Non-Exponential Behavior Near the Critical Point of an Ionic micellar System

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ABSTRACT

The coexistence curv es of the system dodecylammonium Chloride + water + KCl have been obtained from different salt concentration. We found that the asymptotic behavior of the order parameter can be describe using a extended scaling and the usual Ising value for the $\beta = 0.325$ exponent. The static light scattering data for the critical composition are also compatible with the Ising value of $\nu = 0.63$.

Dynamic light scattering results have been obtained near the liquid-liquid critical point. The correlation functions have been found to be single-exponential for temperatures well above critical, while a new decay process at longer times becomes evident at $T-T_c < 4$ K. These correlation functions can be fitted with a double exponential function without systematic trend in the residuals.

The diffusion coefficient associated to concentration fluctuations has been calculated from both relaxation modes. It has been analyzed in terms of the predictions of the mode-coupling theory. The results together with correlation length and the viscosity data, are in good agreement with the calculations.

KEY WORDS: Coexistence curve; critical phenomena; light scattering; micellar solution.

1. INTRODUCTION

The behavior of micellar systems near a critical point has attracted much attention in the last years [1]. Although some experiments lead to critical exponents different to those of the 3-d Ising model, recent experimental work has shown that micellar systems belong to the Ising class [2].

Ionic micellar systems are particularly interesting. They are actually ternary systems including water, a salt and a surfactant. In the case of liquid-liquid equilibrium, it is generally found that the salt concentration is the same in the coexisting phases, in this case the system can be seen as pseudobinary. Furthermore by tuning the ionic strength one can modify the phase behavior of the system. More specifically, one can reduce the difference between the critical point temperature and the Kraff temperature (T_k), where the pure surfactant solid is in equilibrium with the solution. In the limit $|T_c - T_k| \to 0$ the critical point became a critical en point (CEP). Recent experiments and theoretical work indicate that the proximity of a CEP does not affect the critical behavior of the system undergoing a second order phase transition [3,4].

In most cases simple scaling equation have been used to describe the experimental data [2,5,6]. Both static and dynamic light scattering results for micellar systems lead to values of the critical amplitude of the correlation length, ξ, of the order of 1-2 nm, a value which is larger than the one found for mixtures of simple liquids[5,6]. Since the range of validity of simple scaling laws depends on $1/\xi^6$ (Ginzburg´s Criterion) it seems reasonable to expect it to be smaller than in simple liquid mixtures [7]. It is well known that the use of simple scaling laws outside its range of validity leads to effective critical exponents that differ from the 3-D Ising ones. This might lead to values of the exponents ν and γ close to the Fisher-renormalized ones even for relatively small values of $\left(\varepsilon = |T - T_c| / T\right)$, for which simple scaling holds for mixtures of simple fluids.

The critical dynamics of simple binary mixtures has been also studied in detail, and the experimental results show a remarkable agreement with the predictions of mode-coupling and renormalization group theories of dynamic critical phenomena [8]. As

described by Hohenberg and Halperin [9], the key factor for the critical slowing-down of the order parameter fluctuations is the nondissipative coupling between the order parameter and the transverse part of the momentum density.

For binary liquid mixtures, the decay of the order parameter fluctuations $\Gamma(q)$ is most frequently obtained from photon correlation spectroscopy experiments. Despite that the theory predicts the existence of two relaxation modes near a consolute point [9], there is a very limited number of experiments reporting non-single exponential correlation functions $\Gamma^{(2)}(q,t)$ [10,11,12].

In order to shed light to some of the questions mentioned, we have chosen an ionic micellar system: dodecylammonium chloride (DAC) + water + KCl. The system show an upper critical solution temperature (UCST). This critical temperature increase with increasing [KCl], but critical concentration does not seem to change significantly and it is kept constant arround 1.0 wt % of DAC. Fig. 1, show the relative position of the critical line for different salt composition with respect to the Krafft line. The arrows in the Fig. show the three path concentration we choose to carry out both the static and dynamic light scattering measurements. Some off-critical compositions close to that ones, were also measured.

The rest of the paper is organized as follows: Section 2 gives some details of the experimental procedure. The data and the methods followed from the data analysis, and the discussion of the results are given in section 3.

2. EXPERIMENTAL SECTION

The coexistence curve at 0.1 MPa were obtained by the point by point method described elsewhere [13]. The composition of the samples was determined by weight with a precision of $\pm$ 0.5 mg. The samples were placed in a water bath and the temperature was kept constant and measured within a 1mK.

The effect of pressure on the T_c was measured with a technique described previously [14]. The precision was 0.01 MPa over the whole pressure range.

Both Static and Dynamic Light scattering experiments were performed on a Malvern K7032 instrument using and Ar^+ laser operating at 514.5 nm. In order to ensure appropriate temperature control (±0.5 mK) the measuring cell was modified and a Tronac PTC-41 proportional controller with a TCP-25-S probe was used. The temperature was measured with a platinum resistance thermometer.

DAC was synthesized and purified as in previous work [15]. The water was double distilled and deionized (Milli-Q, Ω>10 MS) KCl was Carlo Erba RPE, purity >99%. the mixtures were also prepared by weight with the same mentioned precision. All the light scattering samples were filtrated through a 0.2μm pore size membrane just before use.

3. RESULTS AND DISCUSSION

3.1 Coexistence Curve

We have measured the coexistence curve of the binary system a different salt concentration. Fig. 2, show the phase separation temperature vs the weight fraction of DAC. For a binary mixture near an upper critical solution point temperature (UCST), the shape of the coexistence curve according to the renormalization group (RG) can be described as

$$\Delta\lambda = B_0 t^{\beta}(1 + B_1 t^{\Delta} + B_2 t^{2\Delta} + \ldots) \qquad (1)$$

where $\beta = 0.325 \pm 0.001$ and $\Delta = 0.50 \pm 0.02$ are critical exponents; $t = (T-T_c)/T_c$; B_0, B_1 and B_2 are critical amplitudes.

Table I collects the result of the fit with the Eq. (1). As a example Fig. 3, show the results for [KCl] = 0.30 M. It can be seen that there is a fairly good agreement between the data and Eq. (1) with fixed values of the critical exponents. Although the range of validity of simple scaling is small ($t < 10^{-4}$) when compared with other nonmicellar systems [16], and it seems to decrease as the CEP is approached. Any attempt to fit the curves outside that range leads to effective β values that can be even larger than the mean field value.

