

Solubility of hydrocarbons and light ends in amines

Modelling procedures predict with considerable certainty what the expected hydrocarbon content of any amine solution in a gas processing plant ought to be

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In processing and treating both wellhead and refinery gases for H₂S and CO₂ removal, an unfortunate side effect is the loss of hydrocarbons and other light ends gases that are also soluble to varying degrees. Hydrocarbon solubility is never good news, unless the solvent is intentionally being used for dew point control. Any hydrocarbons that 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 CO₂ and H₂S. It may need to be treated further in a low-pressure absorber to remove H₂S 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.

Once the rich solvent enters the regenerator, its hydrocarbon content is almost completely stripped and it enters the sulphur plant along with the acid gas. Low molecular weight hydrocarbons take up air demand and hydraulic volume in the sulphur plant, lowering sulphur recovery capacity and efficiency. BTEX aromatics are real troublemakers in sulphur plants and can lead to catalyst coking in units with acid gas feeds that are lean in H₂S.

With richer feeds, and especially oxygen-enriched units, temperature moderation 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 mol% 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, sulphide and bisulphide ions, carbonate and bicarbonate and, in the case of primary and secondary amines, amine carbamates. These are all ionic and result in a high total ionic strength. This 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 10 at high loadings.

This article aims to place hydrocarbon and fixed gas solubilities in amine-treating solutions on a solid, generalised footing. The intended result 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

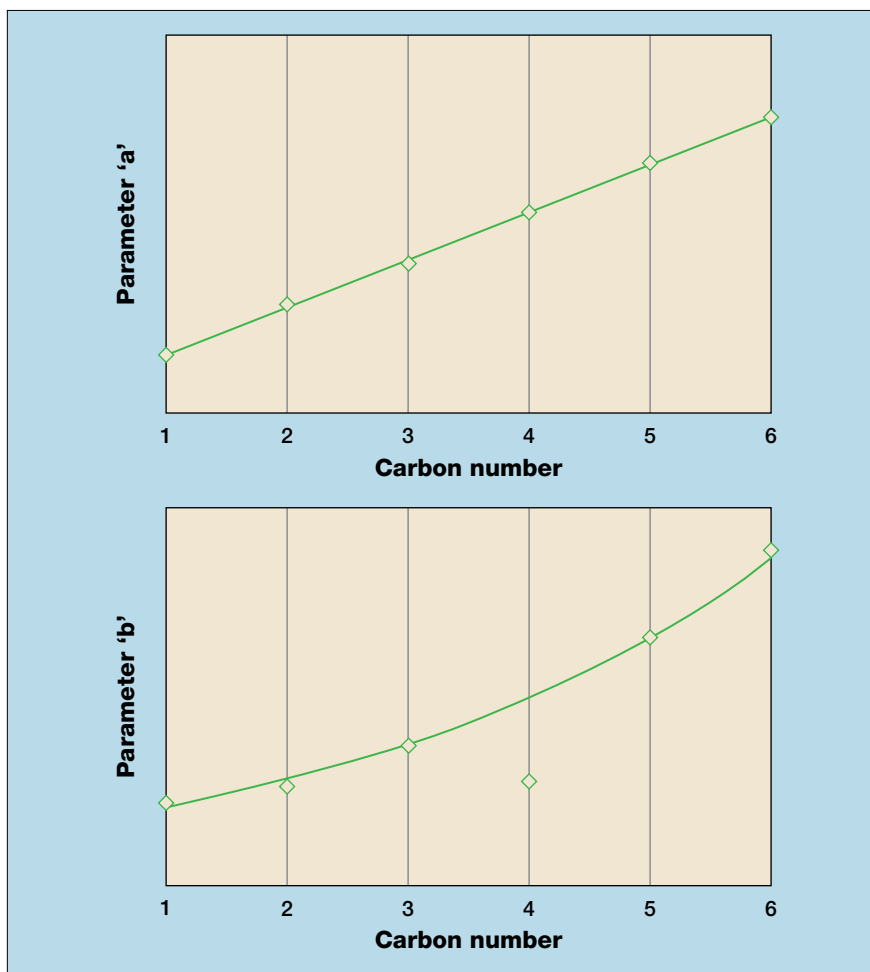


Figure 1 How a and b parameters in the Setschenow (1892) salting-in coefficient correlate with carbon number for the n-alkanes. The value of "b" for n-butane is anomalous and is likely to be wrong

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.

