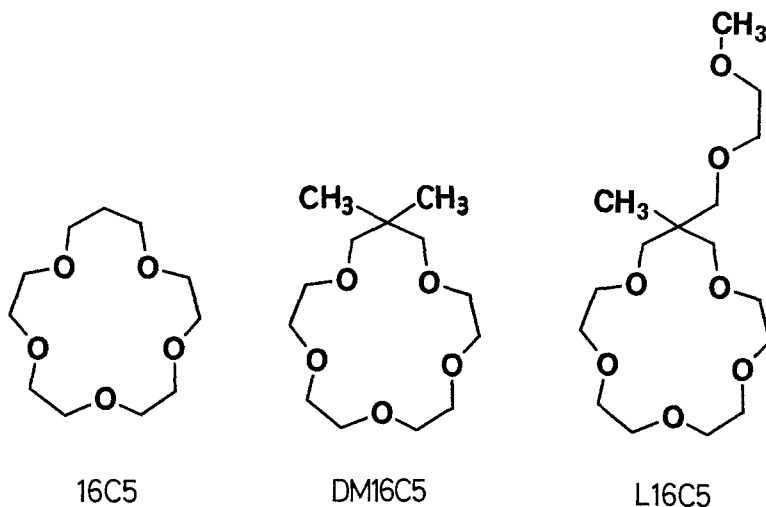


Fig. 1. Structures of 16C5, DM16C5, and L16C5.

of L16C5 and 15,15-dimethyl-16-crown-5 (DM16C5) (Figure 1) with alkali metal ions were determined in acetonitrile (AN) and propylene carbonate (PC) by conductometry at 25°C, and were compared with those in methanol. The solvents were chosen for their low basicities and comparatively high dielectric constants.

2. Experimental

2.1. MATERIALS

The preparation of DM16C5 and L16C5 has been described elsewhere [3]. Extremely pure RbCl and CsCl were purchased from Merck Japan Ltd. RbClO₄ and CsClO₄ were prepared by adding a small excess of HClO₄ to aqueous solutions of RbCl and CsCl, respectively. Lithium, sodium, and potassium perchlorates were obtained from Merck Japan Ltd. All the perchlorates were recrystallized three times from deionized water and, prior to use, dried at 150°C in a vacuum oven.

The method of purification of AN [4] and PC [5] has been described. The middle 70% of the distillate of the solvents was used. Conductivities of the purified AN and PC were less than 2×10^{-7} and $4 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$, respectively.

2.2. APPARATUS AND PROCEDURE

The conductance measurements were conducted using a Fuso conductivity apparatus, model 362A, at $25 \pm 0.005^\circ\text{C}$. Two cells were used with cell constants of 0.21034 ± 0.00003 and $0.090348 \pm 0.000002 \text{cm}^{-1}$.

The experimental procedure to obtain the complex-formation constants of crown ethers with alkali metal ions is as follows. 200 mL of a solution of an alkali metal salt (4.7×10^{-4} – $3.5 \times 10^{-3} \text{M}$; $1 \text{M} = 1 \text{mol dm}^{-3}$) was placed in the cell (volume 300 mL) and its resistance measured. A step-by-step increase in the crown ether

concentration was effected by a rapid transfer from the solution of the crown ether (3.5×10^{-3} – 2.0×10^{-2} M) to the cell using a pipet under a nitrogen atmosphere, until the total concentration of the crown ether was about five times as large as that of the alkali metal salt. The resistance of the solution in the cell was remeasured after each transfer.