The dependence of T_c on the pressure has been studied. In all cases a linear behavior have been found, with a slope $dT_c/dp = (-20\pm1)$ mK/bar, which is independent of the salt concentration. This value along with the critical amplitudes an the result of the light

scattering and the density, allow us to confirm the validity of the two scale universality hypothesis for ionic micellarsystems, obtaining a value of $R_\xi = 0.27 \pm 0.03$.

3.2 Static light Scattering

The total scattered intensity data as a function of the scattering vector for mixture of critical composition have been analyzed in term of the Ornstein-Zernike approximation

$$\frac{I_s(q)}{I_0} = \frac{AT\chi_T}{1+q^2\xi^2} \tag{2}$$

where q= $4\pi n \sin(\theta/2)/\lambda$, λ being the vacuum wave of incident light, n the refractive index of the sample, θ the scattering angle , I_0 the incident light intensity. T is the absolute temperature, ξ the correlation length and χ_T.a generalized susceptibility. The A constant account for the optical properties of the mixture.

The temperature dependence of χ_T and ξ are described by the power laws

$$\begin{aligned} \xi &= \xi_0 \varepsilon^{-\nu} \\ \chi_T &= \chi_{T,0} \varepsilon^{-\gamma} \end{aligned} \tag{3}$$

where ν and γ are universal critical exponents. ξ_0 and $\chi_{T,0}$ are the characteristic critical amplitudes. After correction the data for turbidity, we follow the method described by Sinn and Woermann [17] to obtain ξ, and χ_T (in arbitrary units).

The fit of the ξ and χ_T data using Eq. (2) up to $t \leq 10^{-3}$ yielded values of critical exponents .which are collected in tables II and III. These values of ν and γ are in good agreement with the 3D-Ising prediction (γ=1.241, ν=0.63) for all critical concentration.

The amplitude ξ_0 is similar to that found in another micellar systems[6,18] and is one order of magnitude larger than the one for binary mixtures of simple liquid. The $\varepsilon = \left(|T - T_c|T_c\right)$ range for which constant values of the critical exponents ν and γ are found, is similar to the range found for mixtures of simple liquids.

It can be, also observed that the critical exponents do not show any significant change when the CEP is approaching by reducing [KCl]. This result agrees with the predictions of Fisher and Barbosa [4].

Along with the previous experiments some samples corresponding to off critical composition were also measured. Theses allows us to test the prediction from the so-called linear model [19].

According to the linear model we can describe the correlation length as follows,

$$\xi^2 = \xi_0^2 \frac{V_m}{V_{m,c}} \left[\frac{w_c(1-w_c)}{w(1-w)} \right]^2 \frac{r^{-\gamma}}{1+d_2\theta^2} \tag{4}$$

where V_m y $V_{m,c}$ are the molar volumes of the off-critical and critical mixtures, d_2 is a universal constant and r and θ are parametric variables that we have calculated from the critical temperature and composition.

Fig. 4 shows that the results for all three isochores for [KCl] = 0.30 collapse on a single straight line, confirming the validity of Eq. (4). Similar results were found for other values of [KCl].

3.3 Dynamic light scattering

Dynamic light scattering allow us to measure the temporal autocorrelation function for the thermally induced concentration fluctuations. Experimentally, we obtain the intensity-intensity autocorrelation function $g^{(2)}(\tau)$. This is related to the field-field correlation function, $g^{(1)}(\tau)$, for a ergodic system through the equation:

$$g^{(2)}(\tau) - 1 = \beta \left| g^{(1)}(\tau) \right|^2 \tag{5}$$

Fig. 5 show the normalized intensity correlation function ($g^{(2)}$-1). for some temperatures far and near T_c, and at θ = 90°.

The data collect in this figure shows two different regimes. Far from critical temperature the experimental correlation function are single exponential

However, as T approaches T_c, the correlation functions can no longer be described by a single exponential function. Following the procedure of Rouch et al.[20], we have tried to fit the results using a stretched exponential, but, the residuals still show

systematic trends. Therefore we used a double exponential as Ackerson and Hanley [12] and Hair et al. [10], and Onuki [21]

$$g^{(2)}(t) - 1 = \beta\left[A_{fast}e^{-\Gamma_{fast}t} + A_{slow}e^{-\Gamma_{slow}t}\right]^2 \qquad (6)$$

where Γ_{fast} and Γ_{slow} are the decay rates and A_{fast} and A_{slow} the corresponding amplitudes.

In order to rule out that the fast contribution appearing in our results near T_c is due to multiple scattering, we have carried out measurements for $|T-T_c| < 0.3$ K using cells with three different path lenght of 25, 10 and 3 mm. We have found that within the experimental uncertainty there was no significant change in the relative weight of the two relaxation processes.

The decay rates (Γ_{fast} and Γ_{slow}) obtained fitting the experimental autocorrelation function using Eq. (8) are shown in Fig. 6. It can be observed that the fast mode has a diffusive character through the whole (T,q) experimental range for which two processes are observed. For the sake of comparison, Fig. 6a also shows the decay rate for the temperature farthest away from Tc. The q^2 dependence of Γ_{fast} allows one to define a diffusion coefficient $D_{fast}(T,q) = \Gamma_{fast}(T,q) / q^2$. It must be remarked that there is a smooth transition between the diffusion coefficient D^o obtained from the single exponential correlation functions measured at temperatures far away the critical one and $D_{fast}(T)$ for the temperature interval in which two processes can be separated.

Fig. 6b shows that Γ_{slow} presents a diffusive character only for low q's. The maximum value of q for which a q^2 behavior is observed decreases as T approaches Tc. For high values of q, Γ_{slow} shows a q^3 dependence. This kind of crossover has been extensively discussed in the literature for the decay rate of critical fluctuations [22].

It should also be mentioned that the values of the decay rates corresponding to the fast peaks are similar to those corresponding to the dynamics of micelles in non-critical mixtures, i.e., far from T_c. On the other hand, the values of Γ_{slow} are of the same order of those usually assigned to the concentration fluctuations in near critical micellar systems.

