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Supporting Information: From Absolute Potentials to a Generalized Computational Standard Hydrogen Electrode for Aqueous and Non-aqueous Solvents

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Estimating the Surface Potential

The differences in the absolute potentials predicted by SMD and PCM shown in Table S1 formally corresponds to the difference between inner potential (predicted by SMD) and experimentally accessible outer potential (predicted by PCM).[S1] This relationship between the models could in principle be exploited to estimate the experimentally important surface potential of the proton in different solvents. For this purpose we estimated the inner absolute potential of the proton in water by using the more reliable outer potential computed using CCSD(T)/aug-cc-pvqz/SMD[S2] and the surface potential estimated from the inner and outer potentials in water reported by Kelly et al.[S3] and Trasatti.[S4] This indirect procedure was necessary since the effective outer absolute potential computed directly with the PCM model differs with 4.02 V significantly from the earlier reported value of 4.44 V.[S4] This is not unexpected since the effective absolute potential is known to vary strongly even with very minor changes to the computational protocol such as the choice of reference, the basis set or the electronic structure method.[S2] Owing to the robustness of the conversion factor with respect to the computational setup these uncertainties are unlikely to be present in the computed conversion factors. It must, however, be cautioned that the PCM method is typically somewhat less accurate than the SMD model which will introduce a minor uncertainty in the predicted surface potentials summarized in Table S1. This together with the minor scatter in the conversion factors can result in errors which are of the same magnitude as the surface potential itself. Thus, the predicted surface potentials only correspond to a rough estimate. However, also the surface potentials estimated from experiment in the literature display a large spread. This shows both that different experimental techniques give different values and that the calculation of the surface potential relies on assumptions that have differed over time. A comparison can be found in Table S1

Table S1: Summary of the surface potentials (χ), outer (E_{abs}^{outer}) and inner absolute potentials (E_{abs}^{inner}). Taking advantage of the construction of the implicit solvation models, the outer potential was computed using the PCM solvation while the SMD model was used for the inner potential.[S1] In both cases, computations were performed at the CCSD(T)/aug-cc-pvqz level of theory with formic acid as reference. The outer potential of water was used as reference state and computed from the inner absolute potential of water and the surface potential of water estimated from the inner potential computed by Kelly et al.[S3] and the outer potential reported by Trasatti.[S4]

[(a)]Computed as the sum of E_{abs}^{inner} computed using CCSD(T)/aug-cc-pvqz/SMD and the estimated surface potential of water. [(b)]Estimated from the inner potential reported by Kelly et al.[S3] and the outer potential reported by Trasatti.[S4]

Solvent	E_{abs}^{inner} [V]	E_{abs}^{outer} [V]	χ(computed) [V]	χ(experiment) [V]
Protic solvents				
1-Butanol	4.55	4.64	0.08	
1-Propanol	4.53	4.61	0.08	
1.2-Ethanediol	4.42	4.55	0.13	
Acetic acid	4.78	4.89	0.11	
Aniline	4.86	4.85	-0.01	
Benzylalcohol	4.64	4.69	0.05	
Diethylamine	5.11	5.19	0.08	
Ethanol	4.51	4.59	0.08	-0.30 ([S5]), -0.12 ([S6]), -0.26 ([S7]), -0.21 (,[S8] -0.29)([S9])
Formamide	4.39	4.52	0.13	
Formic acid	4.43	4.54	0.11	
Methanol	4.43	4.57	0.14	-0.23 ([S5]), -0.18 ([S6]), -0.184 ([S7]), -0.13 ([S8,S9])
N-Methylaniline	4.99	4.91	-0.08	
Propanoic acid	5.12	5.22	0.10	
Water	4.14	4.30[(a)]	0.16[(b)]	0.1 ([S10]), 0.06 ([S9]), 0.08 ([S5]), 0.13 ([S5,S6]), 0.14 ([S7])
Aprotic solvents				
1,1,1-Trichloroethane	5.06	4.84	-0.22	
1,4-Dioxane	5.73	5.63	-0.09	
2-Heptanone	4.94	4.71	-0.23	
Acetone	4.83	4.61	-0.22	-0.34 ([S6]), -0.337 ([S7]), -0.32 ([S8]), -0.4 ([S9])
Acetonitrile	4.77	4.56	-0.21	-0.10 ([S11]), -0.108 ([S7])
Anisole	5.26	5.08	-0.18	
Carbontetrachloride	5.73	5.62	-0.11	
Cyclohexane	5.83	5.74	-0.09	
DMF	4.81	4.56	-0.25	-0.26 ([S6]), -0.434 ([S7]), -0.39 ([S8]), -0.46 ([S9])
DMSO	4.80	4.55	-0.25	-0.29 ([S6]), -0.238 ([S7]), -0.19 ([S8]), -0.21 ([S9])
n-heptane	5.90	5.81	-0.08	
Nitrobenzene	4.82	4.56	-0.26	
Nitromethane	4.77	4.56	-0.21	
Pyridine	4.92	4.68	-0.24	
THF	5.04	4.83	-0.21	
Toluene	5.67	5.55	-0.11	
Triethylamine	5.65	5.55	-0.10	

