Hydrocarbon and Fixed Gas Solubility in Amine Treating Solvents: A Generalized Model

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ABSTRACT

Hydrocarbons are sparingly soluble in aqueous solvents and to a first approximation their solubility can be described by the traditional Henry's Law, which linearly relates the mole fraction in water to gas-phase partial pressure. The presence of amines in the aqueous phase increases hydrocarbon solubility over that in water, an effect referred to as "salting-in". Commercial amine treating solutions can contain as much as 25 mol% amine, so it is important to take account of salting-in. The presence of ionic species, on the other hand, has the opposite effect and hydrocarbon solubility is reduced—this is termed "salting-out". The treating solution may be highly loaded with acid gases and therefore it may have high concentrations of numerous ions. The result is significantly reduced hydrocarbon solubility. The once simple ideal-gas, ideal-solution Henry's Law is further complicated by the non-ideal behavior of gases at the high pressures common in gas treating.

This paper provides a generalized approach to representing the equilibrium solubility of hydrocarbons in acid-gas-loaded, high-strength, commercial, amine treating solvents. The methodology is valid for system pressures up to values where the hydrocarbon solubility is so high it begins to compete with the acid gases for a place in the solution and, therefore, it starts to displace acid gas from the solvent. The validity of the generalized model is shown by excellent agreement with GPA, GTI and other data for all generic amines in commercial use over a wide range in concentration and acid-gas loadings. The model correlates all the available data and provides the basis for very reliable hydrocarbon solubility predictions. Finally, using the model in an LNG sweetening application, the implications of salting in and salting out effects are demonstrated in the context of transient operations and foaming in commercial plants.

INTRODUCTION

Wellhead gas in the field is processed in several ways before it is suitable for admission into pipelines for transmission to its point of use. Following an initial treatment to remove brine and sand from the gas, it may be processed cryogenically to remove the heavy hydrocarbons. Next is an acid gas removal step where H_2S content is lowered to meet pipeline specifications and CO_2 is removed to at least the level needed for it to have the required heating value as well as to minimize pipeline corrosion. An amine solvent is most commonly used for acid gas removal. Unfortunately H_2S and CO_2 are not the only components in the gas that are soluble in the treating solvent. Hydrocarbons and fixed gases are also soluble to varying extents depending on the solvent and the particular hydrocarbon species involved. For example, hydrogen and low molecular weight aliphatics have fairly low solubility; whereas, high molecular weight aliphatics and especially aromatic compounds (BTEX) have much greater solubility.

Hydrocarbon solubility is never good news, unless the solvent is intentionally being used for dew point purposes.   Whatever hydrocarbons dissolve into the solvent in the absorber must reappear somewhere else and be discharged from the process. Gas removed from the rich solvent via a flash tank immediately downstream from the absorber (so-called *flash gas make*) is mostly hydrocarbon but with high levels of CO_2 and H_2S. It may need to be treated further in a low pressure absorber to remove H_2S before it can be used as fuel gas, for example, so its flow rate and composition might need to be known with reasonable accuracy.   Incidentally, gas *dissolved* in the amine solvent is not the only way hydrocarbons can enter the flash tank. Carry under of gas entrained (but not dissolved) in the solvent can be a much bigger source than dissolved gas if care is not taken to prevent it. A simple vortex breaker is a common way to minimize, or even eliminate, carry-under entrainment of gas. However, frothy, foamy solvents usually contain large volume fractions of hydrocarbon gases.

Once the rich solvent enters the regenerator, its hydrocarbon content will be almost completely stripped and enter the sulfur plant along with the acid gas. Low molecular weight hydrocarbons will take up air demand and hydraulic volume in the sulfur plant and lower sulfur recovery efficiency. However aromatics (BTEX) are real troublemakers in sulfur plants and can lead to catalyst coking in units with acid gas feeds that are lean in H_2S, while in rich feeds and especially oxygen-enriched units temperature control problems can result. In some cases, heavy hydrocarbons in the right boiling range can be steam stripped and trapped in the overhead circuit of the regenerator, leading to foaming.

A third way for hydrocarbons to remove themselves from the amine treating plant is by periodic foaming events. When conditions are right, hydrocarbons can form a second *liquid* phase. Foaming then becomes almost inevitable, and it is usually alleviated by the spewing of foamy solvent overhead. Although not a solubility issue, foamed solvent may also carry large amounts of hydrocarbons from the absorber bottom and into the flash tank where they contribute in a large way to flash gas make rates far in excess of what would be expected from solubility alone.

