REVIEW PAPER

Modelling of volumetric properties of binary and ternary mixtures by CEOS, CEOS/G^E and empirical models

BOJAN D. DJORDJEVIĆ[*#], SLOBODAN P. ŠERBANOVIĆ[#], IVONA R. RADOVIĆ[#], ALEKSANDAR Ž. TASIĆ and MIRJANA LJ. KIJEVČANIN[#]

Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, P.O. Box 35-03, 11120 Belgrade, Serbia

Abstract: Although many cubic equations of state coupled with van der Waals-one fluid mixing rules including temperature dependent interaction parameters are sufficient for representing phase equilibria and excess properties (excess molar enthalpy H^E, excess molar volume V^E, *etc.*), difficulties appear in the correlation and prediction of thermodynamic properties of complex mixtures at various temperature and pressure ranges. Great progress has been made by a new approach based on CEOS/G^E models. This paper reviews the last six-year of progress achieved in modelling of the volumetric properties for complex binary and ternary systems of non-electrolytes by the CEOS and CEOS/G^E approaches. In addition, the vdW1 and TCBT models were used to estimate the excess molar volume V^E of ternary systems methanol + chloroform + benzene and 1-propanol + chloroform + benzene, as well as the corresponding binaries methanol + chloroform, chloroform + benzene, 1-propanol + chloroform and 1-propanol + benzene at 288.15–313.15 K and atmospheric pressure. Also, prediction of V^E for both ternaries by empirical models (Radojković, Kohler, Jackob–Fitzner, Colinet, Tsao–Smith, Toop, Scatchard, Rastogi) was performed.

Keywords: correlation, prediction, volumetric properties, cubic EOS mixing rules, empirical models, non-electrolyte multicomponent systems.

CONTENTS:

---

* Corresponding author. E-mail: bojan@tmf.bg.ac.yu

[#] Serbian Chemical Society member.

1. INTRODUCTION

CEOS and CEOS/G^E models are widely applied for the representation of vapour–liquid equilibria, VLE, liquid–liquid equilibria, LLE, and other thermodynamic properties of mixtures required for synthesis, design of chemical plants, optimization and development of chemical, gas processing, petrochemical and other industries. Since the first van der Waals-one fluid mixing rule was introduced, continuous effort has been made on the development of new mixing rules. Recently, great advancement was achieved by using G^E mixing rules incorporated into CEOS equations.

The interest was focused on experimental measurements and thermodynamic modelling of mixtures containing various groups of organic compounds: alcohols, aromatics and alkyl chlorides, since they exhibit varying molecular interactions, resulting in specific deviations from ideal behaviour. In addition, these mixtures are important from a practical point of view, due to their diverse industrial applications and presence in main pollution generating industries and processes, causing air, water and soil contamination. Alcohols and aromatics are widely employed in a variety of industrial and consumer applications, such as perfumes, cosmetics, paint, varnish, drugs, fuel, explosives, fats, waxes, resin, plastics, rubber, detergents, DDT, *etc.* Chloroform is applied as a solvent in various industries, *e.g.*, in the extraction of penicillin and other antibiotics in the pharmaceutical industry, for pesticides, fats, oils, rubber, alkaloids, waxes, *etc.* In a mixture with alcohol or benzene, chloroform is widely used as an eluting system, such as, for medical purposes, in radiopharmacy, in chemical reactions, *etc.*; also, chloroform and benzene are very often contained in the wastewater of different industries as pollutants having cancerous features.

One part of the present work is a review of experimental investigations of the volumetric properties of binary and ternary systems, performed at atomspheric pressure using Anton Paar digital vibrating U-tube densimeters: DMA 55[1,2] and DMA 5000,[3–8] with a precision $\pm 1 \times 10^{-5}$ g cm^{-3} and $\pm 1 \times 10^{-6}$ g cm^{-3}, respectively. In both cases, the samples were prepared by weight using mass balances having a precision $\pm 1 \times 10^{-4}$ g. The experimental accuracy achieved by the DMA 55 densimeter was better than $\pm 3 \times 10^{-5}$ g cm^{-3}, while the uncertainty in the density measured by the DMA 5000 densimeter was about $\pm 1 \times 10^{-5}$ g cm^{-3} and the average uncertainty in the excess molar volume was estimated to be $\pm 3 \times 10^{-3}$ cm^3 mol^{-1}.

The other goal of this work was to provide a review of the obtained results in recent investigations performed by the CEOS and CEOS/G^E models on the evaluation of the volumetric properties of binary and ternary mixtures.[2–5,8–13] Also, for the ternary systems methanol + chloroform + benzene and 1-propanol + chloroform + benzene results of the prediction and correlation of V^E values obtained by these models are presented, bearing in mind that previously[6,7] only experi-

mental data were published. In addition, the prediction of V^E values for both ternaries was performed by frequently employed empirical models. Recently, published papers were connected to some advances in describing phase equilibria and excess properties using CEOS/G^E models.[9−13]

2. EVALUATION OF VOLUMETRIC PROPERTIES

2.1. Testing of CEOS and CEOS/G^E models

The ability of composition dependent CEOS (vdW1)[14] and CEOS/G^E mixing rules (Gupta–Rasmunsen–Fredenslund GRF[15] which incorporates the NRTL equation[16] as the G^E model) to correlate the V^E of non-electrolyte binary mixtures was investigated.[9] Very complex systems of diverse structure and complexity were selected: monocyclic ether + n-alkane, + 1-alcohol, + cyclohexane, + toluene. A relatively large number of data points (562) over the entire composition range and in the temperature interval 288.15–308.15 K were covered. The complexity of the chosen systems is characterized by their non-ideal behaviour, exhibiting an asymmetric shape of the V^E – composition relationship having very small or large excess volumes, *etc*. The mentioned data base allowed an analysis of several aspects of the properties of the mixtures: the increase/decrease in the number of the carbon atom chain of the alkane or alcohol series; in addition, diverse structures and complexity of the molecular interactions in the liquid mixtures were examined, which accounted for their ability to affect the V^E–composition behaviour. The influence of the applied mixing rule (CEOS or CEOS/G^E), as well as the influence of the incorporated temperature dependent interaction parameters, on the correlation of the V^E data was tested.[3−5,8]

The results of the investigation[9] lead to the following conclusions: (a) correlation of the data at a single isotherm can be successfully performed using the vdW1 or GRF models with no-temperature dependent parameters of the NRTL equation; (b) however, for the correlation in a temperature range, the obtained results indicate that incorporation of a more flexible mixing rule, which includes all temperature dependent interaction parameters, should be used.

Critical examination of the applicability of the cubic equations of state (CEOS) mixing rules to the representation of V^E data for systems containing dicyclic ethers with alkanes, alcohols and cyclohexane[10] represents a continuation of our effort expended in analyzing V^E data for mixtures of monocyclic ethers with various substances reported previously.[9] Twenty four highly non-ideal mixtures, consisting of 593 data points, were included. Sixteen binaries at 298.15 K and eight systems in the temperature range 288.15–308.15 K were analysed. The V^E––composition dependence for the binaries with dicyclic ethers, mentioned above, were correlated by the Peng–Robinson–Stryjek–Vera cubic equation of state (PRSV CEOS),[17] coupled with two different classes of mixing rules: (a) the composition dependent van der Waals (vdW1) one-fluid models[14] and (b) two types of

the excess free energy mixing rules (CEOS/G^E), the general form based on GRF,[15] as well as the mixing rule of Twu–Coon–Bluck–Tilton (TCBT).[18] Both rules were used with NRTL equation as the G^E model.

According to the obtained results, the following evidence were provided: (*i*) for the correlation of isothermal V^E data at 298.15 K using the CEOS mixing rules for the systems of dicyclic ethers with alcohols and cyclohexane, the use of temperature dependent parameters was not necessary; in addition, it was shown that the correlation of V^E data from a single isotherm can be successfully performed using the GRF model with no temperature dependent parameters in the NRTL equation; (*ii*) for correlation of V^E data of dicyclic ethers with alkanes in the temperature range 288.15–308.15 K, it was found that the use of the new TCBT model with no temperature dependent parameters was adequate. Alternatively, the GRF mixing rule with all temperature dependent parameters worked satisfactorily.

2.2. Binary systems

In this part of research,[1] the effort was directed toward the investigation of the excess molar volume (V^E) of the non-ideal behaviour of two binary mixtures containing alcohol and acetonitrile. The systems methanol + acetonitrile and ethanol + acetonitrile were treated. The density measurements for these systems were performed at 298.15 K and used for the determination of V^E over the entire composition range. During mixing with acetonitrile, which contains a proton acceptor group, a part of the alcohol will tend to dissociate and form other kinds of hydrogen bonds within the molecules. The nature of the mixture was investigated over the composition range. The composition dependence of mixtures was fitted by the Redlich–Kister (RK) polynomial equation.[19] It was shown that the V^E values for both systems are small and that they rise with increasing length of the alkyl chain in the alcohol.

The excess molar volume for the methanol + acetonitrile system is negative over the entire composition range, tending to be skewed toward mixtures rich in acetonitrile. This could be a consequence of the association between the nitrile group and the proton of the methanol hydroxyl group, outweighing the effect of dissociation of the alcohol molecules.

The V^E *vs.* composition curve for the system with ethanol has a S-shaped form; the V^E values are positive in the region of low alcohol concentration, and negative for mole fractions of ethanol higher than 0.35.

The TCBT model was used in an attempt to extend its applicability to the correlation of experimentally obtained V^E data,[11] as described in a previous paper (for the acetonitrile + methanol and acetonitrile + ethanol systems).[1] For the system acetonitrile + methanol, the best results of correlation were obtained by employing the TCBT-2, TCBT-3 and TCBT-5 models, having three, four and

five parameters, respectively. It was shown that improvement of the results by using TCBT-3 and TCBT-5 models was not achieved, comparing to those obtained by the TCBT-2 model. The acetonitrile + ethanol system exhibits S-shaped dependence of V^E on composition. It was shown that the models TCBT-2 and TCBT-3 gave similar results. In addition, the results of the correlation showed that a constant value for the parameter $\alpha_{ij} = 0.3$ should be used.

In conclusion, it can be noticed that, the TCBT models with binary interaction parameters of the vdW fluid gave exceptionally good results for the investigated systems at 298.15 K.

The increased interest in the determination of excess molar volumes was the encouragement to continue work[9–11] on the improvement of the correlation of V^E. Experimental V^E data, calculated from density measurements of the systems methanol + benzene, ethanol + benzene, methanol + chlorobenzene and ethanol + chlorobenzene, at the temperatures 288.15, 293.15, 298.15, 303.15, 308.15 and 313.15 K were presented.[3] The data of the above-mentioned binaries, measured over the entire composition range at the specified temperatures were fitted to the RK equation, with the optimal number of adjustable parameters used according to the F-test.[20] It was observed that, in all cases, V^E increased with increasing temperature. The shape of the V^E–composition relationship can be explained qualitatively on the basis of the following opposite effects, predominant in a certain mole fraction region:[21,22] (a) positive values (in the alcohol lower region) are attributed to rupture or stretch of the hydrogen bonding of self-associated molecules of alcohol; (b) negative values are thought to be due to unlike specific interactions; (c) the geometric fitting of benzene or chlorobenzene into the remaining alcohol structure makes this effect negative to V^E. The magnitude and sign of V^E are a consequence of the contributions occurring in the investigated mixtures.

