



On the Stokes–Einstein relation in glass forming liquids

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Abstract

Nowadays, the experimental evidence of a crossover between two dynamical regimes for supercooled glass-forming liquids at a temperature T_c , $T_c > T_g$, where T_g is the glass transition temperature, has been widely reported in the literature. On one hand, it is a well-known fact that in the region $T_g < T < T_c$, fragile glass forming liquids do not follow the Vogel–Fulcher–Tammann law. On the other hand, in the same region the Stokes–Einstein relation between the viscosity and the translational diffusion coefficient breaks down. Using the temperature derivative analysis, we present, for three glass-forming liquids, an empirical law for $\log_{10} f$, where f is the frequency, and we exhibit the break down of the Stokes–Einstein relation. © 2000 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

The nature of the relaxation processes that occur in a viscous supercooled liquid as it approaches the glass temperature T_g has been extensively studied in the past years. The glass transition point has been usually defined by the temperature T_g at which the viscosity η reaches values of 10^{13} poise.

Different experimental techniques have been used to examine the response function of the system to an external perturbation. In general, it may be described by a stretched

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exponential function, the Kohlrausch–Williams–Watts law [1,2]:

$$\Phi(t) = \Phi(0)\exp(-t/\tau)^\beta,$$

where $\Phi(0) = \Phi(t = 0)$, $0 < \beta \leq 1$, and the parameter τ , which is a function of the temperature, is identified as the average relaxation time of the relevant processes that occur during the glass transition.

Several empirical equations have been proposed to account for the influence of the temperature on the relaxation time which may be also used to describe the behavior of the viscosity of the supercooled liquid. Two of the most important ones emerged through the study of the logarithmic shift factor (LSF),

$$\log a_T = \log \left(\frac{\tau(T)}{\tau(T_s)} \right), \quad (1)$$

where $\tau(T_s)$ is a reference relaxation time at a temperature T_s , and have lead to the Vogel–Fulcher–Tamann (VFT) and the Williams–Landel–Ferry (WLF) equations.

The VFT equation was formulated over 70 years ago to describe the non-Arrhenius behavior of the LSF and the viscosity of several classes of supercooled liquids [3–5], mainly fragile, as they approach the glass temperature T_g ,

$$\tau(T) = \tau_s \exp \left(\frac{B}{T - T_0} \right), \quad (2)$$

where τ_s is a reference relaxation time, and B and T_0 are two independent parameters taken to be nonnegative. T_0 corresponds to the temperature at which τ is infinity. In fact, T_0 has been interpreted as the isentropic temperature, that is, the temperature at which the configurational entropy vanishes.

Thirty years later, Williams et al. [6] proposed an empirical equation to deal with the form for the LSF, specially in polymeric liquids, at a temperature T taking a reference temperature T_s in terms of two parameters, C_1 and C_2 ,

$$\log a_T = \frac{-C_1(T - T_s)}{C_2 + T - T_s}. \quad (3)$$

This equation may be expressed in a semi-universal form if the value of T_s is such that for a large number of glass-forming substances, C_1 and C_2 have constant values [6]. Both VFT, Eq. (2), and WLF, Eq. (3), deal with experimental data corresponding to slow diffusional relaxation processes and have been used to fit data within a range of temperatures $T_g < T < T_g + 50^\circ$.

Recently, experiments have indicated the presence of fast dynamical relaxation processes that take place in the supercooled liquid, and which suggest a new threshold in the glass transition [7–29]. A temperature T_c above T_g , in the range $1.18T_g < T_c < 1.28T_g$ has been found where a cross-over between the two different regimes for the supercooled liquid appears and in which several properties of glass-forming liquids have visible changes in their behavior. Even though the relaxation times do not exhibit any special critical behavior in the vicinity of T_c , a cross-over may be detected by analyzing the derivatives of the relaxation times with temperature. The cross-over becomes more evident in the case of several other experimentally measured properties of the system.

Two of the main features of this cross-over behavior are exhibited on one hand, by the fact that for $T < T_c$, the VFT equation does no longer fit the experimental data for the relaxation times, and on the other hand, a change in the diffusion mechanisms in the glass-forming liquids occurs at temperatures below T_c .

