INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON EQUILIBRIUM DATA*

# CRITICAL EVALUATION OF STABILITY CONSTANTS AND THERMODYNAMIC FUNCTIONS OF METAL COMPLEXES OF CROWN ETHERS

## (IUPAC Technical Report)

*Prepared for publication by*
FRANÇOISE ARNAUD-NEU[1], RITA DELGADO[2,3,‡], AND SÍLVIA CHAVES[3,4]

[1]*Laboratoire de Chimie-Physique, UMR 7512 (CNRS-ULP), ECPM, 25, rue Becquerel, 67087 Strasbourg Cedex 02, France;* [2]*Instituto de Tecnologia Química e Biológica, UNL, Apartado 127, 2781-901 Oeiras, Portugal;* [3]*Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal;* [4]*Centro de Química Estrutural, Av. Rovisco Pais, 1049-001 Lisboa, Portugal*

# Critical evaluation of stability constants and thermodynamic functions of metal complexes of crown ethers

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*Abstract*: Stability constants and thermodynamic functions of metal complexes of crown ethers in various solvents published between 1971 and the beginning of 2000 have been critically evaluated. The most studied crown ethers have been selected: 1,4,7,10-tetraoxacyclododecane (12C4), 1,4,7,10,13-pentaoxacyclopentadecane (15C5), and 1,4,7,10,13,16-hexaoxacyclooctadecane (18C6). The metal ions chosen are: alkali and alkaline earth metal ions, $Ag^+$, $Tl^+$, $Cd^{2+}$, and $Pb^{2+}$. The solvents considered are: water, methanol, ethanol, and their mixtures, as well as acetonitrile, $N,N'$-dimethylformamide, dimethylsulfoxide, and propylene carbonate. The published data have been examined and grouped into two categories, "accepted" and "rejected". The "accepted" values were considered as: (i) recommended (**R**), when the standard deviations (s.d.) on the constant $K$ or on $\Delta_r H$ were $\leq 0.05$ lg unit or $\leq 1$ kJ mol$^{-1}$, respectively; (ii) provisional (**P**), when $0.05 <$ s.d. $\leq 0.2$ for lg $K$ or $1 <$ s.d. $\leq 2$ kJ mol$^{-1}$ for $\Delta_r H$; (iii) recommended 1 (**R1**), if the values were obtained by a single research group, but were considered reliable in comparison with related systems, and considering that the research team usually presents R-level values for other similar systems.

## 1. INTRODUCTION

Crown ethers are compounds with multiple oxygen heteroatoms (3 or more) incorporated in a monocyclic carbon backbone. They were first synthesized by Pedersen in 1967 [67P]. Their generic name originates from their molecular shape, reminiscent of a royal crown. Abbreviated names have been proposed for these compounds in which there is a first figure corresponding to the total number of atoms in the cyclic backbone followed by the letter C (for crown) and then the number of oxygen atoms.

Owing to the nature of their binding sites and to the presence of a hydrophilic cavity delineated by a lipophilic envelope, crown ethers exhibit a strong affinity and high selectivity for alkali and alkaline earth metal ions. They were the first synthetic ligands for which this pronounced selectivity was identified. Crown ethers were extensively studied in parallel with natural ion-selective cyclic antibiotics such as valinomycin or enniatin for which they serve as simple models, helping to explain the transport of these biologically relevant cations and the mechanism of neurotransmission [79LI, 79PL, 87LF, 87PL, 91DV].

Crown ethers have found applications in many areas based on their ability to selectively recognize metal and ammonium ions. In analytical chemistry, their selective metal ion binding properties are exploited in separation and transport processes for the recovery or the removal of cations, in their concentration from very dilute solutions (trace enrichment of radionuclides) and in the design of ion-selective electrodes. They have also been used bonded to the stationary phase in chromatographic techniques. Owing to their ability to dissolve salts in organic media, by reducing the cation/anion interaction (i.e., by shielding the cation and activating the anion), they have been used in many syntheses, and as catalysts in phase-transfer catalysis or enzyme mimics. They also have medical applications as diagnostic or therapeutic agents [79LI, 79PL, 87PL, 89L, 94G].

Since 1967 there has been a growing interest in crown ethers and their complexes; Pedersen's pioneering work, followed by that of Lehn [91DV, 95L] and Cram [97CC], opened up the field of supramolecular chemistry [91V, 95L, 99BG, 00SA]. A great number of crown ether derivatives were thus synthesized, as well as other "coronands" having various other heteroatoms, such as N and S. Their metal complexes, including lanthanides and transition and heavy metal ions, have been extensively studied both in the solid state and in solution. Four reviews of the stability constants of the complexes formed in solution cover the literature until 1993 and span over 500 original references for the simple crown ethers and their benzo and cyclohexyl derivatives [74CE, 85IB, 91IP, 95IP]. Owing to this huge amount of data, the scope of this paper is limited to the most common crown ethers: 1,4,7,10-tetraoxacyclododecane (12C4), 1,4,7,10,13-pentaoxacyclopentadecane (15C5), and 1,4,7,10,13,16-hexaoxacyclooctadecane (18C6). The list of cations is also restricted to alkali and alkaline earth metal ions and to some heavy metal ions such as $Ag^+$, $Tl^+$, $Cd^{2+}$, and $Pb^{2+}$. Although they are not considered as hard cations, the latter are to some extent analogous to the former ones since they possess a spherical symmetry and do not require a specific coordination geometry for complexation. Furthermore, they are often used as competing cations in potentiometric determinations of stability constants of alkali and alkaline earth metal ion complexes. The solvents covered in this review have been limited to those frequently used in equilibrium studies: water, methanol (MeOH), ethanol (EtOH) and their mixtures, acetone (AC), acetonitrile (AN), *N,N'*-dimethylformamide (DMF), dimethylsulfoxide (DMSO) and propylene carbonate (PC). A few data were collected for chloroform ($CHCl_3$), especially in the deuterated form used in NMR experiments, but they were too few to permit recommendations.

## 2. BINDING PROPERTIES OF CROWN ETHERS

In this section, the main conclusions from the many publications on metal ion complexation by crown ethers are briefly summarized. For more detail, readers are directed to the many review articles and books on the subject [e.g., 79M, 89L, 92CS, 96BI].

### Thermodynamic origin of the complex stability

The fundamental equations

$$\Delta_r G^\circ = -RT \ln K \text{ and } \Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$$

show that both enthalpy and entropy contribute to the stability of the complexes. The enthalpy contribution can be obtained experimentally by titration calorimetry or from the temperature dependence of the stability constants (van 't Hoff plots), although the latter tends to be less reliable, especially if $\Delta_r H^\circ$ is not satisfactorily constant over the temperature range investigated, or the temperature range investigated is not sufficient. Complexation enthalpy changes are mainly related to: (i) cation/ligand interactions; (ii) solvation of the metal ion, the ligand, and the metal complexes formed in solution; (iii) repulsion between neighboring donor atoms; and (iv) steric deformation of the ligand. Entropy changes are linked to: (i) change in the number of particles involved in the complexation process and (ii) conformational changes of the ligand accompanying the complexation. In general, there is an enthalpy-driven stabilization, but in some cases—as for highly solvated cations for which complete or partial desolvation is an important step of the complexation process—the stabilization may be entropy-driven. There is often an entropy–enthalpy compensation effect, typical of class A metal ions, in which an enthalpy gain is accompanied by an entropy loss, or vice versa.

### Factors contributing to complexation and selectivity of crown ethers

Crown ethers have a strong affinity for alkali and alkaline earth metal ions and mimic the behavior of natural antibiotics. The main factor governing the binding strength and selectivity is the *size adequacy*

between the cation and the cavity created by the ligand. The cations fitting the cavity best are located in its center and optimize the interactions with the oxygen heteroatoms. Table 1 gives the ionic radii of the cations selected in this paper and the cavity radius of 12C4, 15C5, and 18C6 estimated from CPK molecular models (Corey–Pauling–Koltun models) and, when available, from X-ray crystallographic data [80LI][*]. Accordingly, the highest selectivities are expected when radius ratios are closest to 1.0. However, as can be seen from Tables 6 to 15, deviations are observed (e.g., for the complex of $Na^+$ with 15C5 in different solvents). It has been observed in practice that the size effect is most important for small cations that are able to enter the cavity completely, but other factors must be considered for the larger cations [80LI].

**Table 1** Size parameters of the cations [69SP, 76IT, 80LI] and the ligands [67P, 80LI].

| Cations | Ionic radius/pm | Cations | Ionic radius/pm | Cations | Ionic radius/pm |
|---------|-----------------|---------|-----------------|---------|-----------------|
| $Li^+$  | 74              | $Mg^{2+}$ | 72            | $Ag^+$  | 115             |
| $Na^+$  | 102             | $Ca^{2+}$ | 100           | $Tl^+$  | 150             |
| $K^+$   | 138             | $Sr^{2+}$ | 116           | $Pb^{2+}$ | 120           |
| $Rb^+$  | 149             | $Ba^{2+}$ | 136           | $Cd^{2+}$ | 109           |
| $Cs^+$  | 170             |         |                 |         |                 |

| Ligand cavity radius/pm | | |
|-------------------------|----------------|-------------------|
| 12C4 | 15C5 | 18C6 |
| 60   | 85   | 130  |
| –    | (86–92)[a] | (134–143)[a] |

[a]From X-ray crystallographic data [80LI].

The size adequacy concept must be tuned by the *flexibility* of the ligand, which, at some expense of energy, allows for the accommodation of smaller or greater cations. Nevertheless, ligands such as 12C4 or 15C5 have cavities too small to accommodate some cations (e.g., $Rb^+$ or $Cs^+$). In these cases, the complexation takes place outside the circular bidimensional cavity and the cation completes its coordination sphere with a second ligand, leading to a "sandwich complex". On the other hand, very large ligands (e.g., 30C10) are able to wrap around a small cation like $Na^+$ completely, so as to optimize the metal ion interactions with the donor sites. Thus, selectivity profiles of rigid ligands present *peak selectivities*, whereas more flexible ligands lead to *plateau selectivities* with a general decrease of the extent of complexation [79LI].

The metal-ligand binding energy also depends on the *number of oxygen heteroatoms* present in the macrocyclic structure. This factor determines not only the size of the cavity but also the bond energies with the cation. *Conformational changes* of the ligand as well as *the size of the rings* formed upon complexation may be additional factors that should also be taken into account.

The *nature of the cations* always plays an important role. With alkali and alkaline earth metal ions, which are "hard" acids in the Pearson classification [63P], the bonding with the oxygen heteroatoms is essentially electrostatic in nature and, therefore, the charge density of the cations is dominant. The post-transition series metal ions $Ag^+$, $Pb^{2+}$, and $Tl^+$ are potentially softer and should, in principle, lead to less stable complexes with oxygen donor sites. However, their high polarizability and the covalent character of the bonds that they can establish may lead in some cases to highly stable complexes.

Another very important factor, which needs to be considered in more detail, is *solvation* of the species involved in the complexation, i.e., the ligand, the metal ion, and the complex(es). In sufficiently polar solvents, where the interactions with the counterions are negligible, stability of the complex(es) is

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[*]CPK models give cavity sizes most consistent with the X-ray determinations.

related to the standard Gibbs free energies of solvation of the different species through the following equation:

$$-RT \ln K = \Delta_{bind}G° + \Delta_{solv}G°(ML^{n+}) - \Delta_{solv}G°(M^{n+}) - \Delta_{solv}G°(L) - \Delta_{conf}G°(L)$$

where the terms on the right are, respectively, the free energy for metal-ligand bonding, for solvation of the metal-ligand complex, for metal ion solvation, for ligand solvation, and for ligand conformational changes [77SZ].

Solvent effects are included in Cram's principle of preorganization [91C], which states that both host and guest participate in solvent interactions. However, some simplification can be achieved by assuming no change in conformation between the free and the complexed forms of the ligand. In this case, the solvation energy of the cation becomes the dominant factor in the above equation. In essence, the cation/ligand interactions compete against the solvation of the cation, and the balance between these two effects will be the determining factor for both stability and selectivity. Solvation of the metal ion depends strongly on the ion size. It also depends on the nature of the solvent. Some important solvent parameters are the relative permittivity (dielectric constant) of the solvents $\varepsilon_r$, their dipole moments $\mu$, and, in particular, the Gutmann donor numbers, DN, which are a measure of the electron-donating properties of a solvent [78G]. These are given in Table 2 for the solvents selected in this study.

