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Atmospheric Chemistry and Physics
Discussions

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

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Thank you very much for the constructive comments.

Two main comments are given. Both the comments indicate that the author tries to extract more detail from the results than the data justify. First comment is on the fitting by the three-term van't Hoff equation. Second comment is on the treatment of the salting-out effect. I will replay to each comment as follows.

1. Reply to the comment on the fitting by the three-term van't Hoff equation.

Thank you for the suggestion that the square-root-of-variance of the fitting coefficient should be checked for justifying whether the coefficient should be included in the van't Hoff equation. The square-root-of-variance, that is, standard deviation for each fitting coefficient in equation (12) is as follows:

$\delta \mathrm{a}_1 = 5.50; \delta \mathrm{a}_2 = 8.32; \delta \mathrm{a}_3 = 2.83$

Because the ratio of $\delta \mathrm{a}_3 / a_3$ is 0.148, the three-term van't Hoff equation is thus justified.

According to the referee's comment, I revise the significant figure of each fitting coefficient in equation (13). I set the least digit of the significant figure to the second decimal place so that the values calculated by equation (13) are consistent with the significant figure of K_{H}. Equation (13) is thus as follows:

$$\ln\left(K_{\mathrm{H}}(T)\right) = -49.71 + 77.70 \times (100/T) + 19.14 \times \ln\left(T/100\right) \quad (13)$$

As the referee indicates, there is, however, a small but significant difference in the results at the one temperature where both techniques are used (around 40 °C). This suggests a systematic error in one or both of the methods. In addition, as the referee suggests, if each data is fitted separately, a two-term fit would reproduce the data.

A two-term fit gives equation (A1) for the IGS method and equation (A2) for the PRV-HS method:

$$\ln(K_{\mathsf{H}}(T)) = (-10.43 \pm 0.12) + (22.88 \pm 0.35) \times (100/T) \quad \text{(A1)},$$

$$\ln K_{\mathsf{H}}(T) = (-8.88 \pm 0.12) + (18.51 \pm 0.40) \times (100/T) \quad \text{(A2)},$$

where errors of the fitting coefficients represent standard deviation only for non-linear fitting.

Despite these indication and suggestion, I still think that fitting the three-term van't Hoff equation (equation 12) to the data is reasonable because equation (13) is justified as aforementioned and because the following three reasons additionally support it.

First, even if the data in the IGS method is fitted separately, a three-term fit to the data in the IGS method would be justified as equation (A3), although errors of the fitting coefficients are larger than those in equation (13).

$$\ln(K_{\mathsf{H}}(T)) = (-41.7 \pm 7.2) + (66.8 \pm 10.5) \times (100/T) + (15.1 \pm 3.7) \times \ln(T/100) \quad \text{(A3)},$$

where errors of the fitting coefficients represent standard deviation only for non-linear fitting. Residual mean square of values of K_{H} was 1.19×10^{-8} for equation (A1) and 5.29×10^{-7} for equation (A3).

Second, as seen in Figure 4, if the data for a-seawater at each salinity is fitted separately, the data would be fitted by the three-term van't Hoff equation rather than the two-term van't Hoff equation.

Third, I checked a potential systematic error in the IGS method but did not find it out as follows. Errors of the volumetric flow rate of the gas (F_{meas}) would cause systematic error in the IGS method. But, as described in the experimental section (lines 14-16, on page 4), I had calibrated the soap-bubble meter, which was used to calibrate F_{meas}, by

means of a high-precision film flow meter SF-1U with VP-2U (Horiba, Kyoto, Japan). Other potential systematic error in the IGS method may arise from the redistribution of gaseous CH_2F_2 into the test solution (lines 5-14, on page 5). But if the redistribution of gaseous CH_2F_2 into the test solution was significant, the value of $K_{\mathsf{H}}(T)$ would have been overestimated because equation (6), not equation (7), was used to deduce the K_{H} values in this study. Hence, it cannot be the reason for the difference in the values of K_H obtained around 40 °C between in the IGS method and in the PRV-HS method.

Overall, I think that fitting the three-term van't Hoff equation (equation (12)) to the data is reasonable.

