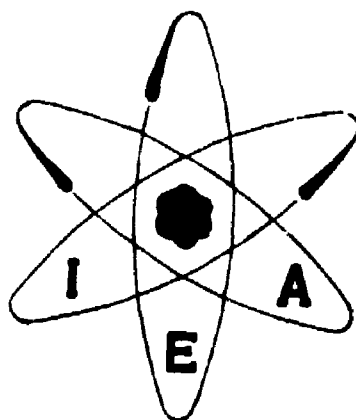


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STUDIED BY NEUTRON TRANSMISSION**

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INSTITUTO DE ENERGIA ATÔMICA
Caixa Postal 11049 (Pinheiros)
CIDADE UNIVERSITÁRIA "ARMANDO DE SALLES OLIVEIRA"
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L. Q. Amaral, R. Fulfaro and L. A. Vinhas

**Coordenadoria de Física Nuclear
Instituto de Energia Atômica
São Paulo – Brasil**

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Abstract

Neutron transmission of the globular compound tert-butanol $(\text{CH}_3)_3\text{COH}$ have been measured in the temperature interval 0°C to 40°C for 6.13 \AA neutrons and in the neutron wavelength range 4 \AA to 7.5 \AA in the liquid and solid states. Results show that the cross-section difference of the state transition in 24°C is 13%, while it is only $\sim 1\%$ at the first order phase transition in 14°C . Evidence of existence of a third crystalline phase with the lowest cross-section has been found. The barrier to interval methyl rotation in the solid state is estimated as $(3.8 \pm 0.5) \text{ kcal/mol}$ and does not change much over the phase and state transitions. The observed dynamical changes must be due to movements of the whole molecule and evidence that tert-butanol is not in the strict sense a plastic crystal. Correlation with heat capacity results is discussed.

1. Introduction

Molecular compounds that form structures with different phases are of prime interest, especially if the phase transition involves a change in the rotational dynamics^(1,2), as occurs with the so called organic globular compounds⁽³⁾. The molecules involved are almost spherical in shape and show in the solid state a phase transition with large entropy change from a crystal II form of low symmetry, stable at low temperature, to a crystal I form with high symmetry and a certain degree of plasticity; the entropy of melting is very small, usually less than 5 eu, following Timmerman's convention, and the triple point is high. The peculiar physical properties of the "plastic" crystal phase have been attributed to orientational disorder and rotation of the molecules about their lattice positions^(3,4,5). Although what actually happens is a small resistance to molecular reorientations, and very seldom free rotation, the solid state transition and the plastic phase are sometimes called rotational.

Compounds of the type $(\text{CH}_3)_3\text{C-X}$, that show also internal methyl rotation, fall usually among the plastic crystals⁽¹⁾ and have been studied⁽³⁾ for $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CN}, \text{SH}$. Tert-butanol $(\text{CH}_3)_3\text{C-OH}$ has been classified⁽⁶⁾ as a globular compound due to its small entropy of fusion; the internal rotation of the methyl groups has been studied by thermodynamic measurements in the gas state⁽⁷⁾, by NMR in the liquid state⁽⁸⁾ and by far infra-red. in the solid state⁽⁹⁾. This compound has a high melting point for the alcohol series (25°C) and a first order phase transition at 13°C , studied by calorimetry⁽¹⁰⁾ and dilatometry⁽¹¹⁾. Heat capacity measurements indicate the existence of a crystal III form over the temperature range 8.5°C to 21.5°C , as an alternative option that could not be reproduced at will. Dilatometric studies mention an "oldness" effect of crystal I. Entropy results⁽¹⁰⁾ show that the phase transitions are not highly energetic, what makes questionable the "plastic" character of the compound, that besides has complex crystalline forms.

Slow neutron transmission measurements in hydrogenous compounds, providing the total incoherent scattering cross section per proton, σ_{H} , can give information on the rotational

dynamics of molecules and molecular groups containing hydrogen atoms^(12,13,14) For sufficiently slow neutrons (energy $\ll 0.025$ eV), σ_H varies linearly with neutron wavelength λ , with slope determined by the inelastic scattering; the main contribution comes from de-excitation of energy levels corresponding to torsional or free rotational motions of the molecule or molecular groups. This slope decreases with increasing effective rotational mass in free rotation⁽¹⁵⁾ and, for a given moment of inertia for rotation, increases with the freedom of motion of the H atoms⁽¹⁶⁾. The slope of $\sigma_H \times \lambda$, at room temperature, has been empirically correlated with the barrier hindering the internal rotation of the molecular groups NH_3 and CH_3 ^(17,18,19). Moreover, the measurement of σ_H as a function of temperature gives information on changes in the freedom of motion of molecules and molecular groups at state and phase transitions^(19,20,21).

