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Ionic Hydration Behavior Derived from Infrared Spectra in HDO

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We have described hydration of ions of different kinds on the basis of infrared spectroscopy and HDO as a probe. Electrolytes with amphiphilic anion have been studied in aqueous solutions of $Mg(C_2H_5SO_4)_2$, $NaC_2H_5SO_4$, $KC_2H_5SO_4$, $NaC_2H_5SO_3$, $KC_2H_5SO_3$, $NaCH_3SO_4$, $NaCH_3SO_3$, $LiCF_3COO$, $NaCF_3COO$, KCF_3COO, and $NaCF_3SO_3$ by means of FTIR spectra of HDO isotopically diluted with H_2O. A procedure has been applied that allowed us to remove the contribution of bulk water and thus to separate the spectra of ion-affected HDO. The results and the known literature data treated in the described way were discussed. Ions of different character have been taken into consideration: mono-, di-, and trivalent, including hydrophobic and amphiphilic ones. Anions and cations appear to have a very different effect on water structure when their polarization power is considered. The energy of affected water H-bonds changes proportionally to the polarization power of anions. On the contrary, cations reveal the zone-type influence. The origin of such hydration behavior and the consequences have been discussed.

1. Introduction

The problem of ion hydration is fundamental to solution chemistry. The theoretical computer simulations in this area need explicit experimental data for comparison of results. The recognition of the hydration process is vital for technology, biochemistry, biology and medicine.

Numerous efforts have been made to rationalize a huge assembly of experimental data on ion hydration accumulated over many years.[1−6] They resulted in several intuitive models of ionic hydration; especially that of Frank and Wen[7] has been highly regarded by solution chemists. This model still provides conceptual guides in interpreting experimental observations the more so as the knowledge of ionic hydration is unsatisfactory on the molecular level. Even highly appreciated direct experimental techniques, like NMR spectroscopy and diffraction methods, provide scarce and ambiguous data because of interpretative problems (for reviews, see refs 8−11). Especially, the influence of ions on water structure is poorly understood.

A well suited method for investigation of solute hydration is vibrational spectroscopy.[12] Spectra of isotopically diluted HDO in H_2O enable us to avoid the number of experimental and interpretative problems connected with H_2O spectra.[13] The OH/OD water vibrations appear to be the most sensitive and ideally suited probe of ionic hydration. To get information about the interactions inside the hydration sphere, the contribution of bulk water should be eliminated from the solution spectrum to obtain the solute-affected water spectrum. The corresponding method of spectral data analysis originates from Kristiansson, Eriksson, and Lindgren works.[14,15] The quantitative versions of this method can be found in refs 16 and 17.

The band position and the band shape of HDO affected by a solute give a measure of water H-bond energy distribution within the solute surrounding. This is based on the experimental Badger-Bauer rule,[18] valid in most cases,[19] which states that the band position of water stretching vibrations changes proportionally to the energy of hydrogen bonds. In the majority of instances, spectral hydration effects for the electrolyte solution can be resolved into anionic and cationic contributions, without additional assumptions. The analysis can be performed for spectra of solutions for the which water/electrolyte molar ratio exceeds 200; it is much less than usually used in diffraction methods.

Until now a relatively large number of ionic hydration spectral data has been obtained using the discussed method of analysis. Most of them arise from Prof. Lindgren's research group of the Institute of Chemistry in Uppsala University. A substantial part of the data has been obtained in our laboratory.

The determined spectral hydration characteristics deals with different kinds of ions: mono-, di-, and trivalent, including hydrophobic and amphiphilic ones. Data for the last group of ions are limited only to the trifluoroacetate (CF_3COO^-)[20] and triflate ($CF_3SO_3^-$)[21,22] anions. The authors of the cited works have stated that water molecules in the vicinity of the CF_3 groups are spectroscopically undistinguishable from bulk water. This conclusion does not correspond with our recent results of spectral hydration studies performed for hydrophobic ions[23,24] and requires an additional explanation. As hydration of amphiphilic molecules is of great importance for biochemistry, colloidal chemistry and surface science, we have now extended the results to give a new insight into this group of ions. It was also tempting to make a comparison with all available spectral data on ionic hydration to draw some general conclusions in this important area. Some corresponding preliminary observations we have discussed in ref 25.

In this paper we have presented the data in such a way as to show the influence of ions of different character on water structure in a uniform fashion. The determined energetic state of water molecules surrounding individual ions is hardly obtainable from any other experimental method, without additional assumptions. The key for the data interpretation seems to be the cooperativity of water hydrogen bonds, already well recognized.[26−28]

The arrangement of the data presented reveals well-marked difference in influencing the surrounding water H-bonds by cations and anions. Among others, the detected difference can explain the more negative enthalpy of hydration of anions with respect to cations of comparable size, observed a long time ago.

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The band model of cation hydration, which results immediately from the experimental spectroscopic data, can verify and quantitatively specify the model of hydration shells arising from Frank and Wen.

2. Experimental Section

2.1. Chemicals and Solutions. D_2O (99.84% deuterium) was produced by Institute of Nuclear Investigation. H_2O used for measurements was twice distilled. Lithium trifluoroacetate, CF_3COOLi (Aldrich, more than 98% pure), and sodium methylsulfonate, CH_3SO_3Na (Aldrich, more than 98% pure), were used without further purification. Sodium methyl sulfate, CH_3SO_4Na (Merck, for synthesis), was recrystallized twice from water. Sodium and potassium trifluoroacetates, CF_3COONa and CF_3COOK, were obtained and purified as described in ref 29. Sodium ethyl sulfate, $C_2H_5SO_4Na$, potassium ethyl sulfate, $C_2H_5SO_4K$, magnesium ethyl sulfate, $(C_2H_5SO_4)_2Mg$, and sodium ethylsulfonate, $C_2H_5SO_3Na$, were obtained by the method of Evans and Albertson[30] described in ref 31. Concentrations of sodium and potassium salt stock solutions were determined gravimetrically as the respective sulfates.[29,31] The concentration of $(C_2H_5SO_4)_2Mg$ stock solution was determined by standard EDTA titration.

Stock solutions with H_2O were prepared for each salt. Sample solutions were made by adding 4% (by weight) of D_2O relative to H_2O ($H_2O + D_2O = 2HDO$, $K \approx 4$) and the reference solutions (without D_2O) by adding the same molar amounts of H_2O. All solutions were prepared by weight and their densities were measured using a bicapillary pycnometer at 25.0 °C.

2.2. IR Measurements and Analysis. FTIR spectra have been measured, handled, and analyzed as described in the ref 24. Analysis has been performed for solution molalities as follows: $(C_2H_5SO_4)_2Mg$ 0, 0.211, 0.417, and 0.570; CF_3COOLi 0, 0.235, 0.469, 0.604, 0.730, 1.005, 1.303, 1.818, 2.919, 3.764, 4.794, 5.794, and 6.726; CF_3SO_3Na 0, 0.386, 0.772, 1.160, and 1.553; CF_3 COONa 0, 0.452, 0.687, 1.155, 1.532, 2.011, 2.975, 4.035, 4.781, 5.646, 6.850, 7.883, 8.771, 9.687, 10.600, and 13.624; CF_3 COOK 0, 0.405, 0.799, 1.216, and 1.539; $C_2H_5SO_4K$ 0, 0.429, 0.840, and 1.267; $C_2H_5SO_4Na$ 0, 0.427, 0.844 and 1.267; CH_3SO_4Na 0, 0.427, 0.834, and 1.271; $C_2H_5SO_3Na$ 0, 0.444, 0.612, and 0.866; CH_3SO_3Na 0, 0.441, 0.607, and 0.860. For $(C_2H_5SO_4)_2Mg$ solutions the approximation of ϵ values vs m has been performed using quadratic regression, for the others using linear regression, in the range of $m < 2$.

3. Results

Figure 1 shows HDO spectra affected by salts with amphiphilic anion for which separation of anion-affected and cation-affected bands was possible. In the case of $Mg(C_2H_5SO_4)_2$ solutions the spectrum shown in Figure 1 corresponds to extrapolated molality, $m \rightarrow 0$. The component band of Mg^{2+}-affected HDO has somewhat higher-frequency position ($\nu_o = 2442 \pm 3$ cm^{-1}) than normally observed (Table 1). For concentrated solution ($m = 0.570$) this component band shifts ca. 12 cm^{-1} more toward higher wavenumbers and the component of anion-affected water shifts ca. 5 cm^{-1} in opposite direction, while the number of affected water molecules (N) decreases by about 0.2. Such spectral behavior was frequently observed[16,32,33] as a result of overlapping of the ion hydration spheres with increasing salt concentration. In the case of $LiCF_3COO$ solutions the component band of Li^+-affected HDO (Figure 1b) reveals much lower frequency than normally observed (Table 1).

