

Letter to the editors

Citation for published version (APA):

Reijenga, J. C. (1994). Letter to the editors. *Chromatographia*, 38(9-10), 658-658.
<https://doi.org/10.1007/BF02277171>

DOI:

[10.1007/BF02277171](https://doi.org/10.1007/BF02277171)

Document status and date:

Published: 01/01/1994

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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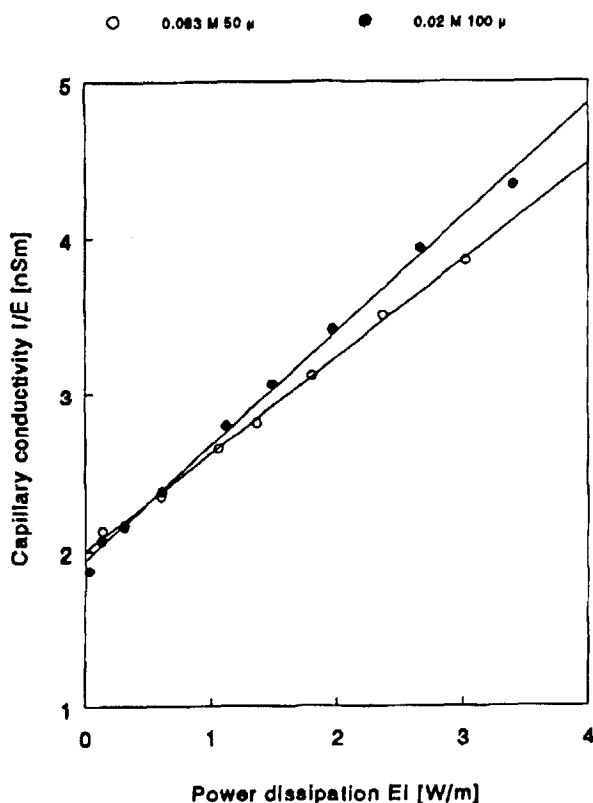
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Letter to the Editors

Sir,

In a recent contribution to *Chromatographia* [1] by Knox and McCormack, temperature effects in Capillary Electrophoresis are determined experimentally, using different voltage drops. The idea is that as the voltage drop decreases, conditions inside the capillary will tend to become ambient. The experimental data for the determination of the average temperature in the capillary, however, requires a different treatment or at least a different way of presentation. This is essentially illustrated in Figure 10 at the end of the manuscript, where the plot of calculated temperature vs power dissipation EI [$W m^{-1}$] results in a straight line. This result is reassuring as several authors in the past have calculated and experimentally verified this fact [2, 3]. As a consequence, it would have been logical to use the same power dissipation as the horizontal coordinate in Figure 1 (u_{eo}), Figure 5 (u_{eo}/E), Figure 6 (I/E) and Figure 7 ($(u - u_{eo})/E$). The reason is that in all four cases, a linear dependence of the Y coordinate with temperature is likely. In the included Figure, for example, the authors's data from their Tables II and III are presented as I/E vs EI . The linear fits are easily extrapolated to zero power dissipation. In addition, the



two lines almost coincide, because the products of ionic strength and square of capillary radius of the two cases are almost equal, a fact not explicitly stated in the manuscript. Coefficients of correlation were 0.9990 and 0.998 respectively.

Finally, a brief remark on the voltage/current dependence. Under method b) it is stated that the buffer conductance is directly proportional to the reciprocal of the buffer viscosity. This is a very misleading statement which in my view requires correction. In reality we have the following two facts:

1. The bulk viscosity η of water depends on the temperature according to the following relation:

$$\frac{1}{\eta} \cdot \frac{\delta\eta}{\delta T} = ca - 0.02 K^{-1}$$

2. The buffer conductance κ depends on the temperature, because all individual mobilities u of the buffer constituents are temperature dependent. This dependence is generally not the same for all ions, but on average:

$$\frac{1}{u} \cdot \frac{\delta u}{\delta T} = ca + 0.02 K^{-1}$$

Whether these two facts are related, remains to be seen. In addition, we must always make a distinction between bulk viscosity (where the above temperature dependence refers to) and wall-surface viscosity (important for electroosmosis). It has been shown [4] that it is possible to change the latter considerably without changing the former. If we change the former, the buffer conductance does not change accordingly.

Summarising: method b) is based on the fact that the buffer conductance κ shows a linear temperature dependence.

References

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