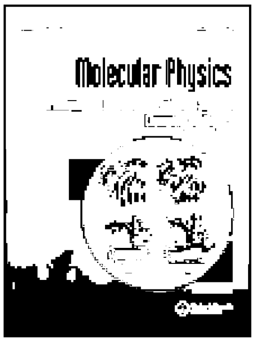

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Neutron diffraction studies of tetrachloride liquids

IV. The molecular beat effect for $TiCl_4/SiCl_4$ and $TiCl_4/SnCl_4$ mixtures

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Neutron diffraction measurements of mixtures of $TiCl_4/SiCl_4$ and $TiCl_4/SnCl_4$ liquids have been made using the total scattering spectrometer of the Harwell Electron Linac. The high Q-value (5–20 Å^{-1}) data exhibit a beat effect and have been analysed in terms of summed molecular form factors. The bond-length parameters are found to be in good agreement with other values and confirm the treatment adopted in the analysis of the data for the pure liquids.

1. Introduction

Tetrachloride liquids are of interest from the structural viewpoint as the molecule is non-spherical but possesses a high degree of symmetry. Various diffraction techniques can be used to obtain the liquid structure factor but one of the most effective methods is thermal neutron scattering. Previous papers in this series [1–3] have emphasized the two basic methods using both steady-state (reactor) and pulsed (linac) neutron facilities. One of the main advantages of the pulsed neutron method results from measurements over a wide Q-value region which enables the molecular form factor $f_1(Q)$ and the intra-molecular bond lengths to be determined to high precision. In paper III, results were presented [3] for the liquids CCl_4, $SiCl_4$, $TiCl_4$, $GeCl_4$ and $SnCl_4$ and these showed that several parameters used in the fit to $f_1(Q)$ needed to be varied in order to obtain satisfactory χ^2-minima. The structural parameters (r_{XCl}) representing the bond length from the chlorine to the central atom was found to be relatively insensitive to the wavelength dependent parameters describing the vibrational motion of the molecule.

In certain cases, it is useful to study liquid mixtures and this technique can be applied successfully to mixtures of tetrachloride liquids, particularly those involving $TiCl_4$ as the negative scattering length of titanium leads to partial cancellation of some interference terms in the diffraction pattern. Preliminary reactor data for special $TiCl_4/SiCl_4$ and $TiCl_4/SnCl_4$ mixtures have been reported

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separately [4] and the present paper concerns an analysis of linac data for the same liquid mixtures.

2. THEORY

The basic theory has been presented in earlier papers and review papers by Powles [5] and Blum and Narten [6]. The measured cross-section is related to the liquid structure factor $S_m(Q)$ which may be divided into the intra-molecular form factor $f_1(Q)$ and the inter-molecular function $D_M(Q)$. At high Q-values the $D_M(Q)$ term is negligible so that the diffraction pattern is characterized by the scattering from an individual molecular unit. For a tetrachloride unit XCl_4, the molecular form factor [5] may be written as

$$f_1(Q)=\frac{1}{(b_X+4b_{Cl})^2}\,[b_X{}^2+4b_{Cl}{}^2+8b_Xb_{Cl}j_0(Qr_{XCl})\exp\left(-\gamma_{XCl}Q^2\right)$$
$$+12b_{Cl}{}^2\,j_0(Qr_{ClCl})\exp\left(-\gamma_{ClCl}Q^2\right)], \qquad (2.1)$$

where b_{Cl} and b_X are the respective coherent scattering lengths for the chlorine and central atoms, r_{XCl} is the bond length with $r_{ClCl}=2\sqrt{\frac{2}{3}}r_{XCl}$ for tetrahedral symmetry and the γ_{XCl} and γ_{ClCl} parameters arise from the vibrational motion. In the analysis of pulsed neutron data obtained for several tetrachloride liquids it was found that the measured cross-section required the use of wavelength dependent γ-factors which could be represented by

$$\gamma=\gamma_0(\alpha+k_\lambda\lambda^n), \qquad (2.2)$$

where γ_0 is proportional to the mean-square amplitude of vibration. The value of α was approximately unity and n was $1{\cdot}8\pm0{\cdot}3$; the k_{XCl} values were approximately 1·9 but the k_{ClCl} values showed more variation (see table 1). The χ^2-fitting procedure gave well-defined values for the r_{XCl} term and these were found to be relatively insensitive to the other parameters.