Spectra in Figure 1b,c generally do not show concentration dependence at the molality range $m < 1.8$, so $\epsilon(\nu_i)$ values have been approximated by the linear regression with m. However, for more concentrated solutions of Li^+, Na^+, and K^+ trifluoroacetates a deviation from the linear correlation has been observed. This seems to correspond to another pattern of the solute–solute organization, resembling micelle type association (see following text). Even for $m < 1.8$ the linear regression of $\epsilon(\nu_i)$ with m is not justified for the region of extraordinarily high-frequency shoulder at ca. 2690 cm^{-1}. This shoulder generally shows Lorentzian shape; only for very diluted solutions has the increased Gaussian character been observed. With increasing molality, the band shifts to higher-wavenumbers and its half-width decreases. Its relative intensity (A) generally increases and depends clearly on the cation: $A(Li^+) \gg A(Na^+) > A(K^+)$.

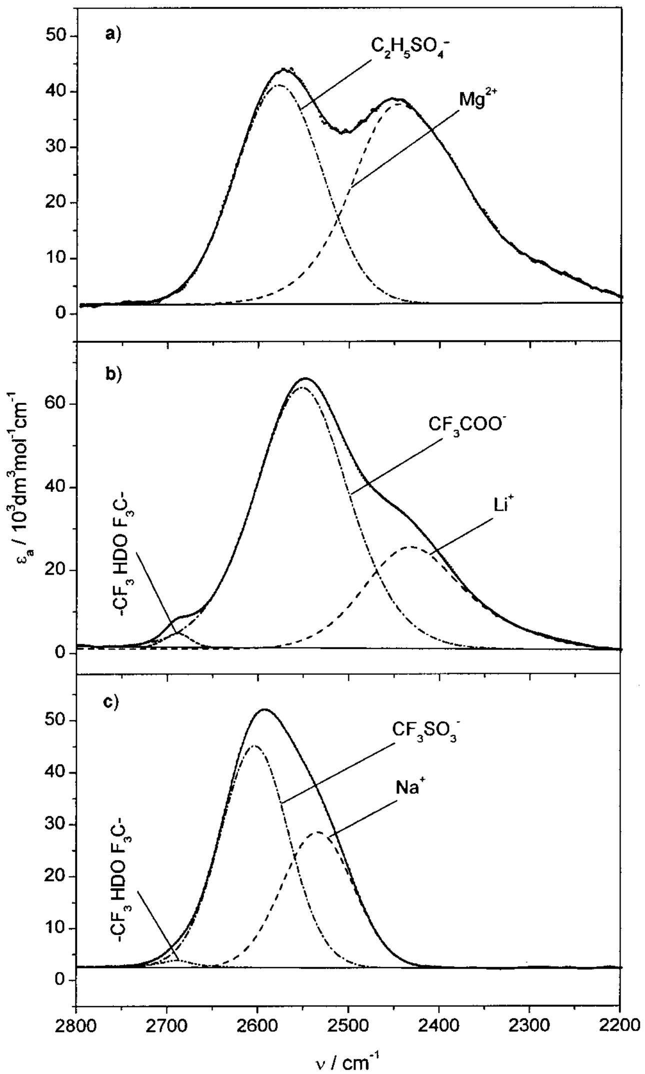

Figure 1. HDO spectra affected by (a) $(C_2H_5SO_4)_2Mg$, $N = 11.4$, (b) CF_3COOLi, $N = 2.0$, and (c) CF_3SO_3Na, $N = 5.6$, at 25.0 °C. The cation-affected (dash line) and the anion-affected (dash–dot line) bands are indicated: solid points, experimental data; permanent line, contour approximated by the sum of component bands. The high frequency shoulder in (b) and (c) arises from HDO molecules imprisoned between CF_3 groups of the anion.

Corresponding band has been observed by Dryjański and Kęcki[34] in saturated solutions and more recently by Bergström and Lindgren[20] in very concentrated solutions of $NaCF_3COO$. After detailed discussion, the latter authors stated that the band arised from water molecules partially screened from interacting with other species by CF_3 ends of aggregated CF_3COO^- anions. We have previously observed[20] the corresponding band for low

TABLE 1: OD Band Position at Maximum of HDO Affected by Anions[a,b]

anion	ν°_{OD} / cm^{-1}	ref[h]
$\mathrm{Ph_4B^-}$	2620 ± 4	23
$\mathrm{PF_6^-}$	2664 ± 4	17
$\mathrm{BF_4^-}$	2647 ± 4	17
$\mathrm{ClO_4^-}$	2630 ± 8	14−17, 22, 23, 32, 33, 40, 48, 53, 60−62
$\mathrm{NO_3^-}$	2595 ± 8	40
$\mathrm{I^-}$	2570 ± 8	40
$\mathrm{Br^-}$	2550 ± 8	24,40,48
$\mathrm{Cl^-}$	2530 ± 8	14, 24, 40, 48
$\mathrm{F^-}$	2450 ± 22	24, 40, 63
$\mathrm{SO_4^{2-}}$	2477 ± 18	40
$\mathrm{CF_3COO^-}$ $(\mathrm{Li^+})^{c,g}$	2552 ± 10, 2690 ± 4^e; $N = 2.5 \pm 0.5$	this work
$\mathrm{CF_3COO^-}$ $\mathrm{Na^+}$ ^{d}	2538 ± 10, 2695 ± 2^e; $N = 5.0 \pm 0.5$	this work, 20^f
$\mathrm{CF_3COO^-}$ $\mathrm{K^+}$ ^{d}	2538 ± 10, 2690 ± 4^e; $N = 5.2 \pm 0.5$	this work
$\mathrm{CF_3SO_3^-}$ $(\mathrm{Ni^{2+}})^c$	2605 ± 1; $N = 7.2 \pm 0.5$	21, 22
$\mathrm{CF_3SO_3^-}$ $(\mathrm{Na^+})^c$	2604 ± 4, 2690 ± 4^e; $N = 5.6 \pm 0.5$	this work
$\mathrm{C_2H_5SO_4^-}$ $(\mathrm{Mg^{2+}})^c$	2582 ± 10; $N = 11.4 \pm 0.5$	this work
$\mathrm{C_2H_5SO_4^-}$ $\mathrm{Na^+}$ ^{d}	2571 ± 8; $N = 4.9 \pm 0.5$	this work
$\mathrm{C_2H_5SO_4^-}$ $\mathrm{K^+}$ ^{d}	2568 ± 8; $N = 5.0 \pm 0.5$	this work
$\mathrm{CH_3SO_4^-}$ $\mathrm{Na^+}$ ^{d}	2572 ± 8; $N = 5.3 \pm 0.5$	this work
$\mathrm{C_2H_5SO_3^-}$ $\mathrm{Na^+}$ ^{d}	2555 ± 8; $N = 4.3 \pm 0.5$	this work
$\mathrm{CH_3SO_3^-}$ $\mathrm{Na^+}$ ^{d}	2559 ± 8; $N = 5.2 \pm 0.5$	this work

[a] Average frequencies calculated on the basis of independent results reported; the scatter of values, estimated or including the extreme values published. [b] In the case of amphiphilic anions, the kind of the cation is also shown as well as the affected number, *N*. [c] The anion-affected band which has been separated from the cation-affected band. [d] The anion-affected and the cation-affected bands, which could not be separated. [e] The OD band which arises from anion aggregates. [f] The authors of this work have used $N = 8.75$, having ν°_{OD} for $\mathrm{CF_3COO^-}$ $\mathrm{Na^+}$ equal to 2529 ± 10 cm^{-1}. [g] ν°_{OD} $(\mathrm{Li^+})$ in that system has a much lower value (2438 ± 10 cm^{-1}) than previously reported (2530 ± 14 cm^{-1})[14,48] (Table 2). [h] Data from Lindgren's laboratory were obtained at 20.0 °C; data from our laboratory were obtained at 25.0 °C.

