Coherent Neutron Scattering from the Binary Ionic Mixture of Ethylammonium Nitrate and Deuterated *n*-Octanol in the Critical Region [1]

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ABSTRACT

We have performed neutron scattering measurements on the mixture of ethylammonium nitrate and deuterated *n*-octanol in order to get information about its microscopic structure in the vicinity of the critical point. Scattering spectra were recorded for wave number transfers q ranging from 0.05 to 0.48 $Å^{-1}$. Samples at the critical salt mole fraction x_c = 0.760, and at three off-critical concentrations (x = 0.299, 0.548 and 0.900) were investigated in their homogeneous phases at various temperatures from T_c + 0.93°C to T_c + 24.12°C, where T_c is the critical temperature. The spectra of the coherent intensity scattered from the critical mixture can be described well by the Fisher-Langer approximation in a wide range of $q\xi$ values, ξ being the critical correlation length. However, an additional shorter characteristic length is needed for a proper description of the coherent spectra over the whole range of q.

KEY WORDS: critical-point phenomena; ionic mixtures; neutron scattering

1. INTRODUCTION

The critical properties of ionic binary mixtures have been studied extensively during the last few years [1-4]. Liquid-liquid phase separation in ionic systems [5,6] has been described as resulting from either *coulombic unmixing* in solvents of low dielectric permittivity ε, for which a strong peak in the pair-correlation function between ions with opposite signs is observed [7,8], or *solvophobic unmixing* in solvents with a large ε value, where a strong correlation between ions with same signs is observed [9].

Among the studied salts which mix with a solvent of low dielectric permittivity and show a liquid-liquid phase separation, a typical example is ethylammonium nitrate (EAN) in *n*-octanol (ε = 8) . The critical properties of this system are well documented. In particular it has a 3-D Ising-type behavior with an upper critical point at a room temperature [10-13]. The present study is concerned with this system.

The main purpose of this neutron scattering study in a relatively large wavenumber range was to get information about short range correlation between the different scattering species present in the mixture. To this end, neutron spectra were measured as a function of temperature in the one-phase region.

In Section 2 we explain how the samples were prepared and characterized. In Section 3, we show that the results of the neutron scattering experiments may be interpreted using very basic physical concepts.

2. SAMPLE PREPARATION AND CHARACTERIZATION

2.1. Sample preparation

EAN ($C_2H_5NH_3^+$, NO_3^-) was prepared by neutralization of ethylamine with nitric acid (Aldrich, Germany) [12,14]. This salt is liquid at room temperature, its melting temperature being close to 14°C. EAN was dried under vacuum and in presence of P_2O_5 for 10 days at room temperature. Then it was filtered through 0.22 μm Millipore filters and frozen into small quantities for storage at 6°C. In order to have high neutron scattering intensities we used deuterated *n*-octanol CD_3 $(CD_2)_7$ OD supplied by Euriso-Top (France) in 0.5 g glass-sealed cells. The isotopic enrichment was 98.6 % and the

chemical purity was better than 98%. Each sample cell was filled up with EAN and deuterated *n*-octanol in a glove box under a dry argon atmosphere.

2.2. Coexistence curve and critical properties

We first measured the coexistence curve of the critical mixture of EAN and deuterated *n*-octanol. The coexistence curve of the non deuterated mixture had been previously measured. The critical salt mole fraction was $x_c = 0.766 \pm 0.002$ and the critical temperature $T_c = 41.788$ °C ± 1.5mK [12]. In contrast, the critical point of the deuterated mixture is $T_c = 29.160$°C ± 2 mK [15] and $x_c = 0.760 \pm 0.002$. The same apparatus was used for both mixtures. It allows the refractive index n, to be measured as a function of temperature in the lower and upper phases by looking for the minimum deviation of a laser beam transmitted through an optical sample cell with a square cross-section [12]. Criticality of the mixture was checked by the appearance of the meniscus in the middle of the sample after a small temperature quench of about 3 mK. Fig.1 shows the normalized coexistence curve (n/n_c vs T/T_c) for the deuterated and non-deuterated mixtures. n_c is the value of the refractive index at T_c. Although a slight asymmetry can be noticed far from T_c, the two curves are identical near T_c. A similar behavior has already been observed in the mixture of isobutyric acid and deuterated water [16]. In this case, the asymmetry of the coexistence curve was explained by the presence of additional species resulting from isotope exchange reactions. Such exchange reactions also occur in our system between the hydroxyl groups of octanol and the ammonium ones of the salt.

The critical exponent β of the EAN - *n*-octanol system has been found to have a value close to that of the 3-D Ising model. Fig. 1 clearly shows that the deuterated system behaves similarly.

The critical properties of the EAN-n-octanol mixture have already been determined by static light scattering [10,13]. The system shows a 3-D Ising-like behavior in a wide range of reduced temperature $\tau = (T - T_c)/T_c$. The same trend holds for the deuterated mixture. However, an increase of the correlation length is noticed. Preliminary static light scattering measurements suggest that $\xi_0 = (6 \pm 1)$ Å which is to be compared to $\xi_0 = (4.6$

± 0.2) Å for the non-deutereted mixture. Details on the experiments and new results will be given in a forthcoming paper [17].

3. SMALL-ANGLE NEUTRON SCATTERING

We used the small-angle spectrometer PACE located at the Laboratoire Léon Brillouin in Saclay (France). This apparatus consists of 30 concentric circular detectors. Neutron scattering measurements were performed for wave number transfers q, ranging from 0.05 and 0.48 $Å^{-1}$. $q = (4 \pi / \lambda) \sin (\theta/2)$ where θ is the scattering angle. The neutron wavelength was $\lambda = 3.7$ Å. A specially designed two-stages thermostat was used for the experiment. The performances and the characteristics of this thermostat are described elsewhere [18]. A large exit aperture allows scattering angles to reach about 20°. The temperature stability of the thermostat is within 0.1 or 0.5 mK, depending on the set-point temperature. Fused-quartz cells (Hellma, Germany) with an optical path of 1 or 2 mm can be housed in a central well machined in the body of the thermostat. In order to have a good temperature stability and to avoid temperature gradients, all the apertures of the thermostat are closed by many fuzed quartz and sapphire windows. In the presently studied q-range, quartz and sapphire do not give Bragg peaks in the scattered spectra.

