Supplementary Information (SI)

for

Refractometric and Conductivity Based Water Cut Measurement Techniques for Stable Emulsions

Mabkhot BinDahbag[1], Dennis Atta[1], Hassan Hassanzadeh[1*]

[1]*Department of Chemical & Petroleum Engineering, Schulich School of Engineering, University of Calgary, Calgary, Alberta T2N 1N4, Canada*

Supplementary Information (SI)

This Supplementary Information (SI) file presents tables containing both raw and calculated data corresponding to the figures included in the main manuscript. The supporting tables provide data for calibration samples and for known and unknown emulsion samples. Additional details about the prepared emulsions are provided beneath each corresponding table.

Accuracy of Boyle's law for liquid volume measurements

The accuracies of Boyle's law, the volumetric method, and the fill-to-full method were evaluated using three different bottle sizes, as shown in **Table A-1**. This table presents the AARD% compared to the actual water volumes.

Corresponding authors: Hassan Hassanzadeh (hhassanz@ucalgary.ca)

Table A-1-Volumes of water measured using three methods and the AARD% relative to the actual volume of water.

Bottle size	V_{water} measured by			Actual V_{water}	AARD relative to actual volumes		
	Boyle's law	Volumetric method	Fill to full method		Boyle's law	Volumetric method	Fill to full method
	mL			mL	%		
100 mL	80.275	81.0	80.022	80.232	0.018	0.319	0.087
500 mL	400.862	404.1	399.783	400.862	0.000	0.269	0.090
1000 mL	801.199	807.5	799.444	801.443	0.010	0.252	0.083
$\sum$ AARD%					**0.028**	**0.840**	**0.260**

Volume measurement for known emulsion samples

Boyle's law parameters obtained during the total volume measurements of emulsion samples were reported in **Table A-2** for known emulsion samples. The experimentally measured emulsion volumes were compared with the corresponding ideal volumes, and the deviations were expressed as the AARD%.

Table A-2-Arithmetic average of volumes measured using Boyle's law method and ideal volumes of known emulsion samples, along with the AARD%.

Sample name	S#	Emulsion	WC	$P_{charging}$	$P_{equilibrium}$	Measured $V_{emulsion}$	Avg. $V_{emulsion}$	Ideal $V_{emulsion}$	AARD
			w/w	psia		mL			%
WCS	1	RO- 40/60 [a]	0.99	18.133	15.048	401.80	401.34	400.92	0.0071
				18.130	15.044	401.33			
				18.080	15.021	400.91			
	2		0.95	18.100	15.030	401.04	401.90	401.80	0.0016
				18.104	15.038	402.12			
				17.991	14.994	402.53			
	3		0.75	18.139	15.082	406.99	407.20	405.87	0.0218
				18.097	15.066	407.23			
				18.167	15.096	407.37			
	4		0.50	18.105	15.091	410.73	411.51	410.90	0.0099
				18.102	15.098	412.05			
				18.019	15.061	411.74			
	5		0.25	18.032	15.101	417.22	416.81	416.02	0.0127
				17.946	15.064	417.20			
				17.954	15.060	416.02			
	6[d]		0.05	23.289	17.406	421.06	421.78	420.12	0.0263
				23.235	17.391	421.70			
				22.993	17.297	422.56			
	7[d]		0.01	17.986	15.114	422.30	421.97	421.01	0.0153
				18.059	15.135	420.67			
				17.990	15.120	422.95			
	8[e]	RO-100 [b]	0.75	24.506	17.649	400.66	400.50	398.73	0.0297
				23.961	17.424	400.51			
				23.697	17.314	400.34			
	9[e]	RO-10/90 [c]	0.75	23.779	17.370	402.15	402.34	401.57	0.0127
				23.894	17.417	402.13			
				23.684	17.338	402.72			
				23.858	18.141	452.74			
				23.004	17.695	450.33			
				23.894	17.417	402.13			
				23.684	17.338	402.72			
						$\sum$ AARD%			**0.1371**

Notes:

- [a] oleic phase is 40/60 wt% toluene/bitumen.
- [b] oleic phase is 100 wt% bitumen.
- [c] oleic phase is 90/10 wt% toluene/bitumen.
- [d] for samples WCS#6 and WCS#7, 100 g of RO water was added to the emulsion sample after measuring its volume to facilitate representative aqueous sampling.
- [e] for samples WCS#8 and WCS#9, 100 g of toluene was added to the emulsion sample after measuring its volume to reduce the viscosity of the oleic phase and enable salt to reach all water droplets in the water-in-oil emulsion.

