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ORIGINAL ARTICLE

NMR study of the stoichiometry and stability of complexation reaction between Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} ions and 60-crown-20 in binary acetonitrile solvent mixtures

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Abstract Proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy was used to study the complexation reaction between Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} ions and 60-crown-20 in a series of binary mixtures of deuterated acetonitrile (AN), nitromethane (NM) and D_2O at 27 °C. Formation constants of the 1:1 complexes were determined through computer fitting of the chemical shift/mol ratio data and found to vary in the order of $Ba^{2+} > Sr^{2+} > Mg^{2+} \approx Ca^{2+}$. The influence of the solvent composition on the stability of the resulting complexes was also discussed. In all cases, the changes in the stability constants with the solvent composition were monotonic and showed a good correlation with the inherent solvation ability of the pure solvents which form the mixture.

Keywords 60-Crown-20 · NMR · Mixed solvents · Complex formation constants

Introduction

After discovery of crown ethers by Pedersen, a considerable progress in macrocyclic chemistry has been made in the past decades [1]. In this regards a lot of data have been published on the equilibrium constants and thermodynamic functions of complex formation of crown ethers with alkali and alkaline-earth metal cations, transition metal ions, lanthanide ions, and small organic molecules [2, 3]. One reason for the interest in this field is that macrocyclic ligands have enhanced the promotion of selective binding and transformation of a large variety of substrates such as inorganic or organic cations, anionic species and neutral molecules [4–6]. Also the complexation reaction of macrocyclic ligands is very useful for construction of selective membrane-sensors for different metal ions [7–10]. Despite the interesting properties of large crown ethers (i.e., larger than 18-crown-6), including their highly flexible geometrics in solution, which lets them adapt their conformation for optimum complexation with guest species, there have been no considerable studies on the complexation reactions of these compounds with metal ions [11, 12]. An example of the structural flexibility of this family can be dibenzo30-crown-10 which forms a 1:1 complex with potassium iodide, in which all ten oxygen's wrap around and bind to the cation in a tennis-ball like conformation [13]. Various techniques have been used to study the complexation of a range of ligands with different cations in a variety of non-aqueous and mixed solvents [14–16]. Among the spectroscopic and electrochemical methods used for the study of metal ion-crown ether complexes, NMR spectroscopy has been found to act as a very sensitive technique for studying the changes in the immediate chemical environment of metal ions in solutions [17, 18]. To the best of our knowledge there are no report on the complexation reaction

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between 60-crown-20 (60C20) and metal ions, we attempted to study the complexation reaction of 60C20 with Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} ions in acetonitrile (AN) and its various mixtures with nitromethane (NM) and deuterated water (D_2O). Since the alkaline earth metal ions used have unsuitable NMR properties such as low receptivity, high quadruple moment, insensitive chemical shifts and etc., we employed ^{1}H-NMR [19] to study the metal-crown ether complexes of interest in acetonitrile (AN), nitromethane (NM) and D_2O mixtures.

Experimental section

Reagent and instrument

The barium perchlorate, calcium perchlorate, magnesium perchlorate and strontium perchlorate were purchased from Merck (Darmstadt, Germany) and used after drying by P_2O_5 in vacuum. Deuterated acetonitrile (AN), nitromethane (NM) and D_2O were purchased from Merck (Darmstadt, Germany). The free 60-crown-20 (60C20) sample was synthesized, purified and dried as described elsewhere [20]. The proton NMR spectra were recorded using a Bruker DPX spectrometer (a frequency of 250.15 MHz) using TMS as the internal standard.

