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Molar Conductance of the Complexes of 18-Crown-6 with Alkaline Earth Metal Ions in Methanol + Water

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The molar conductance of complexes of Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} with 18-crown-6 in 0−90 mass % methanol−water has been measured at temperatures from 278 K to 313 K. The observed molar conductances Λ were found to decrease for mole ratios less than unity. The conductance data have been analyzed using a model involving 1:1 complexation stoichiometry to give the stability constant K and limiting molar conductance Λ_c for each 1:1 complex by using a nonlinear least-squares analysis. The log K values for the resulting 1:1 complexes increased with an increase in methanol concentration and with a decrease in temperature. The stability constants determined for each metal−ligand system at each solvent composition were fitted by the equation $\log K = a/T + b + cT$. Values of $\Delta G°$, $\Delta H°$, $\Delta S°$, and $\Delta C_p°$ have been calculated. The results are discussed in terms of their dependence on temperature and solvent composition. In 0−90 mass % methanol, the complexation process follows the order $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$.

Introduction

There are a number of reports available in the literature on the complexation of 18-crown-6 with alkaline earth metal ions in water and methanol solvents. Most of these reports are concerned with obtaining stability constants at 298 K using various techniques such as spectroscopy (Kashanian and Shamsipur, 1989), conductivity (Chen et al., 1987), and polarography (Blasius et al., 1984), and others are interested in determining thermodynamic parameters, $\Delta H°$ and $\Delta S°$, at 298 K by the method of calorimetry (Izatt et al., 1976; Buschmann, 1985, 1986; Lamb et al., 1980). Most of the research in the area of complexation of metal ions with crown ethers has been carried out to determine stability constants or/and $\Delta H°$ and $\Delta S°$ at 298 K in pure or mixed solvents, but relatively few (Christensen et al., 1974; Izatt et al., 1985, 1991) have dealt with the combined effects of changes in solvent composition and temperature. Thus, there is sparse data on the enthalpy, entropy, Gibbs energy and heat capacity changes of complexation in water−methanol mixtures or other solvents.

The aim of the present work is to determine the temperature and solvent composition dependence of the thermodynamic parameters $\Delta H°$, $\Delta S°$, $\Delta G°$, and $\Delta C_p°$ for the complexation of Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} with 18-crown-6 in water−methanol solvents in the composition range 0−90 mass % of methanol between 278 K and 313 K using the method of conductometry.

Experimental Section

18-Crown-6 (99% purity) was obtained from Janssen Chimica and used without further purification. Methanol (99.8% A. R, C.B.H Lab Chemicals) was used as the solvent for the crown ether. The boiled deionized conductivity water (triply distilled before deionization) was used as an aqueous medium and for preparation of the $MeOH + H_2O$ mixtures. The following salts were obtained from the indicated suppliers: $MgCl_2 \cdot 6H_2O$ and $BaCl_2 \cdot 2H_2O$ (>99% both from B.D.H); $CaCl_2 \cdot H_2O$ (>99%, Fluka AG); $SrCl_2 \cdot 6H_2O$ (AnalaR, Hopkin and Williams Ltd).

The solvents were prepared from known masses of methanol and water. Metal salt solutions of approximately 4×10^{-4} M were prepared by dissolving a known mass of each salt in the $MeOH + H_2O$ mixtures. Similar solutions with the same total salt concentrations were also used as solvents in the preparation of the 18-crown-6 solutions.

Complexation stability constants were determined by conductance measurements as a function of the concentration and temperature. Conductance measurements were carried out using a microprocessor conductivity meter (WTW/LF 537) in the same way as described elsewhere (Sway and Ambushamleh, 1995). The conductivity meter was equipped with a cell (WTW/Tetracon 96) of cell constant 0.609 cm^{-1}. The temperature of the water bath (HAAKE D8) was controlled at ±0.01 K. The cell was calibrated using KCl solutions. Duplicate measurements of each solution were made. The results varied within ±0.1%.

Results and Discussion

In the present work, the 1:1 complexation of an alkaline earth cation, M^{2+} ($M^{2+} = Mg^{2+}$, Ca^{2+}, Sr^{2+}, or Ba^{2+}), with 18-crown-6, L, is assumed. The complexation process is represented by the equilibrium

$$M^{2+} + L \rightleftharpoons ML^{2+} \tag{1}$$

The stability constant K for reaction 1 is given by

$$K = [ML^{2+}]\gamma_{ML}{}^{2+}/[M^{2+}][L]\gamma_{M}{}^{2+}\gamma_{L} \tag{2}$$

where $[ML^{2+}]$, $[M^{2+}]$, [L], and γ denote the concentration of the complex, uncomplexed cation, uncomplexed crown ether, and the activity coefficient of the species indicated, respectively. Since this work has been performed in dilute solutions, it is assumed that the ratio of activity coefficients is unity.

