Mathematical modeling of chemical properties developed over the years, were purely theoretical, empirical or semi-empirical. The first part of this paper is dedicated to extensive application of the new modeling methodology RMM (Shore, 2005) to model experimental data of pure compounds temperature-dependent properties. Refer to Benson-Karhi et al., 2007, for a demonstrative application to modeling water properties. In the second part of this paper we present an original method for temperature-dependent properties prediction. The new method, RMM-QS2PM, which is an original combination of RMM with the QS2PR approach (Shacham et al., 2004), was applied to hydrocarbons. Refer to Shacham et al., 2008, for a demonstrative application to liquid density. In both parts of this research, highly accurate modeling and predictions were generally obtained.

OBJECTIVES
Mathematical modeling of chemical properties is essential for process and product design. Modeling temperature-dependent chemical properties is an ongoing scientific endeavor that spans several centuries. Mathematical modeling and simulation of chemical processes and substances require precise equations to represent the physical and thermodynamic properties as a function of state variables such as temperature. While some models developed over the years originated in purely theoretical arguments, unsatisfactory accuracy obtained via such models had motivated development of alternative models that are either empirical or semi-empirical in nature. In this research we apply three different modeling approaches.

The first approach used TableCurve2D® (henceforth TC), a dedicated software for relational modeling, which ranks thousands of models stored in its data bank according to their goodness-of-fit. The second approach uses “Acceptable models” recommended by
DIPPR®. The latter is a widely used database for constant and temperature-dependent physical properties and the modeling of these properties. The third approach is based on RMM (Response Modeling Methodology) - a new platform for empirical modeling recently developed (Shore, 2005). RMM provides a uniform model (with three variations) to all substances and all properties. The three variations are the two-parameter RMM_2, the three-parameter RMM_3 and the four-parameter RMM_4. The main objective is to demonstrate that RMM results in uniform, accurate, simple and stabilized models compared to other acceptable models.

The number of compounds used at present in industry, or being of its immediate interest, is estimated at around 100,000, while the variety of chemical structures, which are theoretically possible and may eventually interest the industry in the future, are at least several tens of millions. The number of compounds, for which measured data of their properties are available, is at most several thousands, and for some properties even much less. The discrepancy between the number of compounds of interest and the available pure compounds data emphasizes the necessity of being able to predict compounds’ properties (Brauner et al., 2005). In this research we present an original method RMM-QS2PM, which combines the uniformity, simplicity and stability of RMM models with a new constant-properties prediction method, QS2PR (Shacham et al., 2004). This new method was applied to hydrocarbons.

METHODS
This research has two main parts. The first part is dedicated to extensive application of the new modeling methodology RMM to model experimental data of pure compounds temperature-dependent physical and thermodynamic properties. The resulting RMM models are compared to leading models in chemical engineering, some of which are based purely on scientific theory. The comparison is based on advanced empirical models (Burnham and Anderson, 2004).

The second part of this research was dedicated to property prediction using an original combination of RMM with the QS2PR approach (Quantitative Structure-Structure-Property Relationship, Shacham et al., 2004). The latter is a new method for prediction of constant properties of pure "target" compounds, as a function of several predictive compounds having a similar molecular structure. This method enables very accurate prediction of constant properties, like normal boiling point and critical temperature of the "target" compound, as a
function of the respective properties in a small group of predictive compounds. This part of the research presents an original method RMM-QS2PM, which combines the uniformity, simplicity and stability of RMM models with the constant-properties prediction method, QS2PR. This extension of QS2PR to temperature-dependent property prediction has become feasible due to RMM unique advantages, especially the uniformity of the resulting models (which is at odds with the wide variety of model structures prevalent in the chemical engineering literature). This new method was applied to hydrocarbons.

