

SUPPORTING INFORMATION

Elucidating the Fate of Organic Contaminants in Highly Basic Environments for Temperature Swing Solvent Extraction Desalination

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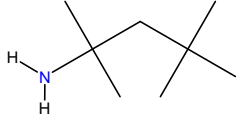
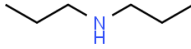
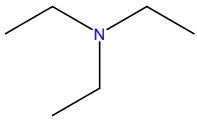
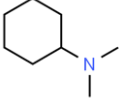
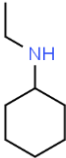
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Table S1. Chemical structures, logarithms of octanol-water partition coefficients (K_{ow}), acid dissociation constants ($pK_{a,1}$ and $pK_{a,2}$), and water solubilities (y_{aq}^{solv}) for amine solvents *tert*-octylamine (TOA), dipropylamine (DPA), triethylamine (TEA), *N,N*-dimethylcyclohexylamine (DMCHA), and *N*-ethylcyclohexylamine (ECHA).

Compound	Chemical Structure	$\log K_{ow}$	$pK_{a,1}^3$ (25 °C)	$y_{aq}^{solv 1,2}$ (25 °C)
TOA		2.58 ⁴	10.7	0.0091
DPA		1.67 ⁵	11.4	0.0434
TEA		1.45 ⁵	10.8	0.0750
DMCHA		2.20 ⁵	10.8	0.0144
ECHA		2.26 ⁵	11.2	0.0208

Characterization of Biphasic Mixture Compositions. Water contents of the organic solvent phases and solvent contents of the aqueous phases were measured using a Karl Fischer titrator (870 KF Titrino plus, Metrohm, Herisau, Switzerland) with the volumetric method and a total organic carbon (TOC) analyzer (QbD1200, Hach, Loveland, CO, United States), respectively. The measured values were statistically indistinguishable from values reported in literature;^{1,2} as such, the latter was utilized in all subsequent analyses. Sodium chloride (NaCl) concentrations of each phase were analyzed by evaporating a known sample weight to remove all water and amine before redissolving the residual salt in deionized (DI) water. Glass pipettes were used to transfer 0.5–1.0 g of sample into a glass vial. The samples were gently evaporated by directing warm air from a hair dryer toward the bottom of the vials for 1 h. NaCl in the resultant solution was quantified using a conductivity meter (Orion Star A121, ThermoFisher Scientific, Waltham, MA, United States).

Analyte concentrations of samples prepared from organic and aqueous phases of the equilibrated biphasic mixtures were characterized using reverse-phase high-performance liquid chromatography (HPLC, UltiMate 3000 with diode array detector, ThermoFisher Scientific). Separation was performed on a Thermo Scientific Acclaim Polar Advantage II HPLC Column (150 mm × 2.1 mm, particle size 2.2 μm) with a flow rate of 0.30 mL/min, injection volume of 25 μL, and a constant column temperature of 40 °C. Mobile phases of 0.1% w/w acetic acid in ultrapure water (Solvent A) and acetonitrile (Solvent B) were utilized. Elution profile gradients and detection wavelengths for each analyte are summarized in Table S1. Peaks were integrated using the Chromeleon software. Calibration curves for each analyte were created with known concentrations of the pure analyte solution under the same HPLC conditions. Aggregate molar balances, i.e., ratio of the sum of moles of analyte in the organic and aqueous phases to moles of analyte in the initial aqueous feed solution, for each experimental condition are reported in Table S2.

Table S2. Elution profile gradients and detection wavelengths for each organic analyte.

Analyte	Elution Profile	Detection Wavelength (nm)
Uracil	Isocratic 20% B for 20 min	267
Caffeine	Isocratic 20% B for 20 min	280
Sulfamethazine	Isocratic 20% B for 20 min	267
Acetaminophen	Isocratic 20% B for 20 min	254
Chloramphenicol	Isocratic 20% B for 20 min	280
Bisphenol-A	Gradient from 40% B to 100% B over 20 minutes	280

Table S3. Molar balance (ratio of the sum of moles of analyte in the organic and aqueous phases, $n_{\text{org}}+n_{\text{aq}}$, to moles of analyte in the initial aqueous feed solution, n_{feed}) for all experimental conditions. Solvents are *tert*-octylamine (TOA), dipropylamine (DPA), triethylamine (TEA), *N,N*-dimethylcyclohexylamine (DMCHA), and *N*-ethylcyclohexylamine (ECHA).

