AUTHORS' REVIEW

Prediction of thermophysical and transport properties of ternary organic non-electrolyte systems including water by polynomials

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Abstract: The description and prediction of thermophysical and transport properties of ternary organic non-electrolyte systems including water by polynomial equations are reviewed. Empirical equations of Radojković *et al.* (also known as Redlich–Kister), Kohler, Jacob–Fitzner, Colinet, Tsao–Smith, Toop, Scatchard *et al.* and Rastogi *et al.* are compared with experimental data of available papers that appeared in well know international journals (Fluid Phase Equilibria, Journal of Chemical and Engineering Data, Journal of Chemical Thermodynamics, Journal of Solution Chemistry, Journal of the Serbian Chemical Society, The Canadian Journal of Chemical Engineering, Journal of Molecular Liquids, Thermochimica Acta, *etc.*). The applicability of empirical models to estimate excess molar volumes, V^E, excess viscosities, $\Delta\eta$, excess free energies of activation of viscous flow, ΔG^{*E}, molar refraction changes on mixing, ΔR, changes in the refractive indices on mixing, Δn_D, changes of isentropic compressibility, $\Delta\kappa_s$, surface tension deviations, $\Delta\sigma$, speed of sound deviations, Δu, relative permittivity deviations, $\sigma\varepsilon_r$, were checked on the series of ternary mixtures of very complex structure, which is described very shortly. The obtained results of prediction are discussed and some recommendations about the use of symmetric or asymmetric models to the possible application to mixtures are made.

Keywords: prediction; thermophysical properties; transport properties; polynomials; ternary non-electrolyte systems.

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1. INTRODUCTION

Reliable thermophysical (the term thermodynamic has also been frequently used, especially when enthalpy and phase equilibria were included in the work) and transport properties of binary, ternary and multi-component systems are of primary interest for synthesis, design and process optimization in chemical, petrochemical and other industries. These properties are important not only for a fundamental understanding of mixing processes, but also in many practical problems concerning fluid phase equilibria, excess functions of solutions, fluid flow, *etc*.

The cost of the various process plants could be much higher if the thermochemical and thermophysical data are unreliable, or thermodynamic methods and models for process simulations are inadequate.

Thermophysical and transport properties can be successfully studied using experimental procedures, macroscopic correlations and predictions, molecular theories or computer simulation. However, no general theory has appeared that could adequately describe the composition dependence of the excess and other properties of liquid mixtures. Therefore, these functional forms are frequently presented by various empirical equations.

Experimental measurements of thermophysical properties of binary systems have been performed extensively in the past, and the obtained data and the parameters of the corresponding models are systematized in various Data Banks, but the experimental data for ternary systems are often scarce and could not be adequate. Moreover, these experimental procedures even with modern instrumentation are frequently very complicated and tend to be expensive and time-consuming.

The design of chemical plants requires very accurate data of the considered properties and reliable correlating models or, in the absence of experimental data, accurate predictive methods are necessary. These methods are the most attractive and powerful approaches among the theoretical methods because they are simple and effective and only require binary information that is relatively easy to obtain. On the other hand, experimental data could be applied to verify experimental equations. In addition, it is important to emphasize that accurate prediction of ternary mixtures containing associating and hydrogen-bonding components is traditionally a difficult thermodynamic problem.

This is one of the main reasons for the primary goals of research and the considerable efforts of researchers and process engineers devoted to the development and improvement of traditional models for correlation and prediction of properties for complex mixtures.

This brief review of several polynomial equations can do no more than summarize some recent activities in the prediction of thermodynamic and transport properties of complex ternary systems, using empirical models that are widely employed today as appeared in well known international journals. This text could be treated as continuation of the V^E predictions performed in the work of McCargar and Acree[1] and an extension to other thermodynamic and transport properties, except the prediction of ternary excess enthalpy data reviewed in an article of Prado *et al.*[2]

2. THERMOPHYSICAL AND TRANSPORT PROPERTIES

In order to estimate the utility of empirical equations to describe thermodynamic and transport behaviour of the ternary systems, the excess, changes of mixing, deviation and other properties can be used. Here, these properties are signed as in original papers, bearing in the mind that frequently for the same property different authors use different names.

Excess molar volume. The excess molar volumes V^E are computed using the equation:

$$V^E = \sum_{i=1}^{n} x_i M_i \left[(1/\rho) - (1/\rho_i) \right] = V - \sum_{i=1}^{n} x_i M_i / \rho_i \quad (1)$$

where ρ_i is the density of a pure component and ρ is the density of a mixture. V is a mixture molar volume, while x_i and M_i are the molar fraction and molar mass of component i. n is the number of components in a mixture.

Excess viscosity. The excess viscosities (or viscosity deviations $\Delta\eta$) are evaluated using the expression:

$$\Delta\eta = \eta - \sum_{i=1}^{n} x_i \eta_i \quad (2)$$

where η_i is the pure component dynamic viscosity and η is the dynamic viscosity of the mixture.

Excess free energies of activation of viscous flow. The excess free energies of activation of viscous flow ΔG^{*E} are obtained from the equation:

$$\Delta G^{*E} = RT \left[\ln(\eta V) - \sum_{i=1}^{n} x_i \ln(\eta_i V_i) \right] \quad (3)$$

where R is the universal gas constant, T is the absolute temperature; V and V_i are the molar volumes of a mixture and a component i, respectively.

Molar refraction changes of mixing. The molar refraction changes of mixing ΔR (molar refractivity deviations) are obtained from:

$$\Delta R = R - \sum_{i=1}^{n} x_i R_i = \frac{n_D^2 - 1}{n_D^2 + 2} V - \sum_{i=1}^{n} x_i R_i \qquad (4)$$

where R and R_i are molar refractions (molar refractivities) of a mixture and a pure component i, respectively, while n_D is the refractive index of the mixture. ΔR can also be calculated using the volume fraction of component i, ϕ_i:

$$\Delta R = R_m - \sum_{i=1}^{n} \phi_i R_i \qquad (5)$$

where

$$R_m = \left(\frac{n_D^2 - 1}{n_D^2 + 1} \right) \left(\frac{\sum_{i=1}^{n} x_i M_i}{\rho_m} \right) \qquad (6)$$

$$R_i = \left(\frac{n_{Di}^2 - 1}{n_{Di}^2 + 1} \right) \left(\frac{M_i}{\rho_i} \right) \qquad (7)$$

and

$$\phi_i = \frac{x_i V_i}{\sum_{i=1}^{n} x_i V_i} \qquad (8)$$

Changes in the refractive indices on mixing. The changes in the refractive indices on mixing, Δn_D, were computed using the equation:

$$\Delta n_D = n_D - \sum_{i=1}^{n} x_i n_{Di} \qquad (9)$$

where n_{Di} is a refractive index of the component i, and n_D is the refractive index of a mixture.

Changes of isentropic compressibilities. The changes of isentropic compressibility (excess isentropic compressibility, κ_s^E, or isentropic compressibility changes of mixing) $\Delta \kappa_s$ were calculated by means of the expression:

$$\Delta \kappa_s = \kappa_s - \kappa_s^{id} = \left(\rho u^2 \right)^{-1} - \kappa_s^{id} \qquad (10)$$

where κ_s is the isentropic compressibility (determined by means of the Laplace Equation $\kappa_s = \rho^{-1} u^{-2}$) and u is the speed of sound of a mixture, while κ_s^{id} is the isentropic compressibility of an ideal mixture.

Surface tension deviations. The surface tension deviations, $\Delta\sigma$, are computed using the equation:

$$\Delta\sigma = \sigma - \sum_{i=1}^{n} x_i\sigma_i \qquad (11)$$

where σ and σ_i are the surface tensions of a mixture and of component i, respectively.

Speed of sound deviations. The speed of sound deviations, Δu, with respect to the ideal behaviour of a mixture are represented using the equation:

$$\Delta u = u - u^{\text{id}} = u - \sum_{i=1}^{n} x_i u_i \qquad (12)$$

where u and u_i denote the speed of sound for a mixture and a pure component i, respectively.

The aforementioned properties of experimental data for binary and ternary mixtures incorporated in this study are given in the cited literature. The excess and derived functions of binary mixtures can be given by the Redlich–Kister Equation:[3]

$$Q_{ij} = x_i x_j \sum_{p=0}^{k} A_p (2x_i - 1)^p \qquad (13)$$

where Q_{ij} represents any of the aforementioned properties; x_i and x_j are the mole fractions of component i and j, respectively, and A_p denotes the polynomial coefficients.

3. PREDICTING EMPIRICAL MODELS

Although it would be possible to evaluate the thermodynamic and transport properties of ternary and multi-component systems from the properties of their pure components, in many cases in practice such calculations could be very inaccurate due to the complex structure of a non-ideal mixture, which is a consequence of the effects of mixing. A successful approach that limits experimental measurements to binary mixtures is to estimate the properties of multi-component systems using only the corresponding properties of the constituent binary systems. The most essential step seems to be that the data reflecting ternary interactions are very weak. It is clear that in this way enormous experimental effort required for ternary data could be saved.

All models could be regarded as physical or/and mathematical models.[4] A physical model describes information gathered by experiments connected to phenomena which occurs in the chemical and related properties. A mathematical

model is based on parameters generated from experimental data or by examination of a physical model.

The herein considered models treated as physical are transformed to mathematical ones in the form of polynomials. These polynomials can then be applied for predictions. The parameters of these models can be generated using experimental data of the corresponding properties obtained from the physical model. It is important to test the quality of predictions performed with data already available or obtained by new measurements. To solve practical problems, it is almost always necessary to develop corresponding computer programs based on knowledge of thermodynamic and transport properties and models relevant for wide complex mixtures of molecular variety.

No general theory exists that would enable the composition dependence of the various properties of liquid mixtures to be adequately presented. In addition to the work of McCargar and Acree,[1] various empirical methods for the prediction of the properties of ternary systems are reviewed in the work of Hillert[4] as analytical numerical and asymmetric methods, including the polynomials treated in the present review.

During the last few decades, several different empirical equations and polynomials have been developed in order to describe the thermodynamic and transport properties of binary and multi-component systems. Most of them, even the very old, are still popular and suitable for the correlation of most binary mixtures. When their parameters evaluated only from binary mixtures are used to predict ternary or multi-component data, the obtained data are not always satisfactory and comparison must be performed to ascertain which polynomials could be recommended to predict ternary data. Some of the polynomials were originally proposed to predict specific properties; however, they should be applicable to any other property included in the consideration.

Frequently used expressions for empirical models are applied here as follows:

I) The Radojković *et al.* model[5] presents an expression proposed by Redlich and Kister.[3] For a ternary system without ternary effects, the excess properties have the following form:

$$Q_{123} = Q_{12} + Q_{13} + Q_{23} \tag{14}$$

where the binary contributions Q_{12}, Q_{13} and Q_{23} are determined directly with Eqs. (1)–(5) and (9)–(12) using the ternary mole fractions x_1, x_2 and x_3 and the coefficients of corresponding binary systems. Some authors introduce this equation as the Redlich–Kister model. This fact is indicated in the present text.