Neutron scattering spectra were measured for samples at the critical salt mole concentration $x_c = 0.760$ as well as at off-critical concentrations x= 0.299, 0.549 and 0.900. The investigated temperature range in the one-phase region was between $(T_c + 0.93)$°C and $(T_c+24.12)$°C.

4. THE RESULTS AND THEIR INTERPRETATION

4.1. Raw data treatment

The raw spectra are first divided by the transmission and the thickness of the sample. The spectrum of the fully assembled thermostat housing the empty cell is then substracted from the sample spectra and the results are normalized to the spectrum of a 1 mm water sample. This allows the scattering data to be corrected for the efficiencies of the various detectors [19].

On general grounds, the neutron scattered intensity can be decomposed as follows

$$I(q) = I_{mix}(q) + I_{mult}(q) + I_{inc} , \qquad (1)$$

where $I_{mix}(q)$ is the scattered contribution from the mixture. In our experiment, multiple coherent scattering $I_{mult}(q)$ may be neglected because for the present system multiple scattering is mainly incoherent . I_{inc} represents incoherent scattering which is almost q-independent.

To obtain the excess coherent-scattering due to mixing $\Delta I_{mix}(q)$, the normalized spectrum of the corresponding ideal mixture $I_{id}(q)$, is substracted from the one of the actual mixture $I_{mix}(q)$

$$\Delta I_{mix}(q) = I_{mix}(q) - I_{id}(q) , \qquad (2)$$

where $I_{id}(q)$ is computed as follows

$$I_{id}(q) = \phi_{EAN} I_{EAN}(q) + (1 - \phi_{EAN}) I_{oct}(q). \qquad (3)$$

ϕ_{EAN} is the volume fraction of the salt. $I_{EAN}(q)$ and $I_{oct}(q)$ are the normalized spectra of the pure salt and of deutereted *n*-octanol, respectively. In this way, the contributions from both incoherent scattering and scattering arising from self-correlations are, in principle, ruled out from $\Delta I_{mix}(q)$. However this is not exactly true for the latter contribution because it is altered by H-D exchange between the hydroxyls and the ammonium groups in the mixture [16,19].

4.2. Data analysis

The spectra $\Delta I_{mix}(q)$ of the excess coherent-scattering at different concentrations and temperatures are shown in Fig. 2. As expected, the scattered intensity at low q values is largest for the critical concentration and increases as the temperature aproaches T_c. In the

following we will focus only on the spectra obtained at the critical concentration, x_c=0.760.

Within the studied q domain, the excess coherent-spectra $\Delta I_{mix}(q)$ may be approximated by the following relation

$$\Delta I_{mix}(q) = \left[(A - a\tau)\tau^{-\gamma} g(q\xi) \right] (1 + \zeta^2 q^2) + (B - b\tau) + (C - c\tau)\zeta^2 q^2 \qquad (4)$$

where A, B, C, a, b and c are constants and $\tau = (T-T_c)/T_c$ is the reduced temperature. a, b and c allow for a possible temperature dependence of the physical parameters involved in A, B and C. γ is the exponent describing the critical temperature behavior of "concentration fluctuations and constant pressure and temperature". $\xi = \xi_0 \tau^{-\nu}$ is their correlation length, ξ_0 being the amplitude and ν the exponent.

The term in the square brackets of Eq. (4) represents the critical scattering from concentration fluctuations. The quantity (B - b τ) is the contribution of both the negative excess-scattering due to H-D exchange and the regular scattering from "density fluctuations at constant concentration and temperature". Note that the critical part of the density fluctuations is almost negligible in the studied temperature range. In the present conditions, the contribution of density fluctuations to ΔI_{mix} (0) is always smaller than 0.01%. However, it is no more negligible at medium q-values.

The terms proportional to $\zeta^2 q^2$ take two effects into account: i) the fundamental q^2 increase of partial structure factors at medium q values approaching the reciprocal mean distance between the scatterers; ii) the q^2 decrease of the form factors of the scattering species present in the mixture. Therefore, ζ may be regarded as an apparent average length typical of short-range contributions to scattering.

For sufficiently high values of $x = q\xi$, the correlation function $g(q\xi)$ can be approximated by the Fisher-Langer expansion [20]

$$g(x) = C_1 (1 + C_2 x^{-(1-\alpha)/\nu} + C_3 x^{-1/\nu}) x^{-(2-\eta)} \quad , \qquad (5)$$

where the coefficients $C_2 = 1.773$ and $C_3 = -2.745$ have been calculated by Bray [21]or a 3-D Ising-like model. According to field theory [22] the values of the critical exponents are $\gamma = 1.240$, $\nu = 0.630$, $\eta = 0.032$ and $\alpha = 0.110$. To within less than 1%, Eq. (5) is expected to be valid for $x \geq 3$ [21, 23].

All the excess coherent-scattering spectra measured at different temperatures were fitted simultaneously [24] to Eqs. (4) and (5). The adjustable parameters were A, a, B, b, C, c and ζ. All the other parameters were assumed to have their theoretical values. The critical temperature T_c was set to its experimental value.

First, we fitted the scattering data for $0.06\ \text{Å}^{-1} \leq q \leq 0.27\ \text{Å}^{-1}$ to the function $F(q) = \left[(A - a\tau)\tau^{-\gamma} g(q\xi) \right] + (B - b\tau)$, i.e. to Eq. (4) with $\zeta = 0$. Fig. 3 shows the quantity $\Delta I_{mix}(q) - F(q)$ as a function of q^2. One clearly notices a q^2 dependence for $q \geq 0.2\ \text{Å}^{-1}$. This emphasized why the $\zeta^2 q^2$ terms in eq. (4) are needed to describe correctly the data in a large q-range.

