

# New gas-water-TEG equilibria

## Gas dehydrators give improved dew point depression when using higher concentrations of triethylene glycol

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NATURAL GAS DEHYDRATION can be required for product specifications well below the conventional 4 to 7 lb/MMscf limit. Most existing triethylene glycol (TEG) design and rating programs use outdated equilibrium data and are not well-suited for getting high dew point depression.

With the improvement in analytical tools available for measurement at low concentrations, considerably improved equilibrium data are now available. This article discusses the equilibrium data used in previous programs along with the evolution of an updated, more accurate program. New predictions are compared with actual operating data. The results show that tools are now available to the hydrocarbon processing industry to predict the interaction between TEG and water vapor in natural gas over a broader range, thereby allowing designs for ultra-low dew point applications to be made with confidence.

### PREVIOUS PROGRAM

Gas dehydrators commonly use TEG. In these dehydrators, the natural gas is contacted with lean TEG, typically in countercurrent absorbers with bubble cap trays or packing. Calculations to determine the number of trays or feet of packing, the required glycol concentration, or the glycol circulation rate, are performed as other typical absorption processes—requiring vapor-liquid equilibrium data.

In absorption calculations, the equilibrium data is expressed usually in terms of component K-values as follows:

$$K = y_w/x_w \quad (1)$$

where

$K$  = equilibrium ratio of water

$y_w$  = mol fraction of water in gas phase

$x_w$  = mol fraction of water in lean glycol

The K-values can be calculated directly from equilibrium data or from various thermodynamic models such as liquid activity correlations or equations of state.

The most commonly used data available in the literature are the equilibrium dew point curves for the natural gas-water-TEG system reported by Worley.<sup>1</sup> These curves were developed in 1966 and are published in the latest edition of the GPSA Engineering Data Book (10th Edition, 1987, Fig. 15-15, represented in Fig. 1 as solid lines). The curves were derived by extrapolating data from field-size pilot plants to an infinite number of trays and to infinite glycol rates. To use

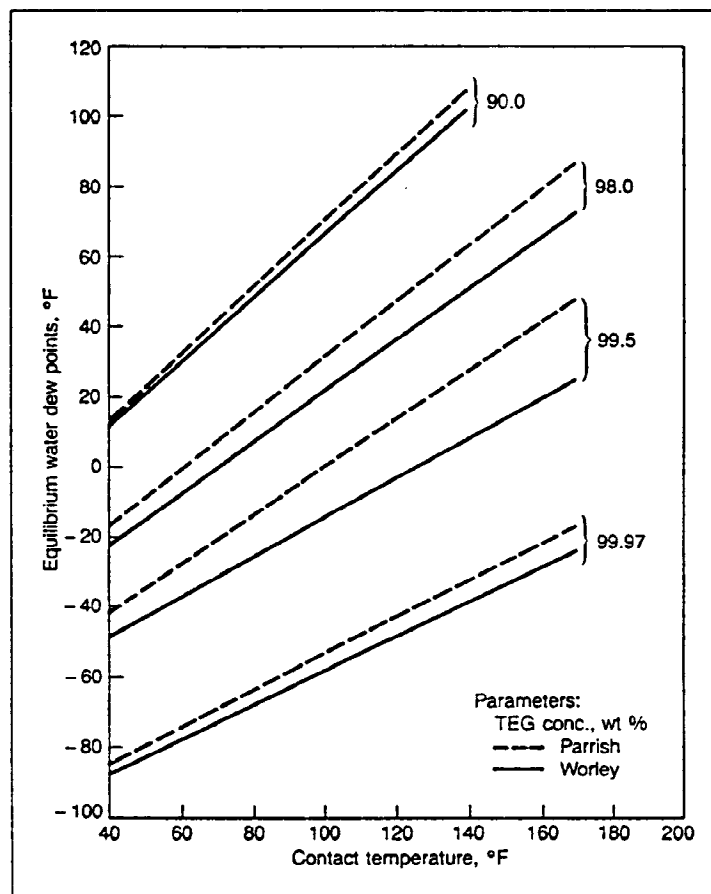


Fig. 1—Worley's curves (solid lines) used for later comparison with Parrish data (dashed lines).