II) The Kohler model[6] aimed at predicting excess properties of ternary systems is given as:

$$Q_{123} = (x_1 + x_2)^2 \, Q_{12}(x_1^a, x_2^a) + (x_1 + x_3)^2 \, Q_{13}(x_1^a, x_3^a) + $$
$$+ (x_2 + x_3)^2 \, Q_{23}(x_2^a, x_3^a) \tag{15}$$

In this equation Q_{ij} refers to a corresponding property Q calculated by x_i^a and x_j^a in the binary mixtures using the following equation:

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

III) The Jacob–Fitzner model[7] for expressing the excess properties of ternary systems takes the form:

$$Q_{123} = \frac{x_1 x_2}{\left(x_1 + \dfrac{x_3}{2} \right)\left(x_2 + \dfrac{x_3}{2} \right)} Q_{12}\left(x_1^b, x_2^b \right) + $$
$$+ \frac{x_1 x_3}{\left(x_1 + \dfrac{x_2}{2} \right)\left(x_3 + \dfrac{x_2}{2} \right)} Q_{12}\left(x_1^b, x_3^b \right) + \tag{16}$$
$$+ \frac{x_2 x_3}{\left(x_2 + \dfrac{x_1}{2} \right)\left(x_3 + \dfrac{x_1}{2} \right)} Q_{23}\left(x_2^b, x_3^b \right)$$

where each binary contribution is evaluated at molar fractions calculated by:

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

IV) The Colinet model[8] can be used for ternary system with six different binary compositions and has the following form:

$$Q_{123} = 0.5\{\left[x_2 \, / (1 - x_1) \right] Q \;(x_1, 1 - x_1) + \left[x_1 \, / (1 - x_2) \right] Q \;(1 - x_2, x_2) + $$
$$+ \left[x_3 \, / (1 - x_1) \right] Q \;(x_1, 1 - x_1) + \left[x_1 \, / (1 - x_3) \right] Q \;(1 - x_3, x_3) + \tag{17}$$
$$+ \left[x_3 \, / (1 - x_2) \right] Q \;(x_2, 1 - x_2) + \left[x_2 \, / (1 - x_3) \right] Q \;(1 - x_3, x_3)\}$$

Equations (14)–(17) are symmetrical in which the three binary mixtures are treated identically.

V) The Tsao–Smith model[9] for ternary system is expressed as:

$$Q_{123} = \left[x_2 \, / (1 - x_1) \right] Q_{12}(x_1^c, x_2^c) + \left[x_3 \, / (1 - x_1) \right] Q_{13}(x_1^c, x_3^c) + $$
$$+ (1 - x_1) Q_{23}(x_2^c, x_3^c) \tag{18}$$

Bearing in mind that this model is asymmetric, binary contributions are alternatively evaluated in following way:

a) $x_i^c = x_1$ and $x_j^c = 1 - x_i^c$ for binaries 1–2 and 1–3, and $x_2^c = 1 - x_3^c = x_2 / (x_2 + x_3)$ for binary 2–3,

b) $x_i^c = x_2$ and $x_j^c = 1 - x_i^c$ for binaries 2–1 and 2–3, and $x_1^c = 1 - x_3^c = x_1 / (x_1 + x_3)$ for binary 1–3,

c) $x_i^c = x_3$ and $x_j^c = 1 - x_i^c$ for binaries 3–1 and 3–2, and $x_1^c = 1 - x_2^c = x_1 / (x_1 + x_2)$ for binary 1–2.

VI) Toop[10] proposed an equation in the following form:

$$Q_{123} = \left[x_2 / (1 - x_1) \right] Q_{12}(x_1^c, x_2^c) + \left[x_3 / (1 - x_1) \right] Q_{13}(x_1^c, x_3^c) + \\ + (1 - x_1)^2 Q_{23}(x_2^c, x_3^c) \tag{19}$$

where binary mole fractions x_i are computed as in the Tsao–Smith model (Eq. (18)). Pelton[11] discussed several models including the Kohler model as a symmetric and the Toop model as an asymmetric model.

VII) The Scatchard *et al.* model[12] is defined by the following expression:

$$Q_{123} = \left[x_2 / (1 - x_1) \right] Q_{12}(x_1^c, x_2^c) + \left[x_3 / (1 - x_1) \right] Q_{13}(x_1^c, x_3^c) + \\ + Q_{23}(x_2, x_3) \tag{20}$$

where x_i^c and x_j^c are computed as in the case of the Tsao–Smith model (Eq. (18)). This model presents a modification of Eq. (14) for ternary mixture of polar + two non-polar liquids.

VIII) The Rastogi *et al.* model[13] is expressed as:

$$Q_{123} = 0.5[(x_1 + x_2)Q_{12}(x_1^a, x_2^a) + (x_1 + x_3)Q_{13}(x_1^a, x_3^a) + \\ + (x_2 + x_3)Q_{23}(x_2^a, x_3^a)] \tag{21}$$

where each binary contribution are evaluated at molar fractions calculated by:

$$x_i^a = 1 - x_j^a = x_i / (x_i + x_j)$$

In some examined articles, other polynomials such as Lark *et al.*,[14] Hillert,[15] Muggianu *et al.*,[16] Knobeloch–Schwartz,[17] Acree *et al.*,[18] Mathieson–Thynne,[19] *etc.*, were also used, but will not be considered herein. Some authors[20–22] divided polynomials into geometrical models and empirical methods. Some of them extended to calculate physicochemical properties of quaternary systems.[20,21] Polynomials are also used for the calculation other thermodynamic properties, such as for example, vapour–liquid and liquid–liquid equilibria.[23,24] On the other hand, more current empirical models were applied to predict ternary properties of alloys, as can be seen in the literature.[25–31] In addition, it is important to emphasize that alternative forms of the empirical equations given in articles of Atik and Lourdani[32,33] could be used.

Quality of the predictions for particular property was estimated by:

Standard deviation:

$$SD = \left(\sum_{i=1}^{N} \left(Q_{123,i}(\exp) - Q_{123,i}(\mathrm{cal}) \right)^2 \Big/ \left(N - p \right) \right)^{1/2} \tag{22}$$

where N is the number of experimental data and p is the number of parameters of a model.

Root-mean-square-deviation:

$$RMSD = \left(\sum_{i=1}^{N} \left(Q_{123,i}(\exp) - Q_{123,i}(\mathrm{cal}) \right)^2 \Big/ N \right)^{1/2} \tag{23}$$

Average absolute deviation:

$$AAD\ (\%) = \frac{100}{N} \sum_{i=1}^{N} \frac{\left| Q_{123}(\exp) - Q_{123}(\mathrm{cal}) \right|_i}{Q_{123,i}(\exp)} \tag{24}$$

4. PREDICTIONS

Alcohol + alcohol + ether ternary systems. Arce *et al.*[34–39] studied excess molar volumes, V^{E}, isentropic compressibility changes of mixing, $\Delta\kappa_{\mathrm{s}}$, and molar refraction changes of mixing, ΔR. The ternary systems were composed from alcohols: methanol, ethanol and 1-butanol and ethers: 2-methoxy-2-methylpropane (MTBE), 2-methoxy-2-methylbutane (TAME) and 2-ethoxy-2-methylpropane (ETBE).

The ternary systems consisted of TAME or MTBE or ETBE as one of the components and two alcohols: *i*) ethanol + methanol,[34,35] *ii*) 1-butanol + methanol[36,37] and *iii*) 1-butanol + ethanol.[38,39]

The V^{E}, ΔR and $\Delta\kappa_{\mathrm{s}}$ values for the investigated mixtures were determined from experimental data of densities, refractive indices and speeds of sound at 298.15 K and atmospheric pressure.

All ternary systems exhibited negative values of V^{E}, while the binary systems containing alcohols showed positive but small values of V^{E}. These negative V^{E} data are a consequence of the open-chain molecules with flexible orientation order that increases with increasing chain length of the alkyl group. It is clear that the tendency of interstitial accommodation of alcohols into the ethers leads to negative values of V^{E}. Properties V^{E}, ΔR and $\Delta\kappa_{\mathrm{s}}$ were calculated using Eqs. (1), (4) and (10), respectively. The excess molar volumes V^{E} for the system ethanol + + methanol + TAME[35] had negative values. The minimum values of V^{E}, around –0.46 cm^3 mol^{-1} were, also, present at around equimolar mixtures with ether and methanol. The deviations in the molar refractions and in the isentropic compressibility were also negative with minimum values of –0.020 and –24, respectively.

As can be seen from Table I the best prediction of V^E for this ternary system was achieved by the polynomial of Radojković *et al.* Adequate predictions of ΔR were provided with the equations of Radojković *et al.*, Jacob–Fitzner and Toop. Radojković *et al.* and Jacob–Fitzner also gave the best predictions of $\Delta\kappa_S$, while the equations of Kohler and of Toop equations functioned somewhat worse. The remaining equations (Colinet, Tsao–Smith, Scatchard *et al.* and Rastogi *et al.*) were unsuitable for the prediction of the $\Delta\kappa_S$ values. It could be concluded that the Scatchard *et al.* and Colinet and Rastogi *et al.* equations were particularly inappropriate for the prediction of V^E, ΔR and $\Delta\kappa_S$ for this ternary system.

TABLE I. The values of standard deviation, SD, of V^E / cm^3 mol^{-1}, $\Delta\kappa_S$ / T Pa^{-1} and ΔR / cm^3 mol^{-1} predicted for the ternary systems ethanol + methanol + MTBE, or + TAME or + ETBE at 298.15 K

Model	Property	MTBE[a]	TAME[a]	ETBE[b]		
Radojković *et al.*	V^E	0.061	0.009	0.021		
	$\Delta\kappa_S$	3	1	3		
	ΔR	0.023	0.004	0.008		
Rastogi *et al.*	V^E	0.148	0.102	0.210		
	$\Delta\kappa_S$	13	5	13		
	ΔR	0.024	0.047	0.013		
Jacob–Fitzner	V^E	0.049	0.031	0.063		
	$\Delta\kappa_S$	2	1	2		
	ΔR	0.023	0.004	0.010		
Colinet	V^E	0.246	0.177	0.300		
	$\Delta\kappa_S$	19	9	17		
	ΔR	0.009	0.09	0.018		
Toop	V^E	0.029	0.033	0.043[c],	0.047[d],	0.104[e]
	$\Delta\kappa_S$	8	4	9	9	6
	ΔR	0.021	0.004	0.009	0.01	0.006
Kohler	V^E	0.017	0.01	0.023		
	$\Delta\kappa_S$	5	3	6		
	ΔR	0.022	0.012	0.009		
Tsao–Smith	V^E	0.078	0.070	0.092[c],	14[d],	0.007[e]
	$\Delta\kappa_S$	13	6	0.099	13	0.007
	ΔR	0.020	0.015	0.10	6	0.007
Scatchard *et al.*	V^E	0.203	0.170	0.234[c],	25,	0.010[e]
	$\Delta\kappa_S$	24	11	0.264	24	0.013
	ΔR	0.021	0.008	0.131	6	0.008

[a]Arce *et al.*[35]; [b]Arce *et al.*[34]; [c]ethanol was the asymmetric component; [d]methanol was the asymmetric component; [e]ETBE was the asymmetric component

For the system 1-butanol + methanol + TAME[36] (Table II) the minimal values of V^E, $\Delta\kappa_S$ and ΔR were some larger ($V^E = -0.56$ cm^3 mol^{-1}, $\Delta\kappa_S = -34$ T Pa^{-1} and $\Delta R = -0.036$ cm^3 mol^{-1}) than the respective values obtained for the system of TAME with ethanol and methanol. The results obtained by polynomials were slightly worse. These equations worked similarly as in the previous

case. The expression of Kohler as the most successful was followed by those of Radojkovic *et al.* and Jacob–Fitzner. The equations of Colinet, Rastogi *et al.* and Scatchard *et al.* produced higher deviations and could not be recommended. However, limitations were achieved by the equations of Toop and Tsao–Smith.

