

Interactive comment on “Experimental determination of Henry’s law constants of difluoromethane (HFC-32) and the salting-out effects in aqueous salt solutions relevant to seawater” by Shuzo Kutsuna

Anonymous Referee #2

Received and published: 25 April 2017

The manuscript by Shuzo Kutsuna entitled “Experimental determination of Henry’s Law constants of difluoromethane (HFC-32) and the salting-out effects in aqueous salt solutions relevant to seawater” describes nice laboratory measurements of Henry’s Law, and modified Setchenov constants as a function of temperature and salinity. The experiments are conducted for a single (constant) mole ratio composed of NaCl, MgCl₂, Na₂SO₄, CaCl₂ and KCl, resembling artificial seawater. The total salt concentration of this mixture is varied to resemble salinity conditions that include salt concentrations found in the ocean (up to 51.3 permille). The range of temperatures probed (276K-353K) provides good signal-to-noise to estimate the enthalpy for dissolution of CH₂F₂

C1

into water. The manuscript argues convincingly, that a single Setchenov salting constant does not describe the salting out effect over the full range of conditions probed. Instead, a parameterization based on a 7-variable global fit is chosen to represent the equilibrium partitioning as a function of salinity, and temperature. This manuscript is suitable for publication in ACP, and I recommend publication after the following comments have been addressed. Comments:

- 1) The overall quality of the measurements seems high, but the manuscript would benefit from an explicit discussion of experimental error. At present, there is essentially no discussion of experimental error. What are the parameters that limit the accuracy of the inert-gas stripping (IGS) method? Of the stripping column apparatus? And of the phase ratio variation headspace method (PRV-HS) method? Do error bars reflect statistics only, or also potential sources of systematic bias?
- 2) The data seems to be precise, but is not necessarily accurate. For example, there does appear to be a small – yet significant – offset between PRV-HS and IGS method in Figure 2 at 312K, where there is overlap between both methods. This offset seems to be significant based on the error bars shown. Is IGS believed to be more accurate, why?
- 3) Does the fit according to (Eq13) take into account the relative weight of error bars?
- 4) What is the reason for the large variation in the size of error bars in Fig. 5?
- 5) The S_{0.5} components of the fit (deviation from Setchenov) is strongest at warm temperatures, and smallest at low temperatures. This is an interesting observation, that warrants discussion. Beyond the empirical finding there is virtually no discussion of these deviations. What are possible causes? What is its relevance?
- 6) The discussion in Sect. 3.3 assumes solubility equilibrium with the atmosphere over the full depth of the ocean mixed layer. How deep is this mixed ocean layer in the model? Concentration gradients in DOC are visible in field data already at a few ten

C2

meters from the ocean surface. Does this mean the model estimates an upper limit?

7) The conclusion that 5% of the atmospheric burden of CH₂F₂ would reside in the ocean mixed layer in the southern semi-hemispheric lower troposphere during winter seems to be an upper limit, and should be worded as such. How much lower could this upper limit be?

8) For a gas with an atmospheric lifetime of 5.4 years, that is mostly emitted in the Northern Hemisphere it seems surprising that the dissolution of CH₂F₂ into the ocean should affect estimates of CH₂F₂ emissions in the Southern Hemisphere and their seasonal variability, because the atmospheric concentrations that reach the Southern Hemisphere are also affected by transport, and chemical removal, and related uncertainties. This should be mentioned.

Specific comments:

P2, L28: 'first' is written twice

P5, L8: add errors for numbers. See comments #1, #2 and add typical values, their units, and uncertainties of variables for the key equations throughout the manuscript.

P7, L6: What statistical test for outliers was applied? Six or fewer points were removed at each temperature. Out of how many? Please add.

Eq(17). For sake of discussion, can a k_S value be given here? And what is the effect of including k_S vs k_{S1}, k_{S2} in the model – does it make a difference?

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-58, 2017.