Tetrahedron Vol. 47, No. 16/17, pp. 2903-2922, 1991
Printed in Great Britain

0040-4020/91 $3.00+.00

CORRELATION ANALYSIS OF STABILITY CONSTANTS OF COMPLEXES FORMED BETWEEN ALKALI METAL CATIONS AND MACROCYCLES

Bo-Long Poh

School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia

(*Received in UK* 18 *December* 1990)

Abstract: The stability constants K_a of 1:1 complexes formed between alkali metal cations and macrocycles are correlated by the equation $\log K_a = m|R_c - R_m| + b$ where R_c and R_m are the radii of the macrocycle cavity and the alkali metal cations respectively, m and b are constants for a given macrocycle.

Introduction. Complexation between alkali metal cations and synthetic macrocycles have been extensively investigated. The stability constants K_a of many such complexes (usually of 1:1 host to guest stoichiometry) have been determined.[1] The log K_a values are usually plotted against the radii R_m of the alkali metal cations. The plots are usually curve shaped, with a maximum at a radius equalling to the radius R_c of the macrocycle cavity. Such plots are of little use for correlating stability constants. In this paper, a better and more useful method of correlating the log K_a data is presented.

Method. Two assumptions (justified by the good correlation results shown later) are made concerning the formation of 1:1 complexes between the alkali metal cations and a given macrocycle. First, the macrocycle maintains the same cavity size in complexing with the different alkali metal cations. Second, two metal cations, one larger and the other smaller, than the macrocycle cavity by the same amount (that is, same $|R_c - R_m|$ absolute value) give complexes of equal stability. These two assumptions lead to the following equation

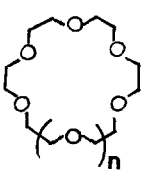
$$\log K_a = m|R_c - R_m| + b \qquad (1)$$

where m and b are constants for a given macrocycle host.

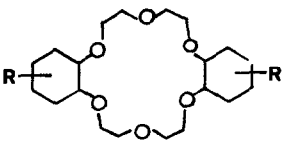
Since the exact value of R_c is not known, R_c is varied until the best correlation between log K_a and $|R_c - R_m|$ is obtained.

Results and Discussion. The log K_a values of 116 complexation equilibria involving 104 macrocycles were correlated using equation 1. A summary of the correlation results is given in Table I and the details of the correlations in Table II. Table III and IV contain the R_m and log K_a values used in the correlations. Some representative plots are shown in Figure 1.

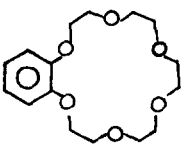
Macrocycles used in the correlations



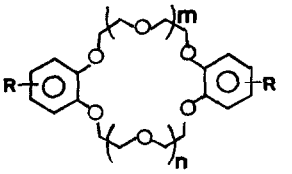
A1 n=0
A2 n=1
A3 n=2



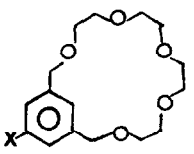
A4 R=H
A5 R=Bu^t



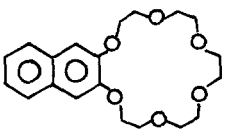
A6



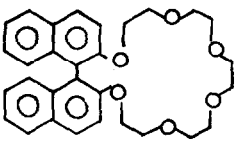
A7 m,n=1, R=H
A8 m,n=3, R=H
A9 m,n=3, R=Me



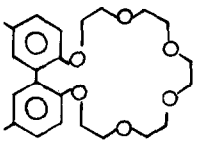
A10 X=H
A11 X=Br
A12 X=Bu^t
A13 X=OMe
A14 X=CN



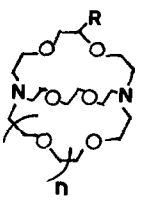
A15



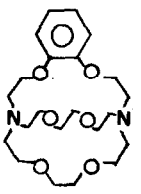
A16



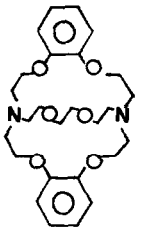
A17



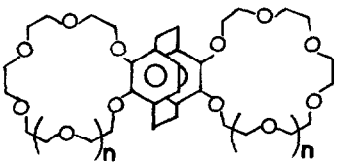
A18 n=0, R=H
A19 n=1, R=H
A20 n=1, R=$C_{10}H_{23}$



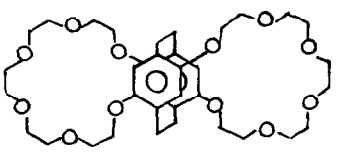
A21



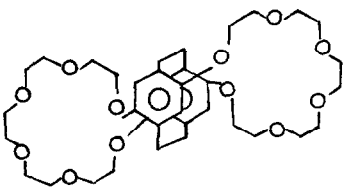
A22



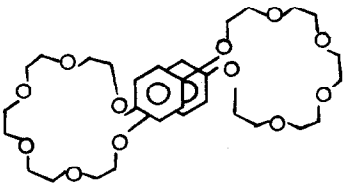
A23 n=0
A24 n=1



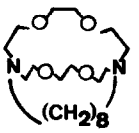
A25



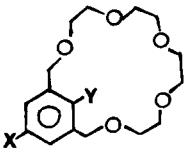
A26



A27

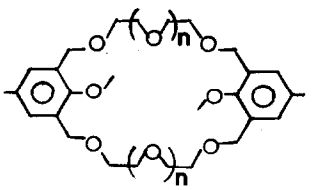


A28

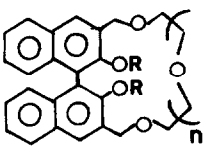


B1 X=H, Y=CO_2Me

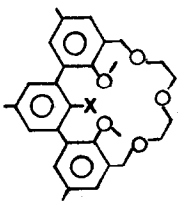
B2 X=Me, Y=OMe



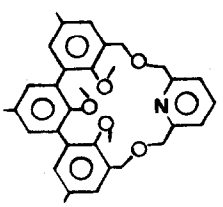
B3 n=0
B4 n=1



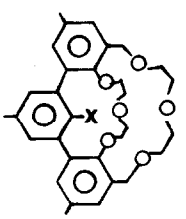
B5 n=2, R=Me
B6 n=3, R=Me
B7 n=2, R=H
B8 n=3, R=H
B9 n=4, R=H



