Small-Angle X-ray Scattering Analysis of Particle Size Distributions of Colloidal ThO₂ Sol

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Small-angle X-ray scattering data were obtained and analyzed from two hydrous ThO₂ sols having differing size distributions of particles. Both the experimental and slit-height-corrected scattering data were employed for analysis. The five independent scattering parameters thus obtained were analyzed in terms of the moments of the size distributions. These data were then converted to size distributions of log normal form. Excellent agreement of these derived size distributions with direct electron-microscopic results could be obtained. An indirect method for the experimental determination of the X-ray transmission by such solutions is also given.

Introduction

For a system of particles of identical shape but having a variation of sizes, small-angle X-ray scattering (SAXS) data can give information concerning the nature of this size distribution if the sizes of the particles fall within a suitable range (approximately 20 to 2000 Å). One of the goals of the SAXS technique during its development has been the realistic and accurate determination of such a size distribution function from an experimentally determined X-ray scattering curve, with a minimum number of assumptions required. An early attempt in this direction was made by Hosemann (1951) who assumed spherical particles having a Maxwellian size distribution, with each particle scattering only as represented by the exponential equation of the Guinier approximation (Guinier & Fournet, 1955). However, even with these very severe restrictions, it is found that it is very difficult to determine from an experimental scattering curve the two parameters defining a Maxwellian size distribution with any accuracy by this method.

A recent procedure has been given by Harkness, Gould & Hren (1969) (hereafter abbreviated HGH) in which only spherical particles having a log normal size distribution function are assumed for the exact evaluation of any experimental SAXS curve. The HGH procedure was shown to give excellent agreement with electron-microscopy results for determination of the size distribution of Guinier–Preston zones in Al–Ag and Al–Zn alloys. HGH pointed out that the assumption of a log normal distribution may best be justified by its wide range of application and its ability to adequately describe the size distributions that arise from nucleation-growth and coarsening processes. Thus, McCurrie & Douglas (1967) determined that a log normal distribution even accurately describes with small dispersity the particle-size distributions that are maintained during the coarsening process of diffusion-controlled amorphous particle growth in a phase-separated glass.

Although the HGH log-normal-distribution determination appears to be the most useful and most accurate SAXS method yet devised from a practical viewpoint, these authors point out that a deficiency of their procedure is that it cannot be accurately applied if the Porod constant $h^2 J(h)$ cannot be experimentally determined over a reasonable $h$ interval. In the present investigation the applicability of the HGH procedure to allow accurate size determinations of some colloidal ThO₂ was evaluated. It was found that although the $h^2 J(h)$ constants could not be evaluated directly, suitable background-scattering corrections could be made to allow their reasonable estimation. With values thus obtained, it was found that particle-size distributions in quite fair agreement with electron-microscopy results were obtained.

Also, during the present study, it was found that the HGH procedure could be extended through employment of the desmeared SAXS data. The equations derived are found to allow different size–moment ratios to be determined from the SAXS data from those derived by HGH. Of particular importance, the present equations do not contain the Porod $h^2 J(h)$ parameter implicity as one of the required experimental SAXS parameters. They thus allow the determination of the parameters defining the log normal distribution function with reasonable accuracy even when the Porod parameter cannot be accurately calculated from the SAXS curves. In the present study it was found that the particle-size distribution calculated by this method was in excellent agreement with electron-microscopy results. Finally, it is of interest to note that by employing both the HGH and the present procedures, four independent and different size–moment ratios can be obtained from the SAXS data when the Porod parameter can be determined. This allows an evaluation of the goodness-of-fit of these parameters to a log normal or other more complex size distribution function.

Moment analysis of SAXS parameters

We define a size distribution function for a polydisperse system of spherical particles, $F(R)$, such that $F(R)dR$...
is the fraction of the particles having radii between \( R \) and \( R + dR \). \( F(R) \) is thus normalized such that \( \int F(R)dR = 1 \). The form of \( F(R) \) need not be specified. The \( n \)th moment of \( R \), \( \langle R^n \rangle \), is given by

\[
\langle R^n \rangle = \int_0^\infty R^n F(R)dR .
\]

For a dilute colloidal sol containing spherical particles having some size distribution, \( F(R) \), SAXS data will give information regarding the ratios of various moments of this distribution, depending upon the method of analysis of the scattering curve and also depending upon whether the desmeared (theoretical) intensity, \( I(h) \), or the experimental (infinite-beam-length) intensity, \( J(h) \), is employed. Here

\[
h = (2\pi/\lambda) (2\theta) = (2\pi/\lambda) (m/d) ,
\]

where \( \lambda \) is the X-ray wavelength, \( 2\theta \) is the scattering angle, \( d \) is the sample-to-receiving-slit distance, and \( m \) is the linear distance of the receiving slit from the centroid of the beam in the plane perpendicular to \( d \).

