The Viscosity Anomaly near the Lower Critical Consolute Point[1]

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ABSTRACT

The shear viscosity measurements for critical mixture 3-methylpyridine + heavy water near lower critical consolute point are reported. The background contribution was constructed based on the viscosity measurements of mixtures with noncritical composition. In the whole investigated temperature range $t_c - t < 15.6$ K the viscosity of critical mixture exceeds background and the critical enhancement is important. The critical increase of viscosity is found in the temperature range $t_c - t < 1.82$ K. The critical exponent $\boldsymbol{y} = 0.043 \pm 0.002$ and wave number $Q = 0.35 \pm 0.05$ nm^{-1} are found.

KEY WORDS: critical behavior; lower critical solution point; viscosity.

1. INTRODUCTION

Shear viscosity η exhibits weak divergence approaching to the critical point from one-phase region. Renormalization group [1] and the mode-coupling [2,3] theories predict the η divergence as

$$\eta = \eta_0 (Q\xi)^z F \qquad (1)$$

where η_0 is the background viscosity, ξ, the correlation length, z is a universal critical exponent, Q is a system dependent wave number, F, crossover function. Theoretical estimates for z give values $z \approx 0.052$ and $z \approx 0.063$ [4]. The latest z value seems to be in better agreement with experimental data [5-8]. The search of connection between the range of viscosity critical behavior, values of system depended parameters with peculiarities of molecular structure and intermolecular interaction is of special interest in view of active investigation of the critical behavior of electrolytes now [9,10]. However the difficulties with determination of background contribution and an ambiguity of crossover from critical to noncritical behavior prevent to obtain sufficient information for such analysis.

The viscosity measurements for binary mixture 3-methylpyridine (MP) with heavy water (HW) in the wide vicinity of the lower critical consolute point are reported in present paper.

2. EXPERIMENT

2.1. Methods

The kinematic viscosity measurements were performed with an quartz Cannon-Tilting type capillary viscometer. The capillary had a length l = 12.5 cm and an internal radius R = 0.032 cm. The volume flowing through the capillary was V = 5.4 cm^3 and the

mean value of the height of the fluid meniscus during an experiment was h = 14.5 cm. The capillary tube had a sudden bottom opening which makes the surface-tension effects negligibly small [11]. The viscometer was calibrated with pro-analysis toluene [12] and with double distilled water [8] in the temperature range 16°C < t < 70°C, taking into account "inlet" correction. The efflux time θ was measured with a stopwatch from 5 to 7 times for every temperature. The upper bound of the accidental error is estimated as 0.1%, while the systematic error 0.3% may be regarded as maximum error of absolute values of kinematic viscosity. The viscometer was immersed in a carefully insulated water thermostat (volume 20 l) with long-time temperature stability ± 0.005K.

The density of mixtures were measured as a function of temperature with pycnometer. It was calibrated and provided the density measurements with the systematic error no more than 0.3%.

2.2. Experimental results for critical mixture

The viscometer was filled with mixture MP + HW with mass fraction of MP, C_c = 0.2997 in according with [13]. Kinematic viscosity was measured for 78 temperatures in the range 24.0°C < t < 39.54°C and demonstrated critical increase in the temperature range 37.72°C < t < 39.54°C.

In order to find the shear viscosity values we performed the density measurements for the critical sample and found the temperature dependence of density $\rho_c(t)$ represented successfully by equation

$$\rho_c(t) = 1.07415 - 4.91 \cdot 10^{-4} t - 3.01 \cdot 10^{-6} t^2 \qquad (2)$$

The obtained temperature dependence of shear viscosity $\eta = \tilde{\nu} \cdot \rho$ is presented in Fig.1.

The critical temperature t_c of the sample was determined by visual observation of the critical opalescence followed by separation of mixture on two liquid phases. Note, that at the temperature slightly higher t_c in the strongly shaken and macroscopically homogeneous mixture we observed a sharp decreasing of efflux time. For our sample we found the critical solution temperature to be equal to t_c =39.540 ± 0.005 °C.

