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Abstract. The structure around lithium ions in solutions of lithium bromide in acetonitrile and water has been studied by neutron diffraction. For this purpose the isotopic first-order difference method has been applied to the lithium ion. For a 0.58 M acetonitrile solution it has been found that the bromide anion enters into the first solvation shell around the lithium ion, whereas in the case of a 1.88 M aqueous solution the first hydration shell of the cation is not disturbed by the anion. The solvation number is approximately 3 in the case of acetonitrile and approximately 4.5 in the case of water.

1. Introduction

Neutron scattering techniques are now frequently used in the study of aqueous electrolyte solutions [1]. In particular, the isotopic first-order difference method has been used by Enderby *et al* [1,2] to examine a great variety of aqueous solutions. Small-angle neutron scattering appears also to be a powerful technique when information about polyelectrolyte solutions [3] is sought. Quasi-elastic neutron scattering turned out to be a convenient method to study the dynamical behaviour of water or hydrogenated particles in solution [4].

Neutron scattering techniques have been rarely applied to non-aqueous electrolyte solutions. However, structure and dynamics of tetraalkylammonium salts in acetonitrile have recently been studied by small-angle [5] and quasi-elastic [6] neutron scattering and the method of differences has been applied to methanol solutions by the Bristol group [7].

In this paper, attention is mainly focused on the study of the solvation of lithium ions in solutions of lithium bromide in acetonitrile. Acetonitrile is an aprotic solvent with a relatively low permittivity (36 at 25 °C) when compared to water. Nevertheless some alkali halides are soluble in acetonitrile up to considerable concentrations. In the case of LiBr, the maximum salt concentration is about 0.6 M.

Several features motivated this work.

(i) The thermodynamic behaviour [8]: Whereas the variation of the osmotic coefficient of an aqueous LiBr solution with concentration shows no peculiarities when

compared to other alkali halides, the osmotic coefficients of the acetonitrile solutions indicate a surprisingly high cation-anion association.

(ii) HNC calculations [8] and a recent microwave study [9] of LiBr in acetonitrile lead also to the conclusion that there is a high ion-pair association but also that there is no significant formation of higher aggregates.

(iii) LiBr in acetonitrile is part of the important industrial system LiBr–acetonitrile–SO_2 which is used as an electrolyte for batteries [10].

In order to get structural information at the microscopic scale, the neutron 'first-order' difference method has been applied to the lithium ion. The isotopes used for this purpose were ^6Li and ^7Li. The total Li^+ radial distribution function $G_{Li}(r)$ can be obtained by this method. As will be demonstrated, the function is dominated by the Li–acetonitrile correlations in the case of an acetonitrile solution and by the Li–water correlations in the case of aqueous solutions. However, in the case where a strong correlation between lithium and bromide ions at short distances occurs, the corresponding Li–Br correlation function can significantly contribute to $G_{Li}(r)$.

2. Experimental procedure

Two solutions were prepared in order to study the solvation of lithium ions in acetonitrile: 0.58 M ^6LiBr and 0.58 M ^7LiBr. The concentration were chosen to be close to saturation in order to get a sufficiently high signal. LiBr was synthesised for both isotopic states starting from enriched $^6Li_2CO_3$ and $^7Li_2CO_3$ originated from CEA. The carbonate salts were brought to reaction with a concentrated HBr solution (Merck, p.a.) which yields the product in solution according to the reaction

$$Li_2CO_3 + 2HBr \rightarrow 2LiBr + H_2O + CO_2.$$
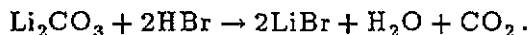
The product was dried and heated to 600 °C under vacuum for several hours and then kept at 300 °C for several days in order to get the unhydrated salt. After pulverisation, the solutions were prepared with purchased deuterated acetonitrile (CEA, 99.6% D, 0.4% H). The concentration of water was found to be less than 100 ppm.