Analyte	Feed Concentration (mg/L)	Temperature (°C)	Solvent	Number of Samples	Molar Balance $[(n_{\text{org}}+n_{\text{aq}})/n_{\text{feed}}]$
Uracil	100	25	TOA	3	0.95 ± 0.01
Caffeine	100	25	TOA	5	0.89 ± 0.05
Sulfamethazine	100	25	TOA	6	0.93 ± 0.03
Acetaminophen	100	25	TOA	3	0.78 ± 0.04
Chloramphenicol	100	25	TOA	3	0.91 ± 0.00
Bisphenol-A	100	25	TOA	3	0.94 ± 0.00
Uracil	100	70	TOA	3	1.05 ± 0.05
Caffeine	100	70	TOA	3	0.79 ± 0.08
Sulfamethazine	100	70	TOA	3	0.94 ± 0.01
Acetaminophen	100	70	TOA	3	0.82 ± 0.02
Chloramphenicol	100	70	TOA	3	0.82 ± 0.00
Bisphenol-A	100	70	TOA	3	0.92 ± 0.05
Caffeine	25	25	TOA	4	0.71 ± 0.14
Caffeine	500	25	TOA	5	0.98 ± 0.06
Caffeine	1,000	25	TOA	3	1.03 ± 0.02
Acetaminophen	25	25	TOA	3	0.79 ± 0.05
Acetaminophen	500	25	TOA	3	0.95 ± 0.04
Acetaminophen	1,000	25	TOA	3	0.98 ± 0.02
Caffeine	100	25	DPA	3	0.72 ± 0.08
Caffeine	100	25	TEA	3	0.81 ± 0.15
Caffeine	100	25	DMCHA	3	0.88 ± 0.05
BPA	100	25	DPA	3	0.77 ± 0.15
BPA	100	25	TEA	3	0.83 ± 0.01
Acetaminophen	100	25	DPA	4	0.81 ± 0.01
Acetaminophen	100	25	ECHA	4	0.95 ± 0.05
Acetaminophen	100	25	DMCHA	4	0.98 ± 0.08

Statistical Analysis and Multiple Linear Regressions. Unpaired two-sample t -tests were conducted for the statistical analyses in this study. The t -statistic, t , is

$$t = \frac{\mu_1 - \mu_2}{\sqrt{\left(\frac{1}{n_1} + \frac{1}{n_2}\right) \left(\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}\right)}} \quad (\text{S1})$$

where μ_i , s_i , and n_i are sample means, standard deviations, and sizes, respectively. Subscripts differentiate the sample populations. Critical t -values, t_c , for a two-tailed t -test with a 95% confidence interval were employed. If $t < t_c$, the null hypothesis cannot be rejected and the quantities are statistically indistinguishable ($p > 0.05$). If $t > t_c$, the null hypothesis is rejected with 95% confidence, and the sample means are considered statistically different.

Multiple linear regressions were performed using the `lm` function in RStudio. All experiments were performed in, at minimum, triplicate. Regressions used data from each individual measurement, and a weighting procedure is, therefore, unnecessary. Slopes, standard errors, t -statistics, and p -value ranges are reported for all coefficients of regression. Intercepts, coefficients of determination (“Multiple R^2 ”), and adjusted coefficients of determination (“Adjusted R^2 ”) are indicated for each regression analysis.

Table S4. Equilibrium analyte mole fractions, x ($\times 10^{-5}$), and distribution coefficients, D (-), at 25 °C in organic solvent and aqueous phases. 100 mg/L analyte aqueous feed solutions were equilibrated with equal weights of solvent *tert*-octylamine (TOA). Bisphenol-A was not detectable in the aqueous phase of the mixtures; “BDL” denotes “Below Detection Limits” and “NA” denotes “Not Available”.