SMD Parameters for Ionic Liquids

Table S2: Summary of the SMD solvation model parameters for ionic liquids. The parameters were taken from Bernales et al.[S12]

Solvent	n	α	β	γ	ε	φ	ψ
[BMIM][BF_4]	1.4215	0.263	0.32	67.07	11.7	0.2	0.267
[BMIM][PF_6]	1.409	0.266	0.216	70.24	11.4	0.177	0.353
[EMIM][DCA]	1.5329	0.229	0.265	66.07	11	0.231	0
[HMIM][NTf_2]	1.4295	0.229	0.265	50.38	12.7	0.111	0.222
[MBPy][BF_4]	1.43	0.229	0.265	61.24	11.5	0.313	0.25

Summary of Absolute Potentials from Literature

Table S3: Summary of earlier reported absolute potentials or relative shifts of the SHE with respect to water.

Solvent	E_{abs} [V]	Relative shift [V]	Surface potential	Source
Water	4.14	–	no	S3
Water	4.44	–	yes	S4
Formamide	4.29	–	yes	S4
Methanol	4.38	–	no	S13
Methanol	4.19	–	yes	S4
Methanol	–	0.109	–	S14
Ethanol	4.21	–	yes	S4
DMSO	3.96	–	no	S13
DMSO	3.83	–	yes	S15
DMSO	–	-0.195	–	S14
Acetonitirile	4.52	–	no	S13
Acetonitirile	4.6	–	yes	S4
Acetonitirile	–	0.479	–	S14
Acetone	4.13	–	yes	S4
Pyridine	–	-0.29	–	S14
[EMIM][NTf_2]	–	0.38	–	S16

Kamlet-Taft Solvtochromic Parameters

Table S4: Summary of used solvatochromic parameters.

Solvent	α	β	π^*	Source
Water	1.17	0.47	1.09	[S17]
Ethanol	0.86	0.75	0.54	[S17]
acetic acid	1.12	0.45	0.6	[S17]
methanol	0.98	0.66	0.6	[S17]
Formic acid	1.23	0.38	0.65	[S17]
Diethylamine	0	0.7	0.24	[S17]
Ethyleneglycol	0.91	0.52	0.92	[S17]
Formamide	0.71	0.48	0.96	[S17]
aniline	0.26	0.5	0.73	[S17]
1-Butanol	0.84	0.84	0.47	[S17]
BenzylAlcohol	0.6	0.52	0.98	[S17]
PropanoicAcid	1.12	0.45	0.58	[S17]
1-Propanol	0.84	0.9	0.52	[S17]
n-MethylAniline	0.17	0.47	0.82	[S17]
Acetone	0.08	0.48	0.71	[S17]
Acetonitrile	0.19	0.4	0.75	[S17]
DMF	0	0.69	0.88	[S17]
DMSO	0	0.76	1	[S17]
Pyridine	0	0.64	0.87	[S17]
Toluene	0	0.11	0.55	[S17]
Triethylamine	0	0.71	0.15	[S17]
THF	0	0.55	0.58	[S17]
Nitromethane	0.22	0.06	0.85	[S17]
N-heptane	0	0	0	[S17]
cyclohexane	0	0	0	[S17]
1,4-Dioxane	0	0.37	0.55	[S17]
1,1,1-TriChloroEthane	0	0	0.49	[S17]
CCl_4	0	0.1	0.28	[S17]
2-Heptanone	0.05	0.48	0.61	[S17]
Nitrobenzene	0	0.3	1.01	[S17]
Anisole	0	0.32	0.73	[S17]
[BMIM][BF_4]	0.63	0.38	1.05	[S18]
[BMIM][PF_6]	0.63	0.19	1.04	[S18]
[EMIM][DCA]	0.53	0.35	1.08	[S18]
[HMIM][NTf_2]	0.65	0.25	0.98	[S18]
[MBPy][BF_4]	–	–	–	–

Effective Absolute Potentials for Computation of Conversion Factors

The conversion factor for the absolute potential relies on the effective absolute potentials computed at the respective levels of theory. For CCSD(T)/SMD, M06-2X/SMD and B3LYP-D3/SMD these data were taken from our earlier work.[S2] In the case of M06-2X/pbf the effective absolute potential was computed using the pKa of formic acid in water as reference following the procedure described in reference.[S2] The used values are summarized in table

Table S5: Effective absolute potentials used to compute the conversion factors between different solvents.

Method	$E_{eff,abs}(SHE; H_2O)$ [V]
CCSD(T)/aug-cc-pvqz/SMD(α= 1.0)	4.14
CCSD(T)/aug-cc-pvqz/SMD(α= 1.1)	4.11
CCSD(T)/aug-cc-pvqz/SMD(α= 1.2)	4.05
CCSD(T)/aug-cc-pvqz/PCM	4.02
M06-2X/6-311++G**/SMD	4.201
B3LYP-D3/6-311++G**/SMD	4.315
M06-2X/6-311++G**/pbf	4.412

