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Present status of the group contribution equation of state VTPR and typical applications for process development

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ABSTRACT

For the development and design of industrial processes the reliable knowledge of thermophysical properties, in particular phase equilibria is most important. Assuming that 1000 components are of technical interest, vapor-liquid equilibrium data for approximately 500,000 binary systems are needed to fit all required binary interaction parameters. Due to the fact that the measurement of all needed properties is nearly impossible, the process engineer depends on factual data banks.

Besides the different phase equilibria, the Dortmund Data Bank as worldwide largest factual data bank for thermophysical properties contains nearly all worldwide available pure component, excess and transport properties. Although more than 66,300 binary VLE data sets for non-electrolyte systems are currently stored in the DDB, in total up to now VLE data for only 13,540 different binary systems are available. The reason is that some systems are very popular and were measured very often, e.g. ammonia – water, ethanol-water and so on. When the 1000 most important components are considered, VLE data for only 8635 binary systems are available. This means for only 1.73% of the systems the required binary interaction parameters can be fitted. Since the assumption of ideal behavior for the missing binary systems can be very erroneous and measurements are very time consuming, predictive group contribution models can be successfully applied to estimate the missing thermophysical properties.

To cover sub- and supercritical conditions, group contribution equations of state have to be applied. They automatically take into account both phases and can be used up to high pressures and supercritical conditions. This allows for example the calculation of phase envelopes. Furthermore, the introduction of Henry coefficients for gaseous compounds is not required. At the same time, enthalpies, heat capacities, densities and so on can be predicted. Today the most sophisticated group contribution equation of state is the volume translated Peng-Robinson group contribution equation of state VTPR. In this paper, typical applications of VTPR for process development are shown and new parameters for 24 additional group combinations are given.

1. Introduction

The volume translated Peng-Robinson group contribution equation of state, VTPR, was already discussed in detail in former publications [1–4] and its performance was demonstrated comparing prediction results with results obtained using the predictive Soave-Redlich-Kwong group contribution equation of state, PSRK [5], and mod. UNIFAC (Do) [6]. Already for a lot of group pairs, VTPR group interaction parameters have been published [7,8]. This paper demonstrates the applicability of VTPR in the area of process design. Nevertheless, a short introduction should be given.

The volume translated Peng Robinson group contribution of state

$$P = \frac{R \cdot T}{(v + c - b)} - \frac{a(T)}{(v + c) \cdot (v + c + b) + b \cdot (v + c - b)} \quad (1)$$

is the result of a systematic further development of the predictive Soave-Redlich-Kwong group contribution equation of state [9]. With the development of VTPR, most of the weaknesses of PSRK could be removed. The introduction of the Twu – alpha function to

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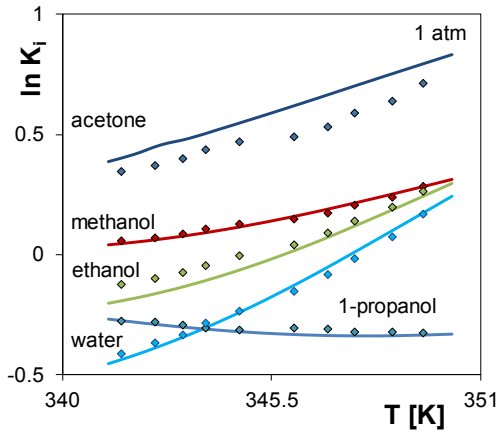

Fig. 1. Experimental data (◆) [17] and predicted K-factors for (by-)products of the Fischer-Tropsch synthesis using VTPR (–).

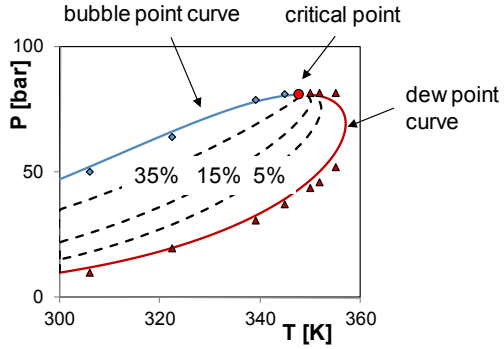

Fig. 2. Experimental data (◆, ▲) [15] and calculated phase envelope of the binary system carbon dioxide (x_1 = 0.7102 [mol/mol]) – *n*-butane (x_2 = 0.2908 [mol/mol]) using VTPR (–). The percentage indicates the amount of the liquid phase in the two phase region.