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Table 1. Data Used for Calculating the Stability Constant, *K*, and Λ_c for Complexation of 18C6 with Alkaline Earth Metal Cations in Water at 298 K for $[SrCl_2\cdot 6H_2O]_0 = 4.08 \times 10^{-4}$ M and $[BaCl_2\cdot 2H_2O]_0 = 4.01 \times 10^{-4}$ M[a]

Sr^{2+} [b]				Ba^{2+} [c]			
$[L]_0/[Sr^{2+}]_0$	$10^4[L]_0$/M	Λ/S cm^2 mol^{-1}	Λcal/S cm^2 mol^{-1}	$[L]_0/[Ba^{2+}]_0$	10^4 $[L]_0$/M	Λ/S cm^2 mol^{-1}	Λcal/S cm^2 mol^{-1}
0.197	0.806	260.73	260.68	0.199	0.795	264.75	264.38
0.374	1.526	258.28	258.32	0.393	1.574	259.95	260.02
0.581	2.370	257.79	257.73	0.581	2.338	256.12	256.24
0.768	3.130	256.32	256.36	0.721	3.088	252.96	253.05
0.950	3.875	255.34	255.32	0.955	3.823	250.36	250.43
1.128	4.606	255.10	255.13	1.135	4.544	248.25	248.32
1.304	5.324	254.61	254.66	1.312	5.252	246.82	246.63
1.477	6.028	254.61	254.63	1.485	5.947	245.18	245.27
1.646	6.719	254.12	254.10	1.656	6.629	244.10	244.17
1.812	7.398	253.63	253.66	1.823	7.298	243.18	243.29
1.976	8.065	253.63	253.65	1.987	7.956	242.62	242.56
2.136	8.719	253.63	253.61	2.184	8.601	241.98	241.95
2.293	9.362	252.65	252.60	2.307	9.236	241.45	241.44
2.448	9.994	252.65	252.57	2.462	9.859	241.05	241.01
2.600	10.615	252.65	252.50	2.615	10.471	240.63	240.64
2.750	11.225	252.65	252.51	2.766	11.073	240.32	240.32
2.897	11.824	251.42	251.65	2.913	11.665	240.05	240.04
3.041	12.414	251.42	251.61	3.058	12.246	239.86	239.79

[a] Λ, observed molar conductivity; Λ_{cal}, calculated molar conductivity; Λ_0, molar conductivity of uncomplexed cation; Λ_c, molar conductivity of the complexed cation; $X^2 = \sum(\Lambda - \Lambda_{cal})^2$. [b] Parameters: $\Lambda_0 = 261.46$ S cm^2 mol^{-1} ; $K = 5.012 \times 10^2$; $\Lambda_c = 250.38$ S cm^2 mol^{-1}; $X^2 = 0.325$. [c] Parameters: $\Lambda_0 = 268.65$ S cm^2 mol^{-1}; $K = 8.01 \times 10^3$; $\Lambda_c = 235.58$ S cm^2 mol^{-1}; $X^2 = 0.250$.

Table 2. Data Used for Calculating the Stability Constant, *K*, and Λ_c for Complexation of 18C6 with Alkaline Earth Metal Cations in 50 mass % Methanol at 298 K for $[SrCl_2\cdot 6H_2O]_0 = 4.09 \times 10^{-4}$ M and $[BaCl_2\cdot 2H_2O]_0 = 3.99 \times 10^{-4}$ M[a]

Sr^{2+} [b]				Ba^{2+} [c]			
$[L]_0/[Sr^{2+}]_0$	$10^4[L]_0$/M	Λ/S cm^2 mol^{-1}	Λcal/S cm^2 mol^{-1}	$[L]_0/[Ba^{2+}]_0$	10^4 $[L]_0$/M	Λ/S cm^2 mol^{-1}	Λcal/S cm^2 mol^{-1}
0.197	0.805	129.47	129.53	0.198	0.790	130.61	130.69
0.389	1.593	127.52	127.48	0.392	1.564	127.60	127.62
0.578	2.367	126.30	126.38	0.583	2.324	124.59	124.65
0.764	3.125	124.58	124.46	0.770	3.069	121.83	121.90
0.946	3.869	123.61	123.53	0.953	3.800	119.82	119.72
1.124	4.599	122.63	122.68	1.133	4.516	118.56	118.59
1.299	5.315	121.65	121.53	1.309	5.220	118.25	118.17
1.471	6.019	121.41	121.38	1.483	5.911	118.05	118.02
1.640	6.709	121.32	121.34	1.653	6.588	118.05	117.99
1.805	7.386	121.23	121.27	1.820	7.254	118.05	117.95
1.968	8.052	121.15	121.18	1.983	7.908	118.05	117.90
2.127	8.705	121.15	121.15	2.145	8.550	118.05	117.85
2.284	9.347	121.15	121.11	2.303	9.180	118.05	117.81
2.438	9.978	121.15	121.09	2.459	9.800	118.05	117.78
2.600	10.598	121.15	121.06	2.611	10.408	118.05	117.76

[a] Λ, observed molar conductivity; Λ_{cal}, calculated molar conductivity; Λ_0, molar conductivity of uncomplexed cation; Λ_c, molar conductivity of the complexed cation; $X^2 = \sum(\Lambda - \Lambda_{cal})^2$. [b] Parameters: $\Lambda_0 = 131.92$ S cm^2 mol^{-1} ; $K = 1.072 \times 10^4$; $\Lambda_c = 120.53$ S cm^2 mol^{-1}; $X^2 = 0.523$. [c] Parameters: $\Lambda_0 = 133.87$ S cm^2 mol^{-1}; $K = 9.211 \times 10^4$; $\Lambda_c = 117.61$ S cm^2 mol^{-1}; $X^2 = 0.102$.