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Kamlet-Taft Equation

The dependence of the absolute potential from the solvatochromic parameters was fitted using the least absolute deviation (LAD) regression method which is less affected by potential outliers. Using this method, the following equation was obtained:

$$E_{abs}(SHE) = (5.90 - 0.6466\pi^* - 0.5930\alpha - 0.6523\beta)V \quad (1)$$

The fit was compared with the regression using the commonly used ordinary least square (OLS) method:

$$E_{abs}(SHE) = (5.87 - 0.7825\pi^* - 0.4648\alpha - 0.5358\beta)V \quad (2)$$

The deviations between the two fits are mainly a result of the significant deviations ($> |0.4\text{V}|$) observed for 1,4-Dioxane and 1,1,1-Trichloroethane. Neglecting these data points, qualitatively similar fits are obtained for the OLS and LAD methods. E.g. the OLS fit changes to:

$$E_{abs}(SHE) = (5.91 - 0.7879\pi^* - 0.4487\alpha - 0.6284\beta)V \quad (3)$$

Within the manuscript only the fit obtained using the LAD method, which includes all data points, is used.

Absolute Potentials - CCSD(T)/SMD(α= 1.0)

Table S6: Predicted absolute potentials in water, non-aqueous solvents and ionic liquids. The absolute potentials (E_{abs}) were obtained using $HCOOH/HCOO^-$ and the CCSD(T)/aug-cc-pvqz/SMD absolute potential in water (E_{abs}=4.14 V) as reference. The conversion factors from water to the solvent of interest ($E_{conversion}$) were obtained using CCSD(T)/aug-cc-pvqz/SMD(α= 1.0).

Solvent	$E_{conversion}$	E_{abs}
Water	0	4.14
Ethanol	0.37	4.51
acetic acid	0.64	4.78
methanol	0.29	4.43
Formic acid	0.29	4.43
Diethylamine	0.97	5.11
Ethyleneglycol	0.28	4.42
Formamide	0.25	4.39
aniline	0.72	4.86
1-Butanol	0.41	4.55
BenzylAlcohol	0.5	4.64
PropanoicAcid	0.5	4.64
1-Propanol	0.40	4.54
n-MethylAniline	0.85	4.99
Acetone	0.69	4.83
Acetonitrile	0.63	4.77
DMF	0.67	4.81
DMSO	0.66	4.8
Pyridine	0.78	4.92
Toluene	1.52	5.67
Triethylamine	1.51	5.65
THF	0.9	5.04
Nitromethane	0.63	4.77
N-heptane	1.76	5.9
cyclohexane	1.69	5.83
1,4-Dioxane	1.59	5.73
1,1,1-TriChloroEthane	0.92	5.06
CarbonTetraChloride	1.59	5.73
2-Heptanone	0.8	4.94
NitroBenzene	0.68	4.82
Anisole	1.12	5.26
$[BMIM][BF_4]$	0.58	4.72
$[BMIM][PF_6]$	0.59	4.73
[EMIM][DCA]	0.63	4.77
$[HMIM][NTf_2]$	0.6	4.75

Solvent	$E_{conversion}$	E_{abs}
[MBPy][BF_4]	0.62	4.76

Absolute Potentials - CCSD(T)/SMD(α= 1.1)

Table S7: Predicted absolute potentials in water, non-aqueous solvents and ionic liquids. The absolute potentials (E_{abs}) were obtained using $HCOOH/HCOO^-$ and the CCSD(T)/aug-cc-pvqz/SMD absolute potential in water (E_{abs}=4.14 V) as reference. The conversion factors from water to the solvent of interest ($E_{conversion}$) were obtained using CCSD(T)/aug-cc-pvqz/SMD(α= 1.1).

Solvent	$E_{conversion}$	E_{abs}
Water	0.00	4.14
Ethanol	0.40	4.54
acetic acid	0.65	4.79
methanol	0.30	4.44
formic acid	0.31	4.45
Diethylamine	0.97	5.11
Ethyleneglycol	0.30	4.44
Formamide	0.26	4.40
aniline	0.77	4.91
1-Butanol	0.44	4.58
BenzylAlcohol	0.54	4.68
PropanoicAcid	0.98	5.12
1-Propanol	0.42	4.56
n-MethylAniline	0.91	5.05
Acetone	0.77	4.91
Acetonitrile	0.70	4.84
DMF	0.75	4.89
DMSO	0.74	4.88
Pyridine	0.86	5.00
Toluene	1.58	5.72
Triethylamine	1.57	5.71
THF	0.97	5.11
Nitromethane	0.71	4.85
N-heptane	1.80	5.94
cyclohexane	1.74	5.88
1,4-Dioxane	1.64	5.78
1,1,1-TriChloroEthane	0.99	5.13
CarbonTetraChloride	1.64	5.78
2-Heptanone	0.87	5.01
NitroBenzene	0.76	4.90
Anisole	1.19	5.33
$[BMIM][BF_4]$	0.63	4.77
$[BMIM][PF_6]$	0.64	4.78
[EMIM][DCA]	0.68	4.82
$[HMIM][NTf_2]$	0.66	4.80

Solvent	$E_{conversion}$	E_{abs}
[MBPy][BF_4]	0.68	4.82

Absolute Potentials - CCSD(T)/SMD(α= 1.2)

Table S8: Predicted absolute potentials in water, non-aqueous solvents and ionic liquids. The absolute potentials (E_{abs}) were obtained using $HCOOH/HCOO^-$ and the CCSD(T)/aug-cc-pvqz/SMD absolute potential in water (E_{abs}=4.14 V) as reference. The conversion factors from water to the solvent of interest ($E_{conversion}$) were obtained using CCSD(T)/aug-cc-pvqz/SMD(α= 1.2).