TABLE 2: OD Band Position at Maximum of HDO Affected by Cations in the First Hydration Sphere (A) and in the Second Hydration Sphere (B)[a]

cation	ν°_{OD} / cm^{-1}	ref[g]
$\mathrm{Bu_4N^+}$ (A)	2523 ± 8	24
$\mathrm{Et_4N^+}$ (A)	2532 ± 12	14, 48
$\mathrm{Ph_4P^+}$ (A)	2534 ± 10, 2680 ± 6^f	23
$\mathrm{Li^+}$ (A/B)^b	2530 ± 14	45
$\mathrm{Li^+}$ (A)	2438 ± 12	this work
$\mathrm{Na^+}$ (A)	2534 ± 8	14, 23, 45, 48, 63, this work
$\mathrm{K^+}$ (A)	2530 ± 14	45
$\mathrm{Mg^{2+}}$ (A)	2428 ± 12	14, 22, 32, 33, 45, 48
$\mathrm{Ca^{2+}}$ (A/B)^b	2540 ± 20	16, 45
$\mathrm{Sr^{2+}}$ (A/B)^b	2529 ± 10	54
$\mathrm{Ba^{2+}}$ (A/B)^b	2537 ±14	14, 48
$\mathrm{Mn^{2+}}$ (A)	2420 ± 12	32, 45, 48, 53, 60
$\mathrm{Fe^{2+}}$ (A)	2419 ± 8	15, 45, 48, 53
$\mathrm{Co^{2+}}$ (A)	2428 ± 8	15
$\mathrm{Ni^{2+}}$ (A)	2418 ± 8	14, 17, 22, 33, 48, 62
$\mathrm{Cu^{2+}}$ (A)	2400 ± 8 (e),^{d} 2530 ± 8 (a)^e	62
$\mathrm{Zn^{2+}}$ (A)	2418 ± 18	14, 32, 45, 48, 61
$\mathrm{Cd^{2+}}$ (A)	2423 ± 8	61
$\mathrm{Hg^{2+}}$ (A)	2416 ± 8	61
$\mathrm{La^{3+}}$ (A)	2421 ± 8	45, 53
$\mathrm{Nd^{3+}}$ (A)	2421 ± 8	53
$\mathrm{Dy^{3+}}$ (A)	2414 ± 8	53
$\mathrm{Yb^{3+}}$ (A)	2414 ± 8	53
$\mathrm{Al^{3+}}$ (A)	2200 ± 20	64, 65
$\mathrm{Cr^{3+}}$ (A)	2200 ± 20	64, 65
$\mathrm{Rh^{3+}}$ (A)	2200 ± 20	64
$\mathrm{Na^+}$ (A/B)^b	2596 ± 10^c	40
$\mathrm{Ni^{2+}}$ (B)	2530 ± 10^c	40
$\mathrm{Al^{3+}}$ (B)	2420 ± 10	64, 65
$\mathrm{Cr^{3+}}$ (B)	2420 ± 10	64, 65
$\mathrm{Rh^{3+}}$ (B)	2420 ± 10	64

[a] Average frequencies calculated on the basis of independent results reported; the scatter of values, estimated or including the extreme values published. [b] The first and the second hydration sphere? (discussion in text). [c] The band assignment is different from that proposed by authors.[40] [d] Water molecules coordinated in equatorial positions. [e] Water molecules coordinated in axial positions. [f] The band of low intensity which has been ascribed to HDO imprisoned between phenyl groups of $\mathrm{Ph_4P^+}$ aggregates. [g] Data from Lindgren's laboratory were obtained at 20.0 °C; data from our laboratory were obtained at 25.0 °C.

concentrated aqueous solutions of $\mathrm{Ph_4PCl}$ (Table 2) and now for much more diluted solutions of trifluoroacetates of $\mathrm{Li^+}$, $\mathrm{Na^+}$, $\mathrm{K^+}$ and also for sodium trifluoromethanesulfonate solutions, $\mathrm{NaCF_3SO_3}$ (Figure 1c). It should be noted that Bergström and Lindgren[21,22] did not observe the high-frequency component in HDO spectra neither in $\mathrm{Ni(CF_3SO_3)_2}$ and $\mathrm{Ba(CF_3SO_3)_2}$ solutions nor in the solid hydrate $\mathrm{La(CF_3SO_3)_3 \cdot 9H_2O}$ in the OH stretching region.

Spectra of ethyl and methyl acetate solutions, shown in Figure 2, do not evidence the high-wavenumber component band at all. Spectra collected in this figure correspond to HDO affected by those electrolytes for which separation of anion-affected and cation-affected component bands was not possible. As can be shown, all the bands are shifted to higher frequency relative to bulk water. The respective band positions are listed in Table 1. There is no marked difference between salts with $\mathrm{Na^+}$ and $\mathrm{K^+}$ cations. The band position for methyl- and ethyl-substituted anions is the same within experimental error. However, the band intensity is higher for ethyl-substituted ones, which corresponds to somewhat smaller *N* values.

4. Discussion

4.1. Anion Hydration. Table 1 lists OD band positions in maximum (ν°_{OD}) of HDO affected by anions of different kinds. Figure 3 correlates the values of ν°_{OD} with polarizing power (q/r) of anions. As can be seen, two groups of anions correlate distinctly: $\mathrm{I^-}$, $\mathrm{Br^-}$, $\mathrm{Cl^-}$, and $\mathrm{F^-}$ halogen anions (correlation line 1) and of $\mathrm{PF_6^-}$, $\mathrm{BF_4^-}$, $\mathrm{ClO_4^-}$, $\mathrm{NO_3^-}$, and $\mathrm{SO_4^{2-}}$ anions (correlation line 2). The amphiphilic anions $\mathrm{CF_3SO_3^-}$, $\mathrm{CF_3COO^-}$, and $\mathrm{C_2H_5SO_4^-}$ and the hydrophobic anion $\mathrm{Ph_4B^-}$ form a separate set. The simplest explanation of the shift of correlation line (2) toward higher frequencies, with respect to correlation line (1), is the higher number of lone electron pairs of anions in group (2). This secures lower partial negative charge on centers of interaction with water.

In the set of anions shown in Figure 3 only $\mathrm{F^-}$ and $\mathrm{SO_4^{2-}}$ interact with water stronger than do water with water molecules (basing on the Badger−Bauer rule). Thus the remaining anions can be considered as water "structure breakers", in the sense of the H-bonds energy between water−anion and between the first hydration sphere and the bulk phase. This term will further be used as referring to energy effects of water hydrogen bonds. The abscissas determined by the intersection of the correlation lines (1) and (2) with ν°_{OD} level of the bulk water (2509 cm^{-1}) in Figure 3 correspond to the anion radii below which water−anion interactions become stronger than water−water interactions. Such "critical radius" for the halogen ions is about 1.6 Å, which is in good agreement with calculations of Bernard and Fowler (∼1.6 Å),[35] NMR investigations by Hindman (∼1.7

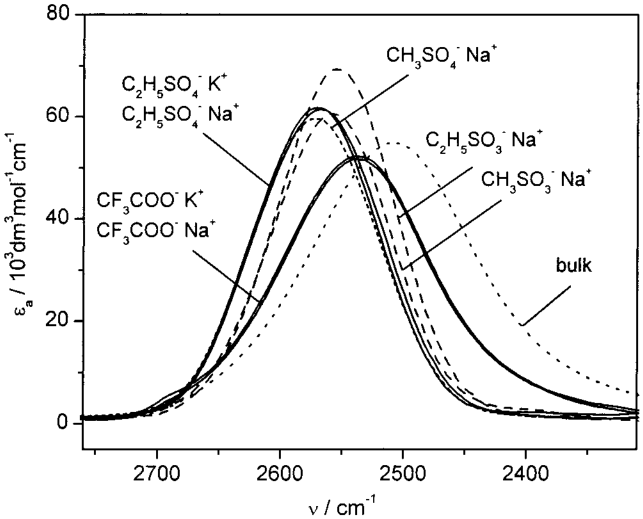

Figure 2. HDO spectra affected by CF_3COOK ($N = 5.2$; solid line), CF_3COONa ($N = 5.0$; solid line), $C_2H_5SO_4K$ ($N = 5.0$; solid line), $C_2H_5SO_4Na$ ($N = 4.9$; solid line), CH_3SO_4Na ($N = 5.3$; short dotted line), $C_2H_5SO_3Na$ ($N = 4.3$; dashed line), and CH_3SO_3Na ($N = 5.2$; dashed line) as indicated, with the bulk HDO (dotted line) for comparison purposes; 25.0 °C.

