

SUPPORTING INFORMATION

Experimental Ternary Diffusion Results

For a mean lysozyme chloride concentration of 0.6 mM and each of the five mean KCl concentrations (0.25, 0.5, 0.9, 1.2, and 1.5 M), Tables S1-5 list experimental parameters for the four experiments performed at each mean composition ($\bar{C}_1$, $\bar{C}_2$). Here, the mean concentration $\bar{C}_i$ is defined as the average of the concentrations of solute i in the top and bottom solutions. For each experiment, we report the concentration differences across the initial free-diffusion boundary, ΔC_1 and ΔC_2 ; pHs of bottom and top solutions; densities of bottom and top solutions, d_{top} and d_{bot} ; the time correction²¹ Δt added to the clock time elapsed after boundary sharpening termination; the number of interference fringes in the Rayleigh optical fringe pattern, J_{measd} ; J_{calcd} (discussed below); the reduced-height-area ratio, $D_{A,measd}$, obtained by extrapolating apparent diffusion coefficients calculated for symmetrical fringe pairs to the center of the Rayleigh pattern (21); and $D_{A,calcd}$, calculated (23) from the ΔC_i and the four $(D_{ij})_V$ and the two R_i values reported in Table 6S for each mean composition. For each experiment, J_{calcd} was taken to be $R_1\Delta C_1 + R_2\Delta C_2$, where the refractive index increments⁷ R_1 and R_2 (Table 6S) were obtained by linear regression of $J_{measd} = R_1\Delta C_1 + R_2\Delta C_2$ using J_{measd} and the corresponding ΔC_1 and ΔC_2 for each set of four experiments at a given mean composition.

Table 6S lists experimental parameters and the volume-fixed $(D_{ij})_V$ values calculated with data from all four experiments at each of the five mean KCl concentrations. Using the concentrations and densities of each prepared solution, the parameters $\bar{d}$, H_1 , and H_2 in $d = \bar{d} + H_1(C_1 - \bar{C}_1) + H_2(C_2 - \bar{C}_2)$ were obtained by linear least-squares at each $\bar{C}_1$ and $\bar{C}_2$, where $\bar{C}_i$ is the average of the mean concentrations $\bar{C}_i$ for all experiments at each mean KCl concentration. Partial molar volumes $\bar{V}_1$ and $\bar{V}_2$ were calculated using Eqs. A-7 in Ref. 16. The partial molar volume of the solvent, $\bar{V}_0$, was calculated from Eqs. 4 and 5 in ref 15.

The quantities S_A and I_A in the ratio S_A/I_A are defined by Fujita and Gosting.²² This ratio is a diagnostic that must be larger than ~ 0.2 if the $(D_{ij})_V$ are to be extracted from fringe position data with satisfactory precision. The quantities λ_1 and λ_2 are the eigenvalues of the matrix of volume-fixed diffusion coefficients.¹⁸

Table 1S. Ternary Experimental Data for 0.6 mM lysozyme chloride-0.25 M KCl - H₂O at 25 °C (Series LKC1)

expt	LKC11	LKC12	LKC13c	LKC14
$\bar{C}_1$ (mM)	0.6000	0.6000	0.6000	0.6000
$\bar{C}_2$ (M)	0.2500	0.2500	0.2500	0.2500
ΔC_1 (mM)	0.4000	0.0000	0.4000	0.0000
ΔC_2 (M)	0.0000	0.1161	0.0000	0.1161
pH bottom	4.49	4.50	4.50	4.50
pH top	4.49	4.45	4.49	4.49
d_{bot} (g cm ⁻³)	1.01205 ₅	1.01390 ₀	1.01204 ₇	1.01391 ₀
d_{top} (g cm ⁻³)	1.01039 ₈	1.00853 ₁	1.01039 ₈	1.00858 ₂
Δt (s)	13	14	17	10
J_{measd}	51.222	52.718	51.257	52.735
J_{calcd}	51.237	52.733	51.242	52.720
D_A (measd) (10 ⁻⁹ m ² s ⁻¹)	0.1329	1.871	0.1322	1.880
D_A (calcd) (10 ⁻⁹ m ² s ⁻¹)	0.1329	1.891	0.1326	1.892