Table 3. Data Used for Calculating the Stability Constant, *K*, and Λ_c for Complexation of 18C6 with Alkaline Earth Metal Cations in 70 mass % Methanol at 298 K for $[CaCl_2\cdot 2H_2O]_0 = 4.06 \times 10^{-4}$ M, $[SrCl_2\cdot 6H_2O]_0 = 4.07 \times 10^{-4}$ M, $[BaCl_2\cdot 2H_2O]_0 = 3.97 \times 10^{-4}$ M[a]

Ca^{2+} [b]				Sr^{2+} [c]				Ba^{2+} [d]			
$[L]_0/[Ca^{2+}]_0$	$10^4[L]_0$/M	Λ/S cm^2 mol^{-1}	Λ_{cal}/S cm^2 mol^{-1}	$[L]_0/[Sr^{2+}]_0$	$10^4[L]_0$/M	Λ/S cm^2 mol^{-1}	Λ_{cal}/S cm^2 mol^{-1}	$[L]_0/[Ba^{2+}]_0$	$10^4[L]_0$/M	Λ/S cm^2 mol^{-1}	Λ_{cal}/S cm^2 mol^{-1}
0.171	0.696	126.21	126.19	0.200	0.815	129.19	129.05	0.200	0.795	131.95	132.03
0.504	2.047	126.08	126.09	0.397	1.614	127.47	127.46	0.397	1.575	129.93	129.64
0.824	3.347	125.99	125.99	0.589	2.397	125.75	125.87	0.589	2.340	127.42	127.31
1.133	4.598	125.89	125.92	0.779	3.169	124.27	124.45	0.778	3.090	125.15	125.06
1.429	5.803	125.80	125.84	0.964	3.919	123.54	123.37	0.963	3.826	123.34	123.11
1.716	6.965	125.80	125.77	1.146	4.659	122.80	122.74	1.145	4.548	122.63	122.43
1.991	8.085	125.80	125.74	1.324	5.384	122.55	122.43	1.324	5.257	122.38	122.33
2.258	9.167	125.80	125.70	1.499	6.096	122.06	122.28	1.498	5.952	122.13	122.29
2.515	10.212	125.80	125.68	1.672	6.797	122.06	122.18	1.670	6.635	122.13	122.28
2.764	11.221	125.80	125.65	1.840	7.482	122.06	122.13	1.839	7.305	122.13	122.27
3.004	12.197	125.80	125.62	2.006	8.156	122.06	122.09	2.005	7.963	122.13	122.26
3.237	13.142	125.80	125.60	2.169	8.818	122.06	122.06	2.168	8.610	122.13	122.26
3.479	14.124	125.80	125.57	2.329	9.468	122.06	122.04	2.327	9.244	122.13	122.25
				2.486	10.107	122.06	122.02	2.484	9.868	122.13	122.25
				2.640	10.735	122.06	122.00	2.639	10.481	122.13	122.25

[a] Λ, observed molar conductivity; Λ_{cal}, calculated molar conductivity; Λ_0, molar conductivity of uncomplexed cation; Λ_c, molar conductivity of the complexed cation; $X^2 = \sum(\Lambda - \Lambda_{cal})^2$. [b] Parameters: $\Lambda_0 = 126.28$ S cm^2 mol^{-1} ; $K = 2.513 \times 10^2$; $\Lambda_c = 121.68$ S cm^2 mol^{-1}; $X^2 = 0.0199$. [c] Parameters: $\Lambda_0 = 130.91$ S cm^2 mol^{-1}; $K = 1.132 \times 10^5$; $\Lambda_c = 121.86$ S cm^2 mol^{-1}; $X^2 = 0.177$. [d] Parameters: $\Lambda_0 = 134.47$ S cm^2 mol^{-1}; $K = 9.550 \times 10^5$; $\Lambda_c = 122.23$ S cm^2 mol^{-1}; $X^2 = 0.683$.

Table 4. Data Used for Calculating the Stability Constant, K, and Λ_c for Complexation of 18C6 with Alkaline Earth Metal Cations in 90 mass % Methanol at 298 K for $[MgCl_2\cdot 6H_2O]_0 = 4.01 \times 10^{-4}$ M, $[CaCl_2\cdot 2H_2O]_0 = 7.94 \times 10^{-4}$ M, $[SrCl_2\cdot 6H_2O]_0 = 4.02 \times 10^{-4}$ M, $[BaCl_2\cdot 2H_2O]_0 = 3.99 \times 10^{-4}$ M[a]