Å)[36] and the thermodynamic considerations presented in the work of Libuś and Chachulska (~1.6 Å).[37]

Extremely weak interaction with water is exhibited by the PF_6^- anion. The $\nu°_{OD}$ value in this case (2664 cm^{-1}) is clearly higher than $\nu°_{OD}$ for HDO molecules which do not form H-bonds with H_2O in water environment (2644 cm^{-1}).[38] Such a high value of $\nu°_{OD}$ can be explained by weaker van der Waals forces between water and the fluorine atoms of the PF_6^- ion than those between water molecules. This explanation also applies to the BF_4^- anion ($\nu°_{OD} = 2647$ cm^{-1}). Nonetheless, weak anion−water hydrogen bonds exist in both the above cases because monomeric HDO molecules closed between $-CF_3$ groups exhibit a band at $\nu°_{OD} \cong 2692$ cm^{-1} (Table 1). The NO_3^- anion is another interesting instance in that group of anions. Data from diffraction studies of water solutions prove that a flat anion interacts with water more strongly in the axial positions (through the nitrogen atom) than in the equatorial plane.[8] Points corresponding to each radius of interaction have been shown in Figure 3. It follows from the correlation that water affected by the anion corresponds mainly to equatorial interactions, whereas water in the axial positions resembles bulk water.[39] This can visualize the physical significance of the affected water spectrum, as well as the difference between the number of affected water molecules (N) and the coordination number (in a sense of the number of nearest neighbors).

The behavior of the amphiphilic anions is the most difficult to rationalize. Only in a few systems studied in this work can the band of anion-affected water be separated from the cation-affected one (Table 1). As can be seen in Figure 3, the $\nu°_{OD}$ values for amphiphilic anions lay below correlation line (2), which seems most suitable for comparison with ions of this type. If we considered the radii of the hydrophilic part of amphiphilic anions in calculation of q/r values only, the points would be shifted toward correlation line (2). Because this is not the case we may anticipate that the interaction with water does not depend on the hydrophilic group only. This suggests that nonpolar groups strengthen the water structure weakened in the surrounding of the polar groups. On the basis of the distance between open points (in the vertical direction), representing q/r values of the hydrophilic part, and the correlation curve (2), it can be estimated that the CF_3 group and the C_2H_5 group shift the band by about 50 and 75 cm^{-1}, respectively, toward lower frequencies. According to the Badger−Bauer rule, these shifts correspond to an increase in the energy of the hydrogen bonds by about 10 and 15 kJ, respectively, per mole of the affected water (for the method of calculation see ref 41).

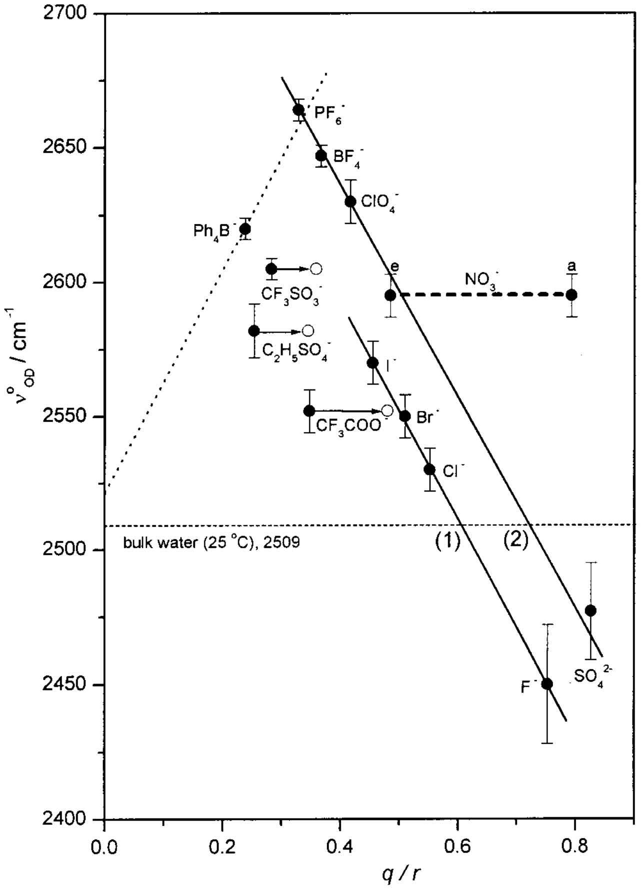

Figure 3. Relationship between $\nu°_{OD}$ for HDO affected by anions and the polarizing power of anions (q/r): the $\nu°_{OD}$ values from Table 1 (●). q = charge number of anions; r/Å = anion radius, based on refs 1, 3, 4, and 8 and data compilation for amphiphilic anions. For NO_3^-, the ionic radii for equatorial (e) and axial (a) positions have been distinguished.[8] (○) Hypothetical positions for $C_2H_5SO_4^-$, $CF_3SO_3^-$, and CF_3COO^- without radius contribution of nonpolar groups (as an approximation, r values for HSO_4^-, HSO_3^-, and $HCOO^-$ were used);[66] the dashed line is the expected approximate relationship for hydrophobic anions (see text).

The main difficulty in separation of the cation- and anion-affected water bands in the case of sodium and potassium salts of amphiphilic anions is their very close position. We also suspect that the presence of nonpolar groups result in increasing ion association, which in turn further complicates separation of the component bands. The conclusion is derived on several premises, which follow from the gathered data: (1) the N values for these salts are rather low (Table 1), which suggests that the same water molecules interact with the cation and the anion simultaneously; (2) the salts having a CF_3 group exhibit a high-energy band, $\nu°_{OD} = 2690-2695$ cm^{-1} (Table 1), which corresponds to HDO molecules trapped between CF_3 groups of anions forming micelle-type aggregates. Association of a counterion is typical of such formations and it clearly depends on the kind of cation.

The only example of a hydrophobic anion in Figure 3 is Ph_4B^-. As can be seen, it strongly weakens water hydrogen bonds ($\nu°_{OD} = 2620$ cm^{-1}). The effect is, however, not as strong as can be expected from the anion radius. This seems to indicate

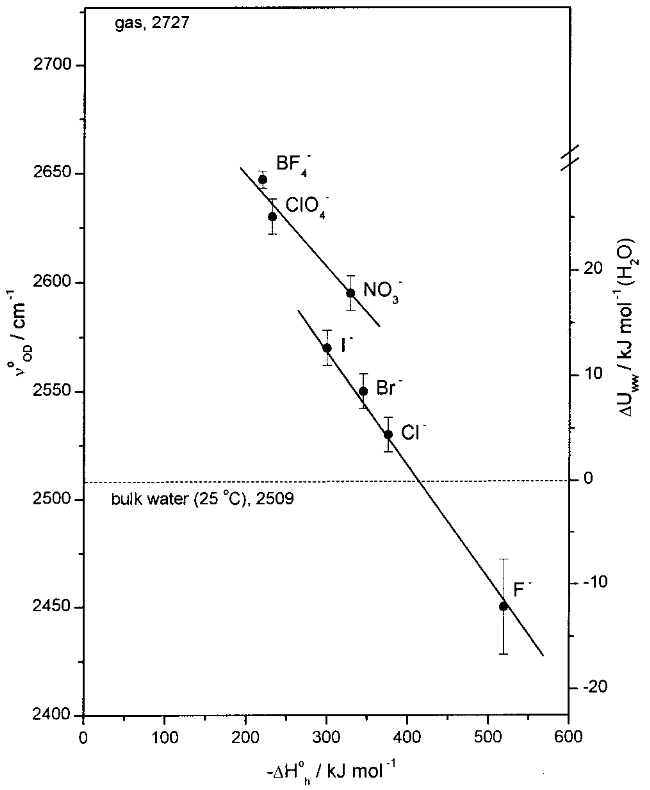

Figure 4. Relationship between $\nu°_{OD}$ for HDO affected by anions and the standard (absolute: $\Delta H°_h(H^+) = -1091$ kJ mol^{-1}) hydration enthalpies of anions, $\Delta H°_h$. $\nu°_{OD}$ values from Table 1; $\Delta H°_h$ values from ref 2. The correlation line is discussed in text. Right axis: scale of the enthalpy change of affected water H-bonds at 25 °C, ΔU_{ww}/kJ mol^{-1}, which corresponds to the scale of $\nu°_{OD}$ (according to the Badger−Bauer rule).

that water molecules surrounding the anion form, to some extent, hydrogen bonds between each other. This may be possible when water molecules tend to be positioned tangentially to the surface of the ion, resulting in sufficiently low orientation energy. The minimum radius for symmetric monovalent anions, above which they can exhibit hydrophobic properties, is estimated to be about 3 Å (Figure 3). The respective band positions for hydrophobic cations, Ph_4P^+ ($\nu°_{OD} = 2530$ cm^{-1})[23] and Bu_4N^+ ($\nu°_{OD} = 2523$ cm^{-1})[24] are clearly at much lower frequencies as compared with the Ph_4B^- anion ($\nu°_{OD} = 2620$ cm^{-1}). Thus, cations have a weaker orientating power than anions. The dashed line in Figure 3 indicates the proposed direction of the band position change with respect to the polarizing power of hydrophobic anions.