Brine salinity measurement for known emulsion samples

Brine salinities for known emulsion samples were determined using three analytical techniques: RI, EC, and gravimetry. The volume of water corresponding to these salinity values was calculated

and reported in **Table A-3**. The accuracy of the measured water volumes was evaluated by comparing them with the actual water volumes in the known emulsion samples, with deviations expressed as the AARD%.

Table A-3-The volume of water obtained using the RI, EC, and gravimetry methods, along with their corresponding AARD% for known emulsion samples prepared for water cut measurements.

Sample name	S#	Emulsion	WC	V_{water} (mL)				AARD (%)		
			w/w	Actual	RI	EC	Gravimetry	RI	EC	Gravimetry
WCS	1	RO- 40/60 [a]	0.99	396.78	399.33	393.47	406.08	0.043	0.056	0.156
	2		0.95	380.7	381.20	376.55	384.83	0.009	0.073	0.072
	3		0.75	300.55	300.88	294.28	302.26	0.007	0.139	0.038
	4		0.50	200.36	197.42	195.12	201.72	0.098	0.174	0.045
	5		0.25	100.18	100.66	97.97	101.59	0.032	0.147	0.094
	6[d]		0.05	20.05	21.14	19.18	21.33	0.362	0.289	0.426
	7[d]		0.01	4.03	4.72	3.01	5.21	1.141	1.687	1.952
	8[e]	RO-100 [b]	0.75	300.57	300.31	294.45	303.29	0.006	0.136	0.060
	9[e]	RO-10/90 [c]	0.75	300.52	300.35	295.19	299.28	0.004	0.118	0.028
$\sum$ AARD%								**1.702**	**2.819**	**2.871**

Notes:

- [a] oleic phase is 40/60 wt% toluene/bitumen.
- [b] oleic phase is 100 wt% bitumen.
- [c] oleic phase is 90/10 wt% toluene/bitumen.
- [d] for samples WCS#6 and WCS#7, 100 g of RO water was added to the emulsion sample after measuring its volume to facilitate representative aqueous sampling.
- [e] for samples WCS#8 and WCS#9, 100 g of toluene was added to the emulsion sample after measuring its volume to reduce the viscosity of the oleic phase and enable the salt to reach all water droplets in the water-in-oil emulsion.

Water cuts measurement for known emulsion samples

Following the determination of the total emulsion volume and the quantification of the aqueous phase, both volumetric (v/v) and mass-based (w/w) water cuts were calculated for the known emulsion samples. The measured volumetric water cuts (v/v) and mass water cuts (w/w) were then compared with the actual (reference) water cut values. The results, including the deviations from the true values, are presented in **Tables A-4** and **A-5**, respectively. The accuracy of the

measurements was assessed by calculating the AARD% to evaluate the performance of the methods used in measuring water cut under the tested conditions.

Table A-4-Volumetric water cuts (v/v) and corresponding AARD% for known emulsion samples measured using RI, EC, and gravimetry techniques compared to actual volumetric water cuts (v/v).