To estimate solubility in amine treating solutions, a good place to start is with the solubility in water because water makes up at least 85 mole% of most treating solutions. However, amines are organic molecules and have a much higher affinity for hydrocarbons than water does. Thus, hydrocarbon solubility in amine treating solvents should be expected to be higher than in water, and the solubility should depend not only on the particular amine but also on its strength. One might say that the amine *salts-in* hydrocarbons. Dissolved acid gases, on the other hand, cause what is termed *salting-out* of hydrocarbons (and fixed gases). When acid gases dissolve in (and react with) the solvent, they produce copious amounts of ionic components such as protonated amine, sulfide and bisulfide ions, carbonate and bicarbonate, and in the case of primary and secondary amines, amine carbamates. These are all ionic, and they result in high total ionic strength. High ionic strength causes dissolved hydrocarbon and fixed gas concentrations to be much lower than would be expected simply on the basis of solubilities in unloaded

amines. Unfortunately, *unloaded* amines are usually what have been used to assess hydrocarbon and fixed gas solubilities in amine treating solutions! *Assessments based solely on unloaded solvent data can be erroneously high by a factor of more than ten at high loadings.*

This article aims to place hydrocarbon and fixed gas solubilities in amine treating solutions on a solid, generalized footing. The intended result is for practitioners is the ability to predict with considerable certainty just what the expected hydrocarbon content of any amine solution in a properly operating plant *ought* to be. This is particularly important for rich solvents under absorber bottom conditions because the rich amine is the normal, unavoidable source of hydrocarbons in flash gas make and Claus plant feed streams. And it is precisely here that ion-induced salting out is at its strongest. The importance of being able to make this prediction accurately is that it provides a quantitative assessment of the situation expected under normal circumstances in a well-managed facility. If the flash gas make rate is higher, there is probably carry-under from the absorber either as entrained gas or as an emulsified second hydrocarbon phase. It points troubleshooting in the right direction, and it also allows a downstream flash gas scrubber to be properly sized.

MODELING AND THEORY

The basis for determining the solubility of any sparingly-soluble gas, i, uses temperature-dependent Henry's-law data for pure water:

$$y_i = \frac{H_i\, PF_i}{\varphi_i P}\, x_i \ \ or \ \ x_i = \frac{\varphi_i P}{H_i\, PF_i}\, y_i$$

Here φ_i is the pure component fugacity coefficient, PF_i is the Poynting factor, and H_i is its Henry's Law constant. In the second form of this equation, x_i in the actual solution is related to the solubility in water, x_i^o, by the Setschenow (1892) salting (in and out) coefficient S_i:

$$S_i = \frac{x_i}{x_i^o} = \frac{y_i H_i^o}{y_i H_i} = \frac{H_i^o}{H_i}$$

Thus, Henry's Law constant in the actual solution is related to the value in water by:

$$H_i = \frac{H_i^0}{S_i}$$

There is extensive literature on the Setschenow (1892) approach (c.f., Harvey and Prausnitz, 1989). The original work of Setschenow provides a method for calculating phase equilibria for systems for which conventional activity-coefficient models are unsuited. The trick, however, is in determining the Setschenow coefficient for the gas of interest. This coefficient consists of contributions from the molecular amine (a salting in contribution) and the various ions (salting out contributions):

$$\ln(S_i) = kC_a - 2.302585\, h\, I$$

where I is the ionic strength[1] and where the sign on hI is negative because of the inverted log_{10} definition in the more-usual, salting-out formulation. The system-dependent parameter h has anion, cation and gas contributions:

$$h = h_- + h_+ + h_g$$

The value of the salting parameter, k, depends on the specific hydrocarbon-amine pair and is also temperature dependent. The salting-out part depends on the specific amine with contributions from protonated amine, carbamate, bicarbonate, carbonate, and in principle at least, on bisulfide and sulfide ions although no measurements appear ever to have been reported of the interactions of HS^- and $S^=$ with any soluble gas.

Salting In

Firstly, it is important to recognize that all salting-in data have been collected for the hydrocarbons in *completely unloaded* amine solvents. Therefore, if simulator comparisons for the rich amine in a flash tank are made, for example, with literature data for the amine in question, the numbers will almost certainly be very different. The literature data ignore the salting out effect of the ions generated by loading the solvent with acid gas and, as will be seen, the effect is very substantial indeed.

Mather and coworkers have correlated the salting in parameter for methane and ethane (Carroll and Mather, 1997), propane (Jou, Critchfield and Mather, 2002) and propylene (Jou and Mather, 2004) in MDEA, DEA, DGA®, MDEA and DIPA according to:

$$\ln(S_i) = kC_a$$

where k ($L \cdot mol^{-1}$) is a linear function of temperature: $k = a + bt(°C)$ with the a and b parameter values shown in Table 1.

Table 1   Parameters in Salting-in Correlation for Public Domain Data on Four Hydrocarbons

	Methane[1]		Ethane[1]		Propane[2]		Propylene[3]	
Amine	a	b	a	b	a	b	a	b
MEA	0.0346	0.000530	0.0509	0.00141	0.153	0	0.0845	0.00084
DEA	0.0380	0.000899	0.1260	0.00148	0.183	0.00169	0.0942	0.00176
DGA®	0.0252	0.00233			0.219	0.00228	0.0412	0.00339
MDEA					0.221	0.00344	0.0100	0.00600
DIPA					0.127	0.00850	0.22	0

[1] Carroll and Mather (1997)
[2] Jou, Critchfield and Mather (2002)
[3] Jou and Mather (2004)

We have developed similar correlations for ethylene, n-butane, 1-butene, n-pentane, benzene, toluene and p-xylene using data confidential to several solvent vendors and which we are not at liberty to divulge.