RESULTS

Applying RMM results summary

In this part 15 different temperature-dependent properties for Oxygen, Argon, Nitrogen and water were investigated. Refer to Benson-Karhi et al., 2007, for a demonstrative application to modeling water, Oxygen, Nitrogen and Argon properties. Altogether 42 different substance-property combinations were investigated (no measured data was found for some of the combinations). Summarizing the results of all 42 combinations points at the following outstanding findings:

1. In the absolute majority of the examined cases RMM model included the minimal number of parameters (simple model).
2. Regarding goodness-of-fit criteria, TC model is the leading model. This result was anticipated since TC suggests a different model for each particular data set.
3. Regarding goodness-of-fit criteria, the RMM model is leading when compared to the model recommended by DIPPR.
4. RMM is also leading, when compared to DIPPR, with respect to the PRESS statistic.
5. The uniformity of the RMM approach extends to its parameters’ values. In most cases (more than 95%) RMM parameters' values are confined to the {-2, 2} range. This stands in stark contrast to parameters’ estimates offered by the other approaches (TC and DIPPR). This RMM unique character has practical advantage in the modeling process.
6. According to the stability criteria relating to the parameters' confidence-interval widths, RMM and DIPPR present similar performances. It should be noted, however, that single parameter instability in RMM, enables retreating to simpler (fewer parameters) stable version of RMM, which still represents good goodness-of-fit performance.
Applying RMM-QS2PM results summary

Out of 36 combinations of target-compound/predictive-compounds/property examined, in 33 combinations, AdjR$^2$ of the predicted model was higher than 0.94, and in 24 combinations it exceeded 0.99. The three cases in which AdjR$^2$ was smaller than 0.94, are characterized by difficulties in finding appropriate data sets for target and predictive compounds. Refer to Shacham et al., 2008, for a demonstrative application to liquid density.

CONCLUSIONS

In the first part of this research RMM was applied to more than 40 data sets associated with temperature-dependent properties of four pure compounds: Oxygen, Argon, Nitrogen and water. In the second part, 144 data sets were analyzed (all the combinations of target-compound/predictive-compounds/properties). Altogether, 184 RMM fittings were performed in this research. Applying RMM to dozens of data sets (in both parts A and B) resulted in, for at least one version of RMM, excellent goodness-of fit with: AdjR$^2 > 0.99$. Furthermore, the relative widths of the parameters’ confidence-intervals, in most cases indicated model stability. This fact in itself demonstrates that applying the new empirical modeling approach, RMM, to chemical engineering has great potential.

Modeling dozens of data sets by RMM emphasized the unique advantages of this method, relative to conventional approaches of property modeling in chemical engineering. The most outstanding advantage of RMM seems to be its uniformity. Applying RMM for any data set is independent of the compound/property combination, and the method allows flexibility in choosing the most appropriate RMM version, according to the available empirical data. The uniformity of the RMM approach extends to its parameters’ values. As realized from the estimates of the RMM parameters, most values are confined to the {-2, 2} range. This stands in stark contrast to parameters’ estimates offered by the other approaches (TC and DIPPR). The practical advantage of this observation can hardly be overestimated. When a model is fit to the data, restricting the search routine to a uniform range for all parameters would almost surely guarantee an optimum global solution (that is, globally best estimates). Such an assertion can hardly be extended to platforms where either different models are used for each property or for each substance-property combination.

Summarizing Part A, comparing RMM to the model offered by TC and DIPPR "Acceptable Model", RMM contains the minimal number of parameters in 85% of the examined data sets. Comparing DIPPR model to RMM, the latter leads regarding goodness-of-fit statistics and in stability statistic. Regarding relative widths of the parameters
confidence-intervals, RMM and DIPPR seem to perform equally well. The RMM models, with their small number of parameters and their uniform models seem to provide an effective tool for empirical modeling of temperature-dependent chemical properties.

Seeing that in 33 combinations of target-compound/predictive-compounds/property out of 36 examined in Part B, AdjR$^2$ of the predicted RMM model was higher than 0.94, and in 73% of the cases it exceeded 0.99, one can say that extending QS2PR to RMM-QS2PM is "working". Extending QS2PR to the prediction of the relational model between temperature and different properties by RMM-QS2PM is possible thanks to the simplicity, stability and accuracy of RMM. These outstanding results, which refer to varying properties, are a breakthrough in the field of property prediction, which up to this point focused on constant properties. RMM-QS2PM demonstrated success in predicting temperature-dependent properties for hydrocarbons open new venues for its application to other varying properties (apart from temperature-dependent properties) and to other groups of pure compounds.

REFERENCES


