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Interrelations Between Shift Factors of Viscoelastic Functions and Apparent Activation Energy of Flow

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SUMMARY

The applicability of an approach is tested experimentally, which interrelates the frequency as well as the temperature shift of isotherm and isochrone viscoelastic data with the apparent activation energy of the viscous flow. The procedure is based on the evaluation of the slopes of isotherms in the log viscoelastic function - log frequency plot and of isochrones in the log function - reciprocal temperature plot. Experimental data demonstrate that the approach applies over the entire temperature range from the high-temperature melt to the glass transition, where the WLF equation fails oftenly. The temperature range of variable activation energy turns out to be substantially smaller than supposed. Above $T_g + 40$ K constant activation energy suffices, suggesting that the range of validity of the EYRING model is quite larger than usually admitted.

CORRELATIONS BETWEEN ACTIVATION OF FLOW AND GLASS TRANSITION

According to the modified ROUSE theory of undiluted polymers in the "free draining" assumption of the bead-spring model for a linear flexible random coil the viscoelastic moduli of polymer melts are related to the relaxation times of p modes of motion, τ_p, by 1) 2)

$$G' = (\rho RT/M)\sum_{p=1}^{N} \omega^2\tau_p^2/(1+\omega^2\tau_p^2) \qquad G'' = (\rho RT/M)\sum_{p=1}^{N} \omega\tau_p/(1+\omega^2\tau_p^2) \quad . \quad (1)$$

G' and G'' are the storage and the loss modulus, resp., M is the molecular weight, ρ the density and ω the angular frequency of the harmonic motion. The relaxation times are dependent on the translational friction coefficient per subunit, ζ_0, on the degree of polymerization, P, and on the root-mean-square end-to-end distance, $\langle h^2\rangle$, by

$$\tau_p = \langle h^2\rangle P\,\zeta_0 Q_e / 6\pi^2 p^2 kT \quad . \quad (2)$$

The factor Q_e represents the enhancement of friction by entanglement restraints 3).

In the range of finite linear viscoelasticity the BOLTZMANN superposition principle holds, which requires implicitly that all relaxation times show identical temperature dependence. Customary this is expressed by the ratio of any specific relaxation time at temperature T to its value at an arbitrarily chosen reference temperature T_0:

$$[\tau_p]_T / [\tau_p]_{T_0} = a_T \quad . \quad (3)$$

Thus a_T is the "shift factor", which allows the superposition of isotherm viscoelastic curves to a composite "master curve" in the logarithmic viscoelastic function - frequency plane.

Since the low-frequency limit of the loss modulus $G'' = \omega\eta_0$, the friction coefficient may be expressed in terms of the steady-state zero-shear viscosity, η_0,

$$\zeta_0 = 36\,\eta_0 M_0 / \rho\,\langle h^2\rangle N_A \quad , \quad (4)$$

Consequently, the relaxation time can be related also to the zero-shear viscosity:

$$\tau_p = 6\,\eta_o M / \pi^2 p^2 \rho R T \qquad (5)$$

It follows that the shift factor a_T can also be expressed by

$$a_T = [\langle h^2\rangle \zeta_o]_T\, T_o \,/\, [\langle h^2\rangle \zeta_o]_{T_o}\, T$$

or

$$a_T = \eta_o T_o \rho_o / \eta_o^{\,o} T \rho \quad , \qquad (6)$$

respectively. Under reduced temperature and density conditions the shift factor is simply given by the ratio of the zero-shear viscosities

$$a_T = [\eta_o / \eta_o^{\,o}] \quad , \qquad (6\,a)$$

with $\eta_o^{\,o}$ the zero-shear viscosity at the reference temperature. As consequence of the BOLTZMANN superposition principle, however, the shift factors apply not only in the range of zero-shear viscosity, but for the entire range of the viscoelastic function above T_g.

A second approach to express relaxation times is related to the thermodynamic probability of configurational changes , Ω, as suggested by GIBBS and DIMARZIO [4]:

$$\tau_p(T) = 1/\Omega(T) \quad . \qquad (7)$$

The probability of configurational changes depends on both the energy of the potential energy barrier between stable configurations, $\Delta\mu$, and the critical configurational entropy, S_c^*, of the smallest cooperative region of configurational redistribution:

$$\Omega(T) = A \exp(-\Delta\mu S_c^* / k T S_c) \quad . \qquad (8)$$

S_c is the temperature dependent molar configurational entropy

$$S_c(T) = \Delta c_p \ln(T/T_2) \qquad (9)$$

and T_2 the thermodynamical equilibrium "freeze in" temperature at which $\Omega(T_2) = 0$. Δc_p is the difference of the heat capacities of the equilibrium melt and of the glass at T_g. T_2 is experimentally not accessible, however. It is stated only that it is situated around T_g - 50 K.