Analyte	Phase	Number of Samples	Mole Fraction, x ($\times 10^{-5}$)	Distribution Coefficient, D (-)
Uracil	Organic	3	0.70 ± 0.02	0.38 ± 0.01
	Aqueous	3	1.84 ± 0.01	
Caffeine	Organic	5	1.47 ± 0.05	6.20 ± 0.32
	Aqueous	5	0.24 ± 0.03	
Sulfamethazine	Organic	6	0.91 ± 0.06	3.09 ± 0.23
	Aqueous	6	0.29 ± 0.03	
Acetaminophen	Organic	3	0.82 ± 0.03	0.89 ± 0.03
	Aqueous	3	0.94 ± 0.07	
Chloramphenicol	Organic	3	1.04 ± 0.01	13.43 ± 0.32
	Aqueous	3	0.08 ± 0.00	
Bisphenol-A	Organic	3	1.60 ± 0.00	NA
	Aqueous	3	BDL	

Table S5. Equilibrium analyte mole fractions, x ($\times 10^{-5}$), and distribution coefficients, D (-), at 70 °C in organic solvent and aqueous phases. 100 mg/L analyte aqueous feed solutions were equilibrated with equal weights of solvent *tert*-octylamine (TOA). Bisphenol-A was not detectable in the aqueous phase of the mixtures; “BDL” denotes “Below Detection Limits” and “NA” denotes “Not Applicable”.

Analyte	Phase	Number of Samples	Mole Fraction, x ($\times 10^{-5}$)	Distribution Coefficient, D (-)
Uracil	Organic	3	0.05 ± 0.00	0.02 ± 0.00
	Aqueous	3	1.97 ± 0.09	
Caffeine	Organic	5	1.91 ± 0.44	5.71 ± 1.10
	Aqueous	5	0.33 ± 0.03	
Sulfamethazine	Organic	6	0.85 ± 0.02	1.82 ± 0.06
	Aqueous	6	0.46 ± 0.01	
Acetaminophen	Organic	3	1.92 ± 0.19	2.89 ± 0.26
	Aqueous	3	0.66 ± 0.04	
Chloramphenicol	Organic	3	1.96 ± 0.00	$2,730 \pm 1,440$
	Aqueous	3	$8.9 \times 10^{-3} \pm 5.8 \times 10^{-3}$	
Bisphenol-A	Organic	3	2.99 ± 0.15	NA
	Aqueous	3	BDL	

Table S6. Coefficients of regression analysis between analyte distribution coefficient, D , in biphasic TOA-water mixtures at 25 °C and analyte property of octanol-water partition coefficient, K_{OW} : $\log \hat{D} = 0.562 \log K_{OW} + 0.396$.

Parameter	Slope	Standard Error	<i>t</i> -statistic	<i>p</i> -value ^a
$\log K_{OW}$	0.562	0.145	3.87	**
(Intercept) ^b	0.396	0.092	4.29	***
Multiple $R^2 = 0.500$		Adjusted $R^2 = 0.467$		

^a Triple, double, and single asterisk indicate *p*-values < 0.001, 0.01, and 0.05, respectively.

^b Vertical axis intercept of the regression equation.

Table S7. Contributions of pK_a variables, ε , to \hat{D} in biphasic TOA-water mixtures at 25 °C; $\varepsilon = -0.108 pK_{a,1} + 0.039 pK_{a,2}$ (Table 2 of the main manuscript)

Analyte	$pK_{a,1}$	$pK_{a,2}$	ε
Uracil	9.23	13.38	-0.475
Caffeine	NA	NA	0.000
Sulfamethazine	6.99	NA	-0.755
Acetaminophen	9.46	NA	-1.022
Chloramphenicol	10.89	13.6	-0.646
BPA	9.78	10.4	-0.651

Table S8. *t*-statistics of unpaired two sample *t*-tests for comparative analyses of distribution coefficients, *D*, at 25 and 70 °C in the TOA-water system. Experimental values and standard errors of *D*s are reported.

Compound	Temperature	Distribution Coefficient, <i>D</i> (-)	<i>t</i> -statistic ^a
Uracil	25 °C	0.38 ± 0.01	45.9 ***
	70 °C	0.02 ± 0.00	
Caffeine	25 °C	6.20 ± 0.32	0.934
	70 °C	5.71 ± 1.10	
Sulfamethazine	25 °C	3.09 ± 0.23	4.25 **
	70 °C	1.82 ± 0.06	
Acetaminophen	25 °C	0.89 ± 0.03	5.50 **
	70 °C	2.89 ± 0.02	
Chloramphenicol	25 °C	13.43 ± 0.32	15.0 ***
	70 °C	2,730 ± 1,440	

^a Triple, double, and single asterisk indicate *p*-values < 0.001, 0.01, and 0.05, respectively.