3. Results and Discussion

The molar conductivity, Λ , vs. $[L]_t/[M]_t$ plots of DM16C5 and L16C5 for PC are given in Figures 2 and 3, respectively, $[L]_t$ and $[M]_t$ denoting total concentrations of a crown ether and an alkali metal, respectively. The experimental plots for AN are similar, and so they have been omitted. In spite of an increase in the crown ether concentration, a negligible change in Λ is found for the L16C5–CsClO₄–PC and –AN systems. Therefore, the determination of complex-formation constants with L16C5 of Cs⁺ in PC and AN was impossible. It can be considered from this that the Cs⁺ complex is unstable or the mobilities of the free Cs⁺ ion and the L16C5 complex are equal. An increase in Λ with an increase in the $[L]_t/[M]_t$ value is observed for the LiClO₄–DM16C5 and –L16C5 systems in PC. The Li⁺ complex is more mobile than the free Li⁺ ion. All the other systems show a decrease in Λ with an increase in the $[L]_t/[M]_t$ value. This indicates that the mobility of the resulting crown ether complex is lower than that of the corresponding free alkali metal ion. For the LiClO₄–L16C5–AN and all the NaClO₄ systems, the slope of each curve changes sharply at $[L]_t/[M]_t = 1$. A stable 1:1 crown ether–alkali metal ion complex is formed in these systems.

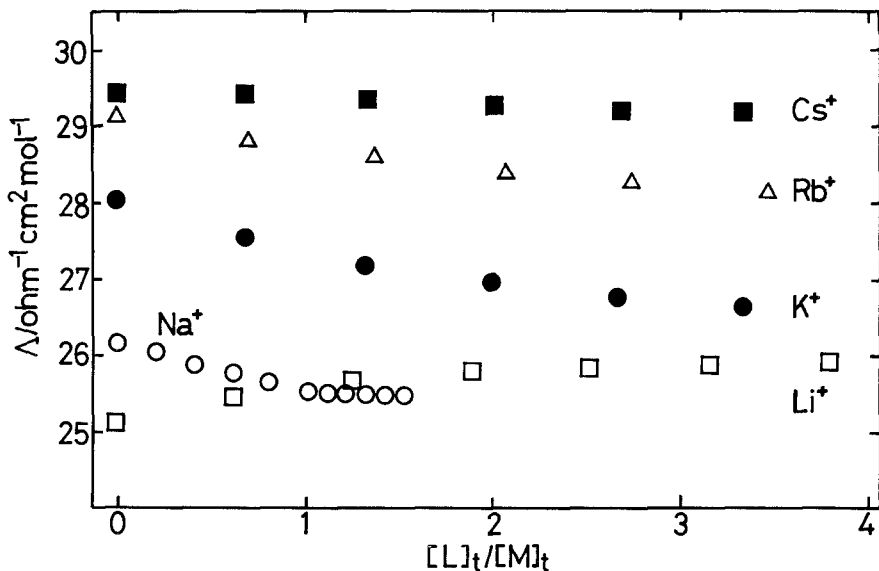


Fig. 2. Λ vs. $[L]_t/[M]_t$ curves for DM16C5–alkali metal perchlorate systems in PC.

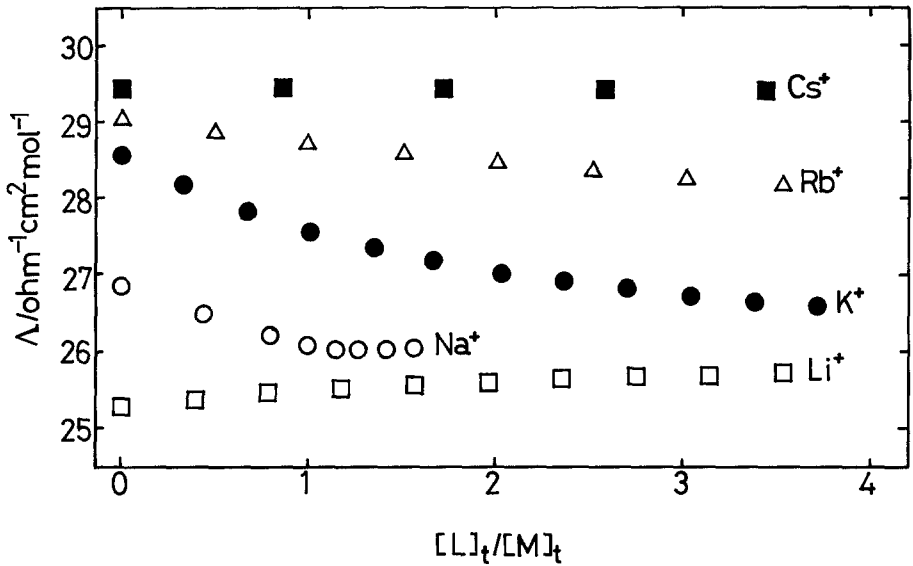
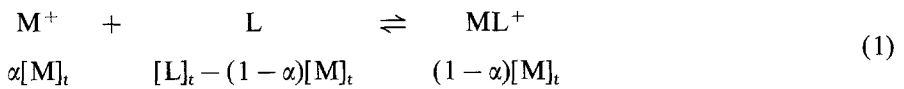