Applying to the glass transition [5] the shift factor is given by the expression

$$\log a_T = -2.303\,(\Delta\mu S_c^* / k)\,\{[1/T_o S_c(T_o)] - [1/T S_c(T)]\} \quad . \qquad (10)$$

Introducing the expression for the temperature dependent molar configurational entropy, equation (10) can be rewritten in the form of the empiric WILLIAM-LANDEL-FERRY relation

$$\log a_T = -a_1 (T - T_o)/[a_2 + (T - T_o)] \quad . \qquad (11)$$

The two constants are

$$a_1 = 2.303\ \Delta\mu S_c^* / \Delta c_p T_o k \ln(T_o/T_2)$$

$$a_2 = T_o\,\{1/[1 + (1 + T_o)/(T - T_o)] \ln(T T_2 / T_o^2)\} \quad . \qquad (12)$$

and it is quite evident that the constant a_2 has the dimension of a temperature.

Starting with equation (6 a) it is obvious that the temperature dependence of the shift factor can be expressed in terms of the temperature dependence of the zero-shear viscosity.

Concerning viscous flow of a fluid, two requirements have to be considered,

- the existence of the necessary "free volume" for the translational movement of the particles, with Ω_v the probability of free volume creation and

- the necessity to "overcome" a potential energy barrier between equilibrium positions of the fluid particles, given by the probability Ω_ε.

Consequently, the probability of viscous flow is given by [6] $\Omega_{fl} = \Omega_v \, \Omega_\varepsilon$. (13)
Therefore two limiting models may be discussed.

In the **first model** the viscous flow depends on free volume creation, i. e. the existent free volume determines the flow. This situation occurs at temperatures near T_g. Than DOOLITTLE's equation [7] applies, which relates the viscosity of the polymer melt in the terminal zone to the ratio of the specific occupied volume, v_{oc} , to the specific free volume, v_f,

$$\eta = A' \exp (B_o v_{oc} / v_f) \quad . \qquad (14)$$

A' and B_o are two empirical constants, the latter near unity. The temperature dependence of the viscosity is exprimed via the temperature dependence of the respective specific volumes

$$v_i = v_{i,o} [1 + \alpha (T - T_o)] \quad , \qquad (15)$$

with $v_{i,o}$ the specific volume at the reference temperature T_o and α the expansion coefficient. The ratio of the specific volumes in equation (14) will be consequently (16)

$$v_{oc} / v_f = (v - v_f) / v_f = \{v_g [1 + \alpha_L (T - T_g)] - v_{f,g} [1 + \alpha_f (T - T_g)]\} / \{v_{f,g} [1 + \alpha_f (T - T_g)]\} \quad .$$

v is the specific volume of the liquid at T, v_g that at T_g. $v_{f,g}$ is the specific free volume at T_g. α_L and α_f are the thermal expansion coefficients of the liquid and of the free volume above T_g.
Introduction of the viscosity ratio, according to equation (6 a) into equation (14) and rearranging yields a WLF equation again:

$$\log a_T = - C_1^g (T - T_g) / [C_2^g + (T - T_g)] \quad . \qquad (17)$$

The constants are given here by the expressions [6]

$$C_1^g = - (B_o / 2.303) [(\alpha_L / \alpha_f) - 1] (v_g / v_{f,g}) \qquad C_2^g = \alpha_f^{-1} \quad . \qquad (18)$$

Substantially simplified expressions for the constants result according to the original paper of WILLIAMS, LANDEL and FERRY [8], when simplifying assumptions are admitted for both the fractional free volume, f, and for the temperature dependence of the fractional free volume,

$$v_{oc} \gg v_f \text{, i. e.} \qquad f = v_f / v = v_f / v_{oc} \qquad (19)$$

and

$$f = f_g + \Delta \alpha_f (T - T_g) \quad . \qquad (20)$$

$\Delta \alpha_f = (\alpha_L - \alpha_G)\, T_g$ is the difference of the expansion coefficients of the polymer melt and of the glass at T_g. The resulting constants are

$$C_1^g = B_o / 2.303 \, f_g \qquad \text{and} \qquad C_2^g = f_g / \Delta \alpha_f \quad . \qquad (21)$$