these curves in dehydrator calculations, K-values are determined by correlating the equilibrium dew point curves with natural gas water content data such as that of McCarthy, et al.,<sup>2</sup> McKetta and Wehe<sup>3</sup> or Bukacek.<sup>4</sup>

Using activity coefficients, an alternative method of calculating K-values for TEG absorbers was developed in 1961 by Scauzillo.<sup>5</sup> Scauzillo used the experimental equilibrium data of Townsend<sup>6</sup> and of Wise, et al.,<sup>7</sup> for the natural gas-water-TEG system to calculate activity coefficients of water in the liquid phase. Townsend's data revealed that the ratio of the water content in equilibrium with a glycol solution to that of the saturated gas was essentially constant for any given glycol concentration. Furthermore, this ratio was equal to the activity of water in the TEG solution, independent of pressure and not significantly affected by temperature in the range of interest. Thus, using the following Eq. 2, Scauzillo derived the expression for the K-values shown in Eq. 3 as follows:

$$\gamma_1 = W_g/(W_1 x_w) \quad (2)$$

$$K = (2.105)(10^{-5})(W_1)(\gamma_1) \quad (3)$$

where

$\gamma_1$  = activity coefficient of water in liquid phase

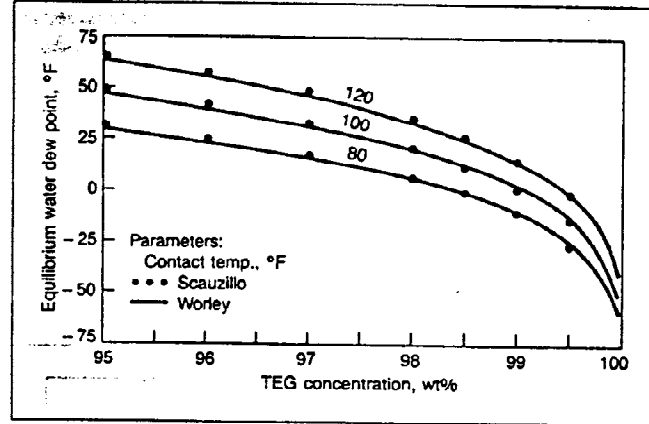


Fig. 2—Dew points calculated by Scauzillo's method ( $P = 1,000$  psia) agree well with Worley's curves.

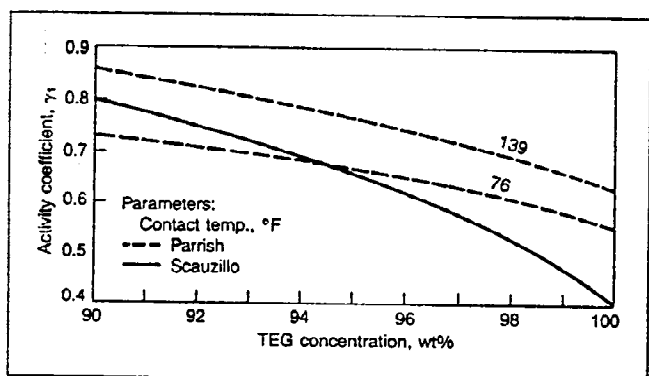


Fig. 3—Scauzillo's activity coefficients for TEG versus water compared with Parrish's data.

$W_g$  = water content in gas phase in equilibrium with lean TEG, lb/MMcf

$W_1$  = water content in gas phase at saturation, lb/MMcf

$x_w$  = mol fraction of water in liquid phase

Using water content data of McCarthy, et al., and K-values calculated by the method just described, Scauzillo presented a graph showing equilibrium dew points available with glycol concentrations of 60 to 99.9 wt% and in the temperature range of 40 to 120°F. Scauzillo's dew point curves closely fit the curves presented by Worley in 1966 as shown in Fig. 2.

Fig. 2 represents the same equilibrium data as in Fig. 1, presented differently to show the minimal disparity between the Scauzillo calculations and the curves presented by Worley.

The author's original program used the Scauzillo method of calculating K-values as its equilibrium basis. Eq. 3 provided a simple means to calculate the equilibrium K-value by use of the activity coefficients which were obtained by curve fitting Scauzillo's original activity coefficient plot shown as a solid line in Fig. 3.