The donor number is defined as the negative enthalpy value for the 1:1 adduct formation between a given electron-pair donor solvent and the standard Lewis acid $SbCl_5$, in dilute solution in the noncoordinating solvent 1,2-dichloroethane, for which a DN[*] of zero is assigned. The units are kcal mol$^{-1}$ for historical reasons. DN reflects the ability of the solvent to solvate cations and other Lewis acids [79R, 99C]. Because solvents with hydroxyl groups, like alcohols and water, solvate $SbCl_5$, their DN values have to be estimated by indirect methods. DN values range from zero, for solvents like hexane or tetrachloromethane, to 61.0 for triethylamine. In general, it is observed that the smaller the value of DN, the more stable the crown ether complex. The acceptor numbers of the same solvents, AN, an empirical parameter like DN, are also given in Table 2. AN measures the power of a given solvent to accept electron pairs as a Lewis acid. AN is a dimensionless number derived by Gutmann and coworkers from the $^{31}P$–NMR chemical shifts produced by the electron-pair acceptance effects of Lewis acidic solvents on dissolved triethylphosphane oxide. AN is defined as 100 times the ratio between the $^{31}P$–NMR chemical shift in a given electron-pair accepting solvent relative to the same in hexane, as reference solvent (AN equal to zero), and the shift of the 1:1 adduct $Et_3PO$–$SbCl_5$, dissolved in 1,2-dichloroethane (AN equal to 100, in order to achieve consistency with the DN scale) [79R, 99C].

**Table 2** Solvent parameters [78G].

| Solvents | $\varepsilon_r$ | $\mu$/D | DN | AN |
|---|---|---|---|---|
| $H_2O$ | 78.3 | 6.07 | 18–33[a] | 54.8 |
| MeOH | 32.66 | 5.7 | 19 | 41.3 |
| EtOH | 24.55 | 5.8 | 31.5 | 37.1 |
| AC | 20.56 | 9.5 | 17 | 12.5 |
| AN | 35.94 | 13.06 | 14.1 | 19.3 |
| DMF | 36.71 | 12.9 | 26.6 | 16.0 |
| DMSO | 46.45 | 13.0 | 29.8 | 19.3 |
| PC | 65.1 | 16.7 | 15.1 | 18.3 |

[a]Depends on how it is assessed, as water reacts with $SbCl_5$.

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[*]The symbols DN and AN do not comply with the normal IUPAC standards for symbols representing quantities (single letters in italic), and have to be considered as an exception of the same sort as pH. The application of the usual convention would be contrary to the universal usage and would also be difficult owing to the different nature of these empirical parameters (DN is a quantity, and AN is a dimensionless number).

However, the assumption of no conformational change of the ligand upon complexation is often invalid. Neither should ligand solvation be neglected, as shown by Popov et al. [88OP] and by Ozutsumi et al. [95OK, 95OKa], even though this factor is, in general, difficult to take into consideration because it requires a detailed knowledge of the ligand structures present in solution.

In solvents that are not easily dissociated, but where ion-pairing may occur, the *nature of the counterion* should become more important [96DN]. Such an effect should also increase with the charge of the cation. However, most authors consider that, analogous to $H_2O$, DMSO, and PC, ion pairing does not take place in solvents like MeOH, AN, and DMF for which $32 < \varepsilon_r < 40$, at least with diluted solutions (concentrations lower than 0.05 M) [95DL]. The situation should be different in AC and EtOH [80SP].

Crown ethers, like macrocycles in general, give rise to a macrocyclic effect that is characterized by an enhanced stability of their complexes as compared to the related open-chain systems. It is often governed by enthalpy changes although it appears as a balance of many antagonistic factors. Among the many factors contributing to this effect is the difference in solvation of the ligands [92CS].

## 3. PRESENTATION OF DATA AND ABBREVIATIONS USED

Only ML and $ML_2$ species, corresponding to the equilibria: $M^{n+} + L \rightleftharpoons ML^{n+}$ and $ML^{n+} + L \rightleftharpoons ML_2^{n+}$ ($M^{n+}$ being the metal ion and L the crown ether) were reported in the publications reviewed. As mentioned previously, "sandwich complexes" tend to form when the size of the metal ion is larger than the cavity size of the macrocycle. They are, therefore, found with the small lig- and 12C4 for all metal ions. In some solvents, they also form with the larger 18C6 and the very large $Cs^+$.

All stability constants, *K*, are given (Tables 6–15) as concentration constants. This means that the activity coefficients were held constant during measurement and that the constants are valid only at the stated ionic strength. The symbols "*I*" and "$I \to 0$" indicate ionic strength and its extrapolation to 0, respectively.

The experimental methods used for the determination of the selected values are denoted by the following symbols:

| | |
|---|---|
| ISE | electromotive force (emf) measurement using ion-selective electrode |
| pot | emf measurement using metal electrode, usually Ag |
| pol | polarography |
| dpp | differential pulse polarography |
| cv | cyclic voltammetry |
| sp | spectrophotometry |
| fluor | fluorimetry |
| NMR | nuclear magnetic resonance spectroscopy |
| cal | calorimetry |
| microcal | microcalorimetry |
| cond | conductimetry |
| ix | ion exchange |
| comp | competition techniques with other metal or ligand |

## 4. DATA EVALUATION CRITERIA

The published data of stability constants and thermodynamic functions of the complexes formed by the selected crown ethers and metal ions have been evaluated using the following main criteria [91KS; 91SM; 96YO; 97LP]:

- Unambiguous definition of complex stoichiometry for the stability constants reported (i.e., ML, $ML_2$, etc.).
- The extent to which essential reaction conditions are specified: the purity of the crown ether and other commercial salts, the grade of the solvent and its purification, the temperature, the ionic strength (see discussion below), the nature of the background electrolyte, the kinetics of the complexation reaction, the ligand-to-metal ratio, the ligand and metal ion concentrations, the type of counterion, etc. The method of standardization of the main solutions, especially the metal ion solutions, should also be indicated.
- The calibration of the apparatus used, when necessary, ought to be clearly described (e.g., the calibration of the electrode system in potentiometric measurements).
- The maintenance of constant temperature and ionic strength during titrations. If a background electrolyte is not used, the working concentrations need to be low (<0.1 M) and clearly indicated, and the experimental procedure must be sufficiently well described for it to be verified that the ionic strength has remained almost constant during the experiment.
- Reliable treatment of the experimental data (e.g., careful consideration of all possible species formed).
- Correct selection of auxiliary data from the literature, when necessary.
- Details of the calculation method used, indicating the name of the program (or a clear description of the unpublished methods if not published). A clear indication of the way standard deviations have been determined, the number of points measured, and the different metal-to-ligand ratios used is also important.

On the basis of these criteria, the published data have been examined and grouped into two categories: "accepted" and "rejected". Among the data that passed this preliminary screening, those exhibiting the best agreement between themselves were selected for further treatment: the values were averaged and calculated standard deviations (s.d.) evaluated, using a single value from each laboratory. The average value is considered as:

- **Recommended** (**R**) when the s.d. $\leq 0.05$ for lg $K$ or $\leq 1$ kJ mol$^{-1}$ for $\Delta_r H$.
- **Provisional** (**P**) when $0.05 <$ s.d. $\leq 0.2$ for lg $K$ or $1 <$ s.d. $\leq 2$ kJ mol$^{-1}$ for $\Delta_r H$.
- **Recommended 1** (**R1**) if the values are presented by a single research group, but considered reliable in comparison with related systems, and considering that the research team usually presents R-level values for other similar systems.

The s.d. for the **R** and **P** values indicates, therefore, an agreement among the selected data and is given in the tables after each averaged value. For the **R1** values, the indicated s.d. is that given by the authors in the original paper, except in the case of inconsistency between the number of significant digits in the value and the s.d.

In a few cases, the criterion $0.2 <$ s.d. $\leq 0.3$ for lg $K$ values was used to indicate values that the present reviewers assess as reliable, taking into account the difficult conditions necessary for the determinations, namely, slow kinetics of complexation, difficult synthesis of the crown ether, which makes replications impossible, competition methods, etc. Such data are not included in the tables, but are given as footnotes. The same treatment has been applied to data from some papers that do not exhibit any obvious errors, but reveal gaps in some important experimental details. Different experimental conditions that are considered reliable, namely, with respect to temperatures or pressure, are also given in footnotes.

The papers with rejected data may, nevertheless, contain important supplementary information that can be useful for readers. Accordingly, all the references checked in the present work have been listed (Tables 3–5), with the indication of the crown ether, the metal ion, and the solvent studied. Difficulties have been experienced in obtaining and translating most of the Chinese papers, and also some Russian and Japanese ones, so this review is limited to the papers referenced.

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**Table 3** References checked for each metal ion and each solvent with 1,4,7,10-tetraoxacyclododecane, 12C4.
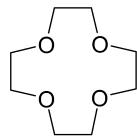


| Cations | Solvents | References |
|---|---|---|
| Li$^+$ | H$_2$O | 85E, 99E |
| | MeOH | 80SP, 87B, 88E, 90E, 93IH, 95AS |
| | AC | 80SP |
| | AN | 80HN, 80SP, 95AS, 95DL, 96DN, 96KAa, 99KC |
| | PC | 80MD, 80SP, 89MG, 95DL, 96DN, |
| Na$^+$ | MeOH | 81IK, 82MRa, 82MY, 83AA, 83GG, 87B, 87ZB, 93BC, 93IH, 95AS |
| | AN | 80HN, 96KA |
| | AN:DMSO | 96KAa |
| | DMF | 96OK |
| | DMSO | 96KA |
| | PC | 80MD |
| K$^+$ | MeOH | 81IK, 82MRa, 82MY, 83AA, 83GG, 87B, 87ZB, 93BC, 95AS |
| | AN | 88Ba |
| | DMF | 96OK |
| | PC | 80MD, 88Ba |
| Rb$^+$ | MeOH | 87B, 87ZB |
| | DMF | 96OK |
| | PC | 80MD |
| Cs$^+$ | MeOH | 87B, 87ZB |
| | DMF | 96OK |
| | PC | 80MD |
| Mg$^{2+}$ | H$_2$O | 85E, 88E |
| | PC | 82MR |
| Ca$^{2+}$ | H$_2$O | 85E, 88E |
| | MeOH | 87B |
| | EtOH | 88SV |
| | PC | 82MR |
| Sr$^{2+}$ | MeOH | 87B |
| | PC | 82MR |
| Ba$^{2+}$ | MeOH | 86Bb, 87B, 87BB, 92BC |
| | AN | 87BB |
| | PC | 82MR, 87BB |
| Ag$^+$ | MeOH | 86Bb, 87B, 92BC, 93BC |
| | AC | 99BS |
| | PC | 89BP, 99BS |
| Pb$^{2+}$ | H$_2$O | 78KK, 85LAa |
| | MeOH | 86Bb |
| | EtOH:H$_2$O | 96SSb |
| | AN:H$_2$O | 96SS |
| | PC | 82MD |
| Tl$^+$ | MeOH | 86Bb |
| | EtOH:H$_2$O | 96SSb |
| | AC | 93JH |
| | AN | 93JH |
| | AN:H$_2$O | 96SSb |
| | PC | 82MD |