Modelling and theory

The basis for determining the solubility of any sparingly soluble gas, i , uses temperature-dependent Henry's Law data for pure water, H_i° and a Setschenow (1892) salting (in and out) coefficient S_i to compute the Henry's Law constant in the actual solution:

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

There is extensive literature on the Setschenow approach.⁴ 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 two terms. There is a contribution from the molecular amine (a salting-in contribution given by kC_a) and the various ions (salting-out contributions):

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

where I is the ionic strength. The system-dependent parameter h has anion, cation and gas contributions:

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

(Ionic strength is defined as $I = \frac{1}{2} \sum m_3 z_3^2$, where m_3 is the molality of the salt ion and z_3 is its charge number.)

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 bisulphide and sulphide ions, although no measurements appear ever to have been reported of the interactions of HS^- and S^{2-} with any soluble gas (a worthy subject for research).

Salting-in

First, it is important to recognise 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, for example, are made 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 co-workers have correlated the salting-in parameter for methane and ethane,³ propane⁶ and propylene⁷ 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: $k = a + bt(^\circ C)$. We have developed similar correlations for ethylene, n-butane, 1-butene, n-pentane, benzene, toluene and p-xylene using data provided confidentially by several solvent vendors.

For light hydrocarbons, 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, 104°F), which is close to many absorber bottom temperatures. In any event, the temperature dependence is weak for propane and propylene so, assuming the correction is temperature independent in those cases, where there are no 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; that is, increasing temperature sensitivity.

A summary of the model's correlation of the data presented in GPA RR-18013 and GPA RR-19510 for MDEA solutions is presented in Figure 2 as representative of the model's quality. Figure 3 provides a similar comparison for H₂ in MEA from Kling and Maurer's 1991 data.⁸

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 flavour for how well a fairly generalised 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 (for instance, Peng-Robinson or Redlich-Kwong-Suave), 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 (worthy subjects for research). In the next section, we shall see that when it comes to the effect of already dissolved acid gases — that is, acid gas loading — on hydrocarbon and fixed gas solubility, the data situation is no better, and in some ways worse.

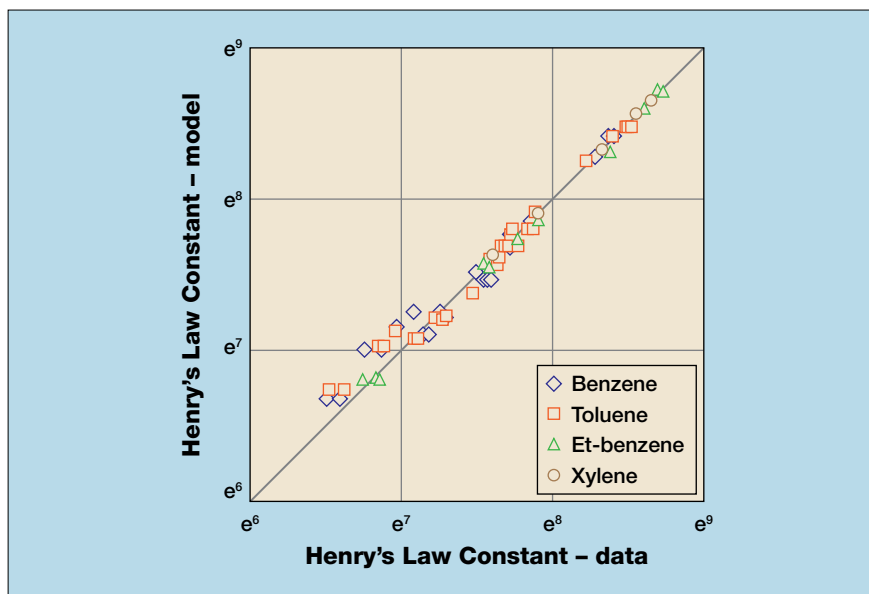


Figure 2 Goodness of fit of the Setschenow (1892) salting-in model to the GPA RR-180 solubility data for BTEX in MDEA from 25 to 120°C. Henry's Law constant is in units of Pa/(mole fraction)

Salting-out

Just as the amine tends to salt in non-polar compounds, a similar trend can be used for describing the salting-out effect that occurs from anions (h_-) and cations (h_+), with a possible contribution also from the soluble gas itself (h_g). The model used in the ProTreat simulator was fitted to the form originally attributed to van Krevelen below, with pairing or mixing rules established that fit the scant data available:

$$\log_{10} \frac{H_i}{H_i^0} = \log_{10} \left(\frac{1}{S_i} \right) = h_i = (h_+ + h_- + h_g)$$