**Absorption calculations.** The major calculation required for TEG units is to determine the circulation rate required to achieve a given dew point depression with a given concentration and number of trays. There are various methods for making this absorption calculation.

Although tray-to-tray calculations could have been performed, the equilibrium data was not believed to be of sufficient accuracy to warrant the effort. Additionally, personal computers at that time were not fast enough to allow the tray-to-tray calculations. Other simplified methods were

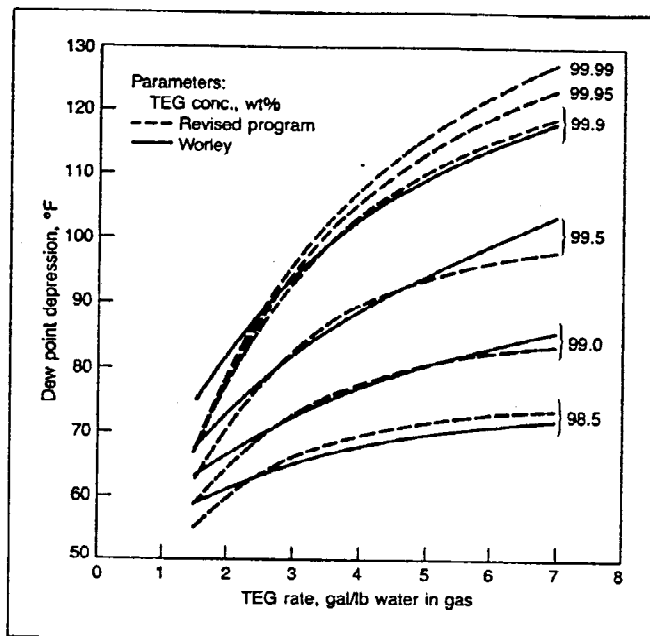


Fig. 4—Example with 6 actual trays and 100°F contact temperature shows effect of higher TEG concentration.

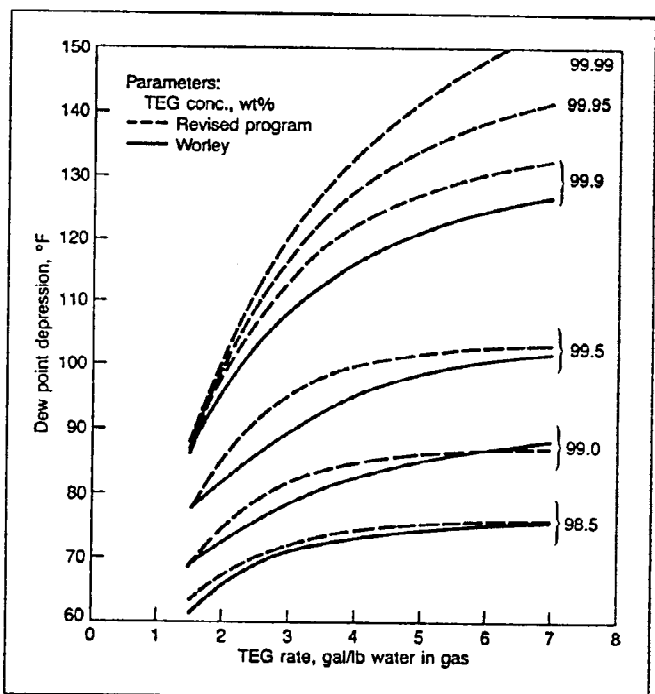


Fig. 5—Example with 8 actual trays, 100°F contact temperature and extended to higher TEG concentrations.

available, such as the McCabe-Thiel graphical method and the Sherwood method.

However, the often used Kremser-Brown method was selected since it is rather accurate for TEG contactor calculations due to the essentially constant absorption factors over the entire column. The accompanying box, "The Kremser-Brown method," provides more details on the reasons for this constant value as well as how the equation is used in the calculations.

