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Study of Complex Formation of n-Alkylammonium Cations by Dibenzo-18-crown-6, Dibenzo-21-crown-7, and Dibenzo-24-crown-8 in Acetonitrile, Nitromethane and Nitrobenzene Solvents and Their Binary Mixtures Using Conductometric Method

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The complex formation of ammonium and four n-alkylammonium perchlorate salts with dibenzo-18-crown-6 (DB18C6), dibenzo-21-crown-7 (DB21C7) and dibenzo-24-crown-8 (DB24C8) was studied by conductometry in acetonitrile (AN), nitrobenzene (NB) and nitromethane (NM) solvents at different temperatures and their binary mixtures at 25°C. The stability constants of the resulting 1:1 complexes were determined and found to decrease in the order: DB21C7 > DB18C6 > DB24C8. Number of hydrogen atoms on the ammonium group available for bonding to the crown ethers was the most important factor in determining complex stability constant.The influence of other factors such as the size of the macrocyclic cavity, steric effect of the alkyl group attached to the $-NH_3^+$ group, and the Gutmann donicity of the solvents on stability of the complexes were studied. In all cases, the stability constants of the resulted complexes in solvents used varied in the order: NB > NM > AN. Standard enthalpies and entropies of the complex formation were obtained from the temperature dependence of the stability constants. Obtained thermodynamic parameters were sensitive to the type of solvent. The enthalpy – entropy compensation effect was investigated in general complexation of cations with crown ethers.

Key words: alkylammonium cations, crown ethers, conductometry, complex stability constant, enthalpy-entropy compensation, solvent effect

Host – guest interactions are important in many biological processes such as enzyme catalysis and inhibition, antibody-antigen interaction and membrane transport [1]. In the chemical sense, the host is usually an organic molecule or anion with specific receptor site while the guest is normally a metal or an organic cation. During the past three decades, a considerable attention has been given on the interaction between macrocyclic polyethers as host and ammonium ion as guest [2–5].

Guest parameters for organic ammonium cations differ from those of metal cations due to different binding mechanism for the two types of guests. Ammonium cation interacts with the macrocycle – donor atoms through hydrogen bond [6–8]. It seems that parameters, which are significant to organic ammonium cation-macrocycle polyether

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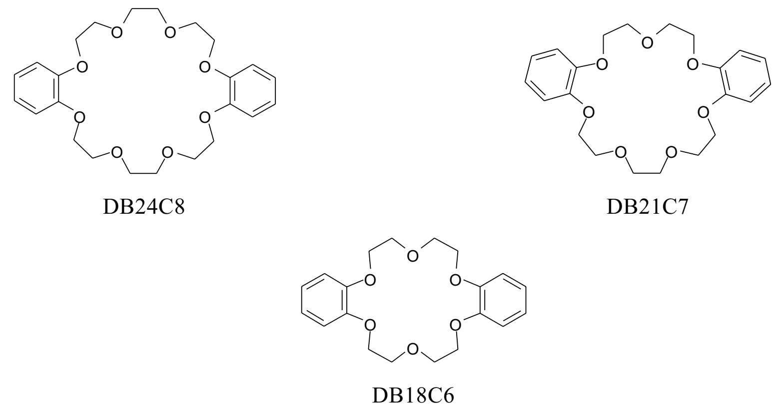
interactions, are number of hydrogen atoms available for hydrogen bonding, steric hindrance of host-guest approach by guest and length of chain of the alkyl group as substituting on amine cation [9].

In the present work, we investigated the effect of these parameters on the n-alkylamine-crown ether interactions. Because most of the previous studies on the complexation of ammonium salt with macrocyclic ligands were limited to aqueous and methanolic solutions [10–15], in this paper we report a conductometry study of organic ammonium complexation with dibenzo-18-crown-6 (DB18C6), dibenzo-21-crown-7 (DB21C7) and dibenzo-24-crown-8 (DB24C8) in nitromethane (NM), acetonitrile (AN), nitrobenzene (NB) and their binary mixtures at different temperatures. The structure of the ligands is given in Figure 1.



DB24C8

DB21C7

DB18C6

Figure 1. Structure of crown ethers.