For light hydrocarbon, apart from the results shown in Table 1, little data seem to exist for the way in which salting-in parameters depend on temperature. Much of the data are at 313.15K (40°C or 104°F) which is close to many absorber bottom temperatures. In any event, the temperature dependence

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[1] Ionic strength is defined as $I = \frac{1}{2}\sum m_s z_s^2$ where m_s is the molality of the salt *ion* and z_s is its charge number.

is weak for propane and propylene, so assuming the correction is temperature independent in those cases without data is unlikely to be a serious deficiency.

Figure 1 provides evidence in support of the premise that information for missing components can be inferred reasonably well by appeal to interpolation, or even extrapolation, based on carbon number within a homologous series. This figure shows that except for *n*-butane which shows an abnormally low temperature dependence of the salting-in parameter (open data point), carbon number offers a reasonable basis for estimating parameters for missing components. Parameter a depends linearly on carbon number (salting-in becomes increasingly significant with increasing molecular weight of the solute gas) while b shows exponential dependence, i.e., increasing temperature sensitivity.
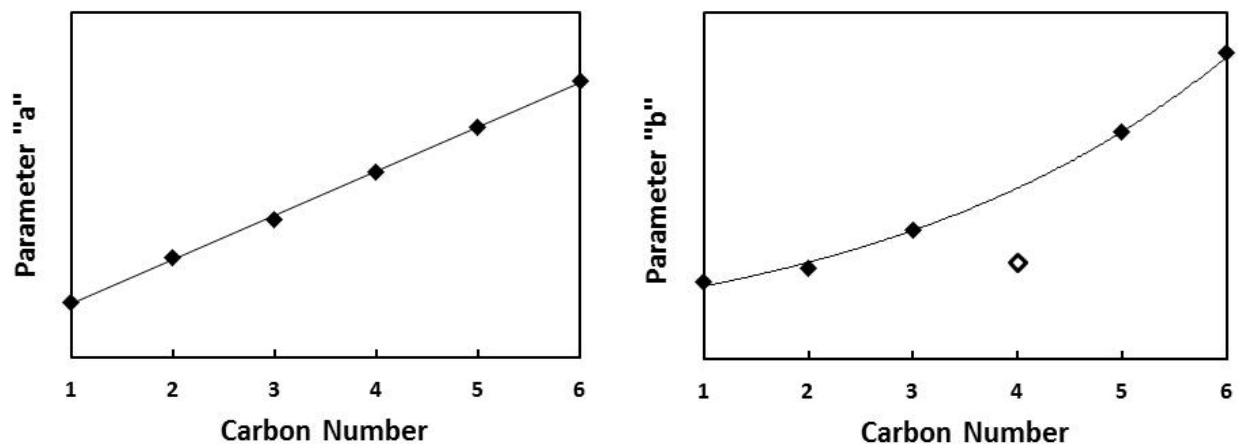

Figure 1   How a and b parameters in the Setschenow (1892) salting-in coefficient correlate with carbon number for the *n*-alkanes

GPA RR-180 (Valtz et al., 2002) report solubility data for BTEX, mostly in water, and in MDEA and DGA® solvent with limited data in DEA, and it includes a small amount of data in MDEA as a function of temperature and amine strength. We have converted the data into Setschenow (1892) salting-in parameter values (S_i) including temperature dependence where available. GPA RR-180 and RR-195 (Mokraoui et al., 2008) data on Henry's Law constants in water as a function of temperature were correlated according to the equation:

$$\ln(H) = A + B\,T + C\,ln(T) + D/T$$

For consistency with the RR-180 data analysis, measured Antoine coefficients for these hydrocarbon components were also correlated. Figure 2 indicates the goodness of fit of the Setschenow BTEX model for MDEA. The benzene and toluene data include measurements of solubility as a function of temperature (25 to 120°C) and amine strength (nominally 2 and 4 molar). For ethyl benzene, measurements are at 60°C and 4.4 molar MDEA only; therefore, we have no choice but to assume the same temperature dependence as toluene. More data are needed. For xylenes, the only solubility measurements are in water, leaving a significant hole in the data.
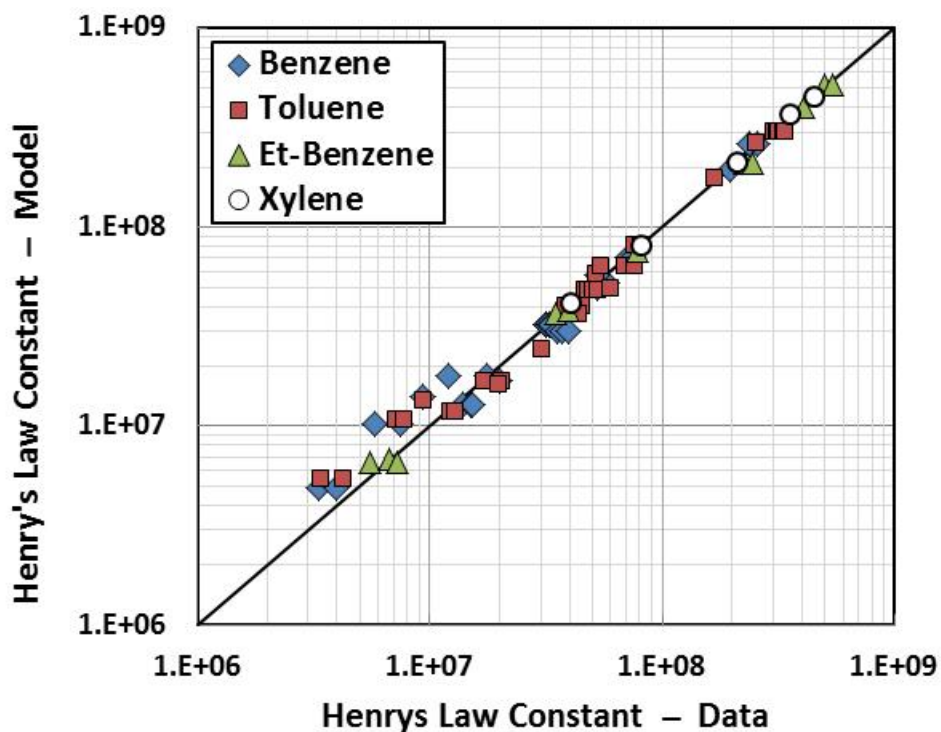
Figure 2   Goodness of fit of the Setschenow (1892) salting-in model to the GPA RR-180 solubility data for BTEX in MDEA from 25 to 120°C. Henry's law constant is in units of Pa/mole fraction.