Table 1. Parameters obtained for neutron diffraction from various tetrachloride liquids [3].

	$TiCl_4$	$SiCl_4$	$SnCl_4$
r_{XCl}/Å	2·169	2·014	2·286
b_X/fm	−3·37	4·149	6·22
w_{Ti}	—	0·552	0·649
$\gamma_{0,XCl}10^3$/Å^2	1·095	1·071	1·053
$\gamma_{0,ClCl}10^3$/Å^2	6·486	3·882	7·284
k_{XCl} (150°)	2·2	1·8	1·9
(90°)	1·6	1·7	1·8
k_{ClCl} (150°)	0·7	1·4	0·6
(90°)	1·0	0·9	0·8

In the case of a liquid mixture the diffraction pattern at high Q-values will depend on the contributions from the separate molecular units. If there is no exchange or association, the effective form factor for the mixture $f_1{}^{\alpha\beta}(Q)$ will be the weighted sum of the two components, i.e.

$$f_1{}^{\alpha\beta}(Q)=w_\alpha f_1{}^\alpha(Q)+w_\beta f_1{}^\beta(Q), \qquad (2.3\,a)$$

where the relative proportions of the XCl_4 and YCl_4 molecules are given by w_α and w_β respectively with $w_\alpha + w_\beta = 1$. The observed cross section per tetrahedral unit can therefore be written as

$$\left(\frac{d\sigma}{d\Omega}\right)^{\alpha\beta}_{\text{self}} + \left(\frac{d\sigma}{d\Omega}\right)^{\alpha\beta}_{\text{int}} = \left(\frac{d\sigma}{d\Omega}\right)^{\alpha\beta} = w_\alpha \left(\frac{d\sigma}{d\Omega}\right)^{\alpha} + (1-w_\alpha)\left(\frac{d\sigma}{d\Omega}\right)^{\beta}. \qquad (2.3\,b)$$

We may now expand this expression using the relation (2.1) and find that the self-terms give

$$\left(\frac{d\sigma}{d\Omega}\right)^{\alpha\beta}_{\text{self}} = 4b_{\text{Cl}}{}^2 + w_\alpha b_{\text{X}}{}^2 + w_\beta b_\gamma{}^2 + \frac{1}{4\pi}\,[4\sigma_{\text{Cl}}{}^i + w_\alpha \sigma_{\text{X}}{}^i + w_\beta \sigma_{\text{Y}}{}^i], \qquad (2.4\,a)$$

where σ^i represents the total bound-atom incoherent scattering cross-section and (after collecting corresponding terms) the interference expression becomes

$$\begin{aligned}\left(\frac{d\sigma}{d\Omega}\right)^{\alpha\beta}_{\text{int}} &= 8b_{\text{Cl}}[w_\alpha b_{\text{X}} j_0(Qr_{\text{XCl}}{}^\alpha)\exp(-\gamma_{\text{XCl}}{}^\alpha\, Q^2) - w_\beta b_{\text{Y}} j_0(Qr_{\text{YCl}}) \\ &\quad \times \exp(-\gamma_{\text{YCl}}{}^\beta\, Q^2)] + 12b_{\text{Cl}}{}^2[w_\alpha j_0(Qr_{\text{ClCl}}{}^\alpha)\exp(-\gamma_{\text{ClCl}}{}^\alpha\, Q^2) \\ &\quad - w_\beta j_0 \exp(-\gamma_{\text{ClCl}}{}^\beta\, Q^2)]. \qquad (2.4\,b)\end{aligned}$$

