Neutron Diffraction Studies of Tetrachloride Liquids †

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Neutron diffraction measurements are reported for VCl_4, CCl_4, $SiCl_4$, $TiCl_4$, $GeCl_4$, $SnCl_4$ and special mixtures of $TiCl_4 + SiCl_4$ and $TiCl_4 + SnCl_4$ using both reactor (steady-state) and linac (pulsed) neutron techniques. Information is extracted for the molecular structure and, in certain cases, for the real-space distribution function of the chlorine atoms.

Neutron diffraction has become an established technique for studying the structural properties of liquids. The earlier measurements on simple monatomic fluids have continued through studies of homonuclear diatomic liquids to experiments on more complex molecular systems. The observed diffraction pattern extends over a wide range of momentum transfer values (typically $Q \sim 0.1$-40 Å^{-1}) due to the contribution from the molecular unit and contains a complicated structure in the low Q-value region ($Q \sim 0.1$-10 Å^{-1}) due to the intermolecular effects arising from correlation of orientation between neighbouring molecules. Current interest in the simulation of liquids by Monte Carlo, molecular dynamics or RISM computations therefore provides motivation for examining the structural properties by direct experimental methods.

Molecules possessing tetrahedral symmetry are the simplest systems in three dimensions possessing a high degree of symmetry. In this respect, the tetrahedral liquids represent a convenient range of materials for systematic study. The properties are listed in table 1 giving relevant structural, physical and neutron scattering information.

Table 1.—Physical constants for various tetrachloride liquids; (ρ_N is the molecular number density).

sample (XCl_4)	$\bar{b}_X$/ fm	r_{XCl}/ Å	ρ/ g cm^{-3}	M/ a.m.u.	ρ_N/ Å^{-3} × 10^{-3}
CCl_4	6.65	1.77	1.59	154	6.18
$SiCl_4$	4.15	2.02	1.48	170	5.21
$TiCl_4$	−3.37	2.17	1.73	190	5.45
VCl_4	−0.41	2.14	1.82	193	5.65
$GeCl_4$	8.19	2.11	1.84	215	5.12
$SnCl_4$	6.22	2.28	2.28	261	5.23

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GENERAL THEORY

The structure factor for a molecular liquid may be written in the form[1]

$$S_m(Q) = \left(\sum_n b_n\right)^{-2} \langle|\sum_n b_n \exp(iQ \cdot r_n)|^2\rangle + N_m^{-1}\left(\sum b_n\right)^{-2} \sum_{\text{inter}}^{N_M} b_i b_j \langle \exp iQ \cdot r_{ij}\rangle$$

where b_i represents the coherent neutron scattering amplitude from the ith nucleus and N_M is the total number of molecules in the system; the summation over n is for the n atoms in the molecule and that over i and j includes all pair contributions to the scattered intensity from different molecules where the exponential phase factors depend on the relative position vector r_n and r_{ij}. The expression is equivalent to separate intra- and intermolecular contributions such that

$$S_m(Q) = f_1(Q) + D_M(Q) = \frac{\sum b^2}{(\sum b)^2} \cdot S(Q)$$

where $f_1(Q)$ is a molecular form factor. For tetrachloride molecules of the form AB_4 this becomes

$$f_1(Q) = \frac{1}{(b_A + 4b_B)^2}[b_A^2 + 4b_B^2 + 8b_A b_B j_0(Qr_{AB}) \exp(-\gamma_{AB}Q^2) + 12_B^2 j_0(Qr_{BB}) \exp(-\gamma_{BB}Q^2)]$$

where r_{AB} is the molecular bond length ($r_{BB} = 2\sqrt{2/3}\, r_{AB}$) and γ is a constant related to the mean-square amplitude of vibration. $D_M(Q)$ is a function which depends on the time-averaged molecular arrangement in the liquid and therefore gives information on the liquid structure as compared with the molecular structure contained in $f_1(Q)$.

For the static approximation, the structure factor is simply related to the observed coherent differential scattering cross-section by

$$\frac{d\sigma}{d\Omega}(\theta, \lambda) = N_m \left(\sum^n b_n\right)^2 S_m(Q)$$

with

$$Q = \frac{4\pi}{\lambda} \sin \theta/2$$

where θ is the scattering angle and λ is the wavelength. In practice, the static approximation is inadequate for most neutron diffraction studies and corrections for inelasticity must be made. These were initially developed by Placzek and have been reviewed in various papers;[1–3] in the case of many molecular systems the application of the corrections is not unambiguously determined but satisfactory approximate procedures have been established.