EXPERIMENTAL

The macrocycles 1,4,7,14,17,20-hexaoxa[7.7]orthocyclophane (DB18C6), 1,4,7,14,17,20,23-heptaoxa [7.10]orthocyclophane (DB21C7) and 1,4,7,10,17,20,23,26-octaoxa[10.10]orthocyclophane (DB24C8) were used (Fluka) as received. NM, AN and NB solvents of analytical grade (Merck) were used. Except of ammonium perchlorate (Fluka), other organic ammonium perchlorate salts (methyl, ethyl, propyl and butyl ammonium perchlorates) were prepared by mixing of appropriate amounts of amine and perchloric acid in water slowly and stirring the mixture for about 0.5 h. The pH of final solution was controlled with pH meter WTW model 535A (Weilheim, Germany) until the precipitate was observed. The resulting salts were filtered and washed with chloroform. The ammonium salts were recrystallized from absolute ethanol and dried in vacuum for 24 h.

The conductance measurements were carried out with a conductometer WTW model LF538 (Weilheim, Germany). A dip-type conductivity cell, made of platinum black, with a cell constant of 1.042 cm^{-1} was used. In a typical experiment, 35 cm^3 of ammonium salt solution (1.0×10^{-4} – 2.0×10^{-4} mol dm^{-3}) in the desired solvent was placed in the titration cell, thermostated in 15, 25, 35 or 45°C and conductance of the solution was measured. Then, a known amount of the macrocycle solution (1.6×10^{-2} mol dm^{-3}) was added into the cell solution in a stepwise manner, using a calibrated micropipette and the conductance of the solution was measured after each addition. The macrocycle solution was added until the desired macrocycle – ammonium ion mole ratio was achieved.

RESULTS AND DISCUSSION

Complex formation of the crown ethers DB18C6, DB21C7 and DB24C8 with n-alkyl ammonium cations (RNH_3^+) in AN, NM and NB solvents was investigated by significant conductance changes at 15, 25, 35 or 45°C. A typical molar conductance-mole ratio plot of complexation of DB21C7 with ammonium ion in NB is shown in Figure 2. Addition of the ligand to cation causes a decrease in the molar conductance of solution. This indicates that the complexed ammonium ion with crown ether has the lower mobility than the solvated NH_4^+ ion. Conductance begins to level off at molar ratios near to unity indicating a 1:1 complex formation. The 1:1 binding of NH_4^+ ion with the crown ethers, L, can be expressed by the following equilibrium:

$$NH_4^+ + L \rightleftarrows NH_4^+L \tag{1}$$

Corresponding equilibrium constant, K_f, can be written as:

$$K_f = \frac{[NH_4^+L]\, f_{NH_4^+L}}{[NH_4^+][L]\, f_{NH_4^+} \cdot f_L} \tag{2}$$

where $[NH_4^+L]$, $[NH_4^+]$ and $[L]$ are the equilibrium molar concentrations of complex, free ammonium ion and free ligand, respectively, and f represents the activity coefficient of the species. Substituting of concentration terms by molar conductance gives:

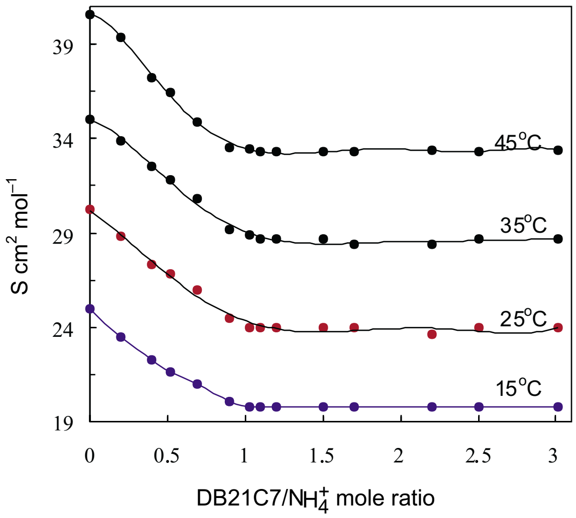


Figure 2. Molar conductance (S cm^{2}mol^{-1}) *vs.* DB21C7 / NH_4^+ mole ratio curve in NB at different temperatures.

$$K_f = \frac{(\Lambda_m - \Lambda_{obs})\, f_{NH_4^+L}}{(\Lambda_{obs} - \Lambda_c)[L]\, f_{NH_4^+} \cdot f_L} \tag{3}$$