TABLE II. The values of the standard deviation, *SD*, of V^E / cm³ mol⁻¹, $\Delta\kappa_s$ / T Pa⁻¹, ΔR / cm³ mol⁻¹ predicted for the ternary systems 1-butanol + methanol + MTBE or + TAME at 298.15 K

Model	Property	MTBE[a]			TAME[a]		
Radojković *et al.*	V^E	0.025			0.027		
	$\Delta\kappa_s$	2			1		
	ΔR	0.007			0.010		
Rastogi *et al.*	V^E	0.210			0.165		
	$\Delta\kappa_s$	19			10		
	ΔR	0.011			0.006		
Kohler	V^E	0.023			0.011		
	$\Delta\kappa_s$	3			2		
	ΔR	0.007			0.010		
Jacob–Fitzner	V^E	0.063			0.030		
	$\Delta\kappa_s$	5			2		
	ΔR	0.008			0.009		
Tsao–Smith	V^E	0.092[c]	0.099[d]	0.109[e]	0.063[c]	0.071[d]	0.087[f]
	$\Delta\kappa_s$	11	12	10	5	6	5
	ΔR	0.007	0.006	0.010	0.013	0.014	0.011
Colinet	V^E	0.299			0.231		
	$\Delta\kappa_s$	30			14		
	ΔR	0.013			0.013		
Toop	V^E	0.044[c]	0.047[d]	0.104[e]	0.036[c]	0.037[d]	0.080[f]
	$\Delta\kappa_s$	8	7	10	3	4	5
	ΔR	0.007	0.006	0.010	0.011	0.011	0.011
Scatchard *et al.*	V^E	0.234[c]	0.264[d]	0.131[e]	0.164[c]	0.197[d]	0.111
	$\Delta\kappa_s$	24	21	12	10	10	7
	ΔR	0.011	0.009	0.010	0.017	0.021	0.011

[a]Arce *et al.*[37]; [b]Arce *et al.*[36]; [c]1-butanol was the asymmetric component; [d]methanol was the asymmetric component; [e]MTBE was the asymmetric component; [f]TAME was the asymmetric component

The third ternary system relates to TAME and 1-butanol and ethanol as the two other components.[38] Minimal values of V^E, $\Delta\kappa_s$ and ΔR were similar to those of the two other ternary systems containing TAME ($V^E = -0.525$ cm³ mol⁻¹; $\Delta\kappa_s = -30$ T Pa⁻¹; $\Delta R = -0.024$ cm³ mol⁻¹). The empirical equations of Radojković *et al.* and Kohler applied to predict V^E, $\Delta\kappa_s$ and ΔR were the best, followed by Jacob–Fitzner (especially adequate for $\Delta\kappa_s$) and Toop equations. The other equations gave evidently higher deviations.

The ternary system of MTBE with the alcohol components ethanol and methanol[35] (Table I) showed larger deviation from ideal behaviour ($V^E = -0.623$ cm³ mol⁻¹) compared to the ternary systems with TAME (-0.455 cm³ mol⁻¹).

The best prediction of V^E was obtained by the Kohler Equation. The Jacob–Fitzner and the Radojković *et al.* Equations achieved the best predictions of $\Delta\kappa_{s123}$, the Kohler and Toop model gave somewhat poorer results, while the remaining models were unsuitable for the prediction of $\Delta\kappa_S$ values. The models of Rastogi *et al.*, Colinet and Scatchard *et al.* are not recommended for the prediction of V^E, $\Delta\kappa_S$ and ΔR for the ethanol + methanol + MTBE system.

The ternary system 1-butanol + methanol + MTBE[37] (Table II) exhibited larger negative values of $V^E = –0.735$ cm^3 mol^{-1}, $\Delta\kappa_S = –68$ T Pa^{-1} and $\Delta R = –0.0376$ cm^3 mol^{-1}. The models of Radojković *et al.* and Kohler, followed by the model of Jacob–Fitzner were the most suitable for the prediction of V^E, $\Delta\kappa_S$ and ΔR. Limitations were found when the models of Toop and Tsao–Smith were used. The models of Colinet, Rastogi *et al.* and Scatchard *et al.* produced high deviations and are not recommended.

The same properties V^E, $\Delta\kappa_S$ and ΔR were predicted for the system ethanol + methanol + ETBE[34] (Table I), which also exhibited high non-ideal behaviour with minimal experimental values: $V^E = –0.8618$ cm^3 mol^{-1}, $\Delta\kappa_S = –54$ T Pa^{-1} and $\Delta R = –0.0457$ cm^3 mol^{-1}. The best predictions of V^E were obtained using the models of Radojković *et al.* and Kohler. The prediction of the Rastogi *et al.*, Scatchard *et al.* and Colinet models for V^E erred significantly. For $\Delta\kappa_S$, the best predictions were obtained by Radojković *et al.* and Jacob–Fitzner followed by the Kohler model. For the prediction of ΔR, most of the models had similar deviations, although the models of Rastogi *et al.*, Scatchard *et al.* and Colinet were again less successful overall.

In conclusion, it is clear that for all the alcohol + alcohol + ether systems studied by Arce *et al.* the models of Radojković *et al.* and Kohler appear to be valid and could be successfully applied for the prediction of this type of ternary systems.

Alcohol + alcohol + cyclic ether ternary systems. Camacho *et al.*[40] investigated the excess molar volumes and excess refractive indices (changes in the refractive indices on mixing) of the *n*-octanol + 1,4-dioxane + 2-butanol system at 298.15 K and atmospheric pressure.

Systems of alcohols and cyclic components are of interest because of their importance for detecting which molecular and structural effects dominate in liquid mixtures. 1,4-Dioxane with two alcohols exhibited relatively large positive values of V^E with a maximum positive experimental value $V^E = 0.675\times10^{-6}$ m^3 mol^{-1}. It is known that alcohols are self-associated substances and that the addition of another compound results in the rupture of hydrogen bonds and an expansion in volume. Also, differences in the sizes of the molecules present lead to interstitial accommodation of molecules and therefore to a negative contribution in V^E. However, this effect is considerably weaker. The difference in free volume between 1,4-dioxane and alcohols also exists. Bearing in mind that excess refrac-

tive indices for the mixtures of alcohols are positive and negative for two binary systems with 1,4-dioxane, the changes in the refractive indices of the ternary system Δn_{D123} are partially negative in accordance with the data of binary mixtures.

Radojković *et al*., Jacob–Fitzner and Tsao–Smith (with 1,4-dioxane as an asymmetric component, option c of Eq. (18)) gave very satisfactory results in the prediction of V^E and Δn_{D123}.

Alcohol + haloalkane + cyclic ether ternary systems. Postigo *et al.*[41] calculated excess molar volume, V^E, viscosity deviations, $\Delta\eta$, and excess free energies of activation of viscous flow, ΔG^{*E} for the ternary system tetrahydrofuran + + 1-chlorobutane + 1-butanol at 283.15, 298.15 and 313.15 K and atmospheric pressure. The ternary V^E data were small, showing both negative and positive values and changing slightly with temperature change. $\Delta\eta$ and ΔG^{*E} were negative at all investigated temperatures. Some effects that influenced these changes include: *i*) the breaking of hydrogen bonding of alcohols, *ii*) the breaking of dipole–dipole specific interactions of the halogenated compound and *iii*) OH–Cl interactions.

Predictions were performed by equations of Radojkovic *et al*., Jacob–Fitzner, Kohler, Tsao–Smith and Rastogi *et al*. The best results were obtained by the Radojković *et al*., Jacob–Fitzner and Kohler Equations at the three investigated temperatures.

In the paper of Mariano and Postigo,[42] V^E, $\Delta\eta$ and ΔG^{*E} were also calculated by empirical equations for ternary system where the alcohol component 1-butanol was exchanged with 2-butanol under the same temperature and pressure conditions as in the previous case. The values of V^E were positive over the entire composition range and increased slightly with increasing temperature. The values of $\Delta\eta$ and ΔG^{*E} were negative at the three considered temperatures. The increase in temperature considerably changed $\Delta\eta$ while ΔG^{*E} was hardly modified.

The positive V^E values showed that effect (i) was dominant.[41] Namely, breakage of the self-associated 2-butanol molecules influences the final V^E values. This effect differs from the effect present in the previous system tetrahydrofuran + + 1-chlorobutane + 1-butanol where the V^E values were negative in the majority of the composition range for all the investigated temperatures. Negative values of $\Delta\eta$ and ΔG^{*E} are in accordance with (*ii*) and (*iii*), as for the previously investigated system (tetrahydrofuran + 1-chlorobutane + 1-butanol)[38] but higher values are a consequence of the presence of the secondary alcohol (2-butanol) in the ternary system,[42] which reduces the OH–Cl interactions.

The best predictions of the ternary V^E, $\Delta\eta$ and ΔG^{*E} values are given by the model of Jacob–Fitzner, followed by those of Radojković *et al*. and Kohler, which are also adequate for the predictions of these properties. The asymmetric

model of Tsao–Smith and symmetric Rastogi *et al*. model produce very high average absolute deviations, and they cannot be recommended for this system.

Alcohol + amine + hydrocarbon ternary systems. Mixtures of alcohols and amines make highly non-ideal systems having large negative excess properties as a consequence of strong cross-association through complex formation by hydrogen bonds. The third component can be a non-polar inert component which acts as order-breaking molecules when mixed with the associating components.

Gardas and Oswal[43,44] studied the volumetric and transport properties of the following ternary systems: *i*) 1-propanol + triethylamine + *cyclo*-hexane, *ii*) 1-propanol + tri-*n*-butylamine + *cyclo*-hexane, *iii*) 1-butanol + triethylamine + cyclohexane and *iv*) 1-pentanol + triethylamine + cyclohexane, at 303.15 K and atmospheric pressure over the whole range of compositions. The values of V^E could be interpreted by several effects: chemical, structural and physical. In the mixtures under investigation, the authors[43,44] explained the influence of the dominate factors on the results of the experimental measurements of the corresponding properties.

Comparison between the ternary systems (*i*) and (*ii*) with 1-propanol as the alcohol component showed that the V^E values are significantly more negative for system (*i*) ($V^E = -1.383$ cm^3 mol^{-1}) than system (*ii*) ($V^E = -0.463$ cm^3 mol^{-1}) indicating that cross-association is more pronounced in the mixture with triethylamine than in the mixture containing tri-*n*-butylamine. However, comparing the values of V^E for the ternaries of triethylamine with different alcohols: 1-propanol (*i*) ($V^E = -1.383$ cm^3 mol^{-1}), 1-butanol (*iii*) ($V^E = -1.535$ cm^3 mol^{-1}) and 1-pentanol (*iv*) ($V^E = -1.567$ cm^3 mol^{-1}), it could be concluded that the V^E values are not much affected by the change in the length of the alcohol from 1-propanol to 1-pentanol. The viscosity deviation, $\Delta\eta$, in these systems were the consequence of molecular interactions as well as of the size and shape of molecules. The ΔG^{*E} values were negative for the three systems containing triethylamine, while the values were both positive and negative for the system containing tri-*n*-butylamine. As pointed out by the authors, the dependence of ΔG^{*E} on composition is complex, depending upon different contributions in the mixture.

Bearing in mind the complex behaviour of the aforementioned systems, it is clear that prediction of V^E, $\Delta\eta$ and ΔG^{*E} by empirical equations was very difficult in all cases, as concluded by the authors. Namely, large standard deviations were obtained when the V^E, $\Delta\eta$ and ΔG^{*E} of viscous flow were predicted by the empirical equations of Kohler, Jacob–Fitzner, Tsao–Smith, Rastogi *et al*. and other applied models containing only binary parameters.

In the work of Kijevčanin *et al.*,[45] excess molar volumes V^E of the ternary system 1-butanol + cyclohexylamine + *n*-heptane were reported at temperatures from 283.15 to 323.15 K. The V^E values of this system are mostly negative

except for the region very close to the binary mixtures of n-heptane with 1-butanol or cyclohexylamine, where changes in the V^E values occurred.

In this system, which exhibited large negative values of V^E with a small influence of temperature, the complexes formed by H-bonding between 1-butanol and cyclohexylamine molecules dominate the behaviour.

Calculation of V^E performed by empirical models showed that satisfactory predictions were obtained by the symmetric equations of Radojković *et al.* and Jacob–Fitzner, whereas the most inadequate estimation by this type of model was with the equation of Rastogi *et al.* For all asymmetric models, better results were obtained with n-heptane as the asymmetric component (Toop and Scatchard *et al.*), especially with the Tsao–Smith model, while quite poor estimations were achieved when 1-butanol was the asymmetric component. When *cyclo*-hexylamine was used as the asymmetric component, some limitations were obtained in the case of the Tsao–Smith model. Increasing of the temperature had no influence on the predictions by the investigated polynomials.