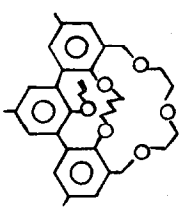
B10 X=OMe
B11 X=OCH_2CHCH_2
B12 X=OH



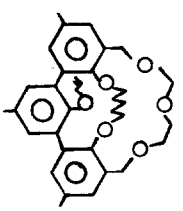
B13



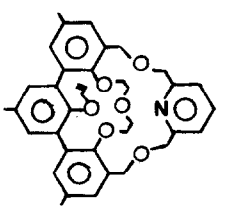
B14 X=OCH_2CHCH_2
B15 X=OH
B16 X=OMe



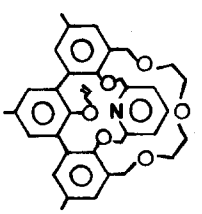
B17



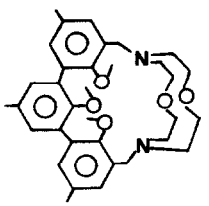
B18



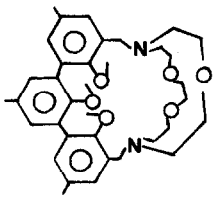
B19



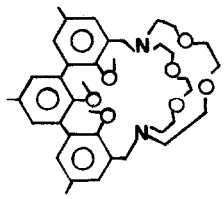
B20



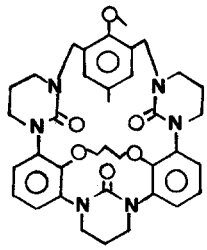
B21



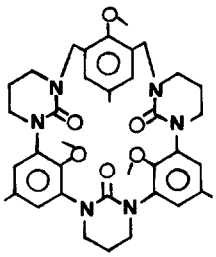
B22



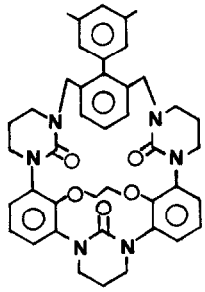
B23



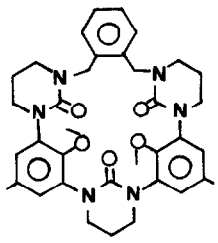
B24



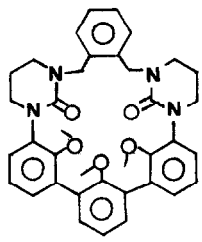
B25



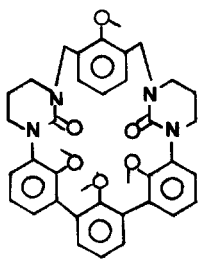
B26



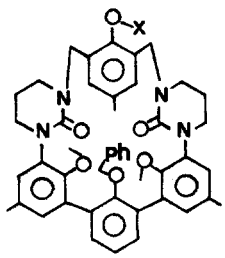
B27



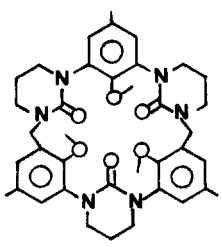
B28



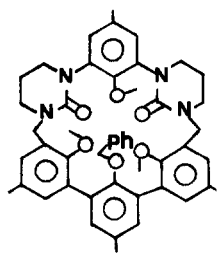
B29



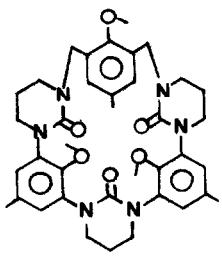
B30 X=H
B31 X=CH_2CHCH_2



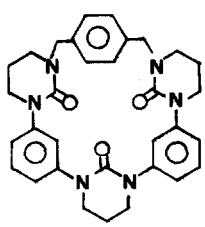
B32



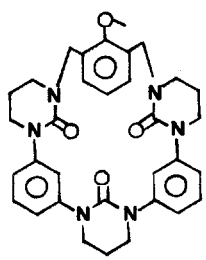
B33



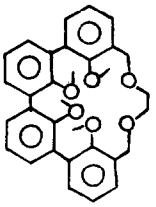
B34



B35

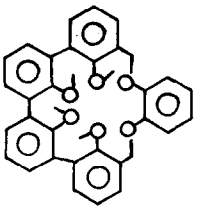


B36

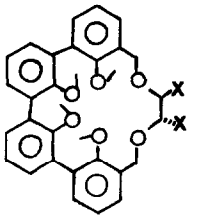


B37

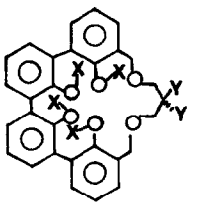
B38 X=Me
B39 X=Et



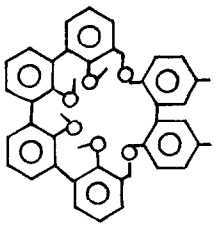
B40



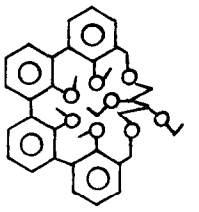
B41 X=CH_2OCH_2Ph



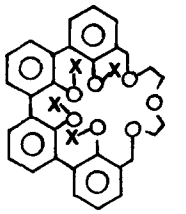
B42 X=Me, Y=H
B43 X=Et, Y=H
B44 X=Me, Y=CH_2OMe



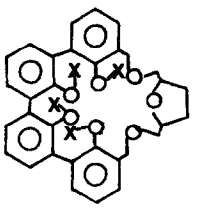
B45



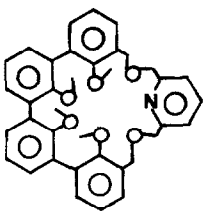
B46



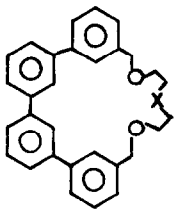
B47 X=Me
B48 X=Et



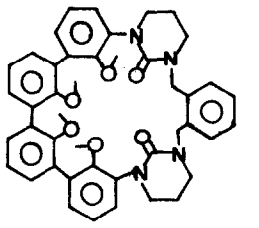
B49 X=Me
B50 X=Et



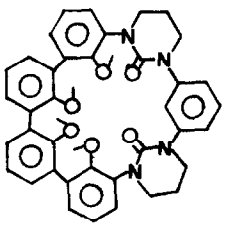
B51



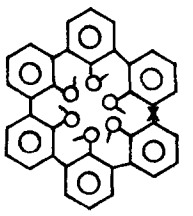
B52 X=S
B53 X=SO
B54 X=SO_2



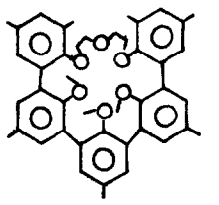
B55



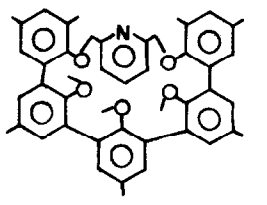
B56



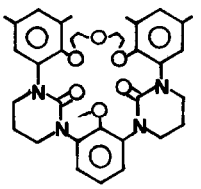
B57 X=CH_2CH_2
B58 X=CH_2SCH_2
B59 X=$CH_2SO_2CH_2$



