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Prediction of excess molar volumes of binary mixtures by Prigogine–Flory–Patterson (PFP) and extended real association solution (ERAS) models*

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Abstract: In this paper, the Prigogine–Flory–Patterson (PFP) theoretical model and the extended real association solution (ERAS) model for the prediction of the excess molar volumes of 17 binary sets of alcohols (methanol, ethanol, propan-1-ol, butan-1-ol, butan-2-ol and pentan-1-ol) with benzene, chlorobenzene, acetonitrile, hexan-1-amine and *n*-heptane were tested at 298.15 K and atmospheric pressure. The binary sets contained 333 experimental data points for 11 different compounds. The ERAS model demonstrated better correlative characteristics for binary mixtures comparing to PFP model. The ERAS model is successfully applied on all binary systems except ethanol + benzene and propan-1-ol + benzene. PFP model gave less satisfactory results for all systems except butan-1-ol + hexan-1-amine, for which obtained results were acceptable.

Keywords: binary mixtures; excess molar volume; prediction model; PFP; ERAS.

INTRODUCTION

Design of process and industrial equipment is based on the knowledge of the thermodynamic properties of fluids. The knowledge of thermodynamic and transport properties of pure components and their mixtures is very important for understanding intermolecular interactions in binary mixtures. Solvent mixtures play an important role in chemical industries and their physiochemical properties often show large deviations from ideal behaviour. Data of this properties are important for various engineering calculations and represent the starting points for the designing, analysis and optimization of technological processes. In addition to the experimental determination of thermodynamic parameters of pure sub-

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stances and their mixtures, it is necessary to develop and test a reliable thermodynamic model to replace, in some cases, very expensive experiments.

Prigogine–Flory–Patterson (PFP) model^{1–7} is the theoretical approach that can describe and predict the non-ideal behaviour of multicomponent systems. On the other hand, the original extended real associated solution (ERAS) model, introduced by Heintz,⁸ combines the association effects arising from hydrogen bonding with free volume effects from the differences of van der Waals interactions between unlike molecules in a mixture. The aim of this work was to test the applicability of these two models to correlate the excess molar volume data of 17 binary systems containing the widely applied organic compounds, alcohols (methanol, ethanol, propan-1-ol, butan-1-ol, butan-2-ol and pentan-1-ol) and benzene, chlorobenzene, acetonitrile, hexan-1-amine and *n*-heptane.^{9–13} The analyzed systems are divided into five groups: alcohols + aromates, alcohols + *n*-alkane, alcohols + amine, alcohols + acetonitrile and amine + *n*-alkane. Selected systems show diverse deviations from ideal behaviour, *e.g.*, highly negative, positive or S-shaped excess molar volumes *vs.* mixture composition curve. In this way, the applicability of the model for a specific type of non-ideal behaviour is confirmed. The modelling was performed at 298.15 K and atmospheric pressure.

MODELLING

In this paper predictive capabilities of PFP and ERAS models were tested for density calculations and excess molar volumes for large number of binary systems based on the previously measured experimental data. The selected systems are characterized by different forms of non-ideal behaviour and the results of this work can show the applicability of both models for different groups of compounds and mixtures.

The PFP model is designed to analyze the thermodynamic functions of the binary systems. This theory is used for interpretation of the measurement results of some excess properties of the binary systems formed by molecular species that differ in size and shape. Pure empirical application of the Flory model⁴ can provide some interesting correlations of excess molar properties for complex mixtures. According to PFP model, the excess molar volume contains three contributions: interactional contribution, a free volume contribution and a pressure contribution. The expression for excess molar volume which separates the three contributions is given as:

$$\frac{V^E}{(x_1V_1^* + x_2V_2^*)} = \frac{(\tilde{V}^{1/3} - 1)\tilde{V}^{2/3}\psi_1\theta_2\chi_{12}}{((4/3)/\tilde{V}^{1/3} - 1)P_1^*} - \frac{(\tilde{V}_1 - \tilde{V}_2)^2((14/9)/\tilde{V}^{1/3} - 1)\psi_1\psi_2}{((4/3)/\tilde{V}^{1/3} - 1)\tilde{V}} + \frac{(\tilde{V}_1 - \tilde{V}_2)(P_1^* - P_2^*)\psi_1\psi_2}{P_1^*\psi_2 + P_2^*\psi_1} \quad (1)$$

where V^E is excess molar volume, x mole fraction, V^* characteristic volume, P^* characteristic pressure, ψ molecular contact energy fraction, θ molecular surface fraction and χ_{12} parameter.