Table 2S. Ternary Experimental Data for 0.6 mM lysozyme chloride - 0.5 M KCl - H₂O at 25 °C (Series LKC3)

expt	LKC31	LKC32	LKC33b	LKC34
$\bar{C}_1$ (mM)	0.6000	0.6000	0.6000	0.6000
$\bar{C}_2$ (M)	0.4999	0.4999	0.4999	0.4999
ΔC_1 (mM)	0.4000	0.0000	0.4000	0.0000
ΔC_2 (M)	0.0000	0.1161	0.0000	0.1161
pH bottom	4.50	4.50	4.50	4.50
pH top	4.50	4.50	4.50	4.50
d_{bot} (g cm ⁻³)	1.02358 ₈	1.02540 ₉	1.02360 ₀	1.02540 ₅
d_{top} (g cm ⁻³)	1.02190 ₉	1.02009 ₈	1.02192 ₆	1.02010 ₅
Δt (s)	17	8	15	7
J_{measd}	52.015	51.550	52.066	51.511
J_{calcd}	52.039	51.525	52.041	51.536
D_A (measd) (10 ⁻⁹ m ² s ⁻¹)	0.1297	1.891	0.1297	1.897
D_A (calcd) (10 ⁻⁹ m ² s ⁻¹)	0.1297	1.917	0.1297	1.917

Table 3S. Ternary Experimental Data for 0.6 mM lysozyme chloride - 0.9 M KCl - H₂O at 25 °C (Series LKC2)

expt	LKC21	LKC22	LKC23	LKC24
$\bar{C}_1$ (mM)	0.5999	0.5999	0.5999	0.5999
$\bar{C}_2$ (M)	0.8999	0.8998	0.8999	0.8999
ΔC_1 (mM)	0.3999	0.0000	0.3999	0.0000
ΔC_2 (M)	0.0000	0.1160	0.0000	0.1161
pH bottom	4.50	4.51	4.49	4.51
pH top	4.49	4.49	4.48	4.50
d_{bot} (g cm ⁻³)	1.04161 ₇	1.04333 ₁	1.04161 ₈	1.04340 ₇
d_{top} (g cm ⁻³)	1.03999 ₈	1.03818 ₉	1.03998 ₄	1.03820 ₂
Δt (s)	13	5	19	7
J_{measd}	51.145	49.957	51.146	49.958
J_{calcd}	51.144	49.943	51.147	49.972
D_A (measd) (10 ⁻⁹ m ² s ⁻¹)	0.1291	1.942	0.1291	1.935
D_A (calcd) (10 ⁻⁹ m ² s ⁻¹)	0.1291	1.968	0.1291	1.967

Table 4S. Ternary Experimental Data for 0.6 mM lysozyme chloride - 1.2 M KCl - H₂O at 25 °C (Series LKC5)

expt	LKC51	LKC52	LKC53b	LKC54
$\bar{C}_1$ (mM)	0.5999	0.5999	0.5999	0.5999
$\bar{C}_2$ (M)	1.1998	1.1997	1.1998	1.1998
ΔC_1 (mM)	0.3999	0.0000	0.3999	0.0000
ΔC_2 (M)	0.0000	0.1161	0.0000	0.1161
pH bottom	4.51	4.48	4.51	4.48
pH top	4.50	4.49	4.49	4.48
d_{bot} (g cm ⁻³)	1.05499 ₇	1.05675 ₀	1.05499 ₃	1.05674 ₈
d_{top} (g cm ⁻³)	1.05336 ₄	1.05162 ₁	1.05336 ₀	1.05162 ₁
Δt (s)	12	5	9	11
J_{measd}	50.997	48.978	51.021	48.930
J_{calcd}	51.008	48.956	51.011	48.950
D_A (measd) (10 ⁻⁹ m ² s ⁻¹)	0.1288	1.971	0.1287	1.972
D_A (calcd) (10 ⁻⁹ m ² s ⁻¹)	0.1288	2.003	0.1288	2.003

