IMPACT OF WETTABILITY ON RESIDUAL OIL SATURATION AND CAPILLARY DESATURATION CURVES

K. J. Humphry[1,*], B. M. J. M. Suijkerbuijk[1], H. A. van der Linde[1], S. G. J. Pieterse[1], and S. K. Masalmeh[2]

[1]Shell Global Solutions International
[2]Shell Development Oman

This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in Napa Valley, California, USA, 16-19 September, 2013

ABSTRACT

In this paper, we supplement capillary desaturation data in the literature with additional wetting systems. The study is performed on Berea sandstone rock samples prepared with different wetting conditions. The rock wettability was characterized with spontaneous imbibition. Residual oil saturations as a function of capillary and Bond number are measured using flooding and centrifuge techniques, respectively, for a wide range of capillary and Bond numbers. We find a strong interrelation between wettability, residual oil saturation, and critical capillary and Bond numbers. As the system becomes less water-wet the residual oil saturation decreases and the critical capillary and Bond numbers increase. We find that the critical capillary or Bond number for strongly water-wet rock is $\sim 10^{-5}$, which is in agreement with data reported in literature. However, for less water-wet rock, the critical capillary or Bond number is higher by at least one order of magnitude. The data presented in this paper indicate that reservoir wettability may significantly impact the design of enhanced oil recovery processes.

INTRODUCTION

Following the water flooding of an oil reservoir the remaining oil saturation (ROS) results from a combination of unswept and swept reservoir areas. In unswept areas of the reservoir the oil saturation, S_{o}, is greater than the residual oil saturation, S_{orw}. In swept areas of the reservoir, a portion of the oil is microscopically trapped in the pore space by capillary forces and S_{o} is greater than or equal to S_{orw}. The challenge for enhanced oil recovery (EOR) is to recover this remaining oil. Unswept oil can be recovered by changing the mobility ratio between water and oil, as in thermal EOR or polymer flooding, or by changing the flooding pathways, as in flow diversion techniques. Microscopically trapped oil can be recovered by changing the balance of forces that hold the oil in place, as in surfactant, solvent, and gas flooding [1].

Microscopically trapped oil is held in place by capillary, or interfacial, forces. To mobilize this trapped oil, viscous or gravity forces need to overcome the capillary forces

holding the oil in place. The ratio between viscous and capillary forces is known as the capillary number, N_{Ca}. This is a dimensionless number given by

$$N_{\mathrm{Ca}} = \frac{v_b\,\mu_b}{\gamma} \tag{1}$$

where v_b is the velocity of the brine phase in the pore, μ_b is the viscosity of the brine phase, and γ is the interfacial tension between the brine and oil phases. The ratio between gravity and capillary forces is known as the Bond number, N_{Bo}. This is a dimensionless number given by

$$N_{\mathrm{Bo}} = \frac{\Delta\rho a k}{\gamma} \tag{2}$$

where $\Delta\rho$ is the absolute difference in density between the brine and oil phases, a is the gravity or acceleration, and k is the permeability of the porous medium to brine. Note that while a number of different, but more or less equivalent, definitions of capillary and Bond number have been proposed in the literature [2], we use the definitions above in this study.

Recovery of microscopically trapped oil is generally studied via desaturation curves. These studies determine the capillary or Bond number above which the residual oil will be remobilized, and the oil saturation as a function of capillary or Bond number. Desaturation curves for strongly water-wet systems using sand packs, outcrop, and reservoir sandstone have been extensively studied, and generally find the critical capillary or Bond number for remobilization of residual oil $\sim 10^{-5}$, with higher values leading to further oil desaturation [3].

Relatively little data is available in the literature for non-water-wet porous media. Desaturation curves have been measured on high permeability model non-water-wet porous media with model fluids [4]. In a recent publication [5], we demonstrated that the critical capillary or Bond number for non-water-wet carbonate rock can be more than two orders of magnitude higher than those reported for water-wet sandstone rock. However, it is unclear if differences between strongly water-wet sandstones and mixed-wet carbonates are due to differences in wetting properties of the rock or differences in pore morphology.