Then, fits to Eq.(4) were performed for $0.06\ \text{Å}^{-1} \leq q \leq 0.46\ \text{Å}^{-1}$. For each temperature the smallest wavenumber used in the fit was such that $q\xi \geq 3$. Fig. 4 shows the computed quantity $g(q\xi)$ together with the experimental points at different temperatures. Eqs. (4) and (5) fit quite well the data in the range $3 \leq q\xi \leq 80$. All the deviations are almost within 1% which is in good agreement with both the data uncertainties and the accuracy of the Fisher-Langer expansion. This confirms the validity of this approximation for $q\xi \geq 3$. The computed value of the correlation length is $\xi_0 = (4.9 \pm 0.1)$ Å, in rough agreement with the results of the preliminary light scattering measurements [17]. The value of the mean characteristic length is found to be $\zeta = (4.0 \pm 0.3)$ Å. This value compares favorably with the distances involved in the system.

In order to check the robustness of the fit we led free the exponent $(2-\eta)$ in eq.(5). The result of the fit gave the value $\eta = 0.03 \pm 0.01$ for the Fisher exponent, $\xi_0 = (4.9 \pm 0.1)$ Å and $\zeta = (4.1 \pm 0.3)$ Å. The computed Fisher exponent is comparable to the theoretical value.

5. CONCLUSION

We studied the ionic mixture of ethylammonium nitrate and deuterated *n*-octanol by means of small-angle neutron scattering up to q = 0.46 $Å^{-1}$. Neutron scattering spectra were recorded in a large temperature domain in the one-phase region at different salt concentrations. The data obtained at the critical salt mole fraction $x_c = 0.760$ run over a relatively large $q\xi$ range ($1.2 \leq q\xi \leq 80$). The excess coherent-spectra can be fitted correctly by the Fisher-Langer expansion for $q\xi \geq 3$. In order to descibe the data in the whole q-range, a characteristic length scale ζ must be introduced in order to take into account the q^2 dependence of the scattered spectra at medium q-values. The value of ζ is found to be about 4 Å.

The results of the fit give a value of the amplitude ξ_0 of the critical correlation length which is comparable to the one inferred from light scattering measurements. The value found for the Fisher exponent is $\eta = 0.03 \pm 0.01$ in fair agreement with the theoretical prediction. These results confirm the 3-D Ising behavior of the mixture previously demonstrated by means of static light scattering. Moreover, they show that the critical domain is very extended as usual for regular binary mixture.

To better characterize the microscopic structure of this system, complementary neutron scattering experiments are planned to be carried out in the near future for q values up to 3 $Å^{-1}$.

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FIGURE CAPTIONS

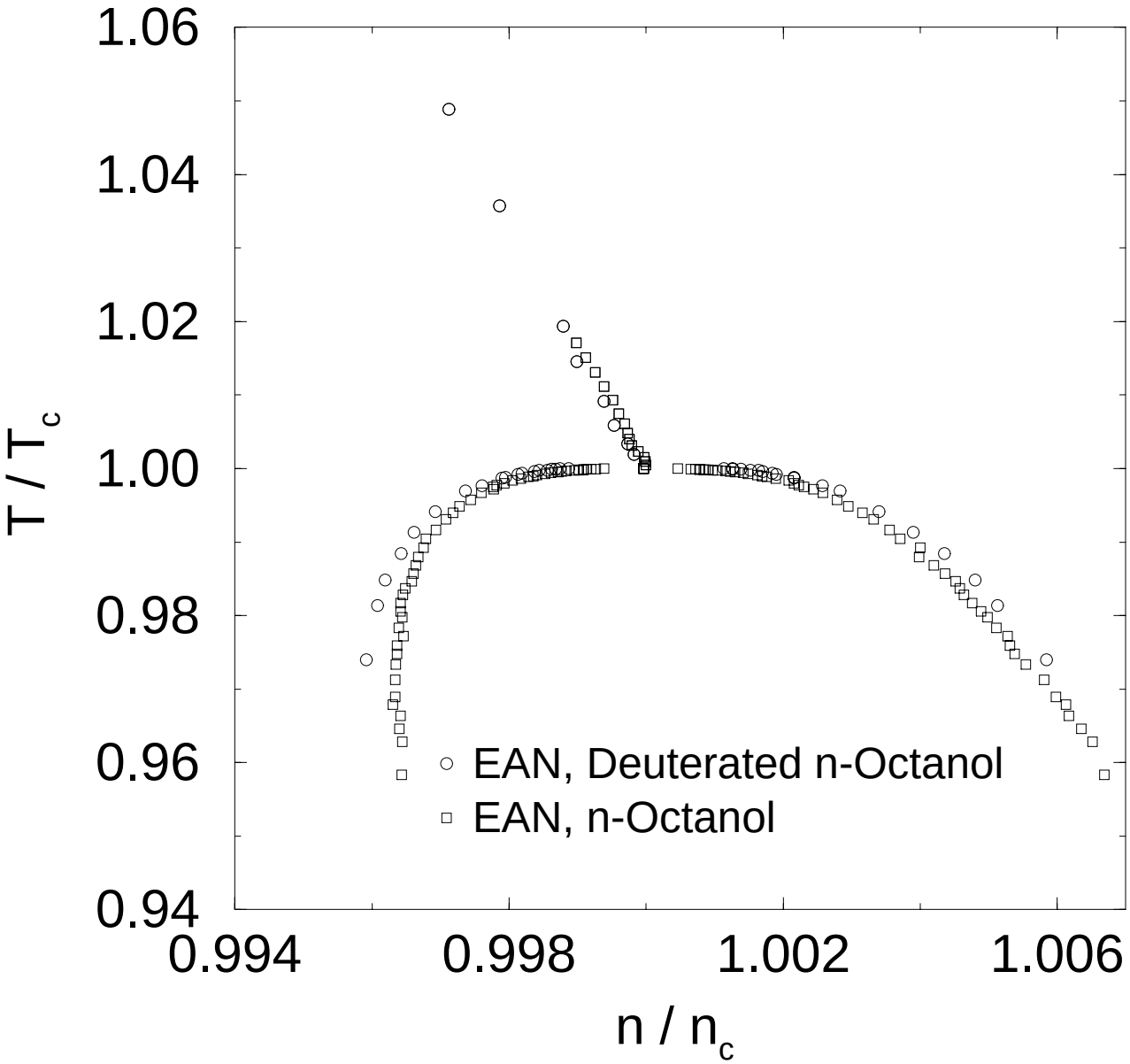
Fig. 1. Normalized coexistence curves (n/n_c vs T/T_c) of the binary ionic mixture of EAN in deutered and non-deutered *n*-octanol. n_c is the value of the refractive index n extrapolated to the critical temperature T_c.