Model validation

In principle, accurate measurements of the low-pressure flash gas produced in a flash tank 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 are 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 stabilises gas-

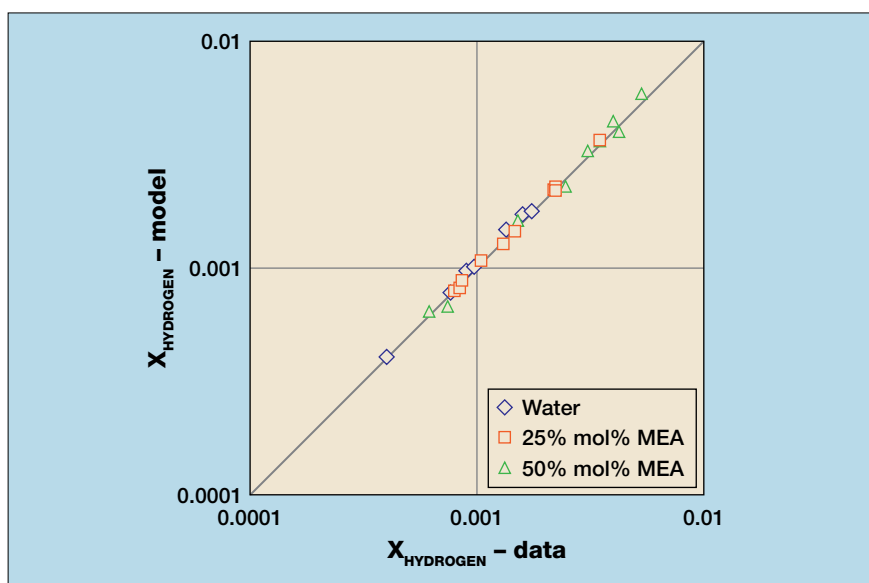


Figure 3 Goodness of fit of the Setschenow (1892) salting-in model to Kling and Maurer's (1991) solubility data for hydrogen in 25 and 50 mol% MEA

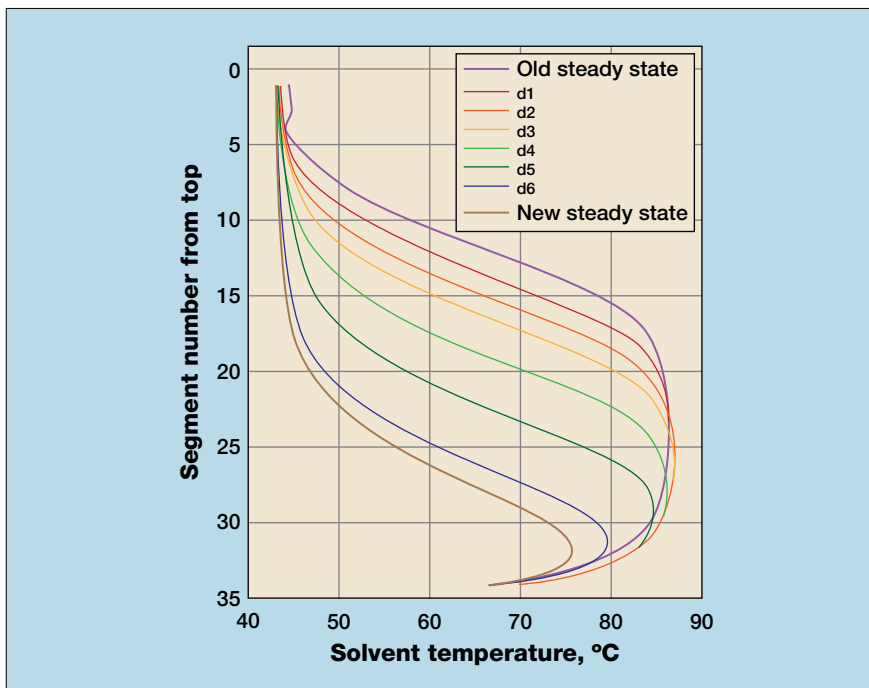


Figure 4 Progression of temperature profiles from one steady state to another

| Inlet gas analysis | | | |
|--------------------|-----------|------------|---------|
| Temperature, °F | 81–85 | | |
| Pressure, psig | 1040–1110 | | |
| Gas flow, MMscfd | 10.9–11.2 | | |
| Composition, mol% | | | |
| 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 |

Table 1

liquid mixtures. It stabilises 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 the effect of molecular weight and temperature.