In order to investigate possible dynamical changes at the state and phase transitions and the behavior of molecular reorientations and methyl internal rotation, this work was undertaken.

II. Experimental

Neutron transmissions in the wavelength interval 3.5Å to 7.5Å were measured using a single crystal spectrometer⁽²²⁾ at the IEA 2 Mw light water reactor. A magnetite crystal monochromator and an appropriate choice of polycrystalline filters of Be and Pb were used to select only neutrons from first order Bragg reflections; the elimination of higher order contamination was checked by total cross section measurements of gold and water. Transmission measurements as a function of temperature were performed with 6.13Å neutrons; for this wavelength the intensity was enough to have in one day a series of measurements covering the whole temperature interval of interest.

The sample was commercial tert-butanol Merck of 99% purity and 0.1% maximum water content. As the behavior of tert-butanol is very sensible to impurities and water content, the conditions of the state transition were checked with the sample pure and with addition of water. Solidification of the pure sample occurred at $\sim 23^\circ\text{C}$, sometimes with supercooling, with quick crystallization at a lower temperature followed by a temperature increase, other times by a slow process while the temperature decreased. Addition of water decreases the solidification point that occurred at 19°C for 1% water, at 13°C for 2% water and at 5°C for 3% water content. The sample was in an aluminium holder while in the liquid state. Temperature in the interval 0°C to 40°C in the sample surroundings were controlled within 2°C by thermocouples attached to the aluminium holder.

The total neutron cross section is given by $\sigma = 1/n T^{-1}/n$, where T is the measured neutron transmission and n is the number of molecules/ cm^2 , obtained from the sample thickness and bulk density. The average scattering cross section per proton, σ_H , is obtained from the total cross section by subtracting the total absorption, proportional to the neutron wavelength, and a constant scattering from the remaining atoms, known from tabulated thermal values⁽²³⁾, and dividing by the number of H atoms in the molecule.

III. Results and discussion

a) Transmission vs temperature

Thirty seven series of independent measurements were taken by cooling and/or heating

after leaving the sample for at least one hour in liquid nitrogen or in a bath of water and ice; results obtained with the two thermal treatments were the same. Tert-butanol is highly hygroscopic and the effect of water contamination was observed in some of the series, when a sample stayed over 24 hours in the sample holder and was heated again to start a new series; these samples presented a variable delay in the solidification point upon cooling and gave on heating results at the same level as at the liquid state over the whole temperature interval. These series have been discarded.

Results obtained for $n\sigma = \ln T^{-1}$ in function of temperature are displayed in figure 1 as average over series of cooling and heating and some separate series that gave too different results to be included in the averages. Errors indicated are statistical; at 30°C, where the number of individual measurements was large enough for calculating the standard deviation of the distribution, the error in the mean value agreed with the statistical error.

Results indicate on cooling an abrupt step at 24°C; the temperature difference from the tabulated melting point (25°C) is probably due to a small water contamination. On heating, the variation was softer, and occurred in the interval 22-24°C. The temperature difference from heating and cooling cannot be ascribed to an error in the temperature measurement, and may be due to a premelting phenomenon or to further water contamination in the cooling process.

The phase transition in the solid state is much less accentuated. It has not been possible to separate the two phases I and II, neither to determine the transition temperatures in each individual series; however, the fluctuations in the values at the same temperature became bigger than the statistical errors in the solid state.

To further determine the conditions of the phase transitions, more 21 independent measurements were performed varying the thermal treatment of the sample, that stayed over at least 24 hours at liquid nitrogen, dry ice, and 20°C. Care has been taken to avoid water contamination and differences in internal pressure. These series evidenced that the phases I and II could be separated, in the limit of the statistical error, once we did not reject the possibility of the liq → II transition, that did not occur in the heat capacity measurements⁽¹⁰⁾.

In four of the 43 useful series, very different results were obtained, that can indicate the existence of a third crystalline phase, suggested by heat capacity measurements⁽¹⁰⁾. Two of the series refer to samples that had stayed over 24 hours in the solid state at 20°C; these have been the conditions on which one of the heat capacity results indicated the crystal III. However, this behavior was not constant, since other phase I measurements after 24, 48 and even more hours did not show any difference. Therefore the "oldness" effect mentioned in the dilatometric study⁽¹¹⁾, which was a constant behavior, cannot be identified with the crystal III hypothesis of the heat capacity measurements. The other two results were obtained on cooling new samples, where there may have occurred liq → III and liq → I → III transitions.