Solvent	$E_{conversion}$	E_{abs}
Water	0.00	4.14
Ethanol	0.41	4.55
acetic acid	0.65	4.79
methanol	0.30	4.44
formic acid	0.31	4.45
Diethylamine	0.97	5.11
Ethyleneglycol	0.30	4.44
Formamide	0.26	4.40
aniline	0.79	4.93
1-Butanol	0.45	4.59
BenzylAlcohol	0.55	4.69
PropanoicAcid	0.98	5.12
1-Propanol	0.43	4.57
n-MethylAniline	0.92	5.06
Acetone	0.79	4.93
Acetonitrile	0.73	4.87
DMF	0.78	4.92
DMSO	0.77	4.91
Pyridine	0.88	5.02
Toluene	1.57	5.71
Triethylamine	1.56	5.70
THF	1.00	5.14
Nitromethane	0.74	4.88
N-heptane	1.78	5.92
cyclohexane	1.73	5.87
1,4-Dioxane	1.63	5.77
1,1,1-TriChloroEthane	1.02	5.16
CarbonTetraChloride	1.63	5.77
2-Heptanone	0.90	5.04
NitroBenzene	0.79	4.93
Anisole	1.20	5.34
$[BMIM][BF_4]$	0.65	4.79
$[BMIM][PF_6]$	0.65	4.79
[EMIM][DCA]	0.70	4.84
$[HMIM][NTf_2]$	0.67	4.81

Solvent	$E_{conversion}$	E_{abs}
[MBPy][BF_4]	0.69	4.83

Absolute Potentials - CCSD(T)/PCM

Table S9: Predicted absolute potentials in water, non-aqueous solvents and ionic liquids. The absolute potentials (E_{abs}) were obtained using $HCOOH/HCOO^-$ and the CCSD(T)/aug-cc-pvqz/SMD absolute potential in water (E_{abs}=4.14 V) as reference. The conversion factors from water to the solvent of interest ($E_{conversion}$) were obtained using CCSD(T)/aug-cc-pvqz/PCM.

Solvent	$E_{conversion}$	E_{abs}
Water	0.00	4.3
Ethanol	0.29	4.59
acetic acid	0.59	4.89
methanol	0.27	4.57
formic acid	0.24	4.54
Diethylamine	0.89	5.19
Ethyleneglycol	0.25	4.55
Formamide	0.22	4.52
aniline	0.55	4.85
1-Butanol	0.34	4.64
BenzylAlcohol	0.39	4.69
PropanoicAcid	0.92	5.22
1-Propanol	0.31	4.61
n-MethylAniline	0.61	4.91
Acetone	0.31	4.61
Acetonitrile	0.26	4.56
DMF	0.26	4.56
DMSO	0.25	4.55
Pyridine	0.38	4.68
Toluene	1.25	5.55
Triethylamine	1.25	5.55
THF	0.53	4.83
Nitromethane	0.26	4.56
N-heptane	1.51	5.81
cyclohexane	1.44	5.74
1,4-Dioxane	1.33	5.63
1,1,1-TriChloroEthane	0.54	4.84
CarbonTetraChloride	1.32	5.62
2-Heptanone	0.41	4.71
NitroBenzene	0.26	4.56
Anisole	0.78	5.08
$[BMIM][BF_4]$	0.48	4.78
$[BMIM][PF_6]$	0.48	4.78
[EMIM][DCA]	0.52	4.82
$[HMIM][NTf_2]$	0.50	4.80

Solvent	$E_{conversion}$	E_{abs}
[MBPy][BF_4]	0.52	4.82

Absolute Potentials - M06-2X/SMD

Table S10: Predicted absolute potentials in water, non-aqueous solvents and ionic liquids. The absolute potentials (E_{abs}) were obtained using $HCOOH/HCOO^-$ and the CCSD(T)/aug-cc-pvqz/SMD absolute potential in water (E_{abs}=4.14 V) as reference. The conversion factors from water to the solvent of interest ($E_{conversion}$) were obtained using M06-2X/6-311++G**/SMD.

Solvent	$E_{conversion}$	E_{abs}
Water	0	4.14
Ethanol	0.40	4.54
acetic acid	0.75	4.89
methanol	0.32	4.46
Formic acid	0.32	4.46
Diethylamine	0.99	5.13
Ethyleneglycol	0.31	4.45
Formamide	0.28	4.42
Acetone	0.75	4.89
Acetonitrile	0.69	4.83
DMF	0.73	4.87
DMSO	0.71	4.85
Pyridine	0.83	4.97
Toluene	1.56	5.70
Triethylamine	1.55	5.69
THF	0.95	5.09
[BMIM][BF_4]	0.63	4.77
[BMIM][PF_6]	0.63	4.77
[EMIM][DCA]	0.68	4.82
[HMIM][NTf_2]	0.65	4.79
[MBPy][BF_4]	0.67	4.81

Absolute Potentials - B3LYP-D3/SMD

Table S11: Predicted absolute potentials in water, non-aqueous solvents and ionic liquids. The absolute potentials (E_{abs}) were obtained using $HCOOH/HCOO^-$ and the CCSD(T)/aug-cc-pvqz/SMD absolute potential in water (E_{abs}=4.14 V) as reference. The conversion factors from water to the solvent of interest ($E_{conversion}$) were obtained using B3LYP-D3/6-311++G**/SMD.