Thus the Guinier radius (for spheres), \( R_G \) or \( R_0 \), results from approximations to a scattering curve at the lowest angles. For an experimental SAXS curve, within the range of validity of the Guinier approximation,

\[
J(h) = J(0) \exp \left(-h^2 R_E/5\right) ,
\]

whereas for a desmeared SAXS curve, with the same restriction,

\[
I(h) = I(0) \exp \left(-h^2 R_D/5\right) .
\]

For a desmeared SAXS curve obtained from spherical particles having any size distribution, \( F(R) \), it has been shown (Guinier & Fournet, 1955) that

\[
R_G^2 = \frac{V_R^2}{\langle R^6 \rangle} = \frac{\langle R^8 \rangle}{\langle R^6 \rangle} ,
\]

where \( V_R \) is the volume of a sphere of radius, \( R \), and the bars denote an averaging. The moments of \( R \) are then as given in equation (1).

Also, for the experimental curve of equation (3), it has been shown (Baur & Gerold, 1964) that

\[
R_E^2 = \langle R^2 \rangle/\langle R^6 \rangle .
\]

It was shown by Porod (1951) that for large values of \( h \), the products \( h^4 I(h) \) and \( h^6 J(h) \) approach constants, such that

\[
K_D = (\pi/4) \lim h^4 I(h) \quad (7a)
\]

\[
K_E = \lim h^6 J(h) . \quad (7b)
\]

Porod (1951) also showed that \( K \) is related to the total surface area, \( S \), of the scattering particles of total volume, \( V \), such that

\[
\frac{V}{S} = \frac{1}{4} \left\langle h^2 J(h)dh/4(1-f)K_E \right\rangle = \frac{1}{4} \left\langle h^2 I(h)dh/4(1-f)K_D \right\rangle ,
\]

where \( f \) is the volume fraction of the scattering particles. For a polydisperse system of spherical particles, equation (8) may be averaged to obtain the average spherical radius, \( P \):

\[
P = \frac{3}{4(1-f)K_E} \left\langle h^2 I(h)dh \right\rangle = \frac{3}{4(1-f)K_D} \left\langle h^2 J(h)dh \right\rangle \quad (9)
\]

\[
P = \left( \frac{3\lambda^2}{8\pi} \right) \left\langle \int_0^\infty m J(m)dm \right\rangle . \quad (10)
\]

With our instrumental arrangement \( d = 210 \text{ mm} \) and \( \lambda = 1.54 \text{ Å} \), and thus with \( m \) expressed in mm, the factor \( (3\lambda^2/8\pi) \) is 38.6. Baur & Gerold (1964) showed that \( P \) is given in terms of the moments of \( R \) by

\[
P = \langle R^3 \rangle/\langle R^5 \rangle \quad (11)
\]

which follows from equation (8).

Finally, we define a mean volume, \( V_D \), by

\[
V_D = \left\langle \frac{3\pi}{2} \right\rangle \left\langle \int_0^\infty h^3 J(h)dh \right\rangle = \left\langle \frac{3\lambda^2 d^2}{16\pi^2} \right\rangle \left\langle \int_0^\infty m^2 J(m)dm \right\rangle . \quad (13)
\]

For our arrangement, the factor \( (3\lambda^2 d^2/16\pi^2) \) is 6.426 \times 10^6. Also for dilute solutions \( 1-f \approx 1 \) in equations (10) and (13). Since \( J(0) \) is proportional to \( V_R^2 \) and the integral (the invariant) to \( V_R \), we obtain in terms of the moments of \( R \)

\[
V_D = \langle R^3 \rangle/\langle R^5 \rangle . \quad (14)
\]

If the electron density of a system of particles remains constant during their precipitation and growth, then the variation in their total number density, \( N \), can be obtained also from the variation in the \( I(0) \), if their size distribution functions, \( F(R) \), have been determined. Thus if \( N_i \) particles having a distribution \( F_i(R) \) yield an \( I_i(0) \),

\[
\frac{N_2}{N_1} = \frac{I_2(0)}{I_1(0)} \left\langle R_i^6 \right\rangle . \quad (15)
\]