**Comparison to actual data.** To determine the accuracy (or indeed the applicability) of a calculation method, one needs to be able to compare the computed results with actual operating data. In our literature search and in discussions with

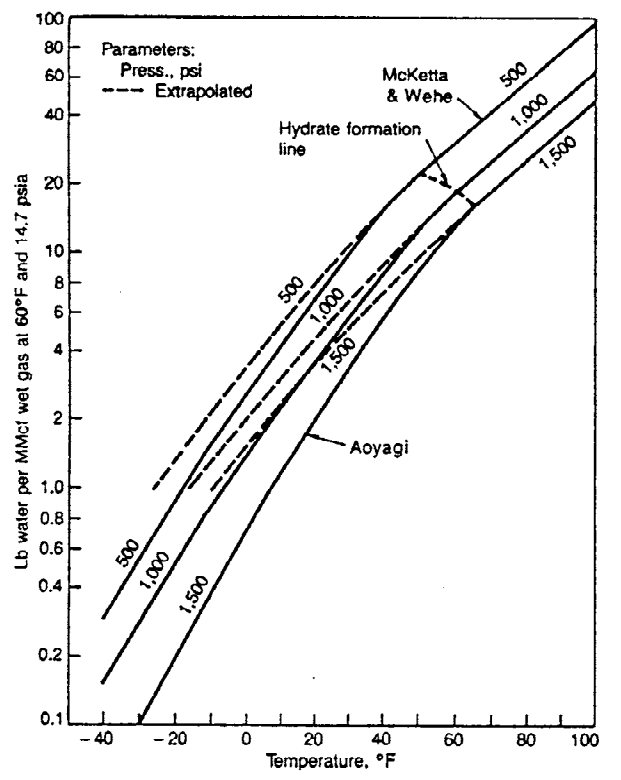


Fig. 6—Water content below hydrate point adjusted by extrapolating earlier data.

operating engineers at major oil companies, we were unable to obtain any more complete data than that of Worley—the same data from which the GPSA equilibrium curves were generated. Worley's data, expressed as operating curves for actual TEG contactors, are reproduced in Figs. 4 and 5 (GPSA Figures 20-40 and 20-41) for 6 and 8 actual trays, respectively. Note that these curves are applicable for 100°F contact temperatures only. Although the curves are 25 years old (1966), they are considered accurate up to lean TEG concentrations of 99.9%. However, extrapolations to higher concentrations have much uncertainty.

Numerous calculations were made with the original glycol program, using the Scauzillo equilibrium data, to provide results for comparison with the Worley operating curves and with more limited data from glycol unit manufacturers. Using the Kremser-Brown method with a constant tray efficiency, poor agreement was initially obtained between the program results and the operating data. However, after incorporating a correlation to adjust the overall column efficiency based on concentration driving forces and other operating parameters, excellent agreement was obtained between the program results and actual operating data.

Many glycol units were designed with this earlier version of the program, which allowed more alternatives to be considered with minimal engineering effort. Increasing confidence in the design program allowed engineers to design units with less excess capacity, thereby reducing capital and operating costs.

## REVISED PROGRAM

Although the earlier program provided exceptional results as compared to the actual field data, there was some concern as to its accuracy at higher glycol concentrations. With publication

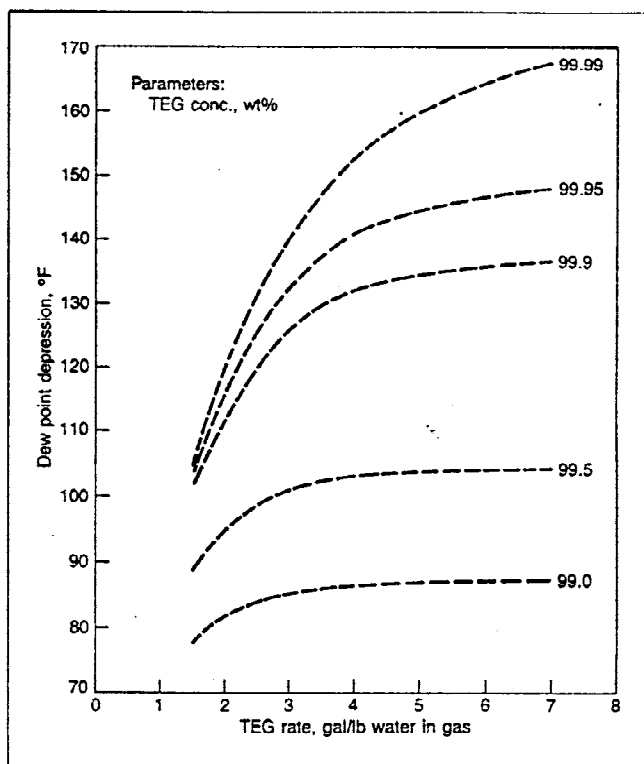


Fig. 7—Example with 10 actual trays, 100°F contact temperature and extended to higher TEG concentrations.

