Supporting information

Experimental determination of Henry's law constants of difluoromethane (CH_2F_2) and the salting-out effects in aqueous salt solutions relevant to seawater

S. Kutsuna

[1]National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, 305-8569, Japan

Correspondence to: S. Kutsuna (s-kutsuna@aist.go.jp)

S1. Equilibrium time for the PRV-HS method experiments

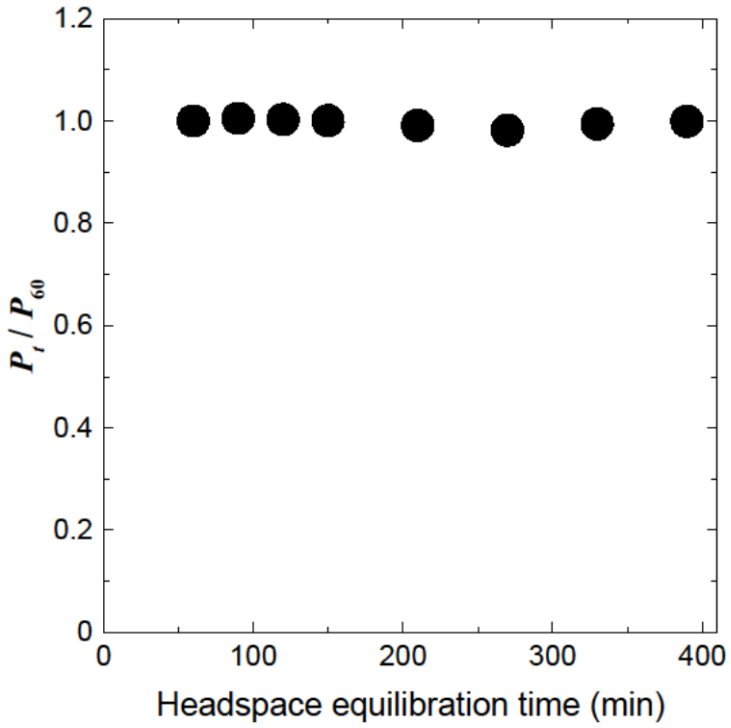

Figure S1. Relative areas of GC-MS peaks for CH_2F_2 versus headspace time duration for equilibration of 9.0 cm^3 of aqueous CH_2F_2 at 353 K.

S2. An example of the IGS method experiments

Figure S2 shows an example of time profile of P_t and how to calculate the k_1 value for the IGS method experiments. The k_1 value at each time was calculated by fitting nearest three data of P_t for each time. The average of the k_1 values is given as the k_1 value for the experimental run. Two standard deviation of the k_1 values gives errors of the k_1 value for the experimental run.