Fig. 3. Λ vs. $[L]_t/[M]_t$ curves for L16C5-alkali metal perchlorate systems in PC.

When a crown ether (L) forms a 1 : 1 complex with a univalent metal ion (M^+), the equilibrium equation is written as



where α is the fraction of free univalent metal ion. The complex-formation constant, K_{ML} , is defined by

$$K_{ML} = \frac{[ML^+]}{[M^+][L]} \quad (2)$$

$$= (1 - \alpha)/\alpha[L].$$

The observed conductivity, κ , is given by

$$\kappa = \kappa_{MA} + \kappa_{MLA} \quad (3)$$

where A^- is an anion, and κ_{MA} and κ_{MLA} denote the conductivities of the univalent metal salt and the univalent metal crown ether salt, respectively. The molar conductivities are written as

$$\Lambda_{MA} = \kappa_{MA}/[M^+] \quad (4)$$

$$= \kappa_{MA}/\alpha[M]_t$$

$$\Lambda_{MLA} = \kappa_{MLA}/[ML^+] \quad (5)$$

$$= \kappa_{MLA}/(1 - \alpha)[M]_t$$

Λ_{MA} and Λ_{MLA} being the molar conductivities of the univalent metal salt and the univalent metal crown ether salt, respectively. As a consequence of Equations 4 and

5, Equation 3 can be transformed into

$$\begin{aligned}\Lambda &= \kappa/[M]_t \\ &= \alpha\Lambda_{MA} + (1 - \alpha)\Lambda_{MLA}.\end{aligned}\quad (6)$$

Equation 2 can be transformed via Equation 6 to give

$$K_{ML} = (\Lambda_{MA} - \Lambda)/(\Lambda - \Lambda_{MLA})[L], \quad (7)$$

where $[L] = [L]_t - [M]_t(\Lambda_{MA} - \Lambda)/(\Lambda_{MA} - \Lambda_{MLA})$. The procedure for obtaining the K_{ML} value is as follows. The Λ_{MLA} value is estimated from the Λ values at the points of large $[L]_t$ to $[M]_t$ ratios. The K_{ML} value of Equation 7 is calculated from this Λ_{MLA} value. The actual K_{ML} and Λ_{MLA} values were obtained by a successive approximation method. By way of example, the actual Λ_{MLA} values of DM16C5- and L16C5-alkali metal chloride complexes in methanol at 25°C are given in Table I [6]. The actual $\log K_{ML}$ values of DM16C5- and L16C5-alkali metal ion complexes in AN and PC at 25°C are listed in Table II, together with the literature values [6].

In each case of K, Rb, and Cs, the $[M]_t$ value of L16C5 is slightly smaller than that of DM16C5; but, the Λ_{MLA} value of L16C5 is much smaller than that of DM16C5 (Table I), indicating that the L16C5 complex is less mobile than the corresponding DM16C5 complex in methanol. This is attributed to the fact that L16C5 is larger in size than DM16C5.