Hydrogen is a component of significant interest to those processing syngas for ammonia and methanol production. Kling and Maurer (1991) have made high quality measurements of the solubility of hydrogen in 25, 50 and 75 mol% (about 53, 77 and 79 wt%) MEA solutions. Temperatures ranged from 50 to 150°C and hydrogen partial pressures from 1.92 to 19.2 MPa (278 to 2,785 psia). We ignored the data for 79 wt% MEA as irrelevant to commercial operations, and then correlated the remainder of the data using the Setschenow (1892) approach. The parity plot of Figure 3 shows an excellent fit of the model to the data. We are unaware of hydrogen data for any other amine solvent. Thus, for other amines there is no alternative to using MEA data until such time as this void is filled by further laboratory measurements.

It is not our intent to enumerate and discuss all the data for all the hydrocarbons and fixed gases in all the amines, but rather to present a flavor for how well a fairly generalized model based on the Setschenow (1892) salting-in and salting-out approach can be made to represent the experimental data, in this case salting-in data. What we have found is that by and large, this approach, combined with a good equation of state (EOS) model for the gas phase (e.g., Peng-Robinson or Redlich-Kwong-Suave EOS) yields an excellent representation of the data. It also became apparent during model development that there are still significant voids in the data even for unloaded aqueous amine solvents. In particular, data for certain of the commercial amines are completely missing (DIPA specifically), and for most of the amines information on the temperature-dependence of solubility is scant where it exists at all. In the next section, we shall see that when it comes to the effect of already-dissolved acid gases, i.e., acid gas loading, on hydrocarbon and fixed gas solubility, the situation is no better, and in some ways worse.
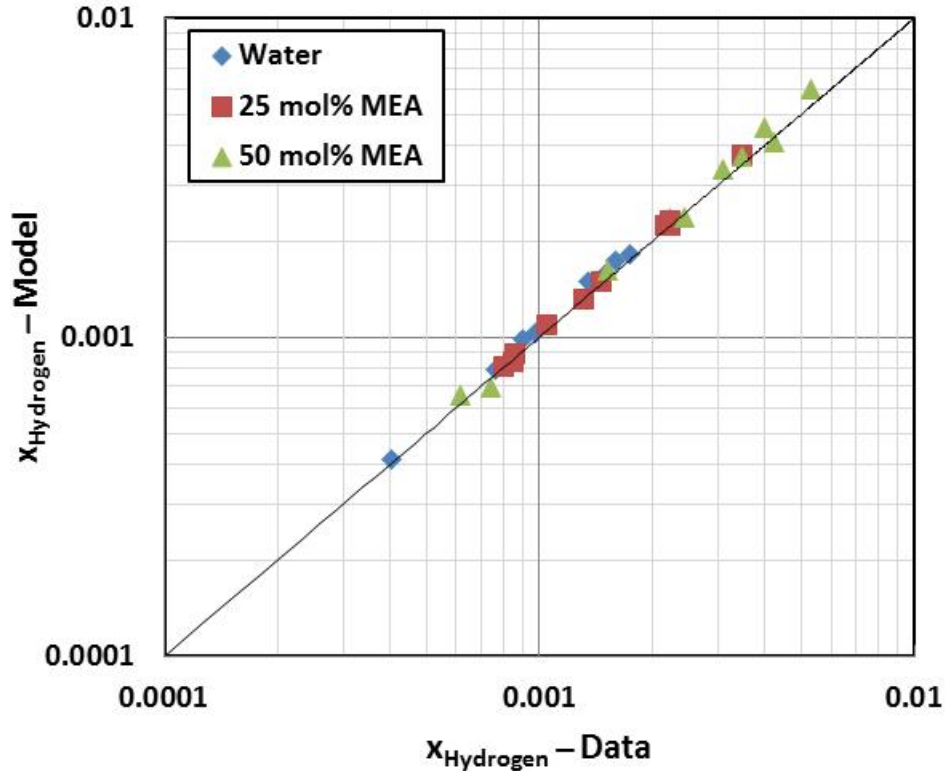
Figure 3   Goodness of fit of the Setschenow (1892) salting-in model to Kling and Maurer's (1991) solubility data for hydrogen in 25 and 50 mol% MEA