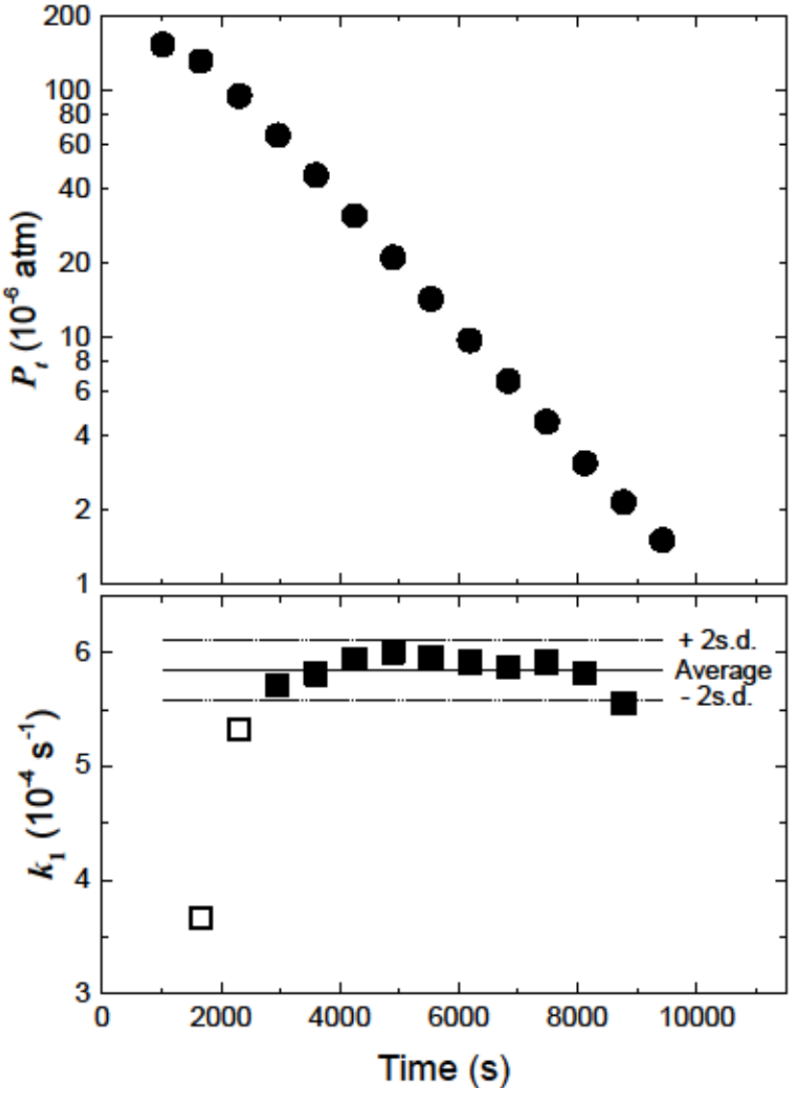

Figure S2. An IGS experimental result for V = 0.350 dm^3 and F = 3.32×10^{-4} dm^3 s^{-1} at 25°C. (upper panel) time profile of P_t; (lower panel) values of k_1 calculated by fitting nearest three data of P_t for each time with respect to Eq. (1).

S3. Results of the PRV-HS method experiments

Figure S3 illustrates the results of a PRV-HS experiment at 313 K. In panel A, peak area (S_{ij}) is plotted against the volume of the CH_2F_2 gas mixture added (v_j) for V_i = 9.0, 7.5, 6.0, 4.5, 3.0, and 1.5 cm^3. For each V_i, the data form a straight line intersecting the origin, indicating that S_{ij} is proportional to v_j for vials with the same value of V_i. The slope (L_i) of each line is obtained by linear regression with respect to Eq. (8), and the reciprocal of the slope (L_i^{-1}) is plotted against the phase ratio (V_i/V_0) in panel B of Fig. S3. Plots of L_i^{-1} and V_i/V_0 obey Eq. (9). Table S1 lists the values of L_i^{-1}, the slopes and the intercepts for linear regression with respect to Eq. (9), and the $K_H(T)$ values calculated from the slopes and the intercepts. Two measurements of $K_H(T)$ were carried out at each temperature.

Furthermore, the $K_H(T)$ values, along with errors of them at 95% confidence level, were also estimated by non-liner fitting of the two datasets simultaneously at each temperature by use of Eq. (11) (Fig. S4). The $K_H(T)$ values and their errors thus estimated are plotted in Fig. 2 and are listed in Table S1.

Table S1. L_i values for various V_i/V_0 ratios at various temperatures, slopes and intercepts for linear regression with respect to Eq. (10), $K_H(T)$ values calculated from the slopes and intercepts, and $K_H(T)$ values and the errors at 95% confidence level estimated by non-linear fitting the two datasets simultaneously at each temperature (Fig. S4) with respect to Eq. (11).