If one of the scattering lengths b_{X} or b_{Y} is negative we may choose the proportions to satisfy the conditions $w_\alpha b_{\text{X}} = -w_\beta b_{\text{Y}}$ and the expression simplifies to

$$\begin{aligned}\left(\frac{d\sigma}{d\Omega}\right)^{\alpha\beta}_{\text{int}} &= 8w_\alpha b_{\text{X}} b_{\text{Cl}} \exp(-\gamma_{\text{XCl}} Q^2)[j_0(Qr_{\text{XCl}}) - j_0(Qr_{\text{YCl}})] \\ &\quad + 12 w_\alpha b_{\text{Cl}}{}^2 \exp(-\gamma_{\text{ClCl}} Q^2)[j_0(Qr_{\text{ClCl}}{}^\alpha) - b_{\text{X}/b\text{Y}}\, j_0(Qr_{\text{ClCl}}{}^\beta)], \qquad (2.4\,c)\end{aligned}$$

where it has been assumed that the γ-factors describing the effects due to the vibrational motion of the two molecular species are of similar magnitude and have the same variation with incident neutron energy. The previous analysis [3] indicated that there was some variation in the k_{XCl} values for different tetrachloride molecules but the differences have a negligible effect on the differential treatment adopted here (see § 5).

The relative size of two molecules has a direct influence on the two combined terms. When the bond lengths are identical ($r_{\text{XCl}} = r_{\text{YCl}}$), the first term disappears and the second term becomes $12b_{\text{Cl}} \exp(-\gamma_{\text{ClCl}} Q^2) j_0(Qr_{\text{XCl}})$ which is equivalent to isomorphous replacement of the X and Y atoms with $\bar{b}_{\text{X}} = 0$. If the bond lengths are different, the periodicity of the oscillations is unequal and the relative phase angle of corresponding oscillations changes as the Q-value increases.

At low Q the ClCl contributions are in phase and therefore give the usual oscillatory form but as the Q-value is increased the relative phase of the two terms grows until the oscillations are out of phase. This partial cancellation condition occurs when

$$Qr_{\text{XCl}} = Qr_{\text{YCl}} \pm n\pi$$

which is at a Q-value given by

$$[Q_0]_{\text{ClCl}} = \frac{n\pi}{\Delta r_{\text{ClCl}}},$$

where

$$\Delta r = r_{\mathrm{XCl}} - r_{\mathrm{YCl}}$$

and

$$\Delta r_{\mathrm{ClCl}} = 2\sqrt{\tfrac{2}{3}}\Delta r.$$

At this point there will be a reduction in the amplitude of the composite pattern and the combined terms will produce a molecular beat effect due to the two different periodicities. A similar situation will occur for the X/YCl contributions but these are initially out of phase due to the choice of $w_\alpha b_{\mathrm{X}} = w_\beta b_{\mathrm{Y}}$ and therefore cancel at low Q-values. The result is that both contributions have an oscillatory form which is modulated by a function that depends on the respective bond length differences. This behaviour is illustrated in figure 1 for a mixture consisting of rigid molecules ($\gamma = 0$) of $\mathrm{TiCl_4}$ and $\mathrm{SiCl_4}$ ($\Delta r = -0{\cdot}155$ Å; $\Delta r_{\mathrm{ClCl}} = -0{\cdot}253$ Å) in the required proportions ($\alpha = 0{\cdot}552$). The top two curves show the combination of terms for the XCl and ClCl interference functions