EXPERIMENTAL

The conventional method of neutron diffraction study is to measure the scattering distribution from the sample using a monochromatic beam from a nuclear research reactor (*i.e.*, fixed λ, variable θ). Alternative methods[4] based on accelerator-driven sources have been developed during the last few years using time-of-flight methods (fixed θ, variable λ) with pulsed neutron beams. In the present series of experiments both methods were used and the results show that the application of both experimental and analytic corrections must be carefully considered if the structural information extracted from the data is to be of high precision. The reactor measurements were made on the hot-source diffractometer (D4) at the

Institut Laue-Langevin, Grenoble, France and the pulsed neutron measurements were made with the total-scattering spectrometer (TSS) at the Electron Linear Accelerator, Harwell, England.

RESULTS AND ANALYSIS

VANADIUM TETRACHLORIDE

It can be seen from table 1 that the coherent scattering amplitude for vanadium is negligibly small in comparison with that of chlorine. The measured diffraction pattern for VCl_4 is therefore dominated by neutron scattering from the chlorine nuclei, and the liquid is effectively a homonuclear system consisting of hollow tetrahedral units of chlorine atoms. The contributions to the structure factor are considerably simplified and the form-factor becomes

$$f_1(Q) = \frac{1}{4}\left[1 + 3\,\frac{\sin Qr_{\mathrm{ClCl}}}{Qr_{\mathrm{ClCl}}}\exp(-\gamma_{\mathrm{ClCl}}Q^2)\right]$$

which is a damped oscillatory wave of fixed periodicity. Since $D_M(Q)$ becomes small at high Q-values, the observed diffraction pattern enables the geometrical parameter r_{ClCl} to be extracted from the data using a χ^2-fitting procedure.

Measurements on a freshly-prepared sample of liquid vanadium tetrachloride in a thin-walled vanadium container were made on the D4 diffractometer using incident wavelengths of 0.5 and 0.7 Å. After correction for container scattering, absorption, multiple scattering and inelasticity (Placzek) effects the normalised structure factor was obtained. The results are shown in fig. 1(*a*) with a form-factor fitted to the data above a Q-value of 6 Å^{-1}. The values of r_{ClCl} obtained from the fit were 3.509 ± 0.015 Å (at 0.7 Å) and 3.484 ± 0.026 Å (at 0.5 Å) which compare satisfactorily with the quoted value of 3.485 ± 0.005 Å from electron diffraction.[5]

Subtraction of the computed $f_1(Q)$ curve enables the $D_M(Q)$ function to be calculated and, since this contains the intermolecular information, it is convenient to determine the real-space distribution by Fourier inversion. For this case, we may express the chlorine–chlorine intermolecular pair correlation function $g_{\mathrm{ClCl}}(r)$, as:

$$d_{\mathrm{ClCl}}(r) = 4\pi r\rho_{\mathrm{Cl}}[g_{\mathrm{ClCl}}(r) - 1] = \frac{8}{\pi}\int_0^{Q_{\max}} QD_M(Q)\sin Qr\,\mathrm{d}Q$$

where ρ_{Cl} is the chlorine number density. This function is shown in fig. 1(*b*) with both data sets superimposed. The agreement is excellent and the pattern exhibits well-defined oscillations extending to 15 Å. The first peak at 3.8 Å arises from chlorine atoms in close proximity and is in good agreement with the van der Waals radius of chlorine which is 1.8 Å. Integration of this peak shows that the number of intermolecular atoms is almost the maximum achieved in a close-packed arrangement, and this implies that there is a preference for an atom to be located in the hollow created by three atoms of the adjacent molecule. The peaks at larger distances exhibit a remarkably regular periodicity and it is difficult to see how this relatively simple pattern could be created by an arrangement of tetrahedral units. Clearly, there is a need for a more detailed examination by computer simulation and for further experiments using pulsed neutrons. Some results for liquid phosphorus which also consists of tetrahedral units (P_4) have been taken and give a substantially different pattern. Data have also been obtained for the distorted tetrahedral molecule $VOCl_3$.