In order to probe the validity of the VFT equation for $\log f$, where f is the frequency, $f \sim \tau^{-1}$, as an appropriate fit for experimental data Stickel et al. [23,24], proposed the temperature-derivative analysis. The frequency f corresponds to the peak of the loss function $\varepsilon''(\omega)$ the imaginary part of the complex dielectric function [23],

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega).$$

The method consists in evaluating three derivatives of a given empirical form for $\log f$:

$$\left(\frac{d \log_{10} f}{dT}\right)^{-1/2}, \tag{4}$$

$$\frac{d}{dT} \left[\left(\frac{d \log_{10} f}{dT}\right)^{-1/2} \right], \tag{5}$$

$$\Theta = \frac{d \log f / dT}{d^2 \log f / dT^2}. \tag{6}$$

In particular, the function Θ represents a very useful mathematical tool to analyze the different regimes in the vicinity of T_c since it supplies information on the rate between the first and second derivatives. If these derivatives are applied to the VFT equation the results are the following:

$$\log_{10}(f_{VFT}) = A - \frac{B}{T - T_0}, \tag{7}$$

$$\left(\frac{d \log_{10} f_{VFT}}{dT}\right)^{-1/2} = B^{-1/2}(T - T_0), \tag{8}$$

$$\frac{d}{dT} \left[\left(\frac{d \log_{10} f_{VFT}}{dT}\right)^{-1/2} \right] = B^{-1/2}, \tag{9}$$

$$\Theta_{VFT} = -\frac{T - T_0}{2}. \tag{10}$$

Thus, the evaluation of Θ may be used to compare a given empirical law with the VFT equation through linearization or by changing the values of the parameters.

Moreover in the last decade, a large amount of experimental studies on the properties of tracer diffusion in supercooled liquids in the glass transition region have been undertaken. The Stokes–Einstein relation between the viscosity and the translational diffusion coefficient,

$$D \sim \eta^{-1} \tag{11}$$

breaks down for $T < T_c$. Instead, it appears that,

$$D \sim \eta^{-\xi} \quad (12)$$

with $\xi < 1$. The value of ξ depends of the glass-forming liquid and of the size of the specific tracer particle [25–29].

In the case of several glass-forming liquids, using the three derivatives Eqs. (4)–(6), it is found that the experimental data for $\log f$ within a range of temperatures $T > T_c$, satisfy the VFT equation. Nevertheless, for $T < T_c$, even though the experimental values for $\log f$ satisfy Eq. (7), the derivatives, (4)–(6) do not have the form for VFT namely, Eqs. (8)–(10). One can thus identify a temperature T_c below which the VFT empirical law is not a good fit.

In this work, using the temperature-derivative analysis proposed by Stickel et al. [23,24], we analyze the behavior of three glass-forming liquids, namely, phenyl salicylate (salol), phenolphthaleine-dimethyl-ether (PDE), and orthoterphenyl (OTP). Using experimental data, [23,24,26,28,30], we present a mathematical form for $\log f$ in the region between T_g and T_c that does not correspond to a VFT equation, and for $T > T_c$ a form which may be actually represented by a VFT type equation. The results obtained for the mathematical form of $\log f$ may be easily extended to find the analytical form of the viscosity in both regions since,

$$\log \frac{f(T)}{f(T^*)} = \log \frac{\eta(T^*)}{\eta(T)}, \quad (13)$$

where T^* may be considered as a reference temperature. We have chosen for T^* the closest available temperature to the corresponding value of T_g for which we have experimental values for the diffusion coefficient in each glass forming liquid.

The value of T_c is generally reported from experiment as the temperature where evidence of a crossover between dynamical regimes appears, specially in the diffusion mechanism. We thus find the value of a temperature T'_c as the temperature where both our empirical forms intersect each other. On the other hand, we study the diffusion mechanisms for both regions by analyzing the validity of the Stokes–Einstein relation by means of the evaluation of the exponent ξ .

2. Results

We have examined the experimental data for $\log f$ in salol and PDE [23,24] and for $\log 1/\eta$ in OTP [30] both in the $T < T_c$ and $T > T_c$ regions.

As far as the behavior in the $T < T_c$ region is concerned, we may propose that for these three liquids an empirical equation of the form

$$\log \frac{f(T)}{f(T^*)} = \log \frac{\eta(T^*)}{\eta(T)} = A(T_a - T)^n + B \quad (14)$$

fits the experimental data. Indeed, in Table 1 we summarize the information on the values of A , T_a , n , and B for the three substances.