Skinner, *et al.*¹² made accurate measurements of the VOC and BTEX components present in the flash gas and degassed solvent in a carefully operated DEA plant. The data ranges in the following tables

| n-C ₆ and BTEX in rich amine from flash tank, ppmw | | |
|---|----------|-------------------|
| | Measured | Generalised 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 |

Table 2

are shown as measured over an eight-hour data collection window. Table 1 shows inlet gas conditions.

Apart from the gas temperature (118°F, 48°C calculated by the ProTreat simulator versus 116–121°F, 46.7–49.4°C 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 generalised model predictions in Table 2. With the exception of ethyl benzene, the generalised solubility model is in solid agreement with the data. The rich amine CO₂ loading was 0.69 for this data set and, at this loading and 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 simply cannot be ignored.

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 generalised model, ProTreat calculated 0.023 MMscfd. Table 3 compares the flash gas analysis with the calculations of the generalised solubility model. For the most part, there is excellent agreement. It should be particularly noted that the CO₂ 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

| Flash tank make gas analysis | | |
|------------------------------|-----------|-------------------|
| | Measured | Generalised model |
| CO ₂ , mol% | 32.5 | 33.98 |
| Methane, mol% | 60.6 | 59.72 |
| Ethane, mol% | 4.4–4.8 | 4.82 |
| Propane, mol% | 0.68–0.73 | 0.96 |
| i-butane, mol% | 0.10–0.11 | 0.07 |
| n-butane, mol% | 0.14–0.15 | 0.18 |
| n-pentane, mol% | 0.03–0.04 | 0.073 |
| n-hexane, ppmv | 162 | 66 |
| Benzene, ppmv | 1000 | 900 |
| Toluene, ppmv | 521 | 466 |
| Et-benzene, ppmv | 17 | 12 |
| m,p-xylenes, ppmv | 95 | 64 |
| o-xylene, ppmv | 14 | 14 |

Table 3

salting-out was severe. The VOC, HAP and fixed gas solubility model is very strong and extremely well qualified to estimate BTEX and most hydrocarbon and fixed gas solubilities with rather high accuracy.

Commercial implications of salting-out

The solubility of benzene in a piperazine promoted MDEA solvent for CO₂ removal in an LNG plant is used 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.¹³ 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 4m-diameter LNG absorber with 16m of IMTP-50 random packing was initially operating under the conditions shown in Table 4. The column was simulated to be producing higher-than-specified CO₂ in the treated gas (1400 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.

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 behaviour of the column, because there is not a direct quantitative correspondence between the number of column

| 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, mol% | | Components | |
| CO ₂ | 5.83 | CO ₂ (loading) | 0.024 |
| C ₁ | 79.04 | MDEA, wt% | 35 |
| C ₂ | 8.26 | Piperazine, wt% | 9 |
| C ₃ | 1.58 | Water | Balance |
| iC ₄ | 0.13 | Wash water | |
| nC ₄ | 0.11 | Temperature, °C | 30 |
| iC ₅ | 0.02 | Pressure, barg | 55.16 |
| nC ₅ | 0.01 | Flow, kg/h | 3044 |
| Benzene | 0.91 | CO ₂ , ppmw | 1 |
| N ₂ | 3.98 | | |
| H ₂ O | 0.13 | | |

Table 4

iterations and time, it does represent a path along which the column could be expected to behave with time.

Figure 4 summarises the progression of the temperature profile over the arbitrary time intervals studied, while Figures 5 and 6 show the benzene concentration profile and the CO₂ 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 (ie, solubility in the amine) is greater at higher temperatures. Thus, higher temperatures mean 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 CO₂ loading profile inside the column is examined that this makes sense.

As Figure 6 shows, the benzene concentration explodes simultaneously with the collapsing CO₂ loading. No longer having a high CO₂ loading in the middle of the