T (K)	L_i (a.u.) *						Eq. (10) Intercept	Eq. (10) Slope	K_H ($M\ atm^{-1}$)		
	V_i/V = 0.421	0.351	0.280	0.210	0.140	0.070			Eq. (10)	Eq. (11)**	Eq. (13)**
353	3.226±0.002	3.270±0.026	3.330±0.004	3.391±0.008	3.462±0.014	3.526±0.009	3.581	–0.870	0.026	0.027 ±0.002	0.031 ±0.003
	2.044±0.006	2.050±0.012	2.112±0.010	2.132±0.009	2.186±0.021	2.209±0.011	2.248	–0.513	0.027		
343	3.000±0.018	3.025±0.009	3.070±0.008	3.089±0.015	3.117±0.015	3.148±0.018	3.179	–0.423	0.031	0.031 ±0.001	0.033 ±0.002
	1.949±0.004	1.955±0.005	1.968±0.003	1.998±0.004	2.020±0.002	2.030±0.009	2.050	–0.258	0.031		
333	3.247±0.018	3.234±0.018	3.243±0.015	3.241±0.010	3.247±0.009	3.223±0.013	3.231	0.034	0.037	0.036 ±0.003	0.037 ±0.002
	3.080±0.009	3.044±0.006	3.082±0.005	3.127±0.009	3.113±0.008	3.134±0.014	3.149	–0.213	0.034		
323	3.208±0.011	3.190±0.008	3.133±0.010	3.134±0.011	3.092±0.008	3.093±0.006	3.055	0.355	0.042	0.043 ±0.002	0.042 ±0.001
	3.357±0.010	3.289±0.014	3.275±0.005	3.233±0.004	3.226±0.016	3.160±0.001	3.135	0.496	0.044		
313	3.245±0.018	3.185±0.013	3.100±0.015	3.022±0.012	2.995±0.012	2.915±0.011	2.848	0.935	0.052	0.052 ±0.003	0.049 ±0.001
	2.162±0.031	2.134±0.010	2.060±0.014	2.029±0.018	1.992±0.010	1.925±0.018	1.896	0.612	0.052		

* Errors are 2σ for the regression only.; ** Errors are those at 95% confidence level for the regression only.