of new, broader ranged equilibrium data by Parrish, et al.,<sup>8</sup> there arose much interest in modifying the program to include the new data which would conceivably allow more accurate calculations for low dew point applications.

Earlier Figs. 1 and 3 show comparisons for the equilibrium values and activity coefficients, respectively, between the newer equilibrium data (dashed lines) and that of Worley (solid lines). The Parrish dew point curves were generated for low pressure systems by using their experimental activity coefficients with a method of equating the vapor phase and the liquid phase fugacities (Appendix B of the Parrish paper). In this method, the water vapor fugacity coefficient ( $\phi^{V_w}$ ) and the Poynting correction factor for the liquid (the exponential term shown later in Eq. 5) were assumed to be unity.

To determine what effects using the activity coefficients given by Parrish might have, equilibrium dew point curves were generated using the Parrish activity coefficients with Eq. 3 and water content data of Bukacek. The calculated dew point values were considerably divergent from the equilibrium dew point curves presented by Parrish, particularly at increasing pressure. Thus, it was concluded that the Parrish dew point curves were not applicable to the high pressure natural gas-water-TEG system, although the experimental activity coefficients for water were considered to be valid and necessary for use in upgrading the equilibrium basis of the program.

**New data for water content.** The initial attempt to use the activity coefficients in the absorption calculations involved the calculation of K-values using the calculation of the fugacity coefficient of water vapor ( $\phi^{V_w}$ ) and the Poynting correction factor as follows:

$$f_w^V = \phi_w^V y_w P \quad (4)$$

$$f_w^L = \gamma_w x_w f_w^{OL} \exp(-PV_w/RT) \quad (5)$$

## The Kremser-Brown method . . .

This method for absorption calculations was used for the following reasons:

- Good agreement when compared to known operating data
- Simplicity and minimal computing time when compared to tray-to-tray calculations
- Accuracy when compared to the Edmister method.

The Kremser-Brown method is based on the following two equations:

$$\frac{Ae^{N+1} - Ae}{Ae^{N+1} - 1} = \frac{y_{n+1} - y_1}{y_{n+1} - y_0} \quad (A)$$

$$Ae = L_d(V_{n+1} K) \quad (B)$$

where

- $Ae$  = average effective absorption factor
- $N$  = number of theoretical trays
- $y_{n+1}$  = mols of absorbed component in inlet gas
- $y_1$  = mols of absorbed component in outlet gas
- $y_0$  = mols of absorbed component in outlet gas at equilibrium
- $L_0$  = mols of lean absorbent
- $V_{n+1}$  = mols of rich gas in inlet
- $K$  = equilibrium value at column conditions (lean glycol in contact with saturated gas).

The right side of Eq. A is normally called the absorption efficiency. Once the absorption factor ( $Ae$ ) has been determined, Eq. B can be used to calculate the circulation rate of the lean absorbent (TEG).

The Kremser-Brown method has the following shortcomings:

- Assumes a constant temperature
- Assumes a constant  $L/V$  ratio
- Assumes an average equilibrium value.

Their insignificance is evidenced by the accuracy of the Kremser-Brown versus the Edmister method.

where

- $f_w^V$  = fugacity of water in vapor phase, psia
- $f_w^L$  = fugacity of water in TEG-water solution, psia
- $\phi_w^V$  = fugacity coefficient of water in vapor phase
- $y_w$  = mol fraction of water in gas
- $x_w$  = mol fraction of water in liquid
- $\gamma_w$  = activity coefficient
- $f_w^{OL}$  = standard state fugacity of water, psia
- $P$  = system pressure, psia
- $T$  = system temperature, °R
- $V_w$  = partial molar volume of water in TEG-water solution, ft<sup>3</sup>/mol

However, the operating curves generated by this method predicted dew point depressions (based on Bukacek water content data) which were in poor agreement with the Worley operating curves, even at the lower glycol concentrations.