Table 5S. Ternary Experimental Data for 0.6 mM lysozyme chloride - 1.5 M KCl - H₂O at 25 °C (Series LKC4)

expt	LKC41	LKC42	LKC43	LKC44
$\bar{C}_1$ (mM)	0.5999	0.5999	0.5999	0.5999
$\bar{C}_2$ (M)	1.4998	1.4998	1.4998	1.4997
ΔC_1 (mM)	0.4000	0.0000	0.4000	0.0000
ΔC_2 (M)	0.0000	0.1661	0.0000	0.1161
pH bottom	4.47	4.50	4.50	4.48
pH top	4.50	4.50	4.49	4.48
d_{bot} (g cm ⁻³)	1.06828 ₅	1.06999 ₈	1.06827 ₄	1.06999 ₈
d_{top} (g cm ⁻³)	1.06663 ₄	1.06490 ₀	1.06662 ₆	1.06488 ₈
Δt (s)	12	5	11	9
J_{measd}	51.806	48.094	50.855	48.112
J_{calcd}	51.827	48.105	51.834	14.102
D_A (measd) (10 ⁻⁹ m ² s ⁻¹)	0.1281	2.011	0.1285	2.010
D_A (calcd) (10 ⁻⁹ m ² s ⁻¹)	0.1281	2.046	0.1281	2.046

Table 6S. Derived Ternary Diffusion Data for 0.6 mM lysozyme chloride - KCl - H₂O at pH 4.5 and 25 °C

Series	LKC1	LKC3	LKC2	LKC5	LKC4
$\bar{C}_1$ (mM)	0.6000	0.6000	0.5999	0.5999	0.5999
$\bar{C}_2$ (M)	0.2500	0.4999	0.8999	1.1998	1.4998
$\bar{d}$ (g cm ⁻³)	1.01122 ₇	1.02275 ₆	1.04080 ₃	1.05417 ₆	1.06745 ₀
H_1 (10 ³ g mol ⁻¹)	4.144	4.196	4.070	4.097	4.127
H_2 (10 ³ g mol ⁻¹)	0.04608	0.04571	0.04491	0.04429	0.04397
$\bar{V}_1$ (cm ³ mol ⁻¹)	10191	10138	10258	10224	10190
$\bar{V}_2$ (cm ³ mol ⁻¹)	28.549	28.916	29.701	30.303	30.610
$\bar{V}_0$ (cm ³ mol ⁻¹)	18.065	18.062	18.052	18.041	18.033
R_1 (M ⁻¹)	128100	130125	127926	127590	129616
R_2 (M ⁻¹)	454.31	443.92	430.23	421.73	414.36
S_A/I_A	2.776	2.845	2.903	2.942	2.996
λ_1 (10 ⁻⁹ m ² s ⁻¹)	0.1278	0.1232	0.1195	0.1170	0.1140
λ_2 (10 ⁻⁹ m ² s ⁻¹)	1.817	1.829	1.864	1.892	1.923
$(D_{11})_V$ (10 ⁻⁹ m ² s ⁻¹)	0.1281±0.0001	0.1237±0.0001	0.1203±0.0001	0.1181±0.0001	0.1155±0.0001
$(D_{12})_V$ (10 ⁻⁹ m ² s ⁻¹)	0.000044±0.000002	0.000049±0.000001	0.000056±0.000002	0.000058±0.000002	0.000062±0.000002
$(D_{21})_V$ (10 ⁻⁹ m ² s ⁻¹)	11.8±0.3	16.9±0.2	26.1±0.3	33.4±0.1	41.9±0.001
$(D_{22})_V$ (10 ⁻⁹ m ² s ⁻¹)	1.817±0.001	1.829±0.001	1.863±0.001	1.891±0.001	1.922±0.001