Experimentally determined enthalpies of ion hydration include the contribution of water−water interaction energy change due to introduction of the ion into the water medium. The energy change should correlate with ion hydration enthalpies. The relationship between the OD band positions of HDO affected by monovalent anions and their hydration enthalpies is presented in Figure 4. It shows that with an increase in the absolute value of hydration enthalpy the water structure breaking effect becomes weaker. Above a threshold value $|\Delta H°_h|$ ca. 420 kJ mol^{-1} the halogen anions reveal a structure making effect.

The energy effect of water interactions change induced by introduction of anion X is given by $N(X)\cdot\Delta U_{ww}$; ΔU_{ww} is the molar H-bonds energy change between ion-affected and pure water. ΔU_{ww} is a measure of water intermolecular interactions because the contribution of van der Waals interactions (14 kJ mol^{-1})[42] may be approximately considered constant and independent of hydrogen bonds energy. The N values for electrolytes are obtained from water "affected spectrum". The division of this value between the cation and the anion can only be made on arbitrary grounds.[43]

The points for halogen anions in Figure 4 form a straight line. This seems to indicate that the product $N(X)\cdot\Delta U_{ww}$ changes linearly with $\Delta H°_h$ in the group. It may represent either an equal number of affected water molecules (N) for the considered anions or a linear change of N with $\Delta H°_h$. The latter case may find justification in the N values determined for Bu_4NX salts in aqueous solutions, where X = Br, Cl, and F.[24] They increase in a series Br < Cl < F and the difference between $N(F^-)$ and $N(Br^-)$ is about 2. This behavior may signify a constant number of affected water molecules in the first anion sphere and a small number in farther spheres, this number increasing proportionally to the polarizing power of the anion and thus with the absolute value of hydration enthalpy. Diffraction studies of solutions and computer simulations predict various values of the hydration number for the halogen anions, ranging from 4 to 9.[8]

We expect that the products $N(X)\cdot\Delta U_{ww}$ plotted vs $\Delta H°_h$ form a correlation curve common to all anions, which is approximately linear for $\Delta U_{ww} < 27.5$ kJ mol^{-1}. Above this value there are no longer water−water hydrogen bonds. If points representing BF_4^-, ClO_4^-, and NO_3^- were to lay on the common correlation curve with halogen anions, then, as follows from Figure 4, lower N values should correspond to the first mentioned group.[44]

4.2. Cation Hydration. Water molecules coordinated by cations are polarized and form hydrogen bonds with water molecules of the second hydration sphere. The energy of these H-bonds depends significantly upon the polarizing power of the cation. Small cations, with high q/r ratios cause strengthening of hydrogen bonds, and they shift the OD band toward lower frequencies. Large cations shift the stretching vibrational band of the coordinated water toward higher frequencies with respect to bulk water. Table 2 lists the OD band positions ($\nu°_{OD}$) of HDO affected by cations obtained up to date, most of the data being determined by Prof. Lindgren's research group. Correlation between the values of $\nu°_{OD}$ and the polarizing power of cations has been presented in Figure 5.

Unlike anions, cations do not change the position of affected water band in a continuous way. The lack of continuity in $\nu°_{OD}$ changes for cations was noticed for the first time by Lindgren with coauthors,[45] basing on the relatively limited set of data available at the time. They indicated two levels: ~2525 and ~2420 cm^{-1}.

As can be seen from Figure 5, the $\nu°_{OD}$ values for cations arrange themselves in several discrete levels and the corresponding energies of water−water intermolecular interactions appear to be quantized. Regularity in the occurrence of these levels may be observed: the ratio of distances between them amounts to 2.0 ± 0.25. We have marked the level $\nu°_{OD} = 2644$ cm^{-1} corresponding to non-hydrogen bonded water molecules in an aqueous environment.[38] The level at $\nu°_{OD} = 2627$ cm^{-1} was additionally postulated on the basis of a detected pattern of regularity in the occurrence of the above-mentioned levels.

The diagram in Figure 5 shows that in aqueous solution a relatively small number of energetic and structural states are preferred. A similar conclusion, as to the angles of interacting molecules, is suggested by the results for other systems with hydrogen bonds and water carried out in matrixes (ref 46 and literature cited therein).

The individual energetic and structural states of HDO molecules diluted in H_2O might be characterized as follows:

The level at $\nu°_{OD} = 2200 \pm 20$ cm^{-1} corresponds to water molecules experiencing a severe electrostriction effect and

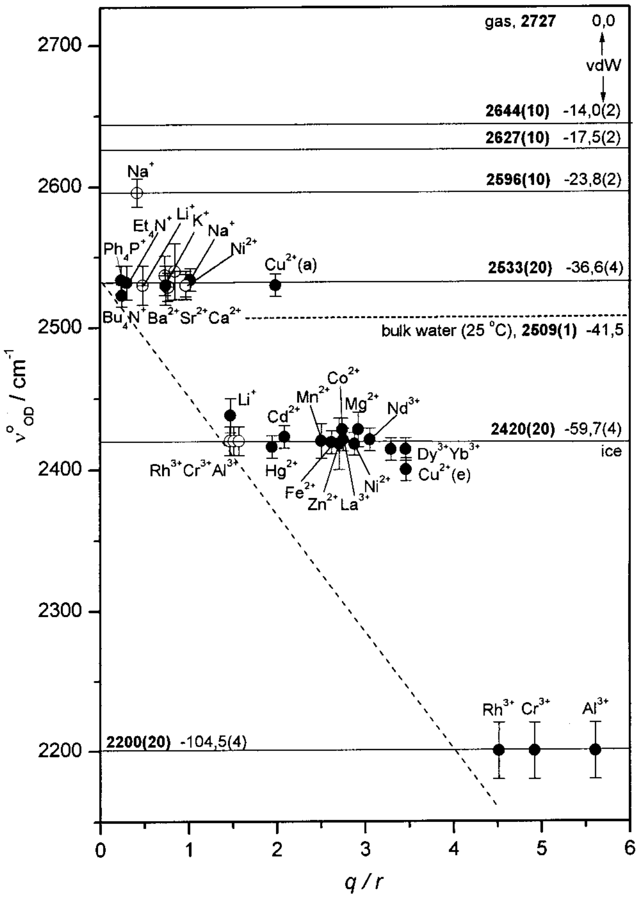

Figure 5. Relationship between $\nu°_{OD}$ for HDO affected by cations and the polarizing power of cations (q/r). $\nu°_{OD}$ values from Table 2. Key: (●) first hydration sphere; (○) second hydration sphere; (⊕) first or the second hydration sphere? (see discussion in text); q is the charge number of cations, r/Å is the the cation Pauling radius.[1,8] In the case of Cu^{2+}, different r values have been used for axial (a) and equatorial (e) positions of elongated tetragonal bipyramid;[8] in the case of Ph$_4$P$^+$, Bu$_4$N$^+$, and Et$_4$N$^+$, the van der Waals radius has been used.[1] For the second hydration sphere of Ni^{2+}, Rh^{3+}, Cr^{3+}, Al^{3+}, and Na$^+$ as well as Li$^+$, Ca^{2+}, Sr^{2+}, and Ba^{2+} the effective radius has been calculated as (r + 1.38 Å), where 1.38 Å is the crystalline radius of water:[2] (dashed line) expected approximate correlation line (discussed in text). Description of the levels: $\nu°_{OD}$ (bold); molar energy of water intermolecular interactions at 25 °C, $-\Delta U_w$/kJ mol^{-1} (normal); vdW is the van der Waals interaction; the scatter of the values (corresponding to the scatter of $\nu°_{OD}$ values) is shown in parentheses.

forming very strong hydrogen bonds between the first and the second hydration sphere. Cations with a high polarizing power, $q/r > 4$, belong to this group (Rh^{3+}, Cr^{3+}, and Al^{3+}). This level may be characterized by the value of intermolecular interaction energy of water, ΔU_w, estimated using the Badger–Bauer rule;[41] $\Delta U_w = -104.5 \pm 4$ kJ·mol^{-1}. Intermolecular distance between water molecules, in terms of the interatomic O···O distance ($R_{O\cdots O}$), can be calculated on the basis of the correlating function of $R_{O\cdots O}$ vs $\Delta\nu°_{OD}$, stated in refs 47 and 48: $R_{O\cdots O} = 2.61 \pm 0.02$ Å.