Fig. 2. Neutron scattered intensity (arbitrary unit) as a function of the wavenumber q. Temperature ranges from T_c + 0.93°C to T_c+24.12°C, T_c being the critical temperature. a) sample at the critical salt mole concentration x_c=0.760, b) x=0.900, c) x=0.548, d) x=0.299.

Fig. 3. Deviation $\Delta I_{mix}(q)$ - F(q) as a function of q^2 for 0.06 $Å^{-1} \leq q \leq 0.48$ $Å^{-1}$ The excess coherent-spectra $\Delta I_{mix}(q)$ are fitted to Eq. (4) with $\zeta = 0$, in the range 0.06 $Å^{-1} \leq q \leq 0.26$ $Å^{-1}$. Notice the q^2 dependence and its temperature variation f or $q \geq 0.21$ $Å^{-1}$.

Fig. 4. a) Computed Fisher-Langer expansion of the correlation function $g(q\xi)$, as a function of $q\xi$. All the spectra measured at different temperatures are fitted simultaneously in the range 0.06 $Å^{-1} \leq q \leq 0.48$ $Å^{-1}$. b) Deviation (%) as a function of $q\xi$. The vertical bars represent the measurement accuracy.

Fig. 1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1.02
1.00
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0.94
T / T_c
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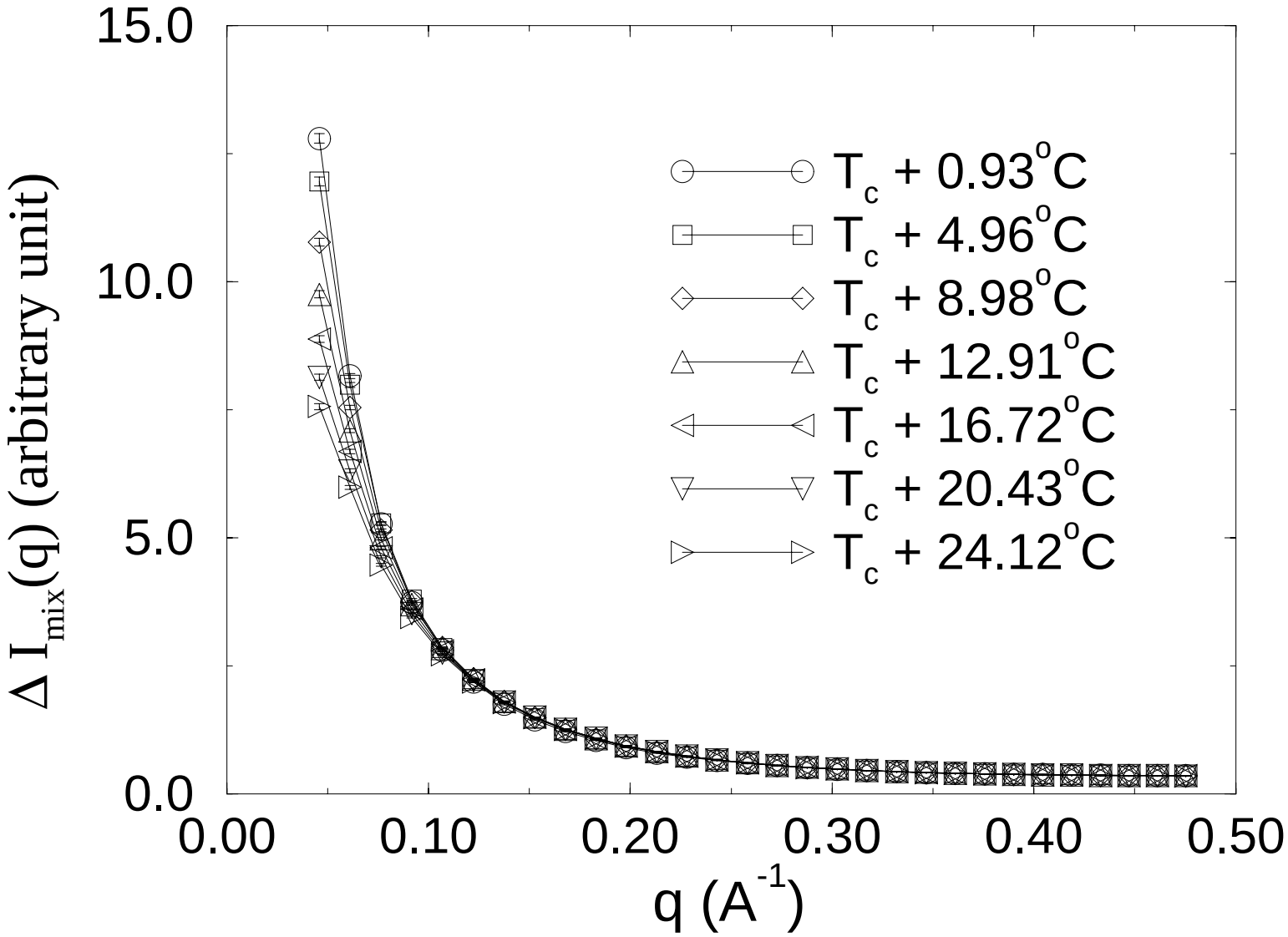
n / n_c
EAN, Deuterated n-Octanol
EAN, n-Octanol