In a similar way solutions in deuterated water (CEA, 99.95% D and 0.05% H) were prepared. In order to compare the solvation of Li^+ with that in acetonitrile solutions, a LiBr salt concentration equal to 1.88 M has been chosen so as to keep equal the ratio between the concentration number of deuterium atoms and the concentration number of Li^+ ions, in both systems.

The atomic concentrations of the four samples are given in table 1.

The neutron scattering experiments were performed on the diffractometer 7C2 situated on the hot source of the Orphée reactor at the laboratoire Léon Brillouin, CEN Saclay [11]. An incident neutron wavelength of 0.712 Å was selected by a Cu 111 monochromator. The scattering intensity was measured simultaneously in the total angular range extending up to 128°, with angular steps equal to 0.2°, by a position-sensitive detector containing 640 cells. This allows us to reach a maximum Q ($= 4\pi \sin(\Theta)/\lambda$, where 2Θ is the diffraction angle) value of 16 Å^{-1}. The solutions were contained in a cylindrical vanadium can of 0.3 cm radius internal. The experiments were performed at room temperature, i.e. (297 ± 1) K. The measured intensities were corrected for instrumental background, container scattering, self-attenuation [12], multiple scattering [13] and were placed on an absolute scale by reference to a vanadium standard [14] (see the Appendix). The neutron scattering and absorption cross sections used in the correction procedure are listed in table 1.

Table 1. Atomic concentrations, neutron scattering lengths and cross sections in barns ($1\ b = 10^{-24}\ cm^2$).

Isotopes	Atomic concen- tration	Coherent scattering length b (10^{-12} cm)	Scattering Mean cross sections (1.8 Å)	Absorption
			(b)	(b)
^{7}LiBr in CD$_3$CN				
^{7}Li (0.999%)	0.00526	−0.2196	1.4390	0.9853
D (0.996%)	0.49470	0.6632	7.9262	0.0018
Br (natural)	0.00526	0.679	5.92	6.9
C (natural)	0.3298	0.6648	5.564	0.0035
N (natural)	0.1649	0.93	11.5	1.9
^{7}LiBr/CD$_3$CN			7.6911	0.3569
^{6}LiBr in CD$_3$CN				
^{6}Li (0.9556%)	0.00526	0.1689	1.0	898.26
D (0.996%)	0.49470	0.6632	7.9262	0.0018
Br (natural)	0.00526	0.679	5.92	6.9
C (natural)	0.3298	0.6648	5.564	0.0035
N (natural)	0.1649	0.93	11.5	1.9
^{6}LiBr/CD$_3$CN			7.6885	5.027
^{7}LiBr in D$_2$O				
^{7}Li (0.999%)	0.0103	−0.2196	1.439	0.9853
D (0.996%)	0.6521	0.6632	7.9262	0.0018
Br (natural)	0.0103	0.679	5.92	6.9
O (natural)	0.3261	0.58	4.234	0.00019
^{7}LiBr/D$_2$O			6.464	0.082
^{6}LiBr in D$_2$O				
^{6}Li (0.9556%)	0.0103	0.1689	1.0	898.26
D (0.996%)	0.6521	0.6632	7.9262	0.0018
Br (natural)	0.0103	0.679	5.92	6.9
O (natural)	0.3261	0.58	4.234	0.00019
^{6}LiBr/D$_2$O			6.460	9.28

3. Results and Discussion

The total structure factor $F(Q)$ of a LiBr solution in acetonitrile is a weighted average of 15 partial structure factors $S_{\alpha\beta}(Q)$, where the subscripts α and β denote the particles involved. The difference between the total structure factors relative to two solutions, identical in all respects except that the isotopic state of Li has been changed, is represented by

$$\Delta S_{\mathrm{Li}}^{\mathrm{AN}}(Q) = A[S_{\mathrm{LiBr}}(Q) - 1] + B[S_{\mathrm{LiLi}}(Q) - 1] + C[S_{\mathrm{LiD}}(Q) - 1]$$
$$+ D[S_{\mathrm{LiC_1}}(Q) - 1] + E[S_{\mathrm{LiN}}(Q) - 1] + F[S_{\mathrm{LiC_2}}(Q) - 1] \qquad (1)$$

