

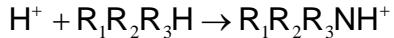
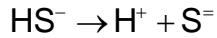
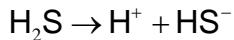
The CONTACTOR™

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Generic MDEA? When, and What Strength?

All amines are selective towards H₂S and most absorb H₂S at more or less the same rate. The selectivity of a particular amine is governed primarily by its chemical reaction rate with CO₂, but also to some extent by the mass transfer characteristics of the contacting device.

During absorption H₂S dissociates to form bisulfide and sulfide ions, and the amine soaks up the released hydrogen ions by neutralization:



Reactions involving hydrogen ions (protons) are instantaneous regardless of the amine, so H₂S absorption rates are not *directly* affected by the particular amine. But the rate of H₂S absorption is definitely affected by (1) mass transfer and (2) phase equilibrium.

H₂S mass transfer is completely controlled by resistance in the gas phase, so the gas-side mass transfer coefficient, k_{GA} , is the important mass transfer parameter, and whatever affects it will affect H₂S absorption. Examples of parameters that affect k_{GA} are gas-phase turbulence levels (type of tower internals) and system pressure.

The other important factor is the equilibrium partial pressure of H₂S over the solvent at local conditions, and this is affected by how much CO₂ is already in the solvent. Thus, too much CO₂ pickup will raise the H₂S backpressure and lower the driving force for H₂S absorption. CO₂ absorption, or more exactly CO₂ slip, will have a profound effect on H₂S removal, and CO₂ slip is all about selectivity.

Unlike H₂S, absorption of CO₂ is affected by (1) reaction kinetics, in addition to (2) mass transfer, and (3) phase equilibrium. To maximize CO₂ slip the amine should be completely

nonreactive towards CO₂ — MDEA fits the bill because it has an extremely small apparent reaction rate constant[†]. Because the reaction is so slow, it has hardly any effect on CO₂ absorption rates, so again what matters is mainly mass transfer and phase equilibrium effects. (This is in complete opposition to the premise on which an equilibrium stage model that purports to account for kinetics is based—see *The Contactor™ Vol. 4, Issue 4, 2010*.)

Absorption rates of CO₂ are controlled by mass transfer resistance in the liquid phase. That's why some amines (such as MDEA and DIPA) are more selective than others (MEA, DGA, DEA for example). DIPA forms a carbamate but it reacts slowly compared with MEA. But MDEA's apparent reaction rate constant is extremely small. Chemical reaction affects liquid-phase mass transfer, and the faster the reaction rate, the larger the effective liquid-side mass transfer coefficient, k_{LA} . Temperature affects the apparent rate constant for MDEA, so k_{LA} is affected, too. But the effect is small because reaction improves the k_{LA} value only a little. Of course, vapor-liquid equilibrium (VLE) continues to play an important role also, and VLE is affected by temperature, amine strength, and the relative liquid loadings of H₂S and CO₂. Heat stable amine salts also affect VLE.

From a mass transfer standpoint, it's obvious that selectivity will be maximized by choosing a solvent that does not react with CO₂. The most obvious choice is MDEA. Unfortunately, for many of us, MDEA has come automatically to mean 50 wt% regardless of the application, but there are lots of instances where the highest strength is not the best choice. Examples include both selective treating as well as straight CO₂

[†] The apparent rate constant is not zero because MDEA slightly catalyzes the bicarbonate ion formation reaction—MDEA is tertiary and does not react directly with CO₂.

removal where MDEA is being considered because of lower regeneration energy needs. Should a high- or low-strength solvent be used? Does it really make that much difference? One of the parameters that can make a difference is solvent viscosity. The resistance to CO₂ absorption is high if $k_{L}a$ is high, and it can be made higher by using a solvent with high viscosity. As Figure 1 shows, this means the highest practical strength. But moderately targeted