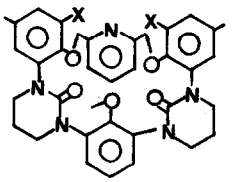
B60



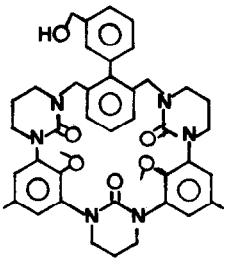
B61



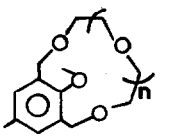
B62



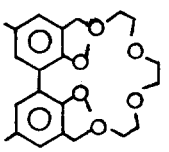
B63 X=Me
B64 X=CH_2OMe



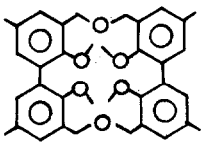
B65



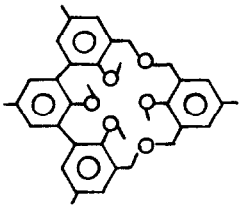
B66 n=2
B67 n=4



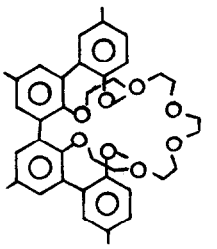
B68



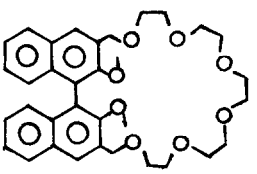
B69



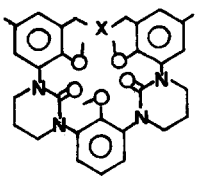
B70



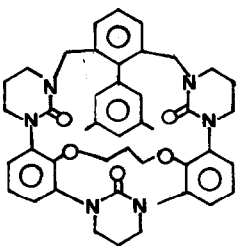
B71



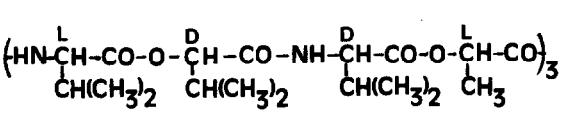
B72



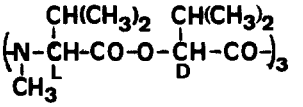
B73 X=O
B74 X=S
B75 X=$C(CO_2Et)_2$
B76 X=1,2-$C_6H_4O_2$



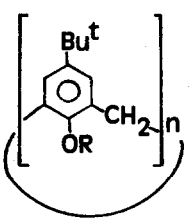
B77



B78



B79



C1 n=4, R=CH_2CO_2Et
C2 n=4, R=CH_2COMe
C3 n=4, R=CH_2COBu^t
C4 n=4, R=CH_2COPh
C5 n=6, R=CH_2CO_2Et

Table I. Summary of Correlation Analysis Results

Compounds	Correlation coefficient: $r \geq 0.99$	$0.95 \leq r \leq 0.99$	$0.90 \leq r < 0.95$	$r < 0.90$	Confidence level (%): ≥ 99	95 to 99	< 95
A series	18	17	5	0	31	9	0
B series	15	43	12	6	59	15	2

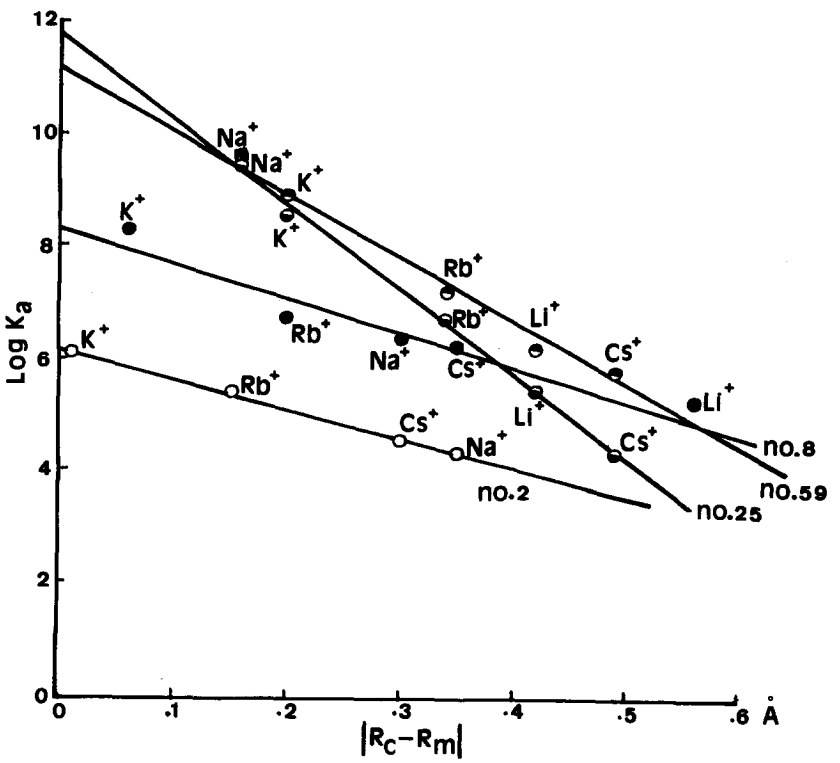


Figure 1. Linear relationship of stability constants of complexes formed between alkali metal cations and macrocycles

Table II. Correlations of Stability Constants[a] of 1:1 Complexes Formed between Alkali Metal Cations and Macrocycles at 25°C