It is noted that equations (5), (6), (11), (14), and (15) are exact, regardless of the nature of the size distribution function, \( F(R) \). Therefore, in principle the simultaneous employment of the first four equations will allow the determination of a four-parameter distribution function. However, in practice it is often not possible accurately to determine experimentally either the parameter \( K \) [equation (7)], or to a lesser extent the integrals in equations (10) and (13). Thus it may be preferable to approximate the actual distribution in terms of a three or two-parameter function which can accurately be experimentally determined from the SAXS
The log normal distribution

A log normal size distribution was thus effectively employed by HGH for analysis of their SAXS data (Harkness, Gould & Hren, 1969). The form of this distribution is

\[
F(R) = \frac{1}{R \ln \sigma \sqrt{2\pi}} \exp \left[ -\frac{\ln R - \ln \mu}{2 \ln^2 \sigma} \right].
\]

where \( \mu \) is the geometric mean of the distribution and \( \sigma \) is the geometric standard deviation of variance. Since the arithmetic mean of the particle sizes, \( \bar{R} \), of this distribution is given by \( \bar{R} = \langle R \rangle \), one obtains by substituting equation (16) into equation (1)

\[
\bar{R} = \exp \left[ \ln \mu + \frac{1}{2} \ln^2 \sigma \right].
\]

One further obtains for the ratio of \( n \)th moment to the \( k \)th moment of \( R 
\[
\langle R^n \rangle / \langle R^k \rangle = \exp \left[ \frac{1}{2}(n-k) \ln \mu + \frac{1}{2} (n^2-k^2) \ln^2 \sigma \right].
\]

With equation (18), the experimentally determined SAXS parameters given by equations (5), (6), (11), and (14) become

\[
\begin{align*}
R_D &= \exp \left[ \ln \mu + 7 \ln^2 \sigma \right], \\
R_E &= \exp \left[ \ln \mu + 6 \ln^2 \sigma \right], \\
P &= \exp \left[ \ln \mu + 2.5 \ln^2 \sigma \right], \\
V_D &= \exp \left[ 3 \ln \mu + 13.5 \ln^2 \sigma \right].
\end{align*}
\]

Only two of these equations are required for the determination of \( \mu \) and \( \sigma \). HGH solved equations (20) and (21) to obtain

\[
\begin{align*}
\ln \mu &= \ln R_E - 1.71 \ln (R_E/P), \tag{23a} \\
\ln^2 \sigma &= (1/3.5) \ln (R_E/P). \tag{23b}
\end{align*}
\]

An attractive alternate choice is equations (19) and (22), which yield

\[
\begin{align*}
\ln \mu &= 0.9333 \ln V_D - 1.8000 \ln R_D, \tag{24a} \\
\ln^2 \sigma &= (1/7.5) (3 \ln R_D - \ln V_D). \tag{24b}
\end{align*}
\]

A third attractive choice for solution is equations (19) and (20), since they require only the determination of Guinier radii from the corresponding experimental and desmeared SAXS curves. These yield

\[
\begin{align*}
\ln \mu &= \ln R_D - 6 \ln (R_D/R_E), \tag{25a} \\
\ln^2 \sigma &= \ln (R_D/R_E). \tag{25b}
\end{align*}
\]

Experimental methods and results

The scattering data were obtained with a commercial Kratky SAXS instrument (sample-to-detector-slit distance of 210 mm), in conjunction with a Kratky high-power copper-anode X-ray tube operated at 35 kV and 38 mA. An entrance slit of 0.040 mm with a detector slit of 0.084 mm was used for all measurements. The slit-height corrections to the experimental scattering curves were made by the least-squares method of Schmidt (1965b), for the case of infinite slit height. Additional details concerning our instrumentation have been previously given (Neilson, 1969), as have been the details of our data reduction and slit-correction procedures (Neilson, 1972).

