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Interactive comment

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 #1

Received and published: 8 March 2017

This is a very well-written paper addressing an important topic in atmospheric chemistry. The title and abstract very clearly indicate the purpose and results of the work. The language is clear and concise throughout. The experimental techniques are relatively new but seem quite appropriate to the determination of solubility of gases at very low partial pressures. The techniques are well referenced and described in sufficient detail for others to reproduce the experiments. The main conclusion of the paper seems to be that the solubility of difluoromethane in seawater (accounting for the salting-out effect) is too low to significantly affect the atmospheric burden. The data clearly support this conclusion, although the reviewer is not qualified to comment in detail on the

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oceanic modeling referred to as AGAGE.

The reviewer finds fault only in that the author tries to extract more detail from the results than the data justify. Lines 6-7 on page 7 are troubling. data points might be eliminated if some systematic error was found and the measurements repeated, but this does not appear to be the case. A glance at Figure 2 gives the reassuring impression that random errors are quite small for both the IGS and PRV-HS methods. However, there is a small but significant difference in the results at the one temperature where both techniques are used. This shows a systematic error in one or both of the methods. Taking either of the data sets in Figure 2 by itself, a linear fit to ln(K) vs (1/T) would be indicated, but with different slopes, hence different enthalpies of solution. It is only when one uncritically joins the data sets that a curve is seen, which seems to justify the use of the third term in the van't Hoff equation, equation 12. In the fitting equation, equation 13, the number of significant figures reported is much higher than justified for the relatively small number of data points. In nonlinear fitting of this type, most programs report the variance associated with each of the fitting coefficients. if the square-root-of-variance is not small compared to the fitting coefficient, that means that the inclusion of that coefficient is probably not justified. The author does not report these results so it is difficult to determine if the three-term van't Hoff equation is justified. The reviewer believes that a two-term fit would be the highest order justified if each data set were analyzed separately.

The treatment of the salting-out effect is similarly overworked. The data in Figure 4 show the expected qualitative trend with respect to increasing salinity and imply small random errors. The plots in Figure 5 clearly show curvature, since the origin is, in effect, a "free" data point. So far, so good. The generalization of the Sechenov equation (equations 18-22) uses more fitting parameters (four salinity parameters for only five measured salinities!) and more significant figures than are justified. In the reviewer's opinion, lines 9-26, page 9 should be eliminated and the author should simply state that ln(Kh/Keq) varies close to the 0.5 power of salinity, in contrast to the Sechenov

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equation. This result is probably new and could be the stimulus for further research.

The paper is almost free of typographical errors. On page 3, line 12, the water quality should be indicated as (resistivity > 18 megohm-cm). On page 6, line 21, "non-linear" is misspelled.

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