No.	Host	Solvent	R_c(A)	n[b]	r[c]	m	b	sd[d]	cl(%)[e]
1	A1	MeOH	1.25	4	0.943	-6.07	4.50	0.31	97.0
2	A2	MeOH	1.37	4	0.999	-5.12	6.15	0.02	99.95
3	A2	H_2O	1.37	4	1.000	-3.63	2.08	0.01	>99.95
4	A2	70% MeOH	1.35	4	0.995	-5.09	4.43	0.06	99.8
5	A2	PC[f]	1.26	4	0.997	-6.11	6.96	0.05	99.8
6	A3	MeOH	1.60	4	0.997	-5.58	5.40	0.09	99.8
7	A4[g]	H_2O	1.34	5	0.994	-2.56	2.06	0.05	>99.95
8	A4	$CDCl_3$	1.32	5	0.958	-5.67	8.25	0.28	99.5
9	A5	H_2O	1.31	4	0.974	-3.79	2.36	0.10	98.5
10	A6	MeOH	1.30	4	0.989	-6.54	6.24	0.07	99.4
11	A6	PC[f]	1.21	4	1.000	-6.26	6.47	0.00	>99.95
12	A6	MeCN	1.23	4	0.992	-5.12	5.99	0.09	99.6
13	A6	MeCN[h]	1.23	4	0.967	-6.57	6.51	0.12	98.1
14	A7	MeOH	1.26	4	0.998	-5.00	5.58	0.03	99.9
15	A8	MeOH	1.48	4	0.979	-6.33	5.12	0.21	98.9
16	A9	MeCN[i]	1.42	4	0.941	-3.91	5.05	0.20	96.8
17	A10	$CDCl_3$	1.47	5	0.987	-4.65	5.35	0.19	99.9
18	A11	$CDCl_3$	1.45	5	0.987	-3.98	4.79	0.16	99.9
19	A12	$CDCl_3$	1.47	5	0.984	-4.16	5.28	0.20	99.8
20	A13	$CDCl_3$	1.46	5	0.984	-3.96	5.33	0.17	99.8
21	A14	$CDCl_3$	1.38	5	0.970	-1.77	4.01	0.09	99.7
22	A15	$CDCl_3$	1.35	5	1.000	-6.40	8.13	0.03	>99.95
23	A16	$CDCl_3$	1.29	5	0.929	-6.12	7.92	0.39	98.8
24	A17	$CDCl_3$	1.28	5	0.976	-4.37	6.47	0.12	99.8
25	A18	MeOH	1.18	5	0.998	-15.2	11.8	0.12	>99.95
26	A18	PC[f]	1.07	5	0.991	-14.9	13.9	0.39	>99.95
27	A18	MeCN	1.17	4	0.986	-17.8	13.8	0.41	99.9
28	A18	$CDCl_3$	1.17	4	0.986	-19.9	15.8	0.43	99.2

Table II. cont.

No.	Host	Solvent	R_c(A)	n[b]	r[c]	m	b	sd[d]	cl(%)[e]
29	A19	MeOH	1.27	5	0.985	-21.1	13.3	0.51	99.9
30	A19	H_2O	1.25	5	0.984	-12.0	6.91	0.28	99.9
31	A19	$CDCl_3$	1.30	4	0.997	-30.1	18.8	0.16	99.8
32	A20	MeOH	1.26	5	0.987	-20.6	12.1	0.29	99.9
33	A21	MeOH	1.24	5	0.990	-21.3	12.4	0.38	99.5
34	A22	MeOH	1.23	5	1.000	-20.7	11.8	0.08	>99.95
35	A23	$CDCl_3$	1.17	5	0.912	-5.30	6.66	0.31	98.2
36	A24	$CDCl_3$	1.38	4	0.993	-4.97	7.12	0.13	99.6
37	A25	$CDCl_3$	1.51	5	0.991	-2.36	5.17	0.09	99.95
38	A26	$CDCl_3$	1.38	5	0.992	-3.99	5.98	0.10	>99.95
39	A27	$CDCl_3$	1.45	4	0.937	-1.83	4.18	0.10	98.2
40	A28	MeOH[j]	1.29	4	0.964	-8.54	5.77	0.24	97.8
41	B1	$CDCl_3$	1.30	4	0.946	-5.09	7.25	0.23	97.2
42	B2	$CDCl_3$	1.38	4	0.990	-3.69	6.17	0.12	99.5
43	B3	$CDCl_3$	1.33	5	0.989	-1.22	3.65	0.03	99.9
44	B4	$CDCl_3$	1.30	5	0.900	-3.00	4.54	0.19	98.0
45	B5	$CDCl_3$	1.30	4	0.980	-6.55	7.90	0.17	99.0
46	B6	$CDCl_3$	1.58	5	0.985	-2.68	6.27	0.14	99.9
47	B7	$CDCl_3$	1.46	4	0.999	-2.08	4.80	0.02	99.95
48	B8	$CDCl_3$	1.56	5	0.978	-2.21	5.55	0.14	99.8
49	B9	$CDCl_3$	k	5	0.963	1.66	2.60	0.15	99.6
50	B10	$CDCl_3$	1.23	5	0.944	-10.7	10.7	0.47	99.2
51	B11	$CDCl_3$	1.21	5	0.973	-11.4	10.6	0.34	99.7
52	B12	$CDCl_3$	1.20	5	0.963	-3.78	6.45	0.13	99.6
53	B13	$CDCl_3$	1.19	5	0.966	-10.1	10.1	0.34	99.6
54	B14	$CDCl_3$	1.24	5	0.984	-11.7	11.4	0.26	99.8
55	B15	$CDCl_3$	1.25	5	0.987	-6.66	8.15	0.14	99.9
56	B16	$CDCl_3$	1.26	5	0.986	-12.6	12.0	0.29	99.9

Table II. cont.