Correlation of the V^E data was performed using the PRSV CEOS coupled with the vdW1 and CEOS/G^E mixing rules introduced by Twu *et al*.[18] (TCBT). The NRTL equation was used as the G^E model. Modelling of the binary V^E data was performed based on two approaches: (a) the temperature independent and (b) temperature dependent vdW1 and TCBT mixing rules. Correlation of the V^E data by temperature independent PRSV CEOS models showed the following: (*i*) for the methanol + benzene system, the three parameter TCBT-3 model was superior; (*ii*) for the ethanol + benzene system, V^E correlation with the two and three parameter TCBT models gave better results than the vdW1-3 model; (*iii*) in the case of the methanol + chlorobenzene system, except for the best TCBT-3 model, all models gave errors which increased with increasing temperature. In addition, the vdW1-3 model can be treated as very satisfactory; (*iv*) for the ethanol + chlorobenzene system, the vdW1-3 and TCBT models functioned quite similar. Correlation of the V^E data by the temperature dependent PRSV CEOS models gave higher errors for the systems with benzene compared to those with chloro-

benzene, because of the S-shaped V^E curves and the considerably lower values of this property. In addition, it could be observed that the three parameter models for both kinds of systems gave better results.

Additional results, related to experimental volumetric determination and thermodynamic modelling based on some CEOS mixing rules for the correlation and prediction of V^E data and the limiting partial excess molar volumes ($\overline{V}_i^{E\infty}$) were also presented.[4] The aim of that investigation was to extend our previous work concerned with the measurements of V^E of methanol + chlorobenzene and ethanol + chlorobenzene[3] to mixtures of some other alcohols, namely 1-propanol, 1-butanol, 2-butanol, 2-methyl-2-propanol, or 1-pentanol, with chlorobenzene, at six temperatures, *i.e.,* 288.15, 293.15, 298.15, 303.15, 308.15 and 313.15 K. Also, density measurements for the 2-methyl-2-propanol + chlorobenzene system were performed at temperatures 303.15, 308.15, 313.15, 318.15 and 323.15 K, since the melting point of 2-methyl-2-propanol is about 298.15 K. All the investtigated systems (except 2-methyl-2-propanol + chlorobenzene system) exhibit S-shaped V^E–composition relationship (in the temperature range of interest for the present work); the system 2-methyl-2-propanol + chlorobenzene exhibited positive V^E values over the entire composition range at each isotherm. Excess molar volumes of the investigated binaries were fitted using the RK equation.

The dependence of V^E on both composition and temperature, for the mixtures studied, can be explained qualitatively as a balance between opposite effects.[4] In addition to aspects of the molecular interactions, mentioned above, the obtained results were theoretically discussed in terms of the chain length of the alcohols, degree of branching in the chain and relative position of the alkyl and OH group in the alcohol. As a consequence of increasing temperature, in general, hydrogen bonding becomes weaker; the molecular interaction energy is lower, leading to an increase of the distance between the molecules, causing the volume to increase. The results of this work show that an order of limiting partial excess molar volume ($\overline{V}_i^{E\infty}$) was established; for example at 298.15 K the following order was recognised: for $\overline{V}_1^{E\infty}$ – ethanol < 1-propanol < 1-butanol ≈ 1-pentanol, whereas for $\overline{V}_2^{E\infty}$ – ethanol > 1-propanol > 1-butanol > 1-pentanol. In addition, the influence of temperature variation on $\overline{V}_i^{E\infty}$ was described and discussed. In addition, the following order of increase of $\overline{V}_1^{E\infty}$ and $\overline{V}_2^{E\infty}$ for mixtures with branched alcohols was noted: primary < secondary < tertiary alcohols.

As mentioned previously,[4] thermodynamic modelling of the experimental V^E data was performed by the PRSV CEOS coupled with two types of mixing rules, vdW1 and TCBT. In both mixing rules, the parameters were used as temperature independent and as temperature dependent ones.

It was shown that for all treated cases, except for the 2-methyl-2-propanol + + chlorobenzene system, which exhibited positive V^E values, the form of the V^E–composition relationship was S-shaped.[4] Modelling of the experimental V^E

data by the mentioned thermodynamic method was applied to each binary system separately and corresponding instructions on the best approach for treating particular data sets was proposed.[4]

2.3. Ternary systems

Excess molar volume data of the ternary system ethanol + 2-butanone + benzene at 298.15 K, which were not available in the literature, were investtigated.[2] In addition, the corresponding binary V^E measurements[2] were compared to the data of other authors reported earlier.[23−27] The binary data were fitted to the RK equation, while for the ternary V^E data, the Nagata and Tamura expression (NT)[28] was employed.

The V^E data of all three binaries were correlated by the vdW and TCBT mixing rules coupled with the PRSV CEOS. For all systems, the best results were obtained by the three-parameter TCBT-3 model, except for the case of the ethanol + 2-butanone mixture, where the vdW1-3 model gave very good results. Prediction and correlation of the ternary V^E data were performed using the corresponding binary parameters. Inspection of the ternary predictions indicates that the use of the vdW1-1 and vdW1-2 models gave fair results, whereas those attained by the vdW1-3 model were very good. Ternary correlation by the TCBT mixing rules, which included a ternary contribution in the NRTL equation, could be estimated as acceptable and mutually very similar.

A systematic study of the excess molar volume for binaries and ternary systems of non-electrolytes was performed.[5] In this work, the densities for the ternary system ethanol + chloroform + benzene and the two corresponding binaries ethanol + chloroform and chloroform + benzene were measured. All these measurements were obtained at the temperatures 288.15, 293.15, 298.15, 303.15, 308.15 and 313.15 K. The related V^E data were obtained from the measured densities. As already was mentioned,[3] thermodynamic investigations of alcohol + aromatic systems are of great importance due to their broad industrial application, as well as because of the complex molecular interactions present in these mixtures. Also the influence of the third component, chloroform, on the interaction between the alcohol and aromatic hydrocarbon in the ternary system was studied.[5] The V^E of the binary mixtures were fitted by the RK equation and the ternary data with the NT equation, while the Radojković *et al.*[29] equation was used for the prediction of the ternary data. Correlation of the binary data was performed by the PRSV CEOS using selected mixing rules: (a) the composition dependent vdW1 and (b) the TCBT mixing rules. Prediction of V^E of the ternary system was performed by the same vdW1 and TCBT models. For the correlation of the ternary V^E data, only the TCBT mixing rules were employed. Inspection of the binary V^E data for ethanol + chloroform shows that the V^E–composition relationship exhibits S-shape curves; also, an increase of V^E with increasing temperature

(from 288.15 to 313.15 K) was found. For the system chloroform + benzene, positive values of V^E were observed over the entire composition range. The highest values were obtained at 288.15 K.

Factors influencing the behaviour of the excess molar volume have already been discussed in the literature for the binary systems ethanol + benzene[3] and ethanol + chloroform.[30] Particularly, in the case of the chloroform + benzene system, some influences can be mentioned as an explanation of the V^E–composition behaviour, for example: (a) the difference between van der Waals volumes[31] of the constituents, (b) the formation of a weak complex between benzene and chloroform[32,33] and (c) the presence of steric hindrance effects in the mixture. The behaviour of the V^E–composition relationship of the ternary system ethanol + chloroform + benzene, in the given temperature range, was discussed in detail.[5] The influence of various factors affecting molecular interactions in the mixture was analysed. It was observed that the highest interactions of the components were obtained when the composition was slightly shifted to a mixture rich in ethanol.

Modelling of the binary V^E data was performed for each isotherm separately over the whole temperature range. The results obtained employing the temperature independent PRSV CEOS models indicate that the three parameter models (vdW1-3 and TCBT-3), for both binaries were the best.

For the prediction of ternary V^E data at the investigated temperatures, the binary interaction parameters of the CEOS models, generated from binary data, were used. The obtained results show that the predictions corresponding to the vdW1-2, vdW1-3 and TCBT-2 models are qualitatively acceptable and approximate to those obtained by the Radojković *et al.*[29] equation. Correlation of the ternary V^E data was performed only by the TCBT model, which included a ternary contribution parameter in the NRTL equation. Fitting of these data could be regarded as fair and similar.

A continual effort to investigate the volumetric properties of binary and ternary mixtures containing different types of organic solvents frequently used in various industries was described.[6] Thermodynamic investigation of alcohols, chloroform and aromatics, either pure or in mixtures, is of considerable interest due to the complex molecular interactions present in these mixtures. Densities for the ternary system methanol + chloroform + benzene and for the binary system methanol + chloroform at 288.15, 293.15, 298.15, 303.15, 308.15 and 313.15 K and atmospheric pressure were measured.[6] From these measurements, the V^E data were calculated. The binary V^E data were fitted using the RK equation, while the NT equation was used for the ternary data. The root-mean-square deviation (RMSD) between the experimental binary data from those computed using the RK equation were 0.0028×10^{-6} m^3 mol^{-1} to 0.0034×10^{-6} m^3 mol^{-1}, whereas for the ternary system, it was in the range: 0.0035×10^{-6} m^3 mol^{-1} to 0.0040×10^{-6} m^3 mol^{-1}.

A further contribution to previous research of the volumetric properties of binary and ternary mixtures containing various alcohols, chloroform and benzene was of primary interest.[7] The density of the ternary system 1-propanol + chloroform + benzene, and the binaries 1-propanol + chloroform and 1-propanol + benzene at the temperatures of 288.15, 293.15, 298.15, 303.15, 308.15 and 313.15 K and atmospheric pressure were measured and used for the calculation of V^E data. The fitting equations for the correlation of binary and ternary V^E data used in the previously discussed work[6] were also employed here. The RMSD of the experimental data from those calculated from the fitting models lay in the ranges: for the 1-propanol + chloroform system, 0.0036 to 0.0038×10^{-6} m^3 mol^{-1}; for the system 1-propanol + benzene, 0.0033 to 0.0044×10^{-6} m^3 mol^{-1}, whereas the RMSD for the ternary system was in the range 0.0039 to 0.0045×10^{-6} m^3 mol^{-1}.

The density of the ternary mixture 1-butanol + chloroform + benzene and the binaries 1-butanol + chloroform and 1-butanol + benzene were measured at six temperatures in the interval 288.15–313.15 K.[8] The corresponding V^E values were calculated from these density measurements and fitted by the polynomial equations: (a) of the RK equation for the binary systems and (b) of the NT equation for the ternary system. Ternary prediction was performed by the equation of Radojković *et al*.[29] The dependence of V^E on composition for the system 1-butanol + chloroform at 288.15, 293.15, 298.15, 303.15, 308.15 and 313.15 K exhibits a S-shaped curve, with a positive maximum and negative minimum values of V^E. It was remarked that these values increase with increasing temperature. The V^E–composition relationships for the system 1-butanol + benzene show positive values that increase with increasing temperature. A qualitative explanation of the V^E–composition relationship could be given on the basis of the opposite contributions, predominating in certain mole fraction regions.[8] The magnitude and sign of V^E have been interpreted as resulting from the balance between these effects.