CARBON TETRACHLORIDE

Liquid carbon tetrachloride has been studied by several workers using both neutron and X-ray diffraction methods. Since it is a two-component material, three partial

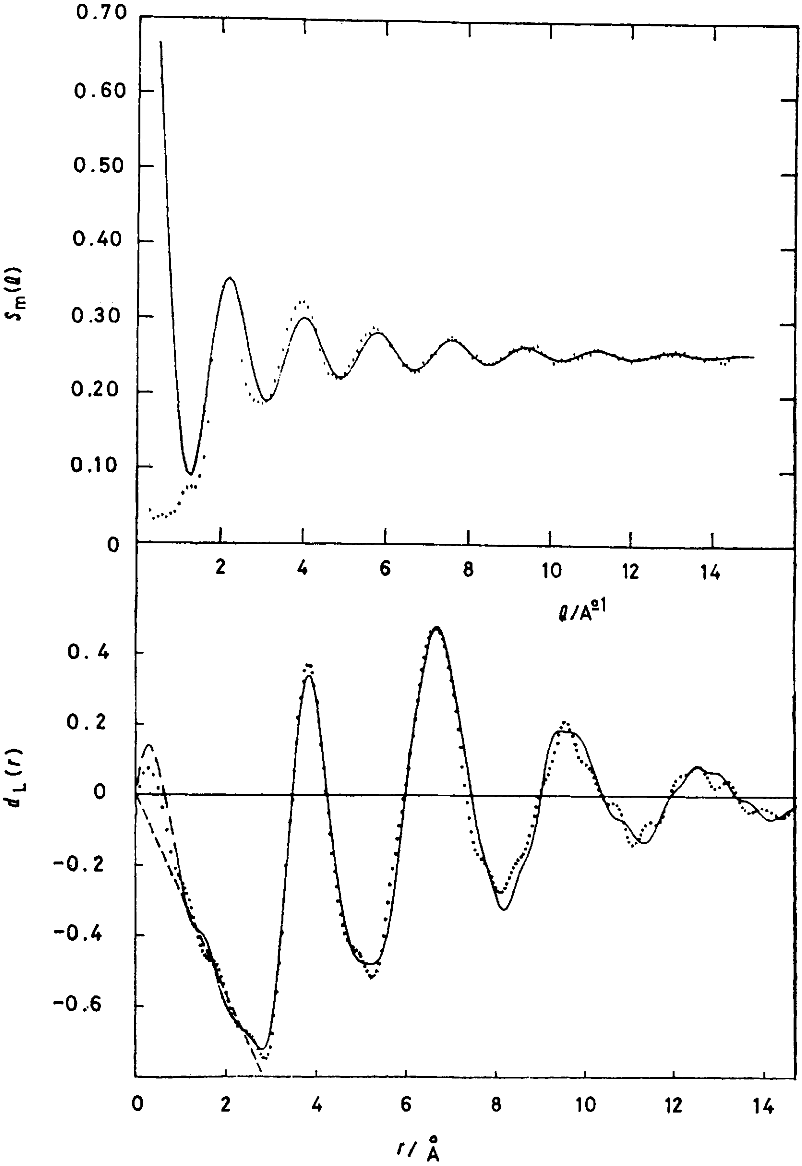

FIG. 1.—Neutron diffraction results for liquid VCl_4. (*a*) Observed diffraction pattern for liquid VCl_4. (*b*) Intermolecular $d_{ClCl}(r)$ distribution obtained from the transform of $D_M(Q)$ data taken at 0.5 and 0.7 Å wavelengths.

structure factors are required to characterise its structure but it is possible to extract useful information from two independent measurements as shown by Narten.[6] Neutron diffraction measurements have been made on liquid CCl_4 using the TSS instrument at the Harwell Linac; the corrected cross-section data for different scattering angles are shown in fig. 2. For this study, the available Q-range is large due to the high flux of epithermal neutrons in the pulsed neutron spectrum[4] so that the diffraction pattern corresponding to the molecular form-factor is well-defined and has visible oscillations extending to 30 $Å^{-1}$. Data in the low Q-value region are contained in the forward-angle detectors and the statistical accuracy is less than at higher angles due to the smaller solid angle, required to provide a suitable Q-resolution.