Mg^{2+} [b]				Ca^{2+} [c]				Sr^{2+} [d]				Ba^{2+} [e]			
$[L]_0/[M^{2+}]_0$	$10^4[L]_0$/M	Λ/S cm^2 mol^{-1}	Λcal/S cm^2 mol^{-1}	$[L]_0/[M^{2+}]_0$	$10^4[L]_0$/M	Λ/S cm^2 mol^{-1}	Λcal/S cm^2 mol^{-1}	$[L]_0/[M^{2+}]_0$	$10^4[L]_0$/M	Λ/S cm^2 mol^{-1}	Λcal/S cm^2 mol^{-1}	$[L]_0/[M^{2+}]_0$	$10^4[L]_0$/M	Λ/S cm^2 mol^{-1}	Λcal/S cm^2 mol^{-1}
0.189	0.759	144.49	144.45	0.172	1.367	126.72	126.71	0.200	0.802	148.85	148.90	0.198	0.793	144.25	144.19
0.375	1.503	144.36	144.38	0.337	2.681	126.60	126.57	0.396	1.588	148.11	148.15	0.393	1.569	143.75	143.80
0.557	2.232	144.28	144.30	0.496	3.946	126.53	126.46	0.587	2.358	147.36	147.41	0.583	2.331	142.75	142.75
0.736	2.948	144.21	144.23	0.650	5.164	126.41	126.35	0.776	3.114	147.11	147.18	0.770	3.079	141.75	141.87
0.911	3.650	144.15	144.17	0.767	6.338	126.28	126.25	0.961	3.856	146.36	146.39	0.953	3.812	141.10	141.05
1.083	4.339	144.09	144.11	0.940	7.470	126.13	126.16	1.142	4.583	145.86	145.95	1.133	4.531	140.75	140.81
1.251	5.015	144.03	144.05	1.077	8.562	126.05	126.04	1.319	5.297	145.86	145.91	1.310	5.237	140.75	140.78
1.417	5.678	143.97	144.00	1.210	9.616	126.02	125.99	1.494	5.998	145.86	145.88	1.483	5.930	140.75	140.78
1.579	6.329	143.93	143.94	1.338	10.635	125.93	125.92	1.666	6.686	145.86	145.87	1.653	6.610	140.75	140.78
1.739	6.969	143.86	143.90	1.462	11.620	125.88	125.85	1.834	7.361	145.86	145.86	1.820	7.278	140.75	140.78
1.895	7.569	143.86	143.86	1.582	12.572	125.84	125.78	1.998	8.025	145.86	145.85	1.984	7.933	140.75	140.78
2.049	8.213	143.86	143.82	1.698	13.494	125.72	125.72	2.321	9.315	145.86	145.85	2.145	8.577	140.75	140.78
2.200	8.819	143.86	143.77	1.810	14.386	125.66	125.66	2.631	10.561	145.86	145.85	2.612	10.442	140.75	140.77
2.349	9.414	143.86	143.74	1.919	15.251	125.60	125.60	3.077	12.351	145.86	145.84	2.909	11.632	140.75	140.77
3.054	12.239	143.86	143.57	2.025	16.089	125.54	125.55	3.501	14.053	145.86	145.85	3.055	12.212	140.75	140.77

[a] Λ, observed molar conductivity; Λ_{cal}, calculated molar conductivity; Λ_0, molar conductivity of uncomplexed cation; Λ_c, molar conductivity of the complexed cation; $X^2 = \sum(\Lambda - \Lambda_{cal})^2$. [b] Parameters: $\Lambda_0 = 144.61$ S cm^2 mol^{-1}; $K = 5.005 \times 10^2$; $\Lambda_c = 141.79$ S cm^2 mol^{-1}; $X^2 = 0.102$. [c] Parameters: $\Lambda_0 = 126.85$ S cm^2 mol^{-1}; $K = 2.712 \times 10^2$; $\Lambda_c = 122.11$ S cm^2 mol^{-1}; $X^2 = 0.0188$. [d] Parameters: $\Lambda_0 = 150.10$ S cm^2 mol^{-1}; $K = 1.853 \times 10^5$; $\Lambda_c = 145.83$ S cm^2 mol^{-1}; $X^2 = 0.423$. [e] Parameters: $\Lambda_0 = 145.50$ S cm^2 mol^{-1}; $K = 3.614 \times 10^6$; $\Lambda_c = 140.72$ S cm^2 mol^{-1}; $X^2 = 0.336$.

Table 5. Dependence of log K for the Complexation of 18-Crown-6 with Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} on Temperature and Composition of Solvent

cation	Mg^{2+}	Ca^{2+}		Sr^{2+}				Ba^{2+}			
mass % MeOH	90	70	90	0	50	70	90	0	50	70	90
					log K						
$T = 278$ K	2.76 ± 0.03	2.63 ± 0.03	3.08 ± 0.04	2.87 ± 0.03	4.34 ± 0.05	5.47 ± 0.05	5.71 ± 0.04	4.34 ± 0.05	5.47 ± 0.05	6.57 ± 0.04	7.12 ± 0.05
$T = 283$ K	2.74 ± 0.02	2.57 ± 0.04	3.05 ± 0.03	2.82 ± 0.04	4.25 ± 0.04	5.36 ± 0.05	5.59 ± 0.05	4.22 ± 0.04	5.33 ± 0.04	6.41 ± 0.05	6.96 ± 0.04
$T = 288$ K	2.72 ± 0.03	2.51 ± 0.04	3.02 ± 0.04	2.77 ± 0.04	4.17 ± 0.05	5.25 ± 0.06	5.47 ± 0.05	4.11 ± 0.04	5.20 ± 0.05	6.26 ± 0.05	6.82 ± 0.04
$T = 293$ K	2.71 ± 0.03	2.46 ± 0.02	3.00 ± 0.05	2.72 ± 0.05	4.09 ± 0.05	5.15 ± 0.03	5.37 ± 0.04	4.01 ± 0.03	5.07 ± 0.04	6.11 ± 0.05	6.68 ± 0.05
$T = 298$ K	2.70 ± 0.04	2.41 ± 0.05	2.97 ± 0.04	2.68 ± 0.03	4.02 ± 0.05	5.05 ± 0.06	5.26 ± 0.05	3.91 ± 0.04	4.96 ± 0.05	5.98 ± 0.06	6.55 ± 0.05
$T = 303$ K	2.68 ± 0.05	2.36 ± 0.04	2.94 ± 0.05	2.64 ± 0.04	3.95 ± 0.05	4.96 ± 0.05	5.16 ± 0.06	3.82 ± 0.03	4.85 ± 0.04	5.85 ± 0.05	6.42 ± 0.04
$T = 308$ K	2.67 ± 0.04	2.31 ± 0.05	2.92 ± 0.04	2.60 ± 0.04	3.88 ± 0.03	4.87 ± 0.06	5.07 ± 0.04	3.73 ± 0.04	4.74 ± 0.05	5.73 ± 0.04	6.31 ± 0.05
$T = 313$ K	2.66 ± 0.04	2.27 ± 0.04	2.90 ± 0.05	2.56 ± 0.05	3.82 ± 0.04	4.78 ± 0.04	4.98 ± 0.05	3.65 ± 0.04	4.65 ± 0.06	5.62 ± 0.05	6.20 ± 0.04