Solvent	$E_{conversion}$	E_{abs}
Water	0	4.14
Ethanol	0.36	4.5
acetic acid	0.63	4.77
methanol	0.29	4.43
Formic acid	0.29	4.43
Diethylamine	0.95	5.09
Ethyleneglycol	0.28	4.42
Formamide	0.25	4.39
aniline	0.71	4.85
1-Butanol	0.4	4.54
BenzylAlcohol	0.49	4.63
PropanoicAcid	0.96	5.1
1-Propanol	0.38	4.52
n-MethylAniline	0.83	4.97
Acetone	0.67	4.81
Acetonitrile	0.62	4.76
DMF	0.65	4.79
DMSO	0.64	4.78
Pyridine	0.75	4.89
Toluene	1.49	5.63
Triethylamine	1.47	5.61
THF	0.87	5.01
Nitromethane	0.62	4.76
N-heptane	1.71	5.85
cyclohexane	1.65	5.79
1,4-Dioxane	1.55	5.69
1,1,1-TriChloroEthane	0.89	5.03
CarbonTetraChloride	1.55	5.69
2-Heptanone	0.77	4.91
NitroBenzene	0.66	4.8
Anisole	1.09	5.23
$[BMIM][BF_4]$	0.57	4.71
$[BMIM][PF_6]$	0.57	4.71
[EMIM][DCA]	0.62	4.76
$[HMIM][NTf_2]$	0.59	4.73

Solvent	$E_{conversion}$	E_{abs}
[MBPy][BF_4]	0.61	4.75

Absolute Potentials - M06-2X/pbf

Table S12: Predicted absolute potentials in water, non-aqueous solvents and ionic liquids. The absolute potentials (E_{abs}) were obtained using $HCOOH/HCOO^-$ and the CCSD(T)/aug-cc-pvqz/SMD absolute potential in water (E_{abs}=4.14 V) as reference. The conversion factors from water to the solvent of interest ($E_{conversion}$) were obtained using M06-2X/6-311++G**/pbf.

Solvent	$E_{conversion}$	E_{abs}
Water	0	4.14
Ethanol	0.48	4.62
methanol	0.45	4.59
Acetonitrile	0.44	4.58
DMF	0.44	4.58
DMSO	0.43	4.57
THF	0.76	4.90
CarbonTetraChloride	1.68	5.82
NitroBenzene	0.45	4.59

Absolute Potentials - LAD Fit

Table S13: Predicted absolute potentials in water, non-aqueous solvents and ionic liquids. The absolute potentials (E_{abs}) were obtained using $HCOOH/HCOO^-$ and the CCSD(T)/aug-cc-pvqz/SMD absolute potential in water (E_{abs}=4.14 V) as reference. The conversion factors from water to the solvent of interest ($E_{conversion}$) were computed from the LAD fit (equation 1) in combination with the solvatochromic parameters in table S4.

Solvent	E_{abs}
Water	4.19
Ethanol	4.55
acetic acid	4.55
methanol	4.50
Formic acid	4.50
Diethylamine	5.29
Ethyleneglycol	4.43
Formamide	4.55
aniline	4.95
1-Butanol	4.55
BenzylAlcohol	4.57
PropanoicAcid	4.57
1-Propanol	4.48
n-MethylAniline	4.96
Acetone	5.08
Acetonitrile	5.04
DMF	4.88
DMSO	4.76
Pyridine	4.92
Toluene	5.47
Triethylamine	5.34
THF	5.17
Nitromethane	5.18
N-heptane	5.90
cyclohexane	5.90
1,4-Dioxane	5.30
1,1,1-TriChloroEthane	5.58
CarbonTetraChloride	5.65
2-Heptanone	5.16
NitroBenzene	5.05
Anisole	5.22
$[BMIM][BF_4]$	4.60
$[BMIM][PF_6]$	4.73
[EMIM][DCA]	4.66
$[HMIM][NTf_2]$	4.72

Total Energies - CCSD(T)/SMD(α= 1.0)

Table S14: Total energies obtained with CCSD(T)/aug-cc-pvqz/SMD(α= 1.0).