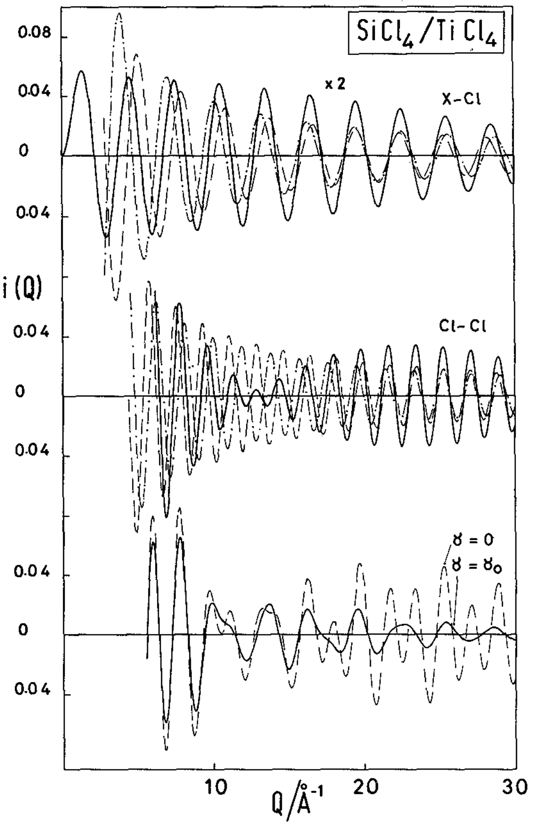

Figure 1. Interference components of the $f_1^{\alpha\beta}(Q)$ form factor for a mixture of rigid ($\gamma = 0$) tetrachloride molecules ($\mathrm{SiCl_4/TiCl_4}$) with $w_{\mathrm{Ti}} = 0{\cdot}552$ (eqn. 2.4 *c*). The top two curves show the XCl and ClCl contributions which sum to give the dashed line of the bottom curve; the effect of introducing thermal vibrations ($\gamma = \gamma_0$) is indicated by the full line in the bottom curve.

respectively and these are combined together to produce the dotted line in the lower curve. If the vibrational effects are incorporated by the inclusion of the appropriate static Debye–Waller factors, γ_0, (see table 1) the solid line in the lower curve is produced. Since the vibrational amplitude is quite large for tetrachloride liquids at room temperature the interference pattern is rapidly damped at high Q-values and the higher order modulation effects are difficult to observe experimentally. Measurements on $TiCl_4/SiCl_4$ and $TiCl_4/SnCl_4$ mixtures were initially made using the reactor technique [4, 7] and gave diffraction patterns which confirmed these predictions but did not have sufficient accuracy for a detailed analysis to be made. It was therefore of considerable interest, to use linac facilities to study the effect, as it is known [8] that this is the most efficient method for neutron data acquisition in the high Q-value region ; a preliminary report of the measurements has been presented earlier [7].

3. EXPERIMENTAL PROCEDURE

The measurements were made on the total-scattering spectrometer (TSS) of the Electron Linac at AERE, Harwell. The liquid mixtures were held in a thin walled vanadium flat plate container of 4 mm thickness mounted at 45° to the incident beam. The same procedure was adopted as described in the first paper [1] of this series and the data were taken during the same experimental period as the measurements on the pure liquids CCl_4, $SiCl_4$, $TiCl_4$, $GeCl_4$ and $SnCl_4$ which were presented [3] in paper III. The data reduction was carried out in a similar manner using the LINDA program [8] ; the normalized cross-sections for the 150° and 90° detectors are shown in figure 2.

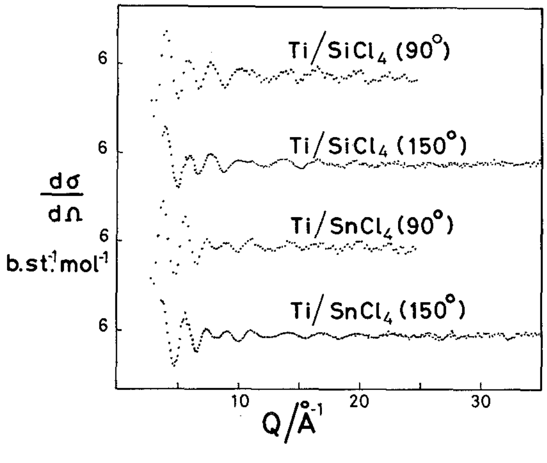

Figure 2. The observed differential scattering cross-section for $TiCl_4/SiCl_4$ ($w_\alpha = 0{\cdot}552$) and $TiCl_4/SnCl_4$ ($w_\alpha = 0{\cdot}649$) mixtures at 150° and 90° scattering angles.

