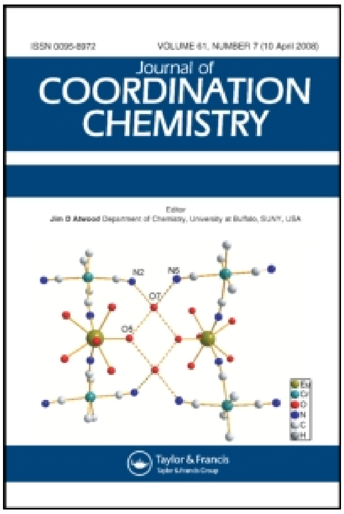

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LITHIUM-7 AND SODIUM-23 NMR STUDIES OF THE COMPLEXATION OF Li^+ AND Na^+ IONS WITH 1,13-DIBENZO-24-CROWN-8 IN BINARY NITROMETHANE–ACETONITRILE MIXTURES

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^{7}Li, ^{23}Na and ^{13}C NMR measurements were used to study the stoichiometry and stability of Li^+ and Na^+ complexes with dibenzo-24-crown-8 in binary nitromethane–acetonitrile mixtures. The resulting chemical shift-mol ratio data clearly reveal the formation of both 1:1 and 2:1 (metal/ligand) complexes in solution. Formation of the two adducts in nitromethane and acetonitrile solutions was further supported by monitoring the molar conductance of Li^+ and Na^+ solutions as a function of macrocycle/metal ion mol ratio. Stepwise formation constants of the 1:1 and 2:1 complexes were evaluated from computer fitting of the NMR mol ratio data to equations which relate observed metal ion chemical shifts to formation constants. In all solvent systems, sodium forms more stable complexes with the crown ether than lithium. There is an inverse linear relationship between the logarithms of the stability constants and the mol fraction of acetonitrile in the solvent mixtures.

Keywords: ^{7}Li, ^{23}Na and ^{13}C NMR; dibenzo-24-crown-8 complexes; stability constants; mixed solvents

INTRODUCTION

Among macrocyclic polyethers (crown ethers), first synthesized by Pedersen,[1] the larger molecules such as dibenzo-30-crown-10 (DB30C10) and

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dibenzo-24-crown-8 (DB24C8) possess particularly interesting properties. These molecules, because of their high degree of flexibility and increased number of donating oxygen atoms in the macrocyclic ring, can twist themselves around metal ions of proper size to form three-dimensional 'wrap around' complexes in which all oxygen atoms of the ring are coordinated to the central cation. Evidence for the formation of such structures both in solution[2–7] and in the solid state[8–10] has been reported. Such three-dimensional complexes may be used as good synthetic models for naturally occurring cyclic antibiotic ionophores.[11] Moreover, the large macrocyclic rings can accommodate two cations, if repulsive forces are not large, as in the case of Na^+ and K^+ complexes with DB24C8[12–15] and DB30C10.[3,16,17]

Alkali metal cation nuclear magnetic resonance is well known as a powerful method for studying thermodynamics,[3–5,17–19] kinetics and mechanism[6,14,15,20–23] of alkali ion complexation with macrocyclic ligands in a wide variety of non-aqueous and mixed solvents. Although the complexation of Na^+ ion with dibenzo-24-crown-8 in various solvents has been studied by different experimental techniques such as polarography,[24–26] conductometry,[27–29] calorimetry,[30] spectrophotometry[31] and ^{23}Na NMR,[3,14,15] evidence for the formation of a 2:1 (Na^+:crown) complex in solution have only been reported by the NMR technique.[14,15] However, information about the complexation of Li^+ ion with dibenzo-24-crown-8 is quite sparse.[25,31] In this paper we report the stoichiometry and stability of Li^+ and Na^+ ion complexes with 1,13-dibenzo-24-crown-8 (DB24C8, **I**) in binary nitromethane-acetonitrile mixtures by ^{7}Li, ^{23}Na and ^{13}C NMR and also by conductometry.

EXPERIMENTAL

1,13-Dibenzo-24-crown-8 (DB24C8, Merck) was purified and dried as described previously.[3] Reagent grade lithium perchlorate and sodium thiocyanate (both from Merck) were purified and dried by previously reported methods.[18,32] Spectroscopic grade nitromethane (NM, Reidel) and acetonitrile (AN, Merck) were used to prepare the solvent mixtures by weight.