In this study, we investigate the effect of wettability on both residual oil saturation and desaturation curves in outcrop Berea sandstone. A number of cores are prepared, and their wetting state is characterized via spontaneous imbibition. The samples are then brought to residual oil saturation using either the centrifuge or unsteady state technique. Desaturation curves are experimentally measured using the centrifuge technique, which gives desaturation curves as a function of Bond number, and the unsteady state technique,

which gives desaturation curves as a function of capillary number. The impact of our results on the design of EOR processes for a reservoir with a given wettability is discussed.

EXPERIMENTAL MEASUREMENTS

Two crude oils, designated B and C, were used in these experiments, as well as *n*-decane. The total acid number (TAN) for the crude oils was measured using ASTM D664 [6]. SARA (Saturates, Aromatics, Resins, and Asphaltenes) analysis was also conducted on the two crude oils. These results are given in Table 1. Three different brines, designated X, Y, and Z, were used in the experiments. The composition of these brines, together with the total dissolved solids (TDS) is given in Table 2. All experiments were conducted at 70°C. Densities and viscosities of the oils and brines at 70°C are given in Table 1 and Table 2 respectively. The interfacial tensions of the brine-oil pairs used in this experimental program were measured using the pedant-drop technique [7], and are reported in Table 3.

Eighteen core plugs (B_01 – B_18) were drilled from two different outcrop blocks of Berea sandstone. Plugs B_01 – B_07 were drilled from a block with porosity, $\phi \sim 0.20$, and permeability, $k \sim 320$ mD. Plugs B_08 – B_18 were drilled from a block with $\phi \sim 0.23$ and $k \sim 100$ mD. The plugs were drilled using tap water and then dried. At this point the plugs are strongly water-wet as they have never been in contact with oil. The properties of the plugs, the brines and the oils used in each plug, and the experimental programs for each of the plugs are given in Table 4. The samples were prepared to initial water saturation (S_{wi}) using either the porous plate technique (B_01 – B_07) or the centrifuge technique (B_08 – B_18). Some core samples were then aged for a period of time, according to Table 4. For plugs containing *n*-decane, aging was not performed, as it was not expected to change the wetting properties of the core [8]. *n*-decane was used as an oil to ensure a strongly water-wet system was included in this study.

In all, five different combinations of brine, oil, and aging were used. These are: Brine Z, Oil C, Aged (ZCA - blue data points); Brine Y, Oil C, Aged (YCA - red data points); Brine X, Oil B, Aged (XBA - green data points); Brine X, Oil B, Unaged (XBU - orange data points); and Brine X, *n*-decane, aging not relevant (XD - purple data points).

Three types of experiments were performed on the initialized core plugs: Amott-type spontaneous imbibition (SI) experiments, multi-speed centrifuge imbibition experiments, and unsteady-state (USS) experiments. Spontaneous imbibition experiments were used to characterize the wettability of the core by assessing both the rate and extent of imbibition [9], while multi-speed centrifuge imbibition experiments and unsteady-state experiments were used to measure capillary desaturation curves.

In Amott or spontaneous imbibition experiments, the plugs were depressurized, and moved to glass jars containing oil at 70°C. Clean Amott cells were weighed and pre-

heated to 70°C. The brines were also heated to 70°C. The plugs were then removed from the glass jars, rolled in dry tissue paper to remove any excess crude, weighed, immersed in brine, transferred to the Amott cell, and returned to the oven at 70°C. Production of oil was then recorded as a function of time until total oil production reached a plateau.

In multi-speed imbibition centrifuge experiments, core plugs were loaded into a centrifuge set to 70°C. The centrifuge was set to the first, lowest speed, and oil production was monitored as a function of time. When oil production reached a plateau, the centrifuge speed was increased. This sequence was repeated until the maximum speed of the centrifuge was reached. For some plugs the range of gravity forces used was increased by replacing the brine with a CsCl solution. In these cases, at the end of the centrifuge run, the plug was removed from the centrifuge and placed into a container containing a 60 wt% CsCl solution. Sufficient time was given to allow the CsCl solution to mix with the brine solution in the plug. The resulting CsCl solution had density $\rho_{\mathrm{CsCl}} = 1.749$ g/cm^3. To ensure complete mixing, this solution was pumped through the core at low flow rates. The plug was loaded again into the centrifuge and imbibition continued, this time using the CsCl solution as the displacing phase.