Comparison of the different data sets shows that the general shapes of the observed patterns are well reproduced in the overlap regions but the amplitudes of the oscillations are not in satisfactory agreement. The use of a conventional form factor is unable to give a fit to the 150° C data as the observed oscillations in the low-Q region have a much smaller amplitude than predicted. This type of behaviour is also observed for the other tetrachloride liquids that have been studied and indicates that the experimental interference function is dependent on the neutron wavelength. It was found that the Debye–Waller factor γ was responsible for this effect and that an improved fit could be obtained by writing

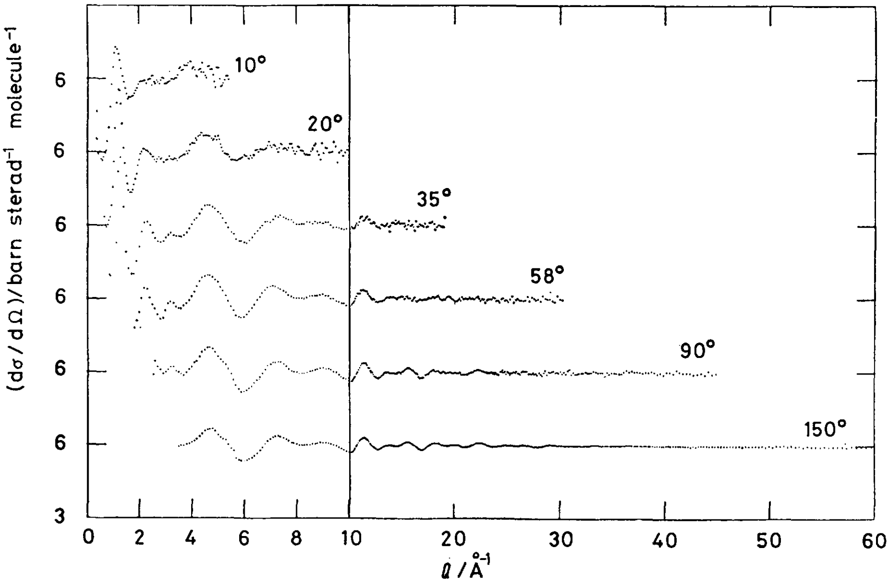

FIG. 2.—Observed diffraction data for liquid CCl_4 obtained at different scattering angles on the Harwell TSS.

$$\gamma = \gamma_0(\alpha_0 + k\lambda^n)$$

where $\gamma_0 = \frac{1}{2}\langle u^2\rangle$ is given by the mean-square amplitude of vibration $\langle u^2\rangle$, α_0 is a constant close to unity and k_λ and n are parameters responsible for the λ-dependence. This type of behaviour has also received some support from the theoretical analysis of inelasticity corrections for molecular gases by Powles.[3] Using this formalism, excellent fits could be achieved over the complete range as shown in fig. 3 where the sensitive function $Qi(Q)$ is displayed; $i(Q)$ is the oscillatory interference function obtained by subtracting the approximately constant contribution of the self-scattering terms from the observed cross-section. The fitted bond-length r_{CCl} was relatively insensitive to the other parameter values and gave the following values: 1.765 ± 0.002 (150°), 1.767 ± 0.006 (90°) and 1.771 ± 0.010 (58°). The combined value of 1.766 ± 0.002 Å is in excellent agreement with other values and shows that pulsed neutron diffraction is capable of determining molecular structure parameters for condensed systems to a high precision. This is a direct result of the short-wavelength neutrons in the epithermal region which permit the measurements to be extended well beyond the Q-values accessible with reactor beams even when a hot-source is used. This capability opens up many possibilities for further investigation and the availability of high intensity pulsed beams in the 1980's with a predicted factor of ×1000 increase over that used in these experiments indicates that the technique can be applied to many related areas.

Although the molecular parameters are well-determined there is inevitably an uncertainty about the extrapolation of the form-factor into the low-Q region. The ability to use this data to extract $D_M(Q)$ functions as for the reactor experiments is of particular importance but we are unable at present to make any definitive statements about this problem. It seems likely that the low statistical accuracy for the forward angle detectors does not enable sufficient information to be extracted from these measurements. This indicates that improved instrumentation will be needed to collect data in this Q-region or alternatively it will be necessary to devise suitable procedures for combining the reactor and linac results. Further work is proceeding in both of these directions.