Dominguez *et al.*[46] measured density of the ternary system 2-butanol + + n-hexane + 1-butylamine at 298.15 and 313.15 K. The V^E values were calculated by the Redlich–Kister and other empirical models given in Table II. The V^E values of this ternary system were characterized by (*i*) negative values in the region where interactions between the hydroxyl (–OH) and amino (–NH$_2$) groups dominated (small mole fraction of n-hexane), (*ii*) positive values in regions were the rupture of the associated structure of 2-butanol in the mixture with n-hexane occurred and (*iii*) when the mole fraction of n-hexane increased the brakeage of cross-hydrogen bonding (OH–NH$_2$), leading to positive values of V^E in the region of low fractions of the other two components. As the results of these facts, the V^E values were negative or positive in the corresponding regions of the triangular diagram. The ternary contribution (V^E–V^E_{bin}) was very high, conditioning higher standard deviations associated with all the considered empirical models. This means that for this ternary system, ternary contributions are important.

Amine/ester/alcohol/hydrocarbon ternary systems. Kwon *et al.*[47] predicted V^E and ΔR values of ternary mixtures of tridodecylamine (alamine 304-1) with 1-octanol, 2-octanol and 1-decanol at 298.15K using the Radojkivić *et al.* equation. Due to the lack of published ternary V^E and ΔR data, the authors estimated the ternary V^E and ΔR data using possible combinations of the correlated binary Redlich–Kister parameters of given sub-binary systems. The results were plotted as isoclines of V^E and ΔR of the ternary systems : Alamine 304-1 + 1-octanol + + 2-octanol, Alamine 304-1 + 1-octanol + 1-decanol, Alamine 304-1 + 2-octanol + 1-decanol and 1-octanol + 2-octanol + 1-decanol.

Different ternary mixtures formed from alcohols, esters and hydrocarbons have been considerably investigated. All the mentioned mixtures consisted of one

associating component (alcohol), a weakly associating polar component (alkyl alkanoate) and a non-polar inert compound (hydrocarbon).

Some studies[48–52] could be of interest in the context of the present paper, bearing in mind that empirical expressions that predict the ternary properties for binary data were applied. Oswal *et al.*[48] gave excess molar volumes, V^E, viscosity deviations, $\Delta\eta$, and excess free energies of activation of viscous flow ΔG^{*E} for two ternary systems: *i*) 1-propanol + ethyl ethanoate + cyclohexane and *ii*) 1-propanol + ethyl ethanoate + benzene. These properties were determined from density and viscosity measurements of ternaries and binaries at 303.15 K. Ghael *et al.*[49] calculated the same properties (V^E, $\Delta\eta$ and ΔG^{*E}) for the ternary systems of ethyl ethanoate + cyclohexane with higher alcohols as the third component (1-butanol or 1-pentanol or 1-octanol) at 303.15 K. The Equations of Redlich–Kister, Kohler, Rastogi *et al.*, Jacob–Fitzner and Tsao–Smith were applied in some studies.[48,49] Casas *et al.*[50,51] reported V^E, $\Delta\eta$ and Δn_D data for the ternary mixture propyl propanoate + 1-hexanol + benzene at 298.15 and 308.15 K. The prediction was performed by models of Jacob–Fitzner, Kohler, Colinet, Tsao–Smith, Toop and Scatchard *et al.*

Investigations of all the aforementioned systems were performed at atmospheric pressure over the whole composition range.

The values of V^E for all mixtures of 1-alcohols with ($C_4H_8O_2$ + c-C_6H_{12}) were large and positive.[48,49] For equimolar composition, the V^E values of the ternary systems C_3H_7OH + $C_4H_8O_2$ + c-C_6H_{12}, C_4H_9OH + $C_4H_8O_2$ + c-C_6H_{12} , C_5H_9OH + $C_4H_8O_2$ + c-C_6H_{12} and $C_8H_{17}OH$ + $C_4H_8O_2$ + c-C_6H_{12} were 0.854, 0.868, 0.832 and 0.812 cm^3 mol^{-1}, respectively. Trend of decreasing V^E values on addition of higher 1-alcohols to the pseudo-binary mixture ($C_4H_8O_2$ + c-C_6H_{12}) could be the consequence of specific interactions between the alcohol and alkanoate molecules and the dilution effect on the breakage of the dipolar-structure in the alkanoate.

V^E values were greatly reduced when cyclohexane replaced benzene.[48,50,51] This indicates that the specific interactions between pairs of molecules alcohol, ethanoate and benzene (beside the disruption of alcohol and ethanoate structures) are significant. Namely, the specific interactions of –n···HO–, –HO···π and/or –n···π types lead to decreases in V^E.

The negative values of $\Delta\eta$ are caused by the destruction of hydrogen bonds in 1-alcohols in mixtures with aromatics, decreasing $\Delta\eta$ when cyclohexane is replaced by benzene. Moreover, the $\Delta\eta$ values are negative in mixtures with heptane because dispersion forces are predominant.

The values of ΔG^{*E} are highly negative for both mixtures with *cyclo*-hexane and benzene and are in accordance with corresponding values and sign of V^E and $\Delta\eta$, which arise due to the structure breakage of both 1-alcohols and ethyl ethanoate molecules.

Changes in refractive indices on mixing, Δn_D, for the ternary mixture propyl propanoate + 1-hexanol + benzene were obtained using experimental values of refractive indices at 298.15 and 308.15 K and atmospheric pressure over the entire range of compositions. The values of Δn_D were negative in the whole region of the ternary mixture.

Polynomial examinations[48,49] of the results for the ternary systems 1-alcohols with ($C_4H_8O_2$ + c-C_6H_{12}) are given in Table III. It could be concluded that the Redlich–Kister model gave smaller values of SD in the prediction of V^E and $\Delta\eta$, while higher values of SD were obtained with the equations of Kohler, Rastogi $et\ al.$, Jacob–Fitzner and Tsao–Smith (Table III). The ternary mixture of 1-propanol with ($C_4H_8O_2$ + c-C_6H_{12}) gave higher values for the best $SD = 0.040$ of the Redlich–Kister model, bearing in mind the maximum value of $V^E = 1.232$ $cm^3\ mol^{-1}$ in accordance to corresponding value $V^E = 0.249\ cm^3\ mol^{-1}$ for the ternary system 1-propanol + $C_4H_8O_2$ with benzene as the third component ($SD =$ $= 0.012$).

TABLE III. The values of standard deviations SD of V^E / $cm^3\ mol^{-1}$, $\Delta\eta$ / mPa s and ΔG^{*E} / J mol^{-1} calculated by polynomials for the ternary systems alcohols (A) + ethyl ethanoate (B) + cyclohexane (C) at 303.15 K

Model	Property	1-propanol (A)[a]	1-butanol (A)[b]	1-pentanol (A)[b]	1-octanol (A)[b]
Redlich–Kister	V^E	0.040	0.035	0.016	0.068
	$\Delta\eta$	0.041	0.012	0.033	0.073
	ΔG^{*E}	151	49	112	107
Kohler	V^E	0.055	0.048	0.028	0.068
	$\Delta\eta$	0.087	0.166	0.231	0.579
	ΔG^{*E}	133	178	257	336
Rastogi $et\ al.$	V^E	0.171	0.187	0.182	0.245
	$\Delta\eta$	0.147	0.206	0.261	0.731
	ΔG^{*E}	248	234	233	218
Jacob–Fitzner	V^E	0.053	0.046	0.026	0.066
	$\Delta\eta$	0.083	0.147	0.205	0.517
	ΔG^{*E}	138	161	239	310
Tsao–Smith	V^E	0.209	0.208	0.222	0.244
	$\Delta\eta$	0.075	0.182	0.250	0.591
	ΔG^{*E}	111	195	277	331

[a]Oswal $et\ al.$[48]; [b]Ghael $et\ al.$[49]

The values of SD for ΔG^{*E} were in the range 49–336 J mol^{-1} for different polynomials. For the mixture 1-butanol with ($C_4H_8O_2$ + c-C_6H_{12}), the smallest value of 49 J mol^{-1} was obtained by the Redlich–Kister model, while in the mixture with benzene, smallest value was 57 J mol^{-1} when the Rastogi $et\ al.$ Equation was applied.

In the mixture propyl propanoate + 1-hexanol + benzene, the ternary contribution,[50,51] given as the difference between the positive and negative experi-

mental value of V^E, and that predicted from the binary mixtures was not large. Bearing in the mind that the influence of this contribution in ternary V^E is insignificant, the prediction performed by the applied polynomials were mostly satisfactory, indicating that for the asymmetric models, the order of the components in the mixtures is essential. A similar conclusion could be reached for the other two properties.

Finally, it could be concluded that predictions with the empirical equations containing only binary parameters gave qualitative representation of V^E, $\Delta\eta$ and ΔG^{*E} for these three ternary systems.

Using different polynomials, Oh *et al.*[52] calculated the standard deviations of V^E and deviations in molar refractivity, ΔR, using measured densities and refractive indices of the ternary mixture dimethyl carbonate + ethanol + 2,2,4-trimethylpentane at 298.15 K. The ternary data showed positive values at all compositions, while deviations in the molar refractivity, ΔR, values were negative. The V^E and ΔR values were predicted using the model of Tsao–Smith, Kohler, Rastogi *et al.* and Radojković *et al.* The Radojkovic *et al.* model provided the best results with standard deviations of 0.0546 and 0.9698 cm^3 mol^{-1} for the ternary V^E and ΔR data, respectively.

Ester + hydrocarbon + aromatic hydrocarbon systems. Pérez *et al.*[53] determined the densities, surface tensions and refractive indices of the ternary system propyl propanoate + hexane + ethylbenzene at 298.15 K and atmospheric pressure over the entire range of composition. The excess molar volume V^E, surface tension deviations $\Delta\sigma_{123}$–$\Delta\sigma_{bin}$ and changes in refractive index of mixing Δn_D were calculated by the polynomials Jacob–Fitzner, Kohler, Colinet, Tsao–Smith, Toop and Scatchard *et al.* Some other empirical equations were also included.

The best results of V^E predictions were obtained with the asymmetric models of Tsao–Smith, Toop and Scatchard *et al.* when hexane was taken as the first component. This ternary system showed a relatively larger ternary contribution $V^E_{123} - V^E_{bin} = -0.07$ cm^3 mol^{-1}, bearing in the mind that the ternary V^E values were mostly lower over the composition range. Similarly, the models of Toop and Scatchard *et al.* gave satisfactory predictions for $\Delta\sigma_{123}$ when propyl propanoate was taken as the first component. In addition, the ternary contribution $\Delta\sigma_{123}$–$\Delta\sigma_{bin}$ was 0.6 mN m^{-1}. In the study of Casas *et al.*,[54] the densities, kinematic viscosities and refractive indices of the ternary system propyl propanoate + + hexane + benzene were measured at 298.25 K and atmospheric pressure over the whole composition range. The excess molar volumes V^E, viscosity deviations $\Delta\eta$ and changes of refractive indices on mixing Δn_D were estimated from the experimental data by the polynomials proposed by Jacob and Fitzner, Kohler, Colinet, Tsao–Smith, Toop and Scatchard *et al.* The asymmetric models again gave better results in the predictions of V^E when hexane was considered as the first component. The ternary contribution $V^E_{123} - V^E_{bin} = -0.155$ cm^3 mol^{-1} was

larger than in the case of the system with ethylbenzene. However, the symmetric model of Jacob–Fitzner gave the most accurate predictions of $\Delta\eta$.

Acrylic ester + alcohol + aliphatic/cyclic/aromatic hydrocarbons. Bahadur and Sastry [55] studied densities (ρ), sound speeds (u), excess volumes (V^E) and $\Delta\kappa_S$ of ternary systems composed of methyl acrylate (MA), 1-alcohols (1-propanol and 1-butanol) and inert hydrocarbons (*n*-hexane, *n*-heptane, cyclohexane, benzene and toluene) at 308.15 K. The following mixtures were treated: *i*) five mixtures of MA + 1-propanol + *n*-heptane, or *cyclo*-hexane, or benzene, or benzene, or toluene and *ii*) five mixtures of MA + 1-butanol with the same inert components as in case (*i*). A qualitative analysis of the V^E and $\Delta\kappa_S$ data of these ternary systems showed that in MA + 1-alcohols + *n*-hexane, or *n*-heptane, or cyclohexane, structure disruptions were more predominant, while in MA + 1-alcohols + benzene or toluene, the weak but specific structure making interactions dominated.