The level at $\nu°_{OD} = 2420 \pm 20$ cm^{-1} corresponds to strong water hydrogen bonds, like those observed in ice:[49] $\Delta U_w = -59.7 \pm 4$ kJ·mol^{-1}, $R_{O\cdots O} = 2.76 \pm 0.02$ Å. It describes interactions of water molecules between the first and the second hydration sphere of divalent transition metal cations, zinc, magnesium, and trivalent lanthanide cations. Furthermore, this level also describes water molecules interacting between the second and the third hydration sphere of trivalent cations, for which the water interacting between the first and the second hydration sphere was already accounted for in level $\nu°_{OD} = 2200 \pm 20$ cm^{-1}.

The level at $\nu°_{OD} = 2533 \pm 20$ cm^{-1} describes water molecules forming slightly weaker hydrogen bonds than those observed in pure water at temperature 25 °C: $\Delta U_w = -36.6 \pm 4$ kJ·mol^{-1}, $R_{O\cdots O} = 2.88 \pm 0.03$ Å. This level characterizes the interactions of water molecules in the first hydration sphere with the second hydration sphere in the case of K$^+$ and Na$^+$. The point corresponding to water molecules coordinated by the Cu^{2+} cation in the axial positions of elongated tetragonal bipyramid (the Jahn–Teller effect) belongs to this level as well. An additional point describes water interacting between the second and the third hydration sphere of the Ni^{2+} cation. We made this assignment[50] contrary to the suggestion of the authors, who obtained the data.[40] It can be estimated that the band intensity of water in the second hydration sphere of Ni^{2+} is less than 10% of the band corresponding to the first hydration sphere. It seems probable for us that other cations from the level $\nu°_{OD} = 2420 \pm 20$ cm^{-1} group exhibit the band of the second hydration sphere within the discussed level. To detect them, studies of electrolyte solutions with an anion, which interacts with water stronger than do water molecules with each other, have to be performed. Otherwise, the presumed weak band of the second hydration sphere of a cation superimposes on the anionic band. To date only three such studies have been conducted, which concerned NiSO$_4$,[40] NaF,[40] and Bu$_4$NF[24] solutions.

Special attention must be paid to Li$^+$, Ca^{2+}, Sr^{2+}, and Ba^{2+} cations, which are characterized by q/r coefficient ranging from 1.3 to 2 and have "transitional" properties. As noticed by Lindgren and coauthors,[45] the bands of water affected by Li$^+$ and Ca^{2+} ions are so broad that they contain the shape of Na$^+$-affected water band in their high-energetic part and a significant contribution of the shape of Mg^{2+}-affected water band in their low-energetic part. The high asymmetry of Ca^{2+} hydration band was also confirmed by our studies.[16] Consequently, it may be considered that the band of water affected by Li$^+$, Ca^{2+}, Sr^{2+}, and Ba^{2+}, observed within the discussed level, is actually a superposition of component bands having their maximum at the $\nu°_{OD}$ characteristic level $\nu°_{OD} = 2420 \pm 20$ cm^{-1} and $\nu°_{OD} = 2533 \pm 20$ cm^{-1}. The intensity of the component band corresponding to water in the second hydration sphere is clearly dominating. Because of the method of ion radius calculation, the water bands affected by Ca^{2+}, Sr^{2+}, and Ba^{2+} have been attributed to the second hydration sphere in Figure 5. The hydration band of CF$_3$COOLi electrolyte shown in Figure 1b reveals the first hydration sphere of Li$^+$ cation, which belongs to the characteristic level $\nu°_{OD} = 2420 \pm 20$ cm^{-1}. The band of the second hydration sphere of the cation, from level $\nu°_{OD} = 2533 \pm 20$ cm^{-1}, is overlapping with the CF$_3$COO$^-$ hydration band.

A separate group is formed by Et$_4$N$^+$, Bu$_4$N$^+$, and Ph$_4$P$^+$ hydrophobic cations. They have different shape of the water hydration band from that for other cations and do not evidence further hydration spheres. As we recently established for the case of Bu$_4$N$^+$,[24] these cations reveal the same average energy of surrounding water H-bonds as that for bulk water (measured by the position of the gravity center of the hydration band, ν^c_{OD}). Simultaneously, water in the hydration sphere forms more H-bonds, which are slightly weaker than in the bulk water. Such behavior results from lack of polarization of water molecules by hydrophobic cations.

The level at $\nu°_{OD} = 2596 \pm 10$ cm^{-1} corresponds to water forming weak hydrogen bonds: $\Delta U_w = -23.8 \pm 2$ kJ·mol^{-1},

$R_{O\cdots O} = 2.99 \pm 0.02$ Å. We introduced this level on the basis of the observation of the hydration spectrum of already mentioned NaF solution, contrary to the authors' [40] interpretation (as in the case of $NiSO_4$). The integrated intensity of the discussed band is higher than the intensity of corresponding Ni^{2+} band. In our opinion, the discussed level reveals the interactions of water in the second hydration sphere of Na^+ cation or (which seems more probable) describes these water molecules in the first hydration sphere which interact more weakly with the cation. It is a well-known fact that alkaline metal cations, with large ionic radii, do not form a well-defined first hydration sphere, which is evidenced by broad distribution of coordination energy and cation–water distance.[8,9,52] Possibly, the discussed level applies to K^+ cation even to a greater extent than to Na^+ but no spectral data confirming this supposition are available.

The level at $\nu°_{OD} = 2627 \pm 10$ cm^{-1} we introduced as a postulate. We expect that it corresponds to water molecules forming hydrogen bonds solely through free electron pairs: $\Delta U_w = -17.5 \pm 2$ kJ·mol^{-1}, $R_{O\cdots O} = 3.06 \pm 0.03$ Å.

The level at $\nu°_{OD} = 2644 \pm 10$ cm^{-1} corresponds to water molecules not forming hydrogen bonds in water environment: [38] $\Delta U_w = -14.0 \pm 2$ kJ·mol^{-1} (the energy of van der Waals interactions), $R_{O\cdots O} = 3.11 \pm 0.03$ Å.

On the basis of a large collection of experimental data belonging to the level at $\nu°_{OD} = 2420$ cm^{-1}, we may assert that its width (± 20 cm^{-1}) is not the result of experimental errors only. A marked regularity in the OD band position connected with the properties of cations may be observed within the width of the level, as long as the compared data are derived from one laboratory.[32,53] Thus, we consider that it is more appropriate to discuss the band position **zones** of $\nu°_{OD}$ values or the corresponding energy **zones** of ΔU_w or ΔU_{ww} values.

The division of stretching frequencies for HDO molecules around cations into two distinct groups at ca. 2420 cm^{-1} and ca. 2530 cm^{-1} has been discussed by Lindgren, Hermansson, and Wójcik,[54] who explained it by the presence or absence of a cation second hydration shell. They suggested that water molecules coordinated trigonally or tetrahedrally in the first hydration sphere give rise to the absorption band at ca. 2420 cm^{-1}. Water molecules trigonally bound to a cation do not reveal additional hydration spheres. Tetrahedrally coordinated molecules could form, through their lone electron pair, hydrogen bonds with molecules from the second sphere. With their OD groups pointed at the cation, they show the absorption band at ca. 2530 cm^{-1}.