where $A = 2c_{\mathrm{Li}}c_{\mathrm{Br}}b_{\mathrm{Br}}\Delta b_{\mathrm{Li}}$, $B = c_{\mathrm{Li}}^2(b_{^6\mathrm{Li}}^2 - b_{^7\mathrm{Li}}^2)$, $C = 2c_{\mathrm{Li}}c_{\mathrm{D}}b_{\mathrm{D}}\Delta b_{\mathrm{Li}}$, $D = 2c_{\mathrm{Li}}c_{\mathrm{C}}b_{\mathrm{C}}\Delta b_{\mathrm{Li}}$, $E = 2c_{\mathrm{Li}}c_{\mathrm{N}}b_{\mathrm{N}}\Delta b_{\mathrm{Li}}$, $\Delta b_{\mathrm{Li}} = b_{^6\mathrm{Li}} - b_{^7\mathrm{Li}}$, and c_{α} is the atomic concentration of species α whose coherent neutron scattering length is b_{α}. The factors A, B, C, D, E and F are given in table 2.

Table 2. Scattering constants for the differences in mb ($1 \text{ mb} = 10^{-27} \text{ cm}^2$).

System	A	B	C	D	E	F
LiBr/CD$_3$CN	0.0152	0.00742	1.41	0.938	0.656	0.938
	H	I	J	K		
LiBr/D$_2$O	0.048	0.00721	3.30	1.44		

It can be shown [15] that the contribution of Placzek corrections to the difference function are negligible to first order. The residual corrections to the experimental difference function may be made by reference to the sum rule

$$\int_0^\infty (S_{\alpha\beta}(Q) - 1)Q^2 \, dQ = -2\pi^2\rho. \tag{2}$$

For example, in the case of the acetonitrile solution this expression can be written as

$$\int_0^\infty \Delta S_{\text{Li}}^{\text{AN}}(Q)Q^2 \, dQ = -2\pi^2\rho(A + B + C + D + E + F). \tag{3}$$

The Fourier transform of $\Delta S_{\text{Li}}^{\text{AN}}(Q)$ gives $G_{\text{Li}}(r)$ (the real-space difference function)

$$G_{\text{Li}}^{\text{AN}}(r) = \frac{1}{2\pi^2\rho r} \int_0^\infty Q\Delta S_{\text{Li}}^{\text{AN}}(Q)\sin(Qr) \, dQ. \tag{4}$$

In the case of acetonitrile solution it gives

$$G_{\text{Li}}^{\text{AN}}(r) = A[g_{\text{LiBr}}(r) - 1] + B[g_{\text{LiLi}}(r) - 1] + C[g_{\text{LiD}}(r) - 1]$$
$$+ D[g_{\text{LiC}_1}(r) - 1] + E[g_{\text{LiN}}(r) - 1] + F[g_{\text{LiC}_2}(r) - 1]. \tag{5}$$

The dominating factors are those related to the correlation of the Li$^+$ ion to the solvent atoms. However, the value of A is not negligible so that a contribution of the pair correlation function $g_{\text{LiBr}}(r)$ can be expected (cf table 2).

In the case of aqueous solutions ten partial structure factors enter into $F(Q)$. The difference is a combination of four structure factors such that

$$\Delta S_{\text{Li}}^{\text{D}_2\text{O}}(Q) = H[S_{\text{LiBr}}(Q) - 1] + I[S_{\text{LiLi}}(Q) - 1] + J[S_{\text{LiD}}(Q) - 1]$$
$$+ K[S_{\text{LiO}}(Q) - 1]. \tag{6}$$

The Fourier transform of $\Delta S_{\text{Li}}^{\text{D}_2\text{O}}$ yields the function $G_{\text{Li}}^{\text{D}_2\text{O}}$ which is given by

$$G_{\text{Li}}^{\text{D}_2\text{O}}(r) = H[g_{\text{LiBr}}(r) - 1] + I[g_{\text{LiLi}}(r) - 1] + J[g_{\text{LiD}}(r) - 1] + K[g_{\text{LiO}}(r) - 1]. \tag{7}$$