All NMR measurements were made on a JEOL FX90Q FT-NMR spectrometer with a field strength of 21.13 kG. At this field, lithium 7, sodium-23 and carbon-13 resonate at 34.77, 23.65 and 22.49 MHz, respectively. A 4.0 M aqueous LiCl solution and a 3.0 M aqueous NaCl solution were used as external reference solutions for ^{7}Li and ^{23}Na chemical shift measurements, respectively. TMS was used as an internal reference in carbon-13 NMR experiments and the corresponding chemical shifts are reported in ppm downfield from TMS. The paramagnetic (downfield) shift from the references is designated as positive. All measurements were carried out at a probe temperature of 27.00 ± 0.05°C.

Conductivity measurements were carried out with a Metrohm 712 conductometer. A dip-type conductivity cell, made of platinum black, with a cell constant of $0.8540\,\mathrm{cm}^{-1}$ was used. In all measurements the cell was thermostatted at 25.00 ± 0.05°C using a Haake D1 thermostat.

RESULTS AND DISCUSSION

Sodium-23 and lithium-7 chemical shifts were measured as a function of the $\mathrm{DB24C8/M^+}$ mol ratio in various binary mixtures of NM and AN at 27°C. In all cases, only one population-average resonance signal was observed, indicating a fast exchange between the solvated and complexed cation sites. The resulting mol ratio plots are shown in Figure 1. It is readily seen that for both $\mathrm{Li^+}$ and $\mathrm{Na^+}$ ions the chemical shift changes obtained in NM are opposite those obtained in AN and the binary mixtures used (*i.e.*, $\mathrm{Na^+}$: paramagnetic shift in NM and diamagnetic in other solvent systems and $\mathrm{Li^+}$: diamagnetic shift in NM and paramagnetic in other solvent systems). A similar opposite trend in the chemical shift changes during the complexation of $\mathrm{Li^+}$ and $\mathrm{Na^+}$ ions with different macrocyclic ligands in NM and AN solutions has been observed and discussed in detail in previous publications.[3,4,19,33–35]

Unlike the cases involved in the formation of strong 1 : 1 complexes, in which the change in chemical shift with ligand/metal ion mol ratio is quite linear at mol ratios <1,[3–5,18,19,32] the mol ratio plots given in Figure 1 show a curved relationship for $0 < \mathrm{DB24C8/M^+} < 1.0$. However, in the cases of the $\mathrm{Na^+}$ complex in all solvent systems and the $\mathrm{Li^+}$ complex in pure NM and 80% NM mixture, a plateau is reached for mol ratios >1.0 due to the quantitative formation of a 1 : 1 complex. Since curved part of the mol ratio plots in the region between 0.0–1.0 usually shows a distinct inflection point at a macrocycle/metal ion mole ratio of about 0.5, it can be logically related to the formation of a 2 : 1 $\mathrm{(M^+)_2DB24C8}$ complex in solution.

It has been shown previously that carbon-13 chemical shifts of the carbons in the ether region of cyclic polyethers are sensitive to the conformational change of the ligands upon complexation with metal ions.[3,36] Thus,