To determine if the Kremser-Brown absorption calculation method was at fault, the Edmister method (a modified Kremser method using an average of the top and bottom absorption factors) was used along with tray-to-tray calculations. Neither of these methods plotted well against the Worley curves, even with the column efficiency correlation used in the previous program or other similar type adjustments.

In trying to determine the reason for the discrepancies, a literature search provided a paper by Aoyagi, et al.<sup>9</sup> that contained more accurate values of the equilibrium water content in natural gas below the hydrate point. Typical water content correlations provide the "metastable" equilibrium value; i.e., the vapor phase in equilibrium over a subcooled liquid. The true hydrate equilibrium values are lower, being the equilibrium value over ice (Fig. 6). The new data were used to obtain actual dew points for calculating the dew point depression and the equilibrium dew point. Although the new

data are for 500, 1,000 and 1,500 psi, this is not limiting, since this is the range of operation of the majority of glycol units.

**Comparison with actual data.** With the new water content data entered into the program, we were able to get exceptionally good agreement between the program results and the Worley curves with all three calculational methods (the Kremser-Brown, Edmister and tray-to-tray calculations) without any correlations for adjusting the column efficiency.

Figs. 4 and 5 show the Worley data (solid lines) versus the values calculated by the program (dashed lines). These curves were calculated with the Kremser-Brown method using an overall column efficiency of 30%.

The curves match well in normal dew point depression ranges but begin to diverge slightly in the extended ranges due to the effect of the newer equilibrium data. Since the agreement is good in the normal operating ranges, we believe the curves beyond the data of Worley to be realistic. Additional curves for 99.95% and 99.99% TEG concentrations are also shown in Figs. 4 and 5. To demonstrate the higher dew point depression calculations, Fig. 7 provides circulation rate curves for the same conditions but with 10 trays.

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## LITERATURE CITED

- 1 Worley, M. S., "Super Dehydration with Glycol," Proceedings of the Gas Conditioning Conference, The University of Oklahoma, Norman, Okla., 1967.
- 2 McCarthy, E. L., Boyd, W. L. and Reid, L. S., "Water Vapor Content of Essentially Nitrogen-free Natural Gas Saturated at Various Conditions of Temperature and Pressure," *AIChE*, Vol. 189 (1950), p. 241.
- 3 McKetta, J. J. and Wehe, A. H., cited by GPSA Engineering Data Book, Fig. 20-h Edition, First Printing, Gas Processors Suppliers Association, Tulsa, Okla., 1987.
- 4 Bukacek, R. F., "1982 Annual Book of ASTM Standards," Part 26, ASTM, Philadelphia, Pa., p. 48.
- 5 Scanzillo, F. R., "Equilibrium Ratios of Water in the Water-Triethylene Glycol-Natural Gas System," *Journal of Petroleum Technology*, July 1961, p. 697.
- 6 Townsend, F. M., "Vapor-Liquid Equilibrium Data for DEG and TEG Water-Natural Gas Systems," Proceedings of the Gas Conditioning Conference, The University of Oklahoma, Norman, Okla., 1953.
- 7 Wise, H., Puck, T. T. and Failey, C. F., "Studies in Vapor Liquid Equilibria. II. The Binary System Triethylene Glycol-Water," *J. Phys. Chem.*, Vol. 54 (1950), p. 734.
- 8 Parrish, W. R., Won, K. W. and Baltatu, M. E., "Phase Behavior of the Triethylene Glycol-Water System and Dehydration/Regeneration Design for Extremely Low Dew Point Requirements," Proceedings of the Sixty-Fifth Annual Convention, Gas Processors Association, San Antonio, Texas, 1986.
- 9 Aoyagi, K., Song, K. Y., Sloan, E. D., Dharmawardhana, P. B. and Kobayashi, R., "Improved Measurement and Correlation of the Methane Gas in Equilibrium With Hydrate," Proceedings of the Fifty Eighth Annual Convention, Gas Processors Association, San Antonio, Texas, 1979.

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