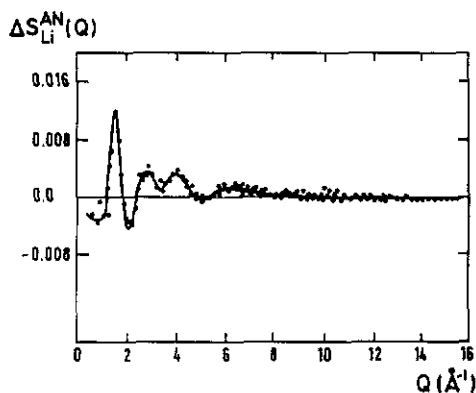**Figure 1.** First-order difference function $\Delta S_{Li}^{AN}(Q)$ for LiBr in CD_3CN. The full circles represent data points, while the full curve is spline fits consistent with $G_{Li}^{AN}(r) = -(A + B + C + D + E + F)$ below $r = 1.8$ Å.

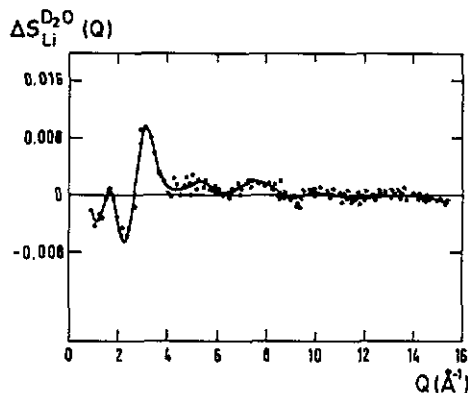**Figure 2.** First-order difference function $\Delta S_{Li}^{D_2O}(Q)$ for LiBr in D_2O. The full circles represent data points, while the full curve is spline fits consistent with $G_{Li}^{D_2O}(r) = -(H + I + J + K)$ below $r = 1.8$ Å.

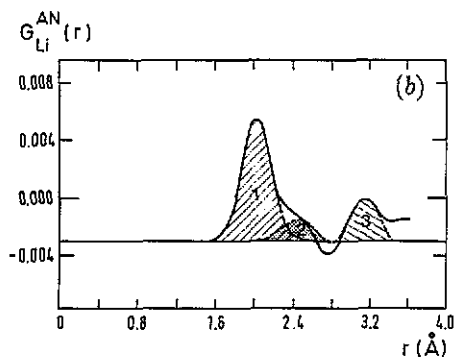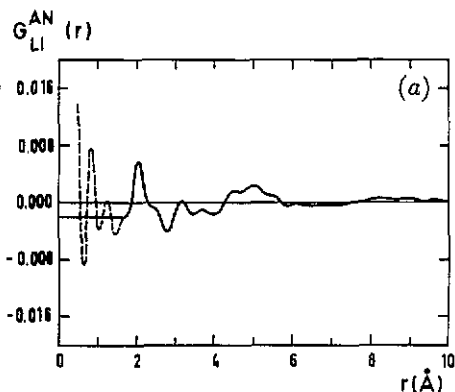**Figure 3.** LiBr in CD_3CN: (a) The total radial correlation function $G_{Li}^{AN}(r)$ obtained by Fourier transformation of the function given in figure 1. (b) Decomposition of $G_{Li}^{AN}(r)$ with three Gaussian peaks corresponding respectively to Li–N (1), Li–Br (2) and Li–C_1 (3) correlations.

The values of the factors H, I, J, and K are given in table 2.

The radial partial pair correlation function $g_{Li\alpha}(r)$ can directly be interpreted according to statistical mechanics as the probability of finding an atom α at a distance r from a central Li^+ ion.