For L16C5, the Λ_{MLA} values of Na and K, the $[M]_t$ values of which are almost the same, are nearly equal. This shows that although K^+ is larger than the 16C5 cavity, K^+ as well as Na^+ , which has the most suitable size for the 16C5 cavity, is effectively screened by the L16C5 and that the moving entities in methanol of the L16C5 complexes with Na^+ and K^+ are almost the same in size.

Plots of the $\log K_{ML}$ vs. ionic radius (r_c) of an alkali metal are given in Figures 4-6. The selectivity sequences of L16C5, DM16C5, and 16C5 for the alkali metal ions are identical regardless of solvent except for the case of the Li^+ - and K^+ -16C5 complexes in PC ($Na^+ > Li^+ > K^+ > Rb^+ > Cs^+$). The selectivities show the size-fit correlation (cavity radius of 16C5 = 0.9 Å [8]). Every crown ether exhibits

Table I. Λ_{MLA} values in CH_3OH at 25°C.

L	MA	Λ_{MLA} ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)	$[M]_t \times 10^4$ (mol dm^{-3})
DM16C5	NaCl	88.960	4.8582
	KCl	85.589	15.463
	RbCl	86.671	9.3724
	CsCl	91.994	8.4140
L16C5	NaCl	76.448	15.299
	KCl	76.555	15.328
	RbCl	79.470	9.1426
	CsCl	86.804	8.3860

Table II. Log K_{ML} values of complexes of DM16C5, L16C5, and 16C5 with alkali metal ions in nonaqueous solvents at 25°C^a

Alkali metal ion	Ionic radius ^b (Å)	AN			PC			CH ₃ OH		
		AN			PC			CH ₃ OH		
		L16C5	DM16C5	16C5 [7]	L16C5	DM16C5	16C5 [7]	L16C5 [2]	DM16C5 [2]	16C5 [7]
Li ⁺	0.74	4.45 ± 0.05	4.1 ± 0.1	4.4 ₈	3.06 ± 0.04	3.13 ± 0.03	3.2 ₅	—	—	—
Na ⁺	1.02	5.0 ± 0.1	4.3 ± 0.1	5.3 ₉	5.2 ± 0.1	4.0 ± 0.1	5.7	3.53 ± 0.01	3.73 ± 0.02	4.10
K ⁺	1.38	3.06 ± 0.02	3.13 ± 0.02	3.5 ₇	2.88 ± 0.02	2.89 ± 0.03	3.3 ₄	2.43 ± 0.01	2.54 ± 0.01	2.9 ₂
Rb ⁺	1.49	2.34 ± 0.03	2.64 ± 0.04	2.9 ₄	2.05 ± 0.03	2.14 ± 0.03	2.5 ₉	2.05 ± 0.03	2.06 ± 0.04	2.4 ₆
Cs ⁺	1.70	—	2.40 ± 0.03	2.3 ₈	—	1.61 ± 0.06	2.1 ₇	1.57 ± 0.05	1.73 ± 0.03	2.0 ₉

^a Each log K_{ML} value is the average of 5–7 measurements. The uncertainties are the standard deviations.^b R. D. Shannon and C. T. Prewitt: *Acta Crystallogr., Sect. B*, **25**, 925 (1969).