2.3. Correction for the influence of shear

The viscosity measurements may be affected when the decay time of the concentration fluctuations becomes comparable to the reversed rate of shear, S^{-1}. The influence of shear for the lower critical consolute temperature as well as for the upper critical temperature appears in enlargement of the one-phase region and deceleration of the critical divergence of viscosity while the critical temperature approaches. From Fig.1 one can see that several experimental points in the range of the reduced temperature $\mathrm{t} \le 3\cdot 10^{-4}$ $\left(\mathrm{t} = \left(t_c - t\right) \big/ \left(t_c + 273.15\right)\right)$ demonstrate above mentioned tendency and correction for shear seems to be important for these data. Approaching t_c the rate of shear produces two effects. The first effect was considered by Oxtoby [14] . It concerns the decreasing of the shear viscosity due to shear $\mathrm{h}(S)$ in comparison with viscosity at zero shear rate $\mathrm{h}(S=0)$:

$$\mathrm{h}(S=0) = \mathrm{h}(S) / \left[1 - \Delta(\mathrm{l})\right] \qquad (3)$$

where the correction $\Delta(\mathrm{l})$ for not very strongly shear ($0.1 < \lambda < 20$) is given by

$$\Delta(\mathrm{l}) = 0.0214 + 0.0266 \log \mathrm{l} + 0.0078 \left(\log \mathrm{l}\right)^2 \qquad (4)$$

λ is a dimensionless parameter, which is related to the shear value S

$$\lambda = \frac{\eta \xi^3 S}{k_B (t + 273.15)} \qquad (5)$$

k_B - the Boltzmann constant. The shear rate S is a transverse velocity gradient and in a capillary viscometer it may be estimated as [8] :

$$S = \frac{4 \rho g h R}{15 \eta l} \qquad (6)$$

where g is the acceleration due to gravity. The shear rate S changes with temperature mainly due to change of shear viscosity and in our case varies within the limits $490 s^{-1} < S < 553 s^{-1}$. The parameter λ diverges strongly near the critical point due to the divergence of the correlation length ξ. In our case the viscosity changes along the way isomorphic to the critical isochore and correlation length varies with reduced temperature τ as

$$\xi = \xi_0 \tau^{-\nu} \qquad (7)$$

where $\nu \approx 0.63$ is the critical exponent and ξ_0 is the amplitude of the correlation length. For mixture MP + HW near the lower critical solution point the ξ_0 value was found from light scattering measurements [15]: $\xi_0 = 4.43 \cdot 10^{-10}$ m. The obtained values of parameters λ indicate that 8 experimental points close to t_c should be corrected to the influence of shear. The corrected values of shear viscosity η_c using Eq. (3) are presented in Fig.1. As we can see from Fig.1 the data corrected for shear following Oxtoby form approximately straight line and the second correction [16] seems to be needless in our case.

2.4. Determination of the regular part

In order to extract the critical part of shear viscosity from the experimental data the background viscosity should be determined in the range far from t_c . Much of the ambiguity is due to lack of knowledge about the range of the critical enhancement which

may stretch over 20 K from t_c [7,10]. Moreover, the form of the background temperature dependence is not well known, especially for associated liquids such as aqueous solutions. Therefore the viscosity for noncritical compositions with mass fraction of MP, C_1 = 0, C_2 = 0.0998, C_3 = 0.1994, C_4 = 0.4003, were measured in the temperature range 24°C < t < 40°C. The measurements of the mixture with higher concentration of MP are useless for our purpose due to nonmonotonic dependence of viscosity upon concentration of organic component in aqueous solutions (see, for instance, [8]). The measurements for noncritical mixtures were done for 20 temperatures similar for 4 mixtures and presented in Table I. The noncritical viscosity data of a mixture with critical composition , C_c = 0.2998, at these temperatures were constructed using quadratic approximation and they are also listed in Table I. The viscosity temperature dependence for mixtures of critical and noncritical composition together with constructed background data for critical composition are shown in Fig.2. The shear viscosity of the critical mixture exceeds the constructed background in the whole temperature range . So the critical enhancement is significant for critical mixture MP+ HW in the wide temperature range (more than 20 K near critical temperature). Therefore, the attempts to estimate background contribution from the data of critical mixture [17] give rise to doubt. Note, that the viscosity data of mixture 2-butoxyethanol + water are not influenced by critical contribution already since the temperature t_c - t = 11 K [8]. The comparison of the known experimental results on aqueous solutions of 2,6-lutidine [18], isobutyric acid [7], butoxyethanol [8] and methylpyridine [this paper] allow to assume that the range of critical enhancement increases with decreasing of absolute value of the solution viscosity.