Stability constants calculations

The 1:1 complex formation reactions can be generally expressed as:

$$60C20 + M^{2+} \rightleftarrows (M - 60C20)^{2+}$$

The formation constants of the resulting 1:1 complexes were calculated using the variation of ^{1}H chemical shift with the $60C20/M^{2+}$ mol ratio. It has been shown that, in the cases where there is a fast exchange between free and complexed metal ion, the observed chemical shift of the resulting single NMR signal is given by Eq. 1 [21]:

$$\begin{aligned}\delta_{obs} = \{[(K_f C_L - K_f C_{M^+} - 1) + (K_f^2 C_{M^+}^2 + K_f^2 C_L^2 \\ - 2K_f C_L^2 - 2K_f^2 C_L C_M + 2K_f C_M + 2K_f \\ + 2K_f C_M + 1)^{1/2}] \times (\delta_L - \delta_{ML})/2K_f C_L\} + \delta_{ML} \qquad (1)\end{aligned}$$

where, K_f is the formation constant for the 1:1 complex, C_L and C_M are the analytical concentration of the 60C20 and M^{2+} ion, respectively, and δ_L and δ_{ML} are the corresponding chemical shifts of 60C20 hydrogen atoms in the pure solvent (free form or in the absence of metal ions) and the limiting ^{1}H chemical shift of $60C20/M^{2+}$ complex (a variable factor). The formation constant of M^{2+}–60C20 complex in different solvent mixtures was calculated by fitting the observed chemical shifts at various M^{2+}/60C20 mol ratios with a nonlinear least-squares program in MATLAB (version 7.8) [22].

Results and discussion

The ^{1}H-NMR spectra of 60C20 in the presence of different concentrations of M^{2+} perchlorate in various binary acetonitrile-solvent mixtures were obtained. Typical spectra are shown in Fig. 1 and the resulting chemical shift versus M^{2+}/60C20 mol ratio plots in some different solvent mixtures is given in Fig. 2. In all solvent mixtures studied, only one population-average signal was observed, indicating that the exchange rate of the cation between the solution bulk and the complexed sites is very fast as compared to the time-scale of the NMR studies. From Fig. 1, it is obvious that the resonance frequency of –CH_2-protons of 60C20 is shifted to the downfield upon adding the M^{2+} ion. Thus, using the chemical shift, one can evaluate the stoichiometry and formation constant of the M^{2+}–60C20 complex. A similar trend is observed in all binary mixtures used.

As seen in the Fig. 2, an increase in the concentration of the cations gradually shifts the proton resonance downfield. In the case of Ba^{2+} and Sr^{2+} after reaching an M^{2+}:60C20 mol ratio of about one; further addition of the cation dose not

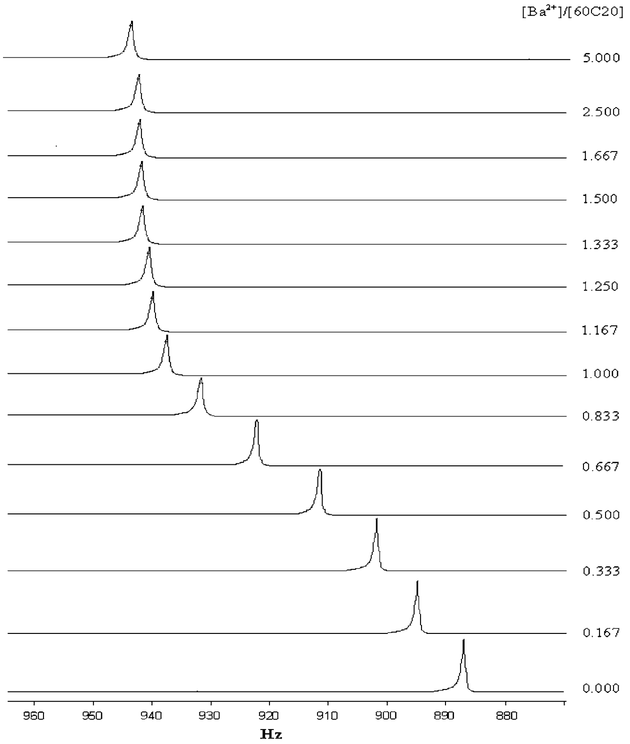

Fig. 1 Proton NMR spectra of 60C20 at various Ba^{2+}/60C20 mol ratio in AN at 27 °C