Table 6. Stability Constants and Thermodynamic Parameters at 298 K for the Complexation of 18-Crown-6 with Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} Cations in Methanol + Water Solvents[i]

cation	solvent	log K	$10^{-3}a$	b	$10^{3}c$	$-\Delta H°$	$-\Delta S°$	$-\Delta G°$	$\Delta C_p°$	method	ref
Mg^{2+}	(90% MeOH)-H_2O	2.70 ± 0.04	0.2929	1.548	0.552	4.67± 0.10	−35.94 ± 0.15	15.41 ± 0.12	6.3 ± 0.1	cond	TW
	MeOH	3.61 ± 0.06								spec	*a*
Ca^{2+}	(70% MeOH)-H_2O	2.41 ± 0.05	1.1869	−2.581	3.380	16.98 ± 0.16	10.85 ± 0.10	13.75 ± 0.15	38.6 ± 0.4	cond	TW
	(70% MeOH)-H_2O	2.51				17.86	11.70			cal	*b*
	(90% MeOH)-H_2O	2.97 ± 0.04	0.5917	0.545	1.470	8.83 ± 0.10	−27.21 ± 0.20	16.94 ± 0.10	16.8 ± 0.3	cond	TW
	MeOH	3.86				11.50	−35.40			cal	*c*
	MeOH	3.87				11.20	−36.00			cal	*d*
	MeOH	3.96								cond	*e*
	MeOH	4.25								spec	*a*
Sr^{2+}	H_2O	2.68 ± 0.03	1.4086	−4.233	7.335	14.50 ± 0.14	−2.65 ± 0.05	15.29 ± 0.12	83.7 ± 0.6	cond	TW
	H_2O	2.72				15.10	−1.25			cal	*f*
	(50% MeOH)-H_2O	4.02 ± 0.05	2.0389	−5.390	8.610	24.40 ± 0.16	4.95 ± 0.08	22.94 ± 0.18	98.9 ± 0.8	cond	TW
	(70% MeOH)-H_2O	5.05	2.5667	−6.511	9.890	32.33 ± 0.15	11.81 ± 0.15	28.81 ± 0.20	112.9 ± 0.9	cond	TW
	(70% MeOH)-H_2O	5.00 ± 0.06				31.30	10.50			cal	*b*
	(90% MeOH)-H_2O	5.26 ± 0.05	2.7518	−7.244	10.98	34.02 ± 0.12	13.40 ± 0.20	30.01 ± 0.15	125.3 ± 1.1	cond	TW
	MeOH	6.50								polg	*g*
	MeOH	5.64								spec	*a*
Ba^{2+}	H_2O	3.91 ± 0.04	3.1417	−11.549	16.50	32.10 ± 0.20	32.85 ± 0.25	22.31 ± 0.10	188.3 ± 1.8	cond	TW
	H_2O	3.87				31.70	33.00			cal	*f*
	(50% MeOH)-H_2O	4.96 ± 0.05	3.7069	−13.183	19.13	38.45 ± 0.16	34.12 ± 0.21	28.30 ± 0.20	218.3 ± 2.3	cond	TW
	(70% MeOH)-H_2O	5.98 ± 0.06	4.2861	−14.932	21.90	44.83 ± 0.18	35.98 ± 0.23	34.12 ± 0.25	249.9 ± 2.1	cond	TW
	(70% MeOH)-H_2O	6.00				44.58	35.50			cal	*b*
	(90% MeOH)-H_2O	6.55 ± 0.05	4.3749	−15.287	24.00	42.96 ± 0.20	18.82 ± 0.18	37.37 ± 0.30	273.8 ± 2.4	cond	TW
	MeOH	7.04				43.55	11.30			cal	*c*
	MeOH	7.31				48.50	23.50			cal	*h*
	MeOH	7.15								spec	*a*

[a] Kashanian and Shamsipur, 1989. [b] Izatt et al., 1976. [c] Lamb et al., 1980. [d] Buschmann 1985. [e] Chen et al., 1987. [f] Izatt et al., 1976. [g] Blasius et al., 1987. [h] Buschmann 1986. [i] The constants of eq 3 and literature values are also tabulated. $\Delta G°$ and $\Delta H°$, units kJ/mol; $\Delta S°$ and $\Delta C_p°$, units J/Kmol; TW, this work; cond, conductivity; spec, spectroscopy; cal, calorimetry; polg, polarography.