**Table 4** References checked for each metal ion and each solvent with 1,4,7,10,13-pentaoxacyclopentadecane, 15C5.
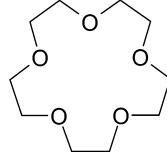


| Cations | Solvents | References |
|---|---|---|
| Li$^+$ | MeOH | 80SP, 87ZB, 95AS, 99WK |
| | MeOH:H$_2$O | 87ZB |
| | EtOH | 99WK |
| | AC | 80SP, 94BC, 99WK |
| | AN | 80HN, 80SP, 88TK, 94DL, 95AS, 96KAa, 99KC, 99WK |
| | DMF | 99WK |
| | DMSO | 99WK |
| | PC | 80SP, 80TY, 89B, 94DL, 95DL, 99WK |
| Na$^+$ | H$_2$O | 76IT, 79HR, 81LP, 82DG, 85BF, 86OE, 93SM |
| | MeOH | 80IY, 80LI, 81IK, 82DG, 82GD, 82IE, 82MK, 82MRa, 82MY, 83GG, 84DI, 84NM, 85Bb, 87AE, 87GH, 87NZ, 92KS, 92TU, 93BC, 95AS, 99WK |
| | MeOH:H$_2$O | 81SD, 82DG, 87KH, 87ZB |
| | EtOH | 81BL, 99WK |
| | AC | 94BC, 99WK |
| | AN | 80HN, 81LP, 82NY, 87BL, 88B, 88OP, 88TK, 95AS, 96KA, 99WK |
| | AN:DMSO | 96KA |
| | DMF | 81LP, 87BL, 99WB, 99WK |
| | DMSO | 81LP, 96KA, 99WK |
| | PC | 80TY, 89B, 99WK |
| K$^+$ | H$_2$O | 76IT, 79HR, 86OE, 93SM |
| | MeOH | 80IY, 80LI, 80PT, 81IK, 82GD, 82IE, 82MK, 82MRa, 82MY, 83GG, 84DI, 84NM, 85Bb, 87NZ, 87ZB, 87ZV, 92KS, 93BC, 95AS, 99WK |
| | MeOH:H$_2$O | 83DD, 87ZB, 87KH |
| | EtOH | 81BL, 99WK |
| | AC | 94BC, 99WK |
| | AN | 80HN, 87BL, 88B, 88Ba, 88TK, 95AS, 99WK |
| | DMF | 87BL, 99WB, 99WK |
| | DMSO | 99WK |
| | PC | 80TY, 88B, 89B, 99WK |
| Rb$^+$ | H$_2$O | 76IT |
| | MeOH | 85Bb, 87ZB, 88TK |
| | MeOH:H$_2$O | 87ZB |
| | AC | 94BC |
| | AN | 88B, 88TK, 91SK |
| | DMF | 96GM, 99WB |
| | PC | 80TY, 89B |
| Cs$^+$ | H$_2$O | 76IT, 79HR, 93SM |
| | MeOH | 80LI, 84DI, 85Bb, 87NZ, 87ZB, 88TK, 99WK |
| | MeOH:H$_2$O | 87KH, 87ZB |
| | EtOH | 99WK |
| | AC | 94BC, 99WK |
| | AN | 88B, 88TK, 91SK, 99WK |
| | DMF | 90SL, 96GM, 99WB, 99WK |

(*continues on next page*)

**Table 4** (*Continued*).

| Cations | Solvents | References |
|---------|----------|------------|
|         | DMSO | 99WK |
|         | PC | 80TY, 89B, 99WK |
| $Mg^{2+}$ | MeOH | 87CB |
|         | PC | 92BS, 92ST |
| $Ca^{2+}$ | $H_2O$ | 86ZK, 90RS |
|         | MeOH | 80LI, 83GG, 84DI, 85Bb, 87CB |
|         | EtOH | 88SV |
|         | AC | 93BD |
|         | PC | 92BS |
| $Sr^{2+}$ | $H_2O$ | 76IT |
|         | MeOH | 80LI, 85Bb |
|         | AC | 93BD |
|         | DMF | 99WB |
|         | PC | 92BS |
| $Ba^{2+}$ | $H_2O$ | 76IT, 00VG |
|         | MeOH | 85Bb |
|         | AC | 93BD |
|         | AN | 88B |
|         | DMF | 99WB |
|         | PC | 92BS |
| $Ag^+$ | $H_2O$ | 76IT |
|         | MeOH | 80LI, 85Bb, 85Bc, 93BC |
|         | EtOH | 98PS |
|         | AC | 99BS |
|         | AN:$H_2O$ | 98MT |
|         | DMF | 99WB |
|         | PC | 83AAa, 89BP, 92ST, 99BS, 00OK |
| $Pb^{2+}$ | $H_2O$ | 78KK, 76IT, 85BF |
|         | MeOH | 85B, 86IC, 87CB |
|         | EtOH: $H_2O$ | 96SSb |
|         | AN:$H_2O$ | 96SS |
|         | PC | 82MD |
| $Tl^+$ | $H_2O$ | 76IT, 85KT |
|         | MeOH | 86IC, 93PS |
|         | EtOH:$H_2O$ | 96SSb |
|         | AN:$H_2O$ | 96SSb, 98MT |
|         | DMF | 88OP |
|         | DMF:AN | 00FM |
|         | PC | 82MD |

**Table 5** References checked for each metal ion and each solvent with 1,4,7,10,13,16-hexaoxacyclo-octadecane, 18C6.
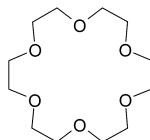


| Cations | Solvents | References |
|---|---|---|
| Li$^+$ | H$_2$O | 80SP, 95KT, 96BC |
| | MeOH | 80SP |
| | AC | 80SP, 94BC |
| | AN | 80HN, 80SP, 96KA, 99KC |
| | CDCl$_3$ | 80BS |
| | DMF | 99WB |
| | DMSO | 77SZ, 80SP |
| | PC | 80SP, 89B, 90S |
| Na$^+$ | H$_2$O | 71F, 76IT, 79HR, 81LP, 81RP, 82DG, 83PK, 84S, 85BF, 85ZP, 86OE, 86S, 89BB, 91E, 91MY, 92OI, 93GB, 93GE, 93SM, 95MV, 96BC, 96EY, 97DT, 97LK, 98KB, 99TM |
| | MeOH | 71F, 77BC, 77CS, 77IL, 77SZ, 79SP, 80IY, 80LI, 80WJ, 82DG, 82HL, 82MRa, 83GG, 83LS, 83PK, 84NM, 85Bb, 85SP, 85ZB, 86AG, 87AE, 87B, 87GH, 89BB, 89E, 90LP, 91LL, 92B, 92KS, 93LT, 96LK, 97LK, 97YY, 98KB, 98SS |
| | MeOH:H$_2$O | 76ITa, 80LV, 82DG, 82HL, 84EK, 89BB, 90MB, 91GT, 92SB, 93LT, 95KZ, 96LK, 97LK, 98KB |
| | EtOH | 81BL, 83PK |
| | EtOH:H$_2$O | 84LA |
| | AC | 81LP, 81RP, 86BP, 94BC |
| | AN | 80KC, 81LP, 81RP, 82NY, 85BP, 86BP, 87BL, 88B, 88OP, 95OKa |
| | AN:H$_2$O | 96EY |
| | CDCl$_3$ | 80BS |
| | DMF | 77SZ, 81LP, 81RP, 81T, 85BP, 87BL, 94OO, 99WB |
| | DMSO | 77SZ, 80KC, 81LP, 81RP |
| | PC | 80KC, 80TY, 81LP, 81RP, 84FL, 85SP, 86BP, 89B, 90S, 95OKa |
| K$^+$ | H$_2$O | 71F, 76IT, 79HR, 82MRa, 83PK, 84S, 84ZB, 85GL, 85TA, 86S, 87MG, 87ZB, 89BB, 91E, 92OI, 92VO, 93SM, 95KT, 95WI, 96BC, 96EY, 96KS, 96SSa, 98BJ, 98KB |
| | MeOH | 71F, 77BC, 77CS, 77IL, 77SZ, 80IY, 80LI, 80PT, 80WJ, 82HL, 82MRa, 83GG, 83LS, 83PK, 83T, 84NM, 85Bb, 85BP, 85TJ, 86AG, 86B, 87AE, 87B, 87GH, 89BB, 89E, 90LP, 91LL, 92B, 92KS, 93LT, 96KS, 96SSa, 97RE, 97YY, 98KB, 98SS, 99RM |
| | MeOH:H$_2$O | 76ITa, 80LV, 82HL, 84EK, 89BB, 90MB, 91GT, 92SB, 93LT, 95KZ, 96KS, 98KB |
| | MeOH:AN | 97RE |
| | MeOH:DMF | 99RM |
| | EtOH | 81BL, 83PK |
| | EtOH:H$_2$O | 84LA |
| | AC | 86BP, 94BC, 96SSa |
| | AN | 80KC, 83T, 85TJ, 86BP, 87BL, 88B, 95OKa, 96SSa, 97RE |
| | AN:DMF | 97RE |
| | AN:H$_2$O | 96EY |
| | CDCl$_3$ | 80BS |

**Table 5** (*Continued*).

| Cations | Solvents | References |
|---|---|---|
| | DMF | 77SZ, 81T, 87BL, 94OO, 96SSa, 97RE, 99RM, 99WB |
| | DMSO | 77SZ, 80KC, 83T, 88FK, 96SSa |
| | PC:DMF | 97RE |
| | PC | 80KC, 80TY, 86BP, 88Ba, 95OKa, 97RE |
| Rb$^+$ | H$_2$O | 76IT, 89BB, 92OI, 95MV, 96BC |
| | MeOH | 77BC, 77CS, 77SZ, 80LI, 83LS, 84ZB, 85Bb, 85ZB, 86B, 87B, 89BB, 91LL, 92B |
| | MeOH:H$_2$O | 76ITa, 89BB, 92GS, 92SB, 95KZ |
| | EtOH:H$_2$O | 84LA |
| | AC | 86BP, 94BC |
| | AN | 88B, 91SK, 95OKa |
| | CDCl$_3$ | 80BS |
| | DMF | 77SZ, 81T, 94OO, 96GM, 99WB |
| | DMSO | 77SZ |
| | PC | 80TY, 86BP, 89B, 95OKa |
| Cs$^+$ | H$_2$O | 71F, 76IT, 79HR, 81RP, 89GS, 92OI, 93SM, 95MV, 96BC |
| | MeOH | 71F, 77BC, 77CS, 77SZ, 80LI, 83LS, 85Bb, 87B, 89BB, 91LL, 92B |
| | MeOH:H$_2$O | 76ITa, 89BB, 92SB, 95KZ |
| | AC | 77MP, 81RP, 86BP, 94BC |
| | AN | 77MP, 81RP, 85BP, 86BP, 88B, 91SK, 95OKa |
| | DMF | 77MP, 77SZ, 81T, 85BP, 90SL, 94OO, 96GM, 99WB |
| | DMSO | 77MP, 77SZ |
| | PC | 77MP, 80KC, 80TY, 86BP, 89B, 95OKa |
| Ra$^+$ | H$_2$O | 85SK |
| Mg$^{2+}$ | H$_2$O | 97BE |
| | MeOH | 87CB, 89KS |
| | MeOH:H$_2$O | 99SS |
| | AN | 91AS, 91SS |
| | AN:H$_2$O | 97BE |
| | DMF | 85BP, 89KS, 91AS, 99WB |
| | DMSO | 89KS |
| | PC | 92BS, 92ST |
| Ca$^{2+}$ | H$_2$O | 76IT, 79HR, 86OE, 87SK, 90RS, 94VBa, 95MV, 95OK, 96BC |
| | MeOH | 80LI, 83GG, 85Bb, 86Ba, 87CB, 89KS, 92B |
| | MeOH:H$_2$O | 76ITa, 99SS |
| | EtOH | 86SR, 87RS |
| | EtOH:H$_2$O | 84LA |
| | AC | 93BD |
| | AN | 91AS, 91SS |
| | DMF | 85BP, 89KS, 91AS, 95OK, 99WB |
| | DMSO | 89KS |
| | PC | 92BS, 92ST |
| Sr$^{2+}$ | H$_2$O | 76IT, 84SL, 85GL, 85SK, 88HD, 89KM, 94VB, 94VBa, 95MV, 95OK, 95WI, 96BC, 99SS |
| | MeOH | 80LC, 80LI, 84BR, 85Bb, 86B, 86Ba, 89KS, 89YK, 92B |
| | MeOH:H$_2$O | 76ITa, 99SS |
| | EtOH | 92MV |
| | EtOH:H$_2$O | 89KM |
| | AC | 93BD |
| | AN | 91AS, 91SS |