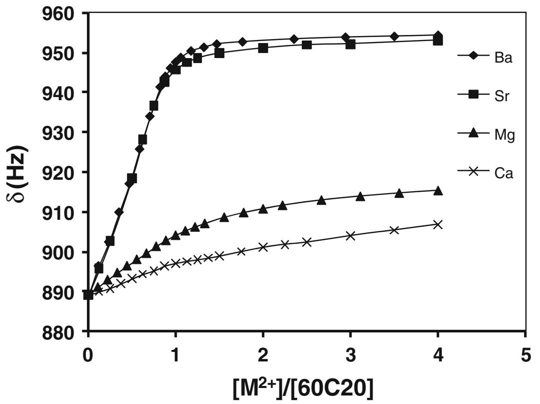

Fig. 2 variation of ^{1}H chemical shift as a function of [M^{2+}]/60C20 mol ratio in AN–NM (75:25) solution at 27 °C

considerably change the resonance frequency, which behavior is indicative of the formation of a 1:1 complex in the solvent mixtures. But in the case of Mg^{2+} and Ca^{2+}, this phenomena was however not observed and the resonance frequency of proton still increased after an M^{2+}:60C20 mol ratio of about one, indicating the formation of weaker complexes between these ions and 60C20 ligand. The formation constants and limiting chemical shifts of the M^{2+}–60C20 complex, evaluated by nonlinear least-squares fitting of the chemical shift–mol ratio data, are listed in Table 1. A sample computer fit of the mol ratio data are shown in Fig. 3. From the data in Table 1, it is obvious that the stability of all 60C20 complexes increased in the order of acetonitrile–D_2O < acetonitrile < acetonitrile–nitromethane. It is well known that the Gutmann donors number of solvent [23] is an important factor in complexation reactions [17–19]. It should be noted that acetonitrile and nitromethane possess similar dielectric constants (i.e., $\varepsilon_{AN} = 37.5$, $\varepsilon_{NM} = 35.6$), but have quite different donors number (i.e., $DN_{AN} = 14.1$ and $DN_{NM} = 2.7$)[23]. Acetonitrile, as a solvent of intermediate solvating ability, can thus compete with the crown ether for metal ions more readily than nitromethane as a solvent of low donicity. In addition, it has been shown that acetonitrile can solvate the macrocyclic ligands to a large extent [24, 25], while nitromethane has no significant interactions with the ligand [2]. Thus, it is expected to observe a rather large increase in the stability of the metal ion–60C20 complexes with addition of nitromethane to acetonitrile solutions. Also, the stability of M^{2+}–60C20 complex were found to rapidly decrease with increasing the D_2O content of the mixed solvent. Water is a solvent of high solvating ability (DN = 33) which can strongly compete with ligands in the complexation process. It is thus reasonable to expect that the addition of water as compared to acetonitrile (DN = 14.1), decreases the extent of interaction between the ligand and cation. Furthermore, the lower dielectric constant of acetonitrile (38.0) in comparison to that of water (78.5) would cause the electrostatic contributions to the bond formation to decrease with decreasing the water content of the solvent mixture. It is interesting to note that there actually was a linear relationship between log K_f and the mol fraction of acetonitrile (X_{CH_3CN}) in the mixed solvent (Fig. 4). It hence seems

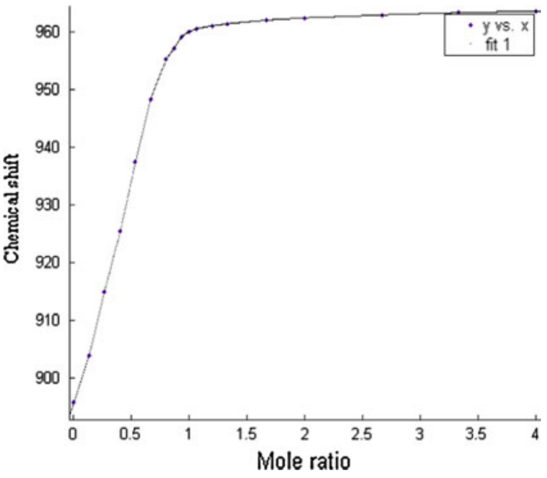

Fig. 3 Computer fit of the variation of the ^{1}H chemical shift of 60C20 as a function of Ba^{2+}/60C20 mole ratio in AN–NM (75:25): (x) experimental data; (*dot line*) theoritical calculated