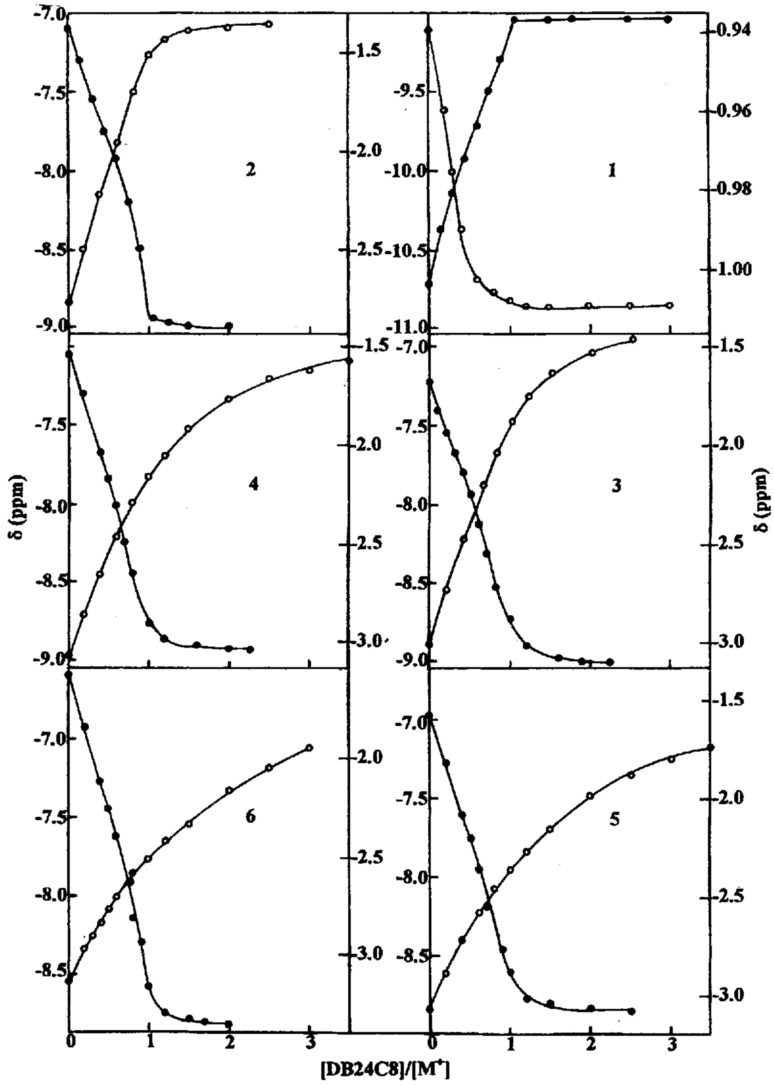

FIGURE 1 Lithium-7 (empty circles, right scale) and sodium-23 (filled circles, left scale) chemical shifts as a function of DB24C8/M^+ mol ratios at 27°C in different NM–AN solvent mixtures. Weight percent of AN in the solvent mixtures is (1) 0, (2) 20, (3) 40, (4) 60, (5) 80, (6) 100. In 3–6, solid lines are the calculated points.

to get further information about DB24C8 interactions with the Na^+ and Li^+ ions in pure AN and NM solutions, we studied the chemical shifts of the polyether chain carbon atoms as a function of metal ion concentrations relative to the concentration of the ligand. A sample mol ratio plot for the

Na^+-DB24C8 system in NM is shown in Figure 2. Other systems studied showed a similar mol ratio pattern. As is clear from Figure 2, the addition of the metal ion to DB24C8 solution results in two conformational changes in the ligand molecule following the formation of both M^+DB24C8 and $(M^+)_2$DB24C8 complexes.

In order to obtain further information about the stoichiometries of the Na^+ and Li^+ complexes with DB24C8 in NM and AN solutions, the molar conductance of metal ion solutions (1.0×10^{-4}–5.0×10^{-4} M) was monitored as a function of ligand/metal ion mol ratios. The resulting molar conductance *vs* DB24C8 to metal ion mol ratios in NM and AN solutions are shown in Figure 3. As is obvious, all mol ratio plots show two sharp infections at ligand to metal ion mol ratios of 0.5 and 1, a fact which strongly supports the NMR data. It should be noted that we have previously observed similar conductance behaviour for the formation of NH_4^+DA18C6 and $(NH_4^+)_2$DA18C6,[37] as well as H_3O^+18C6 and $H_3O^+(18C6)_2$ complexes in non-aqueous solutions.[38,39]

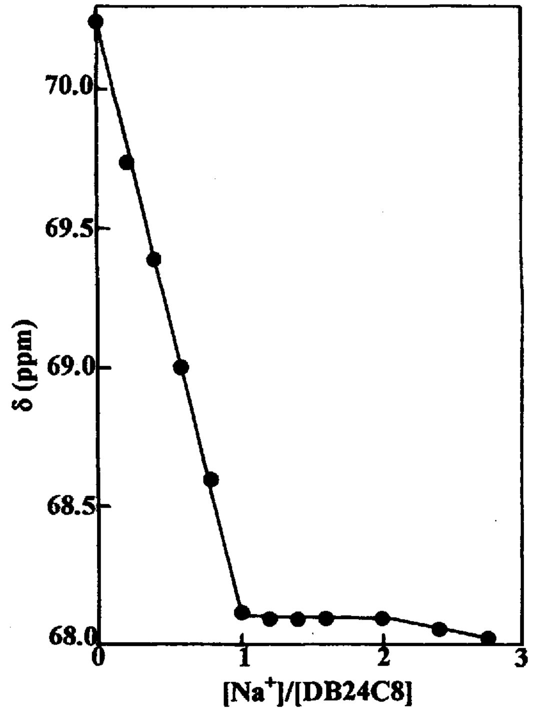

FIGURE 2 Carbon-13 chemical shifts as a function of the Na^+/DB24C8 mol ratio at 27°C in NM solution.