All these results are summarized in Table I, where the values of $\ln T^{-1}$, bulk density and σ are presented for the various phases. Phase III does not have a density measurement, and the density of crystal I has been taken as a lower limit.

The results show that the state transition has a cross section difference of 13%, while the first order phase transition has a cross section difference of ~1%, negligible when compared to the statistical error. Therefore the state transition involves the largest dynamical change,

However, the crystal III form a markedly lower total cross section.

b) Transmission vs wavelength

The values of σ_H obtained from transmission measurements in function of neutron wavelength λ are shown in figure 2 for liquid state (35° C) and solid state (13° C). In view of the results from the preceding section, no attempt was made to separate phases I and II in these measurements. In the solid state the two extreme values obtained with the densities⁽¹¹⁾ of crystal I and crystal II lead to the same slope within the experimental error; a mean value for the density was therefore adopted.

The straight lines are least square fits to the experimental points. As the behavior of σ_H proportional to λ is reached only asymptotically, the value of the slope depends to some extent on the considered wavelength range. In the liquid state the results showed linearity over the whole λ interval. In the solid state the slope decreases with increasing λ ; it has been adopted the best fit for $\lambda > 5\text{\AA}$, since in measurements^(17,18,19) with λ up to 10 \AA linearity was attained about that wavelength. The results for the straight line parameters are shown in Table II

There are two calibration curves relating the slope with the barrier hindering internal rotation: one obtained by Rush^(17,19) for NH_4 from the study of ammonium salts that has also been used for CH_3 and another obtained by Herdade⁽¹⁸⁾ for CH_3 in non-associated liquids. Care must be taken in the utilization of anyone of these calibration curves for tert-butanol.

The slope depends, not directly on the barrier height, but on the structure of energy levels available for energy gain by the neutron, which is determined by the height and functional form of the potencial wall and by the moment of inertia of the rotating group. The correlation between slopes and barriers is reasonable only if the form of the barrier is the same for all compounds.

In the case of the molecular groups NH_4 and CH_3 although the exact shape of the barrier may differ for the two groups, and depends also on the molecular frame, it is usual to assume that both groups experience a threefold cosine barrier in reorienting between equivalent potential minima. For CH_3 , rotation is around the fixed C_3 axes, while for NH_4 rotation is about one of the C_3 axes, with one proton fixed, and there is interchange in the orientation axis about which rotation occurs⁽²⁴⁾ the moments of inertia differ by only 6% ($\sim 4.8 \times 10^{-40}$ g.cm² for NH_4 and $\sim 5.1 \times 10^{-40}$ g.cm² for CH_3). Therefore one would expect calibration curves to be very similar for both groups, specially because the slope is the same for both groups when freely rotating in the gas state.

The discrepancy between the two curves for small barriers, close to the limit of free rotation (< 0.4 kcal/mol) is certainly due to the gas limit used by Rush. For barriers larger than 1 kcal/mol, Herdade's curve gives results larger than the ones from Rush by ~ 1 kcal/mol, what is probably due to a contribution from the molecular movements in the liquid state, since the barrier for hexamethylbenzene in the solid state agrees with Rush's curve.

Therefore, conclusion can be made that Rush's curve can be used for estimating barriers in the solid state, while Herdade's gives results valid for non-associated liquids.

From Rush's curve, the barrier hindering the internal rotation of the methyl groups obtained for tert-butanol in the solid state is (3.8 ± 0.5) kcal/mol

There are still some points to consider about this estimative. Rush's results were taken at 23°C and our measurements are at 13°C ; this represents an absolute temperature difference of $\sim 3\%$. As evidenced by $\sigma_H \times T$ there is no significant change in σ_H over this interval, but this could lead to an underestimation of the barrier by an error smaller than 10%. Another point is that there are really 9 H in the methyl groups and one in OH, and the slope of σ_H reflects the average behavior. As the barrier to the OH rotation in the condensed state⁽⁸⁾ is larger than for CH_3 , this can lead to an overestimation of the barrier by an error not bigger than 10%, that is within the uncertainty of the estimative.

The agreement with the infra-red estimative⁽⁹⁾ for the solid state of 4.1 kcal/mol corroborates the total cross section method and the calibration curves as a valid and complementary technique.