Fig. 2-a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10.0
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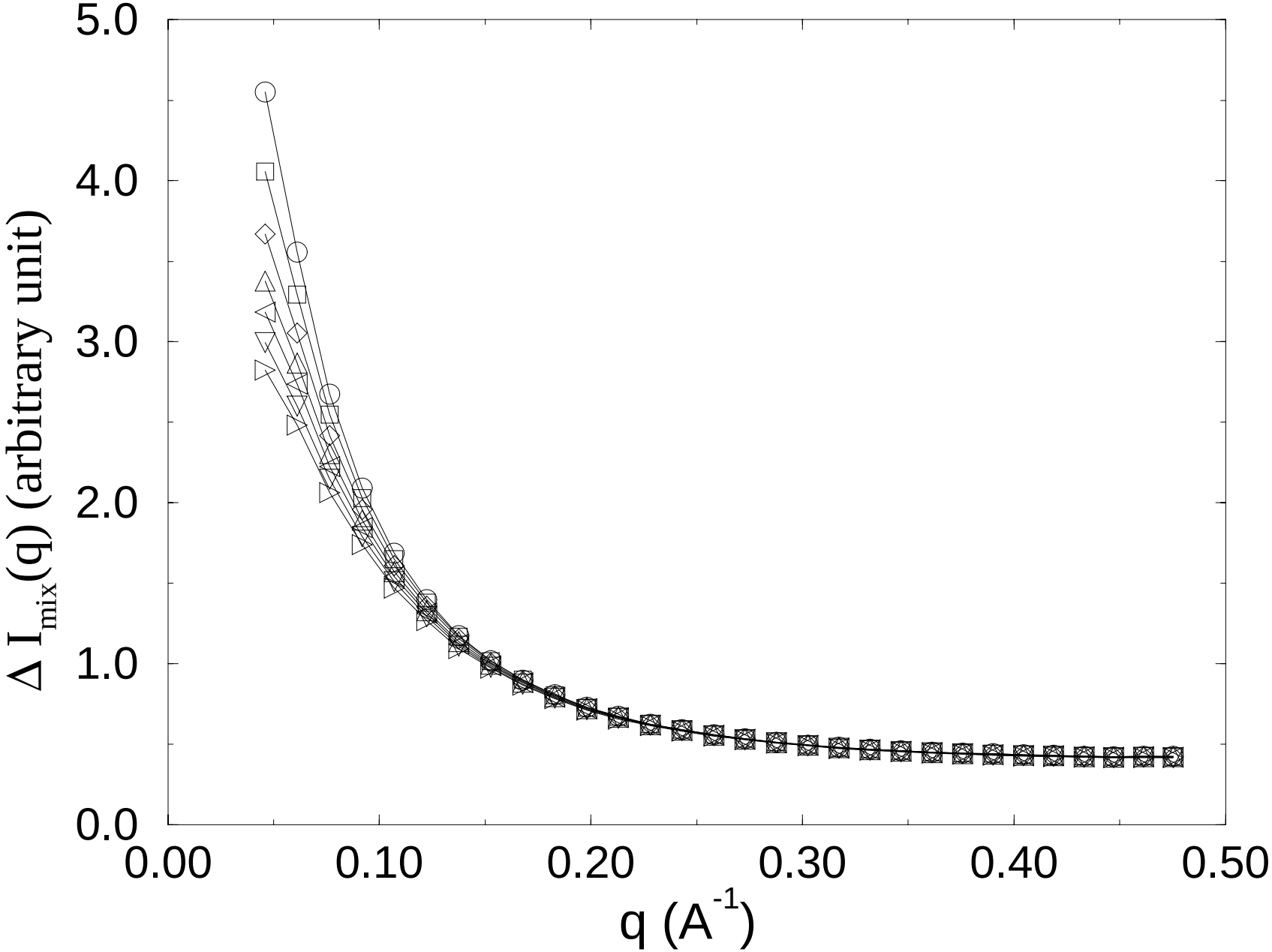
0.10
0.20
0.30
0.40
0.50
q (A-1)
Δ Imix(q) (arbitrary unit)
Tc + 0.93°C
Tc + 4.96°C
Tc + 8.98°C
Tc + 12.91°C
Tc + 16.72°C
Tc + 20.43°C
Tc + 24.12°C

Fig. 2-b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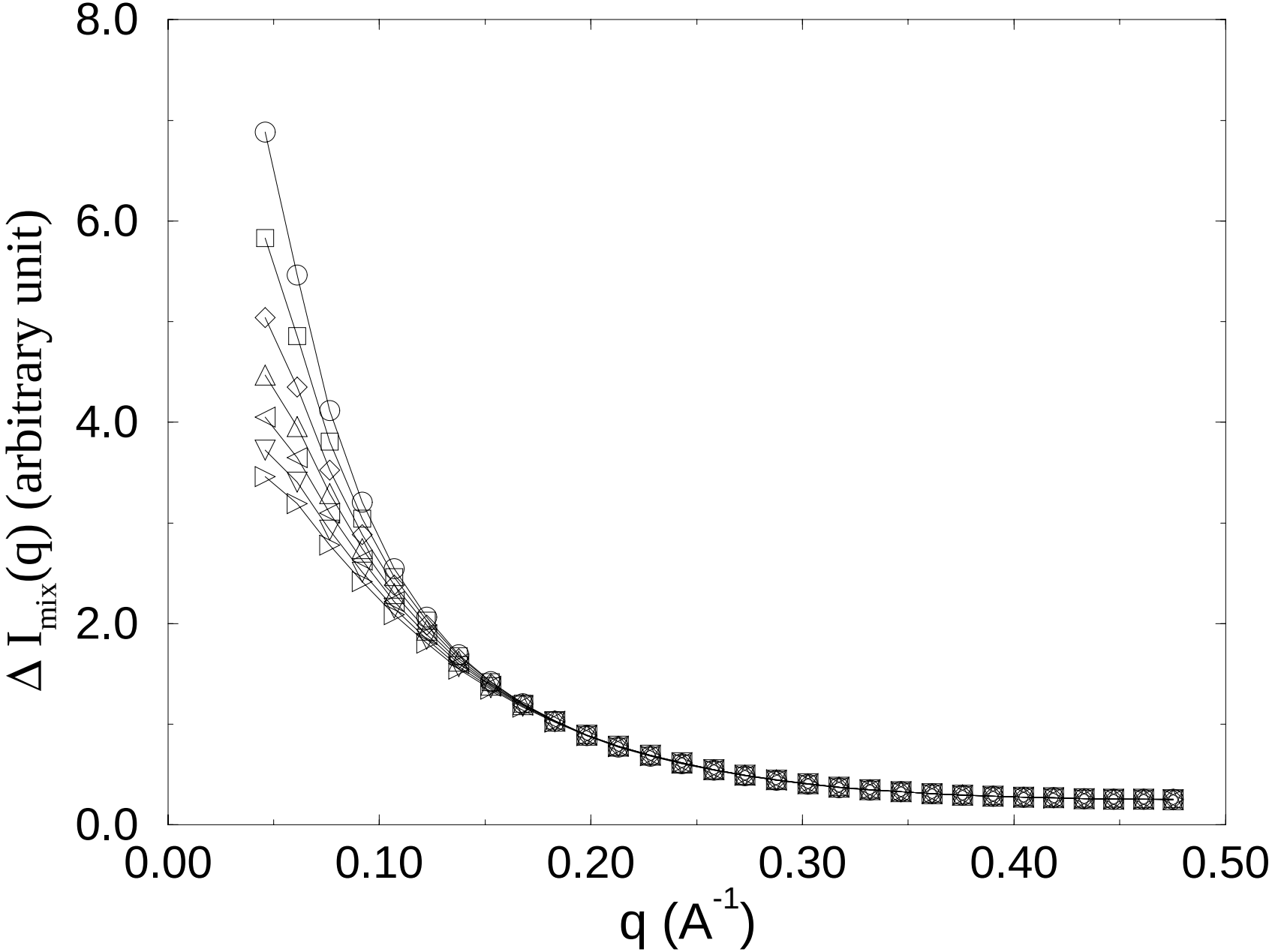
Δ I_mix(q) (arbitrary unit)
q (A^-1)