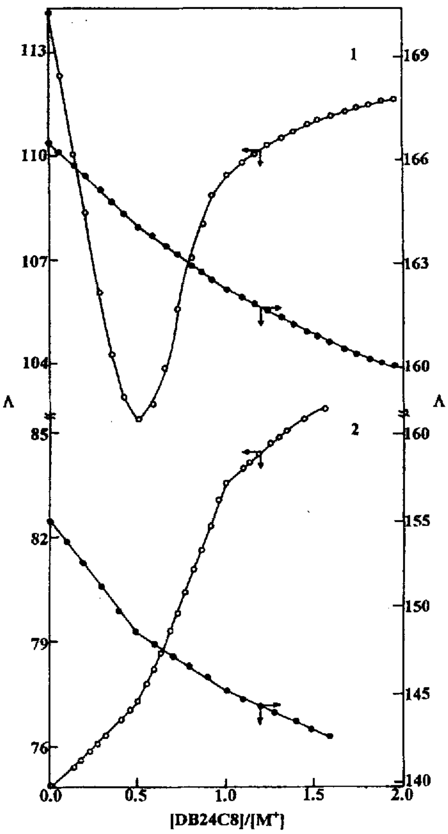

FIGURE 3 Molar conductance (S^{-1} cm^2 mol^{-1}) as a function of DB24C8/Li^+ (1) and DB24C8/Na^+ (2) at 25°C in NM (empty circles) and AN (filled circles) solutions.

In order to calculate the stability constants of the resulting complexes, we assumed a successive 1 : 1 and 2 : 1 complex formation model.

$$M + L = ML \quad K_1 = [ML]/[M][L] \tag{1}$$

$$ML + M = M_2L \quad K_2 = [M_2L]/[M][ML] \tag{2}$$

Here M stands for the Li^+ and Na^+ ions, and L denotes the crown ether used. K_1 and K_2 are stepwise stability constants of the 1 : 1 and 2 : 1 complexes, respectively. The mass balance equations can be written as

$$C_M = [M] + [ML] + 2[M_2L] \tag{3}$$

$$C_L = [L] + [ML] + [M_2L] \tag{4}$$

where C_M and C_L are the analytical concentrations of the metal ion and the crown ether, respectively. Then, the mass balance equations can be solved to obtain an equation for the free metal ion concentration [M], as in (5).

$$\begin{aligned} &K_1K_2[\mathrm{M}]^3 + [K_1K_2(2C_L - C_M) + K_1][\mathrm{M}]^2 \\ &\quad + [1 + K_1(C_L - C_M)][\mathrm{M}] - C_M = 0 \end{aligned} \tag{5}$$

The ^{7}Li and ^{23}Na chemical shift data followed the three-site, fast exchange model of equation (6).[40,41]

$$\delta_{\mathrm{obs}} = \delta_{\mathrm{M}}[\mathrm{M}]/C_M + \delta_{\mathrm{ML}}[\mathrm{ML}]/C_M + \delta_{\mathrm{M2L}}[\mathrm{M_2L}]/C_M \tag{6}$$

where δ_{obs} is defined as the experimental difference in chemical shift obtained by subtracting the reference position from that of the sample. With this definition, a downfield (paramagnetic) shift of the sample results in a positive change in δ_{obs}. The terms δ_{M}, δ_{ML} and δ_{M2L} refer to the chemical shifts of the solvated, 1 : 1 complexed and 2 : 1 complexed metal ion, respectively.

For the evaluation of K_1 and K_2, a non-linear least-squares curve fitting program, KINFIT, was used.[42] Adjustable parameters are the stepwise stability constants and the corresponding chemical shifts (*i.e.*, K_1, K_2, δ_{ML} and δ_{M2L}).

