Attachment 6

Minutes, PCAS Working group meeting

IAPWS Annual Conference, Prague September 3 - 8, 2000

Members present: H. Corti, J. Hruby, U. Franck, J.M.H. Levelt Sengers, V. Majer, M. Nakahara, D. A. Palmer, P. Tremaine

Monday morning, September 4; separate PCAS WG meeting

1. The chairman (D.A. Palmer) opened the session; the agenda for the PCAS WG sessions during the Conference was approved; V. Majer was approved as the clerk of minutes. The minutes of the 1999 (Toronto) PCAS WG meetings were approved

2. The links between activities of PCAS WG and other WGs (PCC, TPWS) were discussed. It was decided that the PCC WG should continue to give guidance on topics of research, which are relevant to physical chemists. V. Majer felt that the input from PCC regarding this aspect is relatively weak. TPWS WG is moving towards projects regarding mixtures ($NaCl+H_2O$, NH_3+H_2O,) and there is certainly an overlap in activities of PCAS and TPWS WGs. A close collaboration and coordination of activities should be established.

3. D. Palmer asked about the relevance of projects regarding sequestration of CO_2. V. Majer mentioned the work performed in Clermont-Ferrand (adsorption of CO_2 in aq. solutions of alkanolamines) and an upcoming analogous project on dissolution of H_2S; in both cases the motivation for these measurements is environmental concerns (elimination of gases causing the greenhouse effect). It would be useful to identify industrial problems regarding aqueous systems and to bring them to the attention of IAPWS; a participation of industrial experts from various fields would be of help.

4. U. Franck suggested as one research topic the investigation of binary systems involving light non-polar compounds (CH_4, CO_2, Ar, N_2) + the light polar compound (H_2O) at supercritical conditions where mixing is unlimited. Particularly, viscosity measurements and examination of the influence of non-polar compound to the dielectric constant of water would be valuable. These data would be certainly of interest to industry (supercritical oxidation)

5. D. Palmer and P. Tremaine raised the question of the future orientation of PCAS WG. Promising topics suggested were: pH measurements at high temperatures, organics in water, ion pairing in compressible water. The relationship to the activities of TPWS WG was discussed.

6. V. Majer suggests as a possible research project, evaluation of high temperature data for dilute aqueous solutions of non-electrolytes and establishment of recommended data on hydration properties. This information is needed for developing and testing new models (based on the FST theory and formulated in terms of hydration

properties) for correlating and predicting standard thermodynamic properties of solutes (and standard chemical potentials) at high temperatures and pressures. P. Tremaine asked for an explanation, as to what would be the role of IAPWS in such a venture and for more precise definition regarding objectives.

7. D. Palmer reported on progress with the preparation of "ATLAS": a monograph consisting of 16 chapters of about 40 book pages, each to be written by two or more experts. An appendix (basically, tables and computer codes) on a CD ROM are also expected. The dead line for submitting the text to press should be November 30, 2002. Finding a good and cooperative publisher is a concern. Sale of 1700 copies per US$ 125 is apparently required for commercial viability of the project. Academic Press and Springer have been approached; the reaction of the former was lukewarm; Springer seems to be much more outgoing, and it was recommended to contact Elsevier.

Tuesday afternoon, September 5, Joint meeting of PCAS and TPWS WGs with a workshop

D. Friend welcomed all participants (about 30 persons present) and announced the program consisting of four sections: 1. guideline on the NH_3+H_2O system, 2. guideline on the NaCl+H_2O critical locus, 3. contributions of young scientists supported by IAPWS on dilute aqueous non-electrolytes, 4. molecular simulation of water substance.

1. D. Friend informed about the status of the NH_3+H_2O system guideline backed by the articles of Tillner-Roth and Friend (JPCRD 27,63,1998 and 27,45,1998). Two contributions relating to this topic are presented:

    a. K. Ogushi *et al*. presented an examination of the *pVTx* properties for the NH_3+H_2O system near the maximum in density; they pointed out the scarcity of data below 273 K for dilute ammonia solutions
    b. F. Marsik (co-authored by Safarik) discussed the critical behavior of the NH_3+H_2O system on the basis of their thermodynamic calculations and stated some differences in the water rich region compared to the Tillner and Roth recommendations.