No.	Host	Solvent	R_c(A)	n[b]	r[c]	m	b	sd[d]	cl(%)[e]
57	B17	$CDCl_3$	1.17	5	0.950	-9.80	8.62	0.42	99.3
58	B18	$CDCl_3$	1.21	5	0.984	-8.42	7.95	0.19	99.9
59	B19	$CDCl_3$	1.18	5	0.994	-11.5	11.2	0.16	>99.95
60	B20	$CDCl_3$	1.22	5	0.986	-9.73	12.4	0.21	99.9
61	B21	$CDCl_3$	0.95	5	0.999	-11.3	15.9	0.14	>99.95
62	B22	$CDCl_3$	1.26	4	0.999	-21.2	20.5	0.12	99.95
63	B23	$CDCl_3$	k	5	0.996	9.77	-0.02	0.28	>99.95
64	B24	$CDCl_3$	1.01	5	0.996	-1.27	9.43	0.02	>99.95
65	B25	$CDCl_3$	1.23	5	0.981	-7.69	12.71	0.19	99.8
66	B26	$CDCl_3$	1.16	5	0.955	-6.74	11.28	0.28	99.3
67	B27	$CDCl_3$	0.76	5	0.973	-5.89	13.3	0.46	99.7
68	B28	$CDCl_3$	0.79	5	0.950	-6.35	12.3	0.49	99.3
69	B29	$CDCl_3$	1.20	5	0.981	-8.34	12.3	0.20	99.8
70	B30	$CDCl_3$	1.17	5	0.915	-7.74	12.8	0.44	98.3
71	B31	$CDCl_3$	1.18	5	0.944	-6.20	10.2	0.27	99.2
72	B32	$CDCl_3$	1.16	5	0.960	-9.77	9.87	0.37	99.5
73	B33	$CDCl_3$	1.13	5	0.910	-9.07	12.1	0.59	98.3
74	B34	$CDCl_3$	1.23	5	0.972	-7.33	12.5	0.22	99.7
75	B35	$CDCl_3$	k	5	0.956	1.67	2.92	0.17	99.4
76	B36	$CDCl_3$	1.31	5	0.992	-3.71	7.49	0.08	>99.95
77	B37	$CDCl_3$	1.16	5	0.952	-12.9	11.1	0.54	99.3
78	B38	$CDCl_3$	1.19	5	0.923	-11.5	10.8	0.60	98.6
79	B39	$CDCl_3$	1.22	5	0.937	-10.9	10.8	0.50	99.0
80	B40	$CDCl_3$	1.13	5	0.898	-6.46	7.18	0.46	97.9
81	B41	$CDCl_3$	1.20	5	0.923	-11.5	10.3	0.59	98.6
82	B42	$CDCl_3$	1.16	5	0.715	-2.64	5.84	0.34	91.4
83	B43	$CDCl_3$	1.38	5	0.932	-0.97	4.61	0.08	98.9
84	B44	$CDCl_3$	1.25	5	0.972	-5.09	6.65	0.16	99.7

Table II. cont.

No.	Host	Solvent	R_c(A)	n[b]	r[c]	m	b	sd[d]	ct(%)[e]
85	B45	$CDCl_3$	1.30	5	0.994	-8.84	9.65	0.12	>99.95
86	B46	$CDCl_3$	1.38	5	0.991	-3.36	6.36	0.09	99.95
87	B47	$CDCl_3$	1.48	5	0.972	-5.95	8.82	0.32	99.7
88	B48	$CDCl_3$	1.57	5	0.975	-4.86	8.38	0.33	99.8
89	B49	$CDCl_3$	1.46	5	0.968	-4.22	9.07	0.27	99.6
90	B50	$CDCl_3$	1.48	5	0.965	-6.07	8.72	0.42	99.6
91	B51	$CDCl_3$	1.55	5	0.998	-2.67	7.41	0.05	>99.95
92	B52	$CDCl_3$	1.46	5	0.978	-3.92	6.99	0.37	99.8
93	B53	$CDCl_3$	1.30	5	0.977	-4.27	6.91	0.18	99.8
94	B54	$CDCl_3$	1.30	5	0.981	-7.27	7.97	0.19	99.8
95	B55	$CDCl_3$	1.19	5	0.989	-8.80	9.28	0.17	99.9
96	B56	$CDCl_3$	1.45	5	0.953	-2.14	6.11	0.16	99.3
97	B57	$CDCl_3$	1.21	5	0.998	-12.2	9.59	0.10	99.95
98	B58	$CDCl_3$	1.32	4	0.985	-7.05	7.94	0.14	99.2
99	B59	$CDCl_3$	1.25	5	0.997	-9.50	8.66	0.09	99.95
100	B60	$CDCl_3$	1.26	5	0.968	-7.53	10.1	0.26	99.6
101	B61	$CDCl_3$	1.22	5	0.855	-8.28	10.8	0.62	96.5
102	B62	$CDCl_3$	1.30	5	0.960	-7.28	9.04	0.27	99.5
103	B63	$CDCl_3$	1.20	5	0.927	-4.83	7.87	0.24	98.7
104	B64	$CDCl_3$	1.21	5	0.926	-4.91	8.56	0.25	98.7
105	B65	$CDCl_3$	1.19	5	0.966	-8.63	12.6	0.29	99.6
106	B66	$CDCl_3$	1.26	4	1.000	-2.17	4.63	0.04	>99.95
107	B67	$CDCl_3$	1.60	4	0.978	-2.83	6.01	0.18	98.8
108	B68	$CDCl_3$	1.31	5	0.979	-4.97	7.54	0.16	99.8
109	B69	$CDCl_3$	1.07	4	0.973	-1.84	3.88	0.09	98.4
110	B70	$CDCl_3$	1.20	5	0.846	-6.42	6.30	0.49	96.2
111	B71	$CDCl_3$	1.23	5	0.976	-10.3	9.81	0.29	99.8
112	B72	$CDCl_3$	1.63	5	0.983	-1.73	5.62	0.11	99.8

Table II. cont.

No.	Host	Solvent	R_c(A)	n[b]	r[c]	m	b	sd[d]	cl(%)[e]
113	B73	$CDCl_3$	1.02	5	0.993	-5.60	14.2	0.15	99.95
114	B74	$CDCl_3$	1.02	5	0.972	-8.31	13.7	0.45	99.7
115	B75	$CDCl_3$	0.82	5	0.983	-5.57	12.1	0.31	99.8
116	B76	$CDCl_3$	0.83	5	0.745	1.51	7.51	0.40	92.0
117	B77	$CDCl_3$	1.19	5	0.883	-5.51	12.7	0.37	97.6
118	B78	MeOH	1.50	4	0.989	-9.80	5.72	0.25	99.4
119	B79	MeOH	1.39	5	0.961	-2.58	3.07	0.16	99.5

[a] Stability constants given in Table IV. [b] Number of points used in the correlation. [c] Correlation coefficient. [d] Standard deviation of the estimate. [e] Confidence level. [f] Propylene carbonate. [g] cis-syn-cis. [h] +0.05 M Bu_4NClO_4. [i] 22°C. [j] +0.01 M Me_4NBr. [k] Correlated with R_m.