Solvent	E(HCOOH) [Ha]	E($HCOO^-$) [Ha]	E($HCOO\cdot$) [Ha]
Ethanol	-189.57408621	-189.11235112	-188.87749451
acetic acid	-189.56565892	-189.09411797	-188.87003779
methanol	-189.5738033	-189.11505833	-188.87617762
Formic acid	-189.56702452	-189.1081478	-188.86814436
Diethylamine	-189.55991468	-189.0762937	-188.86564979
Ethyleneglycol	-189.57027856	-189.11179888	-188.87227371
Formamide	-189.56910505	-189.11185728	-188.87056431
aniline	-189.57047968	-189.09557718	-188.87733304
1-Butanol	-189.57330854	-189.11001616	-188.87707929
BenzylAlcohol	-189.57267101	-189.10600814	-188.87749366
PropanoicAcid	-189.56236258	-189.07829274	-188.8688311
1-Propanol	-189.57371827	-189.11122739	-188.87730365
n-MethylAniline	-189.57037468	-189.09070243	-188.87893458
Acetone	-189.57313707	-189.09925183	-188.88299645
Acetonitrile	-189.57301242	-189.10144394	-188.88197057
DMF	-189.57332334	-189.10022156	-188.88390814
DMSO	-189.57316647	-189.10058295	-188.88379809
Pyridine	-189.5721438	-189.09512414	-188.88301428
Toluene	-189.56665095	-189.06216787	-188.87940234
Triethylamine	-189.56821755	-189.06421378	-188.88124105
THF	-189.57109604	-189.08961339	-188.88235857
Nitromethane	-189.57240422	-189.10065132	-188.88163355
N-heptane	-189.56519265	-189.05223175	-188.87833907
cyclohexane	-189.56518485	-189.05449909	-188.8782308
1,4-Dioxane	-189.56662996	-189.05989643	-188.8797902
1,1,1-TriChloroEthane	-189.57057751	-189.08835205	-188.88168955
CCl_4	-189.56621883	-189.0593826	-188.8790257
2-Heptanone	-189.57215289	-189.09443646	-188.88307018
Nitrobenzene	-189.57221285	-189.09873362	-188.88261807
Anisole	-189.56890951	-189.07936754	-188.88076158
[BMIM][BF_4]	-189.57111172	-189.10140886	-188.87700729
[BMIM][PF_6]	-189.57066438	-189.10083015	-188.87700745
[EMIM][DCA]	-189.57098312	-189.09953287	-188.87749319
[HMIM][NTf_2]	-189.57198736	-189.10150809	-188.87827223
[MBPy][BF_4]	-189.57128562	-189.10014156	-188.87772211
H_2 molecule	-1.1738642		

Total Energies - CCSD(T)/SMD(α= 1.1)

Table S15: Total energies obtained with CCSD(T)/aug-cc-pvqz/SMD(α= 1.1).

Solvent	E(HCOOH) [Ha]	E($HCOO^-$) [Ha]
1,1,1-TriChloroEthane	-189.56812847	-189.08275652
1,4-Dioxane	-189.56539765	-189.05648785
1-Butanol	-189.56940734	-189.1047084
1-Propanol	-189.56974354	-189.10584354
2-Heptanone	-189.56941444	-189.0884249
Acetone	-189.56992543	-189.09290077
aniline	-189.5671972	-189.09013209
Anisole	-189.56689839	-189.07446758
BenzylAlcohol	-189.56888409	-189.10042658
CCl_4	-189.56497508	-189.05594913
ethanol	-189.57004068	-189.10689463
acetonitrile	-189.56948074	-189.09489736
acetic acid	-189.56263561	-189.09021732
formic acid	-189.56981242	-189.11022357
cyclohexane	-189.56408228	-189.05137889
Diethylamine	-189.55759071	-189.07314888
DMF	-189.57024256	-189.09375529
DMSO	-189.57005167	-189.09407334
Ethyleneglycol	-189.56624061	-189.10691766
Formamide	-189.56492959	-189.10685141
HCOOH	-189.56294461	-189.10322256
N-heptane	-189.56416801	-189.0492914
NitroBenzene	-189.56914334	-189.09228211
Nitromethane	-189.56895679	-189.09412397
n-MethylAniline	-189.56733844	-189.08512628
PropanoicAcid	-189.5600933	-189.07521411
Pyridine	-189.56935693	-189.08904638
THF	-189.56861448	-189.0839695
Toluene	-189.56532009	-189.05854875
Triethylamine	-189.56688163	-189.06058413
Water	-189.57029661	-189.11368381
[BMIM][BF_4]	-189.56739889	-189.09545631
[BMIM][PF_6]	-189.56696849	-189.09490643
[EMIM][DCA]	-189.56734811	-189.09353504
[HMIM][NTf_2]	-189.5682594	-189.09539552
[MBPy][BF_4]	-189.56762088	-189.09410641

Total Energies - CCSD(T)/SMD(α= 1.2)

Table S16: Total energies obtained with CCSD(T)/aug-cc-pvqz/SMD(α= 1.2).