Thermodynamic results for the gas state⁽⁷⁾ give a barrier of 3.8 kcal/mol for the internal methyl rotation and NMR results⁽⁸⁾ in the liquid state give a value of 3.4 kcal/mol. Considering the very different methods these results indicate that the internal rotation of the methyl groups is not very sensible to the phase and state transitions. Therefore, the increase in σ_H in the liquid state shall be ascribed to the movements of the whole molecule.

The slope for the liquid state, using Herdade's curve, would give a barrier of ~ 2.5 kcal/mol, a too low result that is partially due to the temperature difference but indicates that the contribution of low-frequency modes to σ_H in tert-butanol is more significant than in the liquids studied by Herdade. The value obtained for the liquid state is consistent with slopes obtained at this laboratory for other alcohols in the liquid state⁽²⁵⁾.

IV. Conclusions

The barrier to methyl rotation in tert-butanol in the solid state is estimated as (3.8 ± 0.5) kcal/mol and does not change much over the phase and state transitions. Comparison with microwave results⁽²⁶⁾ for $(\text{CH}_3)_3\text{CH}$ and $(\text{CH}_3)_2\text{CF}$, respectively 3.9 and 4.3 kcal/mol, shows that the barrier is determined mainly by the interaction forces of the $(\text{CH}_3)_3\text{C}$ group and is almost independent of intermolecular forces and even of the presence of association, that occurs for tert-butanol in the liquid⁽²⁷⁾ and even in the gas state⁽⁷⁾.

The more important dynamical change occurs at the state transition and must be due to movements of the whole molecule. This result evidence that tert-butanol is not in the strict sense a plastic crystal.

Our results confirm the existence of a crystalline phase of difficult reproductibility. The difference in total cross section is probably not due to a change in internal rotation, but indicates a more ordered structure for this crystalline form, that shall have a higher Debye temperature. The reason for the difference in σ , while the heat capacity of the forms III and I are almost the same⁽¹⁰⁾, is an open question.

The fact that the I \rightarrow II transition does not involve great dynamical change, together with

the lower heat capacity results for crystal I, may indicate a pre-transition behavior of crystal II several degrees before the transition, probably for $T > 200$ K. This kind of behavior would indicate cooperative phase fluctuations⁽²⁸⁾

It is felt that there are some common features in behavior for tert-butanol, methanol^(29,30) and ciclo-hexanol⁽³¹⁾, all classified as globular compounds, that seem to be related to the presence of H bonding, and systematic investigation would be worthwhile.

It is hoped that neutron inelastic scattering measurements now in progress will give further information about these questions.

TABLE I

Values of neutron transmission T , bulk density ρ and total cross section σ for the various phases of tert-butanol

	$\ln T^{-1}$	$\rho(\text{g/cm}^3)^{1/3}$	$\sigma(\text{barns})$
liquid	1.60 ± 0.02	0.78	1000 ± 10
crystal I	1.51 ± 0.02	0.84	870 ± 10
crystal II	1.54 ± 0.01	0.87	860 ± 5
crystal III	1.45 ± 0.02	0.84	840 ± 10