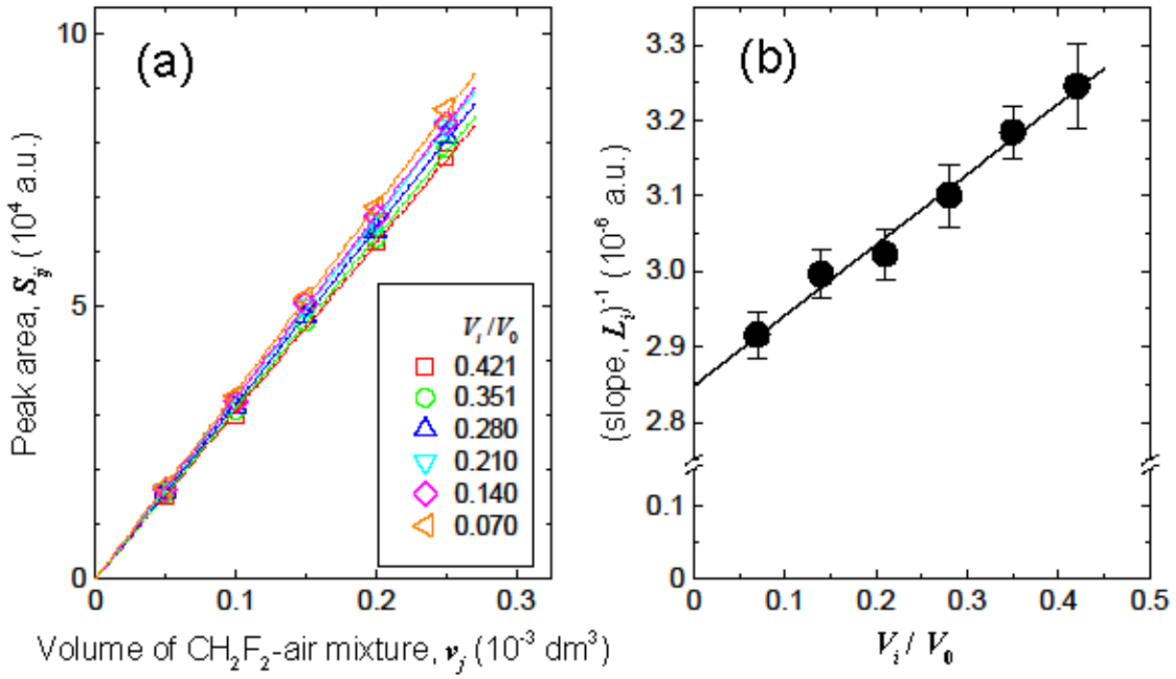

Figure S3. Headspace GC-MS measurements for six series of test samples containing water (V_i in cm^3) to which a CH_2F_2–air mixture was added (v_j in cm^3) at 313 K. (a) Plot of peak area (S_{ij}) versus v_j for test samples containing volume V_i of water. Slope (L_i) was obtained by linear fitting of the data to Eq. (8) for samples of the same V_i. (b) Plot of L_i^{-1} versus V_i/V_0 fitted to Eq. (10).

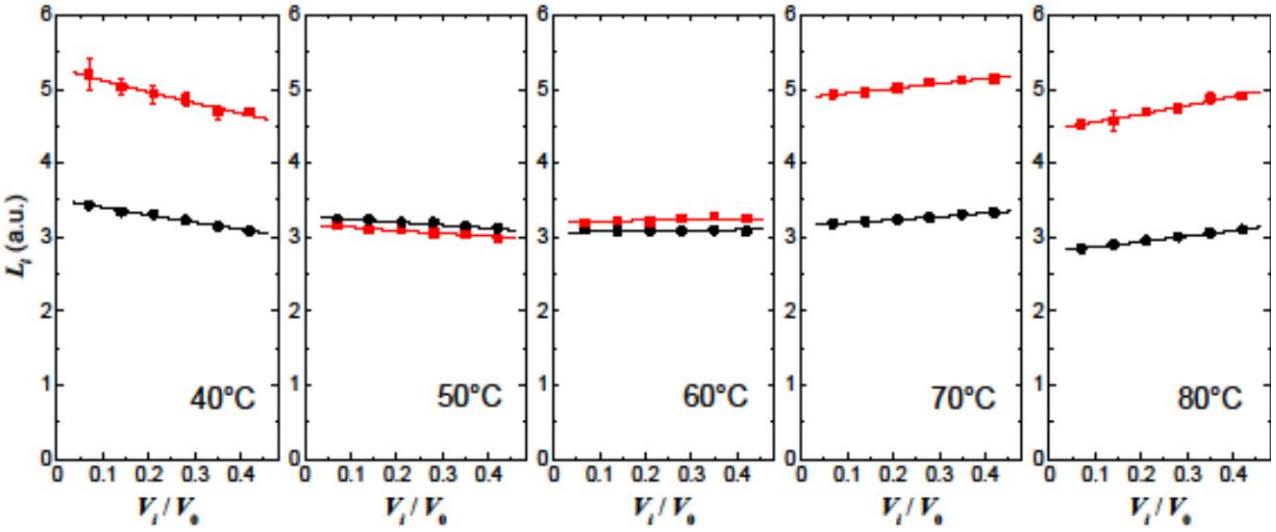

Figure S4. Plot of L_i versus V_i/V_0 for the PRV-HS measurements at each temperature. Bold curves represent the simultaneous fitting of the two datasets at each temperature by Eq. (11).