We suppose that the problem of the cation hydration is of more general nature. The individual cations determine specific arrangement of surrounding water molecules depending on the cation's polarizing power. This arrangement, controlled by water H-bond cooperativity phenomenon, appears to be stable in a relatively broad range of cation electric density. Most probably, this is because of the strong dependence of hydrogen bond energy on the angle of water molecules orientation. As a consequence, the energetic state of water H-bonds arranges in zones. We would suggest considering the correlation in Figure 5 in terms of structural (geometrical) possibilities of transmission of the cation polarizing effect through water H-bonds between the cation hydration spheres.

The dashed line in Figure 5 suggests expected correlation of points in the case of optimal mutual orientation of water molecules in the first and the second hydration spheres. For points situated at higher q/r values with respect to the correlation line (ca. 1.35 and ca. 4.0), a disturbance in transmission of cation polarizing effect to the bulk of the solution is expected. We may expect further hydration spheres in such cases, for which corresponding OD bands would appear at higher levels. Practically, such bands are not frequently observed, because of their low intensity and/or overlapping with the anion-affected water band.

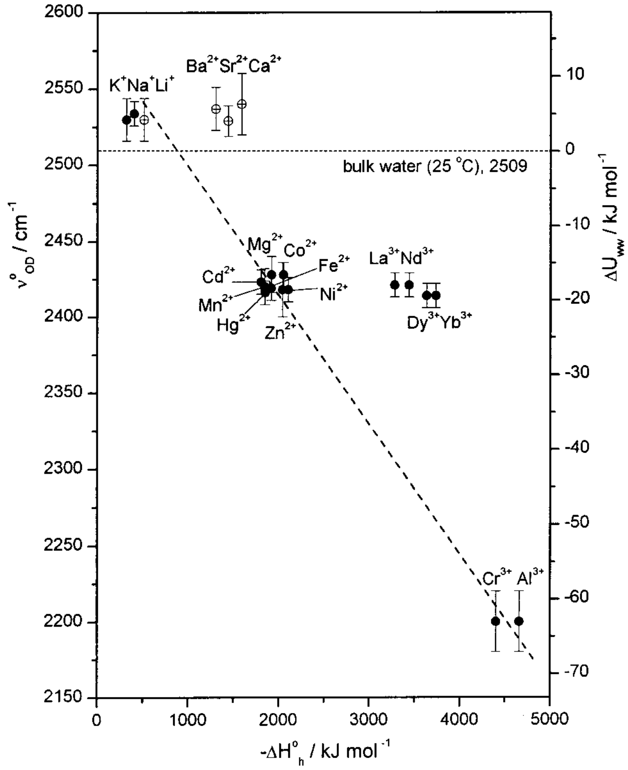

Figure 6. Relationship between $\nu°_{OD}$ for HDO affected by cations in the first hydration sphere (●) and in the first or the second hydration sphere (⊕, discussion in text) and standard (absolute: $\Delta H°_h(H^+) = -1091$ kJ mol^{-1}) hydration enthalpies of cations, $\Delta H°_h$: $\nu°_{OD}$ values from Table 2; $\Delta H°_h$ values from ref 2; the correlation line is discussed in the text. Right axis: the scale of the molar energy change of affected water H-bonds at 25 °C, ΔU_{ww}/kJ mol^{-1}, which corresponds to the $\nu°_{OD}$ scale (according to the Badger-Bauer rule).

Correlation between the positions of OD bands of HDO affected by some cations and experimentally determined enthalpies of hydration[2] has been shown in Figure 6. It is apparent that the points arrange in groups. On the basis of the discussion in the preceding section, it means a similar number of affected water molecules within the group. It must be noticed that points in Figure 6 should be a representation of particular cations; that is, they account for the presence of additional hydration spheres "discovered" and "undiscovered" so far. In such a case, the band position weighed by the integrated intensity of component bands corresponding to all individual hydration spheres would be much more appropriate then $\nu°_{OD}$. This could be simply done by calculating the gravity center of a complex hydration band of the cation, ν^c_{OD}. Unfortunately, there was no possibility to calculate them from the available data.

The correlation line in Figure 6 was plotted so as to connect points corresponding to the same number of affected water molecules in the first hydration sphere of cations. The number of affected water molecules, N, is usually equal to the coordination number in the case of cations of strong coordination power. The course of the correlation line is set by two groups of cations: (a) trivalent cations Cr^{3+} and Al^{3+} and (b) divalent cations of transition metals, zinc, and magnesium. Their unquestionable coordination number is 6.[8,9]

The correlation line runs in the vicinity of points representing alkaline metal cations. Diffraction methods in solutions and computer simulations[8,9] predict coordination number 6 for Na$^+$, 6−8 for K$^+$ and 6 or 4 for Li$^+$, depending on concentration and the properties of solutions. It can be deduced from the correlation that for Li$^+$ number 6 is more appropriate. In that case, however, it accounts also for water molecules in the second hydration sphere. It is not possible that the point corresponding to the band of the first coordination sphere of Li$^+$ (zone 2420 ± 20 cm^{-1}, Figures 1b and 5) represents this cation properly. The concomitant strong band of the second hydration sphere (from the zone 2533 ± 20 cm^{-1}) should be masked by the band corresponding to CF_3COO^--affected water in Figure 1b. According to the proposed correlation in Figure 6, all alkali metals can be considered as structure breakers.

The coordination number for divalent cations Ca^{2+}, Sr^{2+}, and Ba^{2+} is larger than 6.[8,9,55] It cannot be reconciled with the positions of points representing these cations in Figure 5 which correspond to the first hydration sphere. Including the contribution of the band for the first sphere at $\nu^\circ_{OD} = 2420 \pm 20$ cm^{-1} the expected value *of* ν^c_{OD} should be less than 2509 cm^{-1} (the ν°_{OD} value for bulk water). This leads to the conclusion that the discussed cations should be counted among weak "makers" of water structure.

Lanthanide cations form a separate group. From the correlation in Figure 6 it follows clearly that the number of affected water molecules in their first hydration is greater than 6. Spectral analysis performed by Bergström and Lindgren[53] led to the values of 7.8 for La^{3+}, 8.0 for Nd^{3+}, 8.7 for Dy^{3+}, and 8.8 for Yb^{3+}, with a standard deviation of 0.6.

4.3. Comparison of Anion and Cation Hydration. Ion Association. Concluding Remarks. We included a summary of observations for anions and for cations in Figure 7. It combines the data from Figures 3 and 5 concerning the OD band position of HDO affected by anions and cations with respect to the polarizing power of ions, characterized by *q/r* coefficient.

Two different approaches can be made in discussing spectral differences between anion and cation hydration: (1) a stronger polarization of O−H(D) bond of water due to the interaction with an anion (comparison of the slope for the two correlation lines) and (2) the continuity in polarization changes of this bond for anions and lack of such continuity for cations.

The first observation signifies a higher sensitivity of water molecules toward interactions with anions. The noticed differences in values of absolute free energies, enthalpies, and entropies of hydration of anions and cations have led to an apparently similar conclusion. They are generally more negative for anions than for cations of the same ionic radius. The origin of these differences has not been satisfactorily explained so far; attempts to interpret the results have been based on electrostatic models of water molecule interactions. An overview can be found in ref 5. The discussion clearly lacks an adequate account for the structural effects, related to the assemblage of water molecules, in the thermodynamic functions of hydration. For instance, the absolute standard enthalpy of hydration (ΔH°_h) of the F$^-$ anion is ca. 200 kJ·mol^{-1} more negative than that of K$^+$ cation, despite their similar ionic radius.[1] Estimations based on energetic data from Figures 4 and 6, assuming the *N* values for K$^+$ and F$^-$ ions as equal to 6−8 and 6−9, respectively, indicate that the enthalpy effect due to change of hydrogen bonds energy is more negative in the case of F$^-$ by 130−190 kJ·mol^{-1}. Since enthalpies of hydration are determined with ca. 10% accuracy, and the energy relations considered have an approximate character (the Badger−Bauer rule), it may be assumed that the estimated value principally explains the observed difference in ΔH°_h.