In unsteady-state experiments, the core plugs were loaded into a core flooding apparatus set to 70°C. Brine was injected into the core at a fixed rate, and oil production and pressure across the core was monitored as a function of time. When oil production reached a plateau and the pressure drop across the core had stabilized, the brine injection rate was increased. This sequence was repeated until the maximum injection rate of the pumps was reached. For some plugs, the range of viscous forces used was increased by replacing the brine in the injection pumps with brine supplemented with 5000 ppm Floppam 3330S polymer. The polymer was then injected into the core, beginning at a low flow rate. The injection rate of the polymer solution was increased in steps after oil production had reached a plateau and pressure across the core had stabilized. To determine the effective viscosity of the polymer at each injection rate, the pressure drop across the core at the end of each flow rate was recorded, and apparent viscosity was calculated [10].

RESULTS & DISCUSSION

For the spontaneous imbibition experiments, produced oil was recorded as a function of time. The time, t, in the spontaneous imbibition experiments was scaled to form dimensionless time, t_d [11]:

$$t_d = t\sqrt{\frac{k}{\phi}\frac{\gamma}{\mu_b}\frac{1}{{L_c}^2}} \tag{3}$$

where L_c is the length of the core plug and ϕ is the core plug porosity. Spontaneous imbibition results are shown for fifteen plugs as a function of dimensionless time in

Figure 1. For the centrifuge and unsteady-state experiments, oil saturation as a function of capillary or Bond number is shown in Figure 2. S_{wi}, S_{o} after spontaneous imbibition, and S_{orw} for each plug are reported in Table 4.

Three sets of core plugs, XBA, XBU, and XD reached S_{orw} under spontaneous imbibition; no further oil was produced in centrifuge and unsteady state experiments for capillary or Bond numbers less than 10^{-5}. This indicates that these samples are water-wet. However, the "strength" of the water-wetness is not the same for all samples. Faster, earlier production in spontaneous imbibition is an indication of a more water-wet sample [9]. By these criteria, Figure 1 indicates that the most water-wet brine, oil, aging combination in this study is the one that uses *n*-decane, XD. This is also reflected in the desaturation curves in Figure 2: the S_{orw} of the XD core plugs is the highest, as would be expected for a strongly water-wet case [9]. This is understandable, as *n*-decane is not expected to wet the rock surface as it lacks any polar, wettability-modifying components [8].

From spontaneous imbibition production data, the next most strongly-water-wet brine, oil, aging combination studied is XBU: Brine X, Oil B, without aging: These samples show the second fastest spontaneous imbibition. This is also reflected in the S_{orw} for this system, which is the second highest of all the systems included in this study. This is in line with expectations, as it has been established that aging time is required to produce less water-wet samples [12]. The spontaneous imbibition of core plug B_11 is considered to be anomalous, as it shows lower spontaneous imbibition rates and higher S_{orw} than other SBU samples.

The samples from XBA, XBU, and XD all reached S_{orw} during spontaneous imbibition; the measured Amott index for all these samples is 1. However, the desaturation curve and S_{orw} for XBA are significantly different from those for XBU and XD. This shows that differences in critical Bond or capillary number may be observed for samples classified as identically strongly water-wet by the Amott index. This can be clearly seen by comparing the destaration curves of the XD samples, B_12 and B_13, with the XBA samples, B_08 and B_09, in Figure 2. On average, the S_{orw} of the XD samples is 13 saturation units higher than the S_{orw} for the XBA samples, and the critical Bond number for the XD samples is $\sim 10^{-5}$, while the critical Bond number for the XBA samples is $\sim 10^{-4}$. Moreover, the desaturation of the XD samples is complete for a Bond number of $\sim 5 \times 10^{-4}$, while the desaturation of the XBA samples is complete at a Bond number of 10^{-3}.

For the XBU samples, core plug B_16 went directly to the centrifuge after being initialized, while core plug B_11 was subjected to spontaneous imbibition before centrifuge. Despite this difference in sample preparation, and a difference in S_{orw}, B_11 and B_16 have similar desaturation curves.

The samples from ZCA and YCA did not reach S_{orw} during spontaneous imbibition; oil was produced in centrifuge or unsteady state experiments for capillary or Bond numbers less than 10^{-5}. This indicates that theses samples are mixed-wet, or that the Amott index for these samples is less than 1. Moreover, these samples have the slowest oil production in spontaneous imbibition. The S_{orw} of these samples is also the lowest in this study.