S4. Determination of salting-out effects in artificial seawater

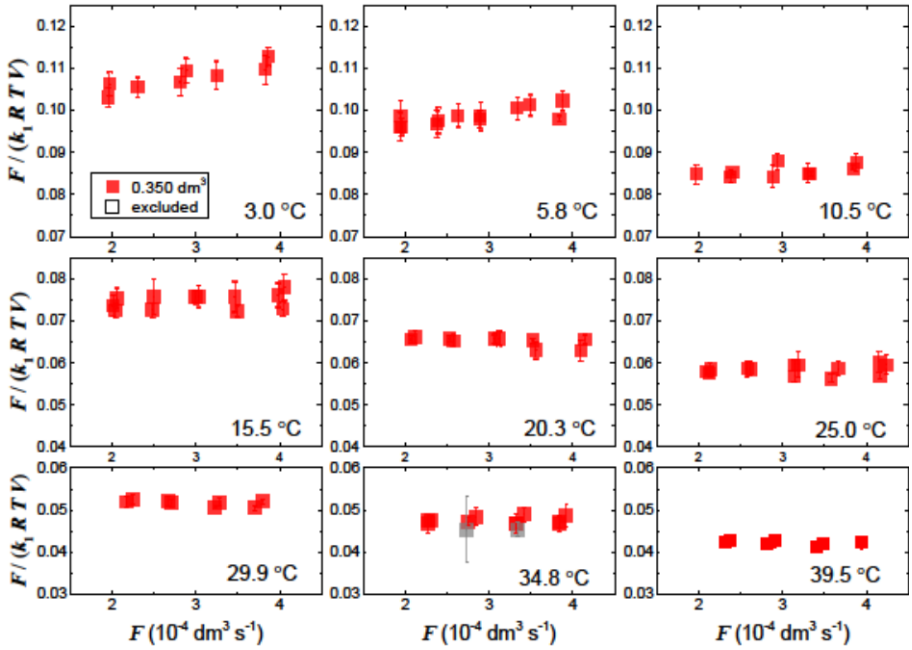

Figure S5. Plots of values of $F/(k_1RTV)$ against F at each temperature for 0.35 dm^3 of a-seawater at 4.452‰. Grey symbols represent the data excluded for calculating the average.

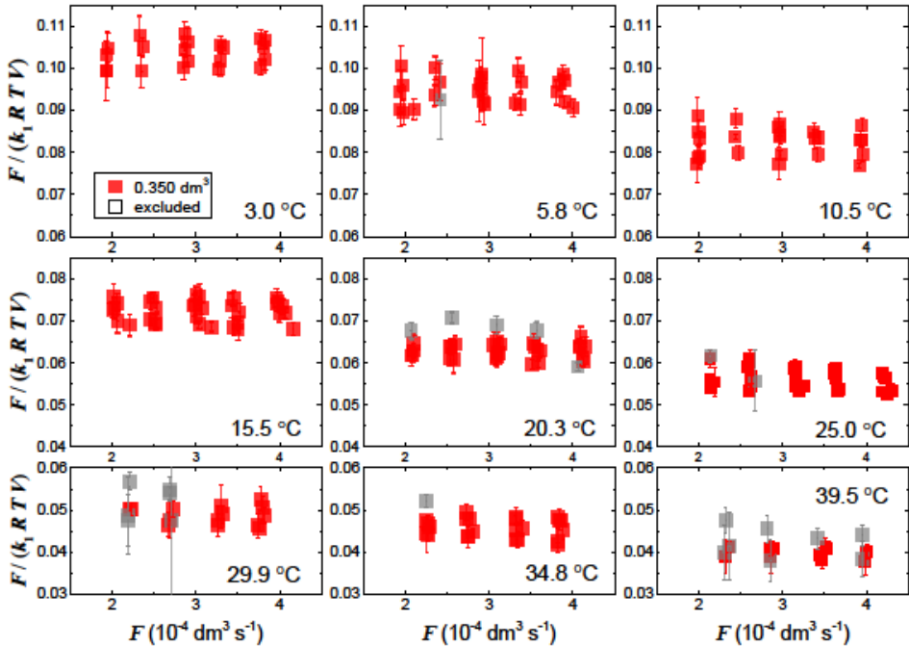

Figure S6. Plots of values of $F/(k_1RTV)$ against F at each temperature for 0.35 dm^3 of a-seawater at 8.921‰. Grey symbols represent the data excluded for calculating the average.