The experimental V^E values for mixtures MA + 1-alcohols + cyclohexane were large and more positive than those with the aliphatic hydrocarbons (*n*-hexane or *n*-heptane). Depolymerisation of the 1-alcohols in the presence of *cyclo*-hexane was found to be stronger than in the presence of *n*-hexane or *n*-heptane molecules. The replacement of aliphatic with aromatic hydrocarbons (benzene or toluene) decreased V^E and even resulted in negative values in the ester + 1-alcohol + toluene mixtures. This is also a consequence of the weak specific interactions of $–OH\cdots\pi$ and $n\cdots\pi$ types between corresponding molecules of the mixtures. Furthermore, additional dipole-induced dipole interactions in MA + + 1-alcohol + toluene mixtures could be possible. The ternary V^E values were predicted with the models proposed by Redlich and Kister, Kohler and Tsao––Smith.

The difference between the experimental and predicted ternary excess values ΔV_{123}^E by polynomials for the systems MA + 1-propanol + hydrocarbons were found mostly between –0.291 and 0.126 cm^3 mol^{-1}. Similarly, for the systems MA + 1-butanol + hydrocarbons, the ΔV_{123}^E values range mostly from –0.095 and 0.188 cm^3 mol^{-1}. In both cases, for some compositions, ΔV_{123}^E values larger than these limits were found. It is clear that all three polynomials gave only quantitative prediction of V^E for the presented ternary mixtures.

Sastry *et al.*[56] measured densities and speeds of sound for 15 ternary mixtures of methyl methacrylate (MMA) + 1 alcohols (1-butanol, 1-pentanol and 1-heptanol) + organic solvents (benzene, toluene, *p*-xylene, ethylbenzene and cyclohexane) at 298.15 and 308.15 K. The V^E and $\Delta\kappa_S$ values were predicted by the Redlich–Kister, Tsao–Smith and Kohler equations.

Experimental values of V^E show that the ternary mixtures of MMA with (1-alcohols + cyclohexane) have more and large positive values than mixtures with other organic solvents. This is a consequence of the fact that the effective

structure-breaking interactions are predominant between unlike molecules of MMA, 1-alcohols and cyclohexane, while the aromatic solvent interact specifically with either MMA or 1-alcohols, as emphasised by the authors.[54]

The difference between experimental and predicted V^E of the investigated mixtures by polynomials were found to change from 0 to 0.008, 0.006 to 0.15 and 0.001 to 0.093 cm^3 mol^{-1}, respectively. These values were obtained by Redlich–Kister equation as compared to the Tsao–Smith and Kohler models. The difference between experimental excess isentropic compressibilities and predicted $\Delta\kappa_S$ was, also, at a minimum with the Redlich–Kister calculated values as compared to those of the other two models.

Aliphatic esters + glycols + aromatic organic solvents. Sastry *et al.*[57] measured densities, ρ, from 298.15 to 313.15 K, speed of sound, u, and relative permittivity, ε_r, at 298.15 and 308.15 K and atmospheric pressure for ternary mixtures of methyl acetate (MA) + diethylene glycol (DG) + nitrobenzene, MA + + triethylene glycol (TG) + chlorobenzene, MA + TG + bromobenzene, MA + + TG + nitrobenzene, ethyl acetate (EA) + TG + chlorobenzene, EA + TG + bromobenzene, EA + TG + nitrobenzene, EA + DG + nitrobenzene, butyl acetate (BA) + TG + chlorobenzene, BA + TG + bromobenzene and BA + TG + nitrobenzene. V^E, $\Delta\kappa_S$ and relative permittivity deviations, $\delta\varepsilon_r$, were predicted employing the Redlich–Kister, Tsao–Smith and Kohler Equations.

Specific structure interactions between the C- and Br-groups of the organic solvents with the carboxyl oxygen of esters, Cl···H–O complexes and dipole–dipole interactions were probably the main factors for the excess values and deviation functions in these mixtures.

The deviations between the experimental and predicted ΔV_{123}^E by Redlich––Kister, Tsao–Smith and Kohler models changed from –0.006 to 0.001, –0.104 to 0.122 and –0.0002 to 0.127 cm^3 mol^{-1} for these models at 298.15 and 308.15 K, respectively.

The Redlich–Kister model predicted the V^E and $\Delta\kappa_S$ value of all mixtures very satisfactorily bearing in mind that the deviation between the experimental and calculated values was close to the uncertainty of these properties. Furthermore, the Tsao–Smith model was a better approximation than the Kohler model in predicting $\Delta\kappa_S$. The deviations $\Delta\varepsilon_r$ between the experimental and calculated values for all models were far larger than the uncertainties. It seems that the deviation $\Delta\varepsilon_r$ is different to the other true excess properties.

Aliphatic/cyclic/aromatic hydrocarbons + alcohol ternary systems. Iglesias *et al.*[58] measured the density, refractive index on mixing and speed of sound of ternary mixture benzene + cyclohexane + 2-methyl-2-butanol at 298.15 K and atmospheric pressure over the entire range of compositions. V^E, Δn_D and $\Delta\kappa_S$ were calculated by means of the polynomials: Kohler, Jacob–Fitzner, Colinet, Tsao–Smith, Toop and Scatchard *et al.* The values of V^E were positive over the

entire composition range. The ternary contribution to V^E had the highest value at low concentrations of 2-methyl-2-butanol, with about 15 % of the total ternary excess volume V^E in the maximum. A similar effect was observed for $\Delta\kappa_s$, while for Δn_D, the ternary contribution was almost negligible.

In the calculation of V^E, the asymmetric Toop and Scatchard *et al.* Equation with benzene as the asymmetric component gave lower deviations with respect to the V^E data. For Δn_D, the asymmetric Tsao–Smith Equation with 2-methyl-2--butanol as the asymmetric component and the symmetric Equations of Kohler, Jacob–Fitzner and Colinet gave the best results. It is important to emphasize that in the range with large absolute values of ternary contributions, the ability of calculations using polynomials is worse because the ternary is not adequately represented as the addition of the binaries. Namely, in this case, the zone of low concentrations of 2-methyl-2-butanol presents insignificant simultaneous ternary interactions.

Aromatic ketone + alcohol + aromatic systems. Prasad *et al.*[59] measured the V^E values of five ternary mixtures of acetophenone + 1-propanol + benzene or substituted benzene (toluene, chlorobenzene, bromobenzene and nitrobenzene) at 303.15 K. The ternary V^E values were predicted by the polynomials of Redlich––Kister, Kohler and Tsao–Smith.

The V^E data were negative over the whole composition range for the ternary systems of acetophenone + 1-propanol with chlorobenzene, bromobenzene, or nitrobenzene, while an inversion in sign occurred at low concentrations of aceto-phenone in mixtures with 1-propanol + benzene or toluene. The V^E data for these mixtures are connected to two opposing contributions: *i*) positive values are a consequence of the rupture of self-associated hydrogen bonds of alcohol and physical dipole–dipole interactions between alcohol monomers and multimers and *ii*) negative values are caused by the formation of $-OH\cdots\pi$ electron hydro-gen-bonded complexes, changes in free volume and interstitial accommodations. In the mixtures of acetophenone + 1-propanol with chlorobenzene, bromoben-zene or nitrobenzene contributions. Contribution (*ii*) is essential for negative V^E values, while both contributions (*i*) and (*ii*) are responsible for the behaviour of the mixtures with benzene and toluene as the third component. A comparison between experimental V^E data of the ternary mixtures and those calculated by the polynomials of Redlich–Kister, Kohler and Tsao–Smith shows that these poly-nomials gave only a qualitative estimation of the V^E in the ternary mixtures.

The estimated results for the ternary mixtures with benzene and toluene showed that somewhat poorer predictions were obtained by all polynomials applied to the mixture with toluene. This was expected bearing in mind that absolute difference of maximum and minimum of the V^E values for this system is higher. When the polynomials were used to predict the V^E values of the systems with chlorobenzene, bromobenzene or nitrobenzene, non-adequate results were

achieved in mixtures with bromobenzene, while the polynomials function better for the prediction of V^E for the system with nitrobenzene than with chlorobenzene. This is a consequence of the fact that the order of the maximum values of V^E is bromobenzene > nitrobenzene > chlorobenzene and that differences between the experimental and calculated ternary V^E values are the smallest for the system with chlorobenzene.

Amide + amide + water system. Han *et al.*[60] reported densities and viscosities at 298.15 K for the ternary system *N,N*-dimethylformamide (DMF) + + *N*-methylformamide (NMF) + water. The excess molar volumes and viscosity deviations were compared with the predicted values using the models of Tsao–Smith, Kohler, Rastogi *et al.* and Radojković *et al.*

The measured V^E data showed negative values over the entire range of composition. This is a consequence of the strong interactions between DMF and water and between NMF and water. Namely, the breaking of H bonding and specific dipole–dipole interactions of the nitrogen compounds are less important than the interactions between the different molecules. The $\Delta \eta$ values were positive over a wide composition range, except in the DMF + NMF rich region, where the $\Delta \eta$ value were negative.

The Radojković *et al.* Equation gave the best predictions with standard deviation of 0.073 cm^3 mol^{-1} and 0.096 mPa s for V^E and $\Delta \eta$, respectively. The other applied polynomials provided poorer results.

n-*Hexanol + ethanenitrile + dichloromethane system.* Aznares *et al.*[61] measured the densities and refractive indices for the ternary system *n*-hexanol + ethanenitrile + dichloromethane at 298.15 K and determined the excess molar volumes, V^E, and the excess refractive indices (changes in the refractive indices on mixing), Δn_D.

The ternary V^E data were positive. *n*-Hexanol is a self-associated molecule and the addition of the other components resulted in a rupture of hydrogen bonding with concurrent expansion in volume. The polynomials of Radojković *et al.*, Jacob–Fitzner, Kohler and Tsao–Smith were used to predict V^E and Δn_D. The equations of Radojković *et al.* and Kohler gave similar and good results for V^E, while the Tsao–Smith model was unsatisfactory in the prediction of Δn_D.

Acetone + alcohol + water system. Iglesias *et al.*[62,63] presented experimental data of densities and refractive indices at 298.15 K and atmospheric pressure for the systems acetone + methanol + 1-propanol, acetone + methanol + water and acetone + methanol + 1-butanol.

The validity of the estimation of the excess V^E values and the refractive indices on mixing Δn_D were examined by the empirical Equations of Kohler, Jacob–Fitzner, Colinet, Tsao–Smith, Toop and Scatchard *et al.* Values of V^E for the system acetone + methanol with water were negative for the entire composition range, due to the strong interactions between water as a proton donor and

acetone as a proton acceptor. The mixture acetone + methanol with 1-propanol or 1-butanol gave similar effects but with a weaker cross association between 1-propanol or 1-butanol and the other two components. Changes of refractive indices were characterized by positive values for all the ternary systems. For the system acetone + methanol with 1-propanol, the best prediction of V^E were obtained by the asymmetric models of Toop and Tsao–Smith with 1-propanol as the asymmetric component in the equations. The symmetric Equations of Kohler, Jacob–Fitzner and Colinet also gave satisfactory results. Minimal values of standard deviations of Δn_D were obtained with methanol as asymmetric component in the Toop and Tsao–Smith models, bearing in mind that all symmetric models were good accordance with experimental data. The lower standard deviations in V^E for the system acetone + methanol with water were obtained by the model of Jacob–Fitzner, Toop and Scatchard *et al.* with methanol as an asymmetric component. The highest values of deviations were achieved by asymmetric models with water as the asymmetric component (or methanol in the Tsao–Smith model).

Better predictions were obtained for Δn_D using Colinet, Jacob–Fitzner and Scatchard *et al.*, Toop (methanol as the asymmetric component in both cases) and Tsao–Smith (acetone as an asymmetric component).