For the scattering measurements the thoria sols were contained in thin-walled Lindemann-type glass capillaries of 0.5 mm i.d. The capillaries were mounted with their lengths precisely parallel to the X-ray beam length and carefully adjusted on the instrument such that the X-ray beam passed along their diameters. It was found difficult to remove and then reposition a capillary at exactly the same position in the beam. Therefore, it is preferable to measure the X-ray transmission of the sample, \( T = \exp (-\mu l) \), which is required for the correction for the effect of the parasitic scattering, without disturbing the position of the capillary. Furthermore, with our arrangement it is not possible to determine \( T \) with any accuracy by the simple measurement of the attenuation of the intensity of the incident beam by the sample, because of the other wavelength components present in the X-ray beam in addition to the K\(_{\alpha}\) radiation. To circumvent this problem, the following method...
was employed which allows the indirect but accurate determination of the degree of attenuation by the sample of just the parasitic intensity, with the sample remaining in its normal scattering position.

Standard-scattering films, obtained by dispersing finely precipitated MgO in collodion, were prepared and mounted on frames. These films could be prepared to exhibit intense scattering at the lower scattering angles, while having transmission values in the range 0-90 to 0-97. The value at an arbitrary scattering angle $T_x$ for a scattering sample, $x$, was determined with the auxiliary use of the standard film, $s$, having a known transmission, $T_s$, as follows. The intensity, $I_x$, scattered by the standard alone was first measured. The capillary was then mounted in its normal position (adjacent to the standard) and the intensity, $I_{xs}$, scattered by both was measured. Finally, the standard was removed and the intensity, $I_x$, scattered by the capillary alone was measured. If $I_p$ is the parasitic scattering measured with no scattering sample in the beam, then the transmission of the unknown $x$ is calculated by

$$T_x = \frac{I_{xs} - I_x T_s}{I_x - I_p T_s}.$$  \hfill (26)

It was found that for flat scattering samples of uniform thickness for which $T$ could be calculated with equation (26) and could also be measured directly by inserting the sample behind the collimation system, the values of $T$ obtained were in agreement within 1%.

Scattering data were obtained for five hydrous ThO$_2$ sols obtained by the refluxing of ThCl$_4$ solutions for times of 1, 2, 4, 9, and 20 h. As determined from the initial ThCl$_4$ concentration, it was concluded that the maximum ThO$_2$ concentration in these sols is in the range of $\frac{1}{2}$ to 1 wt. %. It was determined by Schmidt (1965a) that for ThO$_2$ sols of such concentration, the effect of interparticle interference is negligible, except possibly at the lowest accessible scattering angles. The measured X-ray transmission of these sols when mounted in the 0.5 mm capillaries varied between 0-40 and 0-43, as determined by the above method. These values are thus close to the optimum value of 0-37, and the extent of variation is a measure of both variation of capillary diameter and the precision of their adjustment in the X-ray beam.

The experimental scattering curves obtained from these sols are shown in Fig. 1. The data shown were corrected for the effects of parasitic scattering (see Neilson, 1972), but are without slit-height correction. The scattering curves obtained for the sols of 2 and 4 h reflux times are essentially identical to the plotted 1 h curve, which indicates that no significant colloid formation occurs during these shorter times. The scattering exhibited by the 1 h sol was therefore regarded as arising from density fluctuation effects and from the glass capillary itself. Since scattering of similar magnitude arising from these effects is presumably also superimposed over the particle scattering for the 9 and 20 h sols, the experimental scattering curve of the 1 h sol was subtracted from the curves of the 9 and 20 h sols before calculation of the SAXS size parameters and before applying the slit-height corrections for the particle scattering from these sols. The subsequent discussion and results given for the 9 and 20 h sols refer to data to which this background-scattering correction has been applied.
The Guinier radii for these two sols were determined from both the experimental and slit-height-corrected scattering data. Guinier plots of the experimental data are given in Fig. 2. The radii values thus obtained are given in Table 1, as well as the I(0) values obtained from the corresponding slit-height-corrected data.

<table>
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<th>Parameter</th>
<th>Units</th>
<th>9 h</th>
<th>20 h</th>
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<tr>
<td>€€</td>
<td>(Å)</td>
<td>112</td>
<td>141</td>
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<tr>
<td>€€</td>
<td>(Å)</td>
<td>133</td>
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<tr>
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<tr>
<td>K €€</td>
<td>(m²J)</td>
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<tr>
<td>K €€</td>
<td>(m²J)</td>
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</tr>
<tr>
<td>Q O3</td>
<td>(m²J)</td>
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</table>

The Porod constants, K [equation (7)] were evaluated from both the experimental and slit-height-corrected data for the 20 h sol, but could only be determined with sufficient precision from the experimental data for the 9 h sol. The results are given in Table 1, where

\[ K_E' = \lim \frac{m^3}{J(m)} \]  
\[ K_D' = \lim \frac{m^4}{J(m)}. \]