A coordination number n_{Li}^{α} of atoms α around a central ion Li^+ in a range $r_1 < r < r_2$ can be defined by

$$n_{Li}^{\alpha} = 4\pi\rho c_{\alpha} \int_{r_1}^{r_2} g_{Li\alpha}(r) r^2 \, dr \tag{8}$$

where it is assumed that $g_{Li\beta}(r) = 0$ for all $\beta \neq \alpha$ in the range $r_1 < r < r_2$ (ρ is the total number density of the solution). This means that, for example, for $g_{LiN}(r)$
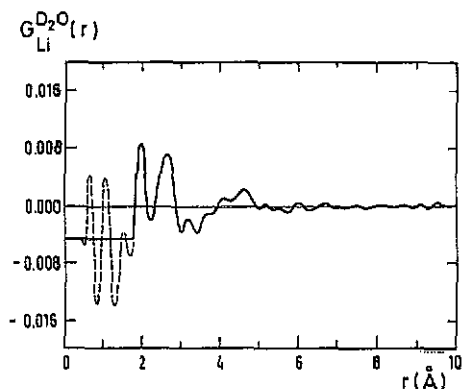
Figure 4. LiBr in D_2O: The total radial correlation function $G_{Li}^{D_2O}(r)$ obtained by Fourier transformation of the function given in figure 2.

(cf equation (5)):

$$g_{LiN}(r) = \frac{G_{Li}^{AN} + (A + B + C + D + E + F)}{E}.$$ (9)

Combining equations (8) and (9) yields

$$n_{Li}^N = \frac{4\pi\rho c_N}{E} \int_{r_1}^{r_2} (G_{Li}^{AN} + A + B + C + D + E + F) r^2 \, dr.$$ (10).

The difference function $\Delta S_{Li}(Q)$ relative to the LiBr solution in acetonitrile is shown in figure 1 and the corresponding function for the aqueous solution in figure 2. The $G_{Li}(r)$ functions, obtained by Fourier transformation are displayed in figure 3(*a*) (acetonitrile solution) and figure 4 (D_2O solution), respectively.

Table 3. Atom–atom distances (in Å) and corresponding coordination numbers derived from experiment.

Atoms	Distance	Coordination number
In CD$_3$CN		
Li–N	2.05	2.9 ± 0.3
Li–Br	2.46	1.0 ± 0.2
Li—C$_1$	3.17	3.4 ± 0.3
In D$_2$O		
Li–O	1.94	4.5 ± 0.5
Li–D	2.58	9.2 ± 0.5

In the case of the organic solution, the $G_{Li}^{AN}(r)$ function shows several resolved peaks which can be interpreted in the following way: From Hartree–Fock calculations [8] it is inferred that Li$^+$ should be solvated by acetonitrile molecules in such a way that the nitrogen atoms are closest to the Li$^+$ ion. The distance Li$^+$–N should be about 2.1 Å. Therefore we assigned the first and highest peak at a distance of 2.05 Å
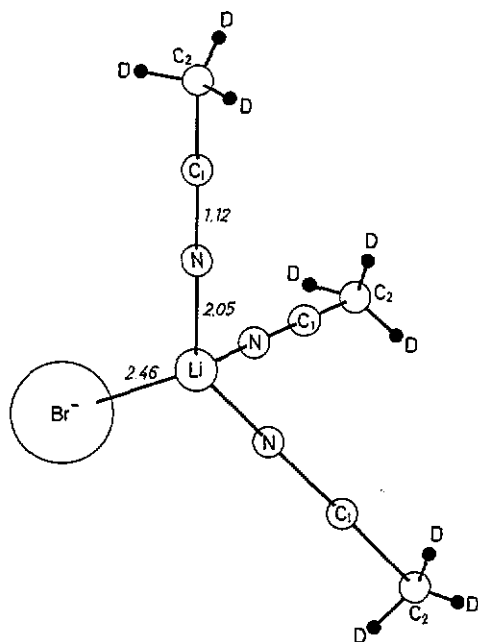
Figure 5. A model proposed for the first nearest neighbours around Li^+ in an acetonitrile solution of LiBr. The centre-to-centre distances (in Å) are inferred from the analysis of the neutron spectra (see table 3).

to the nitrogen atom. Separation and integration of this peak give a coordination number n_{Li}^N of 2.9.