Reduced volume of binary mixture is defined as:¹⁴

$$\tilde{V} = \psi_1\tilde{V}_1 + \psi_2\tilde{V}_2 \quad (2)$$

The characteristic parameters V^* and P^* are obtained from thermal expansion coefficient $\alpha = (1/V)(\partial V/\partial T)_P$ and isothermal compressibility, $\kappa = (1/V)(\partial V/\partial P)_T$:

$$\tilde{V}_i = \left(\frac{1 + ((4/3)\alpha_i T)}{(1 + \alpha_i T)} \right)^3, \quad i = 1, 2 \quad (3)$$

$$V_i^* = V_i / \tilde{V}_i \quad (4)$$

$$P_i^* = \frac{P_i}{\tilde{P}_i} = \frac{T\tilde{V}_i^2\alpha_i}{\kappa_i}, \quad i = 1, 2 \quad (5)$$

The molecular contact energy fraction is calculated by:

$$\Psi_1 = 1 - \Psi_2 = \frac{\phi_1 P_1^*}{(\phi_1 P_1^* + \phi_2 P_2^*)} \quad (6)$$

$$\phi_1 = 1 - \phi_2 = \frac{x_1 V_1^*}{(x_1 V_1^* + x_2 V_2^*)} \quad (7)$$

where ϕ is a hard-core volume fraction.

The molecular surface fraction is calculated by:

$$\theta_1 = 1 - \theta_2 = \frac{S_1 \phi_1}{S_1 \phi_1 + S_2 \phi_2} = \frac{\phi_1}{\phi_1 + (S_2 / S_1) \phi_2} \quad (8)$$

where S_i is the molecular fraction surface/volume ratio for the components determined by Bondi's method.¹⁵

$$\frac{S_1}{S_2} = \left(\frac{V_1^*}{V_2^*} \right)^{-1/3} \quad (9)$$

$$\alpha = - \left(\frac{\partial \ln \rho}{\partial T} \right)_{p,x} \quad (10)$$

$$\kappa = 1 / (u^2 \rho) + \frac{\alpha^2 T}{\rho C_p} \quad (11)$$

The values of the parameters for the pure liquid components and the mixture are obtained using the Flory theory.⁴ The cross-interaction parameter required for the calculation of V^E using PFP theory was derived from values of excess molar volumes at equimolar composition for each mixture.

On the other hand, ERAS model combines real association solution model¹⁶⁻¹⁹ with Flory equation of state. The excess function is written as:

$$V^E = V_{chem}^E + V_{phys}^E \quad (12)$$

where V_{chem}^E is the chemical contribution, mainly due to the association reactions, and V_{phys}^E represents the physical contribution, which results from the physical interactions between molecules:

$$V_{\text{chem}}^E = \tilde{V}_M \left[x_A K_A \Delta v_A^* (\phi_{A1} - \phi_{A1}^0) + x_B K_B \Delta v_B^* (\phi_{B1} - \phi_{B1}^0) + x_A K_{AB} \Delta v_{AB}^* \frac{\phi_{B1}(1 - K_A \phi_{A1})}{V_B V_A^{-1} (1 - K_B \phi_{B1}) + K_{AB} \phi_{B1}} \right] \quad (13)$$

$$V_{\text{phys}}^E = (x_A V_A^* + x_B V_B^*) (\tilde{V}_M - \phi_A \tilde{V}_A - \phi_B \tilde{V}_B) \quad (14)$$

where K_i are the association constants (i is A, B or AB) and it is assumed to be independent of the chain length. Their temperature dependence is given by:

$$K_i = K_0 \exp \left[- \left(\frac{\Delta h_i^*}{R} \right) \left(\frac{1}{T} - \frac{1}{T_0} \right) \right], \quad i = \text{A, B or AB} \quad (15)$$

where K_0 is the equilibrium constant at the atmospheric pressure and standard temperature $T = 298.15$ K and Δh_i^* the enthalpy change of reaction, which corresponds to the hydrogen bonding energy. These reactions are also characterized by the volume change Δv_i^* , related to the formation of the linear chains.

ERAS model is used to correlate the experimental values for the investigated mixtures and needs pure component properties to obtain the characteristic parameters V^* and P^* of each compound. It also needs data for density, ρ , isobaric thermal expansivity, α , and isothermal compressibility, κ , at atmospheric pressure and $T = 298.15$ K.

RESULTS AND DISCUSSION

The goal of this research was to check if PFP and ERAS models are capable to correlate the excess molar volumes of different binary mixtures containing alcohols, aromates, n -alkanes, amines and nitriles. Table I shows the literature density and the molar mass data for all constituents of investigated binary systems at atmospheric pressure and $T = 298.15$ K.