In the system acetone + methanol with 1-butanol, low standard deviations were obtained with the asymmetric models: for the V^E predictions by the Toop and Scatchard *et al.* models (water as the asymmetric component in both cases) and for Δn_D predictions by the Tsao–Smith, Toop and Scatchard *et al.* models (methanol as the asymmetric component).

Water + fluoroalcohol + alcohol/acetone systems. Atik[64] determined V^E for ternary systems of water + 2,2,2,trifluoroethanol with methanol, ethanol, 1-propanol, 2-propanol or acetone at 298.15 K and 101 kPa. All the molecules are polar having a strong self-associative nature and complex formation. Fluoroalcohol is a better proton donor than the hydrocarbon alcohols.

These ternary systems show regions with both negative and positive values of V^E values. The mixtures of water + alcohol + trifluoroethanol and water + acetone + trifluoroethanol involve the disruption and weakening of self-association occurring in water, alcohols and acetone through hydrogen bonding, attributing a combination of strong (water–water) and weak (alcohol–alcohol) association effects.

Estimations of V^E were performed by the Redlich–Kister, Kohler, Jacob––Fitzner, Colinet and Scatchard *et al.* models and by the Mathieson–Thynne and Muggianu *et al.* models, which are the most included here. In all cases, the Redlich–Kister model gave the best predictions, while the Jacob–Fitzner model works satisfactorily in the systems with methanol, ethanol and 1-propanol. The good results obtained with these symmetric models are the consequence of very small ternary contributions to V^E in both the positive and negative regions.

Hydrocarbon + cyclic hydrocarbon + chloroalkane/alcohol system. Souza *et al.*[65] determined V^E at 298.15 K for ternary mixtures *n*-propyl propanoate with cyclohexane, 1-chloro-*n*-hexane and *n*-hexane, with predictions by the Kohler, Jacob–Fitzner, Colinet and Tsao–Smith models. The deviations from the predictions were 3 to 40 times greater than the standard deviation. The asymmetric Tsao–Smith equation presents better results if component 1 was *n*-propyl propanoate. In addition, from the results of V^E for pseudo-binary mixtures, it could be concluded that the symmetric equations do not predict the existence of a maximum. However, the Tsao–Smith equation gives rise to maximums that did not coincide with those obtained from the fittings.

Menaut *et al.*[66] measured the densities of two ternary systems of *cyclo*-hexane + *n*-hexane with 1-chlorohexane or 1-hexanol at 298.15 K. Experimental values of V^E were compared with the results obtained by the empirical equations of Kohler, Jacob–Fitzner, Colinet, Tsao–Smith, Toop and Scatchard *et al.*

Ternary contributions for both mixtures were small but the forms of the positive and negative curves of constant difference between the ternary and binary contributions were completely different. The system with 1-chlorohexane had isolines of negative values for almost the whole composition diagram except near the sub binary mixture of *n*-hexane and 1-chlorohexane. In the system with 1-chlorohexane, the best results for the standard deviation were obtained by the Toop and Scatchard *et al.* models for the mixtures ordered as *cyclo*-hexane + + *n*-hexane + chlorohexane.

In the case of the ternary system with 1-hexanol, an isoline of zero value divided the composition diagram and the symmetric equations of Jacob–Fitzner, Kohler and Colinet all gave better results.

Alcohol + ester + aromatic ternary systems. Rodriguez *et al.*[67] gave experimental data for the density, refractive index and speed of sound of the ternary system dimethyl carbonate + methanol + benzene at 298.15 K and atmospheric pressure over the entire range of composition. The results were used to calculate V^E, Δn_D and $\Delta \kappa_S$ by the same polynomials as in the previous case. The V^E values of this ternary system were positive over most of the composition range, except in the region close to pure methanol, where the sign changed due to interstitial accommodation of methanol molecules into the molecules of other two components For the prediction of V^E, Δn_D and $\Delta \kappa_S$, the asymmetric equations of Toop and Scatchard *et al.* with methanol as the asymmetric component gave good estimations. Calculations of V^E, Δn_D and $\Delta \kappa_S$ by symmetric Equations of Kohler, Jacob–Fitzner and Colinet were also successful.

Alcohol + chloroform + benzene systems. A review paper of Djordjević *et al.*[68] included the application of the polynomials to V^E prediction of two ternary systems of alcohols (methanol and 1-propanol) with chloroform and benzene. The best results were obtained with the a-type Tsao–Smith Equation when

methanol was treated as an asymmetric component. In addition, two other asymmetric equations, the a-type Toop and the a-type Scatchard *et al.* Equations could be recommended. The Radojković *et al.*, Kohler, Jacob–Fitzner, Colinet, b-type Tsao–Smith, b-type Toop and b-type Scatchard *et al.* expressions were satisfactory when chloroform was the asymmetric component, while the models of Rastogi *et al.* and all c-types with benzene as the asymmetric component (Tsao––Smith, Toop and Scatchard *et al.*) gave higher deviations and could not be recommended.

The best agreements with the experimental V^E data for the system 1-propanol + chloroform + benzene were achieved by the a-type asymmetric models of Scatchard *et al.* and Toop with 1-propanol as the asymmetric compound. Satisfactory predictions were obtained using the symmetric equations of Radojković *et al.*, Kohler, Jacob–Fitzner and Colinet. All other asymmetric models work very poorly, whereas the worst results were obtained with the symmetric Rastogi *et al.* model. It could be concluded that for both the studied ternary systems, the majority of the examined predictive models gave adequate predictions of the ternary V^E from the data of their binary subsystems.

In works of Kijevčanin *et al.*[69] and Smiljanić *et al.*,[70] only the Radojković *et al.* model was applied to the prediction of V^E for the ternary systems ethanol and 1-butanol with chloroform + benzene, respectively, and the obtained results could be treated as acceptable, bearing in the mind that the ternary contribution for both systems was relatively small.

Benzene + cyclohexane + hexane ternary system. Dominguez *et al.*[71] determined the κ_s, $\Delta\kappa_s$ and Δu for the ternary mixture benzene + cyclohexane + + hexane at 298.15 K. The polynomials of Redlich–Kister, Tsao–Smith, Kohler and Colinet were used in order to predict $\Delta\kappa_s$ and Δu of this system.

The $\Delta\kappa_s$ and Δu exhibited similar behaviour but with opposite signs. Namely, the region rich in benzene and hexane and poor in cyclohexane gave the most negative $\Delta\kappa_s$, and the most positive Δu values. Predictions of $\Delta\kappa_s$ performed by the Redlich–Kister and Colinet Equations were satisfactory. On the other hand, only the asymmetric Tsao–Smith model was relatively acceptable in predicting Δu. This is consequence of difference between standard deviations of polynomials and those presented by the fitting to the Cibulka Equation showing the existence of molecular interactions between all the molecules present.

Diethylamine + ethyl acetate + n-heptane ternary system. Lillo *et al.*[72] calculated V^E and η^E for the ternary system diethylamine + ethyl acetate + *n*-heptane at 298.15 K. The V^E values were positive over the whole concentration range, indicating that the molecular interactions between the different molecules were weaker than interactions between the molecules in their pure state, showing that repulsive forces dominate in the mixtures. The $\Delta\eta$ values were negative and very small because the dominating repulsive forces decreased the viscosities of the mixtures.

The models of Tsao–Smith, Jacob–Fitzner, Kohler, Rastogi *et al.* and Radojković *et al.* were used to predict V^E and $\Delta\eta$. The Jacob–Fitzner, Radojković *et al.* and Kohler models gave good agreement with the experimental data of this ternary system. The Rastogi *et al.* model exhibited poor results. The Tsao–Smith as an asymmetric model gave lower σ values when diethylamine was the asymmetric component. The other two Tsao–Smith models were not applicable for the prediction of V^E and $\Delta\eta$.

Amine + alcohol + tributylphosphate ternery systems. Kim *et al.*[73] predicted V^E and ΔR for ternary systems tri-octylamine (TOA) + tributylphosphate (TBP) + + 1-octanol, TOA + 1-octanol + 1-decanol, TOA + TBP + 1-decanol and TBP + + 1-octanol + 1-decanol using the Radojković *et al.* model. Prediction for both properties were performed using the correlated Redlich–Kister parameters (Eq. (13)) obtained for the corresponding binary subsystems.

Methyl butanoate + heptane + (octane+cyclooctane + 1-chlorooctane + + 1-octanol). In recent articles,[74–77] presented the results of V^E and $\Delta\eta$ for the ternary systems of (methyl butanoate + heptane) with: *i*) octane, *ii*) cyclooctane, *iii*) 1-chloroctane and *iv*) 1-octanol at four temperatures (283.15, 293.15, 303.15 and 313.15 K) over the whole concentration range and atmospheric pressure were presented.

The obtained results for V^E and $\Delta\eta$ of the ternary systems were used to test the symmetrical (Redlich–Kister, Kohler, Colinet and Rastogi *et al.*) and asymmetrical (Tsao–Smith and Toop) models considered in this work. In addition, the polynomials of Hiller,[15] Muggianu *et al.*,[16] and Acree *et al.*[18] were treated in these papers.[74–77]

In the cases of (*i*)–(*iii*), the authors showed that the maxima and minima for the differences between the ternary properties and the corresponding binary contributions ($V^E_{123} - V^E_{bin}$ and $\Delta\eta_{123} - \Delta\eta_{bin}$) were relatively small, suggesting that the effects due to ternary interactions are of smaller significant.

Binary interactions which dominated in each binaries are the consequence of: *i*) systems of methyl butanoate with *n*-heptane and *n*-octane gave positive V^E values caused by the net rupture of dipole–dipole interactions in methyl butanoate over the molecular packing and heteromolecular dipole–dipole induced interactions, *ii*) in the system *n*-heptane + *n*-octane, molecular packing is the prevalent factor, *iii*) in the system *n*-heptane + cyclooctane, the negative V^E values showed that the packing effect predominated over those due to physical interactions, *iv*) the positive values of V^E for the system methyl butanoate + cyclooctane indicated that the rupture of dipole–dipole interactions between the ester molecules was the predominate factor over the effects of volume contractions and molecular packing, *v*) the negative values of V^E for the system *n*-heptane + 1-chlorooctane showed that the effect of molecular packing was the prevalent factor, *vi*) the positive values of V^E for the system methyl butanoate +

+ 1-chlorooctane suggested that the net rupture of dipole–dipole interactions of the ether molecules prevailed over molecular packing and dipole–dipole interactions of the different molecules, *vii*) for the system methyl butanoate + 1-octanol, the values of V^E were positive and expansive effects connected to the rupture of hydrogen bonds in 1-octanol and dipole–dipole interactions in both components existed and *viii*) the V^E values of the system *n*-heptane + 1-octanol were negative over most of the composition range, indicated that molecular packing was the predominant factor. The breakage of hydrogen bonds at mole fractions of *n*-heptane $x > 0.9$ resulted in positive values of V^E.

Bearing in the mind all these facts, in general, as presented in Table IV, the V^E values for ternary systems with *n*-octane and *cyclo*-octane were predicted reasonably well by all symmetric models, except for the model proposed by Rastogi *et al.* The asymmetric model of Tsao–Smith with the arrangement A + B + + C gave good predictions for both ternary systems, while the Toop model worked satisfactorily only for the mixture with *n*-octane.