    The problem of the value of the universal constant *R* was discussed. It is recommended to accept the proposed guideline with some additional remarks and minor modifications of confidence limits.

2. J. Sengers presented the status of the guideline preparation on the NaCl+H_2O critical locus (up to 30 per cent of NaCl by mass) backed by the article of Povodyrev *et al*. (IJT 20,1529,1999). The problem of describing the critical locus close to 0.4 mass percent in NaCl was emphasized, where the locus seemed to be at the limit of

breaking up into two phases. Crossover behavior seemed to be more like that observed for polymers than in steam (presence of aggregates is apparent from light scattering experiments).

3. V. Majer introduced two talks on dilute aqueous non-electrolytes and provided information on the context in which the work was carried out by Czech investigators at the Blaise Pascal University in Clermont-Ferrand.

    a. L. Hnedkovsky from Prague Institute of Chemical Technology described the Cp. flow calorimeter constructed in France; outlined the new model for calculating heat losses from the cells; and showed examples of data obtained on aqueous solutions of hydroxy and amino derivatives of benzene and toluene. The expected near-critical behavior was discussed and the suitability of a group contribution concept for predicting thermodynamic properties in this family of compounds was demonstrated.
    b. J. Sedlbauer from the University of Liberec discussed various models proposed over recent years for correlating standard thermodynamic properties of aqueous non-electrolytes over a wide range of temperatures and pressures. Examples of test results on the Gibbs free energy were presented and use of a group contribution method for polar aromatics and their polar derivatives was shown.

    A lively discussion followed both contributions regarding calibration of the calorimeter, reliability of results and their processing by correlation techniques.

4. I. Svitchev from Trent University reported on thermodynamic properties of computer simulated water for scientific and engineering use. He recommended the establishment of a group of researchers working under auspices of IAPWS on standardization of thermodynamic and transport properties of computer simulated water. Both non-polarizable SPE and polarizable PPC water models are a good basis for describing real substances. Simulation results can be used in future for supplying data for water and/or aqueous dilute solutions where experiments are difficult or impossible to perform. It is recommended to establish a task group on molecular simulations working on the borderline between TPWS and PCAS WGs.

THURSDAY MORNING, SEPTEMBER 7; SEPARATE PCAS WG MEETING

1. Discussion on the Atlas book was continued during the meeting of the working group. The main points discussed were: what kind of information should be included (additional references and tables)?; what level of the book is appropriate?; how

should it compare with other books published over the past 10 years?, how many references should be included?; and that the PCAS WG should have a leading role in the preparation of the book.

2. D. Palmer announced that he wished to step down after 4 years of chairmanship and M. Nakahara expressed a feeling that a new vice chairman should be appointed. V. Majer was proposed by D. Palmer as the future chairman of PCAS and this proposal was approved by the working group. After a short discussion, S. Lvov was recommended for the vice-chairman position. He was not present in Prague and will be contacted by D. Palmer upon his return to the US.

3. A. Anderko was invited to join the group. He could help to identify issues of interest to the chemical industry and serve as a link between industrial solution chemists and people in academia.

4. The borderline between activities of the WGs PCAS and TPWS and steam was discussed. The general feeling was that the two groups have different approaches towards aqueous systems: focus on physico-chemical description of solutions, interest in dilute systems, understanding of interactions on one side, focus on thermophysical properties of mixtures, equations of state and a more phenomenological engineering approach on the other side. P. Tremaine felt that the PCAS WG should pick up several projects and to work towards a certain well-defined target. M. Nakahara stressed necessity for a better understanding of solutions on a molecular level and to pay more attention also to results from spectroscopic studies.

5. PCAS agreed after a short discussion that the priorities over the next four years should be the following four areas:

    a. pH of water over a wide range of T and p (a specific guideline as an IAPWS document is expected in 1 to 2 years)
    b. establishment of a group contribution scheme based on a theoretically founded model for predicting standard thermodynamic properties of aqueous organic solutes over a wide range of T and p (a guideline as an IAPWS document is expected in 2 to 3 years)
    c. ion association in aqueous alkali metal electrolytes at high temperatures to supercritical conditions (a guideline as an IAPWS document expected in 3 to 4 years).
    d. active participation in the establishment of a new task group on molecular simulation was requested. This task group should be jointly associated with PCAS and TPWS WGs (noting that R. Wood is already active in this area and he is a member of PCAS).