Table 1 Formation constant of 60C20–M^{2+} complex in various binary mixtures at 300 K

Medium	Log K_f ± SD			
	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Pure AN	2.86 ± 0.01	2.26 ± 0.03	4.49 ± 0.08	5.11 ± 0.08
75% AN–25% NM	3.11 ± 0.2	2.57 ± 0.04	4.70 ± 0.10	5.33 ± 0.07
50% AN–50% NM	3.51 ± 0.01	2.93 ± 0.02	5.03 ± 0.09	5.45 ± 0.09
25% AN–75% NM	3.76 ± 0.02	3.25 ± 0.03	5.41 ± 0.08	5.68 ± 0.05
Pure NM	3.93 ± 0.01	3.48 ± 0.03	5.68 ± 0.03	5.89 ± 0.06
75% AN–25% D_2O	2.48 ± 0.02	ND	3.23 ± 0.08	3,56 ± 0,06
50% AN–50% D_2O	ND	ND	2.23 ± 0.06	2.65 ± 0.02
25% AN–75% D_2O	ND	ND	ND	2.18 ± 0.03

ND not determined

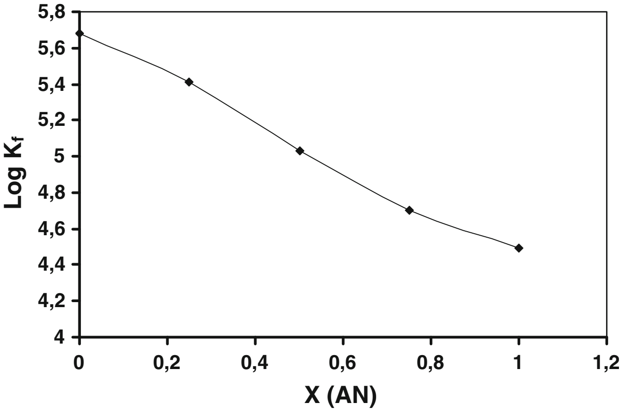

Fig. 4 Variation of stability constant of 60C20–Sr^{2+} complex with the composition of the AN–NM binary system at 27 °C

reasonable to assume that the preferential hydration of the cation is mainly responsible for the monotonic dependence of the stability constants on the solvent composition. The data given in Table 1 revealed that the stability of M^{2+}–60C20 complexes varied in the order of $Ba^{2+} > Sr^{2+} > Mg^{2+} \approx Ca^{2+}$. The stability and selectivity of crown ether complexes with metal cations depend on several factors, including the cavity size of the ligand, the character of the heteroatoms in the polyether ring, spatial distribution of ring binding sites and the cation diameter [26]. The fitness of the cavity size of a macrocyclic compound is an importance factor, which explains the selectivity of crown ether complexes, but large crown ethers (i.e., those larger than 18-crown-6) are very flexible, and contain many oxygen atoms in their rings, which enables them to twist around a metal ion of suitable size to let a maximum number of oxygen atoms in the ring coordinate to the central cations [27]. The selectivity observed for complexes of 60C20 with the alkaline earth metal cations can be attributed to the relative size of the metal ions to the cavity of the polyether ring. Regarding the fact that the ionic radial of the above cations decreases in the order of $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$. The Ba^{2+} ion with the largest ionic size can have a more convenient fitting condition in the ligand cavity, than can the other ions. Mg^{2+} and Ca^{2+} ions have smaller sizes than the cavity and hence cannot properly fit therein. This is while among the two ions, Mg^{2+} ion forms a rather stronger complex than Ca^{2+} ion due to its comparatively higher charge density.