For the investigated ternary system, positive V^E were obtained over most of the composition field, except in the region in the vicinity to 1-butanol in binary mixture with chloroform, where the sign was negative. Maximum V^E values appear close to the binary chloroform + benzene border, suggesting that the unpacking effect, which is a result of complex formation of chloroform + benzene, and the disruptive effect on the self- associated molecules of 1-butanol are more dominant. In addition, an increase of the maximum values of V^E with increasing temperature was remarked, bringing about a diminishing of the negative V^E region. Also, the excess molar volume maximum is located approximately near the centre of the triangular diagram.

V^E Data were used to test the CEOS and CEOS/G^E models for their correlative and predictive abilities.[8] For the correlation of the binary data, PRSV CEOS coupled with temperature independent and temperature dependent mixing rules,

the composition dependent vdW1 and the TCBT models, were used. Correlation of the ternary V^E data was performed by employing the TCBT model, whereas for ternary prediction the vdW1 and TCBT models were used.

3. SIMULTANEOUS CORRELATION OF VLE, H^E AND c_p^E

Considering the fact that phase equilibria: vapour–liquid (VLE), liquid–liquid (LLE), gas solubility and excess properties: excess molar enthalpies (H^E), excess heat capacity (c_p^E), excess molar volume (V^E), *etc.*, of liquid systems are of great importance for the design and operation of industrial processes, as well as the fundamental necessity for a better understanding of molecular interactions in fluid systems from the thermodynamic point of view, simultaneous correlation of two (VLE + H^E, VLE + c_p^E and H^E + c_p^E) and three properties (VLE + H^E + c_p^E) was carried out.[12] For this purpose, the corresponding data of diethers (1,4-dioxane and 1,3-dioxolane) with *n*-alkanes (heptane, octane, nonane and decane) were selected.

VLE and excess properties (H^E and c_p^E) for diether + *n*-alkane systems were simultaneously correlated,[13] employing the CEOS incorporating the activity coefficient model (CEOS/G^E). The approach of Kohler,[34] already used,[35−37] in the form of an empirical equation of the polynomial form, was applied[12] for the simultaneous correlation of the data of the above-mentioned systems. All the coefficients in the expression for the temperature dependent polynomial parameters were generated from the corresponding fits of VLE + H^E, VLE + c_p^E and H^E + + c_p^E or VLE + H^E + c_p^E data.

The calculation results obtained by the Kohler polynomial model were compared with those corresponding to the previously applied CEOS/G^E models (MHV1 and MHV2).[13]

The main results of the investigation on the simultaneous correlation of diverse thermodynamic properties by the Kohler polynomial equation (VLE + H^E, VLE + c_p^E and H^E + c_p^E) for the systems investigated gave very successful results, as was the case with the CEOS/G^E models. However, the correlation of three properties (VLE + H^E + c_p^E) showed that the Kohler model was more suitable than the CEOS/G^E models.

Finally, it can be concluded that the simultaneous correlation of three thermodynamic properties should be further investigated because of its importance from the theoretical and practical points of view.

4. MODELLING OF TERNARIES ALCOHOLS + CHLOROFORM + BENZENE

4.1. Correlation and prediction of V^E by the vdW1 and TCBT models

The general two-parameter cubic equation of state (CEOS) has the form:

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+ub)(V+wb)} \tag{1}$$

where P, T, V, and R denote pressure, temperature, molar volume and gas constant, respectively; the CEOS dependent constants u and w for the Peng–Robinson–Stryjek–Vera (PRSV) equation[17] applied here are: $u = 1 - \sqrt{2}$ and $w = 1 + \sqrt{2}$. For the pure substance, the energy a_i and co-volumen b_i parameters are determined as:

$$a_i(T) = 0.457235 \frac{(RT_{ci})^2}{P_{ci}} [1 + m_i(1 - \sqrt{T_{ri}})]^2 \tag{2}$$

$$b_i = 0.077796 \frac{RT_{ci}}{P_{ci}} \tag{3}$$

$$m_i = k_{0i} + k_{1i}(1 + \sqrt{T_{ri}})(0.7 - T_{ri}) \tag{4}$$

$$k_{0i} = 0.378893 + 1.4897153\omega_i - 0.1713848\omega_i^2 + 0.0196554\omega_i^3 \tag{5}$$

where T_{ci} and P_{ci} are the critical temperature and critical pressure of component i, respectively, T_{ri} denotes the reduced temperature, T/T_{ci}, ω_i is the acentric factor, and k_{1i} represents the pure substance adjustable parameter.[17]

For the determination of the a and b parameters of a mixture, two different types of mixing rules are used: vdW1 and TCBT.

The vdW1 mixing rule[14] is given by the following equations:

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2} \left[1 - k_{ij} + l_{ij}(x_i - x_j)\right] \tag{6}$$

$$b = \sum_i \sum_j x_i x_j (b_i b_j)^{1/2} (1 - m_{ij}) \tag{7}$$

where k_{ij}, l_{ij} and m_{ij} are the binary interaction parameters.

The TCBT mixing rule[18] developed for no reference pressure conditions relates the excess molar Gibbs energy, G^E, with the excess molar Gibbs energy based on the van der Waals reference fluid (vdW), G^E_{vdW}, as:

$$\frac{G^E}{RT} - \frac{G^E_{vdW}}{RT} + (Z - Z_{vdW}) = \ln\left\{\left(\frac{V^*_{vdW} - 1}{V^* - 1}\right)\left(\frac{b_{vdW}}{b}\right)\right\} -$$

$$- \frac{1}{w - u}\left\{\frac{a^*}{b^*}\ln\left(\frac{V^* + w}{V^* + u}\right) - \frac{a^*_{vdW}}{b^*_{vdW}}\ln\left(\frac{V^*_{vdW} + w}{V^*_{vdW} + u}\right)\right\} \tag{8}$$

where G^E_{vdW} is calculated for the PRSV CEOS and $V^* = V/b = Z/b^*$ denotes the reduced liquid volume at the P and T of the mixture. The compressibility factors Z and Z_{vdW} are calculated from Eq. (1) expressed in the Z form. Bearing in mind that V^* does not have an explicit solution, an iterative technique is required for the calculation.

The parameters a_{vdW} and b_{vdW} are determined using Eqs. (6) and (7), while the reduced parameters a^*, b^*, a^*_{vdW} and b^*_{vdW} are obtained from the following equations:

$$a^* = Pa/R^2 T^2 \qquad\qquad b^* = Pb/RT \tag{9}$$

In this paper, the NRTL equation was used as the G^E model:

$$\frac{G^E}{RT} = \sum_i x_i \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_k x_k G_{ki}} \tag{10}$$

For a binary mixture, the following equations are incorporated

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \quad G_{21} = \exp(-\alpha_{12}\tau_{21})$$
$$\tau_{12} = (g_{12} - g_{22})/RT = \Delta g_{12}/RT \quad \tau_{21} = (g_{21} - g_{11})/RT = \Delta g_{21}/RT \tag{11}$$

and for a ternary mixture:

$$\tau'_{ij} = \tau_{ij} + \frac{\sum_{k=1}^{n} x_k \Delta g_{ijk}}{RT} \tag{12}$$

Δg_{12} and Δg_{21} are the binary energy parameters and Δg_{ijk} is the ternary contribution.

For the temperature range, temperature dependent parameters are used in the following manner:

$$Y = Y_1 + Y_2 T \tag{13}$$

where $Y = k_{ij}$, l_{ij}, m_{ij}, Δg_{12} and Δg_{21}. The models used here for all calculations were obtained by applying sets of the corresponding equations as listed in the footnotes of the Tables I–IV. In order to obtain the model parameters or coefficients, the Marquardt optimisation technique[38] was used for the minimization of the objective function given by the equation:

$$OF = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{V^E_{exp} - V^E_{cal}}{V^E_{exp}}\right)^2_i \rightarrow \min \tag{14}$$

The results of the V^E calculation were assessed by the RMSD, defined by the equation:

$$\sigma = \left(\sum_{i=1}^{n}\left(V^E_{exp,i} - V^E_{cal,i}\right)^2 \Big/ n\right)^{1/2} \tag{15}$$

and the percentage average absolute deviation PD(V^E):

$$PD(V^E) = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{V^E_{exp} - V^E_{cal}}{\left(V^E_{exp}\right)_{max}}\right|_i \tag{16}$$

In the present paper, modelling of the previously obtained experimental V^E data[6,7] for two ternary systems: methanol + chloroform + benzene and 1-propanol + chloroform + benzene and their binary constituents: methanol + chloroform, chloroform + benzene, 1-propanol + chloroform and 1-propanol + benzene, was performed by the PRSV CEOS, coupled with two types of mixing rules: vdW1 and TCBT mixing rules. According to the previously established procedure, the parameters in both mixing rules were employed as: (*i*) temperature independent (correlation at each temperature) or (*ii*) temperature dependent (correlation in the temperature range). The values of the model parameters, PD(V^E) and corresponding RMSD for each temperature separately, as well as in temperature range, are given in Tables I and II for the binary systems and in Tables III and IV for the ternary systems.

TABLE I. Correlation of the V^E data by the temperature independent PRSV CEOS models for the investigated binary systems at the temperatures 288.15 to 313.15 K and atmospheric pressure

	$k_{ij,1}$	$l_{ij,1}$	$m_{ij,1}$	$\Delta g_{12,1}$ J mol^{-1}	$\Delta g_{21,1}$ J mol^{-1}	PD(V^E) %	$\sigma \times 10^6$ m^3 mol^{-1}
			Methanol (1) + Chloroform (2)				
			$T = 288.15$ K				
vdW1-2[a]	0.009327		−0.015852			10.54	0.01946
vdW1-3[b]	−0.038847	−0.007914	−0.023699			9.85	0.01836
TCBT-2[c]				0.217463·10^4	−0.756278·10^3	10.94	0.02069
TCBT-3[d]	0.100778			0.521710·10^4	0.127565·10^4	2.01	0.00402
			$T = 293.15$ K				
vdW1-2	0.022390		−0.013519			11.00	0.02005
vdW1-3	−0.039467	−0.009997	−0.024002			9.89	0.01815
TCBT-2				0.207827·10^4	−0.726828·10^3	11.10	0.02067
TCBT-3	0.107533			0.534685·10^4	0.134597·10^4	2.13	0.00433
			$T = 298.15$ K				
vdW1-2	0.035134		−0.011080			11.59	0.02093
vdW1-3	−0.039430	−0.011948	−0.024231			9.93	0.01795
TCBT-2				0.193950·10^4	−0.665477·10^3	11.31	0.02092
TCBT-3	0.109918			0.531074·10^4	0.131166·10^4	1.52	0.00308
			$T = 303.15$ K				
vdW1-2	0.048135		−0.008427			12.45	0.02212
vdW1-3	−0.039532	−0.139192	−0.024516			9.99	0.01770
TCBT-2				0.184834·10^4	−0.633676·10^3	11.50	0.02078
TCBT-3	0.116340			0.544517·10^4	0.135931·10^4	3.34	0.00704
			$T = 308.15$ K				
vdW1-2	0.061420		−0.005532			13.55	0.02371
vdW1-3	−0.040293	−0.016039	−0.024954			10.12	0.01737
TCBT-2				0.175258·10^4	−0.595395·10^3	11.70	0.02048
TCBT-3	0.120553			0.543282·10^4	0.137033·10^4	1.86	0.00372

TABLE I. Continued.