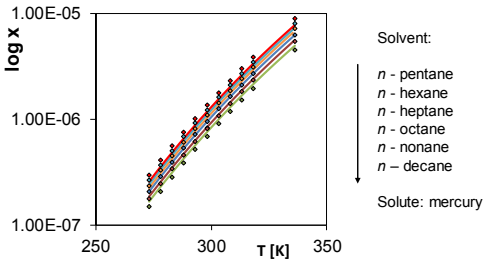

Fig. 4. Experimental (◆) [15] and predicted data for the solubility of mercury in *n*-alkanes using VTPR (–).

take into account the temperature dependency of the attractive parameter *a* [10,11] leads to better results at high reduced temperatures. Furthermore, modern mixing rules for the parameter *a* and *b* suggested by Chen et al. [12] were introduced. In the mixing rule for the *a* – parameter, only the residual part of the excess Gibbs energy is used and the exponent 3 over 4 in the combination rule of the quadratic *b*-mixing rule leads to a significant better description for asymmetric systems [13]. A distinct improvement in the prediction of volume dependent properties could be realized by introducing the concept of volume translation suggested by Peneloux et al. [14]. Finally, the g^E information is taken into account using temperature dependent VTPR parameters which are fitted to a wide range of binary experimental data taken from the Dortmund Data Bank [15] minimizing the following objective function F,

$$F = w_{VLE}\sum \Delta VLE + w_{AZD}\sum \Delta AZD + w_{h^E}\sum \Delta h^E + w_{c_p^E}\sum \Delta c_P^E + w_{GLE}\sum \Delta GLE + w_{\gamma^\infty}\sum \Delta\gamma^\infty + w_{SLE}\sum \Delta SLE + w_{LLE}\sum \Delta LLE = Minimum \quad (2)$$

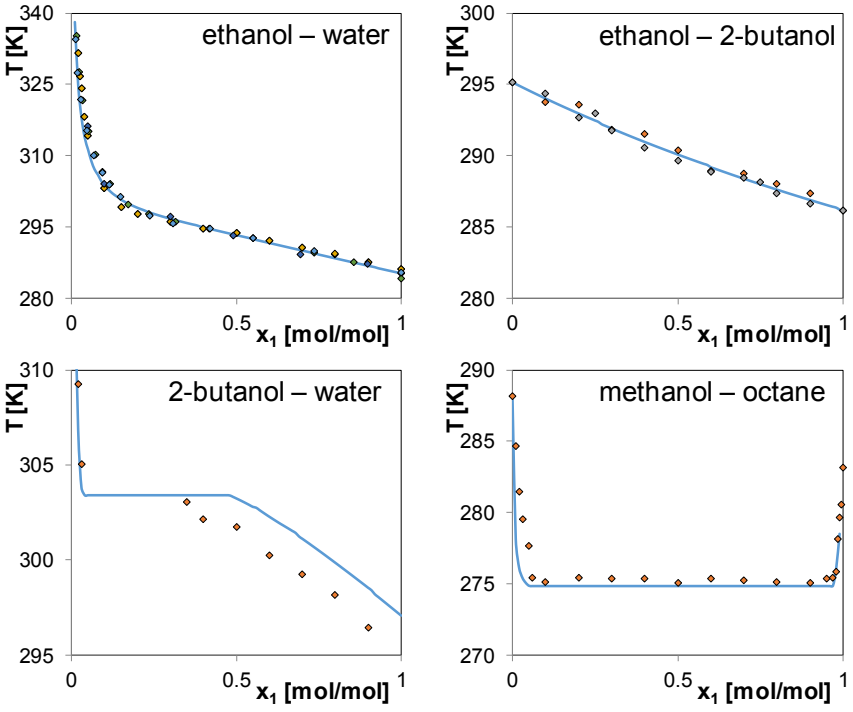

Fig. 3. Experimental (◆) [17] and predicted flash points using VTPR (–).