Solvent	E(HCOOH) [Ha]	E($HCOO^-$) [Ha]
1,1,1-TriChloroEthane	-189.56653636	-189.07781118
1,4-Dioxane	-189.56459196	-189.05331801
1-Butanol	-189.56647306	-189.09892917
1-Propanol	-189.56675432	-189.09999273
2-Heptanone	-189.56763814	-189.08315112
Acetone	-189.56785977	-189.08730317
aniline	-189.56485055	-189.08482824
Anisole	-189.56558738	-189.07007229
BenzylAlcohol	-189.56612967	-189.0947562
CCl_4	-189.56416182	-189.05275866
ethanol	-189.56699856	-189.10097551
acetonitrile	-189.5671864	-189.0890745
acetic acid	-189.5603166	-189.08561889
formic acid	-189.56676567	-189.10470105
cyclohexane	-189.56336116	-189.04845398
Diethylamine	-189.55580071	-189.06931488
DMF	-189.56825002	-189.08812533
DMSO	-189.56803776	-189.08840957
Ethyleneglycol	-189.56315842	-189.10134944
Formamide	-189.56174364	-189.10115957
HCOOH	-189.5598294	-189.09761147
N-heptane	-189.5634978	-189.04652061
NitroBenzene	-189.56715782	-189.08666371
Nitromethane	-189.56670958	-189.088317
n-MethylAniline	-189.56529646	-189.08015084
PropanoicAcid	-189.5583444	-189.07144861
Pyridine	-189.56754993	-189.08372055
THF	-189.56700167	-189.07898575
Toluene	-189.56445008	-189.05520241
Triethylamine	-189.56600843	-189.05722863
Water	-189.5671479	-189.10801739
[BMIM][BF_4]	-189.56474958	-189.08970975
[BMIM][PF_6]	-189.5643248	-189.08917926
[EMIM][DCA]	-189.56482003	-189.08787169
[HMIM][NTf_2]	-189.56567002	-189.08964758
[MBPy][BF_4]	-189.56507318	-189.08841536

Total Energies - CCSD(T)/PCM

Table S17: Total energies obtained at the CCSD(T)/aug-cc-pvqz/PCM level of theory.

Solvent	E(HCOOH) [Ha]	E($HCOO^-$) [Ha]
1,1,1-TriChloroEthane	-189.56992804	-189.09766824
1,4-Dioxane	-189.56565207	-189.06448423
1-Butanol	-189.57141178	-189.10680264
1-Propanol	-189.5715826	-189.10779285
2-Heptanone	-189.57089235	-189.10371572
Acetone	-189.57158118	-189.10778471
aniline	-189.56986162	-189.0972358
Anisole	-189.56843204	-189.08737136
BenzylAlcohol	-189.57099245	-189.10431917
CCl_4	-189.56569375	-189.06487108
ethanol	-189.57174632	-189.10873099
acetonitrile	-189.57198591	-189.11008492
acetic acid	-189.56961891	-189.09563716
formic acid	-189.57193371	-189.10979182
cyclohexane	-189.56517258	-189.05992259
Diethylamine	-189.56781948	-189.08278733
DMF	-189.57200875	-189.11021285
DMSO	-189.57211857	-189.11082515
Ethyleneglycol	-189.57204888	-189.11043716
Formamide	-189.5723646	-189.11218055
HCOOH	-189.57215436	-189.11102373
N-heptane	-189.56488244	-189.05705829
NitroBenzene	-189.57197191	-189.11000641
Nitromethane	-189.57199918	-189.11015926
n-MethylAniline	-189.56949168	-189.09478722
PropanoicAcid	-189.56766629	-189.08160416
Pyridine	-189.57105147	-189.10467293
THF	-189.5700376	-189.09837681
Toluene	-189.56601253	-189.06778033
Triethylamine	-189.5660314	-189.06794989
Water	-189.5722917	-189.11178129
[BMIM][BF_4]	-189.57111172	-189.10140886
[BMIM][PF_6]	-189.57066438	-189.10083015
[EMIM][DCA]	-189.57098312	-189.09953287
[HMIM][NTf_2]	-189.57198736	-189.10150809
[MBPy][BF_4]	-189.57128562	-189.10014156

Gibbs Free Energies - M06-2X/SMD

Table S18: Gibbs Free energies obtained at the M06-2X/6-311++G**/SMD level of theory.

Solvent	G(HCOOH) [Ha]	G($HCOO^-$) [Ha]	G($HCOO\cdot$) [Ha]
Acetone	-189.745182	-189.287267	-189.070766
Ethanol	-189.747416	-189.302075	-189.067507
Acetonitirile	-189.745274	-189.289543	-189.069853
acetic acid	-189.745182	-189.287267	-189.070766
methanol	-189.747414	-189.305184	-189.066837
Diethylamine	-189.732506	-189.265627	-189.055091
DMF	-189.745319	-189.288153	-189.071583
DMSO	-189.745173	-189.288514	-189.071486
Ethyleneglycol	-189.743934	-189.301952	-189.062982
Formamide	-189.742847	-189.302061	-189.061345
Formic acid	-189.74075	-189.298349	-189.05885
Pyridine	-189.744007	-189.283036	-189.070636
THF	-189.742825	-189.277503	-189.069939
Toluene	-189.737814	-189.249916	-189.0668
Triethylamine	-189.739378	-189.251958	-189.068696
H_2 molecule	-1.1697		

Gibbs Free Energies - B3LYP-D3

Table S19: Gibbs Free energies obtained at the B3LYP-D3/6-311++G**/SMD level of theory.