	$k_{ij,1}$	$l_{ij,1}$	$m_{ij,1}$	$\Delta g_{12,1}$ J mol^{-1}	$\Delta g_{21,1}$ J mol^{-1}	PD(V^E) %	$\sigma \times 10^6$ m^3 mol^{-1}
				T = 313.15 K			
vdW1-2	0.073170		–0.002752			14.95	0.02563
vdW1-3	–0.040648	–0.017897	–0.025352			10.29	0.01704
TCBT-2				$0.163854 \cdot 10^4$	$-0.541875 \cdot 10^3$	12.00	0.02036
TCBT-3	0.121939			$0.536275 \cdot 10^4$	$0.130523 \cdot 10^4$	1.87	0.00364
				T = 288.15–313.15 K			
vdW1-2	0.021634		–0.013486			12.94	0.0238
vdW1-3	–0.003207	–0.009216	–0.017999			10.61	0.0194
TCBT-2				$0.163364 \cdot 10^4$	$-0.454764 \cdot 10^3$	25.34	0.0516
TCBT-3	–0.079651			$0.260148 \cdot 10^4$	$-0.332486 \cdot 10^4$	12.31	0.0227
			Chloroform (1) + Benzene (2)				
				T = 288.15 K			
vdW1-2	–0.064033		–0.017573			3.49	0.0076
vdW1-3	–0.008514	–0.004581	–0.008628			2.74	0.0060
TCBT-2				$0.147247 \cdot 10^3$	$0.751000 \cdot 10^5$	1.39	0.0039
TCBT-3	–0.009258			$-0.208918 \cdot 10^4$	$0.260580 \cdot 10^4$	1.25	0.0032
				T = 293.15 K			
vdW1-2	–0.057860		–0.016649			3.65	0.0076
vdW1-3	–0.007256	–0.004148	–0.008197			2.98	0.0062
TCBT-2				$0.135332 \cdot 10^3$	$0.771195 \cdot 10^5$	1.46	0.0038
TCBT-3	0.086805			$0.241585 \cdot 10^4$	$0.126727 \cdot 10^4$	1.38	0.0032
				T = 298.15 K			
vdW1-2	–0.052200		–0.015754			3.81	0.0074
vdW1-3	–0.007308	–0.003688	–0.007991			3.21	0.0063
TCBT-2				$0.123980 \cdot 10^3$	$0.791928 \cdot 10^5$	1.56	0.0037
TCBT-3	–0.010119			$-0.223158 \cdot 10^4$	$0.277009 \cdot 10^4$	1.41	0.0031
				T = 303.15 K			
vdW1-2	–0.047203		–0.014929			3.98	0.0073
vdW1-3	–0.006771	–0.003315	–0.007689			3.45	0.0063
TCBT-2				$0.112960 \cdot 10^3$	$0.811204 \cdot 10^5$	1.67	0.0036
TCBT-3	0.093752			$0.250866 \cdot 10^4$	$0.130924 \cdot 10^4$	1.48	0.0032
				T = 308.15 K			
vdW1-2	–0.042161		–0.014053			4.22	0.0073
vdW1-3	–0.006426	–0.002946	–0.007429			3.76	0.0065
TCBT-2				$0.103211 \cdot 10^3$	$0.834117 \cdot 10^5$	1.89	0.0037
TCBT-3	0.107109			$0.277853 \cdot 10^4$	$0.153623 \cdot 10^4$	1.49	0.0028
				T = 313.15			
vdW1-2	–0.038595		–0.013418			4.55	0.0086
vdW1-3	–0.005877	–0.002714	–0.007144			4.13	0.0069
TCBT-2				$0.936483 \cdot 10^2$	$0.852738 \cdot 10^5$	2.27	0.0043
TCBT-3	0.110792			$0.281775 \cdot 10^4$	$0.155558 \cdot 10^4$	1.57	0.0029

TABLE I. Continued.

	$k_{ij,1}$	$l_{ij,1}$	$m_{ij,1}$	$\Delta g_{12,1}$ J mol^{-1}	$\Delta g_{21,1}$ J mol^{-1}	PD(V^E) %	$\sigma \times 10^6$ m^3 mol^{-1}
				T = 288.15–313.15 K			
vdW1-2	–0.043300		–0.014259			3.93	0.0078
vdW1-3	–0.039939	–0.001267	–0.013681			3.71	0.0072
TCBT-2				–0.173424·10^3	0.310596·10^3	11.27	0.0235
TCBT-3	–0.023914			0.664817·10^3	–0.124516·10^4	3.36	0.0067
			1-Propanol (1) + Chloroform (2)				
				T = 288.15 K			
vdW1-2	0.174217		0.024898			4.38	0.01036
vdW1-3	0.129286	–0.014223	0.017524			3.05	0.00702
TCBT-2				–0.218026·10^4	0.360541·10^4	8.01	0.01908
TCBT-3	–0.054472			0.509984·10^4	–0.429655·10^4	2.19	0.00587
				T = 293.15 K			
vdW1-2	0.173022		0.025272			4.87	0.01113
vdW1-3	–0.225282	–0.126330	–0.033387			1.97	0.00471
TCBT-2				–0.219034·10^4	0.359501·10^4	8.69	0.01969
TCBT-3	–0.069108			0.326820·10^6	–0.216475·10^4	2.67	0.00721
				T = 298.15 K			
vdW1-2	0.171632		0.025609			5.55	0.01186
vdW1-3	–0.223173	–0.122970	–0.034729			1.91	0.00431
TCBT-2				–0.221130·10^4	0.361135·10^4	9.32	0.01985
TCBT-3	–0.067705			0.126275·10^3	–0.218022·10^4	2.96	0.00708
				T = 303.15 K			
vdW1-2	0.170105		0.025914			6.40	0.01274
vdW1-3	–0.220424	–0.119406	–0.036028			1.81	0.00402
TCBT-2				–0.219890·10^4	0.356070·10^4	10.13	0.02085
TCBT-3	–0.065541			0.304066·10^3	–0.221137·10^4	3.47	0.00722
				T = 308.15 K			
vdW1-2	0.168101		0.026105			7.48	0.01370
vdW1-3	–0.215685	–0.115100	–0.037099			1.73	0.00375
TCBT-2				–0.224538·10^4	0.363529·10^4	10.59	0.01972
TCBT-3	–0.066717			0.302224·10^3	–0.220774·10^4	4.14	0.00782
				T = 313.15 K			
vdW1-2	0.166654		0.026414			7.42	0.01484
vdW1-3	–0.212065	–0.111441	–0.038326			1.51	0.00366
TCBT-2				–0.225261·10^4	0.362813·10^4	9.53	0.01992
TCBT-3	–0.072421			0.126495·10^3	–0.220248·10^4	4.21	0.00844
				T = 288.15–313.15 K			
vdW1-2	0.148321		0.021650			16.33	0.0325
vdW1-3	0.083043	–0.025685	0.010283			5.30	0.0107
TCBT-2				–0.220178·10^4	0.356811·10^4	15.05	0.0315
TCBT-3	–0.057814			0.529087·10^4	–0.443514·10^4	5.31	0.0111

TABLE I. Continued.

	$k_{ij,1}$	$l_{ij,1}$	$m_{ij,1}$	$\Delta g_{12,1}$ J mol^{-1}	$\Delta g_{21,1}$ J mol^{-1}	PD(V^E) %	$\sigma \times 10^6$ m^3 mol^{-1}
				1-Propanol (1) + Benzene (2)			
				T = 288.15 K			
vdW1-2	0.099354		0.008781			6.56	0.00943
vdW1-3	–0.087552	–0.043591	–0.017779			3.11	0.00432
TCBT-2				–0.330450·10^3	0.116520·10^4	3.64	0.00528
TCBT-3	–0.007406			–0.103855·10^4	0.171633·10^4	3.47	0.00512
				T = 293.15 K			
vdW1-2	0.102011		0.009528			6.74	0.01071
vdW1-3	–0.082157	–0.041959	–0.017690			3.15	0.00499
TCBT-2				–0.412421·10^3	0.123388·10^4	3.63	0.00594
TCBT-3	–0.010342			–0.145386·10^4	0.214933·10^4	3.46	0.00559
				T = 298.15 K			
vdW1-2	0. 105052		0.010371			6.37	0.01109
vdW1-3	–0.079083	–0.040908	–0.017906			2.32	0.00447
TCBT-2				–0.491062·10^3	0.130171·10^4	2.69	0.00542
TCBT-3	–0.005818			–0.106759·10^4	0.178137·10^4	2.59	0.00502
				T = 303.15 K			
vdW1-2	0.106924		0.011029			6.91	0.01345
vdW1-3	–0.063084	–0.036901	–0.016220			2.94	0.00610
TCBT-2				–0.558168·10^3	0.135830·10^4	3.13	0.00696
TCBT-3	–0.008956			–0.145230·10^4	0.216459·10^4	2.83	0.00623
				T = 308.15 K			
vdW1-2	0.108334		0.011612			6.98	0.01508
vdW1-3	–0.059628	-0.035631	-0.016339			2.95	0.00689
TCBT-2				–0.605775·10^3	0.139267·10^4	3.06	0.00793
TCBT-3	–0.008339			–0.147150·10^4	0.219964·10^4	2.73	0.00676
				T = 313.15 K			
vdW1-2	0.111750		0.012629			6.67	0.01631
vdW1-3	–0.058310	–0.035148	–0.016750			2.97	0.00744
TCBT-2				–0.708732·10^3	0.149942·10^4	3.12	0.00816
TCBT-3	–0.012342			–0.192761·10^4	0.271223·10^4	2.75	0.00709
				T = 288.15–313.15 K			
vdW1-2	0.085992		0.007330			12.42	0.0212
vdW1-3	0.043469	–0.013948	0.000395			4.08	0.0079
TCBT-2				–0.441345·10^3	0.122594·10^4	20.85	0.0356
TCBT-3	–0.044303			0.241384·10^4	–0.273162·10^4	6.13	0.0113

[a]Eqs. (1)-(7), (13), l_{ij} = 0; [b]Eqs. (1)-(7), (13); [c]Eqs. (1)–(11), (13), $k_{ij} = l_{ij} = m_{ij} = 0$; α_{ij} = 0.3 (found by trial and error and set to 0.3 in all cases); [d]Eqs. (1)–(11), (13); $l_{ij} = m_{ij} = 0$; α_{ij} = 0.3.