The method used to calculate the stability constant values from the conductivity data using a nonlinear least-squares technique has been described previously (Sway and Ambushamleh, 1995). The thermodynamic functions $\Delta H°$, $\Delta S°$, $\Delta G°$, and $\Delta C_p°$ for the complexation of 18-crown-6 with alkaline earth cations, namely, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, were calculated using the determined stability constants in the temperature range 278−313 K on solutions containing 0, 50, 70, and 90 mass % of methanol. Tables 1−4 are typical data for the complexation of 18-crown-6 with Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} at 298 K and in 0−90 mass % of methanol. At all temperatures and solvent compositions, Λ decreases with the mole ratio $[L]_0/[M^{2+}]_0$ and starts to level at mole ratio > 1. The decrease in Λ is considered as evidence for the formation of 1:1 complexes. Tables 1−4 show that the experimental and calculated values of Λ are in good agreement. All data obtained in this work, like those in Tables 1−4, were used to calculate the thermodynamic stability constants at various temperatures and solvent compositions. It was impossible to determine the stability constants for the interaction of Mg^{2+} with 18-crown-6 in 0−70 mass % and for Ca^{2+} in 0−50 mass % of methanol because of the constancy of solutions conductivity. The stability constant K decreases with increasing temperature. This indicates that the complexation process is exothermic. Plots of log K versus $1/T$ in 0−90 mass % of methanol for the crown ether with all cations studied were nonlinear. The experimental log K values were fitted to the following empirical expression (Feats and Ives 1956)

$$\log K = a/T + b + cT \tag{3}$$

using a nonlinear regression analysis program. The dependence of the best-fit log K values on temperature and solvent composition is given in Table 5. The log K values of all resulting complexes between Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} ions and 18-crown-6 in 0−90 mass % of methanol at 298 K are presented in Table 6 together with the reported values in aqueous solutions, 70 mass % of methanol and methanol for comparison. The agreement of the log K values in Table 6 with those determined in aqueous solutions and 70 mass % of methanol at 298 K by Izatt et al. (1976) using calorimetry is good, considering the different techniques used in the two studies. The difference in log K values between the present values and those of Izatt et al., (1976) in aqueous solution is 1−4% and 0.3−1% in 70 mass % of methanol.

Table 6 shows that the solvent composition has an important effect on the stability of the resulting complexes. In all cases, the stability of the complexes increases with a decrease in the solvating power of the solvent, as expressed by the Gutmann donor number (Gutmann and Wychera, 1966), where the donor number of methanol is 19.7 and that of water is 33.0. Thus, the solvent mixture with the highest proportion of methanol has the lowest donicity and therefore shows the least competition with the crown molecules for cations, which in turn results in the most stable complex. This explains the low stability of complexes in aqueous solutions based on the log K values obtained in this study. In all solvent compositions, the stability of alkaline earth complexes with 18-crown-6 follows the order $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$.

This stability sequence may be explained in terms of the cationic radii of the alkaline earth metals and the cavity radius of 18-crown-6. Ba^{2+} ion with an ionic radius of 1.35 Å (Shannon, 1976) is positioned inside the cavity of 18-crown-6 with a radius of 1.3−1.6 Å (Frensdorff, 1971), while other cations with smaller ionic sizes such as Mg^{2+}($r = 0.72$ Å), Ca^{2+}($r = 1.0$ Å), and Sr^{2+} ($r = 1.18$ Å) are too small for the cavity of the 18-crown-6, resulting in weaker complexes. To calculate the thermodynamic functions for the complex-

Table 7. Thermodynamic Parameters for the Complexation of 18-Crown-6 with Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} in 0−90 mass % Methanol between 278 K and 313 K[a]