TABLE II

Parameters of straight line $\sigma_H = a + b\lambda$

	a(barns)	b(barns/Å)
liquid	47 ± 1	8.6 ± 0.2
solid	50 ± 2	5.7 ± 0.3

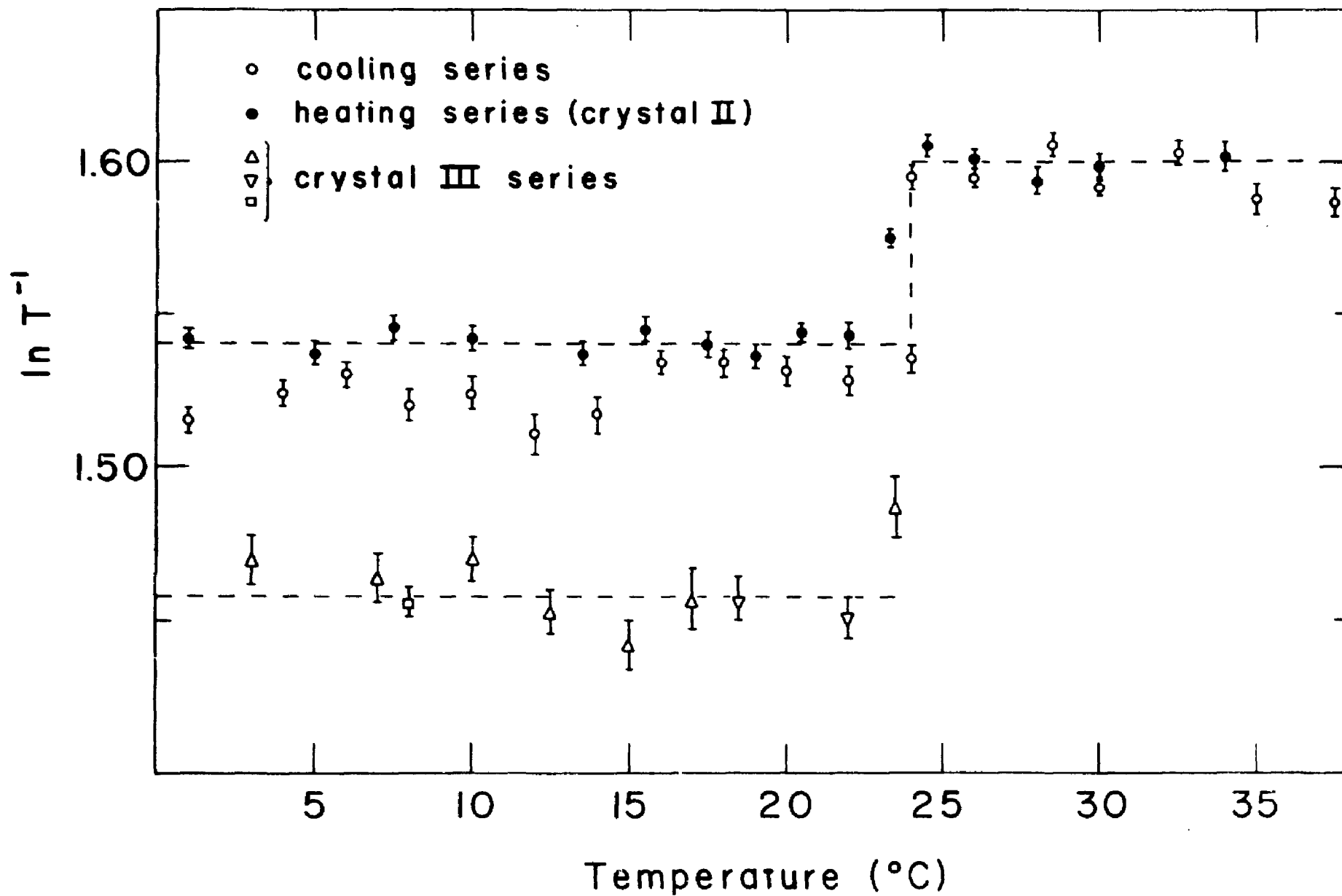


Figure 1 — Results obtained for $n\sigma = \ln T^{-1}$ for tert butanol in function of temperature: Averages over several series of cooling and heating and some series that may correspond to crystal III