For the XBA samples, B_08, B_09, and B_10 have $S_{\mathrm{orw}} \cong 0.35$, while samples B_17 and B_18 have $S_{\mathrm{orw}} \cong 0.26$. There are two possibilities for this difference in S_{orw}. First, B_08, B_09, and B_10 had an aging time of 28 days, while samples B_17 and B_18 had an aging time of 35. It is known that longer aging times result in less water-wet samples [12], which would explain the lower S_{orw} for samples with longer aging times. However, the difference in aging time is not thought to be large enough to lead to such a high difference in S_{orw}. Second, this data may indicate that a combination of spontaneous imbibition and displacement experiment, in this case centrifuge, does not result in the same S_{orw} as a displacement experiment, in this case unsteady state, alone. The spontaneous imbibition may lead to different oil saturation distribution which may impact the final S_{orw} in the following displacement test. This issue needs further investigation in future work.

For the less water-wet core plugs, such as those from ZCA and YCA, the desaturation curves in Figure 2 indicate critical Bond and capillary numbers $\sim 10^{-4} - 10^{-3}$. Desaturation remains incomplete for capillary and Bond numbers as high as $\sim 10^{-2}$. Desaturation curves with these parameters have been observed in oil-wet model systems [4] and in mixed-wet carbonates [5]. The literature data, together with our experimental results, indicates that desaturation curves are primarily a function of wettability rather than of pore structure.

To summarize, the brine, oil, and aging combinations can be ordered from most water-wet to least water-wet as: XD, XBU, XBA, ZCA/YCA.

The results reported in this paper indicate that desaturation is strongly correlated with wettability as the wettability has a strong influence on how oil is trapped and, subsequently, the forces required to remobilize the oil. Mobilization of residual oil requires either higher viscous or gravity forces or a larger reduction in capillary forces as the rock becomes less water-wet and more oil-wet. The data presented in this paper has implications for the design of EOR processes like surfactant or alkaline-surfactant-polymer flooding especially for non-water-wet rock. Such EOR techniques work by changing the balance of forces on capillary trapped oil, where the capillary number is increased via a decrease in surface tension. Therefore, the capillary number required to mobilize trapped oil is significantly higher in less water-wet systems when compared to strongly water-wet systems.

CONCLUSION

This study indicates that there is a strong interrelation between wettability, S_{orw}, and critical capillary and Bond numbers. As the system becomes less water-wet the residual oil saturation decreases and the critical capillary and Bond numbers increase. The residual oil saturation ranged between 15% for the mixed wet samples to nearly 50% for the strongly water-wet samples. Wettability characterization should take into account the rate of spontaneous imbibition in addition to the volume of oil produced during spontaneous imbibition experiments. Weakly water-wet and mixed-wet samples in this study produced more oil, albeit at lower rates, during spontaneous imbibition than strongly water-wet samples.

The critical capillary or Bond number observed for strongly water-wet rock is $\sim 10^{-5}$, which is in agreement with the data reported in literature [3]. However, for less water-wet rock, the critical capillary or Bond numbers may be higher by at least one order of magnitude. Generally, we find reproducibility between core plugs prepared in the same way to be good for both spontaneous imbibition and desaturation experiments, as can be seen in Figure 2.

ACKNOWLEDGEMENTS

We thank Fons Marcelis and Ab Coorn for core plug drilling and characterization.

NOMENCLATURE

a	Gravity or acceleration
k	Permeability to brine
L_c	Core plug length
N_{Ca}	Capillary number
S_{o}	Oil saturation
S_{orw}	Residual oil saturation
S_{wi}	Initial water saturation, as measured after primary drainage
t	Time
t_d	Dimensionless time
v_b	Brine velocity in the pore
γ	Interfacial tension between brine and oil phases
$\Delta\rho$	Absolute density difference between brine and oil phases
μ_b	Viscosity of the brine phase
ρ_{CsCl}	Density of CsCl solution after equilibration with core
ϕ	Porosity

ABBREVIATIONS

EOR	Enhanced oil recovery
IFT	Interfacial tension

ROS	Remaining oil saturation
SARA	Saturates, Aromatics, Resins, and Asphaltenes
SI	Spontaneous imbibition
TAN	Total acid number
TDS	Total dissolved solids
USS	Unsteady state

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* Corresponding author; E-mail address: katie.humphry@shell.com

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Table 1. Properties of oils used in this study. Viscosities and densities are reported for temperatures of 70°C.