So that

$$[L] = C_L - \frac{C_{NH_4^+}(\Lambda_m - \Lambda_{obs})}{(\Lambda_m - \Lambda_c)} \tag{4}$$

where, Λ_m is the molar conductance of ammonium ion before addition of the ligand, Λ_c, the molar conductance of the complexed ammonium ion, Λ_{obs}, the molar conductance of solution during titration, C_L, the analytical concentration of the added crown ether and $C_{NH_4^+}$ is the analytical concentration of ammonium (or n-alkylammonium) ion. By using the dilute amine concentration (2×10^{-4}mol dm^{-3}), the association between amine and perchlorate ions is negligible. Also, it is supposed that activity coefficients of free ammonium cation and in the form of complex are equal, so the activity coefficients in equation (2) are cancelled. The Gen-Plot package [16], from the computer Graphic Service, was used to non-linearly curve fitting of eq. (4). The complex formation constant, K_f, and the estimated Λ_c at points of large crown ether to alkylammonium mole ratios were used as variables. With iterative adjustment of the calculated values of the molar conductance to the observed values and with the estimated K_f and Λ_c at the programm, the stability constant was obtained. Good fits of experimental and calculated data were obtained with assuming 1:1 stoichiometry. All calculated stability constants of alkylamine perchlorate-crown ether complexes in various solvents at 25°C are listed in Table 1.

The most important factor in determining stability constant of alkylamine cations-polyether complexes is the number of hydrogen bonds formed upon complexation [18,19]. All the investigated cations have the $-NH_3^+$ group that might be expected to complex with polyethers. In NB, the trend in log K_f with DB21C7 is shown in sequence: NH_4^+(>6.0) > $CH_3NH_3^+$(5.58) > $C_2H_5NH_3^+$(5.22) ≅ $C_3H_7NH_3^+$(5.19) ≅ $C_4H_9NH_3^+$(4.89). Similar behavior was seen in other studied solvents. Increasing steric bulk of the alkyl(R) group attached to the $-NH_3^+$ group results in a loss of complex stability than the NH_4^+ corresponding complex. Ammonium ion has two distinctive features, which may be important in understanding the above stability trend [16]. NH_4^+ prefers a tetrahedral arrangement of protons about the central nitrogen atom [20,21], that may offer more favorable arrangement for binding the hydrogen atoms to oxygen of polyether especially in DB21C7. Also, it has the capability of hydrogen bonding through three hydrogen atoms with oxygen of polyethers. Goldberg [22] reported nitrogen to oxygen polar interaction to be important component in the structure of tert-butylammonium ion-cyclic polyether complex. The methyl group has a destabilizing effect on the binding ability of the $CH_3NH_3^+$ cation because it causes elongation of the N…O distance, which might be expected to

Table 1. Log K_f of n-alkylammonium cations-crown ethers complexes in nitrobenzene (NB), acetonitrile (AN) and nitromethane (NM) solvents at 25°C.

		Log K_f ± SD		
	Cation	NB (ε = 34.8, DN = 4.4)	NM (ε = 35.87, DN = 2.7)	AN (ε = 36.02,DN = 14.1)
DB21C7	NH_4^+	> 6.0 (> 6.0) [a]	5.88 ± 0.28	4.16 ± 0.02 (4.16± 0.03) [a]
	$MeNH_3^+$	5.58 ± 0.17	4.68 ± 0.05	3.61 ± 0.02
	$EtNH_3^+$	5.22 ± 0.11	4.65 ± 0.05	3.43 ± 0.02
	$PrNH_3^+$	5.19 ± 0.15	4.63 ± 0.08	3.37 ± 0.04
	$BuNH_3^+$	4.89 ± 0.08	4.68 ± 0.09	3.40 ± 0.03
DB18C6	NH_4^+	5.77 ± 0.25 (5.70± 0.01) [a]	5.34 ± 0.18	3.64 ± 0.03 (3.84± 0.03) [a]
	$MeNH_3^+$	5.23 ± 0.15	4.18 ± 0.03	3.03± 0.06
	$EtNH_3^+$	4.84 ± 0.08	4.23 ± 0.05	3.06 ± 0.07
	$PrNH_3^+$	4.67 ± 0.08	4.38 ± 0.05	3.22 ± 0.04
	$BuNH_3^+$	4.62 ± 0.08	4.22 ± 0.07	3.21 ± 0.04
DB24C8	NH_4^+	> 6.0 (> 6.0) [a]	5.66 ± 0.27	3.71 ± 0.02 (3.91± 0.03) [a]
	$MeNH_3^+$	5.00 ± 0.08	4.30 ± 0.04	2.77 ± 0.08
	$EtNH_3^+$	4.97 ± 0.08	4.06 ± 0.05	2.80 ± 0.08
	$PrNH_3^+$	4.67 ± 0.10	4.02 ± 0.07	2.76 ± 0.09
	$BuNH_3^+$	4.64 ± 0.10	4.12 ± 0.06	2.72 ± 0.11

ε = dielectric constant, DN = Gutmann donor number, [17].