Table 1

Values for the coefficients A and B , the exponent n and the temperatures T_a and T^* in Eq. (14), the values of T_g and the reported experimental value for T_c and the intersection temperature T'_c for salol, PDE and OTP

Substance	n	A	B	T_g (K)	T_a (K)	T^* (K)	T_c (K)	T'_c (K)
Salol	2.0	-0.00251	8.6989	220	282	223.33	265	260
PDE	1.5	-0.02506	6.7626	294	340	298.24	325	327
OTP	2.0	-0.00244	10.4113	243	310	244.67	290	283

Table 2

Values for the coefficients C and E and the temperature T_0 in Eq. (15) for salol, PDE and OTP

Substance	C	E (K)	T_0 (K)
Salol	11.585	148	224
PDE	12.161	324	278
OTP	15.253	345	230

On the other hand, in the $T > T_c$ region, the experimental data actually obey a VFT type equation,

$$\log \frac{\eta(T^*)}{\eta(T)} = C - \frac{E}{T - T_0}, \tag{15}$$

where the values of C , E and T_0 for the three supercooled liquids are given in Table 2. It is important to point out that in the case of the VFT equation, the temperature T_0 is usually interpreted as the temperature where the configurational entropy vanishes, with $T_0 < T_g$. Strangely enough in the case of salol we find that $T_0 > T_g$, thus for this liquid T_0 may be considered just as a fitting parameter whose interpretation should be reconsidered.

In Figs. 1–3 we present the plots of Eq. (14) for $T < T_c$ (solid line) and Eq. (15) (dashed line) for $T > T_c$ for salol, PDE and OTP respectively. It is easily seen that there is a small region in the vicinity of T_c where both descriptions overlap. Since T_c is interpreted as the temperature where the crossover between two dynamical regimes occurs, we must find the temperature where both the empirical descriptions Eq. (14) for $T < T_c$ and Eq. (15) for $T > T_c$ intersect each other. Since the description in terms of the derivatives has proved to be useful to distinguish the differences between both regimes, we proceed to find a temperature T'_c where the derivatives Θ , Eq. (6), for both descriptions intersect each other, that is,

$$\Theta_{T < T_c}(T'_c) = \Theta_{T > T_c}(T'_c). \tag{16}$$

We find that for salol, $T'_c = 260$ K, for PDE $T'_c = 327$ K, and for OTP, $T'_c = 283$ K. If we compare these values with the experimentally reported ones, we find that they are in good agreement (see Table 1).

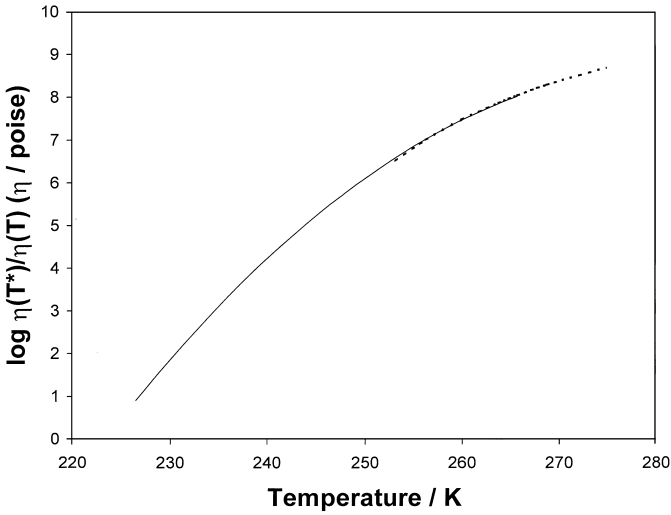


Fig. 1. Plot of $\log \eta(T^*)/\eta(T)$ vs. T in salol given by Eq. (14) in the region $T < T_c$ (solid line) and Eq. (15) for $T > T_c$ (dashed line).