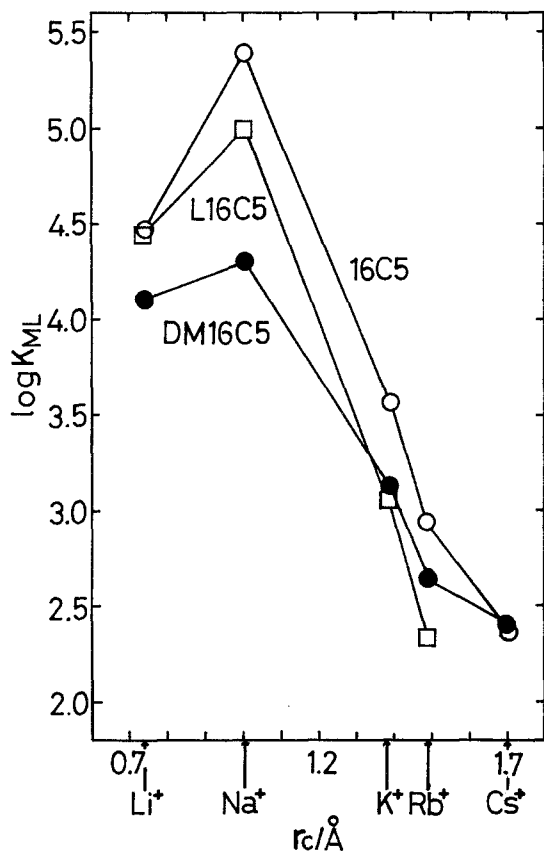


Fig. 4. $\log K_{ML}$ vs. r_c plots for AN.

the highest selectivity for Na^+ . From DM16C5 to L16C5, the selectivity for neighboring alkali metal ions in the periodic table is enhanced in AN and PC, but not always in methanol. No remarkable positive sidearm effect is observed on the selectivity for neighboring alkali metal ions for L16C5 and 16C5. For AN and PC, from the slopes of $\log K_{ML}$ vs. r_c plots between neighboring alkali metal ions (Figures 4 and 5), the selectivity of DM16C5 for neighboring alkali metal ions is the lowest among the three crown ethers except for the case of Rb^+ and Cs^+ in PC. Figure 6 shows that the plots of the three crown ethers are roughly parallel to one another. This indicates that the selectivities of the crown ethers in methanol are almost the same. The selectivities of L16C5 and DM16C5 for the alkali metal ions are governed not by the sidearms but by the cavity size.

16C5 forms the most stable complex with a given alkali metal ion among the three crown ethers. For L16C5 and DM16C5, a positive lariat effect is found only for the cases of a size-fitting cation, Na^+ , in AN and PC and a size-misfitting smaller cation, Li^+ , in AN; the most striking positive lariat effect is observed for Na^+ in PC; in the other cases, L16C5 shows no positive lariat effect.

In general, the stability sequences of a given crown ether-alkali metal ion complex for the solvents are $\text{AN} > \text{PC} > \text{CH}_3\text{OH}$. Exceptions are the L16C5- and

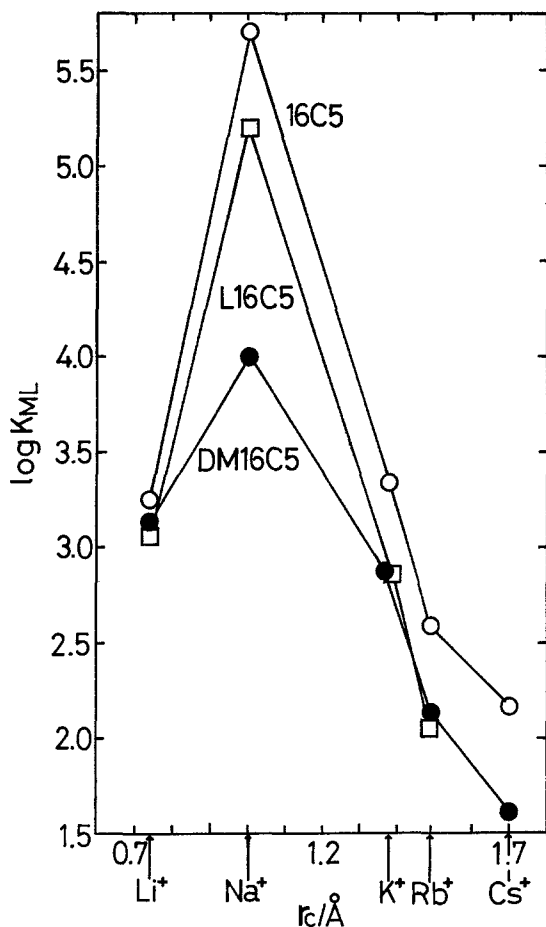
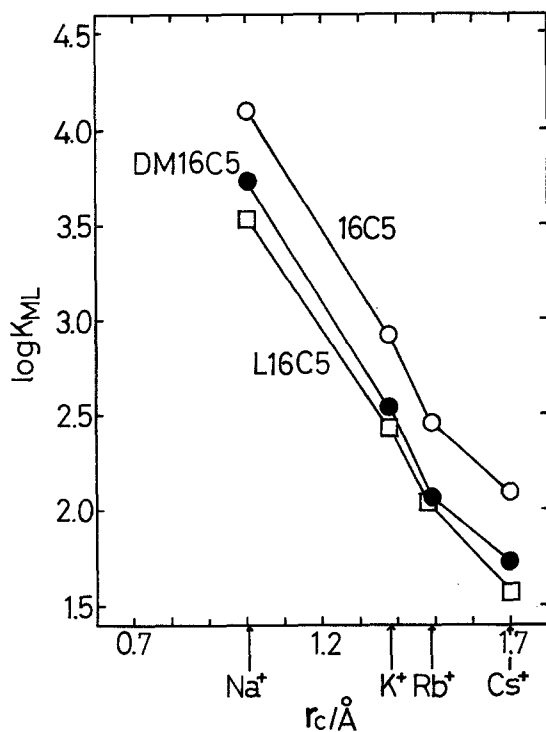