Table III. Radii of Alkali Metal Cations and Some Macrocycles

Cation	Radius (Å)[1]	Macrocycle	Radius (Å)[1,7,8]
Li^+	0.76	A1	0.86 - 0.92; 0.85 - 1.1
Na^+	1.02	A2	1.34 - 1.43; 1.3 - 1.6
K^+	1.38	A3	1.7; 1.7 - 2.1
Rb^+	1.52	A18	1.10
Cs^+	1.67	A19	1.40

Table IV. Stability Constants of 1:1 Complexes Formed between Alkali Metal Cations and Macrocycles at 25°C

No.[a]	Log K_a					Ref.
	Li^+	Na^+	K^+	Rb^+	Cs^+	
1	1.23	3.48	3.39		2.18	1[d]
2		4.36	6.08	5.43	4.60	1
3	-0[b]	0.8	2.03	1.56	0.99	1
4		2.76	4.33	3.46	2.84	1
5		5.46	6.28	5.32	4.5	1
6		2.13	4.32	4.86	5.01	1
7	0.6	1.21	2.02	1.52	1.25	1
8	5.28	6.36	8.30	6.71	6.26	9
9		1.42	2.08	1.53	0.9	1
10		4.29	5.1	4.86	3.88	1
11		5.3	5.4	4.5	3.6	1
12		4.9	5.3	4.4	3.8	1
13		4.90	5.30	4.40	4.05	1
14		4.4	5.0	4.23	3.55	1
15		2.1	4.60	4.6	4.2	1
16[c]		3.60	4.80	4.90	3.80	1
17	2.00	3.23	5.04	4.82	4.70	10
18	2.00	3.04	4.56	4.28	4.16	10
19	2.40	3.20	5.04	4.85	4.70	10
20	2.60	3.41	5.12	4.87	4.74	10
21	3.00	3.20	4.08	3.74	3.52	10
22	4.32	6.08	7.91	7.04	6.08	11
23	4.36	6.23	7.63	5.67	5.76	9
24	4.34	5.22	6.23	5.27	4.71	12
25	5.38	9.48	8.54	6.74	4.33	1
26	9.6	12.8	9.9	7.0	4.9	1
27	6.97	10.7	10.5		4.55	1

Table IV. cont.

No. [a]	Log K_a					Ref.
	Li^+	Na^+	K^+	Rb^+	Cs^+	
28	7.33	12.98	11.22	9.31		13
29	2.6	7.9	10.6	8.98	4.4	1
30	1.25	4.0	5.3	4.06	1.44	1
31		10.56	13.20	12.32	7.55	13
32	2.0	7.0	9.42	7.61	3.21	1
33	2.19	7.50	9.21	7.19	2.98	1
34	2.2	7.5	8.7	5.91	2.61	1
35	4.18	6.24	5.28	4.65	4.38	14
36	4.18	5.18	7.24	$\geqslant$6.42[b]	5.59	14
37	3.49	3.85	4.91	5.14	4.81	14
38	3.63	4.40	6.06	5.47	4.72	14
39	$\leqslant$2.40[b]	3.34	4.10	3.93	3.92	14
40	$<$2.0[b]	3.5	5.2	3.4	2.7	1
41	4.30	5.95	6.09		5.68	2
42	4.00	4.67	6.26		5.06	2
43	2.93	3.30	3.59	3.38	3.28	12
44	2.75	3.70	3.94	3.77	3.79	12
45	4.21	6.09	6.57		5.75	2
46	4.11	4.63	5.98	5.99	5.98	2
47	3.34	3.90	4.61		4.40	2
48	3.85	4.19	5.37	5.35	5.30	2
49	3.69	4.49	5.02	4.94	5.35	2
50	5.11	8.96	8.66	7.66	6.57	15
51	5.04	8.79	8.30	6.96	5.69	15
52	4.78	5.80	5.86	4.99	4.79	15
53	5.41	8.79	7.98	6.60	5.72	15
54	5.51	9.15	9.45	8.34	6.60	15
55	4.96	6.51	7.48	6.15	5.40	15

Table IV. cont.

No. [a]	Log K_a					Ref.
	Li^+	Na^+	K^+	Rb^+	Cs^+	
56	5.34	9.32	10.18	8.64	7.11	15
57	4.20	7.56	6.40	4.76	4.28	15
58	4.18	6.40	6.66	4.98	4.23	15
59	6.23	9.52	8.93	7.20	5.85	15
60	7.70	10.69	10.69	9.36	8.28	15
61	13.79	15.11	11.00	9.75	7.63	13
62	9.79	15.41	>14.57[b]	14.96	12.01	13
63	7.26	9.90	13.93	14.89	15.91	13
64	9.08	9.41	9.00	8.79	8.57	11
65	8.86	11.28	11.43	10.40	9.59	11
66	8.86	10.04	10.18	8.64	7.69	11
67	13.40	11.94	9.08	8.34	8.64	16
68	12.15	11.28	7.91	6.89	7.69	16
69	8.79	10.62	11.15	9.45	8.41	16
70	9.23	12.08	10.52	10.48	9.08	16
71	7.84	9.45	8.79	7.61	7.18	16
72	5.57	8.86	7.61	6.00	5.41	16
73	8.11	11.64	9.59	7.91	7.98	16
74	8.86	11.20	11.34	10.15	9.59	16
75	4.40	4.32	5.28	5.43	5.79	17
76	5.51	6.38	7.34	6.60	6.15	17
77	5.30	9.90	7.84	6.20	5.20	18
78	5.23	9.61	8.04	6.83	5.95	18
79	5.20	9.20	8.62	7.60	6.53	18
80	4.26	7.00	5.15	4.52	4.23	18
81	4.61	9.00	7.67	6.52	5.57	18
82	5.08	5.15	5.74	4.51	4.40	18

Table IV. cont.