For the 20 h sol, the experimental \( m^2J(m) \) data behaved as shown by curve A of Fig. 3, which yielded \( K' = \frac{665 m^2J}{\text{units}} \). If it is assumed that there is present in the scattered intensity an additional constant background of 17 counts/min which must be further subtracted from \( J(m) \), then curve B is obtained which becomes sensibly constant at the larger \( m \) values, yielding the given value of \( K' = \frac{590 m^2J}{\text{units}} \). However, the uncertainty in this value of \( K' \) is thus about 10%. No such correction was necessary for the determination of \( K' \) for the 9 h sol.

The integrals in equations (10) and (13), designated by \( Q_E \) and \( Q_D \) respectively in Table 1 were evaluated in the following manner. The areas under the respective curves were numerically determined from \( m = 0 \) to \( m = b \). These portions of the integrals are designated as \( Q_E1 \) and \( Q_D1 \). The values of \( b \) were chosen within the regions of \( m \) where the Porod relationships [equation (27)] were found to be obeyed. The remainders to these integrals, designated \( Q_E2 \) and \( Q_D2 \), were then determined analytically from the equations

\[ Q_E2 = K_E'/b \]  
\[ Q_D2 = K_D'/b. \]

The value of \( Q_D \) for the 9 h sol could not be determined with sufficient accuracy by this procedure to warrant its inclusion in Table 1.
Data analysis and discussion

The constants $\mu$ and $\sigma$ which characterize the log normal distribution of equation (16) were evaluated from the independent sets of equations (23), (24) and (25) for the 9 and 20 h sols, employing the experimentally determined SAXS parameters, $R_E$, $R_D$, $V_D$ and $P$. The results obtained are given in Table 2.

It was found that the values of $\mu$ and $\sigma$ determined by equation (25) are extremely sensitive to variation in the ratio of $R_D/R_E$. Thus for the 9 h sol, a decrease in this ratio by $10\%$ from that obtained from Table 1 changes $\mu$ from 40 to 75 Å. This unfavorable sensitivity arises from the employment of only the larger moments of $F(R)$ for this particular determination of the distribution parameters. It is estimated that $R_E$ and $R_D$ must each be determined with an accuracy of $1\%$ to ensure an uncertainty of less than $10\%$ in the calculated values of $\mu$ and $\sigma$ by equation (25). This accuracy is probably attained in the values of the radii determined for the 20 h sol. However, for the 9 h sol it is estimated that the uncertainty in $R_E$ and $R_D$ is each about $4\%$. Thus for the 9 h sol it is considered that the values of $\mu$ and $\sigma$ determined from equation (25) are less reliable than those determined from equations (23).

For the 20 h sol the distribution parameters could be determined by the three methods for comparison of results. It was found that the percentage variation of $\mu$ and $\sigma$ with variation of experimental parameters was about the same with employment of either equation (23) or equation (24), and for both cases much less than with equation (25) for variation of the values of $R$. Of the experimentally determined parameters for this sol, it is estimated that the largest uncertainty is in the values of $K'$ [equation (27)], with an uncertainty of about $10\%$. Since $V_D$ is much less sensitive to error in $K'$ than is $P$, it is thus concluded that the most reliable values of $\mu$ and $\sigma$ should be obtained through employment of equations (24).

The distribution function obtained for the 20 h sol for those values of $\mu$ and $\sigma$ as determined by equations (24) is shown in Fig. 4, where the fraction of the particles, $F(R)$, is plotted as a function of their spherical radii, $R$. Also shown in this Figure are the smallest particle sizes as well as the largest particle sizes observed in electron micrographs of the evaporated sol. The agreement appears excellent. The approximate average radius size as estimated from these micrographs is also indicated in Fig. 4, as well as the arithmetic mean, $R$, as determined by equation (17). Again the agreement is considered very good and within the uncertainty of the micrograph value of the average.

The distribution functions obtained for the 20 h sol by employment of the $\mu$ and $\sigma$ parameters are shown in Fig. 5 as obtained from equations (23) (curve A), equations (25) (curve B) and equations (24) (curve C). It is evident that curve C shows a distribution which is in closest agreement with the electron-micrograph results, although even the agreement shown by curves A and B must be considered reasonable. However, with employment of the original value of $K'=665$ obtained without correction of the scattering data (Fig. 3) for evaluation of $P$, the values of the distribution parameters determined by equations (23) are $\mu=60.5$ Å and $\sigma=1.46$ Å. These values yield a size distribution centered at much lower $R$ values than observed, and they indicate the magnitude of the error which may occur when the Porod constant cannot be accurately determined.