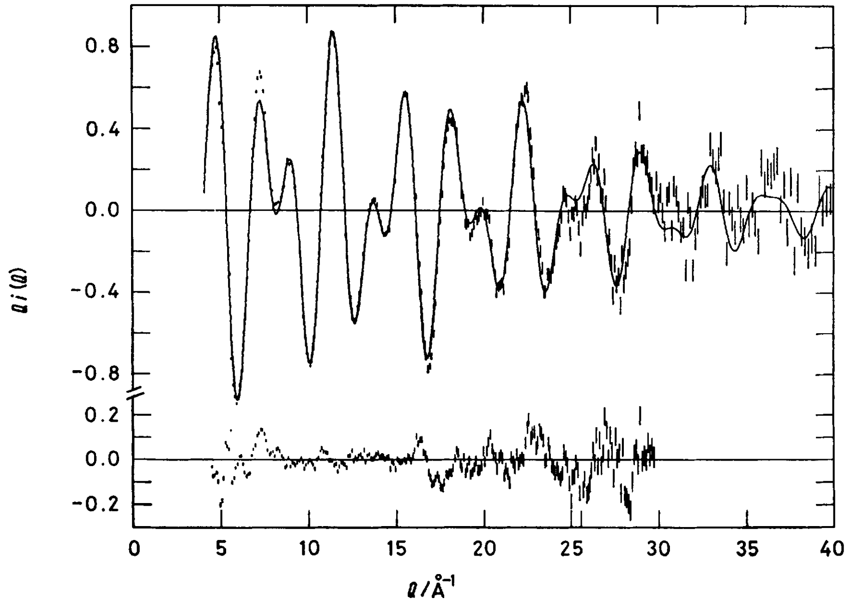

FIG. 3.—$Q_i(Q)$ fit to the 150°C data for CCl_4.

TETRACHLORIDE MIXTURES

The previous two sections have emphasised the complementary nature of the pulsed and steady-state diffraction methods. The simplification obtained for VCl_4 is attractive and presents an interesting possibility for exploitation in a different manner for some of the other liquids. It can be seen from table 1 that the geometrical structure of the molecules is very similar (except for CCl_4) and consequently the molecular arrangement in the liquid is expected to be similar. The major change in the observed diffraction patterns for different tetrachloride liquids arises from the b-value of the central atom which has a large variation (table 1). However, the fact that titanium has a negative b-value provides an opportunity to utilise cancellation effects for terms in the structure factor which involve the central atoms. This method is more familiar in the context of isotopic substitution where the effective b-value is compounded by summation over the individual components

$$\bar{b} = \sum w_i b_i$$

where w_i is a weighting factor. If a mixture of $TiCl_4$ and $SiCl_4$ is prepared, we may assume that this approximates to an isomorphous replacement of silicon and titanium atoms at the centre of each tetrahedral unit such that

$$\bar{b}_X = ab_{Ti} + (1 - \alpha)b_{Si}.$$

Choosing $\alpha = 0.557$ gives $\bar{b}_X = 0$ and the liquid mixture therefore approximates to an assembly of hollow tetrachloride molecules with two slightly different sizes. The effective form-factor will be the weighted sum of the individual $f_1(Q)$ functions, which may be expressed as:[7]

$$f_1(Q) = \alpha[f_1(Q)]_{TiCl_4} + (1 - \alpha)[f_1(Q)]_{TiCl_4}$$

and the interference contribution $i(Q) = S(Q) - 1$ becomes

$$\left(\sum_n b_n^2\right) i(Q) = 8\alpha b_\alpha b_{Cl} \exp(-\gamma_{Cl} Q^2)[j_0(Qr^\alpha_{Cl}) - j_0(Qr^\beta_{Cl})] + \\ + 12\alpha b^2_{Cl} \exp(-\gamma_{ClCl} Q^2)[j_0(Qr^\alpha_{ClCl}) - b_\alpha/b_\beta j_0(Qr_{ClCl})]$$

where the labels α and β represent the different components of the mixture and the difference in the Debye–Waller factors has been neglected.