Although the theory based WLF equations are valid strictly for T_g as the reference temperature only, the empirical relation

$$\log a_T = - C_1^o (T - T_o) / [C_2^o + (T - T_o)] \qquad (17\,a)$$

is used for other reference temperatures, T_o, too. The applicability of the relation generally is claimed for temperatures up to T_g + 100 K. The interdependence between the constants for different reference temperatures

$$C_1^o = C_1^g C_2^g / (C_2^g + T_o - T_g) \qquad C_2^o = C_2^g + T_o - T_g \qquad (22)$$

suggests that a single temperature correction, $T_\infty = T_o - C_2^o$, may be used in the WLF equation.

Consequently, the WLF equation may be written in a form being similar to the empiric VOGEL relation [9], which has been deduced for the temperature dependence of the viscosity:

$$\log a_T = C_1{}^o (T - T_o) / (T - T_\infty) \qquad . \qquad (23)$$

T_∞ is called "VOGEL temperature", which is claimed to be situated in the range of $T_g - 70$ K. The **second model** applies at higher temperatures, where the existence of sufficient free volume implies that overcoming of the potential energy barrier is the rate determining step of the viscous flow exclusively. According to EYRING's theory, when extended to viscous flow of fluids [10], an ARRHENIUS type equation is obtained for the temperature dependence of the zero-shear viscosity

$$\eta_o = [(hN_A / V) \exp(-\Delta S^{\#} / R)] \exp(\Delta H^{\#} / RT)$$

$$\text{or} \qquad \eta_o = B \exp(E / RT) \qquad , \qquad (24)$$

respectively. V is the molar volume, $\Delta S^{\#}$ and $\Delta H^{\#}$ are the activation entropy and enthalpy, resp. In the ARRHENIUS formulation B is considered a temperature invariant constant and E the apparent activation energy of flow. Consequently, the shift factor can be expressed, within the range of validity of ARRHENIUS's law, in the following way:

$$\begin{aligned} \log a_T = \log(\eta_o / \eta_o{}^o) = \log(\eta / \eta^o) &= (E / 2.303 R) [(1/T) - (1/T_o)] \\ &= (-E / 2.303 R T_o)[(T - T_o) / T)] \qquad . \qquad (25) \end{aligned}$$

By comparison with the WLF equation (17a) the two constants can be expressed as

$$C_1{}^o = E / 2.303 R T_o \qquad C_2{}^o = T_o \qquad . \qquad (26)$$

An interdependence between the apparent activation energy of viscous flow and T_g is indicated, if the glass transition temperature, T_g, is considered as reference temperature, instead ot T_o:

$$E / T_g = 2.303 R C_1{}^g \qquad . \qquad (27)$$

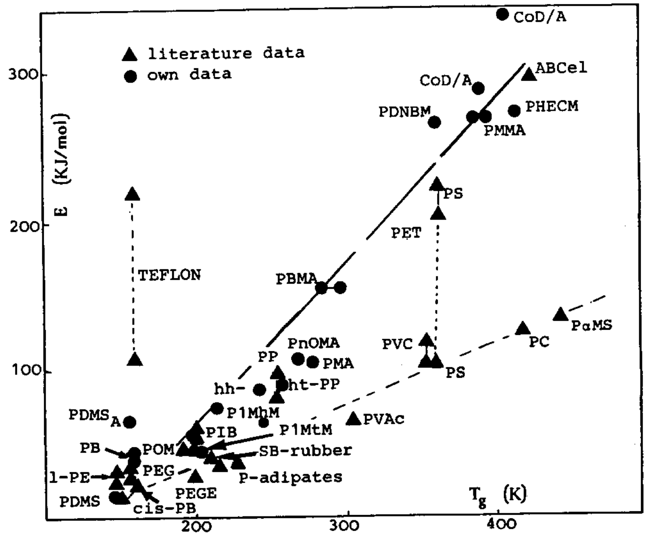

Figure 1: Apparent activation energy of flow, E, versus glass transition temperature, T_g, for various polymers

In Figure 1 both data from literature [11)-13)] and own results are presented to illustrate this correlation. The shape of the Figure remembers on similar attempts of other authors to correlate T_g data of polymers with various characteristics, like melting temperature, solubility parameter or molar cohesive energy [14], and with factors determining the flexibility of macromolecules, respectively [12].