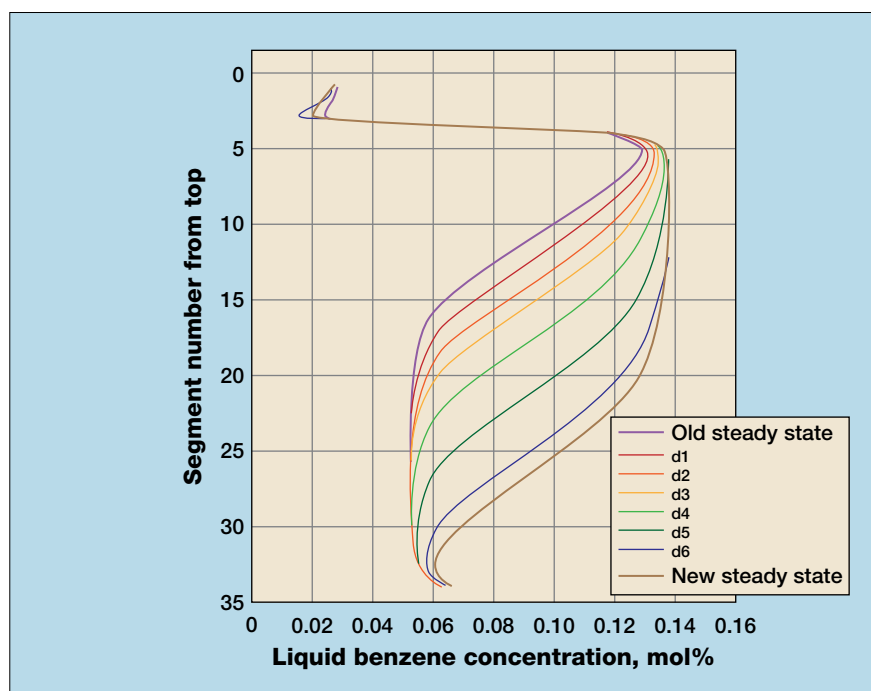


Figure 5 High benzene concentrations building up in the column

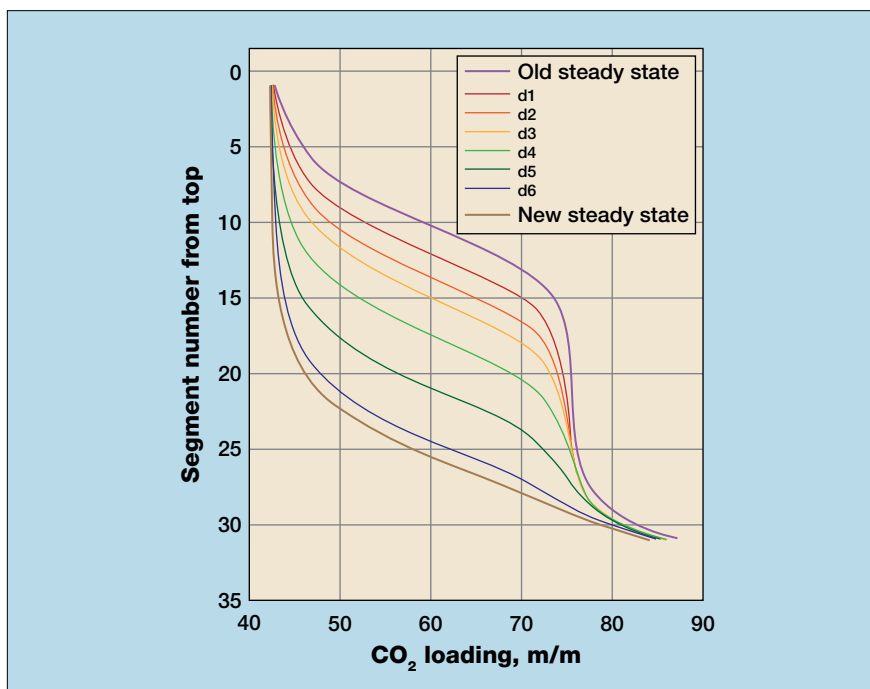


Figure 6 Approach of the CO₂ loading profile to the new steady state

column causes the salting-out effect to shrink dramatically because the lower ionic salt concentrations associated with lower loading cause less desolubilisation. This gives benzene an increased incentive to enter the amine solution and to exhibit much higher levels than when CO₂ 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.

The behaviour of this column may go some way towards explaining the old saying, well known to those who have regularly operated amine units: "Amine units do not like rapid changes". Any rapid change to feed gas CO₂ or H₂S 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 (for instance, an increase in the CO₂ level in the gas or a higher gas rate) will lead to an equally sudden lowering of the equilibrium hydro-

carbon content in a liquid that already 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 liquid hydrocarbon forms, an organic liquid phase will coalesce, surface tension at the 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 may 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 the collection of additional data, especially on the contribution of the sulphide and bisulphide forms of H₂S. This will be especially important for making predictions that can truly pass a rigorous test by regulatory authorities.

ProTreat is a mark of Optimized Gas Treating, Inc. DGA is a mark of Huntsman Corporation.

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