3. ANALYSIS OF CRITICAL CONTRIBUTION

Shear viscosity data η divided on the background contribution η_0 were fitted by the following general equation

$$\frac{\eta_c}{\eta_0} = A\tau^{-y}F \qquad (8)$$

with $A = \left(Q\xi_0\right)^{y/\nu}$ taken as single adjustable parameter, $y = z \cdot \nu$ and F, crossover function. The function F was set to be equal 1 (no crossover) or corresponding to the first term of the Wegner correction-to-scaling to correlation length

$$F = \left(1 + a\tau^{0.5}\right)^{y/\nu} \qquad (9)$$

or corresponding to the dynamic correction-to-scaling [19]

$$F = 1 + a\tau^{0.7} \qquad (10)$$

a is an amplitude of correction. The critical temperature was fixed at its critical value t_c =39.540°C, while the critical exponent y was a free parameter as well as set to theoretical predictions. The results of fits are presented in Table II. The experimental data and several fitting curves are shown in Fig. 3. The value y = 0.0327 (z=0.054) may be certainly rejected as inconvenient. The exponent y = 0.0389 (z=0.062) well fits the data close to the critical point but evidently deviate from experimental data far from critical point. Including the correction with Wegner exponent Δ improves the fit but not enough. The dynamic correction [19] introducing with Eq. (10) leads to the best fit in the whole temperature range but the fit of near critical data becomes worse.

We also fitted our data using the another field variable $\tau' = \left(\frac{T_u - T}{T_u}\right)$, which is usually used for mixtures MP + HW in order to take into account closeness of upper

critical consolute temperature T_u. The results of fits for exponent y and wave number Q appear very similar to those for usual field variable t and some of them are presented in Table II and denoted by stars. Using the value of critical amplitude $x_0 = 0.16nm$ obtained in [17,20] from the fits with field variable t' we can conclude that the most preferable value of wave number Q = 0.352±0.001nm^{-1}. This value well coincides with Q presented in Ref.[17] for several solutions of ternary mixture MP + HW + water, but differs from Q for binary mixture MP + HW. The latest discrepancy may be caused by the worse quality of results namely for this solution, including rough estimate of background. So we can reject any dependence wave number Q on substitution heavy water by water in aqueous solution of pyridines.

Based on the results presented in Table II we conclude that appropriate for our data value of wave number is Q = 0.35±0.05 nm^{-1} . It is rather close to value Q for nitrobenzene+n-hexane [6], electrolytic mixtures [9,10] and two times larger than Q for rather similar aqueous solution of 2-butoxyethanol [8].

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Table I . Shear Viscosity η of MP+HW Mixtures with Different Mass Fractions C_i (i=1...4) of Methylpyridine and Constructed Background Viscosity for Critical Mixture C_c

	$C_1 = 0.$	$C_2 = 0.0998$	$C_3 = 0.1994$	$C_4 = 0.4003$	$C_c = 0.2997$
t,° C	η, cPoise	η, cPoise	η, cPoise	η, cPoise	η , cPoise
24	1.12775	1.47094	1.95381	2.70607	2.3146
25	1.1009	1.43328	1.89887	2.62685	2.2488
26	1.07182	1.38943	1.84568	2.55831	2.1889
27	1.04954	1.35505	1.79443	2.48301	2.1219
28	1.02624	1.32003	1.7507	2.40121	2.0591
29	0.9999	1.28426	1.70024	2.33029	1.9991
30	0.98078	1.25436	1.65577	2.2669	1.9491
31	0.96365	1.2248	1.61515	2.20022	1.8934
32	0.94249	1.19058	1.57783	2.14029	1.8434
33	0.92372	1.16484	1.53762	2.08266	1.7934
34	0.90111	1.13584	1.50185	2.03271	1.7506
35	0.87929	1.1035	1.46666	1.98057	1.7078
36	0.86148	1.08165	1.4338	1.93239	1.665
37	0.84205	1.05542	1.40363	1.88852	1.6307
38	0.82602	1.03352	1.37136	1.84061	1.5893
39	0.80857	1.00748	1.34352	1.80425	1.555
40	0.7907	0.9838	1.31953	1.76458	1.5222

Table II. Parameters Obtained for Different Crossover Functions with Critical Temperature Fixed at the Experimental Value, t_c = 39.54 °C. The Values in Brackets Were Set as Fixed Parameters in Fitting Eq. (8). The sets denoted by star were obtained with field variable t'.