Analysing the results obtained for the system methanol + chloroform by the temperature-independent PRSV CEOS models at each temperature, it is evident that only the three parameter TCBT-3 model worked very well, having errors near or below 2 %, while the results obtained by the two parameter vdW1-2 and TCBT-2 models and three parameter vdW1-3 model are unacceptable. The evident superiority of the TCBT-3 model in comparison with the TCBT-2 model, which is unable to fit the shape of the V^E–x_1 curve is illustrated in Fig. 1a. Over the entire range of temperature, the correlating results attained by all the temperature independent (Table I) or temperature dependent (Table II) models are unsatisfactory.
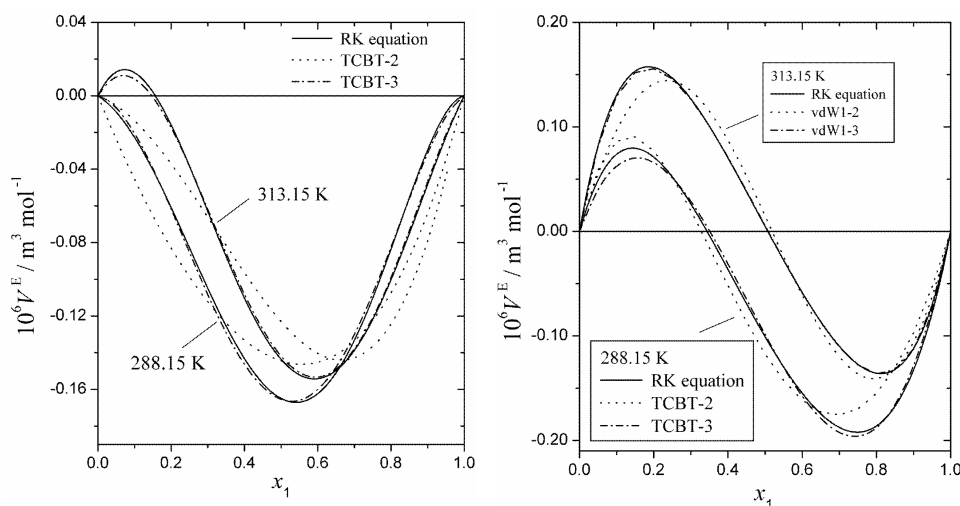

Fig. 1. Correlation of V^E data at 288.15 and 313.15 K by the vdW1 and TCBT models for the binary systems: a) methanol (1) + chloroform (2), b) 1-propanol (1) + chloroform (2). The various types of lines are reported in the legend.

TABLE II. Correlation of the V^E data by the temperature dependent PRSV CEOS models for the investigated binary systems at the temperature range 288.15–313.15 K and atmospheric pressure

	$k_{ij,1}, k_{ij,2}$	$l_{ij,1}, l_{ij,2}$	$m_{ij,1}, m_{ij,2}$	$\Delta g_{12,1}$ / J mol^{-1} $\Delta g_{12,2}$ / J mol^{-1}K^{-1}	$\Delta g_{12,1}$ / J mol^{-1} $\Delta g_{12,2}$ / J mol^{-1}K^{-1}	PD(V^E) %	$\sigma \times 10^6$ m^3 mol^{-1}
				Methanol (1) + Chloroform (2)			
vdW1-2[a]	−0.329138		−0.093779			12.40	0.0224
	0.001237		0.000280				
vdW1-3[b]	−0.201810	0.086387	−0.036700			10.02	0.0178
	0.000540	−0.000330	0.000041				
TCBT-2[c]				$0.234574 \cdot 10^4$	$-0.336333 \cdot 10^4$	20.75	0.0425
				−4.24111	$0.160156 \cdot 10^4$		
TCBT-3[d]	−0.028209			$0.539437 \cdot 10^4$	$-0.804127 \cdot 10^5$	12.82	0.0267
				$0.209787 \cdot 10^4$	$0.507668 \cdot 10^3$		

TABLE II. Continued.

	$k_{ij,1}, k_{ij,2}$	$l_{ij,1}, l_{ij,2}$	$m_{ij,1}, m_{ij,2}$	$\Delta g_{12,1}$ / J mol^{-1} $\Delta g_{12,2}$ / J mol^{-1}K^{-1}	$\Delta g_{12,1}$ / J mol^{-1} $\Delta g_{12,2}$ / J mol^{-1}K^{-1}	PD(V^E) %	$\sigma\times10^6$ m^3 mol^{-1}
			Chloroform (1) + Benzene (2)				
vdW1-2	–0.222941 0.000576		–0.042765 0.000091			3.93	0.0075
vdW1-3	0.002189 –0.000030	–0.029164 0.000085	–0.018467 0.000035			3.38	0.0064
TCBT-2				0.757263·10^3 –2.12153	–0.458710·10^5 0.419412·10^3	1.72	0.0039
TCBT-3	0.001067			0.840710·10^3 –2.26987	–0.476777·10^5 0.427966·10^3	1.76	0.0039
			1-Propanol (1) + Chloroform (2)				
vdW1-2	0.256907 –0.000287					6.02	0.0125
vdW1-3	5.297000 40.17777	1.487200 –0.005164	0.849304 –0.002861			4.89	0.0104
TCBT-2				–0.626817·10^3 –5.39751	0.169979·10^4 6.59297	9.94	0.0196
TCBT-3	–0.071912			–0.935801·10^3 0.384292·10^4	–0.462837·10^4 8.09348	5.04	0.0109
			1-Propanol (1) + Benzene (2)				
vdW1-2	–0.002183 0.000359		–0.028480 0.000130			6.74	0.0130
vdW1-3	–0.258366 0.000626	–0.103036 0.000214	–0.006209 –0.000036			2.96	0.0133
TCBT-2				0.168836·10^4 –7.43558	0.210817·10^3 3.82951	3.89	0.0073
TCBT-3	–0.002192			0.946773·10^3 –5.64250	0.903744·10^3 2.03577	3.98	0.0075

[a]Eqs. (1)–(7), (13), $l_{ij} = 0$; [b]Eqs. (1)–(7), (13); [c]Eqs. (1)–(11), (13), $k_{ij} = l_{ij} = m_{ij} = 0$; $\alpha_{ij} = 0.3$; [d]Eqs. (1)–(11), (13), $l_{ij} = m_{ij} = 0$; $\alpha_{ij} = 0.3$

For the system chloroform + benzene, it can be observed that when the correlation of the V^E data was performed at each temperature, the percentage deviations of the CEOS and CEOS/G^E models were somewhat higher when the temperature was higher. The two parameter vdW1-2 and TCBT-2 models worked very similar to the three parameter vdW1-3 and TCBT-3 models, respectively, with slightly higher errors. In the temperature range, except for TCBT-2, the applied CEOS and CEOS/G^E models gave relatively good results. It is evident from Table II that a significant improvement was achieved when the temperature dependent parameters were introduced only in the TCBT-2 model and partly in the TCBT-3 model, while for the vdW1 models, the errors were slightly better.

For the 1-propanol + chloroform system, it is noticeable that with increasing temperature, the errors incresed as well, except for the vdW1-3 model which be-

comes dominant at higher temperatures. The two parameter vdW1-2 and TCBT-2 models are not suitable at higher temperatures for the correlation of the V^E data for this system. A comparison between the experimental results (RK equation) and the correlating results obtained by the vdW1 and TCBT models at 288.15 and 313.15 K is shown in Fig. 1b. At 288.15 K, the V^E–x_1 curve obtained by the TCBT-2 model cannot satisfactorily describe the S-shape of the experimental values, especially in the extremities, while the TCBT-3 model is more successful. At 313.15 K, the dominance of the vdW1-3 over the vdW1-2 model is evident. In the range of temperature, three parameter models worked better than the two parameter models, but also unsatisfactorily, irrespective of whether temperature dependent parameters were used or not.

When the correlation of the V^E data was performed for 1-propanol + benzene system, at each temperature, relatively similar result around 3 % was obtained with vdW1-3, and both TCBT models, while two parameter vdW1-2 model gave some higher errors. In the temperature range, two parameter temperature independent vdW1-2 and TCBT-2 models worked considerably poorer than three parameter vdW1-3 and TCBT-3 models. Also, it is evident from Table II that considerable improvement was achieved by introducing temperature dependence in vdW1-2 and TCBT-2 models.

Prediction of V^E for the ternary systems methanol (1) + chloroform (2) + benzene (3) and 1-propanol (1) + chloroform (2) + benzene (3) at each temperature over the entire temperature range was performed using the CEOS and CEOS/G^E models, with the binary interaction parameters of these models generated from appropriate binary data. From Table III it is evident that, for both systems, the applied CEOS/G^E models are not suitable for this type of thermodynamic modelling. Much better, but still not acceptable results, were obtained by the vdW1-3 model, while only the simplest vdW1-2 model in the case of the 1-propanol (1) + chloroform (2) + benzene (3) system achieved good results. Correlation of ternary V^E data for these systems was performed using TCBT models adding the ternary contribution in the interaction parameters. Comparing the results obtained by the TCBT-2 and TCBT-3 models for both systems, it is evident that the TCBT-3 model worked slightly better at each temperature and in the temperature interval.

TABLE III. Prediction of V^E by the PRSV CEOS models for the investigated ternary systems

T / K	vdW1-2[a]		vdW1-3[b]		TCBT-2[c]		TCBT-3[d]	
	PD(V^E) %	$\sigma \times 10^6$ m^3 mol^{-1}	PD(V^E) %	$\sigma \times 10^6$ m^3 mol^{-1}	PD(V^E) %	$\sigma \times 10^6$ m^3 mol^{-1}	PD(V^E) %	$\sigma \times 10^6$ m^3 mol^{-1}
Methanol (1) + Chloroform (2) + Benzene (3)								
288.15	12.26	0.02609	14.49	0.03149	HV[g]	0.2618	HV	0.3111
293.15	13.19	0.02685	15.25	0.03178	HV	0.2597	73.91	0.1600
298.15	14.34	0.02825	16.06	0.03227	HV	0.2515	HV	0.3504

TABLE III. Continued.