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The mode-coupling theory predict that the decade rate of the critical fluctuation can be describe to the lowest order in the solutions as:

$$\Gamma_c(q,T) = q^2 D_c K(x) / x \qquad (7)$$

where, $D_c = R_c k_B T/(6\pi\eta\xi)$ and $K(x) = (3/4)\ [1 + x^2 + (x^3 - x^{-1})\tan^{-1}(x)]$ is the Kawasaki universal function with $x = q\xi$. In the preceding expressions $R_c = 1.027$.

In order to probe the validity of Eq. (7) we must calcute D_c. D_c is related to the measured fast and solw modes and to a background contribution D_u, which correspond to the value that the diffusion coefficient would have in absence of any critical perturbation. We can calculate D_u, knowing that at Tc, due to the critical slowing down D_c should be zero. With the value of D_u at Tc and assuming that it does not depend on q (pure diffusive character) we can compute D_c for al the other temperature and q's. We describe extensively this procedure in a previous paper [23].

The calculated values of D_C can be compared with the predictions of the mode-coupling theory. To do so, it is customary to reduce the diffusion coefficient associated to the decay rate as:

$$D^* = D_c\left(6\pi\eta\xi / k_B T R_c\right) = K(x) / x^2 \qquad (8)$$

Fig. 7 shows the fairly good agreement between the results and the predictions given by Kawasaki's function.

It is worth noting that, we have found that D_{fast} is much larger than D_{slow}. As a consequence, over most of the T and q values, we have $D_u \approx D_{fast}$, and therefore $D_C \approx D_{slow}$ (this is so from a numerical point of view but from the physical point, both modes contain part of the critical fluctuations). A complete decoupling of the hydrodynamic modes would allow to interpret the two contributions in Eq.(9) directly in terms of critical and non-critical contributions, a result similar to that of Onuki [21] for $^3He + {}^4He$

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Table I. Results of the fit of the order parameter ($\Delta\lambda = w$) of the system DAC / KCl / H_2O using the equation 1.

[KCl]/ M	T_c / K	B_o	B_1	B_2
0.305	299.448 ± 0.004	6.32 ± 0.03	29.59 ± 0.16	-105 ± 2
0.280	296.202 ± 0.003	6.44 ± 0.02	25.42 ± 0.13	-89.8 ± 1.4
0.260	294.155 ± 0.002	2.73 ± 0.01	105.0 ± 0.5	-291 ± 12

Table II. Results of the fit of the correlation lenght ($\xi(T)$) of the system DAC / KCl / H_2O using the equation 1.

[KCl]/ M	$(T_c - T)_{max}$ / K	ξ_o/nm	ν	T_c / K
0.355	3.6	1.92 ± 0.03	0.630 ± 0.003	305.908 ± 0.003
0.305	3.0	2.31 ± 0.12	0.631 ± 0.010	299.331 ± 0.008
0.255	3.8	2.22 ± 0.05	0.624 ±0.005	292.849 ± 0.005

Table III. Results of the fit of the osmtic susceptibility ($\chi_T(T)$) of the system DAC / KCl / H_2O using the equation 1.

[KCl]/ M	$(T_c - T)_{max}$ / K	$\chi_{To} \cdot 10^{-4}$ / u.a.	γ	T_c / K
0.355	3.6	3.83 ± 0.01	1.20 ± 0.01	305.872 ± 0.00
0.305	3.0	4.1 ± 0.4	1.24 ± 0.02	299.330 ± 0.00
0.255	3.8	4.60 ± 0.09	1.19 ± 0.01	292.840 ± 0.00

FIGURES CAPTIONS

Fig. 1.- Critical (T_c) and Krafft (T_K) emperatures for the DAC + water + KCl systems as a function of the salt concentration, [KCl]. the open circules represents the phase separation temperature. The solid is a linear fit. The open square represent the aproximate coordinates of the CEP. Solid symbol are the Krafft temperatures.

Fig. 2.- Coexistence curve for the system DAC + water + KCl systems as a function of the salt concentration. Open circle are the experimental point. The solid curves are the fit with the equation 2.

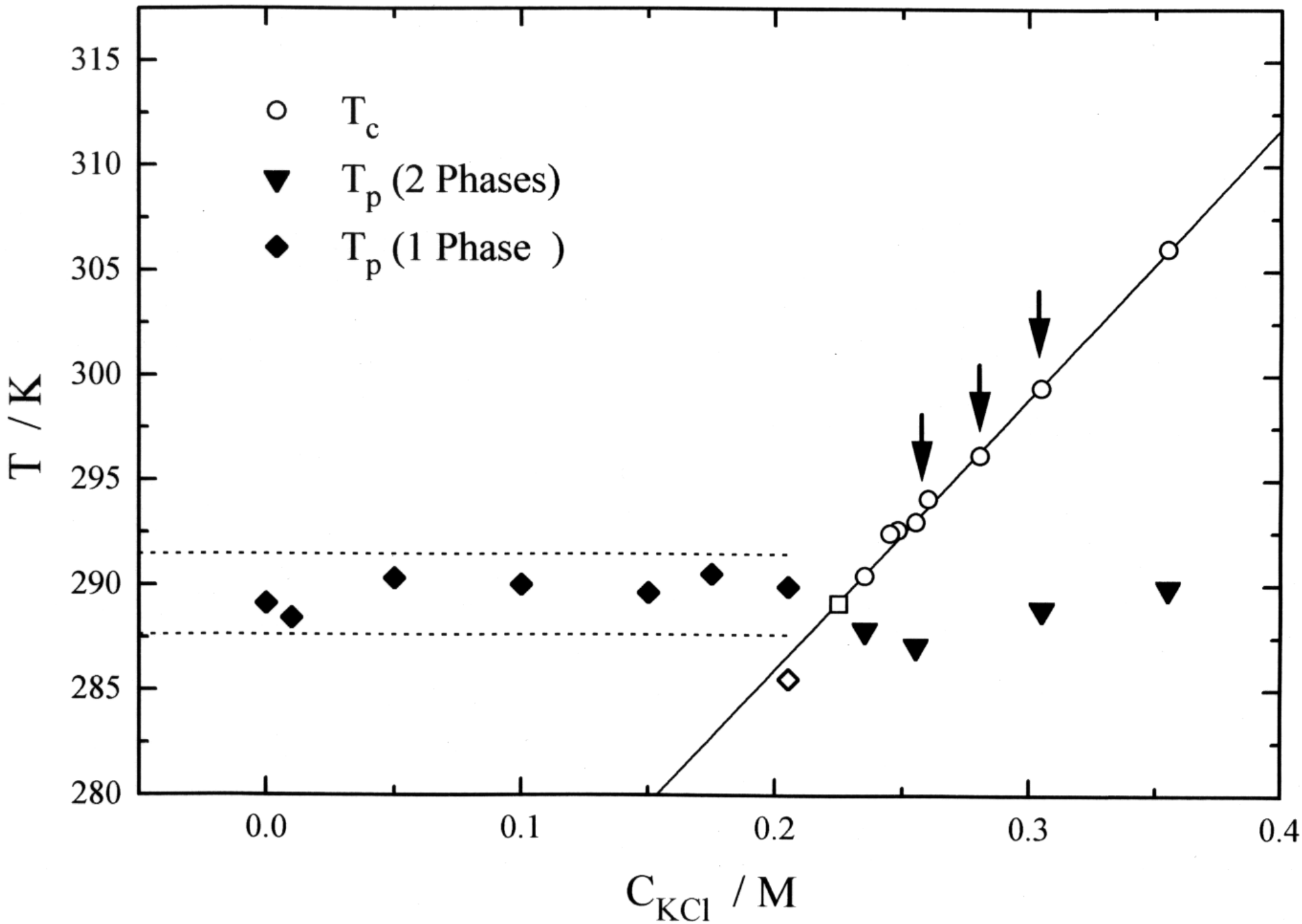
Fig. 3.- Order parmeter for the system DAC+Water +KCl. Symbols areexperimetal data. The dashed line represents single scling fits. Solid lne represents the fit to the equation 1.