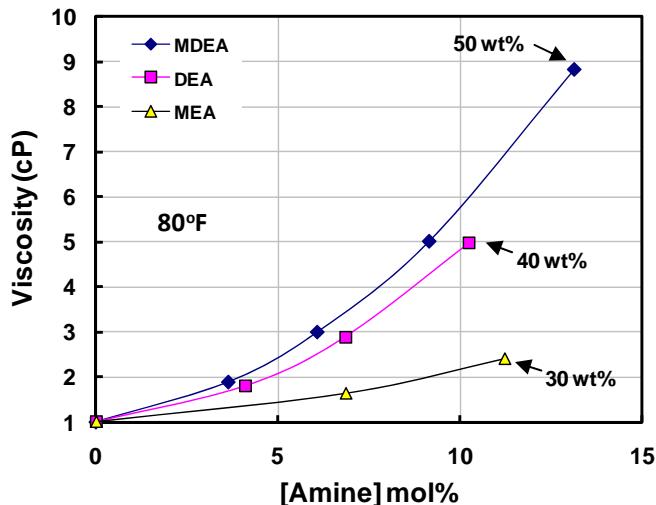


Figure 1 How solvent viscosity depends on strength: MEA, DEA & MDEA at 80°F

selectivity is sometimes desired and in these instances high strength is not necessarily best.

Case Study

A slightly sour gas (150 ppmv H₂S and 5.5% CO₂) is to be treated to < 4 ppmv H₂S and 3% CO₂, then combined with other gas streams before entering the gas transmission line. Gas pressure is 900 psig. A 10°F temperature approach in the lean-rich exchanger is assumed and the solvent flow and reboiler duty are held constant throughout the following comparisons.

The first pass at the design of a 20-tray contactor used 50 wt% MDEA and gave 3.5 ppmv H₂S in the treated gas, but it only got the CO₂ down to 3.3%. Since 50 wt% MDEA fails to work, the designer decided to try boosting the CO₂ kinetics and increasing CO₂ absorption rate by replacing a small amount of the MDEA with an equally small amount of piperazine additive (1.5 wt% piperazine and 48.5 wt% MDEA). But piperazine is such a highly effective promoter that the CO₂ was over absorbed (2.4% in the treated gas) with the result that H₂S could not be reduced below 9.3 ppmv.

This is a direct effect of higher chemical reaction rate, i.e., it's a chemical kinetics effect.

Knowing that high solvent viscosities cause lowered liquid-phase mass transfer coefficients and have a detrimental effect on CO₂ absorption, the suggestion was made to reduce the MDEA strength to 30 wt%. With 30 wt% MDEA, the gas was simulated to treat to 3.3 ppmv H₂S and 2.97% CO₂, meeting both treating goals simultaneously. Could this be an effect of the reduced kinetic rate due to lower amine concentration, or is it mass transfer? The kinetics is already extremely slow and CO₂ absorption is not being enhanced significantly by reaction, so reducing what little reaction rate there is can hardly have much impact. But, as Figure 2 shows, solvent viscosity in the contactor is much reduced. The viscosity of 50 wt% MDEA is 2 to 3

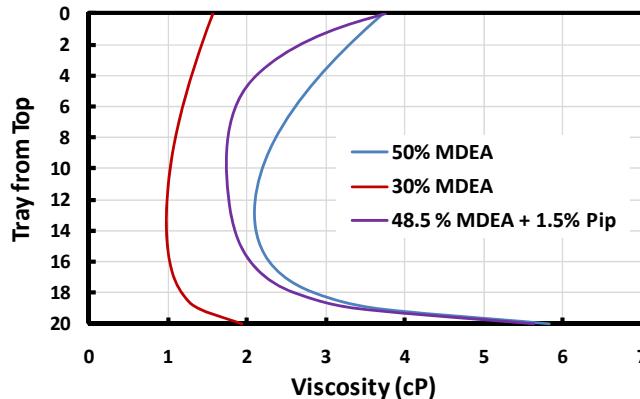


Figure 2 Solvent viscosity profiles in contactor

times higher than 30% solvent. One might have expected the piperazine promoted MDEA to have about the same viscosity as the 50% solvent; however, the extra absorption of CO₂ by piperazine also causes higher temperatures throughout the contactor and this lowers viscosity.

There are two lessons to be learned: (1) 50 wt% MDEA is not the only strength at which MDEA can be used. High strength solvents can be quite viscous, which is detrimental to CO₂ absorption, and (2) Promoters, additives and specialty amines are not always the best first line of defense—there is no substitute for thoughtful consideration and an understanding of what makes amine systems tick.

To learn more about this and other aspects of gas treating, plan on attending one of our seminars. Visit www.ogrt.com/seminars.cfm for details.

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