4. DATA ANALYSIS

In § 3, the form factor was derived for ideal conditions but in practice the variations of the γ-factors has an important effect on the shape of the observed differential cross-sections at high Q-values. The data for the mixture therefore provide an important consistency check on the procedures established for the analysis of the pure liquids. It is convenient to regard the $TiCl_4$ as a reference system (X) and the beat effect arises from a variation in the molecular size which is represented by the parameter $\Delta r = r_{TiCl} - r_{YCl}$ where Y is either Si or Sn. We may simplify further by using the approximate value, $n = 2$ in equation (2.2) so that the damping factor now becomes

$$\exp(-\gamma Q^2) = F \exp(-\gamma_0 Q^2), \tag{4.1 a}$$

where F is a constant for each term given by

$$F = \exp[-\gamma_0 (4\pi)^2 k^2 \sin^2 \theta/2]. \tag{4.1 b}$$

Under these conditions the interference part of the cross-section for the mixture can be written in a suitably parameterized form as

$$\begin{aligned}\left[\frac{d\sigma}{d\Omega}\right]_{\text{int}}^{\alpha\beta} = {} & 8w_\alpha b_X b_{Cl}(A_1 F_{XCl}{}^{\alpha}) \\ & \times \left\{ j_0(Qr_{XCl}) - j_0[Q(r_{XCl} + \Delta r_{XY})] \cdot \frac{F_{YCl} \exp \Delta\gamma_{XCl} Q^2}{F_{XCl}{}^{\alpha} \exp(-\gamma_{0XCl} Q^2)} \right\} \\ & + 12 w_\alpha b_{Cl}{}^2 (A_2 F_{ClCl}{}^{\alpha}) \left\{ j_0(2\sqrt{\tfrac{2}{3}} Q r_{XCl}) - \frac{b_X}{b_Y} j_0[2\sqrt{\tfrac{2}{3}} Q (r_{XCl} \right. \\ & \left. + \Delta r_{XY})] \cdot \frac{F_{ClCl}{}^{\beta} \exp \Delta\gamma_{ClCl} Q^2}{F_{ClCl}{}^{\alpha} \exp(-\gamma_{0ClCl} Q^2)} \right\},\end{aligned} \tag{4.2}$$

where the normalization constants A_1 and A_2 can be combined with the F^{α} parameters to appear as scale factors. Unfortunately the compound expression involving the $(r_{XCl} + \Delta r)$ terms cannot be reduced to a simpler analytic form in order to emphasize the modulation effect on the diffraction pattern.

The results for the pure liquids have been presented earlier (table 1) and the relevant additional numerical values required for analysis of data for the mixtures are given in table 2. The effect of the different Debye–Waller factors

Table 2. Functional constants describing the thermal vibration effects (e.g. 4.2) for special mixtures of $TiCl_4$ with $SiCl_4$ and $SnCl_4$.

	θ/deg	Ti/$SiCl_4$		Ti/$SnCl_4$
$A_1 F_{XCl}{}^{\alpha}$	150		0·702	
	90		0·871	
$R_{XCl}{}^{F} = F_{YCl}{}^{\beta}/F_{ClCl}{}^{\alpha}$	150	1·074		1·062
	90	0·995		0·988
$\gamma_{XCl}{}^{0}$/Å^2			$1{\cdot}095 \times 10^{-3}$	
$\Delta\gamma_{XCl}{}^{0}$/Å^2		$+0{\cdot}024 \times 10^{-3}$		$+0{\cdot}042 \times 10^{-3}$
$A_2 F_{ClCl}{}^{\alpha}$	150		0·512	
	90		0·599	
$R_{ClCl}{}^{F} = F_{ClCl}{}^{\beta}/F_{ClCl}{}^{\alpha}$	150	0·877		1·025
	90	1·267		1·053
$\gamma_{ClCl}{}^{0}$ 10^3/Å^2			6·486	
$\Delta\gamma_{ClCl}{}^{0}$ 10^3/Å^2		+2·604		−0·798

is represented by the ratios $R_{XCl}{}^F = F_{YCl}{}^\beta / F_{XCl}{}^\alpha$ and $R_{ClCl}{}^F = F_{ClCl}{}^\beta / F_{ClCl}{}^\alpha$ which differ from unity.