References

1. Pedersen, C.J.: Cyclic polyethers and their complexes with metal salts. J. Am. Chem. Soc. **89**, 7017–7036 (1967)
2. Izatt, R.M., Bradshow, J.S., Pawlak, K.: Thermodynamic and kinetic data for macrocycle interaction with neutral molecules. Chem. Rev. **92**, 1261–1354 (1992)
3. Karkhaneei, E., Afkhami, A., Shamsipur, M.: Nuclear magnetic resonance study of lithium ion complexes with several crown ethers in binary acetonitrile-nitromethane mixtures. J. Coord. Chem. **39**, 33–42 (2006)
4. Shamsipur, M., Kazemi, S.Y., Azimi, Gh., Madaeni, S.S., Lippolis, V., Garau, A., Isaia, F.: Selective transport of silver ion through a supported liquid membrane using some mixed aza-thioether crowns containing a 1, 10-phenanthroline sub-unit as specific ion carriers. J. Membr. Sci. **215**, 87–91 (2003)
5. Kozlowski, C.A., Kozlowska, J.: PNP-16-crown-6 derivatives as ion carriers for Zn(II), Cd(II) and Pb(II) transport across polymer inclusion membranes. J. Membr. Sci. **326**, 215–221 (2009)
6. Mohapatra, P.K., Lakshmi, D.S., Bhattacharyya, A., Manchanda, V.K.: Evaluation of polymer inclusion membranes containing crown ethers for selective cesium separation from nuclear waste solution. J. Hazard. Mater. **169**, 472–479 (2009)
7. Ganjali, M.R., Rahimi-Nasrabadi, M., Maddah, B., Moghimi, A., Faal-Rastegar, M., Borhany, Sh., Namazian, M.: Sub-micro level monitoring of beryllium ions with a novel beryllium sensor based on 2,6-diphenyl-4-benzo-9-crown-3-pyridine. Talanta **63**, 899–906 (2004)
8. Ganjali, M.R., Hosseini, M., Basiripour, F., Javanbakht, M., Hashemi, O.R., Rastegar, M.F., Shamsipur, M., Buchanen, G.W.: Novel coated-graphite membrane sensor based on *N*, *N*′-dimethylcyanodiaza-18-crown-6 for the determination of ultra-trace amounts of lead. Anal. Chim. Acta **464**, 181–186 (2002)
9. Kantekın, H., Kiliçaslan, M.B., Ağin, F., Alp, H., Ocak, Ü.: New heavy metal ion-selective macrocyclic ligands with mixed-donor atoms and their extractant properties. J. Coord. Chem. **63**, 1921–1932 (2010)
10. Aghaie, M., Giahi, M., Aghaie, H., Arvand, M., Pournaghdy, M., Yavari F.: New Fe(II) ion-selective electrode based on *N*-phenylaza-15-crown-5 as neutral carrier in PVC matrix. Desalination 2009. **247**, 346–354 (2009)
11. Shamsipur, M., Popov, A.: Multinuclear NMR study of dibenzo-30-crown-10 complexes with sodium, potassium, and cesium ions in nonaqueous solvents. J. Am. Chem. Soc. **101**, 4051–4055 (1979)
12. Amini, M.K., Shamsipur, M.: Complex formation of silver, thallium and alkali cations with dibenzo-30-crown-10 in some non-aqueous solutions. Inorg. Chim. Acta **183**, 65–69 (1999)
13. Hasek, J., Hlavata, P., Huml, K.: Complex of potassium thiocyanate and dibenzo[b, q][1, 4, 7, 10, 13, 16, 19, 22, 25, 28]decaoxacyclotriacontane (dibenzo-30-crown-10). Acta Crystallogr. B. **36**, 1782–1785 (1980)
14. Rounaghi, G.H., Nazari, E., Ghaemi, A., Mohajeri, M.: Complexing ability of a macrocyclic ligand, dibenzo-24-crown-8, with $UO2^{2+}$ in some binary mixed non-aqueous solvents. J. Coord. Chem. **63**, 2349–2359 (2010)
15. Rahimi-Nasrabadi, M., Ganjali, M.R., Gholivand, M.B., Ahmadi, F., Norouzi, P., Salavati-Niasari, M.: Cyclic voltammetry investigation of the complex formation between Cu^{2+} and some Schiff bases in binary acetonitrile/dimethylformamide mixtures. J. Mol. Struct. **885**, 76–81 (2008)
16. Rahimi-Nasrabadi, M., Ahmadi, F., Pourmortazavi, S.M., Ganjali, M.R., Alizadeh, K.: Conductometric study of complex formations between some substituted pyrimidines and some metal ions in acetonitrile and the determination of thermodynamic parameters. J. Mol. Liquids **144**, 97–101 (2009)
17. Alizadeh, N.: A comparison of complexation of Li^{+} ion with macrocyclic ligands 15-crown-5 and 12-crown-4 in binary nitromethane–acetonitrile mixtures by using lithium-7 NMR technique and ab initio calculation. Spectrochim. Acta A. **78**, 488–493 (2011)
18. Sahmsipur, M., Shafiee Dastjerdi, L., Alizadeh, N., Bijanzadeh, H.R.: Competitive cesium-133 NMR spectroscopic study of