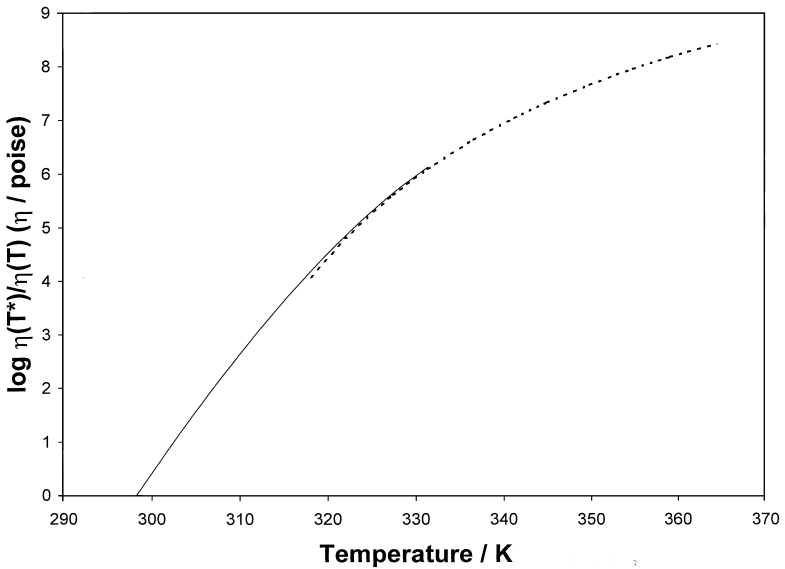


Fig. 2. Plot of $\log \eta(T^*)/\eta(T)$ vs. T in PDE given by Eq. (14) in the region $T < T_c$ (solid line) and Eq. (15) for $T > T_c$ (dashed line).

As mentioned earlier, due to the fast processes that take place for temperatures below T_c , the diffusion processes are such that the Stokes–Einstein relation, Eq. (11) between the viscosity and the diffusion coefficient breaks down, thus obeying the relationship exhibited by Eq. (12).

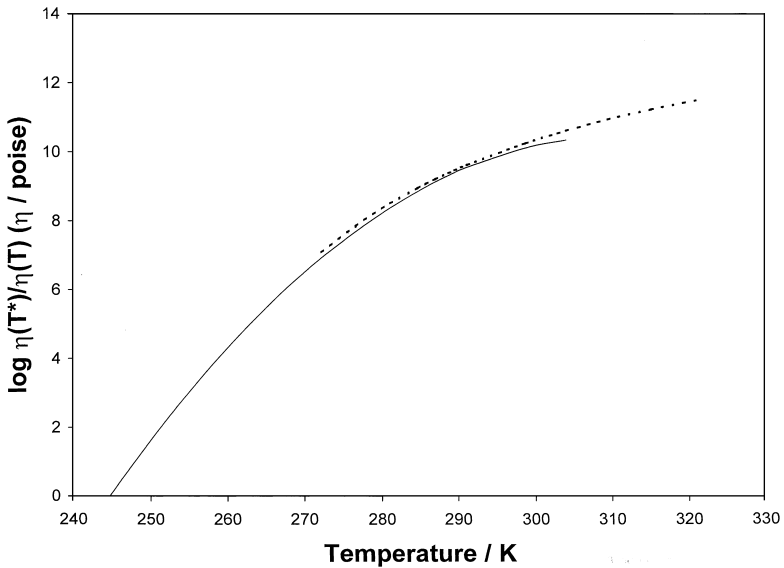


Fig. 3. Plot of $\log \eta(T^*)/\eta(T)$ vs. T in OTP given by Eq. (14) in the region $T < T_c$ (solid line) and Eq. (15) for $T > T_c$ (dashed line).

We have analyzed the relationship between our values of the viscosity, in both regions obtained through our proposed empirical equations and the experimental values for the diffusion coefficient [26,28] as a function of the temperature also in both regions. In order to carry out this analysis, in Figs. 4–6 we plot $\log \eta(T^*)/\eta(T)$ vs. $\log D(T)/D(T^*)$ for salol, PDE and OTP, respectively, using Eq. (14) for $T < T_c$, and Eq. (15) for $T > T_c$, and find that indeed, if we compare the slopes in the $T > T_c$ region, ξ is nearly one for the three glassformers, whereas for $T < T_c$ we obtain a value of $\xi < 1$, where the value of ξ depends both on the tracer and on the substance. In Table 3 we present the values of ξ for both regions and indicate the tracer particle in each case.

The form for the diffusion coefficient clearly indicates that in the range $T_g < T < T_c$ we have a case of an anomalous diffusion process [31]. The exponent ξ may be interpreted as a fractionary scaling parameter in the cross-over region within the framework of a percolation model where the system switches from a translational-rotational coupling regime to a noncoupled regime where a different relaxation process appears. This process may be understood as a progressive freezing of the translational degrees of freedom [32].

3. Discussion

Summarizing, we have exhibited two of the main aspects that indicate the change of the dynamical behavior of a glass forming liquid below T_c , using salol, PDE and OTP as good representative fragile glass-forming liquids.