The X^2-fitting procedure was carried out as described previously and the results are shown in table 3. In the first run (case (*a*)) only the Δr parameter was allowed to vary and the known values of r_{TiCl}, $R_{XCl}{}^F$ and $R_{ClCl}{}^F$ were used. In the further runs (cases (*b*) and (*c*)) the three additional parameters were also allowed to vary but in no case did this lead to any significant reduction of X^2. The results for the $TiCl_4/SnCl_4$ mixtures were in good agreement with predictions from table 2 ; the 150° data gave consistent results to an accuracy of $\pm 0{\cdot}001$ Å whereas the 90° data showed a variation of $-0{\cdot}004$ Å in Δr which was partially compensated by a shift of $+0{\cdot}006$ Å in r_{TiCl}. Similar features were present in the $SiCl_4/TiCl_4$ results although the 150° data show a larger deviation of $\pm 0{\cdot}006$ Å. If it is assumed the r_{TiCl} may be fixed at a constant reference value [3] of 2·169 Å, which also agrees with the electron diffraction results [11], the values of Δr may be used to give the bond lengths for $SiCl_4$ and $SnCl_4$. The accuracy of the Δr determination is shown by the X^2-variation illustrated in figure 3. Using a 10 per cent change in X^2 as the error criteria gives the bond length values and uncertainties listed in table 4. The consistency of the results suggests that the criteria adopted here gives an overestimate of the error values.

Table 3. Parameters given by the χ^2-fitting procedure for data on $Ti/SiCl_4$ and $Ti/SnCl_4$ mixtures : *denotes a fixed value, see text for details.

θ Q Range	Run	r_{TiCl}/Å	Δr/Å	$R_{XCl}{}^F$	$R_{ClCl}{}^F$	χ^2
			Si/Ti			
150°	(*a*)	2·169*	−0·149	1·0735*	0·8765*	19·48
(7–23·9 Å^{-1})	(*b*)	2·169*	−0·150	1·309	0·953	17·51
	(*c*)	2·160	−0·143	1·309*	0·862	16·71
90°	(*a*)	2·169*	−0·154	1·467	1·172	106·5
(7–17·9 Å^{-1})	(*b*)	2·157	−0·145	1·467*	1·044	104·6
150°	(*a*)	2·169*	0·119	0·991	1·298	8·31
(7–23·9 Å^{-1})	(*b*)	2·167	0·20	0·991	1·358	8·27
			Sn/Ti			
90°	(*a*)	2·169*	0·125	0·798	1·312	50·21
(7–17·9 Å^{-1})	(*b*)	2·174	0·122	0·798*	1·170	49·98

The final fit to the 150° data for the $TiCl_4/SnCl_4$ mixture is shown in figure 4 which also includes the data points for the summed diffraction patterns [3] of the two pure liquids with appropriate weighting factors. The agreement between the two data sets is excellent and, although the quality of the fit is very good, it shows that there are some regions where significant systematic deviations from both experimental measurements can be observed ; the 12·5–15·0 Å range shows the differences most clearly. This suggests that a further refinement of the analysis procedure may be possible when a more comprehensive theoretical

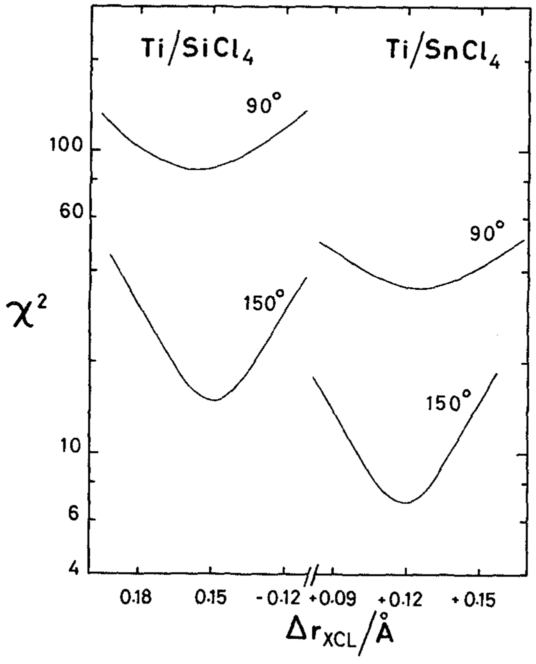

Figure 3. The χ^2-variation for the relative bond length parameter Δr in the fits to $f_1^{\alpha\beta}(Q)$

Table 4. A comparison of bond length values for $SiCl_4$ and $SnCl_4$ obtained using different techniques.