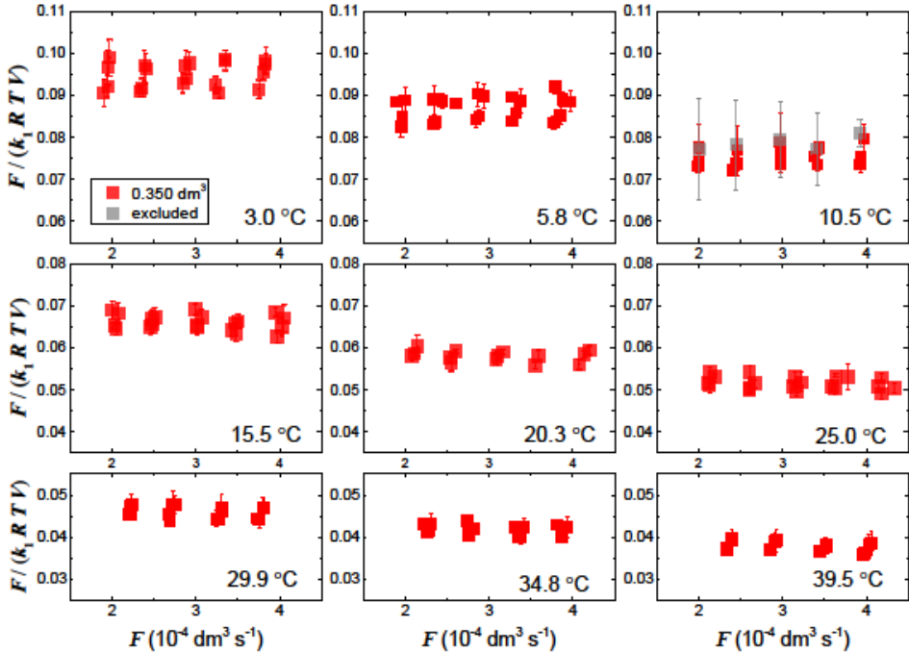

Figure S7. Plots of values of $F/(k_1RTV)$ against F at each temperature for 0.35 dm^3 of a-seawater at 21.520‰. Grey symbols represent the data excluded for calculating the average.

