Supporting Information for:

Kinetics of hydrolysis of 4-methoxyphenyl-2,2-dichloroethanoate in binary water-cosolvent mixtures; the role of solvent activity and solute-solute interactions

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In pure water, the rate constant of the neutral hydrolysis of MPDE is $k_0 = 3.00\times10^{-3}\ \mathrm{s}^{-1}$ at 25.0 °C. The accuracy of the kinetic data is 2-3% for cyanomethane, PEG400, and tetrahydrofuran; and 1-2% for the alcohols.

Table 1. Kinetic Data for Water/Cyanomethane Mixtures

$[H_2O]$ (M)	x_{water}	$\ln(k/k_0)$	$\ln(k/k_0) - 2 \ln a_{water}$
53.8	0.988	-0.261	-0.237
52.1	0.977	-0.545	-0.500
50.35	0.964	-0.844	-0.777
50.25	0.963	-0.925	-0.855
45.2	0.924	-1.94	-1.82
40	0.877	-3.07	-2.90
34.5	0.821	-4.09	-3.91
28.7	0.750	-5.01	-4.82
23.4	0.673	-5.70	-5.50

Table 2. Kinetic Data for Water/PEG400 Mixtures

$[H_2O]$ (M)	x_{water}	$\ln(k/k_0)$	$\ln(k/k_0) - 2 \ln a_{water}$
55.34	0.9999	-0.010	-0.006
52.31	0.9968	-0.301	-0.291
51.13	0.9955	-0.473	-0.461
49.24	0.9933	-0.720	-0.702
46.74	0.9902	-0.968	-0.941
44.7	0.9873	-1.24	-1.20
39.71	0.9793	-1.83	-1.77
37.28	0.9747	-2.18	-2.09
34.24	0.9681	-2.57	-2.45
30.21	0.9575	-3.31	-3.13

Table 3. Kinetic Data for Water/Tetrahydrofuran Mixtures

$[H_2O]$ (M)	x_{water}	$\ln(k/k_0)$	$\ln(k/k_0) - 2 \ln a_{water}$
52.2	0.986	-0.505	-0.481
49.0	0.971	-1.01	-0.960
45.7	0.954	-1.73	-1.66
42.1	0.933	-2.76	-2.66
39.9	0.918	-3.22	-3.11
34.0	0.875	-4.09	-3.96

Table 4. Isobaric activation parameters at 25.0 °C.

cosolvent	x_{water}	$\Delta^{\neq}G$ (kJ/mol)	$\Delta^{\neq}H$ (kJ/mol)	$-T\Delta^{\neq}S$ (kJ/mol)
none	1	87.5	35.1	52.4
cyanomethane	0.922	92.5	35.0	57.5
	0.875	95.1	37.6	57.5
	0.817	97.8	57.4	40.3
PEG400	0.9873	90.5	37.7	52.8
	0.9747	92.9	42.0	50.9
	0.968	94.0	44.8	49.2
tetrahydrofuran	0.971	90.0	40.5	49.5
	0.954	91.8	47.5	44.6
	0.936	93.7	48.5	45.3
	0.918	95.5	44.5	51.0

The accuracy $\Delta^{\neq}G$ of is 0.1 kJ/mol, that of $\Delta^{\neq}H$ and $-T\Delta^{\neq}S$ 1.5 kJ/mol.

Table 5. Kinetic Data for Water/Ethanol Mixtures

x_{water}	$\ln(k/k_0)$	$\ln(k/k_0)$ - 2 ln x_{water}
0.995	-0.0782	-0.0686
0.990	-0.153	-0.132
0.985	-0.238	-0.207
0.980	-0.318	-0.278
0.976	-0.385	-0.336
0.970	-0.490	-0.428

Table 6. Kinetic Data for Water/1-Propanol Mixtures

x_{water}	$\ln(k/k_0)$	$\ln(k/k_0)$ - 2 ln x_{water}
0.997	-0.0683	-0.0622
0.995	-0.127	-0.116
0.992	-0.189	-0.173
0.989	-0.266	-0.243
0.983	-0.394	-0.360

Table 7. Kinetic Data for Water/2-Propanol Mixtures

x_{water}	$\ln(k/k_0)$	$\ln(k/k_0)$ - 2 ln x_{water}
0.995	-0.109	-0.0990
0.990	-0.225	-0.205
0.985	-0.345	-0.315
0.980	-0.480	-0.440
0.975	-0.614	-0.563

Table 8. Kinetic Data for Water/1-Butanol Mixtures

x_{water}	$\ln(k/k_0)$	$\ln(k/k_0)$ - 2 ln x_{water}
0.997	-0.0786	-0.0735
0.995	-0.171	-0.161
0.993	-0.244	-0.229
0.990	-0.337	-0.317
0.987	-0.442	-0.416

Table 9. Kinetic Data for Water/2-Methyl-2-propanol Mixtures

x_{water}	$\ln(k/k_0)$	$\ln(k/k_0)$ - 2 ln x_{water}
0.995	-0.120	-0.110
0.990	-0.261	-0.241
0.985	-0.403	-0.373
0.980	-0.587	-0.546
0.976	-0.749	-0.700