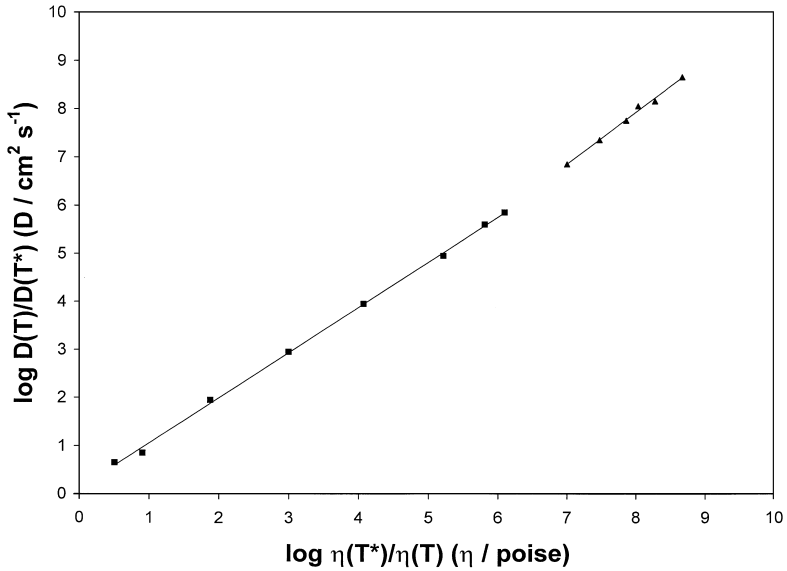


Fig. 4. Experimental translational diffusion coefficient $\log D(T)/D(T^*)$ for TTI as particle tracer in salol [25], \blacksquare for $T < T_c$ and \blacktriangle for $T > T_c$, plotted as a function of the viscosity, $\log \eta(T^*)/\eta(T)$ given by Eq. (14) for $T < T_c$ and by Eq. (15) for $T > T_c$. The solid lines represent the best linear fits in both regions, where the slope are in the $T < T_c$ region $\xi = 0.93$ and for $T > T_c$, $\xi' = 1.06$.

For $T < T_c$ we have found an empirical form for $\log(\eta(T^*)/\eta(T))$, Eq. (14), which indeed deviates from the Vogel–Fulcher–Tammann law. This fact is emphasized by the evidence that in this region the derivative Θ is positive, while the corresponding Θ of a VFT kind of equation is negative [23]. As far as the $T > T_c$ region, a VFT kind of equation, Eq. (15) may be fitted. It still remains to find the proper identification of the temperature T_0 , which is not necessarily an easy task. There has been a tendency of identifying T_0 with the isoentropic temperature, but this fails in the case of salol since $T_g > T_0$. Why this is so is not so clear at present. It is important to point out that as we have seen, there is a small region around T_c where both descriptions, Eqs. (14) and (15) are almost undistinguishable. This may be one of the main reasons for which for many years the VFT description was taken as valid for all temperatures above T_g .

However, it is important emphasize that the empirical law given by Eq. (14) is not necessarily obeyed by any kind of supercooled liquid. In fact, another kind of fragile glasses, propylene carbonate (PPC) and 1-propanol [24], follow a different type of empirical law:

$$\log \frac{\eta(T^*)}{\eta(T)} = F - \frac{G}{(T - T_b)^m} \quad (17)$$

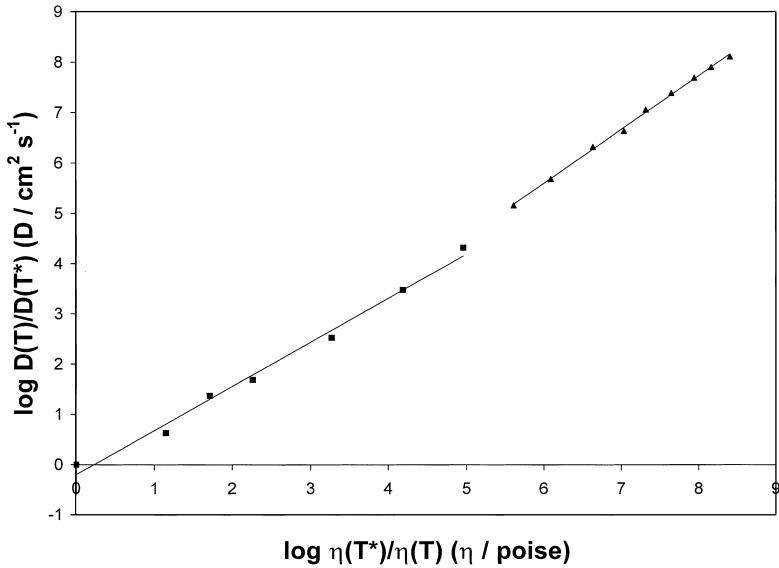


Fig. 5. Experimental translational diffusion coefficient $\log D(T)/D(T^*)$ for ONS-A as particle tracer in PDE [25], ■ for $T < T_c$ and ▲ for $T > T_c$, plotted as a function of the viscosity, $\log \eta(T^*)/\eta(T)$ given by Eq. (14) for $T < T_c$ and by Eq. (15) for $T > T_c$. The solid lines represent the best linear fits in both regions, where the slope are in the $T < T_c$ region $\xi = 0.87$ and for $T > T_c$, $\xi' = 1.06$.

whose Θ is negative. As far as the $T > T_c$ region is concerned, a VFT kind of equation may be fitted.

We have also presented evidence of the failure of the Stokes–Einstein relation when the temperature falls beyond T_c . Our results are in general agreement with those reported in the literature [25–29].

A theoretical description to deal with the dependence of the relaxation times with the temperature is nowadays a great challenge. Several efforts [17,18,23,24,33–35] to explain the role of fast dynamics in terms of the excitation spectrum of glasses have presented two features. On one hand, an anharmonic relaxation-like contribution seems to appear, and on the other, harmonic quasi-local vibrational excitations show up as the “boson peak”. Depending on the ratio between both contributions, different temperature dependences for the relaxation times may be found [33]. A full theoretical interpretation of the proposed equation for the temperature dependence of the relaxation times in the $T < T_c$ region Eq. (14) is an important task in the near future.

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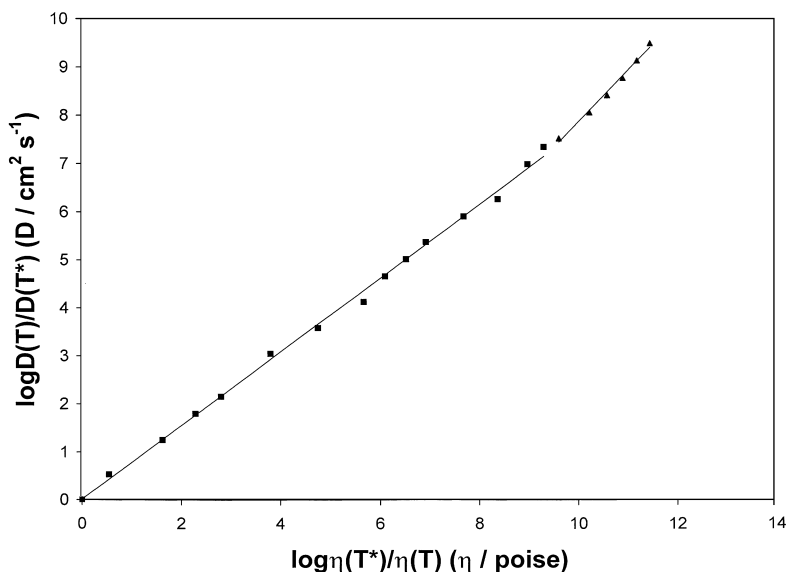


Fig. 6. Experimental translational diffusion coefficient $\log D(T)/D(T^*)$ for TTI as particle tracer in OTP [27], ■ for $T < T_c$ and ▲ for $T > T_c$, plotted as a function of the viscosity, $\log \eta(T^*)/\eta(T)$ given by Eq. (14) for $T < T_c$ and by Eq. (15) for $T > T_c$. The solid lines represent the best linear fits in both regions, where the slope are in the $T < T_c$ region $\xi = 0.76$ and for $T > T_c$, $\xi' = 1.05$.

Table 3

Values of the exponents ξ in the $T < T_c$ region and ξ' for $T > T_c$ in Eq. (12) obtained from Figs. 4–6 for salol, PDE and OTP

Substance	Tracer	$\xi T < T_c$	$\xi' T > T_c$
Salol	TTI	0.93	1.06
PDE	ONS-A	0.87	1.06
OTP	TTI	0.76	1.05

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