[a] = Ref. [7]

result in smaller K_f value of $CH_3NH_3^+$ – crown ether complex in comparing to NH_4^+ – crown ether complex. The data in Table 1 illustrate that lengthening the chain of the R group beyond the α carbon does not appreciably alter stability constant of complex. However, for butylammonium cation, it is seen that the flexible alkyl group can provide an additional hydrogen bond acceptor. With this secondary interaction, the stability constant of the complex is further increased. Similar results had been obtained in the interaction of ethylenoxy side chain with crown ether [23]. It is obvious from Table 1 that log K_f for the reaction of NH_4^+ or other n-alkylammonium cations with DB21C7 are considerably larger than those with DB18C6 or DB24C8. When the polyether is too small to produce a good fit for the ammonium cation (DB18C6 diameter cavity = 2.6 Å; the ammonium ion diameter = 2.9 Å) [24], complexing is expected to be weakened. Furthermore, DB18C6 has less negatively charged oxygen than DB21C7. When the cavity becomes large, *i.e.*, in DB24C8 (diameter cavity > 4 Å), the cation cannot be sufficiently close to the oxygen atoms and the logK_f value is decreased. It seems that the N...O interaction in NH_4^+ – DB18C6 complex acts more efficiently than in corresponding complex with DB24C8, due to shorter N...O distance in the former. Hence, the stability constant of the resulting complexes were found to be decreased in the order DB21C7 > DB18C6 > DB24C8.

The solvent strongly affects the stability constant. Upon complexation, substantial changes must occur in the first solvation shell of both cation and ligand. In general, ligand should be replaced with the solvent molecules in the first solvation shell of the cation. In this study, three solvents, *i.e.*, NB, NM and AN with nearly the same dielectric constant and different donicity number were chosen. In strong solvating solvent such as AN, the complex formation is poor due to highly ordered and tightly bound solvating shell in ammonium ion, whereas in solvents with low donicities, such as NB and NM, a more stable complex is formed. It follows from Table 1, that the stability constants of DB21C7 – alkylammonium cation complexes with selected solvents decrease in the order NB > NM > AN. Although, AN, NB and NM have comparable dielectric constants, the formation constant of the complex in NB, a poor donor solvent, is much higher than that in AN, which has a larger donor number. This indicates that the dielectric constant of the solvent is not the dominant factor in this complexation reaction. Although, the donor ability of NB is greater than NM, but the stability constant of the crown ether-alkylammonium complex in NM is lower than in NB. This behavior may be due to the fact that the NM molecules form a molecular complex with crown ether. In addition, in NB, existence of benzo group in solvent may decrease the N...O interaction, so the stability constant of the complex is increased. The trend in mixture of solvents is similar to that in pure solvents. The variation of the stability constant of NH_4^+ – DB21C7 complex in NB-AN binary system is shown in Figure 3. Similar behavior observed in the other systems, *i.e.*, as the mole fraction of NB and NM increases in AN-NB and AN-NM binary mixtures, the stability constants of the alkylammonium – crown ether complexes increase linearly. Log K_f in binary mixtures are listed in Table 2.

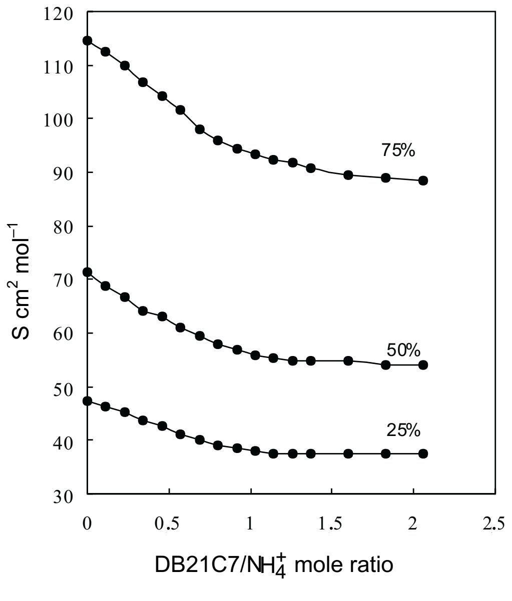


Figure 3. Molar conductance (S cm^{2}mol^{-1}) *vs*. DB21C7 / NH_4^+ mole ratio curve in several NB-AN binary mixtures at 25°C.