Oil	TAN [mg KOH/g]	SARA Saturates [wt%]	SARA Aromatics [wt%]	SARA Resins [wt%]	SARA Asphaltenes [wt%]	Density [g/cm3]	Viscosity [mPa.s]
B	0.014	60.48	32.86	6.43	0.23	0.792	1.08
C	0.100	59.19	36.72	3.87	0.21	0.819	1.59
n-decane	-	-	-	-	-	0.691	0.49

Table 2. Properties of brines used in this study. Viscosities and densities are reported for a temperature of 70°C.

Brine	NaCl [mg/L]	KCl [mg/L]	$MgCl_2.6H_2O$ [mg/L]	$CaCl_2.2H_2O$ [mg/L]	TDS [mg/L]	Density [g/cm^3]	Viscosity [mPa.s]
X	10000	0	70	200	10184	0.990	0.41
Y	638	812	42	183	1608	0.978	0.40
Z	27513	744	2166	7942	35267	1.003	0.41

Table 3: Interfacial tensions of brine-oil pairs used in this study. Interfacial tensions are reported for a temperature of 70°C.

Oil	Brine	IFT [mN/m]
n-decane	X	40
B	X	19
A	Y	15
A	Z	15
A	CsCl	15
B	X + polymer	19

Table 4. Properties of core plugs used in this program with details of initialization and experimental treatment of each core.

Core	Porosity	k [mD]	S_{wi}	S_o after SI	S_{orw}	Brine	Oil	Aging [days]	Measurement	Brine, Oil, and Aging
B_01	0.227	324	0.10	0.47	0.13	Z	C	30	Amott: Brine Z; Centrifuge: Brine Z → CsCl Brine	ZCA
B_02	0.225	314	0.09	0.40	0.14	Z	C	30	Amott: Brine Z; Centrifuge: Brine Z → CsCl Brine	ZCA
B_03	0.225	300	0.18	0.32	-	Z	C	30	Amott: Brine Z	ZCA
B_04	0.226	326	0.10	0.40	0.15	Z	C	30	Amott: Brine Z; Centrifuge: Brine Z → CsCl Brine	ZCA
B_05	0.226	322	0.11	0.39	0.16	Y	C	30	Amott: Brine Y; Centrifuge: Brine Y	YCA
B_06	0.227	340	0.06	0.44	0.21	Y	C	30	Amott: Brine Y; Centrifuge: Brine Y	YCA
B_07	0.224	306	0.07	0.45	0.19	Y	C	30	Amott: Brine Y; Centrifuge: Brine Y	YCA
B_08	0.211	128	0.15	0.35	0.35	X	B	28	Amott: Brine X; Centrifuge: Brine X	XBA
B_09	0.199	125	0.16	0.35	0.35	X	B	28	Amott: Brine X; Centrifuge: Brine X	XBA
B_10	0.208	113	0.16	0.34	0.34	X	B	28	Amott: Brine X; Centrifuge: Brine X	XBA
B_11	0.201	93	0.21	0.45	-	X	B	0	Amott: Brine X; Centrifuge: Brine X	XBU
B_12	0.201	86	0.16	0.47	0.47	X	*n*-decane	-	Amott: Brine X; Centrifuge: Brine X	XD
B_13	0.199	54	0.16	0.49	0.49	X	*n*-decane	-	Amott: Brine X; Centrifuge: Brine X	XD
B_14	0.202	93	0.16	0.43	-	X	B	0	Amott: Brine X	XBU
B_15	0.201	88	0.18	0.46	-	X	B	0	Amott: Brine X	XBU
B_16	0.207	93	0.17	-	0.39	X	B	0	Centrifuge: Brine X	XBU
B_17	0.211	106	0.18	-	0.21	X	B	35	USS: Brine X → Brine X + polymer	XBA
B_18	0.211	96	0.18	-	0.26	X	B	35	USS: Brine X → Brine X + polymer	XBA