TABLE IV. Average percent deviations, *AAD* / %, between the experimental and predicted V^E / cm^3 mol^{-1} and $\Delta\eta$ / mPas values by polynomials for the ternary systems methyl butanoate (A) + *n*-heptane (B) with a third component (C) in the temperature range 283.15 – 313.15 K; for the asymmetrical models, the values depended on the component ordering

Model	*AAD* / %	*n*-Octane(C)[a]	Cyclooctane(C)[b]	1-Chlorooctane(C)[c]	1-Octanol (C)[d]
Redlich–Kister	V^E	1.9	2.0	19.35	45.4
	$\Delta\eta$	6.6	10.95	45	12.35
Kohler	V^E	1.45	5.1	21.35	37.8
	$\Delta\eta$	6.7	14.25	4.1	13.75
Colinet	V^E	1.5	3.45	20.7	38.8
	$\Delta\eta$	6.4	15.15	4.1	15.35
Rastogi *et al.*	V^E	27.2	27.4	65.7	93.5
	$\Delta\eta$	30.05	20.4	33.5	19.6
Tsao–Smith					
A + B + C	V^E	2.2	5.8	10.4	23.6
	$\Delta\eta$	6.55	45.15	13.75	47.15
C + A + B	V^E	21.5	30.65	146.8	204.75
	$\Delta\eta$	20.75	1.1	4.2	0.8
B + A + C	V^E	19.7	37.6	46.85	62.4
	$\Delta\eta$	15.8	45.5	7.35	45.3
Toop					
A + B + C	V^E	2.6	10.65	25.65	48.2
	$\Delta\eta$	6.55	23.1	4.45	23.8
C + A + B	V^E	2.5	3.55	28.8	48.65
	$\Delta\eta$	6.9	2.65	6.0	1.05
B + A + C	V^E	3.2	4.85	10.2	18.5
	$\Delta\eta$	6.5	23.85	3.6	21.9

[a]Matos *et al.*[74]; [b]Trenzado *et al.*[75]; [c]Matos *et al.*[76]; [d]Trenzado *et al.*[77]

The prediction of $\Delta\eta$ for ternary system with *n*-octane was accomplished reasonably well by all the considered symmetric models (except for the Rastogi *et al.* model). All asymmetric models of Toop and the arrangement A + B + C of Tsao–Smith model also produced good prediction.

In the case of ternary system with cyclooctane, the most accurate prediction for $\Delta\eta$ was achieved by the models of Tsao–Smith and Toop with the same arrangement (C + A + B).

Less accurate predictions of the V^E values for ternary system with 1-chloro-octane were obtained when compared to the results of systems with *n*-octane and cyclooctane as the third component, as can be seen from Table IV. In the case of the Tsao–Smith (option A + B + C) and Toop option B + A + C) models predicted results that could be treated as less accurate but satisfactory. Good predictions of $\Delta\eta$ were obtained with symmetric models of Kohler and Colinet and the option (C + A + B) of Tsao–Smith and all options of the Toop model. However, these models gave worse predictions of V^E.

As can be seen from Table IV, predicted results of V^E for the ternary system with 1-octanol as the third component were unsatisfactory. Only the Tsao–Smith and Toop models with the disposition C + A + B gave good prediction of $\Delta\eta$.

Dibutylether + ethanol + aromatic ternary systems. V^E and ΔR values the for the ternary systems dibutylether (DBE) + ethanol + toluene or benzene or 2,2,4-trimethylpentane at 298.15 K were reported.[78–80] The interaction between DBE and ethanol molecules gave negative values of V^E and ΔR. The systems of ethanol with toluene or benzene had positive values of V^E at lower concentrations of ethanol, which changed to negative in the alcohol rich region. The systems of DBE + toluene or benzene show negative values of V^E over the entire range of composition. The binary system of 2,2,4-trimethylpentane + ethanol showed positive V^E values, while the system 2,2,4-trimethylpentane + DBE shows negative values of V^E.

The V^E values for the ternary system with toluene were characterized by negative values, while the other two ternaries showed the appearance of both maximum and minimum values of V^E.

Table V shows that the Radojković *et al.* model provided the best estimation results for the ternary V^E and ΔR values in most cases. The models of Tsao–Smith and Kohler can not be recommended, while the Rastogi *et al.* model gave the best results only for the prediction V^E in the ternary system with toluene.

TAME + ethanol + 2,2,4-trimethylpentane system. Hwang *et al.*[81] determined values of V^E and ΔR data of the ternary systems TAME + ethanol + 2,2,4--trimethylpentane at 298.15 K and compared them with the values predicted by the models of Tsao–Smith, Kohler, Rastogi *et al.* and Radojković *et al.* The V^E of binary system TAME + ethanol at 298.15 K showed negative values over the entire ranges of composition, while the other two binary systems had positive

values of V^E. The positive deviations are caused by dispersive interaction forces between two unlike molecules, while the negative deviations are the consequence of the strong polarity of ethanol molecules. The ΔR of all binary system showed negative values. V^E and ΔR were estimated by aforementioned predictive models. The Radojković *et al.* model provided the best results, as in the case of the ternary system DBE + ethanol + 2,2,4-trimethylpentane (Table V). The other applied models could not be recommended for predictions of V^E and ΔR of this ternary system.

TABLE V. The values of the standard deviations *SD* of V^E / cm³ mol⁻¹, ΔR / cm³ mol⁻¹ calculated by polynomials for the ternary systems DBE (A) + ethanol (B) + third component (C) at 298.15 K

Model	Property	Benzene (C)[a]	Toluene (C)[b]	2,2,4-Trimethylpentane (C)[c]
Tsao–Smith	V^E	0.0837	0.0625	0.1322
	ΔR	1.2977	0.7403	1.7754
Kohler	V^E	0.0524	0.0431	0.0275
	ΔR	0.4779	0.7513	1.7881
Rastogi *et al.*	V^E	0.0624	0.0351	0.0388
	ΔR	1.4336	1.3166	1.2879
Radojković *et al.*	V^E	0.0281	0.0385	0.0273
	ΔR	0.2358	0.0800	0.5962

[a]Han *et al.*[78]; [b]Kwak *et al.*[79]; [c]Lee *et al.*[80]

MTBE + methanol + aromatic hydrocarbon ternary systems. Han *et al.*[82] considered MTBE + methanol in different ternary mixtures with benzene or toluene than the mixtures given in Tables I and II. The V^E and $\Delta\eta$ values at 298.15 K were determined for the ternary systems of MTBE + methanol + benzene and MTBE + methanol + toluene. The values of V^E were negative over the entire range of composition, except for a small region rich of benzene. The $\Delta\eta$ data had small negative values. This is consequence of the molecular interactions between each component which are not very strong in all the binary and ternary systems. The experimental data of V^E and $\Delta\eta$ were compared with the predicted results obtained by the Tsao–Smith, Kohler, Rastogi *et al.* and Radojković *et al.* models. The Kohler and Radojković *et al.* equations provided the best results for both ternary properties.

Formamide + benzene + aromatic amine. In work of Kharat and Nikam,[83] the excess molar volumes and deviations in viscosity of the ternary system aniline + benzene + *N,N*-dimethylformamide at 298.15, 303.15, 308.15 and 313.15 K were calculated by several empirical expressions. At all temperatures, the V^E and $\Delta\eta$ values were negative. The main contribution to the negative values of V^E was the interstitial accommodation of non-associated benzene molecules into aggregates of aniline. This also implies that no complex-forming interactions were present in the system, resulting in negative values of $\Delta\eta$.

The Equations of Radojković *et al.*, Kohler and Scachard *et al.* were applied to predict V^E and $\Delta\eta$. Small deviations between the experimental and predicted values were achieved.

Very good predictions[84] were obtained by the same three equations for V^E and $\Delta\eta$ of the ternary system *N,N*-dimethylformamide + benzene + chlorobenzene at 298.15, 303.15, 308.15 and 313.15 K.

Arylhalide + ether + alcohol/haloalcohol. Atik and Lourdani[32,33] evaluated the V^E of ternary systems α,α,α-trifluorotoluene and ethanol with diisopropyl ether (DIPE) and fluorobenzene[32] and with 2,2,2-trifluoroethanol (TFE)[33] at 298.15 K at a pressure of 101 kPa. When mixing alcohols and ether with fluoro-hydrocarbons, the following specific H bonding appeared: H···O–H, OH···O and O–H···F. These types of effects reflect on the magnitudes of V^E. These self- and cross-H bonding along with dipole–dipole interactions especially contribute to the ternary terms and influence the total packing behaviour of the mixtures.

Predictions were performed by symmetrical (Redlich–Kister, Kohler, Colinet and Jacob–Fitzner) and asymmetrical (Scathard *et al.*, Tsao–Smith and Toop) models. It was shown[32] that for ternary system with fluorobenzene where the ternary contribution terms are higher, better results were obtained by the asymmetrical models, while for systems with TFE,[33] higher errors were achieved by asymmetrical V^E with similar ternary contributions, V^E_{123}.

Atik[85] considered ternary mixtures of fluorobenzene + *tert*-butylmethyl ether and α,α,α,-trifluorotoluene + *tert*-butylmethylether + ethanol at 298.15 K and 0.1 MPa. The structure of these systems are similar to those in previous articles[32,33] of the same author, but the results of the predictions by the equations of Scatchard *et al.*, Tsao–Smith, Toop, Colinet, Jacob–Fitzner and Hillert were better, bearing in the mind that the ternary contributions of these systems were smaller.

Ether + alcohol + hydrocarbon/ionic liquid. The Radojković *et al.* Equation was applied[86,87] to the isolines of V^E and ΔR for the ternary systems: diisopropyl ether (DIPE) + 1-propanol + trihexyletradecylphosphonium [$P_{666,14}$] [TMPP]; *tert*-amylmethyl ether (TAME) + methanol + [$P_{666,14}$] [TMPP], dimethyl carbonate (DMC) + methanol + 1-ethyl-3-methyl-imiduzolium ethyl sulphate (EMISE); DMC + methanol + 1-butyl-3-methylimiduzolium tetrafluoroborate (B_{mim})(BF_4); 2-propanol + water + EMISE and 2-propanol + water + (B_{mim}) (BF_4) at 298.15 K. For all the systems, these properties were negative over the whole concentration range because of attractive interactions, strong polarity of the components and their difference in size, bearing also in the mind the appearance of the strong polarity of the ionic liquids.

Haloalkane + hydrocarbon systems. Matos *et al.*[88] reported V^E at 25 °C and atmospheric pressure for four ternary systems methyl ethanoate + 1-chlorooctane + + (*n*-heptane, *n*-octane, *n*-nonane or *n*-decane). The dominant factors in these

mixtures were the breaking of dipole–dipole interactions in the chloroalkanes and methyl ethanoate molecules. Furthermore, the influence of dispersive effects, heteromolecular interactions and packing molecular efficiency as the molecular size of the components increased resulted in higher positive values of V^E. The results of V^E measurement were compared with equations treated in the present article (Tsao–Smith, Toop, Kohler, Colinet, Rastogi *et al.*) and several other polynomials (Muggianu *et al.*, Hillert, Hwang *et al.* and Oracz).

The best results were obtained by the asymmetrical Tsao–Smith and Toop models and the symmetrical Kohler model. In all cases, the values of V^E_{max} were relatively small and with increasing carbon atomic number in the *n*-alkane, these values became smaller; hence, the results obtained by the polynomials became better.

Amide + cyclic ketone + alkanolamine. Iloukhani and Rakhshi[89] used the polynomial Equations of Kohler and Jacob–Fitzner for predictions of V^E, $\Delta\eta$ and Δn_D for the ternary mixture *cyclo*-hexanone + N,N-dimethylacetamide + N,N-di-ethylethanolamine at 298.15, 308.15 and 318.15 K and at ambient pressure over the whole composition ranges. The positive values of the ternary V^E were the consequence of chemical and structural contributions. Negative values of $\Delta\eta$ and Δn_D showed that the forces between pairs of unlike molecules were less than the forces between like molecules, due to the difference in size and shape of component molecules. The results obtained by both polynomial equations were satisfactory.

Haloalcohol + water + polyether. Esteve *et al.*[90] predicted the V^E values of the ternary system water + 2,2,2-trifluoroethanol + 2,5,8,11,14- pentaoxapenta-decane at 303.15 K by different symmetric and asymmetric empirical equations. Water with these fluoroalkanol and polyether showed negative values of V^E. As 2,5,8,11,14-pentaoxapentadecane is a stronger proton acceptor than 2,2,2-trifluoro-roethanol, their molecules would increase the negative ternary V^E, while associations between the molecules of the fluoroalcohol and poly ether are dominant.