T / K	vdW1-2[a]		vdW1-3[b]		TCBT-2[c]		TCBT-3[d]	
	PD(V^E) %	$\sigma \times 10^6$ $m^3\,mol^{-1}$	PD(V^E) %	$\sigma \times 10^6$ $m^3\,mol^{-1}$	PD(V^E) %	$\sigma \times 10^6$ $m^3\,mol^{-1}$	PD(V^E) %	$\sigma \times 10^6$ $m^3\,mol^{-1}$
Methanol (1) + Chloroform (2) + Benzene (3)								
303.15	15.73	0.03027	17.01	0.03309	HV	0.2483	91.40	0.1881
308.15	17.36	0.03290	17.79	0.03376	HV	0.2441	HV	0.2223
313.15	18.72	0.03494	18.54	0.03446	HV	0.2388	HV	0.2437
288.15–313.15[e]	15.88	0.0316	15.28	0.0305	–	–	16.95	0.0341
288.15–313.15[f]	15.22	0.0300	16.58	0.0329	56.89	0.01148	HV	1.0254
1-Propanol (1) + Chloroform (2) + Benzene (3)								
288.15	3.49	0.00928	18.37	0.05128	HV[g]	0.4008	92.68	0.2534
293.15	4.01	0.01043	23.35	0.06609	HV	0.4096	81.99	0.2215
298.15	4.43	0.01156	24.87	0.06925	HV	0.4215	76.88	0.2089
303.15	4.79	0.01268	24.23	0.06860	HV	0.4270	HV	0.3916
308.15	5.44	0.01441	23.72	0.06851	HV	0.4474	HV	0.4244
313.15	5.85	0.01590	23.35	0.06925	HV	0.4565	HV	0.5184
288.15–313.15[e]	9.06	0.0252	5.35	0.0150	25.72	0.0758	52.84	0.1464
288.15–313.15[f]	4.71	0.0127	15.99	0.0555	87.83	0.2196	71.70	0.1979

[a]Eqs. (1)–(7), (13), $l_{ij} = 0$; [b]Eqs. (1)–(7), (13); [c]Eqs. (1)–(11), (13), $k_{ij} = l_{ij} = m_{ij} = 0$; $\alpha_{ij} = 0.3$; [d]Eqs. (1)–(11), (13), $l_{ij} = m_{ij} = 0$; $\alpha_{ij} = 0.3$; [e]prediction of V^E using temperature independent binary parameters; [f]prediction of V^E using temperature dependent binary parameters; [g]High value

TABLE IV. Correlation of V^E by the PRSV CEOS models for the investigated ternary systems

	Δg_{123} / J mol^{-1} Δg_{132} / J mol^{-1}	Δg_{213} / J mol^{-1} Δg_{231} / J mol^{-1}	Δg_{312} / J mol^{-1} Δg_{321} / J mol^{-1}	PD(V^E) / %	$\sigma \times 10^6$ $m^3\,mol^{-1}$
Methanol (1) + Chloroform (2) + Benzene (3)					
T = 288.15 K					
TCBT-2[a]	$-0.216001 \cdot 10^4$ $0.330521 \cdot 10^3$	$0.331983 \cdot 10^4$ $-0.305165 \cdot 10^4$	$-0.895245 \cdot 10^3$ $-0.685207 \cdot 10^5$	3.00	0.00757
TCBT-3[b]	$-0.181584 \cdot 10^4$ $-0.220503 \cdot 10^4$	$-0.486347 \cdot 10^3$ $0.246196 \cdot 10^4$	$-0.175874 \cdot 10^4$ $-0.112493 \cdot 10^4$	1.73	0.00423
T = 293.15 K					
TCBT-2	$-0.204943 \cdot 10^4$ $0.143604 \cdot 10^4$	$0.223202 \cdot 10^4$ $-0.227332 \cdot 10^4$	$-0.415594 \cdot 10^3$ $-0.698775 \cdot 10^5$	2.89	0.00722
TCBT-3	$0.371297 \cdot 10^4$ $0.235339 \cdot 10^4$	$0.269915 \cdot 10^4$ $0.185877 \cdot 10^4$	$-0.518535 \cdot 10^4$ $-0.169579 \cdot 10^4$	1.61	0.00384
T = 298.15 K					
TCBT-2	$-0.191181 \cdot 10^4$ $-0.396537 \cdot 10^3$	$0.152833 \cdot 10^4$ $-0.187830 \cdot 10^4$	$0.178648 \cdot 10^3$ $-0.715393 \cdot 10^5$	2.87	0.00707
TCBT-3	$-0.548621 \cdot 10^4$ $0.500719 \cdot 10^4$	$0.127889 \cdot 10^3$ $-0.510516 \cdot 10^4$	$-0.217509 \cdot 10^4$ $0.353247 \cdot 10^4$	1.57	0.00345

TABLE IV. Continued.

	Δg_{123} / J mol⁻¹ Δg_{132} / J mol⁻¹	Δg_{213} / J mol⁻¹ Δg_{231} / J mol⁻¹	Δg_{312} / J mol⁻¹ Δg_{321} / J mol⁻¹	PD(V^E) / %	$\sigma \times 10^6$ m³ mol⁻¹
Methanol (1) + Chloroform (2) + Benzene (3)				
T = 303.15 K				
TCBT-2	$-0.181260 \cdot 10^4$ $0.120825 \cdot 10^3$	$0.153214 \cdot 10^4$ $-0.214668 \cdot 10^4$	$0.245954 \cdot 10^3$ $-0.737614 \cdot 10^5$	3.00	0.00719
TCBT-3	$-0.690601 \cdot 10^4$ $0.800038 \cdot 10^3$	$-0.164110 \cdot 10^4$ $0.787850 \cdot 10^2$	$0.694574 \cdot 10^4$ $0.234458 \cdot 10^4$	1.57	0.00340
T = 308.15 K				
TCBT-2	$-0.170755 \cdot 10^4$ $0.177365 \cdot 10^3$	$0.146794 \cdot 10^4$ $-0.221035 \cdot 10^4$	$0.362709 \cdot 10^3$ $-0.757075 \cdot 10^5$	3.17	0.00746
TCBT-3	$-0.733523 \cdot 10^4$ $0.543242 \cdot 10^3$	$-0.152677 \cdot 10^4$ $0.690292 \cdot 10^3$	$0.729489 \cdot 10^4$ $0.315206 \cdot 10^4$	1.85	0.00397
T = 313.15 K				
TCBT-2	$-0.159713 \cdot 10^4$ $0.130813 \cdot 10^4$	$0.200236 \cdot 10^4$ $-0.271314 \cdot 10^4$	$-0.227257 \cdot 10^2$ $-0.785854 \cdot 10^5$	3.52	0.00793
TCBT-3	$-0.865464 \cdot 10^4$ $0.131091 \cdot 10^3$	$-0.146771 \cdot 10^4$ $0.218790 \cdot 10^4$	$0.931429 \cdot 10^4$ $0.433321 \cdot 10^4$	1.84	0.00399
T = 288.15–313.15 K[c]				
TCBT-3	$-0.643200 \cdot 10^4$ $-0.147793 \cdot 10^4$	$-0.416194 \cdot 10^4$ $-0.508707 \cdot 10^4$	$0.925400 \cdot 10^4$ $0.831354 \cdot 10^4$	4.54	0.0110
T = 288.15–313.15 K[d]				
TCBT-2	$-0.102981 \cdot 10^4$ $0.237608 \cdot 10^4$	$-0.112302 \cdot 10^4$ $-0.150594 \cdot 10^4$	$0.108598 \cdot 10^4$ $-0.687462 \cdot 10^5$	6.91	0.0159
TCBT-3	$-0.297640 \cdot 10^3$ $-0.156207 \cdot 10^4$	$0.860895 \cdot 10^5$ $0.112204 \cdot 10^4$	$0.112204 \cdot 10^4$ $0.942530 \cdot 10^5$	4.45	0.0110
1-Propanol (1) + Chloroform (2) + Benzene (3)				
T = 288.15 K				
TCBT-2	$0.228110 \cdot 10^4$ $-0.144128 \cdot 10^3$	$-0.404970 \cdot 10^4$ $0.402080 \cdot 10^4$	$-0.805761 \cdot 10^3$ $-0.151393 \cdot 10^4$	3.09	0.00947
TCBT-3	$-0.537758 \cdot 10^4$ $-0.414362 \cdot 10^4$	$0.564205 \cdot 10^4$ $0.626995 \cdot 10^4$	$-0.694120 \cdot 10^4$ $-0.575803 \cdot 10^3$	1.78	0.00496
T = 293.15 K				
TCBT-2	$0.220340 \cdot 10^4$ $-0.182405 \cdot 10^3$	$-0.361646 \cdot 10^4$ $0.406272 \cdot 10^4$	$-0.949869 \cdot 10^3$ $-0.102617 \cdot 10^5$	3.05	0.00926
TCBT-3	$0.821370 \cdot 10^4$ $-0.233635 \cdot 10^4$	$0.758260 \cdot 10^4$ $0.735235 \cdot 10^4$	$-0.500333 \cdot 10^4$ $-0.193503 \cdot 10^4$	1.43	0.00414
T = 298.15				
TCBT-2	$0.226181 \cdot 10^4$ $-0.153375 \cdot 10^3$	$-0.379604 \cdot 10^4$ $0.408361 \cdot 10^4$	$-0.952405 \cdot 10^3$ $-0.323087 \cdot 10^4$	3.04	0.00943
TCBT-3	$0.838612 \cdot 10^4$ $-0.638441 \cdot 10^4$	$-0.305674 \cdot 10^4$ $0.745891 \cdot 10^4$	$0.357589 \cdot 10^4$ $-0.170838 \cdot 10^4$	1.70	0.00489

TABLE IV. Continued.

	Δg_{123} / J mol^{-1} Δg_{132} / J mol^{-1}	Δg_{213} / J mol^{-1} Δg_{231} / J mol^{-1}	Δg_{312} / J mol^{-1} Δg_{321} / J mol^{-1}	PD(V^E) / %	$\sigma \times 10^6$ m^3 mol^{-1}
1-Propanol (1) + Chloroform (2) + Benzene (3)				
	T = 303.15 K				
TCBT-2	$0.229285 \cdot 10^4$ $-0.265356 \cdot 10^3$	$-0.396769 \cdot 10^4$ $0.420063 \cdot 10^4$	$-0.859157 \cdot 10^3$ $-0.121934 \cdot 10^5$	2.85	0.00909
TCBT-3	$-0.524865 \cdot 10^4$ $0.111767 \cdot 10^5$	$-0.311913 \cdot 10^4$ $-0.376340 \cdot 10^4$	$0.533207 \cdot 10^4$ $0.832227 \cdot 10^4$	1.69	0.00485
	T = 308.15 K				
TCBT-2	$0.233657 \cdot 10^4$ $-0.202952 \cdot 10^3$	$-0.393679 \cdot 10^4$ $0.420418 \cdot 10^4$	$-0.983846 \cdot 10^3$ $-0.907649 \cdot 10^4$	2.93	0.00924
TCBT-3	$-0.552509 \cdot 10^4$ $0.116962 \cdot 10^5$	$0.304273 \cdot 10^4$ $-0.402050 \cdot 10^4$	$0.519002 \cdot 10^4$ $0.887191 \cdot 10^4$	1.71	0.00515
	T = 313.15 K				
TCBT-2	$0.236775 \cdot 10^4$ $-0.277245 \cdot 10^3$	$-0.385129 \cdot 10^4$ $0.395861 \cdot 10^4$	$-0.830860 \cdot 10^3$ $0.861178 \cdot 10^2$	2.84	0.00937
TCBT-3	$-0.631254 \cdot 10^4$ $0.989397 \cdot 10^4$	$0.126667 \cdot 10^5$ $-0.115236 \cdot 10^5$	$-0.832791 \cdot 10^4$ $0.965200 \cdot 10^4$	1.80	0.00557
	T = 288.15–313.15 K^c				
TCBT-2	$0.295533 \cdot 10^4$ $0.276140 \cdot 10^4$	$-0.306031 \cdot 10^4$ $0.246993 \cdot 10^4$	$-0.101354 \cdot 10^4$ $-0.537722 \cdot 10^4$	12.26	0.0344
TCBT-3	$-0.516953 \cdot 10^4$ $-0.495301 \cdot 10^4$	$0.823286 \cdot 10^4$ $0.836822 \cdot 10^4$	$-0.561513 \cdot 10^4$ $-0.692308 \cdot 10^3$	2.57	0.0077
	T = 288.15–313.15 K^d				
TCBT-2	$0.244863 \cdot 10^4$ $0.589126 \cdot 10^2$	$-0.461499 \cdot 10^4$ $0.458958 \cdot 10^4$	$-0.125297 \cdot 10^4$ $0.940416 \cdot 10^5$	3.65	0.0107
TCBT-3	$0.928149 \cdot 10^4$ $0.145152 \cdot 10^4$	$0.523491 \cdot 10^4$ $-0.450387 \cdot 10^4$	$-0.197974 \cdot 10^4$ $0.568441 \cdot 10^5$	2.88	0.0085