During the curve fitting process, the free metal ion concentration, [M], was calculated from equation (5) by a Newton-Ralphson procedure. Once the value of [M] had been obtained, the concentration of all other species involved were calculated from the mass balance equations, using the estimated values of K_1 and K_2 at the current iteration step of the program. Refinement of the parameters was continued until the sum-of-squares of the residuals between the observed and calculated (from equation (6)) chemical shifts for all experimental points was minimized. The output of the program KINFIT comprises the refined parameters, the sum-of-squares and the standard deviation of the data. All stepwise stability constants as well as δ_{M}, δ_{ML} and δ_{M2L} are summarized in Table I. Our assumption of 1 : 1 and 2 : 1 stoichiometries for the resulting complexes seems reasonable in the light of fair agreement between the observed and calculated chemical shifts (see Figures 1(3) to 1(6)).

The data given in Table I indicate that, in all solvent mixtures used, $\mathrm{Na^+}$ forms more stable 1 : 1 and 2 : 1 complexes than $\mathrm{Li^+}$ with DB24C8. The ionic radius of the metal ions is expected to play a fundamental role in complexation from the viewpoints of both ionic solvation and ease of binding

TABLE I Stepwise stability constants and limiting chemical shifts (ppm) for Na^+ and Li^+ complexes with DB24C8 in various NM–AN mixtures at 27°C[a].

Solvent composition		Na^+					Li^+				
%*AN*	X_{AN}	δ_M	$\log K_1$	δ_{ML}	$\log K_2$	δ_{M2L}	δ_M	$\log K_1$	δ_{ML}	$\log K_2$	δ_{M2L}
0	0.00	−10.73	>8	−9.12	>6		−0.93	5.08 (0.07)	−1.09 (0.01)	3.38 (0.07)	−1.00 (0.02)
20	0.27	−7.10	>7	−9.08	>5		−2.78	4.41 (0.04)	−1.34 (0.02)	2.48 (0.05)	−2.09 (0.03)
40	0.50	−7.23	6.53 (0.05)	−9.04 (0.02)	4.77 (0.04)	−7.92 (0.02)	−3.02	3.16 (0.04)	−1.33 (0.01)	< 1	
60	0.69	−7.05	5.95 (0.05)	−8.93 (0.02)	3.80 (0.07)	−7.81 (0.02)	−3.06	2.73 (0.03)	−1.31 (0.01)	< 1	
80	0.86	−6.96	4.39 (0.04)	−8.88 (0.03)	2.55 (0.05)	−7.66 (0.03)	−3.10	2.31 (0.05)	−1.28 (0.02)	< 1	
100	1.00	−6.61	3.60 (0.10)	−8.81 (0.03)	1.22 (0.07)		−3.15	1.93 (0.03)	−0.92 (0.05)	< 1	

[a] Values in parentheses indicate standard deviations.

with the donating oxygen atoms of the macrocyclic ring. Lithium ion has much stronger ionic solvation than does Na^+. Since complex stability is a balance between the cation-ligand and cation-solvent interactions, the stronger solvation of Li^+ ion will result in weaker complexes with DB24C8.

In the case of 1 : 1 complexes, it has been clearly shown that for large crown ethers which are capable of forming three-dimensional of 'wrap around' complexes with ions, cationic size will strongly influence complex formation.[3,4] Complexation of a large crown ether by a cation of appropriate size results in the formation of a stable 'wrap around' complex. The crystal structure[10] of such a three-dimensional complex between DC24C8 and Na^+ showed that the 24-membered ring adopts a conformation that allows all eight oxygen atoms of the macrocyclic ring to be coordinated to the central Na^+ ion. However, if the ring size is much larger than the cation, (*e.g.*, in the case of the Li^+-DB24C8 system), the ligand can still form such a three-dimensional structure, but the oxygen atoms of the ligand are in close proximity and the resulting repulsive forces weaken the complex.

It is interesting to note that the crystal structure of the 2 : 1 sodium *o*-nitrophenolate complex with DB24C8[13] reveals the partition of the large crown ether molecule into two distinct and symmetrical regions in which each sodium ion is hexacoordinated to the anion and four ether oxygens of the ring. However, to the best of our knowledge, there is no reported evidence for the formation of a 2 : 1 $(Li^+)_2$-DB24C8 complex.

The data in Table I clearly indicate the effect of solvent properties on the stability of the resulting complexes between Li^+ and Na^+ and DB24C8.