2. Reply to the comment that the treatment of the salting-out effect is overworked.

The referee points out the treatment of the salting-out effect is overworked. I agree on this point. The referee has the opinion that lines 9-26, page 9 should be eliminated and the author should simply state that $\ln(K_H/K_{eq})$ varies close to the 0.5 power of salinity. Thank you for the opinion. According to the referee's opinion, almost all the data in Figure 5 is found to be fitted using only one parameter as follows.

According to the referee's opinion, I eliminate equations 18 - 21. Instead, I represent $\ln(K_{\mathsf{H}}/K_{\mathsf{eq}})$ by equation A4:

$$\ln(K_{\mathsf{H}}(T)/K^{S}_{\mathsf{eq}}(T)) = k_{\mathsf{s1}} \times S^{0.5} \quad \text{(A4)}$$

where $k_{\mathsf{s1}} = a_{\mathsf{s1}} \times (100/T)$.

Equation (A4) is used to estimate the amount of CH_2F_2 dissolved in the ocean mixed layer in Sect. 3.3. Fitting equation (A4) to all the data in Figure 5 gives $a_{\mathsf{s1}} = 0.1343 \pm 0.0013$ (equation (A5)). Errors are standard deviation only for non-linear fitting.

$$\ln\left(K_{\mathsf{H}}(T)/K^{S}_{\mathsf{eq}}(T)\right) = (0.1343 \pm 0.0013) \times (100/T) \times S^{0.5} \quad \text{(A5)}$$

This fitting reproduces all the data, except for two data at 39.5 °C, in Figure 5, as indicated in Figure 5m. Only one parameter (a_{s1}) is thus found to be required for fitting almost all the data in Figure 5.

Combining equations (13) and (A5) gives equation (A6):

$$\ln\left(K^{S}_{\mathsf{eq}}(T)\right) = -49.71 + (77.70 - 0.134 \times S^{0.5}) \times (100/T) + 19.14 \times \ln(T/100) \quad \text{(A6)}$$

Based on equation (A6), values of K^{S}_{eq} and the amount of $\mathrm{CH_2F_2}$ dissolved in the ocean mixed layer will be recalculated and the manuscript will be revised.

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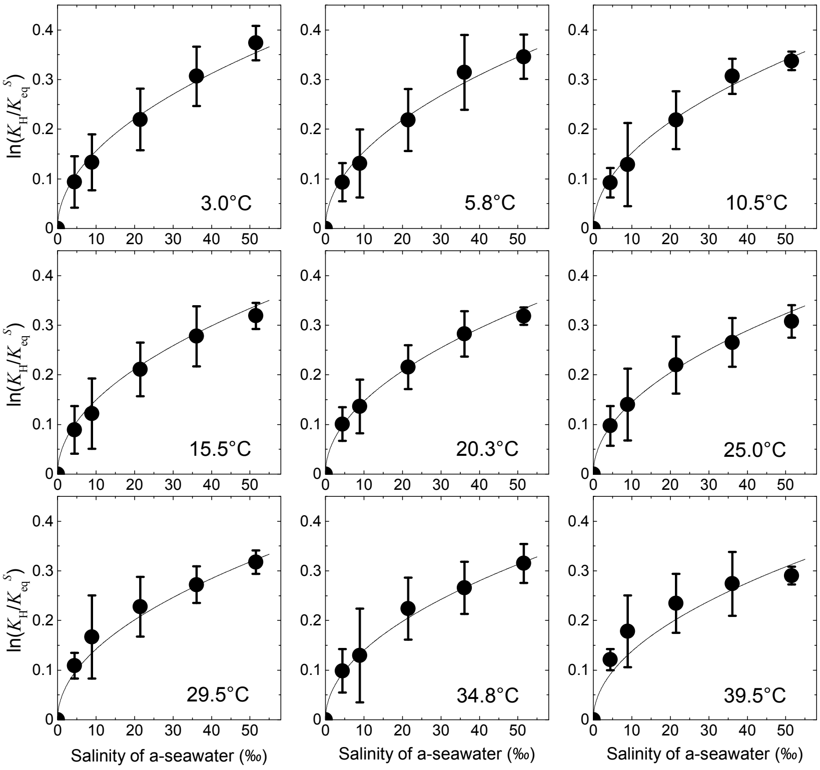

Fig. 1. (Fig. 5m) Plots of ln(KH(T)/KHS(T)) vs. salinity in a-seawater at each temperature. Bold curves represent the fitting obtained by Eq. (A5)