**Table 5** (*Continued*).

| Cations | Solvents | References |
|---------|----------|-----------|
| | DMF | 85BP, 89KS, 91AS, 95OK, 99WB |
| | DMSO | 89KS |
| | PC | 92BS, 92ST |
| $Ba^{2+}$ | $H_2O$ | 76IT, 82YM, 85GL, 85SK, 88HD, 90BW, 94VBa, 95MV, 95OK, 95WI, 96BC, 98BJ, 98SS, 99BS, 99SS |
| | MeOH | 77IL, 80LI, 82HL, 84BR, 85Ba, 85Bb, 86B, 86Ba, 86Bb, 89KS, 92B |
| | MeOH:$H_2O$ | 76ITa, 82HL, 99SS |
| | AC | 86BP, 93BD |
| | AN | 86BP, 88B, 91AS, 91SS |
| | DMF | 85BP, 89KS, 91AS, 95OK, 99WB |
| | DMSO | 89KS |
| | PC | 86BP, 92BS, 92ST |
| $Cd^{2+}$ | $H_2O$ | 85LAa, 92ZQ, 99TM, 00KT |
| | MeOH | 98RH |
| | MeOH:$H_2O$ | 97SA |
| | DMF | 96RE |
| | PC:DMF | 96RE |
| | PC | 96RE |
| $Pb^{2+}$ | $H_2O$ | 76IT, 76KK, 82YM, 85BF, 85LAa, 87IB, 88HA, 91PS, 92ZQ, 95WI, 97SA |
| | MeOH | 85B, 86Bb, 86IC, 87CB |
| | MeOH:$H_2O$ | 76ITa, 87IB, 97SA |
| | EtOH:$H_2O$ | 96SSb |
| | AN | 96RE |
| | AN:DMSO | 96RE |
| | AN:$H_2O$ | 91PS, 94RA, 96SS |
| | DMF | 85BP, 96RE |
| | DMSO | 96RE |
| | PC:DMF | 96RE |
| | PC | 96RE |
| $Ag^+$ | $H_2O$ | 71F, 76IT, 97SA, 97VO, 99LP, 00BS |
| | MeOH | 77ILa, 80KC, 80LI, 85Bb, 86Bb, 90LP, 92B, 99LP |
| | MeOH:$H_2O$ | 97SA, 99LP |
| | EtOH | 98PS, 00BS |
| | EtOH:$H_2O$ | 84LA |
| | AC | 93JH, 99BSa, 00BS |
| | AN | 88CR, 96BG, 00BS |
| | DMF | 86PA, 93JH, 99WB, 00BS |
| | DMSO | 77SZ, 00BS |
| | PC | 80KC, 89BP, 92ST, 99BSa, 00BS |
| $Tl^+$ | $H_2O$ | 76IT, 76KK, 81RP, 84P, 84ZB, 85KT, 91PS, 92ZQ, 95WI |
| | MeOH | 74CG, 80KC, 80WJ, 86Bb, 86IC, 88LFa, 90LP, 93LK, 93PS |
| | MeOH:$H_2O$ | 93LK |
| | EtOH | 74CG, 93LK |
| | EtOH:$H_2O$ | 93LK, 96SSb |
| | AC | 81RP, 85LA, 86BP, 92LL, 93JH |
| | AC:$H_2O$ | 92LL |
| | AN | 81RP, 86BP, 91LK, 91SS, 92LL, 93JH, 96RE |
| | AN:DMF | 00FM |
| | AN:DMSO | 96RE |

**Table 5** (*Continued*).

| Cations | Solvents | References |
|---------|----------|-----------|
| | AN:$H_2O$ | 91PS, 92LL, 96SSb |
| | DMF | 77SZ, 81RP, 85LA, 88LFa, 88OP, 91LK, 91SS, 93JH, 96RE |
| | DMSO | 81RP, 91LK, 92LL |
| | DMSO:$H_2O$ | 92LL |
| | PC:DMF | 96RE |
| | PC | 80KC, 91LK, 96RE |

Tables 6–15 collect all the selected values of lg $K$, $\Delta_r H$, and $T\Delta_r S$, each table corresponding to a different solvent, starting by water (Table 6), followed by methanol (Table 7) and its mixtures with water (Table 8), then ethanol (Table 9) and its mixtures with water (Table 10). The other tables follow the alphabetical order of the remaining solvents: acetone (Table 11), acetonitrile (Table 12), *N*,*N*′-dimethylformamide (Table 13), dimethylsulfoxide (Table 14), and, finally, propylene carbonate (Table 15).

**Table 6** Recommended and provisional data for 12C4, 15C5, and 18C6 complexes in water at 25 °C and ionic strength 0–0.1 M.

| Cations | Species | lg $K$ (Evaluation) | References | $-\Delta_r H$ (Evaluation) kJ mol$^{-1}$ | $T\Delta_r S$ kJ mol$^{-1}$ | References |
|---------|---------|---------------------|------------|------------------------------------------|-----------------------------|------------|
| | | | 12C4 | | | |
| Pb$^{2+}$ | ML | 2.00 ± 0.05 (R1) | 78KK | | | |
| | | | 15C5 | | | |
| Na$^{+}$ | ML | 0.8 ± 0.2 (P) | 76IT, 79HR, 82DG, 85BF | 6.3 ± 0.2 (R1) | −1.7 | 76IT |
| K$^{+}$ | ML | 0.75 ± 0.08 (P) | 76IT, 79HR | 17.2 ± 0.4 (R1) | −12.9 | 76IT |
| Cs$^{+}$ | ML | 0.8 ± 0.2 (P) | 76IT, 79HR | 5.4 ± 0.8 (R1) | −0.8 | 76IT |
| Sr$^{2+}$ | ML | [a] | | 3.8 ± 0.4 (R1) | | 76IT |
| Ba$^{2+}$ | ML | 1.69 ± 0.06 (P) | 76IT, 00VG | 4.6 ± 0.4 (R) | 5.0 | 76IT, 00VG |
| Ag$^{+}$ | ML | [b] | | [b] | | |
| Tl$^{+}$ | ML | [c] | | [c] | | |
| Pb$^{2+}$ | ML | 2.0 ± 0.1 (P) | 76IT, 78KK | 13.6 ± 0.1 (R1) | −2.5 | 76IT |
| | | | 18C6 | | | |
| Na$^{+}$ | ML | 0.8 ± 0.2 (P) | 76IT, 79HR, 85BF, 92OI, 95MV, 96EY, 99TM | 11 ± 2 (P) | −6 | 76IT, 92OI, 95MV |
| K$^{+}$ | ML | 2.05 ± 0.04(R)[d,e] | 71F, 79HR, 82MRa, 85TA, 87MG, 87ZB, 92OI, 92VO, 95WI, 96SSa | 25.0 ± 0.9 (R)[e,f] | −13.3 | 76IT, 82MRa, 85TA, 92OI, 92VO, 95WI, 96SSa |
| Rb$^{+}$ | ML | 1.51 ± 0.08 (P)[g] | 76IT, 92OI, 95MV | 16.0 ± 0.5 (R)[g] | −7.4 | 76IT, 95MV |
| Cs$^{+}$ | ML | 0.96 ± 0.03 (R) | 76IT, 79HR, 92OI, 95MV | 17 ± 1 (P)[h] | 12 | 76IT, 92OI, 95MV |
| Ca$^{2+}$ | ML | 0.5 ± 0.1 (P) | 87SK, 95MV, 95OK | | | |
| Sr$^{2+}$ | ML | 2.75 ± 0.05 (R)[i,j] | 76IT, 95MV, 95OK, 96BC, 99SS | 15.1 ± 0.5 (R)[i,j] | 0.6 | 76IT, 95MV, 95OK, 99SS |
| Ba$^{2+}$ | ML | 3.79 ± 0.05 (R)[k,l] | 76IT, 90BW, 94VBa, 95OK, 96BC, 99BS | 31.7 ± 0.8 (R)[k,l] | −10.1 | 76IT, 90BW, 94VBa, 95OK, 96BC, 99BS, 99SS |
| Ag$^{+}$ | ML | 1.50 ± 0.03 (R) | 76IT, 97SA, 00BS | 9 ± 1 (R) | −1 | 76IT, 97SA, 99LP, 00BS |
| Tl$^{+}$ | ML | 2.2 ± 0.1 (P)[m] | 76IT, 76KK, 84P, 84ZB | 20 ± 2 (P)[m] | −7 | 76IT, 76KK, 84P |
| Pb$^{2+}$ | ML | 4.24 ± 0.02 (R)[n] | 76IT, 88HA, 97SA | 22 ± 2 (P)[n] | 2 | 76IT, 97SA |

(*continues on next page*)

**Table 6** (*Continued*).

[a] The value of lg $K = 1.95 \pm 0.08$ can be treated as reliable [76IT].

[b] The values of lg $K$ / $-\Delta_r H$ : $0.94 \pm 0.08$ / $13.5 \pm 0.1$ could be treated as reliable [76IT].

[c] Divergent values from [76IT] and [85KT]; the most reliable value seems to be $1.23 \pm 0.04$ [76IT]; the corresponding $-\Delta_r H$ value is $16.8 \pm 0.2$.

[d] Values of lg $K$ at other temperatures [85TA]: $2.29 \pm 0.01$ (10 °C); $2.25 \pm 0.01$ (15 °C); $2.14 \pm 0.01$ (20 °C); $1.94 \pm 0.01$ (35 °C); $1.79 \pm 0.02$ (45 °C).

[e] Values of lg $K$ / $-\Delta_r H$ at $p = 1.52$ MPa and different temperatures [95WI]: $1.74 \pm 0.06$ / $26.3 \pm 0.6$ (50 °C); $1.43 \pm 0.08$ / $27.9 \pm 0.9$ (75 °C); $1.14 \pm 0.08$ / $30 \pm 1$ (100 °C); $0.86 \pm 0.09$ / $33.5 \pm 0.9$ (125 °C).

[f] Values of $-\Delta_r H$ at other temperatures [92VO]: $23.6 \pm 0.4$ (35 °C); $22.3 \pm 0.2$ (45 °C).

[g] Values of lg $K$ / $-\Delta_r H$ at other temperatures [95MV]: $1.47 \pm 0.02$ / $15.3 \pm 0.2$ (35 °C); $1.38 \pm 0.02$ / $14.7 \pm 0.1$ (45 °C).

[h] Values of $-\Delta_r H$ at other temperatures [95MV]: $15.0 \pm 0.2$ (35 °C); $13.95 \pm 0.06$ (45 °C).

[i] Values of lg $K$ / $-\Delta_r H$ at other temperatures [95MV]: $2.64 \pm 0.02$ / $13.9 \pm 0.1$ (35 °C); $2.56 \pm 0.02$ / $13.1 \pm 0.1$ (45 °C).

[j] Values of lg $K$ / $-\Delta_r H$ at $p = 1.52$ MPa and different temperatures [95WI]: $2.51 \pm 0.01$ / $15.9 \pm 0.2$ (50 °C); $2.32 \pm 0.01$ / $17.2 \pm 0.3$ (75 °C); $2.14 \pm 0.01$ / $18.9 \pm 0.4$ (100 °C); $1.96 \pm 0.02$ / $21.2 \pm 0.4$ (125 °C).

[k] Values of lg $K$ / $-\Delta_r H$ at other temperatures [95MV]: $3.68 \pm 0.04$ / $29.3 \pm 0.2$ (35 °C); $3.52 \pm 0.04$ / $28.1 \pm 0.4$ (45 °C).

[l] Values of lg $K$ / $-\Delta_r H$ at $p = 1.52$ MPa and different temperatures [95WI]: $3.46 \pm 0.01$ / $29.4 \pm 0.1$ (50 °C); $3.12 \pm 0.01$ / $28.7 \pm 0.2$ (75 °C); $2.83 \pm 0.01$ / $29.3 \pm 0.4$ (100 °C); $2.57 \pm 0.01$ / $31.3 \pm 0.6$ (125 °C).

[m] Values of lg $K$ / $-\Delta_r H$ at $p = 1.52$ MPa and different temperatures [95WI]: $2.01 \pm 0.01$ / $19.4 \pm 0.3$ (50 °C); $1.78 \pm 0.02$ / $20.2 \pm 0.3$ (75 °C); $1.57 \pm 0.03$ / $21.2 \pm 0.5$ (100 °C); $1.38 \pm 0.03$ / $22.4 \pm 0.5$ (125 °C).

[n] Values of lg $K$ / $-\Delta_r H$ at $p = 1.52$ MPa and different temperatures [95WI]: $3.98 \pm 0.01$ / $21.5 \pm 0.2$ (50 °C); $3.73 \pm 0.01$ / $22.4 \pm 0.4$ (75 °C); $3.49 \pm 0.01$ / $24.2 \pm 0.5$ (100 °C); $3.27 \pm 0.02$ / $26.9 \pm 0.6$ (125 °C).