Fig. 4.- Test of the validity of Eq.(6) (linear model equation of state) for describing the off-critical results in the vicinity of the critical point for c = 0.30. Symbols correspond to different weight fractions of DAC (in percent)

Fig. 5.- Experimental correlation functions for the DAC + water + KCl (0,3 M) system at different temperatures and fixed scattering angle of 90°. Only part of the experimental data are shown for the sake of clarity. Note that for temperatures far from the critical one the correlation function shows a single exponential decay, while near T_c there are two decays. The inset shows the short time behavior in detail. The line corresponds to the fit to Eq.(9),. for ΔT = 18.28 K. Symbols correspond to ΔT (K): ■ 18.28, ● 13.41, 8.53, □ 3.83, o 2.92, Δ 2.46, ∇ 0.98, ◊ 0.60, X 0.40, + 0.29. The data shown for ΔT(K) = ∇ 12.618, ◆ 7.63, x 7.09, and + 6.01 are those obtained at the laboratory of Prof. D. Woermann (Cologne, Germany).

Fig. 6.- (a) Decay rate corresponding to the fast relaxation mode for two temperatures within the interval for which two modes can be resolved. For the sake of comparison the results for a far from critical temperature (where single exponential behavior is found) are also included. (b) Decay rate corresponding to the slow relaxation mode. Note that, within the experimental range, there is a crossover from a q^2 to a q^3 behavior. Lines are aid for the eyes.