Solvent	G(HCOOH) [Ha]	G($HCOO^-$) [Ha]	G($HCOO\cdot$) [Ha]
Ethanol	-189.827407	-189.382146	-189.1518
acetic acid	-189.818803	-189.363872	-189.144189
methanol	-189.827306	-189.384812	-189.150676
Formic acid	-189.820651	-189.377959	-189.142705
Diethylamine	-189.812791	-189.346005	-189.139564
Ethyleneglycol	-189.823827	-189.381568	-189.146799
Formamide	-189.822714	-189.381628	-189.145134
aniline	-189.823156	-189.365229	-189.151089
1-Butanol	-189.826564	-189.379812	-189.151337
BenzylAlcohol	-189.825707	-189.37575	-189.151577
PropanoicAcid	-189.81513	-189.34795	-189.142681
1-Propanol	-189.827007	-189.381023	-189.151586
n-MethylAniline	-189.822689	-189.360274	-189.152457
Acetone	-189.82549	-189.368809	-189.156424
Acetonitrile	-189.825543	-189.370985	-189.155484
DMF	-189.825635	-189.369769	-189.157371
DMSO	-189.825484	-189.370126	-189.157268
Pyridine	-189.824356	-189.364689	-189.156413
Toluene	-189.818356	-189.331823	-189.152487
Triethylamine	-189.819925	-189.33387	-189.154336
THF	-189.823214	-189.359201	-189.155699
Nitromethane	-189.824732	-189.370191	-189.155122
N-heptane	-189.816789	-189.321923	-189.151358
cyclohexane	-189.816806	-189.324178	-189.151264
1,4-Dioxane	-189.818291	-189.329557	-189.152855
1,1,1-TriChloroEthane	-189.82269	-189.357944	-189.15502
CCl_4	-189.817896	-189.329048	-189.152092
2-Heptanone	-189.824358	-189.36401	-189.156464
Nitrobenzene	-189.824515	-189.368278	-189.156067
Anisole	-189.820857	-189.348975	-189.153995
[BMIM][BF_4]	-189.823966	-189.371068	-189.150895
[BMIM][PF_6]	-189.823523	-189.370494	-189.1504
[EMIM][DCA]	-189.823738	-189.369158	-189.15128
[HMIM][NTf_2]	-189.824784	-189.371136	-189.152092
[MBPy][BF_4]	-189.82406	-189.369771	-189.151523
H_2 molecule	-1.181000		

Gibbs Free Energies - M06-2X/pbf

Table S20: Gibbs Free energies obtained at the M06-2X/6-311++G**/pbf level of theory.

Solvent	G(HCOOH) [Ha]	G($HCOO^-$) [Ha]
Water	-189.752601	-189.321669
Ethanol	-189.755377	-189.314918
methanol	-189.755655	-189.316401
Acetonitrile	-189.755673	-189.316827
DMSO	-189.755856	-189.3174
DMF	-189.755554	-189.316563
THF	-189.753266	-189.302785
CCl_4	-189.74686	-189.26234
Nitrobenzene	-189.755452	-189.316325
H_2 molecule	-1.16971	

Zero-point energy and Entropy Corrections for CCSD(T)

Table S21: Zero-point energy and entropy contributions (298.15 K; 1 bar) for CCSD(T) computations. The data were obtained at the B3LYP-D3/6-311++G**/SMD level of theory. All values are in Ha.

Solvent	HCOOH	$HCOO^-$	$HCOO\cdot$
Ethanol	0.009241	-0.003535	-0.004942
acetic acid	0.009156	-0.003544	-0.00497
methanol	0.009228	-0.003473	-0.004998
Formic acid	0.00916	-0.003522	-0.005046
Diethylamine	0.009073	-0.003559	-0.004993
Ethyleneglycol	0.009205	-0.003485	-0.005017
Formamide	0.009205	-0.003479	-0.005024
aniline	0.009251	-0.0036	-0.004844
1-Butanol	0.009247	-0.003545	-0.004935
BenzylAlcohol	0.009279	-0.003558	-0.004897
PropanoicAcid	0.009132	-0.003518	-0.004947
1-Propanol	0.009244	-0.00354	-0.004938
n-MethylAniline	0.009329	-0.003646	-0.00481
Acetone	0.009226	-0.003719	-0.00475
Acetonitrile	0.009165	-0.003694	-0.004754
DMF	0.009213	-0.003719	-0.004818
DMSO	0.009215	-0.003715	-0.004817
Pyridine	0.009225	-0.003726	-0.004822
Toluene	0.00925	-0.003744	-0.004872
Triethylamine	0.009247	-0.003745	-0.004878
THF	0.009225	-0.003738	-0.004837
Nitromethane	0.009336	-0.003696	-0.004745
N-heptane	0.009248	-0.003756	-0.00489
cyclohexane	0.009251	-0.00375	-0.004883
1,4-Dioxane	0.009255	-0.003743	-0.004876
1,1,1-TriChloroEthane	0.009223	-0.003741	-0.004837
CCl_4	0.009247	-0.003749	-0.004878
2-Heptanone	0.009218	-0.003733	-0.004829
Nitrobenzene	0.00922	-0.003715	-0.004808
Anisole	0.009243	-0.003738	-0.004845
[BMIM][BF_4]	0.009243	-0.003593	-0.004858
[BMIM][PF_6]	0.009243	-0.003593	-0.004856
[EMIM][DCA]	0.009223	-0.003618	-0.004839
[HMIM][NTf_2]	0.009216	-0.003619	-0.00485
[MBPy][BF_4]	0.009216	-0.003621	-0.004846
H_2 molecule	-0.001429		