Fig. 2-c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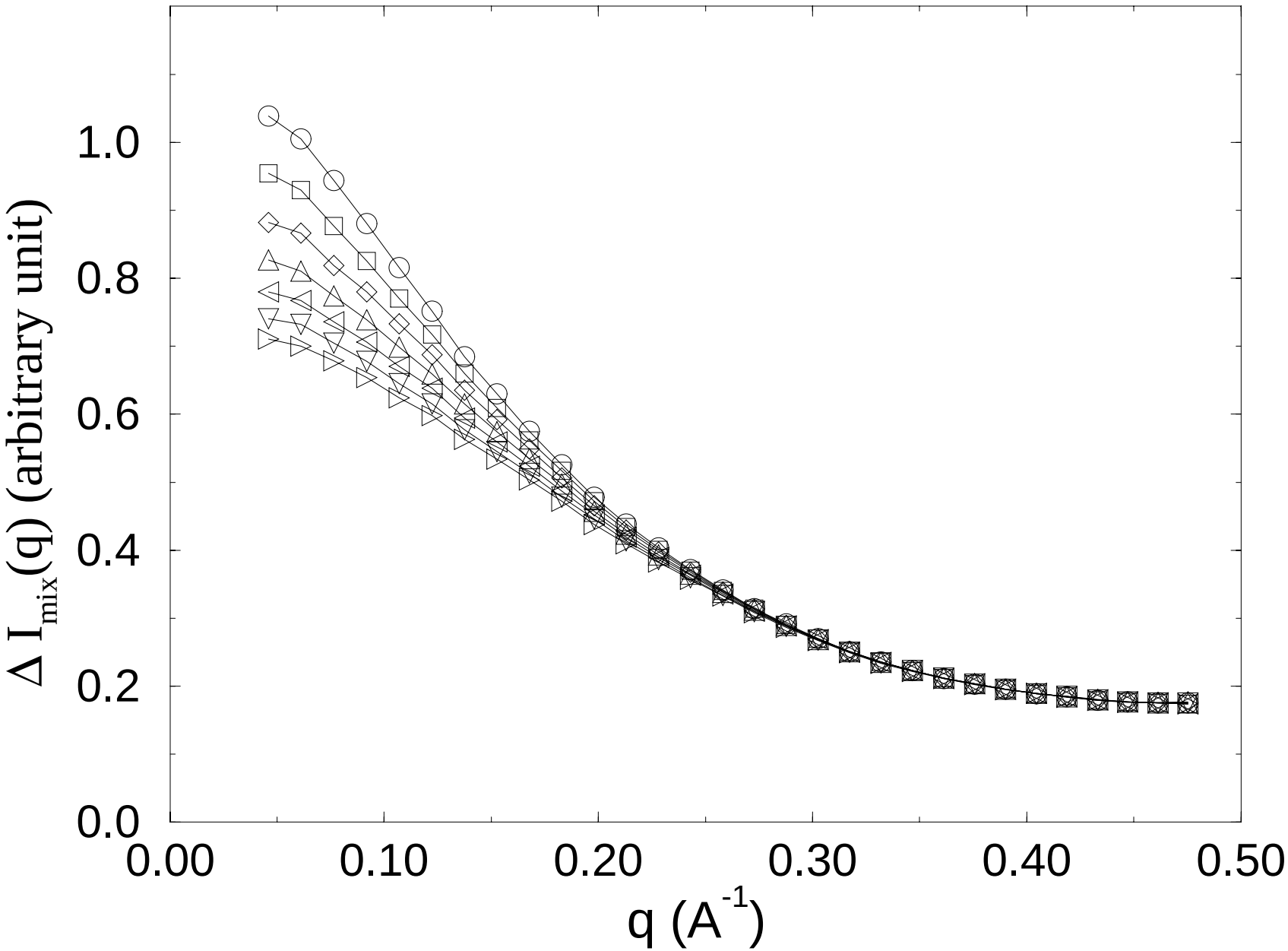
q (A^-1)