Fig. 7.- Reduced diffusion coefficient associated to the concentration fluctuations. The continuous line corresponds to the Kawasaki function arising from the mode coupling theory. Note that the D_c^* have been calculated using independent experimental values of the viscosity and of the static correlation length.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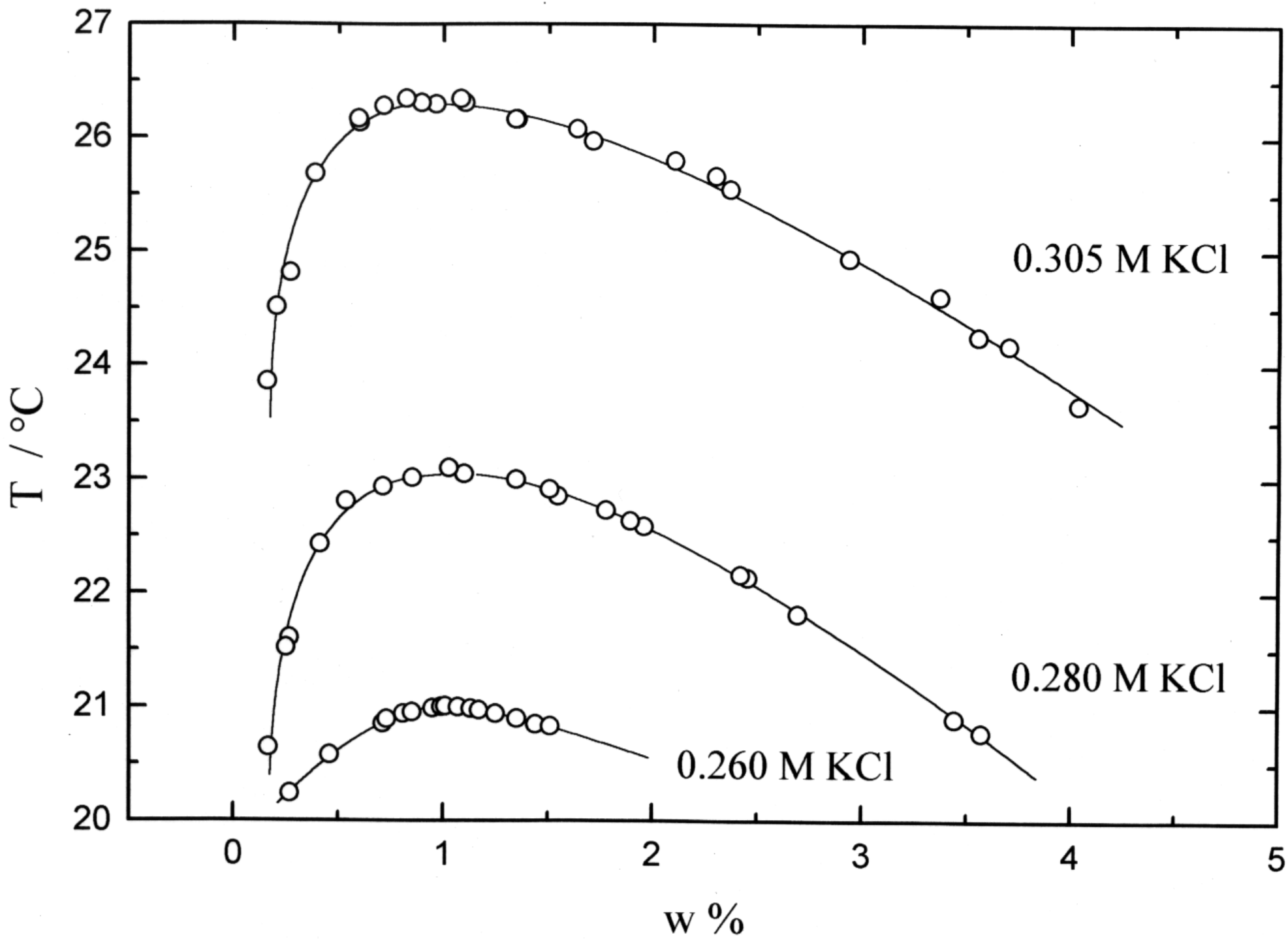
C_{KCl} / M
T_c
T_p (2 Phases)
T_p (1 Phase)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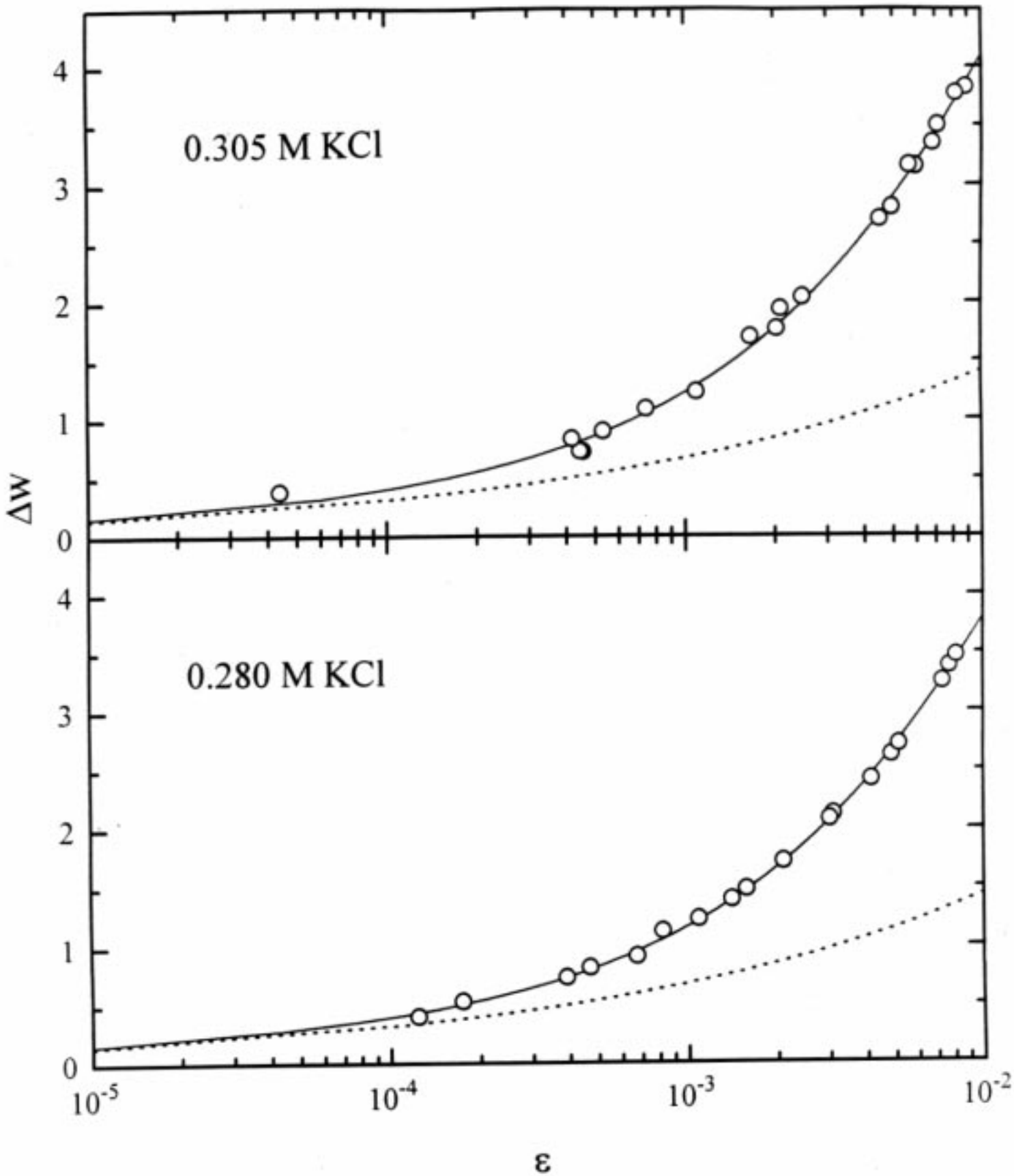
0.260 M KCl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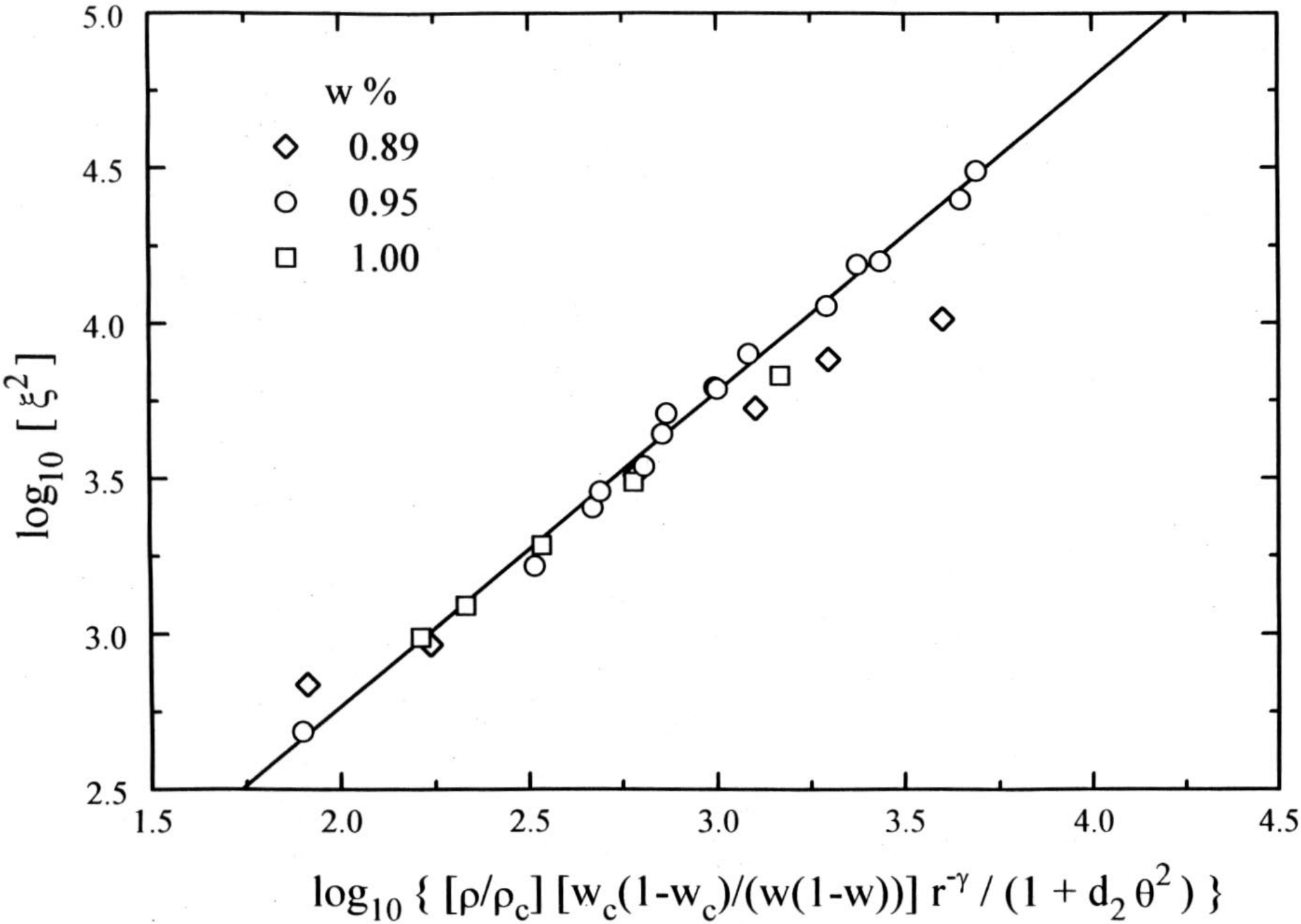