Salting-Out

At first glance, salting out is almost as straightforward as salting in. The salting-out contributions arise from anions (h_-) and cations (h_+), with a possible contribution from the soluble gas itself (h_g). However, no data are available for the soluble gases of interest (mostly aliphatic and aromatic hydrocarbons) so nothing can be done apart from ignoring the contribution. The most common way to express salting out is:

$$\log_{10} \frac{H_i}{H_i^o} = \log_{10}\left(\frac{1}{S_i}\right) = hI = (h_+ + h_- + h_g)I$$

where for a single ionic "compound", M^+X^-, the ionic strength is I. The so-called van Krevelen parameters, h_+, h_- and h_g, correspond to contributions of the cation, anion and gas to the coefficient h. In terms of the Setschenow constant as we have already defined it, this must be inverted and rewritten as the natural logarithm:

$$\ln(S) = -\ln(10)\, h\, I = -2.302585(h_+ + h_- + h_g)I$$

In systems containing a single amine the only cation of significance is the protonated amine, AmH$^+$ (the hydrogen ion concentration is quite negligible). However, we are immediately confronted with a dilemma: even in single amine systems, anions include HS$^-$, and HCO$_3^-$ and, if the amine is

primary or secondary, the carbamate of the amine, AmCOO⁻ may be at high concentration, too. The Setschenow (1892) equation is written for a *single anion-cation pair* so it is certainly not clear how one is to account for the various anions. In mixed amine systems the situation is even more complicated. Joosten and Danckwerts (1972) proposed that for such mixed electrolytes, *each neutral ion pair* (called a salt) should be separately accounted for:

$$log_{10} \frac{H_i}{H_i^o} = \sum_{salts} h_{salt} I_{salt}$$

However, in mixed amine systems, for example, there are ions such as HS⁻ and HCO3⁻ that are in some sense *shared* by each amine in the system, so how to assign pairing is even less clear. Nevertheless, speciation is always fully known so once the basis for anion-cation pairing is decided, the actual pairing itself is straightforward. We have gone to great lengths to develop logical pairing rules that make sense chemically for solutions containing single as well as multiple amines.

Barrett (1966) has determined values for the van Krevelen parameters for numerous mono- and multi-valent cations (most of no pertinence to gas treating), several anions with only $CO_3^=$ of gas treating interest, and the gases H_2, O_2, CO_2, N_2O, H_2S, NH_3, C_2H_2 and SO_2. No data appear ever to have been measured for any other hydrocarbons and fixed gases *and such data are needed*. Their availability would enhance the reliability of calculations on the solubility of gases in loaded amine solvents. The amount of dissolved gas species exiting an absorber in the rich solvent is determined by absorber bottom conditions of temperature and especially acid gas loading; in other words, by the concentrations of carbamates and protonated amines.

Browning (1993) used the analogy between nitrous oxide (N_2O) and CO_2 to infer the effect of CO_2 loading on the physical (Henry's law) solubility of CO_2 in aqueous MEA, DEA and MDEA. He determined h_+ and h_- parameter values for several protonated amines, their carbamates, and HCO_3^-. Table 2 shows the results together with 95% confidence limits. This work goes some way toward filling the gap at least for MEA, DEA and MDEA; however, the temperature dependence of most van Krevelen parameters remains unknown.

Table 2   Values of h_+ and h_- for Various Ion Pairs in Amine Systems

Ion	$h_\pm$ (L/gmol)
MEAH⁺	0.055 ± 0.006
DEAH⁺	0.047 ± 0.005
MDEAH⁺	0.041 ± 0.007
NH4⁺	0.028
MEACOO⁻	0.054 ± 0.003
DEACOO⁻	0.043 ± 0.003
HCO3⁻	0.073 ± 0.025

Browning also determined N_2O solubility in the pure MEA, DEA and MDEA for use in a model for blends involving these amines in water. He gathered no information for DGA® solvent, DIPA or piperazine; however, given the small variation between amines shown by the results in Table 2, one might assume them to have the same values as DEA, MDEA, and MEA (similar molecular weights), respectively. On the other hand, piperazine being a diamine has three protonated forms (mono-protonated, di-protonated, and mono-protonated carbamate) and it exists in mono- and di-carbamate forms, too. So the situation with piperazine is about as complex as it could possibly be in an amine system. Fortunately, and with the exception of high-strength piperazine for carbon capture, piperazine in

most gas treating applications is a relatively low concentration additive so its contribution to salting-in is less than that of other ionic species. In carbon capture, one usually is not interested in the solubility of hydrocarbons and fixed gases at all, so there the issue is moot.

Despite the foregoing, there is certainly room for improvement in enumerating the effect of acid gas loading on salting-out. Data for other amines such as DIPA and especially piperazine would be beneficial. Values for the van Krevelen parameter for most gases remains unknown and there are no data whatsoever on the effect of the HS^- ion on salting out. This is an area that cries out for laboratory work to provide the data needed for an even more accurate prediction of BTEX solubility in amine treating solvents, for example. Work with CO_2 is logistically simple; H_2S presents a challenge, but a quite manageable one.