**Table 7** Recommended and provisional data for 12C4, 15C5, and 18C6 complexes in methanol (MeOH) at 25 °C and ionic strength 0–0.1 M.

| Cations | Species | lg $K$ (Evaluation) | References | $-\Delta_r H$ (Evaluation) kJ mol$^{-1}$ | $T\Delta_r S$ kJ mol$^{-1}$ | References |
|---|---|---|---|---|---|---|
| | | | 12C4 | | | |
| Li$^+$ | ML | [a] | | | | |
| Na$^+$ | ML | $1.5 \pm 0.2$ (P) | 82MRa, 82MY; 87B | $11 \pm 2$ (P) | $-2.2$ | 82MRa, 87B |
| | ML$_2$ | $2.2 \pm 0.1$ (P) | 82MRa, 82MY; 87B | $30 \pm 2$ (P) | $-18$ | 82MRa, 87B |
| K$^+$ | ML | $1.60 \pm 0.07$ (P) | 82MRa, 82MY, 87B, 87ZB, 93BC | | | |
| | ML$_2$ | [b] | | | | |
| Rb$^+$ | ML | $1.65 \pm 0.05$ (R1) | 87ZB | | | |
| | ML$_2$ | $0.87 \pm 0.05$ (R1) | 87ZB | | | |
| Cs$^+$ | ML | $1.62 \pm 0.05$ (R1) | 87ZB | | | |
| | ML$_2$ | $0.82 \pm 0.05$ (R1) | 87ZB | | | |
| | | | 15C5 | | | |
| Li$^+$ | ML | $1.24 \pm 0.05$ (R) | 87ZB, 95AS | | | |
| Na$^+$ | ML | $3.32 \pm 0.12$ (P) | 82GD, 82MRa, 82MY, 84DI, 85Bb, 93BC, 95AS | $22.5 \pm 0.4$ (R) | $-3.6$ | 82MRa, 84DI, 85Bb |
| | ML$_2$ | $2.5 \pm 0.2$ (P) | 82MRa, 85Bb | $10 \pm 1$ (R1) | $5$ | 85Bb |
| K$^+$ | ML | $3.5 \pm 0.2$ (P) | 82GD, 82MRa, 82MY, 84DI, 85Bb, 87ZB, 93BC | $32.4 \pm 0.4$ (R) | $-12.2$ | 82MRa, 84DI, 85Bb |
| | ML$_2$ | $2.5 \pm 0.2$ (P) | 84DI, 82MY, 85Bb, 87ZB, 93BC | | | |
| Rb$^+$ | ML | $2.80 \pm 0.08$ (P) | 87ZB, 88TK | | | |
| | ML$_2$ | $2.23 \pm 0.05$ (R1) | 87ZB | | | |
| Cs$^+$ | ML | $2.69 \pm 0.08$ (P) | 84DI, 87ZB, 88TK | [d] | | |
| | ML$_2$ | [c] | | | | |
| Ca$^{2+}$ | ML | $2.2 \pm 0.2$ (P) | 80LI, 83GG, 85Bb, 87CB | $8 \pm 2$ (P) | $5$ | 80LI, 85Bb |
| Ag$^+$ | ML | $3.62 \pm 0.02$ (R) | 80LI, 85Bb | $27.2 \pm 0.3$ (R) | $-6.6$ | 80LI, 85Bb |
| | ML$_2$ | [e] | | | | |
| Tl$^+$ | ML | $3.31 \pm 0.02$ (R1) | 86IC | $36.40 \pm 0.02$ (R1) | $-17.52$ | 86IC |

(*continues on next page*)

**Table 7** (*Continued*).

| Cations | Species | lg $K$ (Evaluation) | References | $-\Delta_r H$ (Evaluation) kJ mol$^{-1}$ | $T\Delta_r S$ kJ mol$^{-1}$ | References |
|---|---|---|---|---|---|---|
| Pb$^{2+}$ | ML | 3.6 ± 0.2 (P) | 85B, 86IC, 87CB | 27 ± 2 (P) | −6 | 85B, 86IC |
| | | | 18C6 | | | |
| Na$^+$ | ML | 4.35 ± 0.04 (R)[f] | 71F, 79SP, 80WJ, 82HL, 82MRa, 85Bb, 85SP, 85ZB, 92B, 98SS | 35 ± 1 (R) | −10 | 82HL, 83LS, 85Bb, 97LK |
| K$^+$ | ML | 6.11 ± 0.05 (R)[g] | 71F, 80LI, 82MRa, 83T, 86B, 92B, 97RE, 98SS | 55.3 ± 0.7 (R) | −20.5 | 80LI, 90LP, 92B, 96SSa, 97RE |
| Rb$^+$ | ML | 5.4 ± 0.1 (P) | 77BC, 80LI, 85ZB, 92B | 50.0 ± 0.4 (R) | −19.2 | 80LI, 85Bb, 92B |
| Cs$^+$ | ML | 4.6 ± 0.2 (P) | 71F, 80LI, 83LS, 87B, 91LL | 47.2 ± 0.3 (R1) | −21.0 | 80LI |
| | ML$_2$ | 2.06 ± 0.05 (R1) | 80LI | 13.9 ± 0.6 (R1) | −2.1 | 80LI |
| Ca$^{2+}$ | ML | 4.0 ± 0.2 (P) | 80LI, 85Bb, 87CB, 89KS, 92B | 11.3 ± 0.3 (R) | 11.5 | 80LI, 85Bb |
| Sr$^{2+}$ | ML | | | 36.6 ± 0.6 (R) | | 80LI, 85Bc |
| Ba$^{2+}$ | ML | 7.2 ± 0.1 (P) | 80LI, 85Ba, 86B, 89KS | 47 ± 2 (P) | −6 | 80LI, 85Ba, 85Bb, 86B |
| Ag$^+$ | ML | 4.61 ± 0.04 (R) | 80KC, 80LI, 85Bb, 90LP, 92B | 39 ± 1 (R) | −13 | 80LI, 85Bb, 90LP |
| Tl$^+$ | ML | 5.27 ± 0.05 (R) | 80KC, 86Bb, 86IC | 44 ± 1 (R) | −14 | 86IC, 90LP |
| Pb$^{2+}$ | ML | [h] | | [h] | | |

[a]The value of 1.32 ± 0.01 can be treated as reliable [95AS].
[b]Values of $K_2$ from [87B] and [93BC] seem too high; a good estimation could be 0.5 ± 0.3.
[c]Divergent values for ML$_2$ species; the value 1.82 [87ZB] is the most likely.
[d]Value of 31.9 ± 0.1 can be treated as reliable [84DI].
[e]lg $K_2$ = 3.07 ± 0.05 can be treated as reliable [85Bc].
[f]Study of the effect of the ionic strength in TBAH, 25 °C, all values of lg $K$ with standard deviation of ± 0.02 [79SP]: 4.33 (0.005 M); 4.32 (0.01 M); 4.30 (0.03 M); 4.29 (0.05 M); 4.27 (0.08 M); 4.28 (0.10 M); 4.22 (0.20 M); 4.17 (0.30 M); 4.13 (0.40 M); 4.09 (0.50 M).
[g]Values of lg $K$ at other temperatures [97RE]: 6.39 ± 0.04 (15 °C); 5.76 ± 0.05 (35 °C); 5.44 ± 0.06 (45 °C).
[h]Values of lg $K$ = 6.99 ± 0.05 and $-\Delta_r H$ = 45 ± 1 can be treated as reliable [86Bb].

**Table 8** Recommended and provisional data for 15C5 and 18C6 complexes (ML) in methanol/water (MeOH/H$_2$O) mixtures, 25 °C and ionic strength 0–0.1 M.

| Cations | MeOH % | lg $K$ (Evaluation) | References | $-\Delta_r H$ (Evaluation) kJ mol$^{-1}$ | $T\Delta_r S$ kJ mol$^{-1}$ | References |
|---|---|---|---|---|---|---|
| | | | 15C5 | | | |
| Li$^+$ | 70 wt | 1.02 ± 0.05 (R1) | 87ZB | | | |
| Na$^+$ | 20 wt | 1.49 ± 0.01 (R1) | 82DG | | | |
| | 40 wt | 1.71 ± 0.01 (R1) | 82DG | | | |
| | 60 wt | 2.21 ± 0.01 (R1) | 82DG | | | |
| | 70 wt | 2.32 ± 0.05 (R1) | 87ZB | | | |
| | 80 wt | 2.65 ± 0.01 (R1) | 82DG | | | |
| | 90 wt | 2.96 ± 0.01 (R) | 81SD, 87KH | | | |
| K$^{+ a,b}$ | 70 wt | 2.79 ± 0.05 (R1) | 87ZB | | | |
| Cs$^+$ | 90 wt | 2.10 ± 0.01 (R1) | 87KH | | | |
| | | | 18C6 | | | |
| Na$^+$ | 70 wt | 2.76 ± 0.02 (R1) | 76ITa | 20.5 ± 0.5 (R1) | −4.8 | 76ITa |
| | 80 vol | 3.05 ± 0.01 (R1) | 95KZ | 23.3 ± 0.5 (R1) | −5.9 | 95KZ |
| | 90 wt | 3.66 ± 0.02 (R1) | 82HL | 27.8 ± 0.3 (R1) | −6.9 | 82HL |

(*continues on next page*)

**Table 8** (*Continued*).

| Cations | MeOH % | lg $K$ (Evaluation) | References | $-\Delta_\mathrm{r}H$ (Evaluation) kJ mol$^{-1}$ | $T\Delta_\mathrm{r}S$ kJ mol$^{-1}$ | References |
|---|---|---|---|---|---|---|
|  | 90 vol | 3.50 ± 0.05 (R1) | 80LV |  |  |  |
|  | 99 wt | 4.33 ± 0.02 (R1) | 82HL | 33.9 ± 0.2 (R1) | −9.2 | 82HL |
| K$^+$ | 70 wt | 4.33 ± 0.05 (R1) | 76ITa | 39.3 ± 0.5 (R1) | −14.6 | 76ITa |
|  | 80 vol | 4.70 ± 0.02 (R1) | 95KZ | 45.3 ± 0.2 (R1) | −18.5 | 95KZ |
|  | 90 vol | 5.23 ± 0.04 (R1) | 80LV |  |  |  |
|  | 99 wt | 6.05 ± 0.05 (R1) | 82HL | 55.3 ± 0.3 (R1) | −20.8 | 82HL |
| Rb$^+$ | 70 wt | c |  | 38.8 ± 0.3 (R1) |  | 76ITa |
|  | 80 vol | 3.99 ± 0.03 (R1) | 95KZ | 36.6 ± 0.4 (R1) | −13.8 | 95KZ |
| Cs$^+$ | 70 wt | 2.84 ± 0.01 (R1) | 76ITa | 33.9 ± 0.1 (R1) | −17.7 | 76ITa |
|  | 80 vol | 3.40 ± 0.03 (R1) | 95KZ | 27.7 ± 0.8 (R1) | −8.3 | 95KZ |
| Mg$^{2+}$ | 90 wt | 2.70 ± 0.04 (R1) | 99SS | 4.7 ± 0.1 (R1) | 10.7 | 99SS |
| Ca$^{2+}$ | 70 wt | 2.46 ± 0.05 (R) | 76ITa, 99SS | 17.4 ± 0.5 (R) | −3.4 | 76ITa, 99SS |
|  | 90 wt | 2.97 ± 0.04 (R1) | 99SS | 8.8 ± 0.1 (R1) | 8.1 | 99SS |
| Sr$^{2+}$ | 50 wt | 4.02 ± 0.05 (R1) | 99SS | 24.4 ± 0.2 (R1) | −1.5 | 99SS |
|  | 70 wt | 5.03 ± 0.03 (R) | 76ITa, 99SS | 31.8 ± 0.5 (R) | −3.1 | 76ITa, 99SS |
|  | 90 wt | 5.26 ± 0.05 (R1) | 99SS | 34.0 ± 0.1 (R1) | −4.0 | 99SS |
| Ba$^{2+}$ | 50 wt | 4.96 ± 0.05 (R1) | 99SS | 38.4 ± 0.2 (R1) | −10.2 | 99SS |
|  | 70 wt | d | 99SS | 44.7 ± 0.2 (R) |  | 76ITa, 99SS |
|  | 90 wt | 6.56 ± 0.09 (P) | 82HL, 99SS | 43.1 ± 0.5 (R) | −5.7 | 82HL, 99SS |
|  | 99 wt | e |  | e |  |  |
| Ag$^+$ | 50 wt | 2.45 ± 0.04 (R1) | 97SA | 16 ± 1 (R1) | −2 | 97SA |
|  | 70 wt | 2.95 ± 0.05 (R1) | 97SA | f |  |  |
|  | 90 wt | 3.85 ± 0.05 (R1) | 97SA | g |  |  |
| Pb$^{2+}$ | 50 wt | 5.12 ± 0.03 (R1) | 97SA | h |  |  |
|  | 70 wt | 6.50 ± 0.02 (R1) | 97SA | 37.9 ± 0.5 (R) | −0.8 | 76ITa, 97SA |
|  | 90 wt | 6.70 ± 0.03 (R1) | 97SA | h |  |  |

[a]A value of 3.00 ± 0.08 can be treated as reliable for 90 wt [87KH].
[b]ML$_2$ species have been postulated in 70 wt, lg $K_2$ = 2.0 ± 0.05 [87ZB] and in 90 wt, lg $K_2$ = 2.2 ± 0.2 [87KH].
[c]The value 3.5 ± 0.1 can be treated as reliable [76ITa].
[d]The value 5.98 ± 0.06 can be treated as reliable [99SS].
[e]The values of lg $K$ / $-\Delta_\mathrm{r}H$ of 7.03 ± 0.06 / 43.4 ± 0.6 can be treated as reliable [82HL].
[f]The value of $-\Delta_\mathrm{r}H$ = 23 ± 2 can be treated as reliable [97SA].
[g]The value of $-\Delta_\mathrm{r}H$ = 34 ± 2 can be treated as reliable [97SA].
[h]The values of $-\Delta_\mathrm{r}H$ = 30 ± 2 (50 wt) and −43 ± 2 (90 wt) can be treated as reliable [97SA].