Comparison of the predictions of the symmetrical Redlich–Kister (*i.e.*, Radojković *et al.*), Kohler, Muggianuet *et al.* and Colinet and the asymmetrical Tsao–Smith, Toop, Scachard *et al.* and Hillert) models showed that the smallest standard deviation was obtained by the Hiller eEquation with water as the first component. In all cases, the results of the asymmetrical models with water as first component were satisfactory. The Redlich–Kister model was the only symmetrical model that gave similarly good predictions.

The same empirical equations as in the article of Esteve *et al.*,[90] were used in work of Olive *et al.*[91] to predict ternary excess viscosities of the system trifluo-roethanol + water + tetraethylene glycol dimethyl ether at 303.15 K. In this case, the Colinet Equation showed the best results with smallest standard deviation. Of the symmetric models, only the Kohler Equation gave satisfactory agreement,

while the asymmetric model of Toop and Hillert could be treated similarly when trifluoroethanol was the first component.

Methyl acetate + methanol + n-*alcohols*. Rodrigez *et al.*[92] applied the predictive methods (Kohler, Jacob–Fitzner, Colinet, Tsao–Smith, Toop, Scachard *et al.*) to determine V^E and Δn_D for the ternary mixture methyl acetate + methanol + ethanol at 298.15 K. The ternary mixture showed positive values of V^E over most of the triangular diagram, suggesting the different closeness of the packing of the molecules as consequence of the different chain molecular lengths of the *n*-alcohols. In the evaluation of V^E, both types of models (symmetric and asymmetric) showed lower standard deviations. In the prediction of Δn_D, better results were achieved by symmetric and type b asymmetric models, where component b is methanol.

Canosa *et al.*[93] extended their investigation of V^E and Δn_D to ternary mixtures of methyl acetate + methanol with 2-propanol at 298.15 K. The ternary V^E becomes more positive than in the case of the mixture methyl acetate + methanol with ethanol.[92] Namely, molecular packing is more difficult at low amounts of methanol when the *n*-alcohol chain increases due to steric hindrance. In addition, high values of V^E for intermediate regions could appear because of a weakening of the H-bonds between the carboxyl group and the OH group. Finally, in dilute regions of 2-propanol or methyl acetate, the capacity of accommodation is similar as in the case of the smaller ethanol molecules.[92]. The estimations were performed using the same equations as in the previous work.[92]

The best prediction of the ternary V^E was realised with the symmetric Jacob––Fitzner and Tsao–Smith models when methyl ethanoate was the asymmetric component. For Δn_D estimation, better results were obtained with methanol as the asymmetric component. The ternary contribution of V^E is relatively small, and the highest value (–0.04 cm^3 mol^{-1}) was obtained in an approximately equimolar ternary composition. This fact could be the reason for the satisfactory results obtained with all the symmetric models.

Canosa *et al.*,[94] as a continuation of previous articles,[92,93] treated the ternary V^E of the system methyl acetate + methanol with 2-butanol at 298.15 K. The best predictions of V^E were obtained by the symmetric equations[93] and the asymmetric Scatchard *et al.* and Toop Equations with methanol and the Tsao–Smith equation with methyl acetate as the asymmetric component. The highest ternary contribution ΔV^E (–0.030 cm^3 mol^{-1}), detected at approximately equimolar composition, was some what smaller that in system with 2-propanol (0.04 cm^3 mol^{-1}),[93] giving better overall predictions.

Iglesias *et al.*[95] reported experimental densities, refractive indices of mixing and derived properties V^E and Δn_D of the ternary system methyl acetate + methanol + 1-butanol at 298.15 K and 1 atm. over the whole composition range.

These derived properties were predicted by the same models as in the previous studies.[92–94]

The V^E values were positive over the entire range of the calculations. This behaviour could be explained by certain disruptions of the associated alcohol molecules and polar association of the methyl acetate molecules or by rupture of the interaction of the methyl acetate and methanol molecules. Moreover, in accordance with corresponding region of ternary concentrations, the following effects should be taken into consideration: *i*) contractive trend due to the small size of the alcohol molecule and interaction of –OH group and ester groups and *ii*) the steric hindrance caused by the non-polar characteristics of the hydrocarbonated chain.

The good prediction results obtained by the symmetric models of Kohler, Jacob–Fitzner and Colinet, and the asymmetric models of Scatchard *et al.* and Toop (except with methanol as asymmetric component), could be explained by the facts that ternary contribution of V^E was relatively small compared to the binary and ternary values of V^E. Namely, ternary contribution is almost negligible except in the zone of low concentration of 1-butanol, thus the binary interactions determine the final excess value of ternary V^E. Standard deviations of these models are very similar to that obtained by the Cibulka Equation used for correlation of the ternary V^E data.

Amide + cyclic ketone + n-*alcohols*. Venkatesu and Prabhakara Rao[96] measured the V^E values of ternary liquid mixtures of *N,N*-dimethylformamide and *cyclo*-hexane with *n*-propanol, *n*-butanol, *n*-pentanol and *n*-hexanol as a function of composition at 303.15 K. The V^E values were positive in all cases except at a lower mole fraction of *N,N*-dimethylformamide in the system with *n*-propanol. The positive values of V^E showed that the effect of structure breaking of the components was dominant in the mixtures and increased with increasing chain length of the *n*-alcohols. Analysis of the results indicated good agreement between the measured V_{123}^E values and those predicted from the Redlich–Kister Equation in all ternary systems.

Haloalkane + ester + amine. Iloukhani and Khanlarzadeh[97] applied some geometrical and empirical models to V^E for ternary (1-chlorobutane + 2-chlorobutane + 2-butylamine; 1-chlorobutane + 2-chlorobutane + butyl acetate; 2-chlorobutane + butylamine + butyl acetate) and the quaternary system (1-chlorobutane + 2-chlorobutane + butylamine + butyl acetate) at 298.15 K. Prediction of the ternary systems was realised by different geometrical models (Kohler, Jacob––Fitzner, Rastogi *et al.* and Radojković *et al.*). The best results were obtained by the Kohler and Radojković *et al.* Equations. Estimation of V^E for the quaternary system was achieved by symmetrical (Redlich–Kister, Kohler, Lakhalpan and Colinet) and asymmetrical (Tsao–Smith, Toop, Hilert, Scatchard *et al.* and Knobeloch–Schwartz) models. The best result was obtained by the Tsao–Smith Equation.

5. CONCLUDING REMARKS

1. The choice of liquid mixtures in the present review (organic non-electrolytes and water) was based on their important application in the chemical and other industries. The thermodynamic and transport properties of multicomponent systems and their analysis in terms of various types of models are important for chemical processes. The search for models capable of correlating the molecules structure and macroscopic properties of liquids and predicting the behaviour of multicomponent mixtures are of primary interest for many investigators.

2. Properties considered in this work (ρ, V^E, Δn_D, Δu, $\Delta \eta$, ΔG^{*E}, ΔR, $\Delta \kappa_S$ and ε_r) are sensitive to different kinds of complexity of liquid mixtures and have often been used to investigate molecular packing, molecular motion and various types of intermolecular interactions and their strength, influenced by the size and chemical nature of different molecules. Assuming that the interactions in a ternary mixture are mostly dependant on the interactions in the binary ones, the use of polynomials was considered to test these methods of predicting ternary properties from binary data.

3. Extensive studies of the current status of the methods for the modelling of the aforementioned properties led to conclusion that, in spite of many years of contribution and development in these fields, there is still no general model that could be capable for the prediction within the accuracy of experimental measurements. Moreover, the success in application of each model is limited to a particular case due to the type and complexity of the systems and the number of their components.

4. The main reason for very extensive application of various polynomials lies not in the theoretical sophistication of this approach, but in the fact that the binary data are more accurately represented in the prediction of multicomponent mixtures. Unlike other approaches frequently used, the polynomials do not require a specific functional form of the equation and do not limit the number of adjustable parameters. The herein treated asymmetric models indicated: *i*) the different contribution of one of the binary constituents, *i.e.*, a pair which does not include a polar component and *ii*) the order of components in the mixture. For symmetric models, all three binary systems were considered identically.

5. Ternary contribution which represents the difference between the experimental value and that predicted from the binary mixtures is the main factor indicating the quality of the polynomial predictions. The following notices are essentials:

– When ternary contributions are relatively small (including positive and negative values), then the effects due to ternary interactions are less important. In these cases, the results obtained by the polynomials are generally very good, particularly when using ordered symmetric models. The standard deviations in

some cases are very close to those obtained by fitting equations, such as the Cibulka, Singh or Nagata equations.

– Larger absolute values of the ternary contribution result in poorer estimations by the polynomials due to the fact that these ternary mixtures are not adequately represented only by the binary sub-systems because stronger ternary molecular interactions exist. Furthermore, unsatisfactory predictions are obtained when the difference in the experimental maximal and minimal ternary values of V^E are large.

– Various factors in connection with position of the ternary contribution (asymmetric, change of sign, magnitude of maximum or minimum) could be important for good predictions. In some cases, asymmetric models gave satisfactory results.

6. The influence of higher temperatures on the calculation by polynomials the errors only slightly. The higher values of the ternary contribution resulting by increasing the temperature lead to poorer prediction. When ternary contribution in ternary diagrams changes sign, the errors of the predictions could be decreased.

7. Results obtained by asymmetric models can be very different:

– For the same ternary system, the best prediction is achieved for one thermodynamic or transport property but the worst for any other.

– Change of temperature changes the quality of the prediction.

– Possible arrangement of the components as the asymmetric one frequently produces results which are completely different. For this reason, it is necessary to use all three components as asymmetric for the prediction.

– Different asymmetric models can give very dissimilar results when the same asymmetric component is applied in testing the same ternary system.

– When the ternary contribution is small, the order of the components in the mixtures could be essential for the asymmetric models.

8. In many cases, the Radojković *et al.* model, or the same model used as the Redlich–Kister model, could be recommended for the prediction of ternary properties as the simplest expression among those presented in this review.

ИЗВОД

ПРЕДСКАЗИВАЊЕ ТЕРМОФИЗИЧКИХ И ТРАНСПОРТНИХ СВОЈСТАВА ТРОЈНИХ
ОРГАНСКИХ НЕЕЛЕКТРОЛИТНИХ СИСТЕМА, УКЉУЧУЈУЋИ ВОДУ, ПОМОЋУ
ПОЛИНОМА

БОЈАН Д. ЂОРЂЕВИЋ, МИРЈАНА Љ. КИЈЕВЧАНИН, ИВОНА Р. РАДОВИЋ, СЛОБОДАН П. ШЕРБАНОВИЋ
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У овом прегледном раду је дат опис и предсказивање термофузичких и транспорт-
них својстава тројних органских неелектролитних система, укључујући и воду помоћу
полинома. Емпиријске једначине Радојковића и сар. (односно Redlich–Kister), Kohlera,
Jacob–Fitznera, Colineta, Tsao–Smitha, Toopa, Scatcharda и сар. и Rastogia и сар. су поре-
ђене са расположивим експерименталним подацима објављеним у познатим међународ-
ним часописима (*Fluid Phase Equilibria*, *Journal of Chemical and Engineering Data*, *Journal
of Chemical Theromodynamics*, *Journal of Solution Chemistry*, *Journal of the Serbian Chemical
Society*, *The Canadian Journal of Chemical Engineering*, *Journal of Molecular Liquids*, *Thermo-
chimica Acta* и др.). Применљивост емпиријских модела на одређивање допунске молар-
не запремине, V^E, допунских вискозности, $\Delta\eta$, допунске слободне енергије активације
вискозног тока, ΔG^{*E}, промене моларне рефракције мешања, ΔR, промене индекса
рефракције при мешању, Δn_D, промене изентропске компресибилности, $\Delta\kappa_s$, одступање
површинског напона, $\Delta\sigma$, одступање брзине звука, Δu, и одступање релативне permitiv-
ности, $\sigma\varepsilon_r$, проверена је на серији тројних смеша врло сложене структуре које су и
елементарно описане. Добијени резултати предсказивања су продискутовани и дате су
извесне препоруке за коришћење симетричних и несиметричних модела и могућој
успешној примени на смеше.

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