The CONTACTOR™

Published Bimonthly by Optimized Gas Treating, Inc.
Volume 6, Issue2, March, 2012

VOC and HAP Emissions

Regulated pollutants include volatile organic compounds (VOCs) such as hexane, and Hazardous Air Pollutants (HAPs) mainly benzene, toluene, ethylbenzene and the xylenes (the so-called BTEX components). ProTreat® accurately models the solubility of these chemicals in all amine treating solutions and triethylene glycol (TEG) dehydrating agent Solubility models are based on the results of GPSA research projects; in other words, on the gold standard of measured VOC/HAP and HC data. But ProTreat goes a step further—it accurately accounts for acid gas solvent loadings on HC and VOC/HAP solubility.

The ProTreat solubility database for these kinds of components consists of various GPSA research reports, specifically RR-131 for solubilities in TEG, RR-137 and RR-149 for MEG (available soon in Version 5.2), and RR-161, RR-180, and RR-195 for amines plus about 20 data sources in the literature[†].

The root of all thermodynamic information lies in laboratory measurements but to be used in process simulation, the data must be converted to a computational model that accurately represents and reproduces the underlying data. The ProTreat solubility model rests on Henry's Law of solubility of gases in liquids. It is modified to account for vapor-phase nonideality through the Peng-Robinson equation of state (EOS). Liquid phase nonideality is handled by an activity coefficient model in the case of TEG, and by Setchenov[‡] salting-in and salting-out parameters for amines. The salting-*in* parameter accounts for the higher solubility of most gases in amines compared with water (the amine is organic and has higher solubility for organic gases than water does). The salting-*out* parameters account for reduced solubility in the presence of substantial concentrations of various ions.

The sum and substance of all this is that ProTreat models very accurately the solubilities of gases in amines and glycols, and accounts for the effect of acid gas loading, amine concentration, temperature and even heat stable salts. Models are regressed to all the GPSA research report data (the gold standard) and therefore can be expected to predict VOC and HAP emissions accurately.

Figure 1 is a comparison between ProTreat calculated solubilities of BTEX in TEG (lines in the figure) and the solubility data reported in RR-131. It

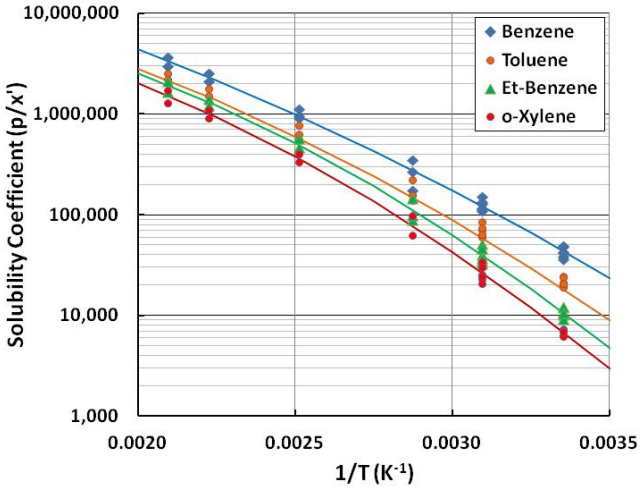

Figure 1 Solubility of BTEX in TEG Solutions

can be seen that as one should expect from a realistic model, the predicted behavior exactly tracks through the center of the data for each of the BTEX components shown. This is an activity coefficient model that correctly accounts for interactions between the dissolved gases and the

[†] e.g., Carroll, J.J. & A.E.Mather, J. Chem. Eng. Data, *43*, 781 (1998); Carroll, J.J. & A.E.Mather, AIChE Journal, *37,* 511 (1992); Jou, F.-Y., J.J.Carroll & A.E.Mather, Fluid Phase Equilibria, *116,* 407 (1996).

[‡] Setchenov, M., Ann. Chim. Phys., Über die Konstitution der Salzlosungen auf Grund Ihres Verhaltens zu Kohlensäure, *25*, 226 (1892).

(moisture-containing) TEG. The non-aromatic hydrocarbons to C8 use the same model.