**Table 9** Provisional data for 15C5 and 18C6 complexes in ethanol (EtOH) at 25 °C and ionic strength 0–0.1 M.

| Cations | Species | lg $K$ (Evaluation) | References | $-\Delta_\mathrm{r}H$ (Evaluation) kJ mol$^{-1}$ | $T\Delta_\mathrm{r}S$ kJ mol$^{-1}$ | References |
|---|---|---|---|---|---|---|
|  |  | 15C5 |  |  |  |  |
| Ag$^+$ | ML | a |  |  |  |  |
|  |  | 18C6 |  |  |  |  |
| Ag$^+$ | ML | 3.5 ± 0.1 (P)$^{b}$ | 98PS, 00BS | 30.5 ± 0.6 (R) | −10.5 | 98PS, 00BS |

[a]Values at different temperatures can be treated as reliable [98PS]: 3.23 ± 0.04 (10 °C), 3.12 ± 0.06 (25 °C), 2.89 ± 0.05 (40 °C), 2.70 ± 0.05 (55 °C). A value of $-\Delta_\mathrm{r}H$ = 21.4 ± 0.5 has been obtained from the temperature dependence of lg $K$.
[b]Values of lg $K$ at other temperatures : 3.62 ± 0.05 (10 °C), 3.06 ± 0.07 (40 °C), and 2.88 ± 0.08 (55 °C) can be treated as reliable [98PS].

**Table 10** Recommended data for 12C4, 15C5, and 18C6 complexes (ML) in ethanol/water mixtures, 25 °C and ionic strength 0–0.1 M.

| Cations | EtOH % | lg $K$ (Evaluation) | References | $-\Delta_r H$ (Evaluation) kJ mol$^{-1}$ | $T\Delta_r S$ kJ mol$^{-1}$ | References |
|---------|--------|---------------------|------------|------------------------------------------|------------------------------|------------|
| | | | 12C4 | | | |
| Tl$^+$ | 90 wt | a | | | | |
| Pb$^{2+}$ | 90 wt | 3.23 ± 0.04 (R1) | 96SSb | | | |

[a]A value of 2.18 ± 0.06 can be treated as reliable [96SSb].

**Table 11** Recommended and provisional data for 12C4, 15C5, and 18C6 complexes in acetone (AC) at 25 °C and ionic strength 0–0.1 M.

| Cations | Species | lg $K$ (Evaluation) | References | $-\Delta_r H$ (Evaluation) kJ mol$^{-1}$ | $T\Delta_r S$ kJ mol$^{-1}$ | References |
|---------|---------|---------------------|------------|------------------------------------------|------------------------------|------------|
| | | | 12C4 | | | |
| Li$^+$ | ML | a | | a | | |
| Ag$^+$ | ML | 2.17 ± 0.05 (R1) | 99BS | | | |
| | ML$_2$ | b | | | | |
| | | | 15C5 | | | |
| Li$^+$ | ML | 3.42 ± 0.04 (R1) | 94BC | 12.9 ± 0.5 (R1) | 6.6 | 94BC |
| Na$^+$ | ML | c | | 27.3 ± 0.4 (R1) | | 94BC |
| K$^+$ | ML | 4.26 ± 0.05 (R1) | 94BC | 26.9 ± 0.5 (R1) | –2.6 | 94BC |
| Rb$^+$ | ML | 4.34 ± 0.03 (R1) | 94BC | 24.3 ± 0.3 (R1) | 0.5 | 94BC |
| Cs$^+$ | ML | 3.68 ± 0.04 (R1) | 94BC | 19.4 ± 0.4 (R1) | 1.6 | 94BC |
| Ca$^{2+}$ | ML | 4.01 ± 0.05 (R1) | 93BD | 35 ± 1 (R1) | –12 | 93BD |
| Ag$^+$ | ML | 4.52 ± 0.02 (R1) | 99BS | d | | |
| | | | 18C6 | | | |
| Na$^+$ | ML | 4.46 ± 0.04 (R1) | 94BC | 34.0 ± 0.5 (R1) | –8.7 | 94BC |
| K$^+$ | ML | 5.89 ± 0.02 (R1) | 94BC | 50.6 ± 0.4 (R) | –17.0 | 94BC, 96SSa |
| Rb$^+$ | ML | 5.16 ± 0.03 (R1) | 94BC | 47.8 ± 0.6 (R1) | –18.5 | 94BC |
| Cs$^+$ | ML | 4.51 ± 0.04 (R1) | 94BC | 52.8 ± 0.4 (R1) | –27.2 | 94BC |
| Ca$^{2+}$ | ML | 5.07 ± 0.05 (R1) | 93BD | 39 ± 1 (R1) | –10 | 93BD |
| Sr$^{2+}$ | ML | 5.31 ± 0.05 (R1) | 93BD | 52 ± 1 (R1) | –22 | 93BD |
| Ba$^{2+}$ | ML | 7.35 ± 0.05 (R1) | 93BD | 61 ± 1 (R1) | –19 | 93BD |
| Ag$^+$ | ML | 5.1 ± 0.2 (P) | 93JH, 99BSa | 36 ± 2 (P) | –7 | 99BSa, 00BS |

[a]The values of lg $K$ / $-\Delta_r H$ at 27 °C 1.62 ± 0.03 / 13.4 ± 0.8 can be treated as R1 [80SP].
[b]A value of lg $K_2$ = 2.98 ± 0.06 can be treated as reliable [99BS].
[c]A value of 4.26 ± 0.06 can be treated as reliable [94BC].
[d]A value of 31 ± 2 can be treated as reliable [99BS].

**Table 12** Recommended and provisional data for 12C4, 15C5, and 18C6 complexes in acetonitrile (AN) at 25 °C and ionic strength 0–0.1 M.

| Cations | Species | lg $K$ (Evaluation) | References | $-\Delta_r H$ (Evaluation) kJ mol$^{-1}$ | $T\Delta_r S$ kJ mol$^{-1}$ | References |
|---------|---------|---------------------|------------|------------------------------------------|------------------------------|------------|
| | | | 12C4 | | | |
| Li$^+$ | ML | 3.4 ± 0.1 (P) | 80HN, 95AS, 96DN, 99KC | 21.9 ± 0.8 (R1) | –2.8 | 96DN |

(*continues on next page*)

**Table 12** (*Continued*).

| Cations | Species | lg $K$ (Evaluation) | References | $-\Delta_r H$ (Evaluation) kJ mol$^{-1}$ | $T\Delta_r S$ kJ mol$^{-1}$ | References |
|---|---|---|---|---|---|---|
| Na$^+$ | ML | 3.31 ± 0.01 (R1) | 80HN | | | |
| K$^+$ | ML | 2.40 ± 0.02 (R1) | 88Ba | 9.5 ± 1 (R1) | 4.2 | 88Ba |
| | ML$_2$ | 2.29 ± 0.05 (R1) | 88Ba | 14.5 ± 1 (R1) | −1.4 | 88Ba |
| Ba$^{2+}$ | ML | 4.12 ± 0.05 (R1) | 87BB | 42.5 ± 1 (R1) | −19.0 | 87BB |
| Tl$^+$ | ML | 4.01 ± 0.02 (R1) | 93JH | | | |
| | | | 15C5 | | | |
| Li$^+$ | ML | 4.3 ± 0.2 (P)$^a$ | 94DL, 99WK | | | |
| Na$^+$ | ML | 5.1 ± 0.2 (P) | 80HN, 82NY, 88B, 88OP, 88TK | 26 ± 2 (P) | 3 | 82NY, 88B, 88OP |
| K$^+$ | ML | 4.2 ± 0.2 (P) | 88B, 88TK | 32 ± 1 (R1) | −8 | 88B |
| Rb$^+$ | ML | 3.6 ± 0.2 (P) | 88B, 88TK, 91SK | 29 ± 1 (R1) | −9 | 88B |
| Cs$^+$ | ML | 3.0 ± 0.1 (P) | 88B, 88TK, 91SK | 28 ± 1 (R1) | −11 | 88B |
| | | | 18C6 | | | |
| Li$^+$ | ML | $^b$ | | | | |
| Na$^+$ | ML | 4.6 ± 0.1 (P) | 80KC, 82NY, 88B, 88OP | −2 ± 1 (R) | 28 | 82NY, 88B, 95OKa |
| K$^+$ | ML | 5.76 ± 0.08 (P) | 80KC, 83T, 88B, 97RE | $^c$ | | |
| Rb$^+$ | ML | 5.1 ± 0.2 (P) | 88B, 95OKa | 14 ± 1 (P) | 15 | 88B, 95OKa |
| Cs$^+$ | ML | $^d$ | | 17 ± 1 (P) | | 88B, 95OKa |

$^a$The value of 4.96 ± 0.05 at 27 °C can be treated as reliable [96KAa].
$^b$The value at 27 °C lg $K$ = 2.32 ± 0.05 (R) can be treated as reliable [80SP, 96KA].
$^c$The value of $-\Delta_r H$ = 14 ± 3 can be treated as reliable [88B, 95OKa, 96SSa].
$^d$The values of lg $K$ = 4.36 ± 0.08 at 25 °C [95OKa] and 4.8 ± 0.2 at 22 °C [85BP] can be treated as reliable.

**Table 13** Recommended and provisional data for 12C4, 15C5, and 18C6 complexes in DMF at 25 °C and ionic strength 0–0.1 M.

| Cations | Species | lg $K$ (Evaluation) | References | $-\Delta_r H$ (Evaluation) kJ mol$^{-1}$ | $T\Delta_r S$ kJ mol$^{-1}$ | References |
|---|---|---|---|---|---|---|
| | | | 12C4$^a$ | | | |
| | | | 15C5 | | | |
| Cs$^+$ | ML | $^b$ | | | | |
| | | | 18C6 | | | |
| Na$^+$ | ML | 2.5 ± 0.1 (P)$^c$ | 81T, 94OO, 99WB | $^d$ | | |
| K$^+$ | ML | 4.2 ± 0.1 (P)$^e$ | 81T, 94OO, 96SSa, 97RE | 38.1 ± 0.8 (R) | −14.1 | 94OO, 96SSa, 99RM, 99WB |
| Rb$^+$ | ML | 4.0 ± 0.1 (P) | 81T, 94OO, 99WB | 43 ± 2 (P) | −20 | 94OO, 99WB |
| Cs$^+$ | ML | 3.64 ± 0.02 (R) | 81T, 94OO, 99WB | 49.2 ± 0.8 (R) | −28.4 | 94OO, 99WB |
| Ca$^{2+}$ | ML | | | 3 ± 1 (R) | | 95OK, 99WB |
| Sr$^{2+}$ | ML | 2.92 ± 0.02 (R1)$^f$ | 95OK | 22.6 ± 0.2 (R1) | −5.9 | 95OK |
| Ba$^{2+}$ | ML | 3.9 ± 0.2 (P)$^g$ | 95OK, 99WB | 44.4 ± 0.1 (R1) | −22.2 | 95OK |
| Ag$^+$ | ML | 2.6 ± 0.2 (P) | 93JH, 99WB, 00BS | | | |
| Tl$^+$ | ML | 3.6 ± 0.1 (P)$^h$ | 85LA, 88OP, 91SS, 93JH | | | |

**Table 13** (*Continued*).

| Cations | Species | lg $K$ (Evaluation) | References | $-\Delta_r H$ (Evaluation) kJ mol$^{-1}$ | $T\Delta_r S$ kJ mol$^{-1}$ | References |
|---------|---------|---------------------|------------|------------------------------------------|------------------------------|------------|
| Pb$^{2+}$ | ML | 3.7 ± 0.1 (P)$^i$ | 85BP, 96RE | | | |

[a]Values of lg $K_1$ / lg $K_2$ for alkali metal ions can be treated as reliable [96OK]: 0.43 ± 0.08 / 1.7 ± 0.1 (Na$^+$), 0.68 ± 0.07 / 0.5 ± 0.3 (K$^+$), 0.66 ± 0.05 / – (Rb$^+$), 0.56 ± 0.06 / 0.6 ± 0.2 (Cs$^+$).
[b]Value of 0.91 ± 0.04 can be treated as reliable [90SL].
[c]Value at 28 °C can be treated as reliable: 2.23 ± 0.04 [81RP].
[d]The value of $-\Delta_r H = 19 ± 3$ can be treated as reliable [94OO, 99WB].
[e]Values of lg $K$ at other temperatures can be treated as reliable [97RE]: 4.59 ± 0.08 (15 °C), 4.03 ± 0.09 (35 °C), and 3.74 ± 0.08 (45 °C).
[f] Value at 30 °C can be treated as reliable: lg $K = 2.67 ± 0.04$ [91AS].
[g]Value at 30 °C can be treated as reliable: lg $K = 3.81 ± 0.03$ [91AS].
[h]Value at 28 °C can be treated as reliable: lg $K = 3.35 ± 0.06$ [81RP].
[i]Value at 22 °C.