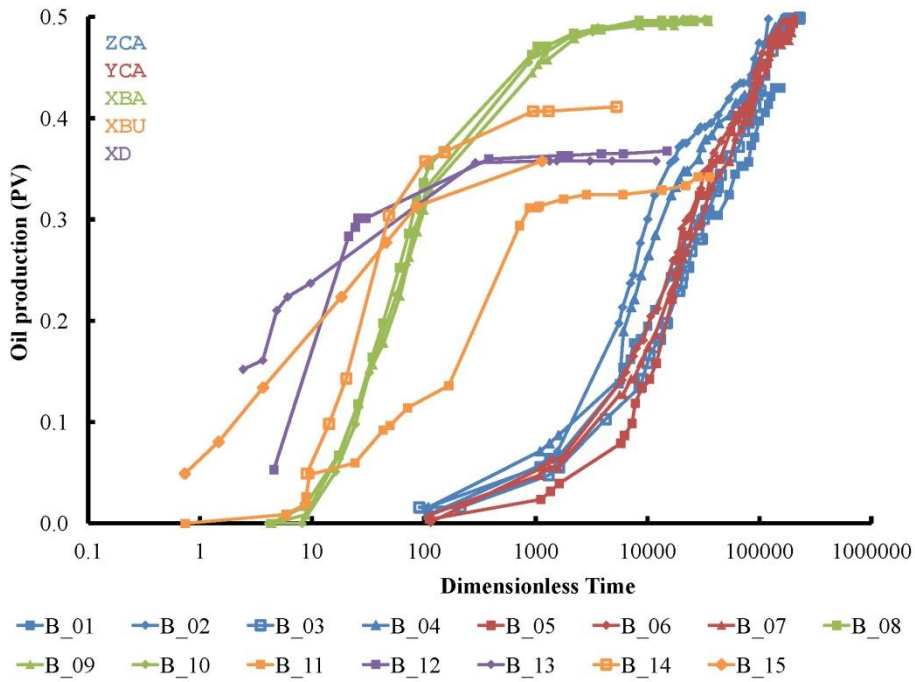

Figure 1. Spontaneous imbibition curves as a function of dimensionless time.

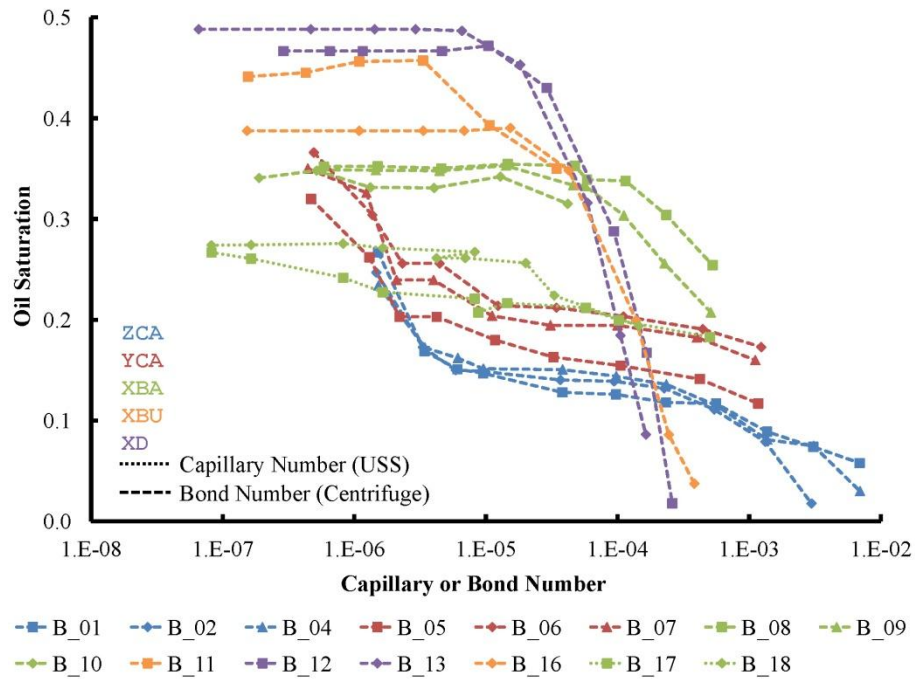

Figure 2. Desaturation curves as a function of capillary or Bond number.