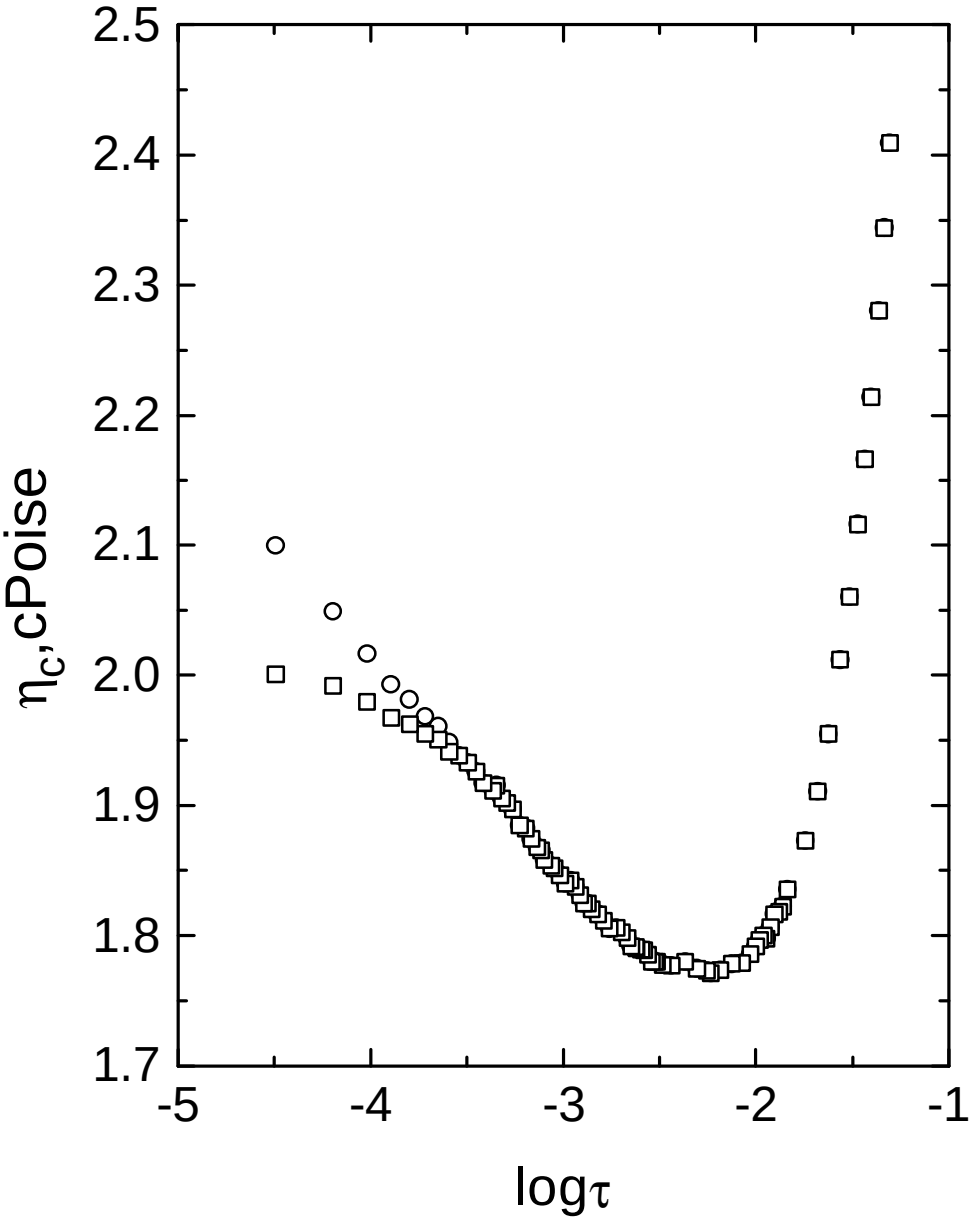
N	Crossover function	y	A	a	Q nm^{-1}	χ^2
1	F=1	(0.0327)	0.94893	-	0.822	3.14
2	F=1	(0.04095)	0.9009	-	0.453	1.66
3	F=1	0.03889	0.91273	-	0.514	1.57
4	Eq. (9)	(0.0327)	0.95537	-1.88485	0.937	2.50
5	Eq. (9)	(0.04095)	0.89555	1.64137	0.414	1.41
6	Eq. (9)	0.04531	0.86294	4.2754	0.291	1.30
7	Eq. (10)	(0.0327)	0.95397	-0.22068	0.911	2.62
8	Eq. (10)	(0.04095)	0.8968	0.1966	0.423	1.33
9	Eq. (10)	0.04351	0.8797	0.33066	0.353	1.21
10*	Eq. (10)	(0.0327)	0.90386	-0.46534	0.892	2.62
11*	Eq. (10)	(0.04095)	0.83881	0.7345	0.419	1.34
12*	Eq. (10)	0.04343	0.82013	1.108	0.352	1.22

FIGURE CAPTIONS

Fig.1. The experimental shear viscosity data of critical mixture (quadrangles) and data corrected for shear following Eq. (3) (circles).

