

SUPPORTING INFORMATION:

Investigation of the Effects of Solvent-Mismatch and Immiscibility in Normal-Phase × Aqueous Reversed-Phase Liquid Chromatography

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Table S1: Summary of chromatographic parameters as observed for the propoxylate separations with varying sample diluent (corresponding to Figure 1 of the manuscript).

Injection solvent	Breakthrough?	Injection solvent retained?	PO peak (retained)*		Comment
			T_R	$W_{0.5}$	
Reference conditions	No	No	2.712	0.023	
Methanol	No	No	2.712	0.035	
Acetonitrile	No	No	2.708	0.045	
Isopropanol	No	No	2.708	0.028	
Tetrahydrofuran	Yes	No	2.575	0.035	
Dichloromethane	No	Yes	2.700	-	Broad analyte peaks, $W_{0.5}$ not determined
Chloroform	No	Yes	2.704	-	Broad analyte peaks, $W_{0.5}$ not determined
<i>n</i> -Hexane	No	Yes	2.574	0.025	
Isooctane	No	Yes	2.543	0.027	

* Values in min.

Table S2: Summary of chromatographic parameters as observed for the separations of a standard mixture with varying sample diluent (corresponding to Figure 2 of the manuscript).

Injection solvent	Break-through?	Injection solvent retained?	Peak 1 (benzylalcohol)*		Peak 2 (benzaldehyde)*		Peak 3 (2-nitrotoluene)*		Comments
			T_R	$W_{0.5}$	T_R	$W_{0.5}$	T_R	$W_{0.5}$	
Reference conditions	No	No	1.2	0.017	1.511	0.02	2.001	0.021	
Methanol	Yes	No	1.206	0.033	1.512	0.027	1.998	0.021	Fronting analyte peaks
Acetonitrile	Yes	No	1.208	0.055	1.512	0.034	1.998	0.023	Fronting analyte peaks
Isopropanol	Yes	No	1.202	0.099	1.508	0.061	1.994	0.023	Fronting analyte peaks
Tetrahydrofuran	Yes	No	1.202	0.101	1.508	0.061	1.996	0.022	Fronting analyte peaks
Dichloromethane**	No	Yes	-	-	-	-	-	-	
Chloroform**	No	Yes	-	-	-	-	-	-	
<i>n</i> -Hexane	No	Yes	1.027	0.019	1.318	0.045	1.879	0.116	
Isooctane	No	Yes	1.031	0.021	1.321	0.036	1.862	0.100	

*: values in min.

** : due to overlap in retention between the analyte peaks and injection solvent signal, T_R and $W_{0.5}$ could not be determined.

Table S3: Summary of chromatographic parameters as observed for the separations of a standard mixture with varying sample diluent (corresponding to Figure 3 of the manuscript).

Injection solvent	Breakthrough?	Injection solvent retained?	PO peak (retained)*		Comment
			T_R	$W_{0.5}$	
Reference conditions (ACN as %B)	No	No	1.148	-	Individual ethoxylate peaks not resolved
Dichloromethane (ACN as %B)	No	Yes	1.139	-	Distribution eluted as one peak at onset of DCM elution
Chloroform (ACN as %B)	No	Yes	1.246	-	Distribution eluted as one peak at onset of CHCl_3 elution
Reference conditions (MeOH as %B)	No	No	2.038	0.030	
Dichloromethane (MeOH as %B)	No	Yes	1.969	0.039	
Chloroform (MeOH as %B)	No	Yes	1.984	0.033	

*: values in min.