^{a}Eqs. (1)–(13), $k_{ij} = l_{ij} = m_{ij} = 0$, $\alpha_{ij} = 0.3$; ^{b}Eqs. (1)–(13), $l_{ij} = m_{ij} = 0$, $\alpha_{ij} = 0.3$; ^{c}correlation of V^E using prediction results obtained with temperature independent binary parameters; ^{d}correlation of V^E using prediction results obtained with temperature dependent binary parameters

4.2. Prediction of V^E by empirical models

An attractive alternative to the CEOS and CEOS/G^E models is the prediction of V^E for multicomponent systems performed by empirical equations existing in the literature.

Frequently used expressions for these models are as follows:

i) The Radojković *et al.* model[29]

$$V_{123}^E = V_{12}^E + V_{13}^E + V_{23}^E \tag{17}$$

in which the binary contributions V_{ij}^E are determined directly using the ternary mole fractions;

ii) The Kohler model[34]

$$V_{123}^E = \left(x_1 + x_2\right)^2 V_{12}^E(x_1^a, x_2^a) + \left(x_1 + x_3\right)^2 V_{13}^E(x_1^a, x_3^a) + \left(x_2 + x_3\right)^2 V_{23}^E(x_2^a, x_3^a) \quad (18)$$

Kohler's equation is symmetric, treating all binaries identically. The mole fractions in binary contributions are $x_i^a = 1 - x_j^a = x_i / \left(x_i + x_j\right)$;

iii) The Jacob–Fitzner model[39]

$$V_{123}^E = x_1 x_2 \Big/ \left[\left(x_1 + x_3/2\right)\left(x_2 + x_3/2\right)\right] V_{12}^E(x_1^b, x_2^b) +$$
$$+ x_1 x_3 \Big/ \left[\left(x_1 + x_2/2\right)\left(x_3 + x_2/2\right)\right] V_{13}^E(x_1^b, x_3^b) + \quad (19)$$
$$+ x_2 x_3 \Big/ \left[\left(x_2 + x_1/2\right)\left(x_3 + x_1/2\right)\right] V_{23}^E(x_2^b, x_3^b)$$

where $x_i^b = 1 - x_j^b = \left(1 + x_i - x_j\right)/2$;

iv) The Colinet model[40]

$$V_{123}^E = 0.5 \left\{ \begin{array}{l} \left[x_2/\left(1-x_1\right)\right]V^E(x_1, 1-x_1) + \left[x_1/\left(1-x_2\right)\right]V^E(1-x_2, x_2) + \\ + \left[x_3/\left(1-x_1\right)\right]V^E(x_1, 1-x_1) + \left[x_1/\left(1-x_3\right)\right]V^E(1-x_3, x_3) + \\ + \left[x_3/\left(1-x_2\right)\right]V^E(x_2, 1-x_2) + \left[x_2/\left(1-x_3\right)\right]V^E(1-x_3, x_3) \end{array} \right\} \quad (20)$$

v) The Tsao–Smith model[41]

$$V_{123}^E = \left[x_2/\left(1-x_1\right)\right]V_{12}^E(x_1^c, x_2^c) + \left[x_3/\left(1-x_1\right)\right]V_{13}^E(x_1^c, x_3^c) + \left(1-x_1\right)V_{23}^E(x_2^c, x_3^c) \quad (21)$$

Bearing in mind that this model is asymmetric, the binary contributions are evaluated in following manner:

a) $x_i^c = x_1$ and $x_j^c = 1 - x_i^c$ for binaries 1–2 and 1–3, and $x_2^c = 1 - x_3^c = x_2/\left(x_2 + x_3\right)$ for binary 2–3 (option *a* in Table V)

b) $x_i^c = x_2$ and $x_j^c = 1 - x_i^c$ for binaries 2–1 and 2–3, and $x_1^c = 1 - x_3^c = x_1/\left(x_1 + x_3\right)$ for binary 1–3 (option *b* in Table V)

c) $x_i^c = x_3$ and $x_j^c = 1 - x_i^c$ for binaries 3–1 and 3–2, and $x_1^c = 1 - x_2^c = x_1/\left(x_1 + x_2\right)$ for binary 1–2 (option *c* in Table V)

vi) The Toop model[42]

$$V_{123}^E = \left[x_2/\left(1-x_1\right)\right]V_{12}^E(x_1^c, x_2^c) + \left[x_3/\left(1-x_1\right)\right]V_{13}^E(x_1^c, x_3^c) + \left(1-x_1\right)^2 V_{23}^E(x_2^c, x_3^c) \quad (22)$$

in which the binary mole fractions are computed as in the Tsao–Smith model (Eq. (21)).

vii) The Scatchard model[43]

$$V_{123}^E = \left[x_2/\left(1-x_1\right)\right]V_{12}^E(x_1^c, x_2^c) + \left[x_3/\left(1-x_1\right)\right]V_{13}^E(x_1^c, x_3^c) + V_{23}^E(x_2, x_3) \quad (23)$$

where x_i^c and x_j^c were computed as in the case of the Tsao-Smith model (Eq. (21)).

viii) The Rastogi model[44]

$$V_{123}^E = 0.5\left[\left(x_1 + x_2\right)V_{12}^E(x_1^a, x_2^a) + \left(x_1 + x_3\right)V_{13}^E(x_1^a, x_3^a) + \left(x_2 + x_3\right)V_{23}^E(x_2^a, x_3^a)\right] \quad (24)$$

where $x_i^a = 1 - x_j^a = x_i/\left(x_i + x_j\right)$.

TABLE V. Prediction of the V^E data by the empirical models for the investigated ternary systems

Model	$\sigma \times 10^6$ / m³ mol⁻¹					
	Methanol (1) + Chloroform (2) +Benzene (3)					
	T / K					
	288.15	293.15	298.15	303.15	308.15	313.15
Radojković	0.0336	0.0340	0.0344	0.0350	0.0358	0.0363
Kohler	0.0309	0.0310	0.0312	0.0315	0.0320	0.0320
Jacob–Fitzner	0.0336	0.0340	0.0344	0.0350	0.0358	0.0363
Colinet	0.0294	0.0294	0.0296	0.0300	0.0305	0.0304
Tsao–Smith[a]	0.0078	0.0077	0.0078	0.0080	0.0083	0.0092
Tsao–Smith[b]	0.0318	0.0329	0.0339	0.0352	0.0365	0.0372
Tsao–Smith[c]	0.0516	0.0517	0.0519	0.0520	0.0520	0.0518
Toop[a]	0.0254	0.0242	0.0231	0.0219	0.0208	0.0194
Toop[b]	0.0311	0.0324	0.0338	0.0355	0.0375	0.0391
Toop[c]	0.0350	0.0354	0.0360	0.0366	0.0376	0.0379
Scatchard[a]	0.0256	0.0245	0.0234	0.0222	0.0211	0.0198
Scatchard[b]	0.0315	0.0328	0.0343	0.0362	0.0384	0.0402
Scatchard[c]	0.0373	0.0378	0.0385	0.0393	0.0405	0.0409
Rastogi	0.0528	0.0516	0.0506	0.0498	0.0493	0.0486
	1-Propanol (1) + Chloroform (2) + Benzene (3)					
Radojković	0.0302	0.0304	0.0312	0.0319	0.0326	0.0339
Kohler	0.0304	0.0303	0.0308	0.0310	0.0310	0.0321
Jacob-Fitzner	0.0302	0.0304	0.0312	0.0319	0.0326	0.0339
Colinet	0.0274	0.0275	0.0280	0.0282	0.0285	0.0294
Tsao–Smith[a]	0.0348	0.0349	0.0347	0.0350	0.0349	0.0354
Tsao–Smith[b]	0.0424	0.0417	0.0414	0.0408	0.0395	0.0394
Tsao–Smith[c]	0.0538	0.0524	0.0515	0.0501	0.0484	0.0476
Toop[a]	0.0159	0.0165	0.0171	0.0181	0.0187	0.0201
Toop[b]	0.0491	0.0501	0.0514	0.0526	0.0536	0.0554
Toop[c]	0.0409	0.0413	0.0424	0.0431	0.0437	0.0453
Scatchard[a]	0.0158	0.0163	0.0166	0.0176	0.0180	0.0192
Scatchard[b]	0.0531	0.0540	0.0555	0.0567	0.0580	0.0598
Scatchard[c]	0.0399	0.0408	0.0422	0.0433	0.0444	0.0465
Rastogi	0.0581	0.0585	0.0595	0.0610	0.0633	0.0660

[a]Methanol or 1-propanol is the asymmetric components; [b]chloroform is the asymmetric component; [c]benzene is the asymmetric component

As can be seen from Table V, the best results of V^E predictions for the system methanol + chloroform + benzene were obtained with the a-type Tsao–Smith Equation. This a-type asymmetric model assumes that component shown as first in the numbering (methanol) is the asymmetric component. This type is the most adequate, giving the best agreement with the experimental data for this system. In addition, two other asymmetric expressions, the a-type Toop and the a-type Scatchard Equation, produced lower RMSD and could be recommended. The Radojković, Kohler, Jacob–Fitzner, Colinet, b-type Tsao–Smith, b-type Toop and b-type Scatchard function satisfactorily, while the other models present clearly higher deviations and can not be recommended.