**Table 14** Recommended data for 15C5 and 18C6 complexes in DMSO at 25 °C and ionic strength 0–0.1 M.

| Cations | Species | lg $K$ (Evaluation) | References | $-\Delta_r H$ (Evaluation) kJ mol$^{-1}$ | $T\Delta_r S$ kJ mol$^{-1}$ | References |
|---------|---------|---------------------|------------|------------------------------------------|------------------------------|------------|
| | | | 15C5 | | | |
| Na$^+$ | ML | $^a$ | | | | |
| | | | 18C6 | | | |
| Na$^+$ | ML | 1.43 ± 0.05 (R1)$^b$ | 80KC | | | |
| K$^+$ | ML | 3.25 ± 0.04 (R) | 80KC, 83T | 27.6 ± 0.5 (R1) | –9.1 | 96SSa |
| Cs$^+$ | ML | 3.04 ± 0.02 (R1) | 77MP | | | |
| Ag$^+$ | ML | 1.56 ± 0.05 (R1) | 00BS | 1.0 ± 0.4 (R1) | 7.9 | 00BS |

[a] The value at 27 °C can be treated as R1: 1.17 ± 0.01 [96KA].
[b]The value of lg $K = 1.41 ± 0.07$ (28 °C) can be treated as reliable [81RP].

**Table 15** Recommended and provisional data for 12C4, 15C5, and 18C6 complexes in propylene carbonate (PC) at 25 °C and ionic strength 0–0.1 M.

| Cations | Species | lg $K$ (Evaluation) | References | $-\Delta_r H$ (Evaluation) kJ mol$^{-1}$ | $T\Delta_r S$ kJ mol$^{-1}$ | References |
|---------|---------|---------------------|------------|------------------------------------------|------------------------------|------------|
| | | | 12C4 | | | |
| Li$^+$ | ML | 2.87 ± 0.06 (P) | 80MD, 96DN | 17 ± 1 (R1) | –0.6 | 96DN |
| Na$^+$ | ML | | | | | |
| | ML$_2$ | $^a$ | | | | |
| K$^+$ | ML | 2.08 ± 0.06 (P) | 80MD, 88Ba | $^c$ | | |
| | ML$_2$ | $^b$ | | | | |
| Rb$^+$ | ML | 1.69 ± 0.04 (R1) | 80MD | | | |
| Cs$^+$ | ML | 1.43 ± 0.05 (R1) | 80MD | | | |
| Mg$^{2+}$ | ML | $^d$ | | | | |
| | ML$_2$ | | | | | |
| Ca$^{2+}$ | ML | | | | | |
| | ML$_2$ | $^e$ | | | | |
| Sr$^{2+}$ | ML | 5.29 ± 0.05 (R1) | 82MR | | | |
| | ML$_2$ | $^f$ | | | | |
| Ag$^+$ | ML | 3.9 ± 0.1 (P) | 89BP, 99BS | | | |

(*continues on next page*)

**Table 15** (*Continued*).

| Cations | Species | lg $K$ (Evaluation) | References | $-\Delta_r H$ (Evaluation) kJ mol$^{-1}$ | $T\Delta_r S$ kJ mol$^{-1}$ | References |
|---|---|---|---|---|---|---|
| | ML$_2$ | 3.5 ± 0.2 (P) | 89BP, 99BS | | | |
| Tl$^+$ | ML | g | | | | |
| Pb$^{2+}$ | ML | h | | | | |
| | ML$_2$ | | | | | |
| | | | 15C5 | | | |
| Li$^+$ | ML | 4.14 ± 0.09 (P) | 80TY, 89B, 94DL | 21 ± 1 (R) | 3 | 89B, 94DL |
| Na$^+$ | ML | i | | i | | |
| K$^+$ | ML | 3.6 ± 0.2 (P) | 80TY, 89B | k | | 89B |
| | ML$_2$ | j | | | | |
| Cs$^+$ | ML | l | | 17 ± 1 (R1) | | 89B |
| Ag$^+$ | ML | 6.27 ± 0.03 (R) | 89BP, 99BS | 41.2 ± 0.9 (R1) | −5.4 | 99BS |
| | ML$_2$ | m | | | | |
| Tl$^+$ | ML | 5.29 ± 0.02 (R1) | 82MD | | | |
| | ML$_2$ | 1.45 ± 0.04 (R1) | 82MD | | | |
| | | | 18C6 | | | |
| Li$^+$ | ML | 2.74 ± 0.05 (R) | 89B, 90S | 17 ± 1 (R1) | −1 | 89B |
| Na$^+$ | ML | 5.5 ± 0.2 (P) | 80KC, 80TY, 84FL, 90S, 95OKa | 29 ± 1 (R) | 2 | 89B, 95OKa |
| K$^+$ | ML | 6.2 ± 0.1 (P)[n] | 80KC, 80TY, 88Ba, 90S, 95OKa, 97RE | 46.3 ± 0.9 (R) | −10.9 | 88Ba, 95OKa |
| Rb$^+$ | ML | 5.33 ± 0.07 (P) | 80TY, 89B, 95OKa | 44 ± 1 (R) | −14 | 89B, 95OKa |
| Cs$^+$ | ML | 4.50 ± 0.02 (R) | 80KC, 80TY, 89Ba, 95OKa | 43.3 ± 0.4 (R) | −17.6 | 89B, 95OKa |
| Mg$^{2+}$ | ML | 2.94 ± 0.05 (R1) | 92BS | 30 ± 1 (R1) | −14 | 92BS |
| Ca$^{2+}$ | ML | 3.75 ± 0.07 (P) | 92BS, 92ST | 38.5 ± 1 (R1) | −17.1 | 92BS |
| Sr$^{2+}$ | ML | | | 59 ± 1 (R1) | | 92BS |
| Ba$^{2+}$ | ML | o | | o | | |
| Ag$^+$ | ML | 7.0 ± 0.1 (P) | 80KC, 89BP, 99BSa | 49.6 ± 0.8 (R1) | −9.7 | 99BSa, 00BS |
| Tl$^+$ | ML | 7.13 ± 0.05 (R1) | 80KC | | | |

[a]The values of lg $K_1$ / lg $K_2$ and of 3.5 ± 0.2 / 2.8 ± 0.2 (pot) can be treated as reliable [80MD].
[b]Evidence for a 1:2 complex with lg $K_2$ = 2.65 ± 0.02 [88Ba].
[c]Values of $-\Delta_r H_1$ = 14.6 ± 2 and $-\Delta_r H_2$ = 8.7 ± 2 can be treated as reliable [88Ba].
[d]lg $K_1$ = 2.61 ± 0.08 and lg $K_2$ = 3.6 ± 0.2 can be treated as reliable [82MR].
[e]lg $K_1$ = 5.53 ± 0.06 and lg $K_2$ = 4.0 ± 0.1 can be treated as reliable [82MR].
[f]Evidence for a 1:2 complexes with lg $K_2$ = 2.6 ± 0.1 [82MR].
[g]A value of 3.71 ± 0.06 can be treated as reliable [82MD].
[h]Values of lg $K_1$ = 7.68 ± 0.09 and lg $K_2$ = 4.0 ± 0.2 can be treated as reliable [82MD].
[i]The values of lg $K$ / $-\Delta_r H$ of 4.87 ± 0.05 / 32 ± 2 can be treated as reliable [89B].
[j]Values of lg $K_2$ = 2.84 ± 0.05 and $-\Delta_r H_2$ = 30 ± 2 can be treated as reliable [88Ba].
[k]A value of 30 ± 2 can be treated as reliable [89B].
[l]A value of 3.39 ± 0.05 can be treated as reliable [89B].
[m]lg $K_2$ = 1.77 ± 0.01 has also been found [89BP].
[n]Values of lg $K$ at other temperatures [97RE]: 6.43 ± 0.07 (15 °C), 5.85 ± 0.05 (35 °C), and 5.55 ± 0.05 (45 °C).
[o]The values of lg $K$ = 11.6 ± 0.1 and $-\Delta_r H$ = 64 ± 1 can be treated as reliable [92BS].

**Table 16** Experimental conditions of papers selected for critical evaluation in Tables 6 to 15.

| Temperature/ °C | $I$/M or $c$/M (medium) | Counterion | Experimental methods | Ref. |
|---|---|---|---|---|
| 25 | $2 \times 10^{-4} - 1 \times 10^{-2}$ | $Cl^-$ | ISE | 71F |
| 25 | 0.1 | $Cl^-$ or $ClO_4^-$ | cal | 76IT |
| 25 | 0.1 | $Cl^-$ or $ClO_4^-$ | cal | 76ITa |
| 25 | 0.1/TEAP | – | pol | 76KK |
| 25 | $\leq 10^{-2}$ | $Cl^-$ | ISE | 77BC |
| 25 | $\leq 0.1$ | $TPB^-$ | $^{133}Cs$ NMR | 77MP |
| 25 | 0.1/TEAP | $NO_3^-$ | pol | 78KK |
| 25 | $\leq 0.1$ | $Cl^-$ | ISE (cation exch.) | 79HR |
| 25 | $\leq 0.1$/TBAH | – | ISE | 79SP |
| 25 | $1.9 - 3.3 \times 10^{-3}$ | $I^-$, $TPB^-$ | cond | 80HN |
| 25 | $\leq 0.1$ | $ClO_4^-$ or $NO_3^-$ or pic | ISE or $Ag^+$ elect. | 80KC |
| 25 | 0.1 | $Cl^-$ or $ClO_4^-$ or $NO_3^-$ | cal | 80LI |
| 25 | 0.1/TMAB | $Cl^-$ | ISE | 80LV |
| 25 | 0.1/TEAP | $ClO_4^-$ | pot | 80MD |
| 27 | $\leq 0.02$ | $ClO_4^-$ | $^7Li$ NMR | 80SP |
| 25 | $\leq 5 \times 10^{-4}$ | $ClO_4^-$ | cond | 80TY |
| 25 | $\leq 0.1$ | – | fluor | 80WJ |
| 28 | $\leq 0.1$ | $ClO_4^-$ | $^{205}Tl$ NMR | 81RP |
| 25 | $4 - 5 \times 10^{-4}$ | $ClO_4^-$ | cond | 81T |
| 25 | $2 \times 10^{-4} - 1 \times 10^{-2}$ | – | ISE | 82DG |
| 25 | $2 \times 10^{-4} - 1 \times 10^{-2}$ | $Cl^-$ | ISE | 82GD |
| 25 | $\leq 0.1$ | $Cl^-$ | cal | 82HL |
| 25 | 0.1/TEAP | $CF_3SO_3^-$ | pot comp | 82MR |
| 25 | $\approx 10^{-3}$ | $Cl^-$ | pot/cal | 82MRa |
| 25 | $2 \times 10^{-4} - 1 \times 10^{-2}$ | $Cl^-$ | ISE | 82MY |
| 10, 25, 40 | 0.01/TEAP | – | ISE | 82NY |
| 25 | $2 \times 10^{-4} - 1 \times 10^{-2}$ | $Cl^-$ | ISE | 83GG |
| 25 | $\leq 0.1$ | – | cond | 83LS |
| 25 | $\leq 0.1$ | $Cl^-$ | cond | 83T |
| 25 | 0.1 | $Cl^-$, $I^-$ | cal | 84DI |
| 25 | 0.1/TEAP | $ClO_4^-$ | ISE | 84FL |
| 25, 35, 45, 55, 65 | 0.02 | $ClO_4^-$ | $^{205}Tl$ NMR | 84P |
| 25 | 0.1/TMAH | – | pol | 84ZB |
| 25 | $\leq 0.1$ | $ClO_4^-$ | cal comp | 85Ba |
| 25 | 0.05/TEAP | $NO_3^-$, $ClO_4^-$ | pot (comp Ag+) | 85Bb |
|  | $0.5 - 8 \times 10^{-3}$ | $NO_3^-$, | cal |  |
| 25 | 0.1/TEAP | $ClO_4^-$ | ISE | 85BF |
| 22 | $\leq 0.01$ | $TPB^-$ | $^{133}Cs$ NMR or $^{23}Na$ NMR comp | 85BP |
| 25 | $\leq 0.02$ | $ClO_4^-$, $NO_3^-$ | $^{133}Cs$ or $^{205}Tl$ NMR | 85LA |
| 25 | $\leq 0.1$ | $SCN^-$ | $^{23}Na$ NMR | 85SP |
| 10, 15, 20, 25, 35, 45 | $\leq 5 \times 10^{-3}$ | $Cl^-$ | cond | 85TA |
| 25 | 0.1/TEAI | $Cl^-$ | pol | 85ZB |
| 25 | $\leq 0.1$ | – | cal comp | 86B |
| 25 | 0.05/TEAP | – | ISE | 86Bb |
|  | $\leq 0.1$ | $ac^-$ or $NO_3^-$ | cal |  |
| 25 | 0.1 | $ClO_4^-$ or $NO_3^-$ | cal | 86IC |
| 25 | $\leq 0.1$ | $NO_3^-$, $TPB^-$, $Br^-$, $I^-$ | cond | 87B |