Table 2. Log K_f of n-alkylammonium cations-crown ethers complexes in AN-NB and AN-NM binary mixtures at 25°C.

		Log K_f ± SD				
Ligand	Solvent	NH_4^+	$MeNH_3^+$	$EtNH_3^+$	$PrNH_3^+$	$BuNH_3^+$
DB21C7	Pure NB	>6	5.58 ± 0.17	5.22 ± 0.11	5.19 ± 0.15	4.89 ± 0.08
	75% NB + 25% AN	5.38 ± 0.14	5.01 ± 0.07	4.96 ± 0.07	4.67 ± 0.06	4.64 ± 0.07
	50% NB + 50% AN	5.03 ± 0.09	4.58 ± 0.03	4.30 ± 0.04	4.21 ± 0.02	4.24 ± 0.02
	25% NB + 75% AN	4.65 ± 0.05	4.07 ± 0.02	3.90 ± 0.02	3.80 ± 0.02	3.86 ± 0.02
	Pure AN	4.16 ± 0.02	3.61 ± 0.02	3.43 ± 0.02	3.37 ± 0.04	3.40 ± 0.03
	Pure NM	5.88 ± 0.28	4.68 ± 0.05	4.65 ± 0.05	4.63 ± 0.08	4.68 ± 0.09
	75% NM + 25% AN	5.34 ± 0.26	4.41 ± 0.07	4.32 ± 0.06	4.31 ± 0.08	4.41 ± 0.09
	50% NM + 50% AN	4.74 ± 0.05	4.19 ± 0.02	4.05 ± 0.04	4.01 ± 0.03	4.06 ± 0.03
	25% NM + 75% AN	4.39 ± 0.03	3.76 ± 0.02	3.62 ± 0.03	3.61 ± 0.03	3.64 ± 0.04
	Pure AN	4.16 ± 0.02	3.61 ± 0.02	3.43 ± 0.02	3.37 ± 0.04	3.40 ± 0.03
DB18C6	Pure NB	5.77± 0.25	5.23 ± 0.15	4.84 ± 0.08	4.67 ± 0.08	4.62 ± 0.08
	75% NB + 25 % AN	4.76 ± 0.07	4.50 ± 0.04	4.37 ± 0.04	4.32 ± 0.06	4.27 ± 0.05
	50% NB + 50% AN	4.48 ± 0.04	3.92 ± 0.03	3.88 ± 0.02	3.83 ± 0.03	3.79 ± 0.03
	25% NB + 75% AN	4.02± 0.02	3.40 ± 0.02	3.47 ± 0.03	3.49 ± 0.03	3.48 ± 0.02
	Pure AN	3.64± 0.03	3.03 ± 0.06	3.06 ± 0.07	3.22 ±0.04	3.21 ± 0.04
	Pure NM	5.34 ± 0.18	4.18 ± 0.03	4.23 ± 0.05	4.38 ± 0.05	4.22 ± 0.07
	75% NM + 25% AN	4.73 ± 0.16	3.82 ± 0.05	3.89 ± 0.07	4.06 ± 0.05	3.95 ± 0.07
	50% NM + 50% AN	4.02 ± 0.03	3.44 ± 0.04	3.55 ± 0.05	3.66 ± 0.05	3.65 ± 0.05
	25% NM + 75% AN	3.70± 0.03	3.13 ± 0.05	3.15 ± 0.07	3.27 ± 0.06	3.22 ± 0.06
	Pure AN	3.64 0.03	3.03 ± 0.06	3.06 ± 0.07	3.22 ± 0.04	3.21 ± 0.04
DB24C8	Pure NB	>6	5.00 ± 0.08	4.97 ± 0.08	4.67 ± 0.10	4.64 ± 0.10
	75% NB + 25% AN	5.14 ± 0.11	4.23 ± 0.03	4.18 ± 0.04	4.14 ± 0.05	4.12 ± 0.04
	50% NB + 50% AN	4.75 ± 0.06	3.82 ± 0.02	3.44 ± 0.02	3.38 ± 0.04	3.45 ± 0.04
	25% NB + 75% AN	4.29 ± 0.03	3.27 ± 0.02	3.06± 0.03	2.95 ± 0.04	2.92 ± 0.04
	Pure AN	3.71 ± 0.02	2.77 ± 0.08	2.80 ± 0.08	2.76 ± 0.09	2.72 ± 0.11
	Pure NM	5.66 ± 0.27	4.30 ± 0.04	4.06 ± 0.05	4.02 ± 0.07	4.12 ± 0.04
	75% NM + 25% AN	4.40 ± 0.05	3.88 ± 0.06	3.73 ± 0.10	3.68 ±0.10	3.76 ± 0.05
	50% NM + 50% AN	4.74 ± 0.05	3.45 ± 0.05	3.39 ± 0.09	3.30 ± 0.08	3.48 ± 0.07
	25% NM + 75% AN	3.91 ± 0.03	3.11 ± 0.06	3.09 ± 0.10	3.07 ± 0.10	2.91 ± 0.10
	Pure AN	3.71 ± 0.02	2.77 ± 0.08	2.80 ± 0.08	2.76 ± 0.09	2.72 ± 0.11