No. [a]	Log K_a					Ref.
	Li^+	Na^+	K^+	Rb^+	Cs^+	
83	4.08	4.15	4.70	4.40	4.34	18
84	4.23	5.45	6.18	4.99	4.58	18
85	4.85	7.18	8.20	7.49	6.46	18
86	4.38	5.04	6.43	5.93	5.26	18
87	4.18	6.54	8.15	8.18	8.08	18
88	4.74	5.15	7.81	8.04	7.88	18
89	6.41	6.76	8.88	8.96	8.04	18
90	4.76	5.20	8.51	8.36	7.62	18
91	5.34	5.91	7.00	7.32	7.08	18
92	4.45	4.89	6.81	6.74	6.20	18
93	4.53	5.82	6.18	5.77	5.45	18
94	4.04	6.20	6.76	6.08	5.20	18
95	5.34	7.99	7.48	6.26	5.26	18
96	4.77	4.92	6.11	5.86	5.72	18
97	4.11	7.40	7.48	5.64	4.04	19
98	<4.40 [b]	5.86	7.40	6.74	5.34	19
99	4.11	6.38	7.48	6.15	4.54	19
100	6.00	8.56	8.95	8.04	7.32	20
101	6.28	9.80	9.08	7.92	7.90	20
102	4.89	7.34	7.63	7.11	6.65	20
103	5.46	7.23	6.89	6.15	5.94	20
104	6.04	7.88	7.54	6.95	6.62	20
105	8.95	11.08	11.32	9.28	8.69	9
106	3.58	4.15	4.32		3.70	12
107	3.46	4.66	5.26		5.81	12
108	4.76	6.39	7.20	6.28	5.71	12
109		3.79	3.38	2.91	2.85	12
110	2.91	5.69	4.82	3.94	3.94	12

Table IV. cont.

No. [a]	Log K_a					Ref.
	Li^+	Na^+	K^+	Rb^+	Cs^+	
111	5.01	7.69	8.52	6.28	5.49	12
112	4.11	4.52	5.36	5.29	5.56	2
113	12.67	14.28	12.15	11.15	10.76	21
114	11.57	13.99	10.04	9.15	8.86	21
115	11.79	11.15	8.49	7.98	7.76	21
116	7.61	7.48	9.08	8.49	8.41	21
117	9.96	12.23	11.49	10.84	10.62	11
119		0.88	4.7	5.19	4.36	1
120	1.28	2.4	2.92	2.74	2.34	1

[a] The numbering corresponds to that in Table II. [b] Not used in the correlation because of uncertainty in the value. [c] 22°C. [d] Average log K_a value is used whenever more than one value is listed in all the data taken from ref. 1.

The macrocycles are divided into two groups: (1) the ligating atoms are part of the macrocyclic ring structure (A1 to A28); (2) some or all of the ligating atoms are not part of the macrocyclic ring structure (B1 to B79). The first group of macrocycles give good correlations (Table I). There is not a single correlation (out of a total of forty) with a correlation coefficient $r < 0.90$ and a confidence level less than 95%. Some of the macrocycles in the second group have methyl substituents attached to their ligating atoms. These methyl groups may give rise to steric hindrance if they point into the cavity and resulting in poorer correlations. However, the results (Table I) show that steric effect is probably not serious because, on the whole, good correlations are still obtained. Only six correlations have $r < 0.90$ (no. 80, 82, 101, 110, 116 and 117) and two with a confidence level less than 95% (no. 82, 116). It is difficult to state with certainty the reason(s) for these few poorer correlations. Steric factor is unlikely to be the reason for the poor correlation obtained for no. 82 (Table II) since the macrocycle B42 is very similar to B43 which gives a satisfactory correlation in no. 83. Sometimes the accuracy of the experimental log K_a values could be a contributing factor. For example, the earlier log K_a value for Rb^+ in no. 43 was given by Cram and coworkers[2] as 3.23 instead of their more recent value of 3.38 (Table IV, no. 43). If the earlier log K_a value for Rb^+ were used, a poorer correlation for no. 43 is obtained (R_c = 1.33 Å, n = 5, r = 0.921, m = -1.12, b = 3.59, Sd = 0.08 and confidence level = 98.5%).

Table V. Comparison of Observed[a] and Calculated[b] Log K_a Values for the NH_4^+ Complexes

No.[c]	Log K_a	No.[c]	Log K_a	No.[c]	Log K_a	No.[c]	Log K_a
1	3.03(3.41)[d]	43	3.28(3.53)	67	8.64(9.34)	92	6.36(6.87)
2	4.20(5.84)	44	3.93(4.15)	68	7.61(8.24)	93	5.71(6.35)
3	1.16(1.86)	45	5.90(7.33)	69	9.74(10.4)	94	5.70(7.03)
6	3.27(4.45)	46	5.68(6.20)	70	10.5(10.8)	95	6.38(7.17)
7	0.8(1.83)	47	3.77(4.74)	71	7.54(8.62)	96	5.48(6.07)
8	7.83(7.63)	48	4.85(5.26)	72	6.30(7.24)	97	4.98(6.90)
15	2.4(4.80)	49	4.71(4.96)	73	8.04(9.34)	98	6.08(7.16)
17	5.06(5.16)	50	7.18(8.59)	74	10.5(11.1)	99	5.49(6.95)
18	4.60(4.71)	51	6.54(7.94)	75	5.87(5.31)	100	7.52(8.80)
19	5.08(5.11)	52	4.69(5.58)	76	6.15(7.05)	102	6.61(8.09)
20	5.09(5.21)	53	6.34(7.71)	77	6.36(7.61)	103	6.67(6.76)
21	4.03(3.92)	54	7.54(9.22)	78	6.74(8.06)	104	6.96(7.48)
22	6.96(7.62)	55	6.00(6.95)	79	7.36(8.56)	105	9.99(10.6)
23	6.51(6.99)	56	8.11(9.84)	81	6.64(7.69)	106	3.62(4.26)
24	5.50(5.82)	57	4.88(6.07)	83	4.20(4.56)	107	5.11(5.53)
31	12.6(14.9)	58	4.88(6.10)	84	5.46(5.74)	108	5.78(6.94)
35	4.38(4.01)	59	6.74(8.37)	85	7.26(8.50)	109	3.28(3.22)
36	6.65(6.87)	60	9.30(10.4)	86	6.40(6.19)	111	6.43(7.75)
37	5.25(4.98)	62	13.6(16.9)	87	7.82(8.52)	112	5.06(5.27)
38	5.71(5.78)	63	14.8(13.9)	88	7.53(7.70)	113	10.9(11.9)
39	3.96(4.15)	64	8.79(8.89)	89	8.04(8.94)	114	9.74(10.3)
41	5.70(5.79)	65	10.5(11.2)	90	7.88(8.42)	115	8.04(8.68)
42	5.56(6.05)	66	9.23(9.46)	91	6.80(7.09)	118	1.67(5.03)
						119	1.92(2.97)

[a] The references are given in Table IV. [b] Using the correlation lines given in Table II; the Rm value for NH_4^+ is 1.43 Å (ref. 22). [c] The numbering corresponds to that in Table II. [d] Calculated values in parentheses.