Fig. 2-d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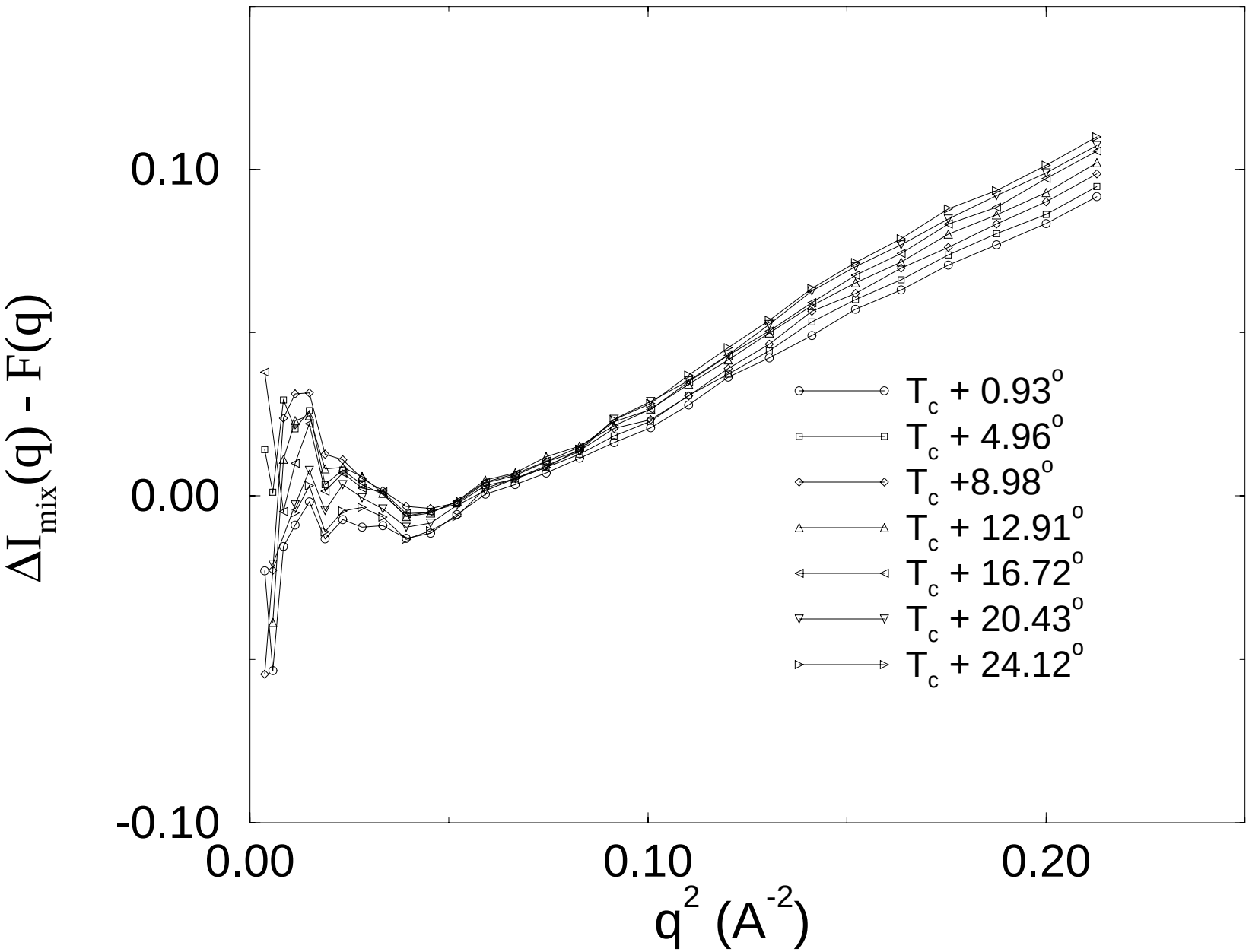
Δ I_mix(q) (arbitrary unit)
q (A^-1)

Fig. 3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0.10
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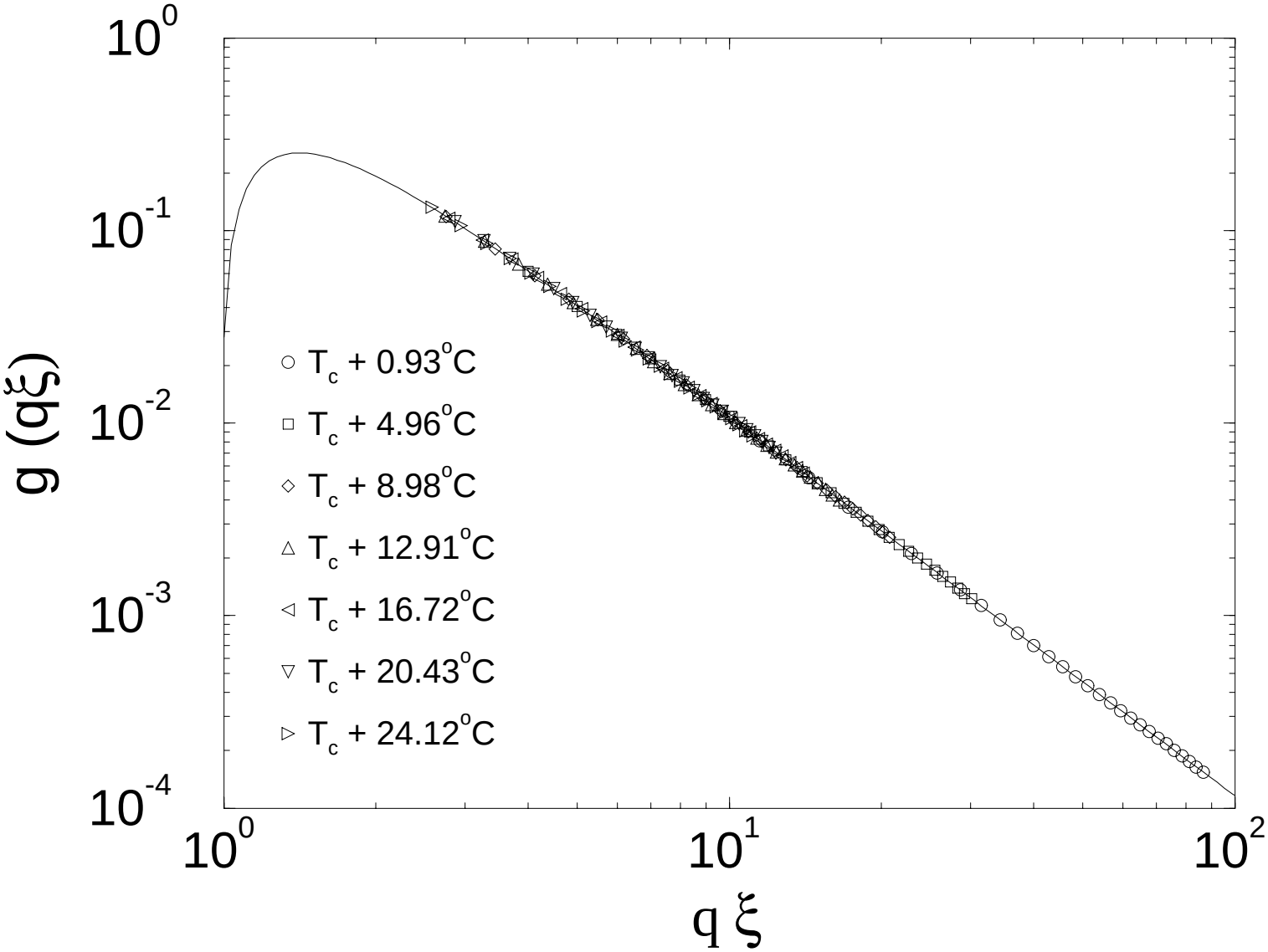
$\Delta I_{mix}(q) - F(q)$
q^2 (A^{-2})
T_c + 0.93°
T_c + 4.96°
T_c +8.98°
T_c + 12.91°
T_c + 16.72°
T_c + 20.43°
T_c + 24.12°