From an x-ray study on pure acetonitrile the mean distance between the nitrogen and the first carbon atom C_1 within an acetonitrile molecule is known. This experimental value has been found equal to 1.15 Å [16] while *ab-initio* calculations yield 1.14 Å [8]. Indeed, the $G_{Li}^{AN}(r)$ function shows a peak at 3.17 Å. The distance between the nitrogen peak and this peak is 1.12 Å which is in good agreement with the N–C_1 distances quoted above. Therefore we assigned the peak at 3.17 Å to the Li–C_1 correlation. Integration yielded a coordination number of 3.4. The same coordination numbers of approximately 3 for N and C_1 are a further argument for the assignement of the two peaks at 2.05 Å and 3.17 Å to the Li–N and Li–C_1 correlations, respectively.

The nitrogen peak is perturbed by a small peak having its maximum at 2.46 Å. By symmetrizing the nitrogen peak, the neighbouring peak can be separated. The latter is supposed to reflect the correlation between lithium and a bromide counter-ion (see figure 3(b)). The coordination number n_{Li}^{Br} of 1.0 at such a small distance can only be explained by an extremely high peak in the corresponding ion–ion pair correlation function $g_{LiBr}(r)$ [8]. In a more chemical picture this is a strong indication of a very high association in the sense of ion-pair formation. The coordination number of approximately one for the bromide ion around lithium completes the picture assumed for the first solvation sphere (cf figure 5). It shows that Li^+ has a first solvation shell of tetrahedral geometry in which one of the four solvent molecules is replaced by a bromide ion.

The peak at 3.69 Å and further peaks between 4.3 and 5.8 Å are much more difficult to interpret. They probably represent correlations between Li^+ and the CD_3 groups of the acetonitrile molecules—expected around 4.6 Å—or contributions of the

second solvation sphere which enters partially into the first shell. For this first neutron scattering study of an acetonitrile solution we restrict our interpretation to the first three peaks. The distances and coordination numbers are compiled in table 3.

The $G_{Li}^{D_2O}(r)$ function of the aqueous solution displays the expected simple structure: one peak at a distance of 1.94 Å and a second one at $r = 2.58$ Å. The first one can be assigned to the correlation Li–O, the second one to the correlation Li–D. The coordination numbers are 4.5 ± 0.5 in the case of oxygen and 9.2 ± 0.5 in the case of hydrogen, yielding a hydration number of 4.5. The distances and the hydration numbers are in excellent agreement with the results relative to other aqueous lithium solutions [17, 18].

4. Conclusion

The result of the present neutron scattering study shows that the structure of solvation of a lithium ion in deuterated acetonitrile is different from that in water. In the aqueous solution the first solvation sphere around Li^+ consists of four or five solvent molecules whereas in the organic solution the first nearest neighbours are three acetonitrile molecules and one bromide ion. This particular behaviour of the organic solution is in agreement with the protophobic character of acetonitrile which is known from other techniques [19]. A detailed theoretical interpretation of the Li^+ solvation and LiBr association in acetonitrile and their consequences on the thermodynamical properties of the solution will be given in an other paper [8].

Appendix

The raw data were corrected for multiple scattering and absorption and normalized by the methods referred in the text. The multiple scattering can be considered isotropic and is treated as a constant to be subtracted from the data, after correction for attenuation.

The normalization of the data was performed with respect to a vanadium standard and was independent of the multiple scattering correction made to the samples. The normalization was, however, dependent on the attenuation corrections made to the samples, especially when the absorption cross section is not small [20]; it also depends on the attenuation and the multiple scattering corrections made to the vanadium scattering.