On the other hand, it is also evident that the C_1 constant of of the WLF equation cannot be admitted an" universal" constant. It is a factor, which varies between certain limits, depending on the nature of the polymers. For the greater part of polymers, however, a constant factor seems to be applicable within certain limits. This observation is in accordance with statements of ADAM and GIBBS [5] and of SCHWARZL and ZAHRADNIK [15] concerning the non-universal character of WLF constant, as admitted by FERRY in the third edition of his book too [2]. As a general rule it can be stated, however, that the temperature coefficient of viscous flow of a polymer is as higher as higher its glass transition temperature. When writing the WLF equation (17 a) in the form

$$\log a_T = \{-C_1^{\,o}T/[C_2^{\,o} + (T - T_o)]\}[(T - T_o)/T] \qquad (28)$$

and comparing with the ARRHENIUS type relation (25), it is obvious that the activation energy of viscous flow is a temperature dependent factor, $E = E(T)$:

$$E(T) = 2.303\,RT_oC_1^{\,o}T/[C_2^{\,o} + (T - T_o)] = 2.303\,RT_oC_1^{\,o}T/(T - T_\infty) \quad . \qquad (29)$$

Consequently, the two ranges of viscous flow are delimited by the different nature of the activation energy within both regimes. Constant activation energy of flow, at higher temperatures, implies a stationary flow mechanism. The monotonic increase of the activation energy when approaching T_g suggests a gradual change in the flow mechanism, as predicted in the range of validity of the WLF relation. This monotonic change is not confirmed generally by experimental data. Especially at temperatures nearest T_g more or less pronounced discrepancies have been found between experimental shift factors and those calculated applying the WLF relation [15].

EXPERIMENTAL APPROACH FOR SHIFT FACTORS VIA ACTIVATION ENERGY

Experimental data substantiate that the ARRHENIUS law for viscous flow applies in the terminal zone, whereas the WLF equation is considered to be valid mainly for the glass transition region. It has been shown by us recently that in the terminal zone an a_F shift of isochrone viscoelastic data along the reciprocal temperature axis can be performed, besides the usual a_T shift of isotherm data along the log frequency axis. Isochrone mastercurves may be constructed in this way [16]. This is demonstrated in Figure 2 for G' of a poly(isobutylene), where the activation energy is temperature invariant. Consequently, isotherm and isochrone mastercurve are transformable into one-another by rescaling of the abscissa. The measurements have been performed in the excentric rotating disk mode. Due to slipping of the sample between the plates the glass plateau could not been reached. The composite curves are flattened at high frequencies and low temperature, consequently.

Figure 2 makes evident that the a_T shift corresponds to a frequency difference between the isotherms in double logarithmic scale, whilst the a_F shift manifests a $\Delta(1/T)$ differnce between the isochrones in log storage modulus - reciprocal temperature scale. Both differences are measured for arbitrarily chosen constant value of the respective modulus. Thus we may write for the shifts of the data

$$\log a_T = (\Delta \log\omega)_{G'_a} \quad \text{for isotherms and} \quad a_F = (\Delta T^{-1})_{G'_a} \quad \text{for isochrones,} \qquad (30)$$

G'_a being the arbitrarily chosen constant value of the modulus. In terms of the above defined shift factors the ARRHENIUS law (25) may be formulated

$$\log a_T = a_F E/2.303\,R \quad , \qquad (31)$$

corresponding to

$$(\Delta \log \omega)_{G'_a} = (E/2.303\,R)(\Delta T^{-1})_{G'_a} \quad . \qquad (32)$$

Equation (31) makes evident that both shift factors are interrelated by the activation energy of viscous flow. This means that, within the range of validity of ARRHENIUS's law, the shift of isotherms as well as of isochrones is governed only by the constant activation energy of flow, and that composite curves can be drawn using an unique shift principle [17].