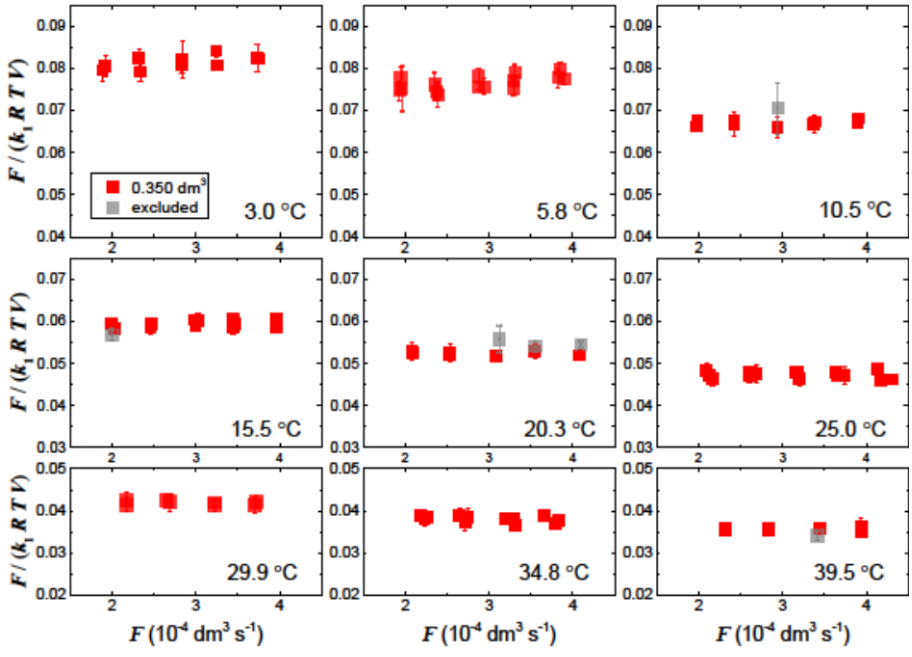

Figure S8. Plots of values of $F/(k_1RTV)$ against F at each temperature for 0.35 dm^3 of a-seawater at 51.534‰. Grey symbols represent the data excluded for calculating the average.

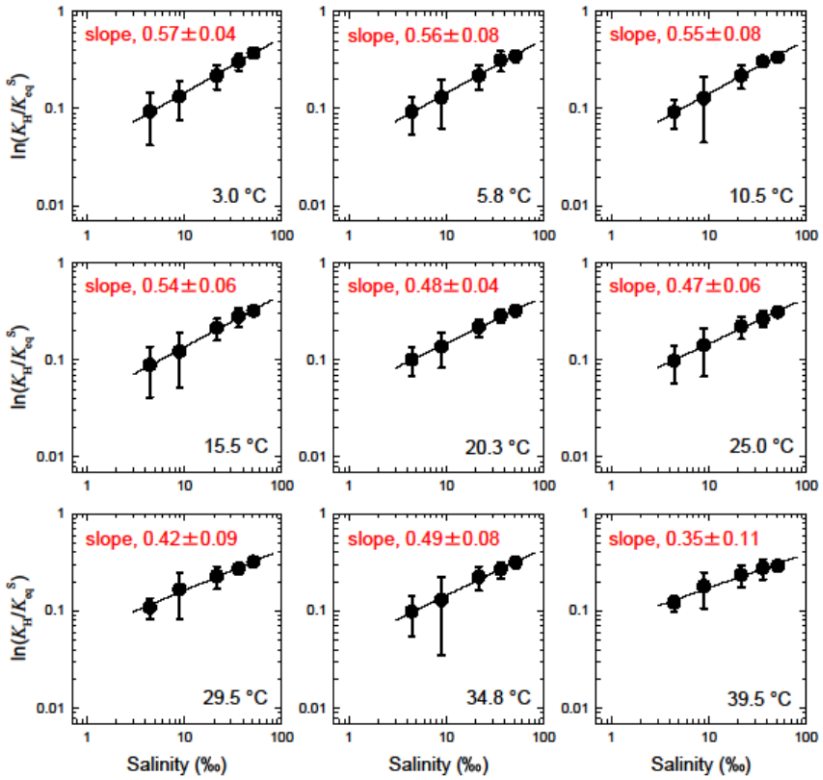

Figure S9. log-log plots for $\ln(K_H(T)/K_H^S(T))$ vs. salinity in a-seawater at each temperature. Bold lines represent the fitting obtained by a liner regression. Errors are those at 95% confidence level for the regression only.

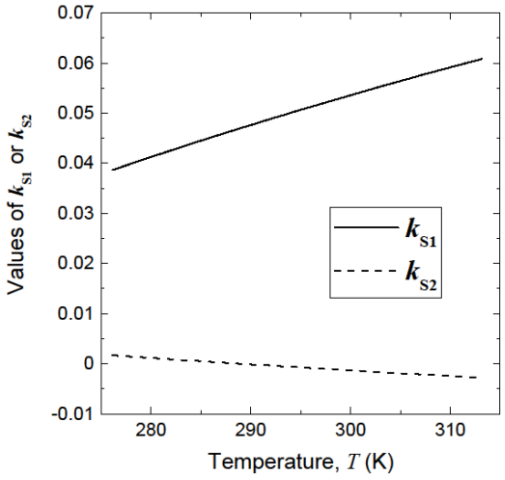

Figure S10. Plots of k_{s1} and k_{s2} (coefficients in Eq. (18)) against temperature.