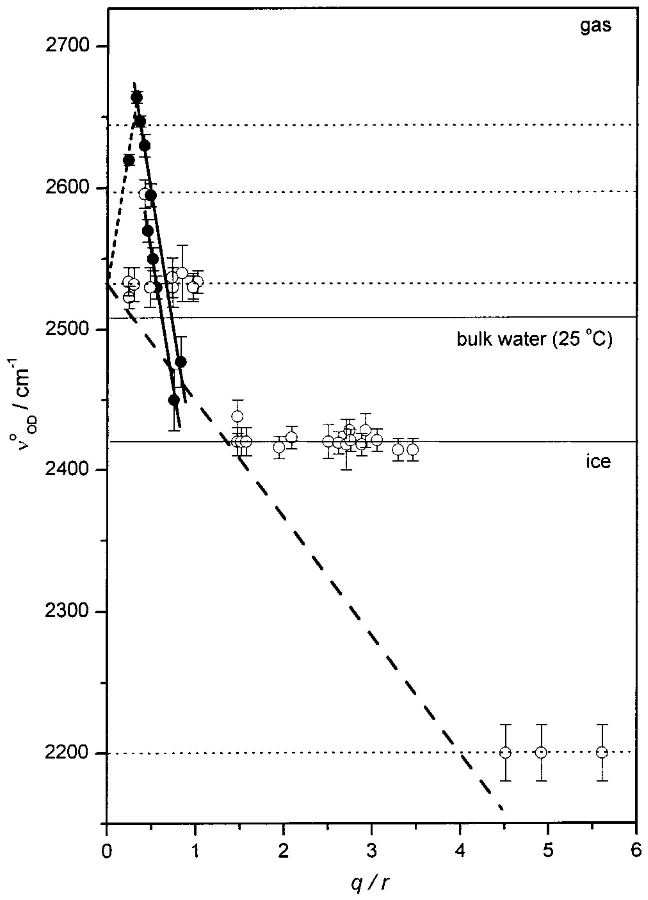

Figure 7. Relationship between ν°_{OD} for HDO affected by anions (●) or by cations (○) and the polarizing power of cations (*q/r*). Data from Figures 3 and 5 have been compared; the points for amphiphilic anions and cation Cu^{2+} have been omitted as not typical examples; the correlation lines as in Figures 3 and 5.

The second aforementioned difference is likely to be explained by the ease of adaptation of water molecules coordinated by an anion, but not by a cation, to the structure of the bulk solution. We consider two reasons that contribute to this phenomenon: (a) formerly noticed[4,5] less hindered rotation around the anion−water interaction axis and (b) greater possibility of changing the anion−water interaction angle than that for cation−water interaction (mainly due to anions' larger ionic radius).

As a consequence of generally larger anionic radii and the observations mentioned above, anions have been more often considered as destroying the water structure. Vibrational bands of anion-affected water molecules are much narrower than the bands of water affected by cations. This is in agreement with the established rule[56] of linear increase of the bandwidth with the band shift toward lower wavenumbers. Therefore, the direct influence of cation on the water spectrum was not noticed in early works: the band of water influenced by the cation is obscured by the bulk water absorption. Instead, the ability to "split" the water band was assigned to anions;[57] Kęcki[58] considered also the influence of a cation on this effect.

Hydration of ions discussed till now refers to solutions at low concentrations or even extrapolated to the infinite dilution. The influence of ion association on the water spectrum has been analyzed previously.[32,33] The observed spectral changes have been interpreted in terms of chemical equilibrium between water molecules affected by (a) anion, (b) cation, (c) anion and cation and (d) bulk water.[33] Instance (c) corresponds to outer-shell ion association. It is worth stressing that water molecules affected simultaneously by an anion and a cation give a band whose position changes in a continuos manner, depending on the properties of ions separated by water molecules in question.[32] Water in solid hydrates behaves similarly.[47]

When purely electrostatic aspects of ion association are neglected, the structural enthalpy effect promotes the association between ions, which exhibit a similar band position of affected water (Figure 7). Cations of well-defined first hydration sphere (water characterized by the 2420 ± 20 $\mathrm{cm^{-1}}$ zone) have the second hydration sphere at 2533 ± 20 $\mathrm{cm^{-1}}$ zone. The energy state of water molecules in this region is similar to that of water affected by most anions. This promotes outer-shell ion association. If water molecules in the first hydration sphere of cations belong to the 2533 ± 20 $\mathrm{cm^{-1}}$ zone (alkali metals cations), the possibility of forming contact ion pairs increases. Infrared hydration studies performed by Max and Chapados, using ATR sampling of ordinary (H_2O) water, deal with these particular electrolyte cases; ref 59 and references therein. Salts with amphiphilic anions exhibit a particular tendency toward association.

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(41) $\Delta U_{\mathrm{w}} = \Delta U_{\mathrm{vdW}} - a\Delta\nu^{\circ}_{\mathrm{OD}}$, where ΔU_{vdW} is the energy of van der Waals interactions of water in water ($-14\ \mathrm{kJ \cdot mol^{-1}}$),[42] $\Delta\nu\ ^{0}_{\mathrm{OD}}$ is the shift of OD band in relation to the position corresponding to the state of HDO without hydrogen bonds in water, equal to $(2644 - \nu^{\circ}_{\mathrm{OD}})$ [$\mathrm{cm^{-1}}$], a is the proportionality coefficient, equal to $(\Delta H_{\mathrm{v}} - RT - |\Delta U_{\mathrm{vdW}}|)/(2644 - 2509)$ [$\mathrm{kJ\ mol^{-1}\ cm}$], where ΔH_{v} is the enthalpy of vaporization of water at 25 °C, equals 44.01 $\mathrm{kJ \cdot mol^{-1}}$,[1] RT is the work of gas expansion, 2509 $\mathrm{cm^{-1}}$ is the $\nu\ ^{0}_{\mathrm{OD}}$ value for pure water at 25 °C.

(42) Kleeberg, H.; Koçak, O.; Luck, W. A. P. *J. Solution Chem.* **1982**, *11*, 611.

(43) Contrary to the attitude presented in works of Lindgren et al. (started from ref 17) we consider the ways of division questionable because: (1) there are no good grounds to assign the N value to any ion that could serve as a reference point, having in mind that "affected number" does not correspond to "hydration number"; (2) the studied solutions (of molality at least 0.2 $\mathrm{mol\ kg^{-1}}$) are by 2 orders of magnitude more concentrated than "dilute electrolyte solutions" for which additivity of the cation and anion can be justified; (3) the necessity of assumption the orientation of HDO molecule with respect to the interacting anion (see ref 17).

(44) The result of band shape analysis and assumption of coordination number for a respective cation leads to $N \cong 2$ for the BF_4^-, ClO_4^-, and NO_3^-.[17,32,45] Assuming that the axis of the interacting anion−water molecular system is consistent with the axis of the O−H(D) bond, the above value of N should by multiplied by 2. This is because the probability of a HDO molecule interacting through the OD group with the anion equals to $^1/_2$. This procedure was used in works of the Lindgren's group (ref 45 and references therein).

(45) Lindgren, J.; Kristiansson, O.; Paluszkiewicz, C. *Interactions of Water in Ionic and Nonionic Hydrates;* Kleeberg, H., Ed.; Springer-Verlag: Berlin, Heidelberg, 1987; p 43.

(46) Luck, W. A. P. *The Fundamental Spectrum of Water and Solutions.* In *Structure of Water and Aqueous Solutions*; Luck, W. A. P., Ed.; Chemie-Physik Verlag: Berlin, 1973; p 221

(47) Berglund, B.; Lindgren, J.; Tegenfeldt, J. *J. Mol. Struct.* **1978**, *43*, 169.

(48) Kristiansson, O.; Eriksson, A.; Lindgren, J. *Acta Chem. Scand.* **1984**, *A38*, 613.

(49) Falk, M. *Can. J. Chem.*, **1971**, *49*, 1137.

(50) In the authors' [40] opinion the discussed band, observed in the spectrum of water affected by $NiSO_4$ salt, should be ascribed to the water molecules in the first hydration sphere of the SO_4^{2-} anion. The authors, on the basis of the results of MD simulation of $HCOO^-$ ion hydration, assume that this band corresponds to OD oscillators of HDO molecule interacting with the SO_4^{2-} anion through the OH group. This interpretation would apply to the situation, when hydrogen bonding of water with a Lewis base through the OH group would be stronger than the relevant water−water interaction. On the basis of our own results, in the case of Bu_4NF solutions[24] as well as for water-DMSO mixtures,[51] we had not noticed such an effect.

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(52) Heinzinger, K.; Pálinkás, G. In *Interactions of Water in Ionic and Nonionic Hydrates*; Kleeberg, H., Ed.; Springer-Verlag:, Berlin, Heidelberg, 1987, p. 1.

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