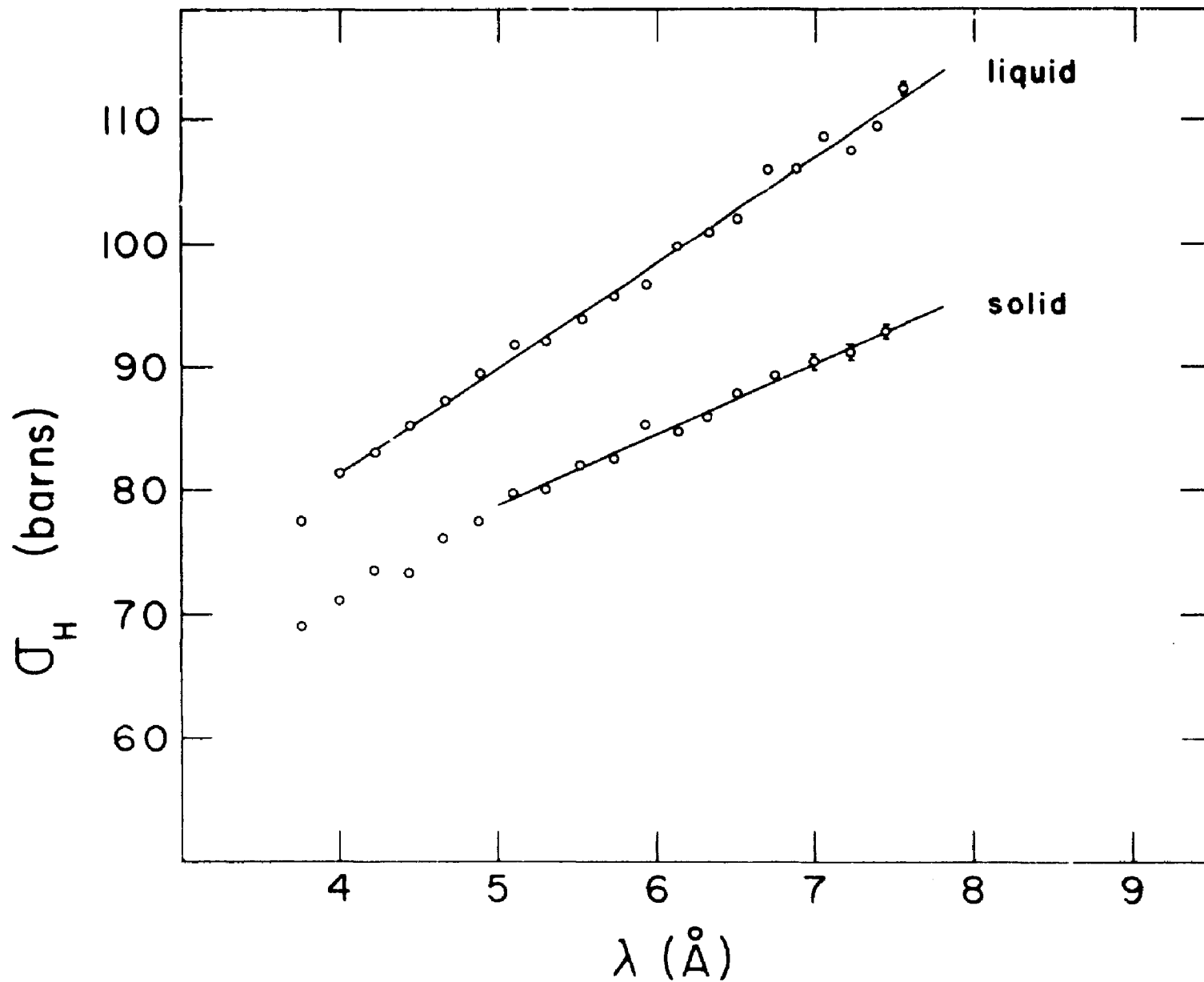


Figure 2 – Scattering cross sections per hydrogen atom σ_H as a function of neutron wavelength and least square fits. A mean density, adopted for the solid state

RESUMO

Foi medida a transmissão do composto globular tert-butanol $(\text{CH}_3)_3\text{COH}$ para neutrons de $6,13\text{\AA}$ no intervalo de temperatura de 0°C a 40°C e para neutrons com comprimento de onda no intervalo de 4\AA a $7,5\text{\AA}$ nos estados sólido e líquido. Os resultados mostram uma diferença de 13% na seção de choque na mudança de estado em 24°C e de apenas $\sim 1\%$ na transição de fase de primeira ordem em 14°C . Existe indicação da existência de uma terceira fase cristalina, com a menor seção de choque. A barreira para rotação interna dos grupos metil no estado sólido é estimada em $(3,8 \pm 0,5)$ kcal/mol, e não é muito afetada pelas transições de fase e de estado. As alterações dinâmicas observadas devem ser devidas a movimentos da molécula toda e evidenciam que o tert-butanol não se enquadra entre os cristais plásticos típicos. É discutida a correlação com resultados de calor específico.

RÉSUMÉ

On a mesuré la transmission du composé globulaire tert-butanol $(\text{CH}_3)_3\text{COH}$ pour les neutrons de $6,13\text{\AA}$ dans l'intervalle de température de 0°C a 40°C e pour neutrons avec longueur d'onde dans l'intervalle de 4\AA à $7,5\text{\AA}$ dans les états solide e liquide. Les résultats montent une différence de 13% en la section efficace dans le changement d'état à 24°C e de seulement $\sim 1\%$ dans la transition de phase de première ordre à 14°C . On a obtenu évidence de l'existence d'une troisième phase cristalline, avec la plus basse section efficace. La barrière pour la rotation interne des groupes methyl dans l'état solide est estimée en $(3,8 \pm 0,5)$ kcal/mol, et elle ne change pas beaucoup dans les transitions de phase et d'état. Les alterations dynamiques observées doivent être attribuées aux mouvements de la molécula toute entière et evidencient que le tert-butanol n'est pas dans le sens restrict un cristal plastique. On discute la correlation avec les résultats de chaleur spécifique.

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