Sample name	S#	Emulsion	WC	WC (v/v)				AARD% relative to actual WC		
			w/w	Actual	RI	EC	Gravimetry	RI	EC	Gravimetry
WCS	1	RO- 40/60 [a]	0.99	0.990	0.995	0.980	1.012	0.036	0.063	0.149
	2		0.95	0.947	0.949	0.937	0.958	0.007	0.074	0.071
	3		0.75	0.741	0.739	0.723	0.742	0.014	0.160	0.016
	4		0.50	0.488	0.480	0.474	0.490	0.107	0.184	0.035
	5		0.25	0.241	0.242	0.235	0.244	0.020	0.160	0.081
	6[d]		0.05	0.048	0.050	0.045	0.051	0.333	0.314	0.398
	7[d]		0.01	0.010	0.011	0.007	0.012	1.126	1.694	1.927
	8[e]	RO-100 [b]	0.75	0.754	0.750	0.735	0.757	0.035	0.165	0.030
	9[e]	RO-10/90 [c]	0.75	0.748	0.747	0.734	0.744	0.017	0.131	0.040
$\sum$ AARD%								**1.695**	**2.945**	**2.747**

Notes:

- [a] oleic phase is 40/60 wt% toluene/bitumen.
- [b] oleic phase is 100 wt% bitumen.
- [c] oleic phase is 90/10 wt% toluene/bitumen.
- [d] for samples WCS#6 and WCS#7, 100 g of RO water was added to the emulsion sample after measuring its volume to facilitate representative aqueous sampling.
- [e] for samples WCS#8 and WCS#9, 100 g of toluene was added to the emulsion sample after measuring its volume to reduce the viscosity of the oleic phase and enable the salt to reach all water droplets in the water-in-oil emulsion.

Table A-5-Mass water cuts (w/w) and corresponding AARD% for known emulsion samples measured using RI, EC, and gravimetry techniques compared to actual mass water cuts (w/w).

Sample name	S#	Emulsion	WC	WC (w/w) obtained from				AARD% relative to actual WC		
			w/w	Actual	RI	EC	Gravimetry	RI	EC	Gravimetry
WCS	1	RO- 40/60 [a]	0.99	0.990	0.997	0.982	1.013	0.043	0.056	0.156
	2		0.95	0.950	0.951	0.940	0.960	0.009	0.073	0.072
	3		0.75	0.750	0.751	0.734	0.754	0.007	0.139	0.038
	4		0.50	0.500	0.493	0.487	0.503	0.098	0.174	0.046
	5		0.25	0.250	0.251	0.244	0.254	0.032	0.147	0.094
	6[d]		0.05	0.050	0.053	0.048	0.053	0.363	0.288	0.428
	7[d]		0.01	0.010	0.012	0.008	0.013	1.150	1.679	1.953
	8[e]	RO-100 [b]	0.75	0.750	0.749	0.735	0.757	0.006	0.136	0.060
	9[e]	RO-10/90 [c]	0.75	0.749	0.749	0.736	0.746	0.003	0.117	0.027
$\sum$ AARD%								**1.711**	**2.809**	**2.874**

Notes:

- [a] oleic phase is 40/60 wt% toluene/bitumen.
- [b] oleic phase is 100 wt% bitumen.
- [c] oleic phase is 90/10 wt% toluene/bitumen.
- [d] for samples WCS#6 and WCS#7, 100 g of RO water was added to the emulsion sample after measuring its volume to facilitate representative aqueous sampling.
- [e] for samples WCS#8 and WCS#9, 100 g of toluene was added to the emulsion sample after measuring its volume to reduce the viscosity of the oleic phase and enable the salt to reach all water droplets in the water-in-oil emulsion.

Salinity-RI calibration curve for unknown emulsion samples

The salinity–RI calibration curve was established using 10 mL of the aqueous phase collected from each of the first four unknown emulsion samples (UES#1–#4). Sodium chloride was added to the calibration samples: 0.3 g was added to the first group (RICS#1, #3, #5, #7), and 0.6 g was added to the second group (RICS#2, #4, #6, #8). The weight of salt added, and the corresponding volume of brine used to prepare each calibration solution are reported in **Table A-6**. Brine salinities were calculated for these prepared concentrations, and subsequently, RI values were measured for each solution. A correlation between measured salinity and RI was then developed, yielding the calibration curve used to estimate the aqueous-phase salinity in unknown emulsion samples. This calibration relationship ensures accurate determination of salinity from RI measurements during the analysis of emulsions with unknown composition.

Table A-6-Weights of NaCl, source of aqueous phase, and volumes of brine used for generating salinity-RI calibration curve for unknown emulsion samples.