complexation of different metal ions with dibenzo-21-crown-7 in acetonitrile-dimethylsulfoxide and nitromethane-dimethylsulfoxide mixtures. Spectrochim. Acta A **69**, 1265–1270 (2008)

19. Shamsipur, M., Talebpour, Z., Alizadeh, N.: NMR study of the stoichiometry, stability, and ligand interchange of silver ion-hexathia-18-crown-6 complex in binary dimethyl sulfoxide solvent mixtures at 300 K. J. Sol. Chem. **32**, 227–238 (2003)
20. Gibson, H.W., Bheda, M.C., Engen, P., Shen, Y.X., Sze, J., Zhang, H., Gibson, M.D., Delaviz, Y., Lee, S.H., Liu, S., Wang, L., Nagvekar, D., Rancourt, J., Taylor, L.T.: Synthesis and characterization of large (30–60-Membered) aliphatic crown ethers. J. Org. Chem. **59**, 2186–2196 (1994)
21. Roach, E.T., Handy, P.R., Popov, A.I.: Study of the interaction of lithium ion with pentamethylenetetrazole by lithium-7 NMR. Inorg. Nucl. Chem. Lett. **9**, 359–363 (1973)
22. Ahmadi, F., Jafari, B.: Voltammetry and spectroscopy study of in vitro interaction of fenitrothion with DNA. Electroanalysis. **23**, 675–682 (2011)
23. Gutmann, V.: The donor–acceptor approach to molecular interactions. Plenum, New York (1978)
24. Gokel, G.W., Cram, D.J., Liotta, C.L., Harris, H.P., Cook, F.L.: 18-Crown-6 [1, 4, 7, 10, 13, 16-hexaoxacyclooctadecane]. Org. Synth. **56**, 30–33 (1977)
25. Joshaghani, M., Gholivand, M.B., Ahmadi, F.: Spectrophotometric and conductometric study of complexation of salophen and some transition metal ions in nonaqueous polar solvents. Spectrochim. Acta A **70**, 1073–1078 (2008)
26. Izatt, R.M., Pawlak, K., Bradshaw, J.S., Bruening, R.L.: Thermodynamic and kinetic data for macrocycle interactions with cations and anions. Chem. Rev. **91**, 1721–2085 (1991)
27. Strasser, B.O., Popov, A.I.: Influence of solvent properties on the kinetics of complexation of the sodium ion with 18-crown-6. J. Am. Chem. Soc. **107**, 7921–7924 (1985)