Thermodynamic parameters, entalphy (ΔH) and entropy (ΔS), for the 1:1 complexation of n-alkylammonium cations with crown ethers in different solvents were evaluated from the corresponding log K_f at different temperatures by applying a linear least squares analysis according to the Vant'Hoff equation:

$$2.303\log K_f = -\Delta H/RT + \Delta S/R \qquad (5)$$

Plots of log K_f *vs.* 1/T for all complexes were linear and ΔH and ΔS values for interaction of crown ethers with alkylammonium cations studied were found and listed in Table 3. The interpretation of ΔH and ΔS values is a somewhat complex task because these values arise from a combination of various phenomena that, taken together, control complexation equilibria. ΔG value is estimated from ΔH and ΔS values. Table 3 clearly shows $|\Delta G|$ that values for DB21C7 complexation reactions are significantly higher than those for DB18C6 or DB24C8. Izatt *et. al* [25] had shown that sometimes ΔH and ΔS compensate each other with ΔH or ΔS being the dominate quantity in determining the magnitude of log K_f [26,27]. Plot of ΔH *vs*. TΔS for the data points in Table 3 in NM and NB solvents is shown in Figure 4. Data points give a good fit ($r > 0.94$) to a straight line with a slope 0.97 and intercept of 25.8.

Table 3. Thermodynamic parameters for complexation of n-alkylammonium cations with crown ethers in NB, NM and AN solvents at 25°C [a,b].