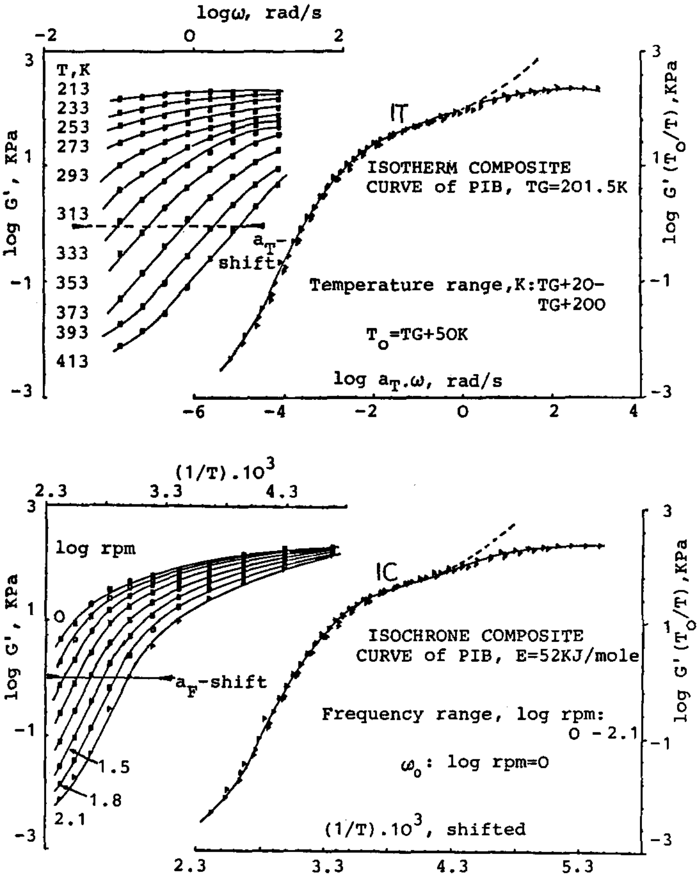

Figure 2: Construction of isoterm and isochrone mastercurves for poly(isobutylene), M_n = 12000

As long as the superposition principle holds, the shift factors are not depending on the arbitrarily chosen value of the viscoelastic function. The parallelity of two curves is assured if for any couple of identic ordinates the slopes of the respective curves are identical. Consequently, in reduced coordinates, isotherms of identical slope $[\partial \log G' / \partial \log \omega]_T$ are a_T-shifted along the frequency axis, whilst isochrones of identical slope $[\partial \log G' / \partial (1/T)]_\omega$ are a_F-shifted along the reciprocal temperature axis.

Viscoelastic data may be represented spatially in log viscoelastic function - log frequency - reciprocal temperature - coordinates. It has been demonstrated that the slopes of the isochrone and of the isotherm viscoelastic functions in a given point are also connected via activation energy of flow [18]:

$$\frac{[\partial \log G' / \partial (1/T)]_\omega}{[\partial \log G' / \partial \log \omega]_T} = E(T) / 2.303 R . \quad (33)$$

Equation (33) does not imply, however, a constant activation energy of viscous flow. This assumption is connected only with the EYRING model. The above equation is useful to deliminate the temperature regimes, where the two models are valid. The EYRING model will be the determining one as long as the activation energy derived from ratio of the slopes of the isochrone and the isotherm curves at a given point of the viscoelastic function surface is a temperature independent constant. On the other hand a temperature dependent E-value suggests that the DOOLITTLE model applies, and that the viscoelastic behaviour of the polymer is depending mainly on the disponible free volume for configurational redistribution.

The discussed approach for evaluation of temperature dependent viscoelastic data offers the chance to rediscuss literature data on the viscoelastic properties of polymers in the vicinity of the glass transition. Data of FERRY et al. for poly(butylmethacrylate) (PBMA) [19] and poly(n-octylmethacrylate) (PnOMA) [20] as well as of SCHWARZL and ZAHRADNIK for poly(methylmethacrylate) (PMMA) [15] have been used. It may be stated that in the latter case the shift factors calculated by our method are in agreement with the experimental ones, whereas the WLF equation failed at lower tures, as evidenced by the respective authors [15].