Sample Name	S#	Source aqueous phase	W_{NaCl}	V_{brine}	Avg. RI	C_{NaCl}
			g	mL	nD	$g_{NaCl/L_{brine}}$
RICS	1	UES#1	0.3209	10.25	1.33863	31.307
	2	UES#1	0.6138	10.35	1.34324	59.304
	3	UES#2	0.3056	10.25	1.33841	29.815
	4	UES#2	0.6184	11.5	1.34231	53.774
	5	UES#3	0.3187	10.3	1.33857	30.942
	6	UES#3	0.6075	10.75	1.34279	56.512
	7	UES#4	0.3021	10.25	1.33831	29.473
	8	UES#4	0.6017	10.4	1.34210	57.856

Salinity-EC calibration curve for unknown emulsion samples

The salinity–EC calibration curve was developed using four calibration samples (EC calibration samples, ECCS#1–#4). Each calibration sample consisted of a 35 mL aqueous phase taken from the final collected unknown emulsion sample (UES#24). Sodium chloride was added to three of the samples: 1 g of NaCl to the second sample (ECCS#2), 2 g to the third sample (ECCS#3), and 3 g to the fourth sample (ECCS#4), while the first sample (ECCS#1) remained free of NaCl. The weight of salt added, source of aqueous phase, and the volume of brine used to prepare each solution are reported in **Table A-7**. Brine salinities of these samples were calculated, and the corresponding EC values were measured using conductivity meter. The obtained salinity values were then correlated with the measured EC to establish a calibration relationship. This curve is used to determine the salinity of the aqueous phase in unknown emulsion samples by measuring their EC, enabling accurate and reliable phase characterization.

Table A-7-Weights of NaCl and volumes of brine used for generating salinity-EC calibration for unknown emulsion samples.

Sample name	S#	Source aqueous phase	W_{NaCl}	V_{brine}	Avg. EC	C_{NaCl}
			g	mL	µS/cm	g_{NaCl}/L_{brine}
ECCS	1	UES#24	0.0000	35.055	216	0.0000
	2	UES#24	1.0853	35.912	47543	30.221
	3	UES#24	2.0038	36.001	81473	55.659
	4	UES#24	3.1069	36.549	117349	85.006

Water cut measurement for unknown actual emulsion samples

For unknown actual emulsion samples, the salinity and volume of the aqueous phase were determined using two indirect methods—RI and EC—based on the previously established calibration curves. The measured aqueous-phase volumes obtained from these methods are reported in **Table A-8**, alongside the aqueous-phase volumes determined by the centrifuge method.

Table A-8-Volumes of emulsions (achieved from Boyle's law) and volumes of aqueous phase for each unknown emulsion sample obtained using RI, EC, and centrifuge techniques collected during the SAGD experiment.