Table S9. Coefficients of regression analysis between ratios of distribution coefficients at 25 °C to 70 °C, $D^{25\text{ °C}}/D^{70\text{ °C}}$, in biphasic TOA-water mixtures and the associated changes in aqueous phase acidity, $\Delta\text{pH}^{\text{aq}}$, and logarithms of analyte acid dissociation constants, $\Delta\text{p}K_{\text{a},1}$ and $\Delta\text{p}K_{\text{a},2}$: $\log D^{25\text{ °C}}/D^{70\text{ °C}} = 15.72 \Delta\text{pH}^{\text{aq}} - 1.273 \Delta\text{p}K_{\text{a},1} - 0.652 \Delta\text{p}K_{\text{a},2} - 12.446$.

Parameter	Slope	Standard Error	<i>t</i> -statistic	<i>p</i> -value ^a
$\Delta\text{pH}^{\text{aq}}$	15.719	1.225	12.829	***
$\Delta\text{p}K_{\text{a},1}$	-1.273	0.376	-3.385	**
$\Delta\text{p}K_{\text{a},2}$	-0.652	0.210	-3.104	*
(Intercept) ^b	-12.446	1.028	-12.111	***
Multiple $R^2 = 0.956$		Adjusted $R^2 = 0.941$		

^a Triple, double, and single asterisk indicate *p*-values < 0.001, 0.01, and 0.05, respectively.

^b Vertical axis intercept of the regression equation.

Table S10. *t*-statistics of unpaired two sample *t*-tests for comparative analyses of distribution coefficients, *D*, and molar partition ratios, *K*, for acetaminophen and caffeine at different feed analyte concentrations. Note that because caffeine molecules remain neutral, i.e., do not protonate or deprotonate, in the investigated systems, *D* and *K* are, therefore, equivalent. Solvent *tert*-octylamine (TOA) were equilibrated with equal weights of aqueous feed solutions of 20, 100, 500, and 1,000 mg/L analyte. Experimental means and one standard deviations of *D* and *K* are reported.

Compound	Feed Analyte Concentration (mg/L)	log <i>D</i>	<i>t</i> -statistic	log <i>K</i>	<i>t</i> -statistic ^a
Caffeine	20	0.54 ± 0.08	2.58 *	0.54 ± 0.08	2.58 *
	100	0.79 ± 0.02		0.79 ± 0.02	
	100	0.79 ± 0.02	0.93	0.79 ± 0.02	0.93
	500	0.86 ± 0.03		0.86 ± 0.03	
	500	0.86 ± 0.03	0.61	0.86 ± 0.03	0.61
	1,000	0.83 ± 0.00		0.83 ± 0.00	
Acetaminophen	20	-0.12 ± 0.01	3.80 **	2.15 ± 0.01	2.47 *
	100	-0.06 ± 0.00		2.19 ± 0.00	
	100	-0.06 ± 0.00	2.78 *	2.19 ± 0.00	19.1 ***
	500	-0.04 ± 0.00		2.09 ± 0.01	
	500	-0.04 ± 0.00	22.9 ***	2.09 ± 0.01	4.17 *
	1,000	0.06 ± 0.00		2.07 ± 0.00	

^a Triple, double, and single asterisk indicate *p*-values < 0.001, 0.01, and 0.05, respectively.

Table S11. Experimental distribution coefficients, D , for analytes caffeine, acetaminophen, and bisphenol-A across amine solvents of *tert*-octylamine (TOA), *N,N*-dimethylcyclohexylamine (DMCHA), *N*-ethylcyclohexylamine (ECHA), dipropylamine (DPA), and triethylamine (TEA). Aqueous feed solutions of 100 mg/L caffeine, 20 mg/L acetaminophen, or 100 mg/L bisphenol-A were equilibrated with equal weights of solvents at 25 °C. Bisphenol-A was not detectable in the aqueous phase of the TOA and DMCHA mixtures; thus, distribution coefficients could not be calculated and are indicated by “NA” for “Not Applicable”. Caffeine and bisphenol-A were not measured for ECHA, and acetaminophen was not measured for DMCHA.

Compounds	Feed Analyte Concentration (mg/L)	Solvent	Distribution Coefficient, D (-)
Caffeine	100	DPA	3.25 ± 0.34
		TEA	1.15 ± 0.21
		TOA	6.20 ± 0.32
		DMCHA	4.48 ± 0.68
Acetaminophen	20	DPA	0.25 ± 0.02
		ECHA	0.51 ± 0.02
		TOA	0.68 ± 0.06
		DMCHA	1.09 ± 0.02
Bisphenol-A	100	DPA	$5,400 \pm 3,700$
		TEA	110 ± 10
		TOA	NA
		DMCHA	NA

Table S12. Coefficients of regression analysis between analyte distribution coefficient, D , in biphasic solvent-water mixtures and analyte properties of octanol-water partition coefficient, K_{OW} , and acid dissociation constants, $K_{a,1}$: $\log \hat{D} = 1.117 \log K_{OW} - 0.147 pK_{a,1} + 0.623$.