	Mg^{2+}	Ca^{2+}		Sr^{2+}				Ba^{2+}			
mass % MeOH	90	70	90	0	50	70	90	0	50	70	90
$T = 278$ K											
$10^{-3}a$	0.2929	1.1869	0.5917	1.4086	2.0389	2.5667	2.7518	3.1417	3.7609	4.2861	4.3749
b	1.548	−2.581	0.545	−4.233	−5.390	−6.511	−7.244	−11.549	−13.183	−14.932	−15.287
10^3C	0.552	3.380	1.470	7.335	8.610	9.890	10.980	16.500	19.130	21.900	24.000
$-\Delta H^\circ$	4.80 ± 0.10	17.72 ± 0.16	9.15 ± 0.10	16.12 ± 0.14	26.30 ± 0.14	34.51 ± 0.15	36.44 ± 0.12	35.74 ± 0.20	42.67 ± 0.16	49.66 ± 0.18	48.25 ± 0.20
$-\Delta S^\circ$	−35.52 ± 0.15	13.44 ± 0.10	−26.08 ± 0.20	2.96 ± 0.05	11.54 ± 0.08	19.38 ± 0.15	21.81 ± 0.20	45.47 ± 0.25	48.76 ± 0.21	52.76 ± 0.23	37.20 ± 0.18
$-\Delta G^\circ$	14.69 ± 0.12	14.00 ± 0.15	16.40 ± 0.10	15.28 ± 0.12	23.10 ± 0.18	29.12 ± 0.20	30.39 ± 0.15	23.10 ± 0.10	29.06 ± 0.20	34.97 ± 0.25	37.90 ± 0.30
ΔC_p°	5.9 ± 0.1	36.0 ± 0.4	15.6 ± 0.3	78.1 ± 0.6	91.7 ± 0.8	105.3 ± 0.9	116.9 ± 1.1	175.7 ± 1.8	203.7 ± 2.3	233.1 ± 2.1	255.5 ± 2.4
$T = 283$ K											
$-\Delta H^\circ$	4.76 ± 0.10	17.54 ± 0.16	9.08 ± 0.10	15.72 ± 0.14	25.84 ± 0.16	33.98 ± 0.15	35.85 ± 0.12	34.85 ± 0.20	41.64 ± 0.16	48.48 ± 0.18	46.96 ± 0.20
$-\Delta S^\circ$	−35.62 ± 0.15	12.80 ± 0.10	−26.37 ± 0.20	1.56 ± 0.05	9.89 ± 0.08	17.49 ± 0.15	19.70 ± 0.20	42.32 ± 0.25	45.10 ± 0.21	48.57 ± 0.23	32.61 ± 0.18
$-\Delta G^\circ$	14.85 ± 0.12	13.93 ± 0.15	16.53 ± 0.10	15.28 ± 0.12	23.03 ± 0.18	29.04 ± 0.20	30.29 ± 0.15	22.87 ± 0.10	28.88 ± 0.20	34.73 ± 0.25	37.71 ± 0.30
ΔC_p°	6.0 ± 0.1	36.6 ± 0.4	15.9 ± 0.3	79.5 ± 0.6	93.3 ± 0.8	107.2 ± 0.9	119.0 ± 1.1	178.8 ± 1.8	207.3 ± 2.3	237.3 ± 2.1	260.1 ± 2.4
$T = 288$ K											
$-\Delta H^\circ$	4.73 ± 0.10	17.36 ± 0.16	9.00 ± 0.10	15.32 ± 0.14	25.37 ± 0.16	33.44 ± 0.15	35.25 ± 0.12	33.95 ± 0.20	40.60 ± 0.16	47.29 ± 0.18	45.65 ± 0.20
$-\Delta S^\circ$	−35.72 ± 0.15	12.14 ± 0.10	−26.65 ± 0.20	0.15 ± 0.05	8.25 ± 0.08	15.60 ± 0.15	17.61 ± 0.20	39.16 ± 0.25	41.44 ± 0.21	44.38 ± 0.23	28.01 ± 0.18
$-\Delta G^\circ$	15.00 ± 0.12	13.84 ± 0.15	16.65 ± 0.10	15.27 ± 0.12	23.00 ± 0.18	28.95 ± 0.20	30.16 ± 0.15	22.68 ± 0.10	28.67 ± 0.20	34.46 ± 0.25	37.60 ± 0.30
ΔC_p°	6.1 ± 0.1	37.3 ± 0.4	16.2 ± 0.3	80.9 ± 0.6	95.0 ± 0.8	109.1 ± 0.9	121.1 ± 1.1	181.9 ± 1.8	211.0 ± 2.3	241.5 ± 2.1	264.7 ± 2.4
$T = 293$ K											
$-\Delta H^\circ$	4.70 ± 0.10	17.17 ± 0.16	8.91 ± 0.10	14.92 ± 0.14	24.89 ± 0.16	32.89 ± 0.15	34.64 ± 0.12	33.03 ± 0.20	39.53 ± 0.16	46.07 ± 0.18	44.32 ± 0.20
$-\Delta S^\circ$	−35.83 ± 0.15	11.50 ± 0.10	−26.93 ± 0.20	−1.25 ± 0.05	6.60 ± 0.08	13.70 ± 0.15	15.50 ± 0.20	36.00 ± 0.25	37.77 ± 0.21	40.18 ± 0.23	23.42 ± 0.18
$-\Delta G^\circ$	15.20 ± 0.12	13.80 ± 0.15	16.83 ± 0.10	15.26 ± 0.12	22.95 ± 0.18	28.90 ± 0.20	30.07 ± 0.15	22.49 ± 0.10	28.43 ± 0.20	34.28 ± 0.25	37.48 ± 0.30
ΔC_p°	6.2 ± 0.1	37.9 ± 0.4	16.5 ± 0.3	82.3 ± 0.6	96.6 ± 0.8	110.9 ± 0.9	123.2 ± 1.1	185.1 ± 1.8	214.6 ± 2.3	245.7 ± 2.1	269.3 ± 2.4
$T = 303$ K											
$-\Delta H^\circ$	4.64 ± 0.10	16.78 ± 0.16	8.75 ± 0.10	14.07 ± 0.14	23.90 ± 0.16	31.76 ± 0.15	33.39 ± 0.12	31.15 ± 0.20	37.35 ± 0.16	43.57 ± 0.18	41.58 ± 0.20
$-\Delta S^\circ$	−36.04 ± 0.15	10.20 ± 0.10	−27.49 ± 0.20	−4.06 ± 0.05	3.30 ± 0.08	9.91 ± 0.15	11.29 ± 0.20	29.68 ± 0.25	30.45 ± 0.21	31.80 ± 0.23	14.23 ± 0.18
$-\Delta G^\circ$	15.55 ± 0.12	13.69 ± 0.15	17.06 ± 0.10	15.32 ± 0.12	22.91 ± 0.18	28.78 ± 0.20	29.94 ± 0.15	22.16 ± 0.10	28.14 ± 0.20	33.94 ± 0.25	37.25 ± 0.30
ΔC_p°	6.4 ± 0.1	39.2 ± 0.4	17.1 ± 0.3	85.1 ± 0.6	99.9 ± 0.8	114.8 ± 0.9	127.4 ± 1.1	191.5 ± 1.8	222.0 ± 2.3	254.1 ± 2.1	278.5 ± 2.4
$T = 308$ K											
$-\Delta H^\circ$	4.61 ± 0.10	16.59 ± 0.16	8.66 ± 0.10	13.65 ± 0.14	23.40 ± 0.16	31.18 ± 0.15	32.75 ± 0.12	30.19 ± 0.20	36.23 ± 0.16	42.29 ± 0.18	40.18 ± 0.20
$-\Delta S^\circ$	−36.15 ± 0.15	9.56 ± 0.10	−27.76 ± 0.20	−5.46 ± 0.05	1.65 ± 0.08	8.02 ± 0.15	9.20 ± 0.20	26.52 ± 0.25	26.79 ± 0.21	27.60 ± 0.23	9.63 ± 0.18
$-\Delta G^\circ$	15.75 ± 0.12	13.62 ± 0.15	17.22 ± 0.10	15.32 ± 0.12	22.87 ± 0.18	28.87 ± 0.20	29.90 ± 0.15	22.00 ± 0.10	27.95 ± 0.20	33.80 ± 0.25	37.21 ± 0.30
ΔC_p°	6.5 ± 0.1	39.9 ± 0.4	17.3 ± 0.3	86.5 ± 0.6	101.6 ± 0.8	116.6 ± 0.9	129.5 ± 1.1	194.6 ± 1.8	225.6 ± 2.3	258.3 ± 2.1	283.1 ± 2.4
$T = 313$ K											
$-\Delta H^\circ$	4.57 ± 0.10	16.38 ± 0.16	8.57 ± 0.10	13.21 ± 0.14	22.89 ± 0.16	30.59 ± 0.15	32.09 ± 0.12	29.20 ± 0.20	35.09 ± 0.16	41.00 ± 0.18	38.75 ± 0.20
$-\Delta S^\circ$	−36.26 ± 0.15	8.91 ± 0.10	−28.05 ± 0.20	−6.87 ± 0.05	−0.003 ± 0.08	6.12 ± 0.15	7.09 ± 0.20	23.36 ± 0.25	23.12 ± 0.21	23.41 ± 0.23	5.04 ± 0.18
$-\Delta G^\circ$	15.94 ± 0.12	13.60 ± 0.15	17.32 ± 0.10	15.34 ± 0.12	22.90 ± 0.18	28.65 ± 0.20	29.84 ± 0.15	21.87 ± 0.10	27.87 ± 0.20	33.68 ± 0.25	37.16 ± 0.30
ΔC_p°	6.6 ± 0.1	40.5 ± 0.4	17.6 ± 0.3	87.9 ± 0.6	103.2 ± 0.8	118.5 ± 0.9	131.6 ± 1.1	197.8 ± 1.8	229.3 ± 2.3	262.5 ± 2.1	287.7 ± 2.4