Sample	r_{SiCl_4}/Å	Reference	r_{SnCl_4}/Å	Reference	Method
Pure liquids	2·018 ±0·003	[8]	2·281 ±0·004	[10]	e^-
	2·014 ±0·004	[3]	2·284 ±0·006	[3]	n/150°
	2·013 ±0·009	[3]	2·289 ±0·011	[3]	n/90°
Liquid mixtures	2·015 ±0·009	This paper	2·284 ±0·009	This paper	n/150°
	2·013 ±0·018	This paper	2·292 ±0·019	This paper	n/90°

treatment of the neutron scattering process is established. The agreement of parameter values and observed diffraction patterns for the mixtures and pure liquids provides a satisfactory confirmation of the analysis procedures adopted in the earlier papers [1, 3]. The accuracy of the bond length determination is finally limited only by the low statistics in the high-Q region of the diffraction pattern. The availability of new pulsed neutron facilities [12] should enable the

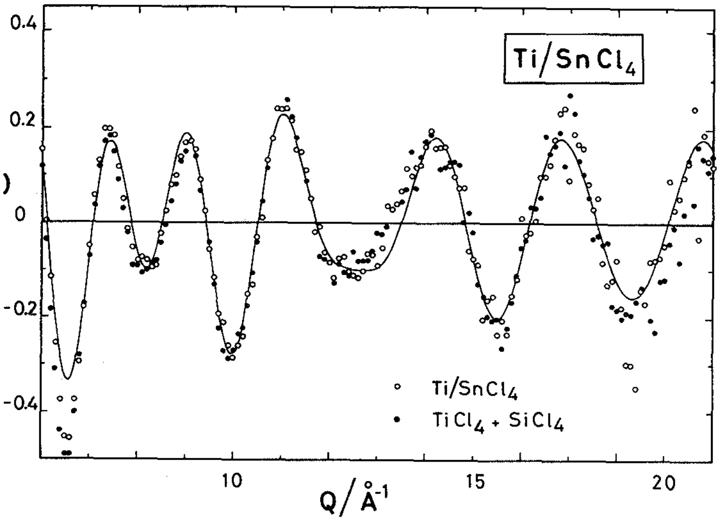

Figure 4. Comparison of the fitted curve, $f_1^{\alpha\beta}(Q)$ to the experimental data at 150° for the $TiCl_4/SnCl_4$ mixture and the combined measurements for $TiCl_4$ and $SnCl_4$ pure liquids [3].

counting statistics to be greatly improved with a consequent reduction in the error values. The reference treatment therefore enables the bond lengths to be put on an absolute scale without some of the problems associated with recoil corrections that were discussed earlier [1].

5. Conclusions

The measurements have demonstrated that diffraction studies of mixed molecular systems can be undertaken and that modulation effects in the diffraction pattern are produced if the molecules are of similar structure. The present experiments have been conducted on samples containing nuclei with negative scattering lengths (Ti) and this has resulted in a simplified diffraction pattern due to cancellation effects in the coherent scattering. The extraction of structural information in the form of bond length differences has been shown to give results that are in agreement with data obtained from a full analysis of the diffraction measurements of the pure liquids. This procedure minimizes the problems encountered in accurately characterizing the energy dependence of the vibrational damping factor and the possible recoil corrections. The method is likely to have wider applications, particularly in the study of more complicated molecular structures where the two components are of very similar structure. The use of materials with negative coherent scattering lengths is not essential for the successful application of the method as difference function procedures, more often applied to isotopic studies, can also be used for the high Q-value region if adequate counting statistics are achieved. It is anticipated that this method will be of relevance to systems where the molecular conformation is more variable and may possibly be used to study structural change caused by temperature and pressure variation. The method may also be applied to chemical systems in which structural changes due to solvent interactions are important.

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[12] HOBBIS, L. C. W., REES, G. H., and STIRLING, G. C. (editors), 1977, Rutherford Lab. Report RL-77-064/C ; this proposed facility has now been financed and construction has started.