Among different factors in solution,[43] certainly of vital importance is the ability of solvent molecules to solvate ionic species and thus to compete with the ligands for the cation.[3,4,7,18,19,27,31,37] Of course, the interaction of some solvents with macrocyclic ligands[44] is of equal importance, although much less appreciated. Thus, the thermodynamic stability of alkali ion-macrocycle complexes is not just a measure of the absolute strength of ion–dipole interactions between the cation and the local -CH_2-O-CH_2- groups of the crown ethers,[1,45] but a measure of the relative strength as compared to ionic solvation.

From Table I, it is obvious that the stepwise stability constants decrease drastically with increasing fraction of AN in the solvent mixtures. It is well known that the Gutmann donor number of solvents[46] is an important measure in complexation reactions.[3,4,6,7,32,37,39,40] It should be noted that while AN and NM possess about the same dielectric constants (*i.e.*, $\varepsilon_{AN} = 37.5$

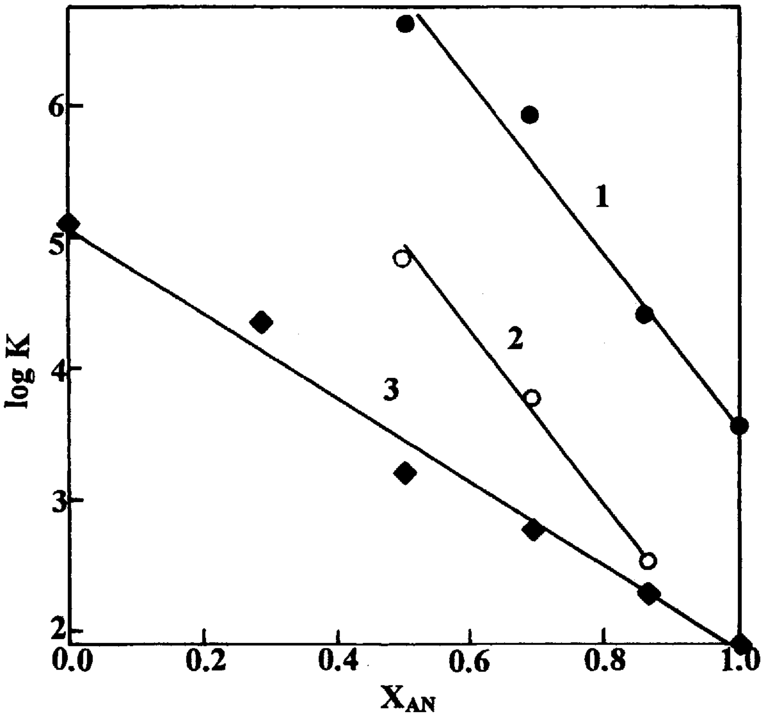

FIGURE 4 Variation of log K of DB24C8 complexes with Li^+ and Na^+ with X_{AN} in the binary NM–AN mixtures: (1) log K_1 for Na^+DB24C8; (2) log K_2 for $(Na^+)_2$ DB24C8; (3) log K_1 for Li^+DB24C8.

and $\varepsilon_{NM} = 35.6$), their solvating abilities are quite different.[46] AN is a solvent of much higher Gutmann donor number (DN = 14.1) than NM (DN = 2.7) so that it can more strongly compete with the crown ether molecules for the alkali ions used. Thus it is not unexpected to observe a rather large decrease in stability of the 1 : 1 and 2 : 1 complexes with increasing amounts of AN in the solvent mixtures.

It is interesting to note that there is actually a linear relationship between the logarithm of the stepwise stability constants of the complexes and the mol fraction of AN, X_{AN} (see Figure 4). We have frequently witnessed similar behaviour for different metal ion-ligand systems in various mixed solvents.[31,47–52] Such monotonic behaviour could be related to the preferential solvation of the cations by AN molecules. This is also consistent with the observed changes of δ_M with solvent composition. From the data given in Table I it is obvious that for both Li^+ and Na^+ ions, addition of only 20% (by wt) of AN to NM changes the δ_M values characteristic for NM solution to values very close to those for AN solution; further addition of AN does not change the δ_M values much. Such variation of δ_M seems to further support the preferential solvation of both lithium and sodium ions by AN molecules in the mixed solvents.

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