MODEL VALIDATION

In principle, accurate measurements of the make gas from a low-pressure flash tank located immediately downstream from a high pressure absorber should provide an excellent test of any model for hydrocarbon and inerts solubility in a treating solvent. All too often, however, such data is suspect because of the propensity of the solvent coming from the absorber sump to contain *entrained* gas. Any foaming tendency is likely to exacerbate such carry-under because foaming stabilizes gas-liquid mixtures. It stabilizes not just foams (structures of liquid films enveloping large volumes of gas), but also dilute emulsions containing gas in the form of small bubbles dispersed in liquid. These emulsions of entrained gas are carried from the column in the rich solvent and are separated in the downstream flash tank. When this happens, it results in falsely-high gas concentrations that are mistakenly interpreted as *dissolved* gas. In fact, measured gas make rates and compositions almost always consist of dissolved plus some entrained gas, and such data can be quite erroneous and misleading. To add further fuel to the fire, many refinery amine systems contain multiple amine contactors that feed a common rich amine flash drum. When the flash gas is metered, it usually is not compensated for mole weight or temperature impacts.

Skinner et al. (1996) made accurate measurements of the gas make and degassed solvent from the flash tank in a carefully-operated DEA plant. The objective was to obtain accurate data on the disposition of VOC and BTEX components absorbed by the solvent under actual operating conditions. The data ranges in the following tables are shown as measured over an 8 hour data collection window. Table 3 shows inlet gas conditions.

Table 3   Inlet Gas Analysis

Temperature (°F)		81–85	
Pressure (psig)		1,040–1,110	
Gas Flow (MMscfd)		10.9–11.2	
Composition (mole %)			
Water	0.00632	n-Pentane	0.456
CO_2	6.90	n-Hexane	0.0700
Methane	83.30	Benzene	0.0344
Ethane	6.41	Toluene	0.0213
Propane	1.82	Et-Benzene	0.00074
i-Butane	0.449	m-Xylene	0.00404
n-Butane	0.530	o-Xylene	0.00091

Apart from the gas temperature (118°F calculated by the ProTreat® simulator vs. 116–121°F measured) nothing else concerning the treated gas was reported. However, the measured *n*-C6 and BTEX content of the rich amine leaving the absorber itself is compared with generalized model predictions in Table 4. With the exception of ethyl benzene, the generalized solubility model is in solid agreement with the data. The rich amine CO_2 loading was 0.69 for this data set and at this loading and the bottoms temperature, the salting out parameter value is 1.45. In other words, the solubility of the gases involved was roughly 1.45 times *lower* than would be predicted in the unloaded solvent—obviously, salting *out* can be a huge correction and it simply cannot be ignored!

Table 4   n-C6 and BTEX in Rich Amine from Flash Tank (ppmw)

	Measured	**Generalized model**
n-Hexane	nd–0.02	0.001
Benzene	23–27	28
Toluene	10–14	16.3
Et-Benzene	0.2–0.4	0.004
m,p-Xylenes	1.6–2.6	2.3
o-Xylene	0.6–0.9	0.51

The rich amine went to a zero-duty flash drum operating at 106.5 psig. The flash gas make rate was estimated at 0.025 MMscfd at the plant site. Using the generalized model, ProTreat calculated 0.023 MMscfd. Table 5 compares the flash gas analysis with the calculations of the generalized solubility model. For the most part there is excellent agreement. It should be particularly noted that the CO_2 loading of the rich amine from the flash drum was 0.69 at an amine strength of 21.4 wt% so the ionic concentration was quite high and salting out was severe. The VOC, HAP, and fixed gas solubility model is very strong and is extremely well-qualified to estimate BTEX and most hydrocarbon and fixed-gas solubilities with rather high accuracy.

Table 5   Flash Tank Make Gas Analysis

	Measured	**Generalized Model**
CO_2 (mol%)	32.5	33.98
Methane (mole %)	60.6	59.72
Ethane (mole %)	4.4–4.8	4.82
Propane (mole %)	0.68–0.73	0.96
i-Butane (mole %)	0.10–0.11	0.07
n-Butane (mole %)	0.14–0.15	0.18
n-Pentane (mole %)	0.03–0.04	0.073
n-Hexane (ppmv)	162	66
Benzene (ppmv)	1,000	900
Toluene (ppmv)	521	466
Et-Benzene (ppmv)	17	12
m,p-Xylenes (ppmv)	95	64
o-Xylene (ppmv)	14	14

Harvey and Prausnitz (1989) state that using Setschenow constants allows good agreement with experiment at very high salt concentrations, where salting-out is usually under-predicted. They claimed good results for phase equilibria in a natural-gas/brine system at high pressures. We concur with that finding in the context of heavily acid-gas-loaded amine solutions.

COMMERCIAL IMPLICATIONS OF SALTING OUT

Salting out can dominate the effect even of temperature on hydrocarbon solubility in an amine treating solvent. Here we use the solubility of benzene in a piperazine promoted MDEA solvent for CO2 removal in an LNG plant as an example of just how much salting out matters. It is known that the solubility of benzene in MDEA is an increasing function of temperature (Valtz et al., 2002). The question is the extent to which this higher solubility is mitigated by salting out from the high salts content caused by high solvent loading at the rich end of an absorber.