Parameter	Slope	Standard Error	t -statistic	p -value ^a
$\log K_{OW}$	1.12	0.076	14.8	***
$pK_{a,1}$	-0.147	0.019	14.8	***
$pK_{a,2}$	NA	NA	NA	NA
(Intercept) ^b	0.623	0.120	5.20	***
Multiple $R^2 = 0.866$		Adjusted $R^2 = 0.858$		

^a Triple, double, and single asterisk indicate p -values < 0.001, 0.01, and 0.05, respectively.

^b Vertical axis intercept of the regression equation.

Table S13. Coefficients of regression analysis between analyte distribution coefficient, D , in biphasic tert-octylamine-water mixtures, analyte properties of octanol-water partition coefficient, K_{OW} , and acid dissociation constants, $K_{a,1}$, and solvent property of solubility in water, y_{aq}^{Solv} (which can be alternatively expressed as a fitted function of solvent hydrophobicity and solvent acidity, Table S14): $\log \hat{D} = 1.323 \log K_{OW} - 0.180 pK_{a,1} - 5.900 \hat{y}_{aq}^{Solv} + 0.414$.

Parameter	Slope	Standard Error	<i>t</i> -statistic	<i>p</i> -value ^a
$\log K_{OW}$	1.32	0.067	19.7	***
$pK_{a,1}$	-0.180	0.015	-11.8	***
$pK_{a,2}$	NA	NA	NA	NA
\hat{y}_{aq}^{Solv}	-5.90	1.08	-5.45	***
(Intercept) ^b	0.414	0.096	4.30	***
Multiple $R^2 = 0.930$		Adjusted $R^2 = 0.923$		

^a Triple, double, and single asterisk indicate *p*-values < 0.001, 0.01, and 0.05, respectively.

^b Vertical axis intercept of the regression equation.

Table S14. Coefficients of regression analysis between solvent solubility in water and solvent properties of octanol-water partition coefficient, K_{OW} , and acid dissociation constants, K_a : $\hat{y}_{aq}^{Solv} = -0.173 \log K_{OW} - 0.100 pK_a + 1.404$.

Parameter	Slope	Standard Error	<i>t</i> -statistic	<i>p</i> -value ^a
$\log(K_{OW})$	-0.173	0.005	26.6	***
pK_a	-0.100	0.004	-36.3	***
(Intercept) ^b	1.404	0.053	-23.9	***
Multiple $R^2 = 0.975$		Adjusted $R^2 = 0.974$		

^a Triple, double, and single asterisk indicate *p*-values < 0.001, 0.01, and 0.05, respectively.

^b Vertical axis intercept of the regression equation.

Table S15. *t*-statistics of unpaired two sample *t*-tests for comparative analyses of distribution coefficients, *D*, and molar partition ratios for acetaminophen and caffeine at different feed salt concentrations. Aqueous feed solutions of 1,000 mg/L analyte were equilibrated with equal weights of *tert*-octylamine (TOA) solvent at 25 °C. Experimental mean and one standard deviation of *D* are reported.

Compound	Feed Salt Concentration (mol NaCl/L)	Distribution Coefficient, <i>D</i> (-)	<i>t</i> -statistic ^a
Acetaminophen	0.0	1.15 ± 0.05	24.9 ***
	0.5	0.44 ± 0.04	
	0.5	0.44 ± 0.04	5.49 ***
	1.0	0.75 ± 0.12	
	1.0	0.75 ± 0.12	7.94 ***
	4.0	1.50 ± 0.18	
	0.0	1.15 ± 0.05	4.28 ***
	4.0	1.50 ± 0.18	
Caffeine	0.0	6.59 ± 0.30	3.28 *
	0.5	12.7 ± 4.51	
	0.5	12.7 ± 4.51	0.24
	1.0	13.3 ± 2.71	
	1.0	13.3 ± 2.71	3.45 *
	4.0	20.1 ± 2.86	

^a Triple, double, and single asterisk indicate *p*-values < 0.001, 0.01, and 0.05, respectively.

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