Sample name	S#	$V_{emulsion}$	W_{NaCl}	RI method			EC method			Centrifuge method
				RI	C_{NaCl}	V_{water}	EC	C_{NaCl}	V_{water}	V_{water}
		mL	g	nD	g_{salt}/L_{brine}	mL	µS/cm	g_{salt}/L_{brine}	mL	mL
UES	1	747.250	34.9934	1.34289	57.177	595.90	84086	58.984	577.14	611.87
	2	772.862	35.0198	1.34330	59.673	570.72	85713	60.164	565.93	582.86
	3	736.969	34.9700	1.34420	65.133	520.79	91765	64.550	525.64	550.38
	4	763.044	35.0029	1.34357	61.297	554.91	88581	62.242	546.24	491.87
	5	773.525	35.1145	1.34308	58.313	585.99	83880	58.835	580.64	529.82
	6	773.421	35.0204	1.34300	57.806	589.69	83873	58.830	579.14	546.86
	7	773.765	35.2744	1.34289	57.156	600.90	83654	58.672	584.96	591.74
	8	773.447	35.0759	1.34530	71.810	472.29	102691	72.468	467.86	462.84
	9	727.514	35.2066	1.34389	63.225	540.62	92999	65.444	521.74	590.28
	10	729.438	35.1881	1.34399	63.854	534.85	89278	62.747	544.57	552.78
	11	710.155	35.0028	1.34679	80.882	416.63	114243	80.840	416.86	466.87
	12	826.761	35.1997	1.34506	70.369	483.99	101620	71.692	474.77	484.78
	13	798.724	35.0011	1.34704	82.425	408.51	118341	83.810	401.49	419.87
	14	823.706	35.0886	1.34461	67.609	502.82	98158	69.183	491.02	494.83
	15	780.227	35.0638	1.34545	72.744	465.86	104597	73.850	458.64	476.84
	16	751.983	35.0159	1.34487	69.232	489.64	100448	70.842	478.14	494.86
	17	887.418	35.1332	1.34425	65.437	520.71	96015	67.630	503.30	543.81
	18	770.647	35.1593	1.34634	78.142	433.74	111052	78.527	431.53	484.80
	19	795.744	35.3067	1.34404	64.159	534.03	91712	64.512	531.02	546.73
	20	838.337	35.2099	1.34364	61.723	554.22	90248	63.451	538.69	582.77
	21	816.541	35.3544	1.34251	54.843	628.36	79564	55.707	618.35	642.71
	22	774.492	35.5500	1.34191	51.189	678.10	74253	51.858	669.14	642.62
	23	1039.631	35.2974	1.34005	39.864	869.17	58028	40.100	863.97	840.73
	24	740.993	35.2974	1.34250	54.782	628.06	78691	55.075	624.63	612.73

Using the measured aqueous phase volumes and the total emulsion volume, the volumetric water cuts (v/v) were calculated for each sample. The resulting volumetric water cuts (v/v) derived from the three methods—RI, EC, and centrifuge—are summarized in **Table A-9**. These results allow for a comparative assessment of the accuracy and reliability of the RI and EC techniques.

Table A-9-Volume of water and volumetric water cut (v/v) obtained using RI, EC, and centrifuge methods, for unknown emulsion samples.

Sample name	S#	$V_{emulsion}$	Calculation obtained from RI		Calculation obtained from EC		Calculation obtained from centrifuge	
			V_{water}	WC	V_{water}	WC	V_{water}	WC
		mL	mL	v/v	mL	v/v	mL	v/v
UES	1	747.25	595.90	0.80	577.14	0.77	611.87	0.82
	2	772.86	570.72	0.74	565.93	0.73	582.86	0.75
	3	736.97	520.79	0.71	525.64	0.71	550.38	0.75
	4	763.05	554.91	0.73	546.24	0.72	491.87	0.64
	5	773.52	585.99	0.76	580.64	0.75	529.82	0.68
	6	773.42	589.69	0.76	579.14	0.75	546.86	0.71
	7	773.77	600.90	0.78	584.96	0.76	591.74	0.76
	8	773.44	472.29	0.61	467.86	0.60	462.84	0.60
	9	727.52	540.62	0.74	521.74	0.72	590.28	0.81
	10	729.43	534.85	0.73	544.57	0.75	552.78	0.76
	11	710.16	416.63	0.59	416.86	0.59	466.87	0.66
	12	826.76	483.99	0.59	474.77	0.57	484.78	0.59
	13	798.72	408.51	0.51	401.49	0.50	419.87	0.53
	14	823.63	502.82	0.61	491.02	0.60	494.83	0.60
	15	780.3	465.86	0.60	458.64	0.59	476.84	0.61
	16	751.9	489.64	0.65	478.14	0.64	494.86	0.66
	17	887.5	520.71	0.59	503.30	0.57	543.81	0.61
	18	770.6	433.74	0.56	431.53	0.56	484.80	0.63
	19	795.8	534.03	0.67	531.02	0.67	546.73	0.69
	20	838.3	554.22	0.66	538.69	0.64	582.77	0.70
	21	816.5	628.36	0.77	618.35	0.76	642.71	0.79
	22	774.5	678.10	0.88	669.14	0.86	642.62	0.83
	23	1039.7	869.17	0.84	863.97	0.83	840.73	0.81
	24	740.9	628.06	0.85	624.63	0.84	612.73	0.83