Fig. 4-a


10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
g (qξ)
○ T_c + 0.93°C
□ T_c + 4.96°C
◇ T_c + 8.98°C
△ T_c + 12.91°C
◁ T_c + 16.72°C
▽ T_c + 20.43°C
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10^0
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q ξ
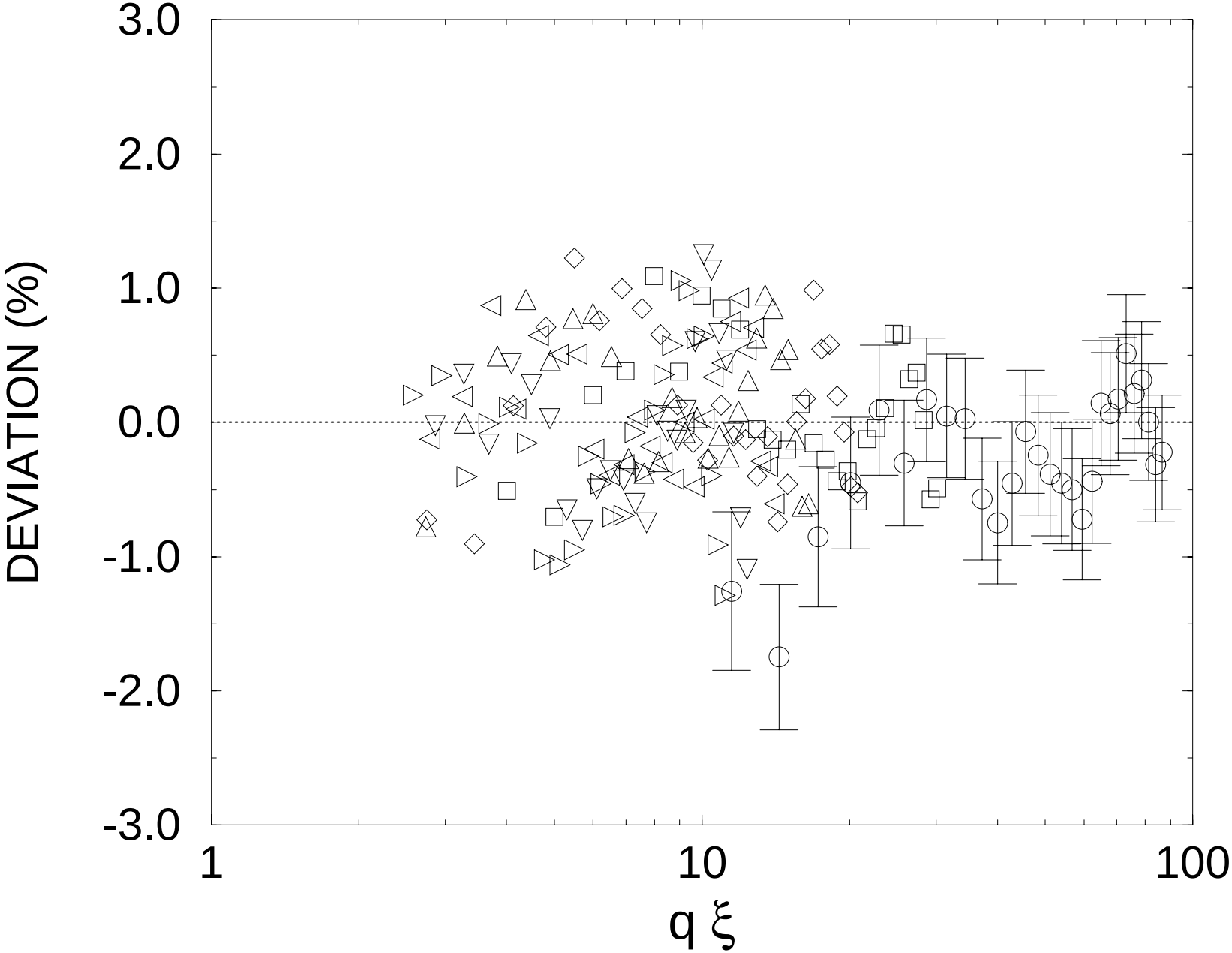
Fig. 4-b