Steric factor is expected to be significant in the case of the functionalized calixarenes (C1 - C5) since some of the flexible chains attached to the ligating oxygen atoms point into the cavity defined by the ligating oxygen atoms.[3,4] The reported log K_a data[5] of these macrocycles are poorly correlated by equation 1.

When the cavity size adopted by the macrocycle for complexation is larger than the size of the largest alkali metal cation Cs^+ and the first assumption given earlier is still valid, the correlation equation becomes

$$\log K_a = mR_m + b \qquad (2)$$

Three of the complexation equilibria (no. 49, 63 and 75) are better correlated by equation 2.

The NH_4^+ cation is not included in the correlation because, unlike the alkali metal cations, it uses four hydrogen atoms instead of the central charged nitrogen atom to coordinate to its ligating atoms. The log K_a values for the NH_4^+ complexes calculated from the correlation lines in Table II are given in Table V. The differences between the observed and calculated values are higher than the standard deviations of the estimate in Table II.

The other two metal cations, Ag^+ and Tl^+, are also not included in the correlations because they are soft cations, unlike the alkali metal cations which are hard.[6] They generally deviate from the correlation lines of the alkali metal cations, as shown by a comparison of their observed and calculated log K_a values (Table VI).

Table VI. Comparison of Observed[a] and Calculated[b] Log K_a Values for Ag^+ and Tl^+ Complexes

No.[c]	Log K_a (Ag^+)	Log K_a (Tl^+)	No.[c]	Log K_a (Ag^+)	Log K_a (Tl^+)
1	3.62(3.89)[d]	4.6; 5.26(5.48)	14	4.04(5.05)	3.86(4.38)
2	4.58(5.02)		15	4.45(4.99)	2.4(4.80)
3	1.55(1.28)	2.27(1.61)	25	14.0(11.3)	
5	7.10(6.29)	7.13(5.49)	26	18.6(12.7)	
6	2.46(2.89)		27	8.9(13.4)	12.3(7.93)
7	1.7(1.57)	1.8(1.65)	29	12.1(10.8)	10.1(8.4)
10		4.60(4.93)	33	11.8(10.5)	7.9(6.9)
13		5.70(4.74)	118	3.90(2.29)	4.06(5.72)

[a] The references are given in Table IV. [b] Using the correlation lines given in Table II; the R_m values for Ag^+ and Tl^+ are 1.15 and 1.50 Å respectively.[1] [c] The numbering corresponds to that in Table II. [d] Calculated values in parentheses.

Conclusion. The stability constants of 1:1 complexes formed between alkali metal cations and macrocycles are satisfactorily correlated by equation 1 when the macrocycles do not have flexible chains that will interfer with their cavity size defined by the ligating atoms.

Acknowledgement. The author thanks the Universiti Sains Malaysia for a Short Term Research Project Grant.

References

1. Izatt, R.M., Bradshaw, J.S., Nielsen, S.A., Lamb, J.D., Christensen, J.J., Sen, D., Chem. Rev., 1985, 85, 271.
2. Koenig, K.E., Helgeson, R.C., Cram, D.J., J. Am. Chem. Soc., 1976, 98, 4018.
3. McKervey, M.A., Seward, E.M., Ferguson, G., Ruhl, B., Harris, S.T., J. Chem. Soc., Chem. Commun., 1985, 388.
4. Ferguson, G., Kaitner, B., McKervey, M.A., Seward, E.M., J. Chem. Soc., Chem. Commun., 1987, 584.
5. Schwing, M.J., Arnaud, F., Marques, E., Pure & Appl. Chem., 1989, 61, 1597.
6. Pearson, R.G., J. Chem. Educ. 1968, 45, 581.
7. Weber, E., Vögtle, F., Topics in Current Chemistry, 1981, 98, 18.
8. Lehn, J.M., Sauvage, J.P., J. Am. Chem. Soc., 1975, 97, 6700.
9. Cram, D.J., Katz, H.E., Dicker, I.B., J. Am. Chem. Soc., 1984, 106, 4987.
10. Moore, S.S., Tarnovski, T.L., Newcomb, M., Cram., D.J., J. Am. Chem. Soc., 1977, 99, 6398.
11. Doxsee, K.M., Feigel, M., Stewart, K.D., Canary, J.W., Knobler, C.B., Cram, C.D., J. Am. Chem. Soc., 1987, 109, 3098.
12. Koenig, K.E., Lein, G.M., Stuckler, P., Kaneda, T., Cram, C.D., J. Am. Chem. Soc., 1979, 101, 3553.
13. Cram, D.J., Ho, S.P., J. Am. Chem. Soc., 1986, 108, 2998.
14. Helgeson, R.C., Tarnowski, T.L., Timko, J.M., Cram, D.J., J. Am. Chem. Soc., 1977, 99, 6411.
15. Lein, G.M., Cram, D.J., J. Am. Chem. Soc., 1985, 107, 448.
16. Cram, D.J., Dicker, I.B., Lauer, M., Knobler, C.B., Trueblood, K.N., J. Am. Chem. Soc., 1984, 106, 7150.
17. Nolte, R.J.M., Cram, D.J., J. Am. Chem. Soc., 1984, 106, 1416.
18. Artz, S.P., Cram, D.J., J. Am. Chem. Soc., 1984, 106, 2160.
19. Cram, D.J., de Grandpre, M., Knobler, C.B., Trueblood, K.N., J. Am. Chem. Soc., 1984, 106, 3286.
20. Katz, H.E., Cram, D.J., J. Am. Chem. Soc., 1984, 106, 4977.
21. Bryant, J.A., Ho, S.P., Knobler, C.B., Cram, D.J., J. Am. Chem. Soc., 1990, 112, 5837.
22. Frensdorff, H.K., J. Am. Chem. Soc., 1971, 93, 600.