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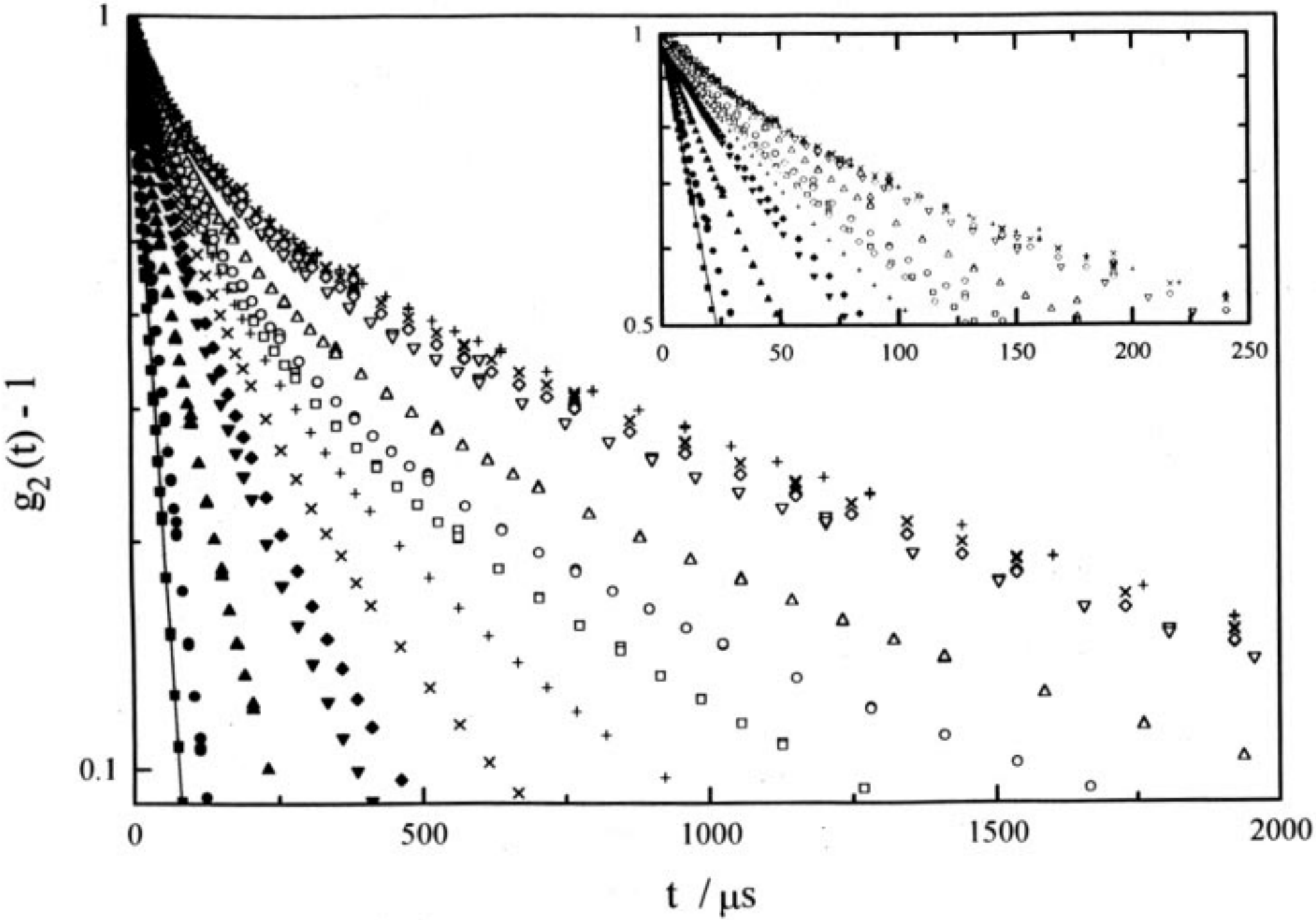
$\log_{10}[\xi^2]$
$\log_{10}\{[\rho/\rho_c][w_c(1-w_c)/(w(1-w))]\, r^{-\gamma}/(1+d_2\theta^2)\}$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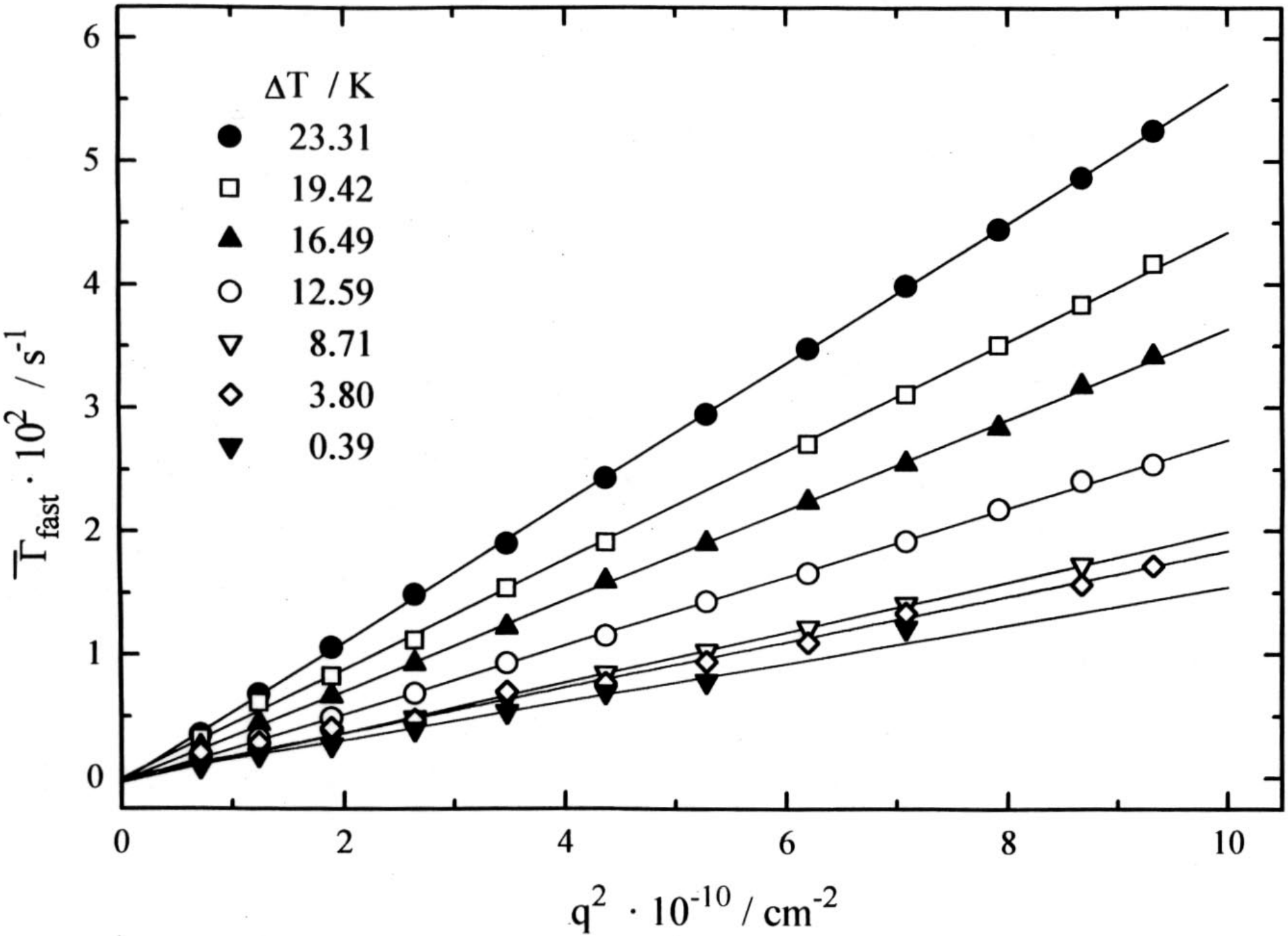