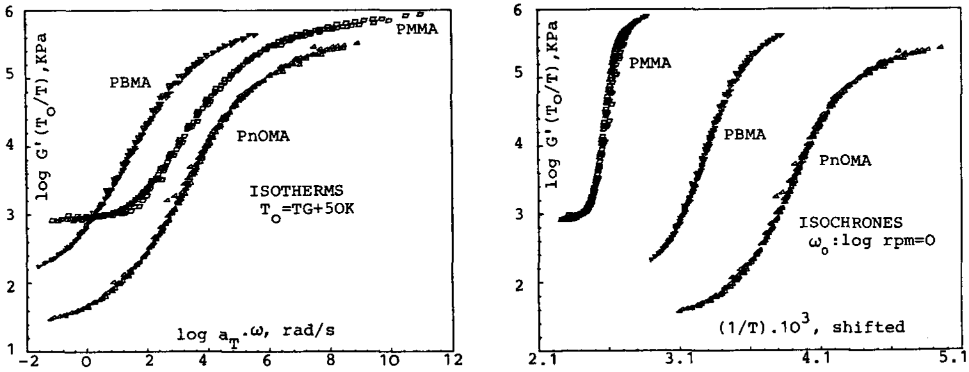

Figure 3: Isotherm and isochrone mastercurves for PMMA (Solvic 229) PBMA (M_w = 3050000) and PnOMA (M_w = 3620000). Reference temperature and frequency indicated

In Figure 4 the activation energies used to evaluate the shift factors in the range near T_g are shown for the composite curves presented in Figure 3. These activation energies were evaluated by the trial-and-error method. Calculations according to equation (33), from the slopes of the isochrones and the isotherms at a given point in the viscoelastic master surface, yielded somewhat higher values [22].

It is remarkable that the range of variable activation energy of flow, and that of the applicability of the WLF relation, is relatively narrow. A customary constant activation energy is reached already above T_g + 40 K. At least for the studied polymers the range of the DOOLITTLE model and of the related WLF equation is much smaller as supposed usually.

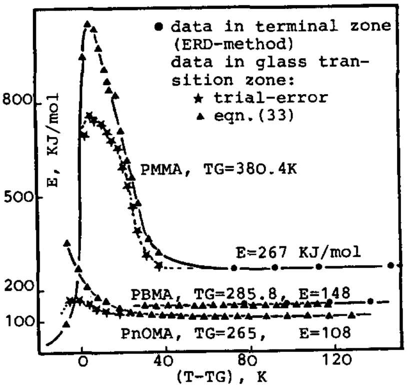

Figure 4: Apparent activation energy of flow versus T - T_g for the polymers indicated in Figure 3

According to equation (33) the activation energy of flow is given by the ratio of the two slopes of isochrones and isotherms. The correlation between the slopes of composite curves for the storage modulus and the activation energy in the final zone of viscous flow is illustrated in Figure 5. It is evident that the slope of the isotherms is nearly identical for all polymers studied. Some influence of polydispersity is suggested by ONOGI et al. [21]. On the other hand, the slope of the isochrones is strongly dependent on the activation energy of flow and - via this activation energy - on T_g (comp. Figure 1). This is not surprising, because the shift is efected versus 1/T. This means that the isochrones of dynamic viscosity are shifted along the slope of the zero shear viscosity or along the slope given by the activation energy of viscous flow, as demonstrated by SCHNEIDER and CANTOW [16].

The same regularities are evidenced also by the composite curves in the glass transition range, as shown by the data in Figure 3. For both the transition zone from the glassy state to the rubber plateau as well as for the terminal zone of viscous flow the temperature coefficient of viscoelastic properties seems to increase in parallel to the glass transition temperature of the respective polymer.

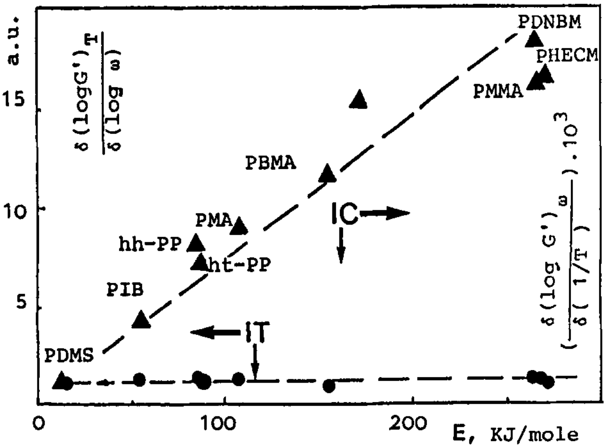

Figure 5: Correlation between the slope of composite curves for the storage modulus and the activation energy in the final zone of viscous flow. Measurements of the authors [22].

On the contrary, the steepness of the transitions in the frequency range is invariant essentially [21].

In conclusion the linear viscoelastic behaviour can be interpreted unequivocally by the apparent activation energy of viscous flow. The proposed method is satisfactory also at very low temperatures near T_g, where the WLF equation oftenly fails. The EYRING model applies down to temperatures T_g + 40 K.

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