The best agreement with experimental V^E data for the system 1-propanol + + chloroform + benzene, as shown in Table V, was achieved by the asymmetric models: the a-type of Scatchard and the a-type of Toop, having in both cases 1-propanol as the asymmetric component. Satisfactory results were obtained using the symmetric models of Radojković, Kohler, Jacob–Fitzner and Colinet. All other asymmetric equations worked very poorly, whereas the worst predictions were obtained with the symmetric Rastogi model. It can be concluded that for both studied ternary systems, the majority of the examined predictive models gave adequate predictions of V^E from the data of their binary sub-systems.

Comparison of the results achieved by the empirical models and the CEOS and CEOS/G^E models leads to the following remarks: for the methanol + chloroform + benzene system, the results obtained by both CEOS models (vdW1-2 and vdW1-3) are of the same quality compared with those attained by the majority of the empirical models (an exception is the a-type Tsao–Smith model). For the 1-propanol + chloroform + benzene system, the vdW1-2 model worked signifycantly better than the vdW1-3 one and all empirical models. The applied CEOS/G^E models, as it was already mentioned, are not suitable for this type of estimations for the ternary systems examined here.

5. CONCLUSION

In the last decades, powerful thermodynamic models (G^E, CEOS, polynomials, *etc.*) have been developed. Firstly, the achievement was mainly directed to the correlation, prediction, cross prediction and simultaneous fitting of VLE, LLE, H^E, c_p^E, *etc.* However, until the employment of CEOS/G^E models, which are no longer limited to non-polar systems, the range of applicability could not be extended to very complex mixtures with polar components over wide ranges of pressure and temperature, including the critical region. This rapid progress was imposed by a specific behaviour of G^E on the CEOS model through its additional flexible mixing rules. The accurate results of the CEOS/G^E models, such as the TCBT-3 model, used in correlating and predicting V^E for diverse, strongly non-ideal systems over a large range of temperature, are very promising. In addition, the range of their applicability could be extended to other thermodynamic properties (H^E, c_p^E, *etc.*) and, as the most important, to mixtures which hitherto could not be successfully represented by CEOS. Based on the results of this study, it can be concluded that the CEOS/G^E mixing rules have an advantage over the vdW1-one fluid mixing rules for almost all the here investigated binary and ternary systems and in some cases the improvement was quite significant. The results obtained using the TCBT model with an insignificant change of parameters, generated from an individual isotherm, support the opinion that the influence of temperature on the CEOS/G^E parameters is reduced, enabling extrapolation over wider ranges of temperature. A number of the examined empirical models, especially some of the

asymmetric ones, such as Tsao–Smith, Toop and Scathhard, allowed adequate prediction of V^E of ternary mixtures from the data of binary subsystems. However, the reliability that most of the empirical polynomials employed exhibited suggests that no unique equation can represent the diverse types of complex systems.

ИЗВОД

МОДЕЛОВАЊЕ ВОЛУМЕТРИЈСКИХ СВОЈСТАВА БИНАРНИХ И ТЕРНЕРНИХ СМЕША ПОМОЋУ CEOS, CEOS/G^E И ЕМПИРИЈСКИХ МОДЕЛА

БОЈАН Д. ЂОРЂЕВИЋ, СЛОБОДАН П. ШЕРБАНОВИЋ, ИВОНА Р. РАДОВИЋ, АЛЕКСАНДАР Ж. ТАСИЋ И МИРЈАНА Љ. КИЈЕВЧАНИН

Технолошко–мешалуршки факулшеш, Универзишеш у Београду, Карнегијева 4, 11000 Београд

Иако су правила мешања базирана на кубним једначинама стања и van der Waals-један флуид правилу мешања, која укључују температурно зависне параметре, довољна за прорачун равнотеже пара–течност и допунских својстава (допунска моларна енталпија H^E, допунска моларна запремина V^E, итд.), проблеми настају при корелисању и предсказивању термодинамичких својстава сложених смеша у различитим интервалима температуре и притиска. Велики напредак је остварен приступом базираном на CEOS/G^E моделима. Овај рад представља преглед доприноса у последњих шест година наше истраживачке групе у моделовању волуметријских својстава сложених бинарних и тернерних система нееелектролита помоћу CEOS и CEOS/G^E приступа. Посебно, vdW1 и TCBT модели су примењени за израчунавање V^E података тернерних система метанол + хлороформ + бензен и 1-пропанол + хлороформ + бензен, као и одговарајућих бинарних система метанол + хлороформ, хлороформ + + бензен, 1-пропанол + хлороформ и 1-пропанол + бензен у интервалу температуре 288.15– –313.15 K и на атмосферском притиску. Такође, извршено је и предсказивање V^E података за оба тернерна система емпиријским моделима (Radojković, Kohler, Jackob–Fitzner, Colinet, Tsao–Smith, Toop, Scatchard и Rastogi).

REFERENCES

1. I. R. Grgurić, A. Ž. Tasić, B. D. Djordjević, M. Lj. Kijevčanin, S. P. Šerbanović, *J. Serb. Chem. Soc.* **67** (2002) 581
2. I. R. Grgurić, S. P. Šerbanović, M. Lj. Kijevčanin, A. Ž. Tasić, B. D. Djordjević, *Thermochim. Acta* **412** (2004) 25
3. S. P. Šerbanović, M. Lj. Kijevčanin, I. R. Radović, B. D. Djordjević, *Fluid Phase Equilib.* **239** (2006) 69
4. I. R. Radović, M. Lj. Kijevčanin, E. M. Djordjević, B. D. Djordjević, S. P. Šerbanović, *Fluid Phase Equilib.* in press
5. M. Lj. Kijevčanin, S. P. Šerbanović, I. R. Radović, B. D. Djordjević, A. Ž. Tasić, *Fluid Phase Equilib.* **251** (2007) 78
6. M. Lj. Kijevčanin, M. M. Djuriš, I. R. Radović, B. D. Djordjević, S. P. Šerbanović, *J. Chem. Eng. Data* **52** (2007) 1136
7. M. Lj. Kijevčanin, I. M. Purić, I. R. Radović, B. D. Djordjević, S. P. Šerbanović, *J. Chem. Eng. Data* **52** (2007) 2067

8. J. D. Smiljanić, M. Lj. Kijevčanin, B. D. Djordjević, D. K. Grozdanić, S. P. Šerbanović, *Int. J. Thermophys.*, in press
9. M. Lj. Kijevčanin, B. D. Djordjević, S. P. Šerbanović, I. R. Grgurić, A. Ž. Tasić, *Physic. Chem. Liquids* **42** (2004) 147
10. M. Lj. Kijevčanin, B. D. Djordjević, S. P. Šerbanović, I. R. Grgurić, A. Ž. Tasić, *Physic. Chem. Liquids* **44** (2006) 233
11. I. R. Grgurić, A. Ž. Tasić, B. D. Djordjević, M. Lj. Kijevčanin, S. P. Šerbanović, *J. Serb. Chem. Soc.* **68** (2003) 47
12. M. Lj. Kijevčanin, S. P. Šerbanović, I. R. Radović, B. D. Djordjević, A. Ž. Tasić, *J. Serb. Chem. Soc.* **71** (2006) 807
13. S. P. Šerbanović, I. R. Grgurić, M. Lj. Kijevčanin, A. Ž. Tasić, B. D. Djordjević, *Korean J. Chem. Eng.* **21** (2004) 858
14. Y. Adachi, H. Sugie, *Fluid Phase Equilib.* **23** (1986) 103
15. P. A. Gupta, P. Rasmussen, A. Fredenslund, *Ind. Eng. Chem. Fundam.* **25** (1986) 636
16. H. Renon, J.M. Prausnitz, *AIChE J.* **14** (1968) 135
17. R. Stryjek, J. H. Vera, *Can. J. Chem. Eng.* **64** (1986) 323
18. C. H. Twu, J. E. Coon, D. Bluck, B. Tilton, *Fluid Phase Equilib.* **158**–**160** (1999) 271
19. O. Redlich, A. Kister, *Ind. Eng. Chem.* **40** (1948) 345
20. P. R. Bevington, D. K. Robinson, *Data Reduction and Error Analysis for the Physical Sciences*, McGraw-Hill, Singapore, 1994
21. T. M. Letcher, J. A. Nevines, *J. Chem. Thermodyn.* **26** (1994) 697
22. R. Tanaka, S. Toyama, *J .Chem. Eng. Data* **42** (1997) 871
23. J.–P. E. Grolier, G. C. Benson, P. Picker, *J. Chem. Eng. Data* **20** (1975) 243
24. T. M. Letcher, J. A. Nevines, *J. Chem. Eng. Data* **40** (1995) 293
25. J. Inarrea, J. Valero, P. Perez, M. Gracia, C. G. Losa, *J. Chem. Thermodyn.* **20** (1988) 193
26. K. N. Marsh, C. Burfitt, *J. Chem. Thermodyn.* **7** (1975) 955
27. R. Malhotra, B. S. Mahl, Int. Data Ser. Sel. Data Mixtures Ser. A 1 (1991) 52
28. I. Nagata, K.Tamura, *J. Chem. Thermodyn.* **22** (1990) 279
29. N. Radojković, A. Tasić, D. Grozdanić, B. Djordjević, D. Malić, *J. Chem. Thermodyn.* **9** (1977) 349
30. P. P. Singh, B. R. Sharma, K. S. Sidhu, *Can. J. Chem.* **56** (1978) 2127
31. T. E. Daubert, R. P. Danner, *Physical and Thermodynamic Properties of Pure Chemicals; Data Compilation*, Hemisphere Publishing Corporation, New York, 1989
32. J.-P. E. Grolier, G. Roux–Desgranges, Z. S. Kooner, J. F. Smith, L. G. Hepler, *J. Solution Chem.* **16** (1987) 745
33. H. Nomura, S. Koda, Y. Miyahara, *J. Chem. Phys.* **65** (1976) 4339
34. F. Kohler, *Monatsh. Chem.* **91** (1960) 738
35. P. K. Talley, J. Sangster, C. W. Bale, A. D. Pelton, *Fluid Phase Equilib.* **85** (1993) 101
36. M. Dominguez–Perez, S. Freire, J. J. Llano, E. Rilo, L. Segade, O. Cabeza, E. Jimenez, *Fluid Phase Equilib.* **212** (2003) 331
37. A. Touriño, M. Hervello, V. Moreno, G. Marino, M. Iglesias, *J. Serb. Chem. Soc.* **69** (2004) 461
38. D. W. Marquardt, *J. Soc. Ind. Appl. Math.* **2** (1963) 431
39. K. T. Jakob, K. Fitzner, *Thermochim. Acta* **18** (1977) 197
40. C. Colinet, *Ph.D. Thesis*, University of Grenoble, France, 1967
41. C. C. Tsao, J. M. Smith, *Chem. Eng. Prog. Symp. Series* **49** (1953) 107
42. G. W. Toop, *Trans. TMS-AIME* **233** (1965) 850
43. G. Scatchard, L. B. Ticknor, J. R. Goates, E. R. McCartney, *J. Am. Chem. Soc.* **74** (1952) 3721
44. R. P. Rastogi, J. Nath, S. S. Das, *J. Chem. Eng. Data,* **22** (1977) 249.