In Fig. 6 are shown the size distribution functions obtained for the 9 and 20 h sols with the employment of the $\mu$ and $\sigma$ values determined by equation (23). The relative variation in the number density of particles between the 20 h sol, $N_{20}$, and the 9 h sol, $N_{9}$, was determined from equation (15) with these data, employing the relationship

$$\ln \left[ \frac{\langle R_E^2 \rangle}{\langle R_D^2 \rangle} \right] = 18[\ln^2 \sigma_1 - \ln^2 \sigma_2] + 6[\ln \mu_1 - \ln \mu_2]. \quad (29)$$

The result is $N_{20}/N_{9}=0.63$, which suggests that for the reflux time between 9 and 20 h particle coarsening or agglomeration is the predominant process.

Finally, we note that in the SAXS study of ThO$_2$ sols made by Schmidt (1965a), a value for the radius of gyration of his $\neq 500$ sol was obtained which yielded a much larger particle dimension than the dimensions derived from the other SAXS data. Schmidt therefore concluded that the value of this radius of gyration was possibly in error. However, from the values of $V_P$ and $R^2$ which he reported, with the assumption of spherical particles we calculate $V_D=0.523 \times 10^6$ and $R_D=163$. With these values, from equation (24) we then obtain $\mu=22.7$ Å and $\sigma=1.70$ Å. These parameters yield a size distribution function which appears to be quite reasonable and compatible with his other results. This points out that it may be misleading to
employ only the Guinier radius rather than the entire size distribution for purposes of interpretation.

Conclusions

The results obtained indicate that the employment of suitable parameters obtained solely from experimental SAXS data will yield particle-size distributions which are in excellent agreement with those determined by electron microscopy. The SAXS results further indicate that during the precipitation of the ThO₂ sol, the actual particle-size distribution may be closely approximated by a log normal distribution.

It is further concluded that the HGH procedure will yield a fair-size distribution function for the precipitating ThO₂ sols only if a suitable correction is applied during the evaluation of the Porod constant. A more accurate distribution function is obtained by determination of the volume parameter defined in the text. Finally, the simultaneous employment of the Guinier radii determined from both the experimental and desmeared SAXS curves, both of which can be determined very rapidly and accurately, can yield a distribution function which may be as accurate as that determined by the HGH procedure, but which is less accurate, however, than the more lengthy procedure employing the volume parameter.

The hydrous ThO₂ sols which were investigated were prepared and provided by C. P. Hansen. Mr Hansen also kindly provided the electron microscopy results which were discussed. Also thanks are due to T. J. Whitacre for carrying out the experimental work and for obtaining the X-ray scattering data.

References


X-ray Diffraction Studies of Alkali Halide Solutions

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Alkali halide aqueous solutions (LiCl, LiBr, NaCl, NaBr) have been investigated by X-ray diffraction in order to clarify the structural features of these systems (the existence of ordered local structures, their stability, geometry, etc.). The cation–H₂O interaction is particularly evident for the Li⁺ ions, for which a well resolved peak at 2.1 Å is apparent in the correlation function. It is shown that the ions give rise to a considerable disturbance of the solvent structure, in fact the ‘order range’ in the solutions appears to be shorter than in pure water. The high coordination numbers of the Cl⁻ and Br⁻ ions could be due to close packing of solvent molecules or hydrated cations around the anions.

Introduction

X-ray diffraction has often been used in studies of hydration phenomena in alkali halide solutions, particularly in connexion with the determination of the so-called coordination numbers (Brady, 1958; Lawrence & Kruh, 1967; Licheri, Piccaluga & Pinna, 1972). In the present paper we study some alkali halide solutions and examine in a more general way the problem of the structure of these systems: the existence of ordered local structures, their stability, geometry and resolution with different structural techniques. The last question is extremely interesting, because in our opinion, unless it is carefully considered diffractometric information can be used incorrectly.

Experimental

In Table 1 we report the analytical data of the solutions studied. The temperature of the samples was 24 ± 1 °C.

Table 1. Normality N, and molar salt content, expressed as x in the composition (AB)ₓ·(H₂O)_{1-x} of the solutions studied

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<th>AB</th>
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