Fig. 5. $\log K_{ML}$ vs. r_c plots for PC.

16C5- Na^+ complexes for PC and AN and a DM16C5- Cs^+ complex for CH_3OH and PC. The stability sequences are completely the reverse of the donor-number sequences of the solvents ($\text{AN} < \text{PC} < \text{CH}_3\text{OH}$ [9]). The stability of the crown ether-alkali metal ion complex depends largely on the donor number of the solvent. The dielectric constants (ϵ_r) of AN, PC, and methanol at 25°C are 35.95 [10], 64.4 [11], and 32.6 [12], respectively. Thus, there is no correlation between the stability of the crown ether-alkali metal ion complexes and the dielectric constant of the solvent.

As can be seen from Table III, the $K_{ML}(M_1^+)/K_{ML}(M_2^+)$ ratio of L16C5 or 16C5 varies very much with the solvent in the cases of $M_1 = \text{Na}$, $M_2 = \text{K}$ and $M_1 = \text{Na}$, $M_2 = \text{Li}$, but that of DM16C5 does so only slightly and remains almost constant when $M_1 = \text{Na}$, $M_2 = \text{Li}$ and $M_1 = \text{Na}$, $M_2 = \text{K}$, respectively, where Na^+ and Li^+ are size-fitting and size-misfitting smaller cations, respectively. For the size-misfitting larger cations K^+ , Rb^+ , and Cs^+ , the $K_{ML}(M_1^+)/K_{ML}(M_2^+)$ ratio of the crown ether hardly varies with the solvent in the cases of

Fig. 6. $\log K_{ML}$ vs. r_c plots for methanol.Table III. $K_{ML}(M_1^+)/K_{ML}(M_2^+)$ values at 25°C

M_1	M_2	L	AN	PC	CH ₃ OH
Na	Li	L16C5	4	138	—
		DM16C5	2	7	—
		16C5	8	282	—
Na	K	L16C5	87	209	13
		DM16C5	15	13	15
		16C5	66	229	15
K	Rb	L16C5	5	7	2
		DM16C5	3	6	3
		16C5	4	6	3
Rb	Cs	L16C5	—	—	3
		DM16C5	2	3	2
		16C5	4	3	2

$M_1 = K$, $M_2 = Rb$ and $M_1 = Rb$, $M_2 = Cs$. It is interesting that the ratio for DM16C5 is nearly constant regardless of the solvent.

Notes and References

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