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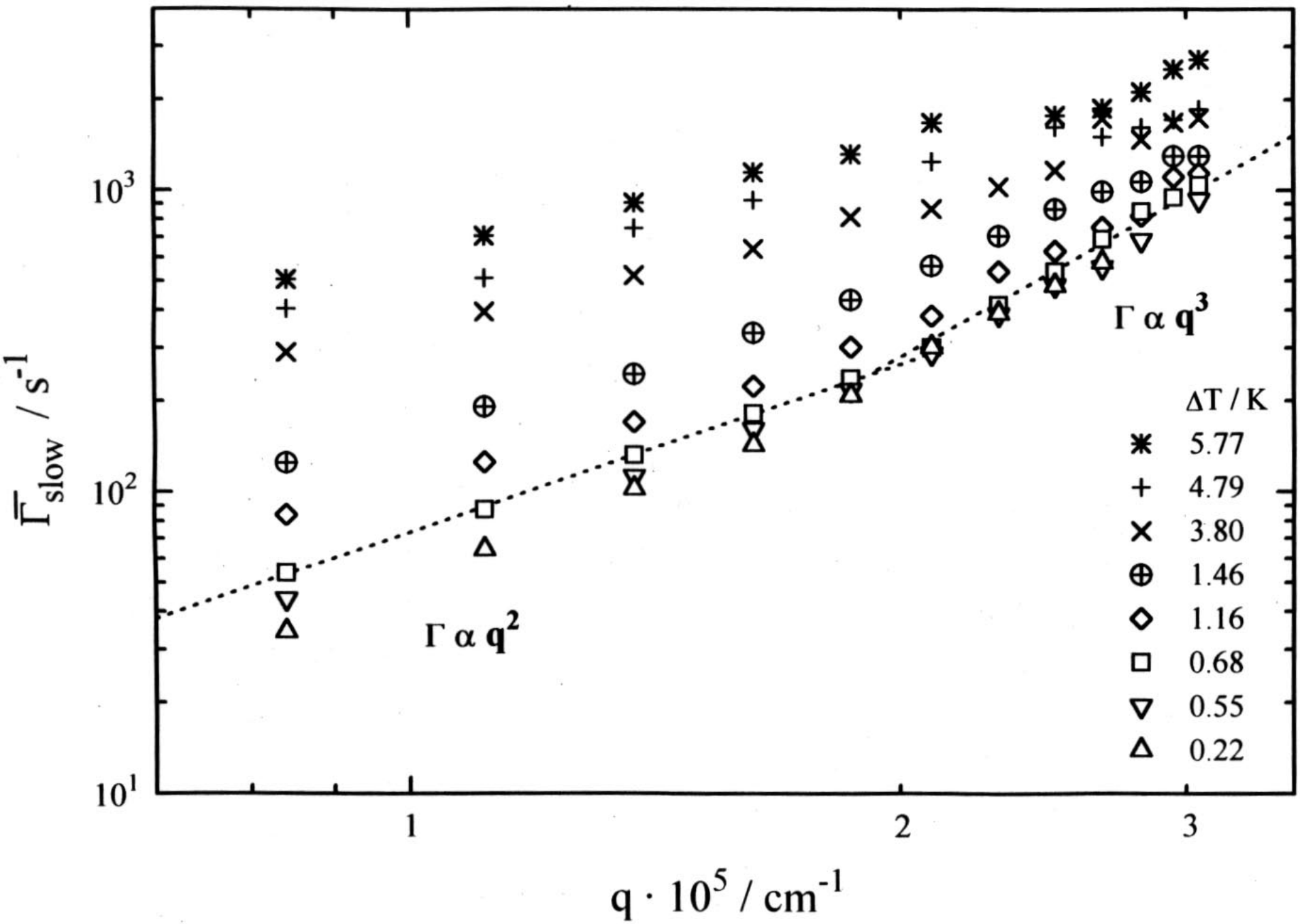
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1.16
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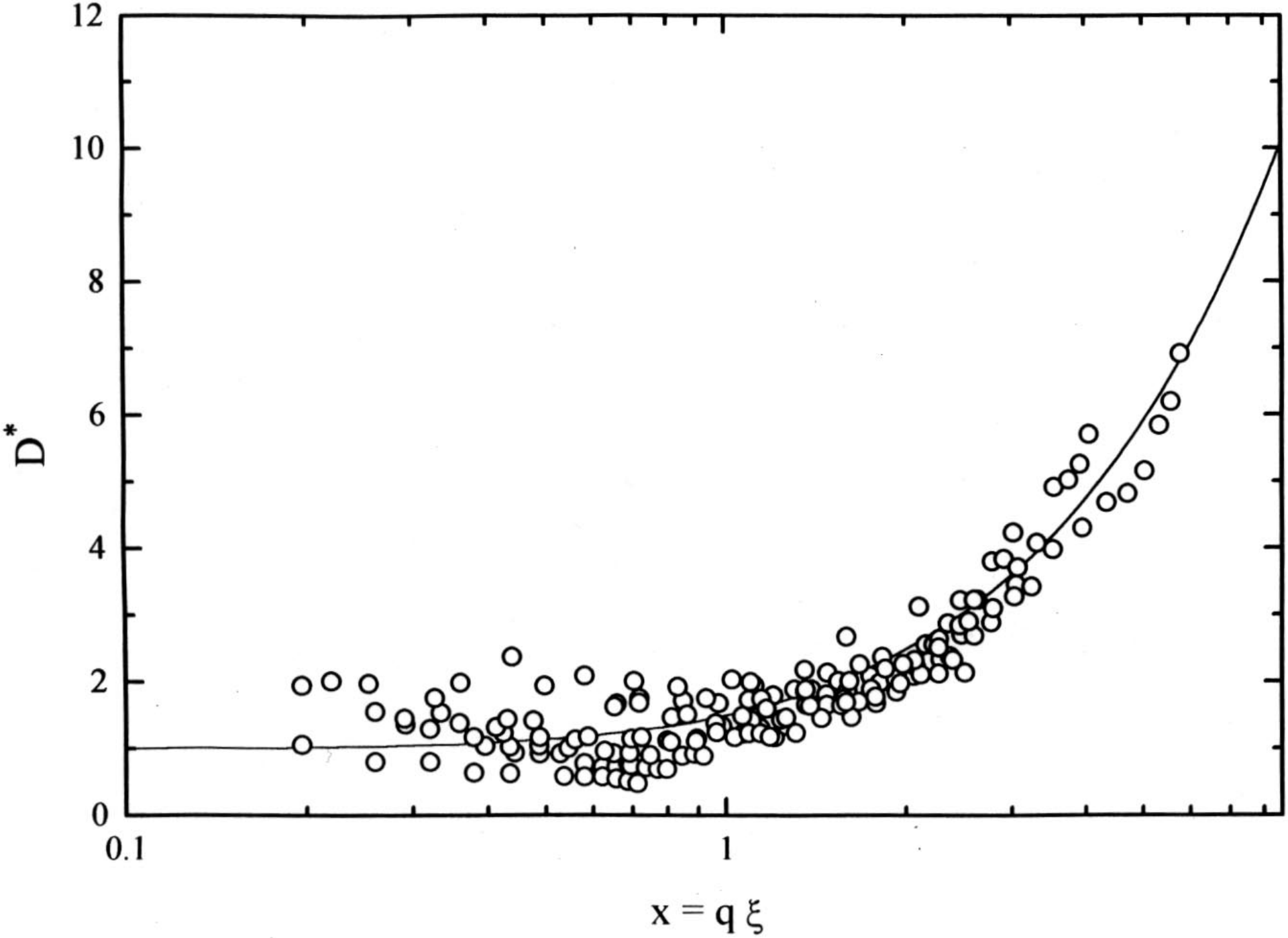
0.55
0.22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