A 4-m diameter LNG absorber with 16 m of IMTP-50 random packing was initially operating under the conditions shown in Table 6. The column was simulated to be producing higher-than-specified CO_2 in the treated gas (1,400 ppmv) caused by a slightly starved amine supply. Low amine flow resulted in a large, broad, internal temperature bulge. It was believed at the time by the plant operators that the higher benzene solubility at higher temperatures would result in a large internal concentration of benzene trapped inside the column.

Table 6 Absorber Inlet Streams

Inlet Gas		Solvent	
Temperature (°C)	33.3	Temperature (°C)	43
Pressure (barg)	50.4	Pressure (barg)	61.04
Flow (kg/h)	582,450	Flow (kg/h)	900,000
Components (mole %)		Components	
CO_2	5.83	CO_2 (Loading)	0.024
C1	79.04	MDEA (wt%)	35
C2	8.26	Piperazine (wt%)	9
C3	1.58	Water	Balance
iC4	0.13		
nC4	0.11	**Wash Water**	
iC5	0.02	Temperature (°C)	30
nC5	0.01	Pressure (barg)	55.16
Benzene	0.91	Flow (kg/h)	3,044
N_2	3.98	CO_2 (ppmw)	1
H_2O	0.13		

This hypothesis was tested by taking the converged column results from the initial "starved" solvent condition, and perturbing the solvent flow in the ProTreat simulator from 900,000 kg/h to 1,000,000 kg/h using a "Restart" feature. The Restart feature allows a previously converged column profile to be used as the starting conditions for a new simulation. By stopping the "Restart" simulation after various numbers of iterations along the path to convergence and capturing the results, an unsteady state path of the temperature and concentration profiles could be studied. While this case study does not necessarily represent the true time-dependent behavior of the column because there is not a *direct* quantitative correspondence between the number of column iterations and time, it does represent a path along which the column could be expected to behave temporally.

Figure 4 summarizes the progression of the temperature profile over the arbitrary time intervals studied, while Figures 5 and 6 show the benzene concentration profile and the CO_2 loading profiles,

respectively, in the solvent inside the column over the same window. ***Despite the collapsing temperature profile, benzene actually is predicted to increasingly accumulate to quite high levels inside the column!*** This was completely counter to our expectations which were derived from knowing that benzene salting in (i.e., solubility in the amine) is greater at higher temperatures. Thus, higher temperature means benzene salts in more, and conversely, lower temperatures (which are what is seen here) should mean benzene salts in less (has lower solubility). In fact, at first glance the opposite happens. It is not until the CO_2 loading profile inside the column is examined that this makes sense.
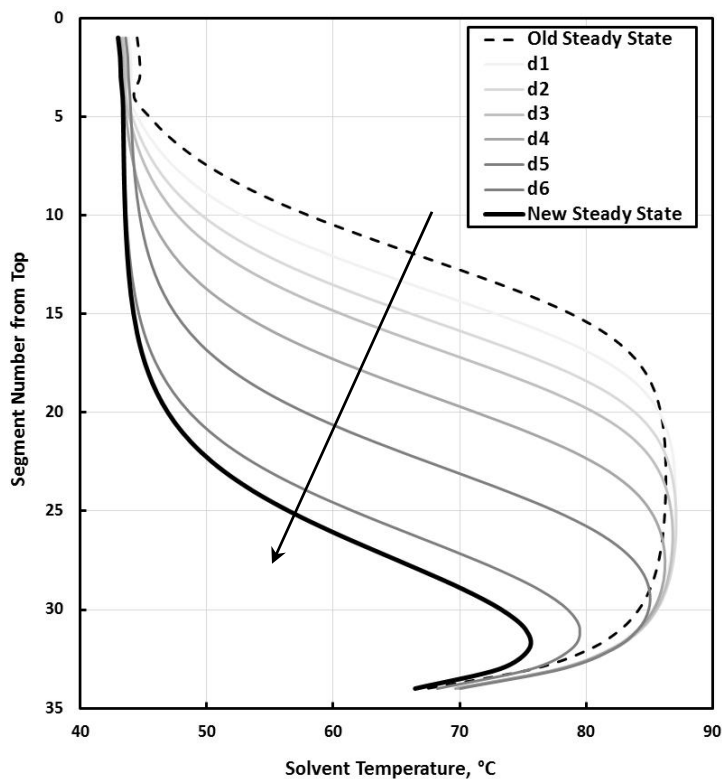