Measurements have been made on special mixtures of $SiCl_4 + TiCl_4$ ($\alpha = 0.557$) and $SnCl_4 + TiCl_4$ ($\alpha = 0.648$) using the 0.5 Å beam on the D4 diffractometer. Fig. 4(*a*) shows the results for $SiCl_4 + TiCl_4$ with the fitted molecular form-factor. It can be seen that the $f_1(Q)$ curve is not a simple damped oscillatory curve but exhibits a " molecular beat " effect due to the difference in the r_{ClCl} values of the two components. This phenomenon can be more clearly seen in linac measurements on these mixtures and may be used to provide very accurate information on bond–length differences. The $D_M(Q)$ function can be evaluated in the same manner as for VCl_4 and has a similar shape; the $d_L(r)$ functions obtained by Fourier transformation are shown in fig. 4(*b*). The basic pattern is similar to that of fig. 1(*b*) but there are some interesting differences. In both cases, the first peak is located at 3.95 Å corresponding to two chlorine atoms in close proximity but is at a larger distance than in VCl_4. For the $SnCl_4 + TiCl_4$ mixture this peak is broader and of lower amplitude, which suggests that the molecules are less inter-locked than in the other cases. The second peak also occurs at a higher value for the mixtures and has a lower amplitude, which is a further indication that the disorder introduced by the packing of the different sized molecules has a direct effect on the distribution function. There is also some evidence for an asymmetric distortion of the peak shape but this could possibly arise from ripples introduced by the Fourier transform or the presence of residual terms involving the central atom contributions. Model simulations of these liquid mixtures would help to elucidate some of the problems regarding the interpretation of the data.

TETRACHLORIDE LIQUIDS

The pure tetrachloride liquids are of interest in themselves and the complete range have been studied with the TSS; several (three) have also been studied with the D4 diffractometer for a restricted Q-range (≤ 5 Å^{-1}). The cross-section results for the reactor measurements are shown in fig. 5(*a*). The sharp main peak occurs just above 2 Å^{-1} and is followed by a second broad oscillation at about 4 Å^{-1} where the maximum in the molecular form-factor occurs. Below 2 Å^{-1}, there are marked changes as $SiCl_4$ has a prominent pre-peak at 1.1 Å^{-1}; the corresponding peak for $SnCl_4$ is much smaller and is completely absent for $TiCl_4$; there is also evidence for a very minor peak in the VCl_4 data. The significance of these differences is difficult to assess as the behaviour shows no systematic correlation with molecular size or the *b*-value of the central atom. The low Q-value of this peak suggests that it is connected with some long-range behaviour as it represents an effective periodicity of 5.7 Å in real space. Fig. 5(*b*) shows a comparison of the cross-section data for the mixed tetrachlorides with corresponding data for an artificial mixture obtained by summing the experimental results for the separate components in the correct proportions. The two curves are in remarkably close agreement except for the low Q-value region. The differences are probably related to changes in the molecular orientation for each of the species but the information does not permit a simple interpretation and requires a more detailed analysis of the intermolecular terms for each system.

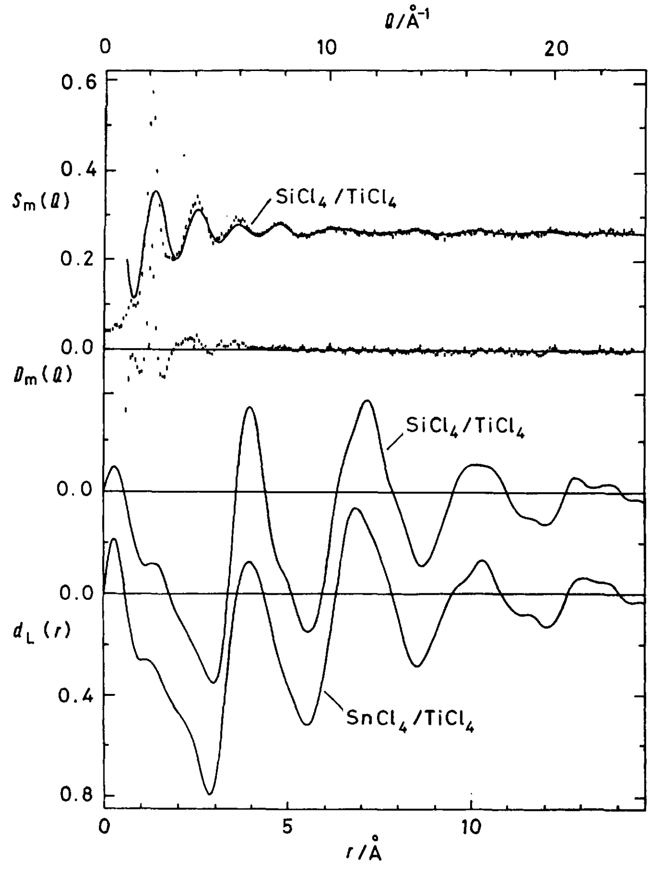

FIG. 4.—Neutron diffraction results for the $SiCl_4$ + $TiCl_4$ mixture. (*a*), $S_m(Q), f_1(Q)$ and $D_M(Q)$ data; (*b*), $d_L(r)$ function obtained from the transform of the $D_M(Q)$ data; the results for the $SnCl_4$ + $TiCl_4$ data are also shown.

