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To whom it may concern

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Review of the Habilitation Thesis “Acid-Base Equilibria at the Nanoscale” by Dr. Peter Kosovan

Dear Evaluation Committee, Ladies and Gentlemen,

Dr. Peter Kosovan's contribution to the scientific community deals with the in-depth understanding of acidity (and basicity) in complex nanoscopic environments. While the pH of dilute solutions of weak monoacids (or bases) is well understood from an idealized thermodynamic point of view (since the establishment of the Henderson-Hasselbalch equation more than 100 years ago), the mutual influence of the acidic moieties in polyacids gives an already more complicated scenario. A (limited) theoretical understanding of the counterion condensation and titration behavior of polyacids was created by Katchalsky and coworkers 70 years ago. However, the behavior apart from linear polyacids remained obscured until the last two decades. E.g. branching can lead to further deviations from ideal behavior. Into this scenario, the independent scientific work of Dr. Kosovan sets in.

On this journey, he gives also theoretical impulses, as he is one of the few researchers who points out that the effective pK_a and effective pH provide equivalent descriptions for the same behavior (page 17). He investigated the protonation of a single acidic group in a charged environment and detected a shift of the titration curve not only by simulations but also by experiments using fluorescence spectroscopy. He investigated the titration behavior of various polyacids with different branching. Most prominently, he analyzed the protonation behavior of different peptides again with experiment and simulation. He extracted (sometimes subtle) changes in the polyampholytic behavior dependent on the difference of the involved pK_a s. The presence of already oppositely charged entities facilitates the ionization, as also seen for mixtures of oppositely charged polyions (polyelectrolyte complex). As a rather recent field of research, he is devoted to study two-phase systems where either a certain species cannot partition between different compartments (like in the

case of a dialysis setup or in the case of a gel in combination with supernatant). Here, the Donnan equilibrium needs to be taken into account. In some cases, the system can generate salt for its own Donnan equilibrium by adjusting the ionization equilibrium. In future, it could be nice to see also effects on the reservoir size on the establishment of a Donnan equilibrium.

Conceptually, he tackled the problem mainly with help of computer (Monte-Carlo) simulations. He does not only use existing simulation methods, but he is also very active in simulation method development like for the "Grand-Reaction Ensemble", which is suitable to investigate phase separated systems. As mentioned already above, he combined nicely the simulation results with experiments not only from the literature, but also from collaboration partners and eventually from his own group. Hence, Dr. Kosovans group belongs to the very few groups world-wide which are experts both in simulations and lab-scale experiments. Combined with this excellency, an increasing pace of publishing can be seen in his track record. Furthermore, he was invited to give several presentations and I remember well the time, when he visited my former university as an internationally distinguished expert on acid-base equilibria. At that time, he could help other simulation groups to set up similar simulation capacities on reactive systems.

His habilitation thesis is well written and I was delighted to see that he manages to take the reader along the line, even when the reader starts reading in a later chapter (like when omitting the method part). In some cases, the presentation shows imperfections, which might be partially caused by a faulty representation in certain pdf programs. Hence, the figure captions could sometimes carry more information, which might be otherwise buried in hidden insets of the figures (e.g. the color code in Figure 4.7 is not totally clear to me in addition to the difference between top and bottom row; is Figure 4.10 really dealing with positively charged stars?). In any case, these observations are absolutely minor compared to the overall impact given by Dr. Kosovan.

Hence, I fully recommend the acceptance of the habilitation thesis and the promotion of Dr. Kosovan to become an associate professor. I am already now curious, which charge effects he will unravel in future.

Sincerely,

Prof. Dr. Felix Plamper