Figure 4   Progression of Temperature Profiles from One Steady State to Another

As shown in Figure 6, the benzene concentration explodes simultaneously with the collapsing CO_2 loading. No longer having high CO_2 loading in the middle of the column causes the salting out effect to shrink dramatically because the lower ionic salt concentrations associated with lower loading cause less desolubilization. This gives benzene increased incentive to enter the amine solution, and to exhibit much *higher* levels than when CO_2 is present, *even though the temperatures there are much lower* and on that account solubility should be *lower*. In summary, lower temperatures imply lower solubility, but lower loading implies higher solubility—in the present case the effect on solubility of salting out far and away dominates over the effect of temperature.
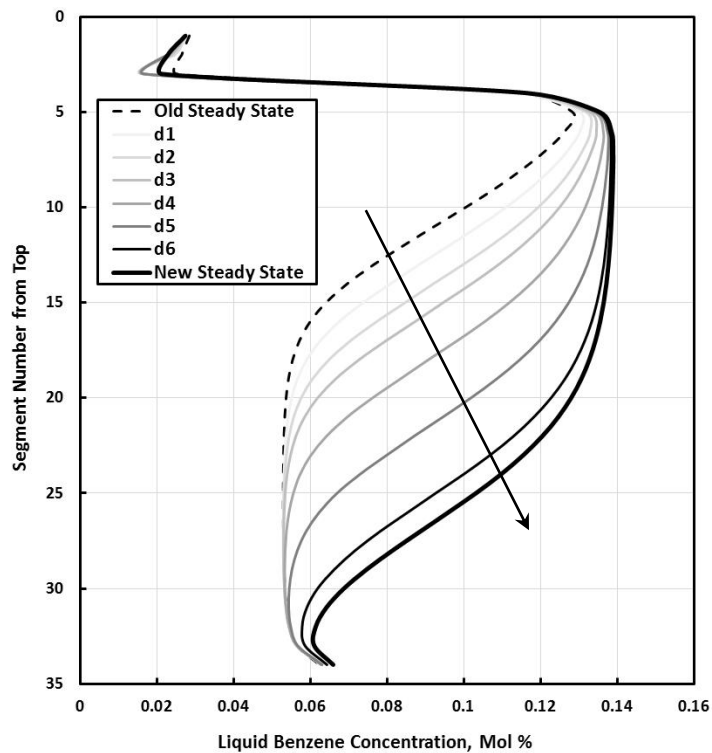
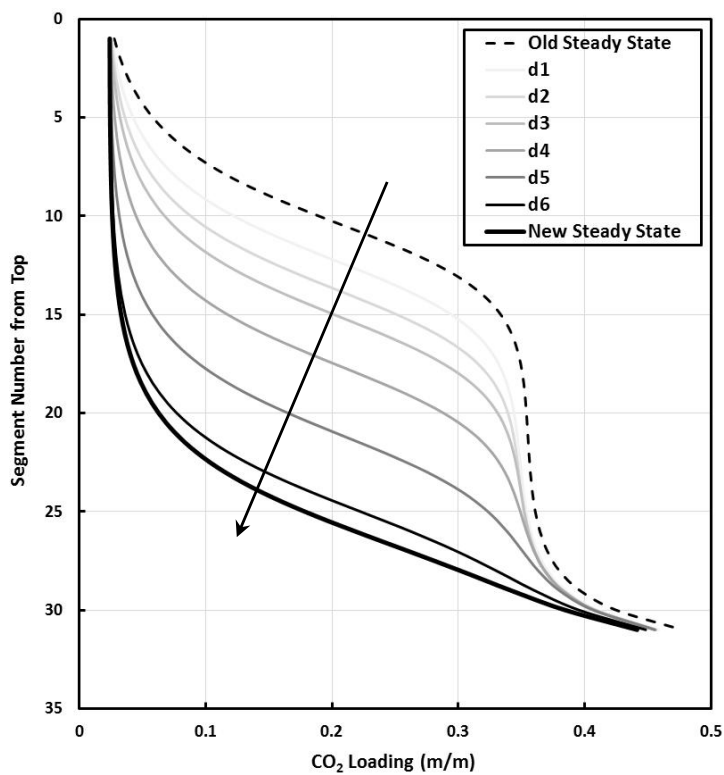Figure 5   High Benzene Concentrations Building up in the Column

Figure 6   Approach of the CO$_2$ Loading Profile to the New Steady State

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Conditioning Conference, Norman, Oklahoma, February, 2013

The behavior of this column may go some way towards explaining the old saying, well known to those who have regularly operated amine units, that "Amine units do not like rapid changes". Any rapid change to feed gas CO_2 or H_2S content, amine temperature, or amine flow rate that will rapidly swing the column's internal temperature profile will also rapidly swing the amount of hydrocarbon stored inside the column. It is easy to imagine situations in which a sudden change in a variable (e.g., an increase in the CO2 level in the gas, or a higher gas rate) will lead to an equally sudden lowering of the equilibrium hydrocarbon content in a liquid that contains hydrocarbon at a high pre-change level. In other words, the solubility limit will be exceeded locally. If the rate of hydrocarbon mass transfer from the liquid back into the gas occurs more slowly than a liquid hydrocarbon can form, then an organic liquid phase will coalesce, surface tension at gas-liquid interface will drop, and the energy needed to expand the froth will fall dramatically. Thus, the froth on trays can be expected to turn to foam which will eventually be ejected from the column.

CONCLUSIONS

A good hydrocarbon solubility model in amine systems will properly take into account salting *out* effects as well as salting *in* effects. The VLE data for salting out parameters (and to a much lesser extent, salting in effects) are scarce and the industry would stand to benefit significantly from collection of additional data, especially on the contribution of the sulfide and bisulfide forms of H_2S. This will be especially important for making predictions that can truly pass a rigorous test by regulatory authorities.

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