(*continues on next page*)

**Table 16** (*Continued*).

| Temperature/ °C | *I*/M or *c*/M (medium) | Counterion | Experimental methods | Ref. |
|---|---|---|---|---|
| | 0.05/TEAP or TEAN | | ISE | |
| 25 | 0.02–0.03 | $ClO_4^-$ | cal | 87BB |
| 25 | 0.1/TEAI or TBAP | – | pol | 87CB |
| | ≤0.1 | $Cl^-$ | cond | |
| 25 | ≤2 × 10^{-3} | $Cl^-$ | ISE | 87KH |
| 25 | 0.05 | $pic^-$ | ix | 87MG |
| 25 | ≤0.03 | $Cl^-$, $NO_3^-$ | cal | 87SK |
| | 0 (extrapolation) | $Cl^-$, $NO_3^-$ | $^{43}$Ca NMR | |
| 25 | 5 × 10^{-4} – 1 × 10^{-3} | $Cl^-$ | cond | 87ZB |
| 25 | 0.05/TEAP | | ISE | 88B |
| | ≤0.1 | $TPB^-$ | cal comp | |
| 25 | 0.05/TEAP | $ClO_4^-$ | ISE | 88Ba |
| | ≤6 × 10^{-3} | | cal | |
| 25 | 0.1/HNO_3 | – | pol | 88HA |
| 25 | ≤0.1 | $ClO_4^-$ | $^{23}$Na or $^{205}$Tl NMR | 88OP |
| 25 | 6 × 10^{-4} | $ClO_4^-$ | cond | 88TK |
| 25 | 0.05/TEAP | | ISE | 89B |
| | ≤2.5 × 10^{-3} | $ClO_4^-$, $TPB^-$ | cal | |
| 25 | 0.1/TEAP | $ClO_4^-$ | ISE | 89BP |
| 25 | <1 × 10^{-4} | $Cl^-$ | sp comp | 89KS |
| 25 | → 0 | $Cl^-$ | cond | 89YK |
| 25 | ≤0.1 | $Cl^-$ | cal | 90BW |
| 15, 20, 25, 30, 35 | 4 – 6 × 10^{-4} | $ClO_4^-$ | cond | 90LP |
| 25 | ≤0.01 | $ClO_4^-$, $SCN^-$ ($K^+$) | cond | 90S |
| 25 | 0.05 | $I^-$, $ClO_4^-$ | $^{133}$Cs NMR | 90SL |
| 25 | 0.05/TBAP | $Cl^-$ | pol (DME) | 91LL |
| 25 | 5 × 10^{-3} | $Cl^-$, $TPB^-$ | $^{133}$Cs NMR | 91SK |
| 25 | 0.05/TEAP | $ClO_4^-$ | pol comp | 91SS |
| 25 | 0.05/TEAN or TEAP | – | ISE | 92B |
| | ≤2.0 × 10^{-3} | $NO_3^-$, $TPB^-$ | cond | |
| | ≤6 × 10^- | $NO_3^-$, $TPB^-$ | cal | |
| 25 | ≤3.0 × 10^{-3} | $ClO_4^-$ | cal comp or direct | 92BS |
| 23 | 0.05/TBAP | – | pol | 92LL |
| 25 | 0.1/TEAC | $Cl^-$ | cal | 92OI |
| 25 | ≤5 × 10^{-4} | $ClO_4^-$ | cond | 92ST |
| 25, 35, 45 | ≤0.1 | $NO_3^-$ | cal | 92VO |
| 25 | 1 – 2 × 10^{-3} | $TPB^-$ | cond | 93BC |
| | 0.05/TEAP | – | pot | |
| 25 | ≤6 × 10^{-3} | $ClO_4^-$, $TPB^-$ | cal comp or direct | 93BD |
| 25 | ≤1 × 10^{-4} | $ClO_4^-$ | cond | 93JH |
| 25 | 0.05/TEAP | | ISE | 94BC |
| | ≤6 × 10^{-3} | $ClO_4^-$ ($Na^+$), $CF_3(CF_2)_3SO_3^-$, $TPB^-$ ($K^+$), $TPB^-$ ($Rb^+$, $Cs^+$) | cal | |
| 25 | 0.8 – 1 × 10^{-3} | $AsF_6^-$, $BF_4^-$, $CF_3SO_3^-$ | cal | 94DL |
| 25 | 0.1/TEAP | $Cl^-$ | cal | 94OO |
| 15, 25, 35, 45 | ≤0.0025 | $Cl^-$ | cal | 94VB,94VBa |
| 25 | 2.5 – 2.9 × 10^{-3} | $ClO_4^-$ | cond | 95AS |

(*continues on next page*)

**Table 16** (*Continued*).

| Temperature/ °C | *I*/M or *c*/M (medium) | Counterion | Experimental methods | Ref. |
|---|---|---|---|---|
| 25 | ≤0.1 | $NO_3^-$ | cal | 95KZ |
| 15, 25, 35, 45 | ≤0.1 | $Cl^-$ | cal | 95MV |
| 25 | 0.1/TEAC ($H_2O$) 0.1/TEAP (DMF) | $Cl^-$, $Br^-$, $NO_3^-$, $ClO_4^-$ | cal | 95OK |
| 25 | 0.05/TEAP | $ClO_4^-$ | cal | 95OKa |
| 25 | 0.005 | $Cl^-$, $ClO_4^-$, $SCN^-$ | cal | 95WI |
| 50, 75, 100, 125 | | $NO_3^-$ | isoth flow cal[a] | |
| 25 | 0.1 / TMAH | $ClO_4^-$, $NO_3^-$ | cal | 96BC |
| 25 | <$10^{-3}$ | $AsF_6^-$, $BF_4^-$, $CF_3SO_3^-$, $ClO_4^-$ | microcal | 96DN |
| 10, 15, 25, 35, 45 | ≤0.01 | – | ISE | 96EY |
| 27 | ≤0.005 | $ClO_4^-$ | ^{7}Li NMR | 96KA |
| 22 | 0.025/TBAP | $ClO_4^-$ | pol (dpp) | 96RE |
| 25 | 0.025/TMAC ≤0.1 | $Cl^-$, $ClO_4^-$, $SCN^-$ | ISE cal | 96SSa |
| 25 | 0.03/TEAP | $NO_3^-$ | pol | 96SSb |
| 15–45 | <0.015 | $NO_3^-$ | cal | 97LK |
| 15, 25, 35, 45 | ≤$5 \times 10^{-4}$ | $ClO_4^-$ | cond | 97RE |
| 15–35 | ≤$4 \times 10^{-4}$ | $NO_3^-$ | cond | 97SA |
| 10, 25, 40, 55 | 0.05/TEAP | $NO_3^-$ | ISE | 98PS |
| 25 | 0.05/TEAI | – | ISE | 98SS |
| 25 | ≤$5 \times 10^{-3}$ 0.05/TEAP | $Cl^-$, $Br^-$, $I^-$ | cal pot | 99BS |
| 25 | 0.05/TEAP ≤$5 \times 10^{-3}$ | $NO_3^-$, $TPB^-$, $CF_3SO_3^-$ | ISE cal | 99BSa |
| 25 | 0.1/TEAP | $Cl^-$ | ISE | 99KC |
| 15, 25, 35, 45 | ≤0.1 | $NO_3^-$ | cal | 99LP |
| 15, 25, 35, 45, 55 | ≤$5 \times 10^{-4}$ | $ClO_4^-$ | cond | 99RM |
| 25 | ≤0.01 | $Cl^-$ | cond | 99SS |
| 25 | ≤0.01 | $Cl^-$ | cond | 99TM |
| 25 | ≤$5 \times 10^{-3}$ | $TPB^-$ | cal | 99WB |
| 25 | 0.1/TEAP | $ClO_4^-$ | cv | 99WK |
| 25 | 0.05/TEAP ≤$5 \times 10^{-3}$ | $NO_3^-$, $TPB^-$, $CF_3SO_3^-$ | pot cal | 00BS |
| 25, 35, 45 | ≤$2 \times 10^{-2}$ | $Cl^-$ | cal | 00VG |

[a]Pressure: $p$ = 1.52 Mpa.

Abbreviations used: TEAC: tetraethylammonium chloride; TEAI: tetraethylammonium iodide; TEAN: tetraethylamonium nitrate; TEAP: tetraethylammonium perchlorate; TBAH: tetrabutylammonium hydroxide; TBAP: tetrabutylammonium perchlorate; TMAB: tetramethylammonium bromide; TMAH: tetramethylammonium hydroxide; TPB: tetraphenylborate; pic: picrate; comp: competition.

The reviewers have tried to avoid recalculations to a preselected ionic strength so the data listed mostly correspond to values determined experimentally at ionic strength ≤0.1 M (see above). Experimental conditions used in papers selected for critical evaluation are summarized in Table 16.

## Remarks on ionic strength conditions

The following considerations may explain why in some cases we have considered in our first selection, values that were not determined in controlled ionic strength conditions.

As mentioned before, many techniques have been used to determine stability constants of crown ether complexes. Measurements by electrochemical methods (potentiometry, polarography, cyclic voltammetry, etc.) are generally carried out in the presence of a great excess of an inert electrolyte vs. the reactants, which maintains the ionic strength and hence the activity factors ($f_i$) and allows for the determination of conditional stability constants $K$, defined in terms of concentration ratios.

$$K^\circ = \frac{\left(ML^{n+}\right)}{\left(M^{n+}\right)(L)} = K \frac{f_{ML^{n+}}}{f_{M^{n+}} f_L}$$

where the brackets mean the activity of the species.

In some other techniques (conductometry, calorimetry, NMR, etc.) the use of a background electrolyte is less obvious or at least less frequent and the experimental requirements for the determination of conditional stability constants may not be achieved.

However, in the case of neutral ligands such as crown ethers and in the absence of a background electrolyte, the following considerations can be taken into account.

For low concentrations values ($<10^{-3}$ M), the activity coefficients can be calculated by the Debye–Hückel limiting law:

$$\lg f_i = -A z_i^2 \sqrt{I}$$

where $A$ is a parameter depending only on the solvent and the temperature. In these conditions, the activity coefficient of the ligand can be considered as unity ($f_L = 1$) and, if the metal ion and the complex have the same charge (which is the case for ML and $ML_2$ complexes reported in this review), $f_{M^{n+}}$ and $f_{ML^{n+}}$ have similar values. Consequently, the conditional stability constants can be approximated to thermodynamic constants $K^\circ$ ($I \approx 0$).

For higher concentrations, the activity coefficients must be calculated from the general Debye–Hückel equation involving the ion-size parameter $a$ of the species:

$$\lg f_i = -A Z_i^2 \frac{\sqrt{I}}{1 + B a \sqrt{I}}$$

In these conditions, $f_{M^{n+}}$ and $f_{ML^{n+}}$ can no longer be considered as equal and $f_L$ may also differ from unity. The stability constants thus will vary with the ionic strength and differ from the thermodynamic value. However results of Popov et al. [79SP], performed in methanol for the system 18C6/Na$^+$, have shown that the value of the stability constant remains reasonably constant and close to the thermodynamic value in the ionic strength range of 0.005 to 0.1 M ($\lg K = 4.30 \pm 0.02$ for the studied complex). It is only at higher ionic strengths that the $K$ value begins to decrease appreciably [79SP, 85ZP, 99BS].

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