In the first-order difference functions ΔS shown in figures A1 and A2 it can be noticed that there is a characteristic bend, which is stronger in D_2O where the atomic fraction of lithium is approximatively twice as great for D_2O solution as for the acetonitrile solution, but stays relatively low (see table 1). These bends are thought
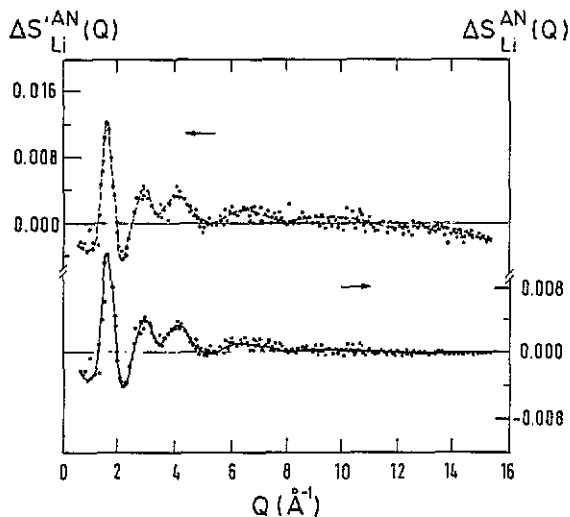
Figure A1. First-order difference functions for LiBr in CD_3CN. (– – –) $\Delta S_{Li}^{\prime AN}(Q)$: before correction; (——) $\Delta S_{Li}^{AN}(Q)$: after correction.
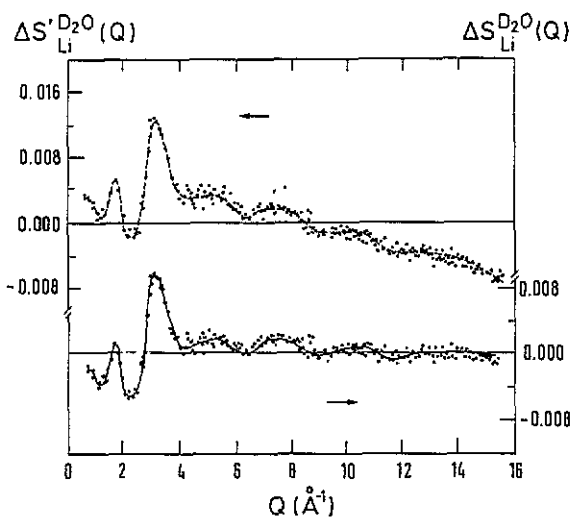

Figure A2. First-order difference functions for LiBr in D_2O. (– – –) $\Delta S_{Li}^{\prime D_2O}(Q)$: before correction; (——) $\Delta S_{Li}^{\prime\prime D_2O}(Q)$: after correction.

to originate from the approximations used in the scattering corrections, which result in the incomplete cancellation of the 'self'-scattering terms in the difference function, when a highly absorbing isotope (^6Li) is used in the presence of light atoms. A significant distorsion of the 'distinct' scattering terms, which contain the structural information, is not expected. We have to correct the first-order difference functions. Actually, no practical theory exists that could be used to carry out these residual corrections in a completely proper way. Therefore we have chosen an empirical method. It gives:

(i) for $\Delta S_{Li}^{AN}(Q)$

$$\Delta S_{Li}^{AN}(Q) = \Delta S_{Li}^{\prime AN}(Q)(1 - 0.004Q^2) - 8.57 \times 10^{-5} \qquad \text{(A1)}$$

(ii) for $\Delta S_{\mathrm{Li}}^{\mathrm{D_2O}}$:

$$\Delta S_{\mathrm{Li}}^{\mathrm{D_2O}}(Q) = \Delta S_{\mathrm{Li}}^{\prime\mathrm{D_2O}}(Q)(1 - 0.0002Q^2) + 0.0007Q - 0.00524 \qquad (A2)$$

where $\Delta S'$ are the difference functions before the corrections.

The coefficients in the two expressions (A1) and (A2) are adjusted in a way that $\Delta S_{\mathrm{Li}}^{\mathrm{AN}}(Q)$ and $\Delta S_{\mathrm{Li}}^{\mathrm{D_2O}}(Q)$ verify the sum rule of the Q-space data. In figures A1 and A2 we give a comparison between the first-order difference functions obtained before and after the corrections.

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