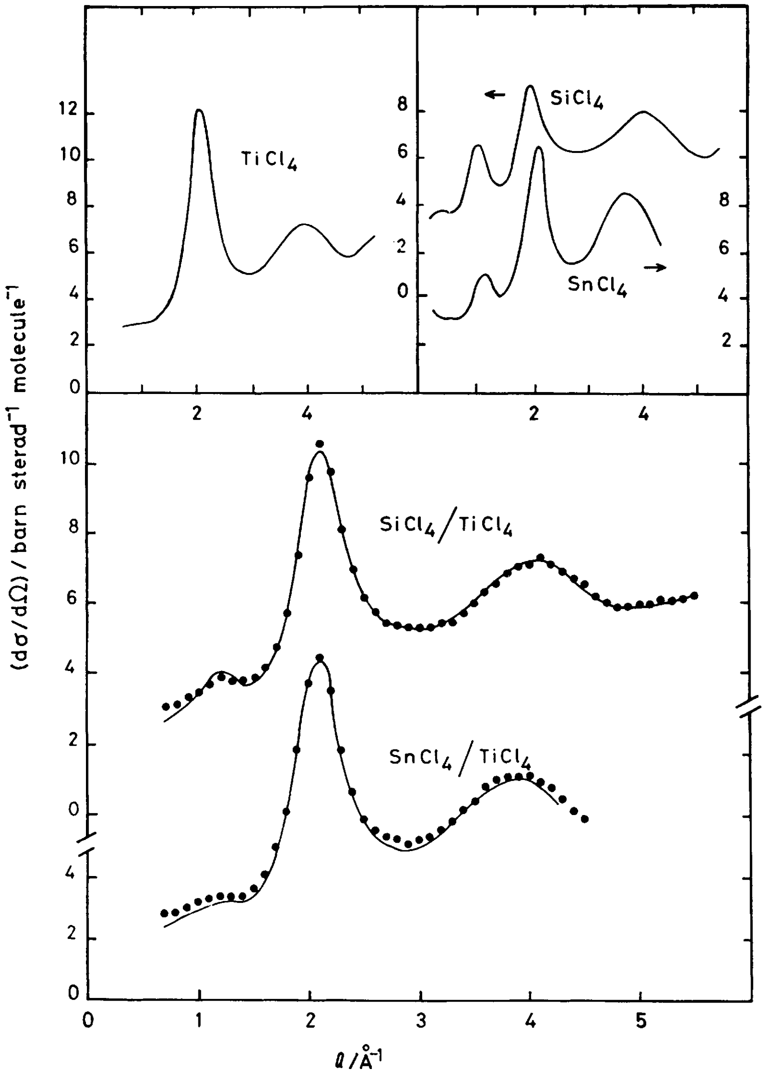

Fig. 5.—Diffraction measurements for tetrachloride liquids (*a*) and mixtures (*b*): see text for details.

CONCLUSIONS

The present study shows that a combination of pulsed and steady-state techniques for neutron diffraction from tetrachloride liquids can provide interesting information on both the inter- and intra-molecular structure. There remain some uncertainties about the corrections for wavelength-dependent effects observed in the data and the pulsed neutron technique cannot be satisfactorily used, at present, for measurements in the low-Q region (≤ 4 Å^{-1}). A complete pair-distribution function for chlorine–chlorine atoms has been obtained for VCl_4 and shows oscillations extending to 15 Å^{-1}. Similar results have been obtained for special mixtures of $SiCl_4$ + $TiCl_4$ and $SnCl_4$ + $TiCl_4$. The results for the pure tetrachloride liquids contain a mixture of the partial structure factors and do not permit a simple analysis to be made. Further analysis in conjunction with X-ray data should permit two of the pair correlation functions (Cl—Cl and X—Cl) to be approximately determined. Some preliminary molecular dynamics calculations for VCl_4 have been carried out[8] and analysis for the other liquids will be continued.

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