Ligand	–ΔG	–ΔH	TΔS	Cation/ Solvent
DB21C7	20.8 ± 0.7	18.5 ± 0.1	2.3 ± 0.3	MeNH_3^+, AN
	20.1 ± 0.3	18.2 ± 0.4	1.9 ± 0.4	EtNH_3^+, AN
	19.0 ± 1.0	20.5 ± 0.2	–1.5 ± 0.7	PrNH_3^+, AN
	19.4± 0.1	14.6± 0.3	4.8 ± 0.1	BuNH_3^+, AN
	26.6 ± 0.2	11.1± 0.1	15.5± 0.4	MeNH_3^+, NM
	26.4 ± 0.1	10.3 ± 0.2	16.1± 0.1	EtNH_3^+, NM
	27.2 ± 0.3	10.6 ± 0.1	16.6 ± 0.1	PrNH_3^+, NM
	25.4 ± 0.2	11.3 ± 0.1	14.1 ± 0.3	BuNH_3^+, NM
	29.4 ± 0.2	13.9 ± 0.2	15.5 ± 0.1	MeNH_3^+, NB
	30.6 ± 0.7	12.7 ± 0.4	15.9 ± 0.4	EtNH_3^+, NB
	27.9 ± 0.8	12.0 ± 0.2	15.9 ± 0.1	PrNH_3^+, NB
	28.6 ± 0.1	13.9 ± 0.2	14.7 ± 0.1	BuNH_3^+, NB
DB18C6	18.6 ± 0.6	15.7 ± 0.6	2.8 ± 0.6	MeNH_3^+, AN
	17.6 ± 0.7	13.7 ± 0.2	3.9 ± 0.2	EtNH_3^+, AN
	17.6 ± 0.2	11.7 ± 0.1	5.9 ± 0.1	PrNH_3^+, AN
	17.5 ± 0.8	27.9 ± 0.5	–10.4 ± 0.5	BuNH_3^+, AN
	23.8 ± 0.1	19.2 ± 0.1	4.6 ± 0.1	MeNH_3^+, NM
	24.5 ± 0.2	16.9 ± 0.1	7.6 ± 0.1	EtNH_3^+, NM
	24.8 ± 0.6	15.8 ± 0.2	9.0 ± 0.2	PrNH_3^+, NM
	24.0 ± 0.2	15.7 ± 0.2	8.3 ± 0.2	BuNH_3^+, NM
	29.0 ± 0.5	13.9 ± 0.7	15.1 ± 0.1	MeNH_3^+, NB
	28.3 ± 1.2	13.7 ± 0.8	14.6 ± 0.5	EtNH_3^+, NB
	26.8 ± 0.2	13.2 ± 0.1	13.6 ± 0.1	PrNH_3^+, NB
	26.5 ± 0.3	13.2 ± 0.1	13.3 ± 0.1	BuNH_3^+, NB
DB24C8	15.7 ± 0.2	13.9 ± 0.2	1.8 ± 0.2	MeNH_3^+, AN
	16.0 ± 0.2	12.9 ± 0.1	3.1 ± 0.2	EtNH_3^+, AN
	16.0 ± 0.2	14. 0 ± 0.2	2.0 ± 0.2	PrNH_3^+, AN
	15.8 ± 0.2	16.2 ± 0.1	–0.4 ± 0.1	BuNH_3^+, AN
	24.6 ± 0.1	18.3 ± 0.1	6.3 ± 0.1	MeNH_3^+, NM
	23.3 ± 0.3	13.8 ± 0.1	9.5 ± 0.1	EtNH_3^+, NM
	23.1 ± 0.5	18.5 ± 0.1	4.6 ± 0.1	PrNH_3^+, NM
	23.4 ± 0.1	14.1 ± 0.4	9.3 ± 0.1	BuNH_3^+, NM
	29.1± 0.3	29.5 ± 0.5	–0.4 ± 0.5	MeNH_3^+, NB
	28.0 ± 0.3	29.2 ± 0.2	–1.2 ± 0.8	EtNH_3^+, NB
	27.1 ± 0.3	28.7 ± 0.2	–1.6 ± 0.2	PrNH_3^+, NB
	26.7 ± 0.3	26.9 ± 0.4	–0.2 ± 0.3	BuNH_3^+, NB

[a] Values in KJ mol^{-1}

[b] Results represent the averages of triplicate measurements and the uncertainties are the corresponding standard deviations.

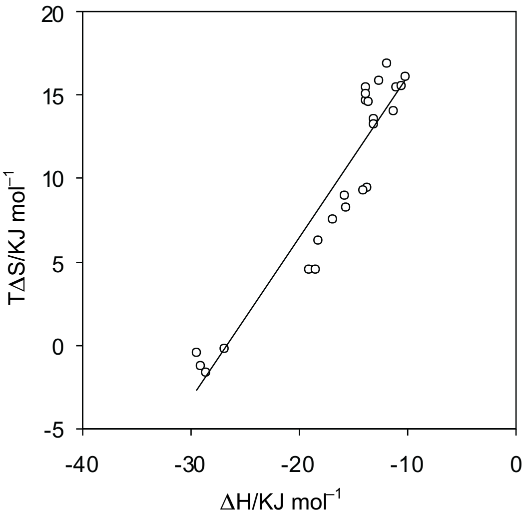


Figure 4. Plot of TΔS *vs.* ΔH for 1:1 complexation of alkylammonium cations with crown ethers in NB and NM.

The data in AN solvent showed a clear non-compensating behavior. This shows that even though compensation processes are more likely to be observed, the phenomenon of entropy-enthalpy compensation is not universal and thermodynamically necessary, but is determined by a particular pattern of molecular interactions. Since the thermodynamic parameters are governed by several factors, more studies must be done to a better understanding of the nature of the ion-molecular interactions, which control the magnitudes and signs of the non-compensating behavior in entropy and enthalpy.

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