Figure 2 is a sample plot comparing the ProTreat model for benzene solubility in Benzene-Toluene-EthylBenzene-MDEA mixtures with data from RR-180. On average, predicted K-values (ratio of y_i/x_i) are within about 5% of measured data. The results shown here are quite typical of K-value correlations for all VOCs and BTEX components in MDEA and all other amines.

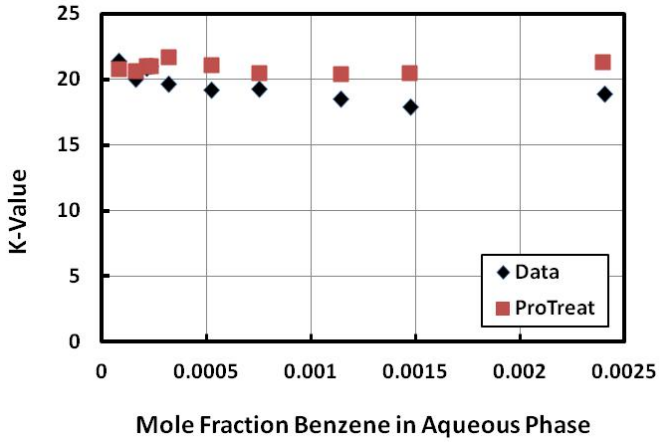

Figure 2 Predicted and Measured K-values for Benzene in BTEX-MDEA-H_2O at 0.5 MPa and 333K

The following case[§] Is the basis for a comparison with ProTreat® predictions of the disposition of VOC and BTEX measured in a DEA plant. The data ranges In the following tables are shown as measured over an 8 hour data collection window. Table 1 shows inlet gas conditions.

Table 1 Inlet Gas Analysis

Temperature (°F)		81–85	
Pressure (psig)		1040–1110	
Gas Flow (MMscfd)		10.9–11.2	
Composition (mol%)			
Water	0.00532	n-Pentane	0.456
CO2	6.9	n-Hexane	0.07
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 by ProTreat vs. 116–121°F measured) nothing else concerning the treated gas is reported. However, the measured n-C6 and BTEX content of the rich amine leaving the absorber is compared with ProTreat predictions in Table 2

Table 2 n-C6 and BTEX in Rich Amine (ppmw)

	Measured	ProTreat®
n-Hexane	nd–0.02	0.238
Benzene	23–27	31.06
Toluene	10–14	18.32
Et-Benzene	0.2–0.4	0.439
m,p-Xylenes	1.6–2.6	2.28
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 flow was estimated at 0.025 MMscfd at the plant site—ProTreat calculated 0.0229 MMscfd. Table 3 compares the flash gas analysis with ProTreat simulation. For the most part there is excellent agreement. It should particularly be noted that the CO_2 loading of the rich amine was 0.68 at an amine strength of 21.4 wt% so the ionic concentration was quite high and salting out was severe. ProTreat's VOC, HAP and hydrocarbon model is quite strong. ProTreat is well qualified to estimate reliably BTEX and most hydrocarbon and inert-gas solubilities.

Table 3 Flash Gas Analysis

	Measured	ProTreat
CO_2 (mol%)	32.5	33.2
Methane (mol%)	60.6	58.35
Ethane (mol%)	4.4–4.8	4.67
Propane (mol%)	0.68–0.73	0.939
i-Butane (mol%)	0.10–0.11	0.068
n-Butane (mol%)	0.14–0.15	0.17
n-Pentane (mol%)	0.03–0.04	0.07
n-Hexane (ppmv)	162	64
Benzene (ppmv)	1,000	880
Toluene (ppmv)	521	455
Et-Benzene (ppmv)	17	11.7
m,p-Xylenes (ppmv)	95	62
o-Xylene (ppmv)	14	13.9

~.~

Plan to attend our workshop in Abu Dhabi (25–26 March 2012) or a free seminar in Houston, Denver, Calgary and elsewhere. For details, visit www.ogtrt.com/seminars

ProTreat® and ***The Contactor***™ are trademarks of Optimized Gas Treating, Inc.

[§] Skinner, F.D., D.L.Reif, & A.C.Wilson, *BTEX and Other VOC Emissions from a Natural Gas Amine Treater*, Topical Report to Gas Research Institute, GRI Project Number 5094-220-2796, Feb 1996.