Fig.2. Temperature dependence of the viscosity of mixtures of different compositions : C_1 = 0 (set 1), C_2 = 0.0998 (set 2), C_3 = 0.1994 (set 3), C_4 = 0.4003 (set 4), C_c = 0.2998 (set 6) and constructed background contribution to viscosity of critical mixture C_c = 0.2998 (set 5).

Fig. 3. Analysis of singular contribution to the viscosity of critical mixture. The experimental data points are presented by circles; fits 1, 3 and 9 from Table II are shown by dot, dash and solid lines, respectively.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η_c,cPoise
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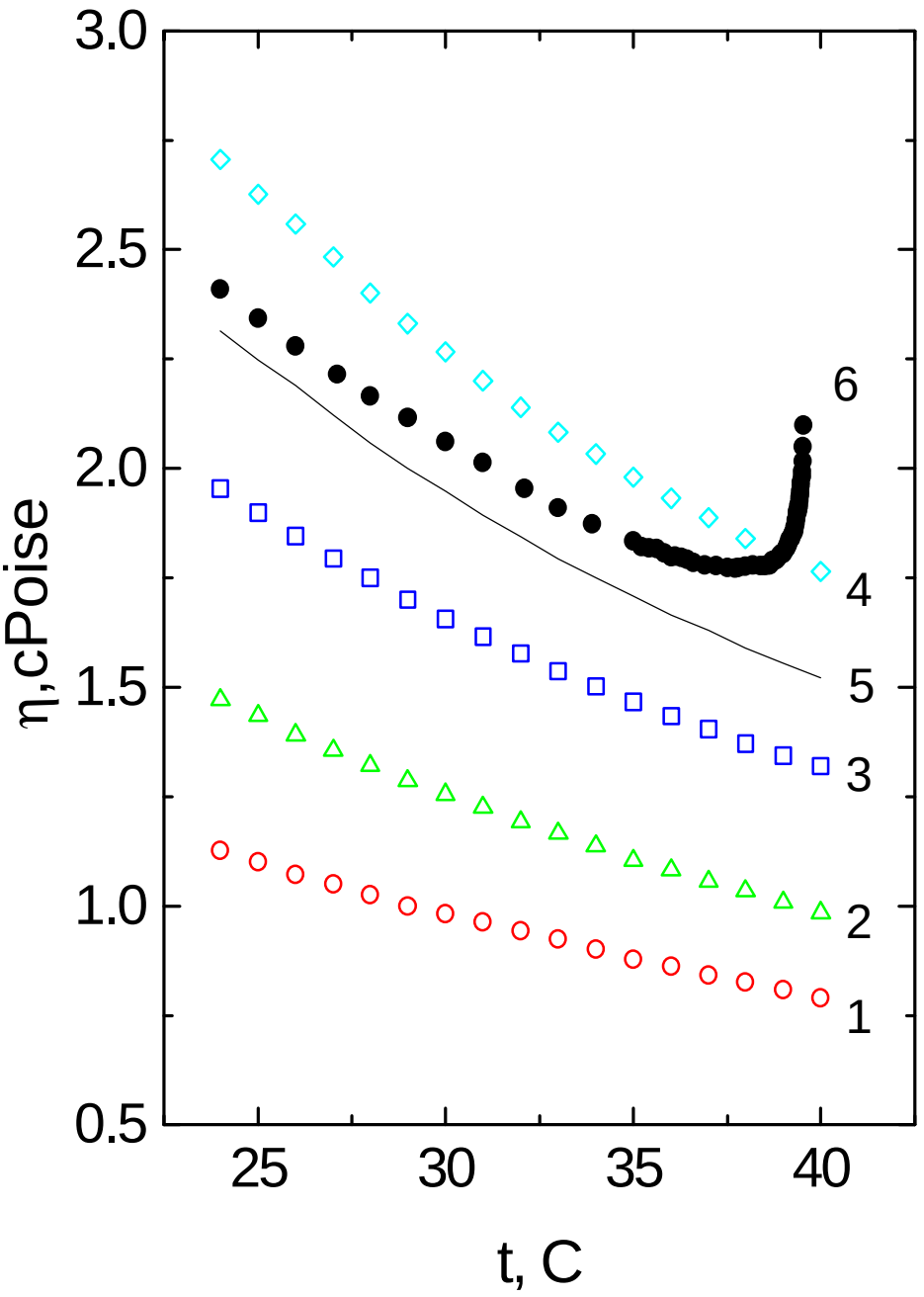
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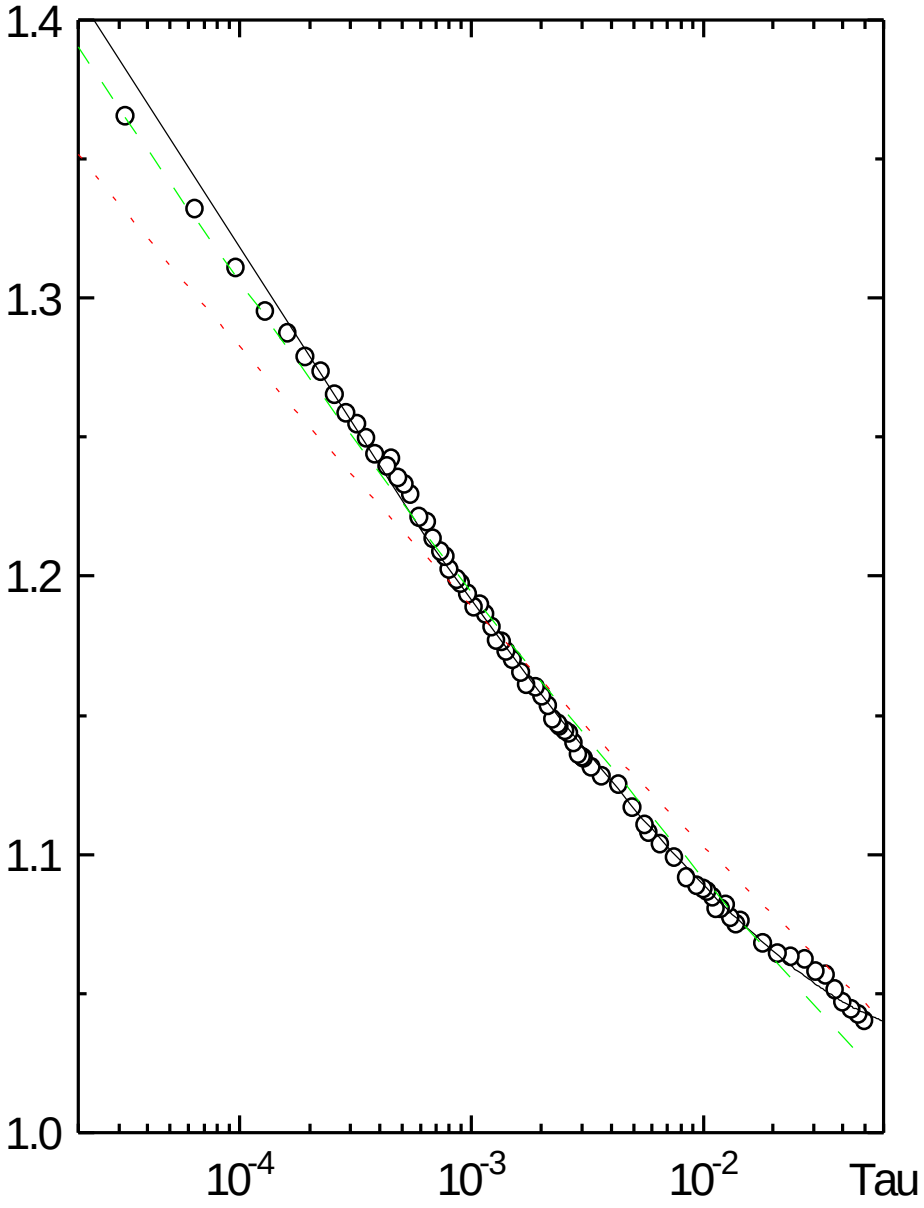
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