[a] The constants of eq 3 are tabulated. Units: ΔH° and ΔG°, kJ mol^{-1}; ΔS° and ΔC_p°, J mol^{-1} K^{-1}.

ation process at different temperatures, the following expressions were derived from eq 3

$$\Delta H° = -2.303R(a - cT^2) \tag{4}$$

$$\Delta S° = 2.303R(b + 2cT) \tag{5}$$

$$\Delta G° = -2.303R(a + bT + cT^2) \tag{6}$$

$$\Delta C_p° = 4.606RcT \tag{7}$$

where a, b, and c are empirical coefficients resulting from the best fit of log K with temperature in eq 3. The calculated values at 298 K of $\Delta H°$, $\Delta S°$, $\Delta G°$, and $\Delta C_p°$ are given in Table 6 together with the information available in the literature. Those functions calculated at other temperatures for each solvent composition are summarized in Table 7.

The values of $\Delta H°$ and $\Delta S°$ for the complexation of 18-crown-6 with Ca^{2+}, Sr^{2+}, and Ba^{2+}in aqueous solution and 70 mass % of methanol are in good agreement with those reported by Izatt et al. (1976) at 298 K (Table 6). The difference in $\Delta H°$ values between the present values and those of Izatt et al. (1976) in aqueous solution is 1−4% and 0.6−3% in 70 mass % of methanol, while for those of $\Delta S°$ the difference ranges between 0.5 and 7% in aqueuoes solution and 1.4 and 7% in 70 mass % of methanol. The $\Delta H°$ and $\Delta S°$ values for the Ba^{2+} complex in water at 298 K are more negative than those of the Sr^{2+} complex. This indicates that the formation of the Ba^{2+} complex is exothermic and stable compared to the Sr^{2+} complex. Table 7 shows that $\Delta H°$ and $\Delta S°$ of the Ba^{2+} complex become more negative than those of the Sr^{2+} complex in water as the temperature decreases. This suggests that the Ba^{2+} complex becomes more stable and more solvated in water with decreasing temperature. This is in accord with the formation of the complex ML^{2+}, shown by eq 1, which results in a more ordered state of the system as the solvent molecules are replaced by a cation in the crown ether cavity. Therefore, the stability sequence in water based on log K, $\Delta H°$, and $\Delta S°$ values are $Ba^{2+} > Sr^2$. The $\Delta C_p°$ value for the Ba^{2+} complex in water is larger and more positive than that of the Sr^{2+} complex at 298 K, as shown in Table 6, indicating that the enhancement of the structure of water by hydrogen bonds is more than that of Sr^{2+} complex.

The dependence of $\Delta H°$ values for $Sr^{2+}$and Ba^{2+}complexes on solvent composition in the range 0−90 mass % methanol at 298 K and other temperatures is shown in Tables 6 and 7. It is obvious that the addition of methanol up to 90 mass % is accompanied by more negative $\Delta H°$ values for the Ba^{2+}complex than those of the Sr^{2+} complex. This behavior is in agreement with the chemical contribution (nonelectrostatic), which suggests stronger Ba^{2+} complex solvation than Sr^{2+} complex solution.

Inspection of Table 6 in 90 mass % of methanol shows that in going toward smaller cations such as Mg^{2+} and Ca^{2+}, the $-\Delta H$ decreases and the ΔS becomes positive. This behavior is different from that of other cations for which the ΔS values are negative and indicates that these cations are not interacting strongly with all the available complexing sites in the crown ether.

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