TABLE I. Densities, ρ , and molar masses, M , of the pure compounds at 298.15 K and atmospheric pressure

Compound	$\rho / \text{g cm}^{-3}$	$M / \text{g mol}^{-1}$
Methanol ⁹	0.78665	32.04
Ethanol ⁹	0.78525	46.07
Propan-1-ol ¹⁰	0.799692	60.09
Butan-1-ol ¹¹	0.805762	74.12
Butan-2-ol ¹²	0.802528	74.12
Pentan-1-ol ¹³	0.810968	88.15
Acetonitrile ⁹	0.77669	41.05
Hexan-1-amine ¹¹	0.760128	101.19
Benzene ¹⁰	0.873582	78.11
Chlorobenzene ¹³	1.101038	112.56
n -Heptane ¹¹	0.679494	100.02

The values of parameters for the pure liquid components required for both PFP and ERAS models were obtained from the literature.²⁰⁻²⁶ Table S-I of the Supplementary material to this paper lists the literature for pure component data,

self-association constant, K , thermal expansion coefficient, α , isothermal compressibility κ , reduced pressure P^* , reduced volume V^* , molar enthalpy change of association, Δh^* , molar volume change of association, Δv^* , and surface volume ratio S at atmospheric pressure and $T = 298.15$ K.

The PFP parameter, χ_{12} , in Eq. (1), can be calculated at given temperature by fitting the experimental excess molar volumes of binary mixture over the entire composition range. The values of the interaction parameter χ_{12} for the studied mixture have been calculated using the equimolar V^E values and they are listed in Table S-II (Supplementary material) together with the equimolar values for all contributions to V^E (interactional, free volume and P^* effect contribution). The parameters K_{AB} , Δv_{AB}^* , and X_{AB} in the ERAS model were correlated and listed in Table S-III (Supplementary material).

The quality of the fit for the applied models was estimated by the standard deviation, σ and average percent deviation, D :

$$\sigma = \left[\frac{\sum_{i=1}^N (V_{\text{exp}}^E - V_{\text{cal}}^E)^2}{N - npar} \right]^{0.5} \quad (16)$$

$$D = \frac{100}{N} \sum_{i=1}^N \left| \frac{V_{\text{exp}}^E - V_{\text{cal}}^E}{V_{\text{exp}}^E} \right| \quad (17)$$

where $npar$ is the number of parameters.

The obtained results with PFP and ERAS models, for all systems, are listed in Table II. The results obtained for the selected binary systems, representing each group of analyzed binary mixtures, are presented in Figs. 1–7.

The systems selected for the analyses are divided into five groups: alcohols + aromates, alcohols + n -alkane, alcohols + amine, alcohols + acetonitrile and amine + n -alkane. Selected systems show different deviations from ideal behaviour, *e.g.*, negative, positive or S-shape (positive and negative) V^E vs. x_1 curves. In all cases the ERAS model was significantly superior comparing to PFP model.

The systems of alcohols with aromates were the largest group in this research, *i.e.*, five systems with benzene and six systems with chlorobenzene were analyzed. The systems of analyzed alcohols with chlorobenzene exhibit S-shape V^E vs. x_1 curve. As it was already discussed in the literature¹⁰ the addition of large amounts of chlorobenzene to a pure alcohol induces the de-polymerization of normal alcohols, resulting in volume expansion and positive V^E values. The contraction in volume is characteristic for higher alcohol concentrations due to the

formation of OH–Cl atom hydrogen bonded complexes, between an alcohol and chlorobenzene. Structural effects can also contribute to closer geometrical packing and volume contraction, which is the prevailing factor in the mixture with methanol, since methanol is the smallest molecule. The systems with benzene (Figs. 1 and 2) also show sigmoidal V^E vs. x_1 curves, but the negative effects are less pronounced comparing to the equivalent systems with chlorobenzene. The possible interactions between alcohols and benzene aromatic ring are the OH- π type²⁷, which are much weaker comparing to OH-Cl interactions between alcohols and chlorobenzene. It is obvious that PFP model is not capable to correlate V^E experimental data of those systems, with errors exceeding 100 % (Fig. 2). On the other hand ERAS model was rather successful in some cases. For the alcohol + chlorobenzene the systems percentage deviations are ranged from about 7 to 15 %, while for the alcohol + benzene systems the deviations were higher especially for the systems containing ethanol or 1-propanol (see Fig. 2). Although the errors for the ethanol + benzene system are high (10.97 %), Fig. 1 confirms that ERAS model fits experimental point rather well, except in the dilute regions.

TABLE II. Average relative deviation, D and the standard deviation, σ obtained with PFP and ERAS models

Mixture	PFP		ERAS	
	$D / \%$	$\sigma / \text{cm}^3 \text{mol}^{-1}$	$D / \%$	$\sigma / \text{cm}^3 \text{mol}^{-1}$
Methanol + benzene ²⁷	103.25	60.097	10.97	0.0017
Ethanol + benzene ²⁸	203.20	51.452	217.45	0.0276
Propan-1-ol + benzene ⁹	1120.70	37.7	181.05	0.0203
Butan-1-ol + benzene ²⁹	56.65	21.7	12.65	0.0096
Butan-2-ol + benzene ³¹	18.34	9.55	6.71	0.0194
Methanol + chlorobenzene ²⁷	865.59	13.7	7.28	0.0030
Ethanol + chlorobenzene ²⁷	202.61	17.6	14.02	0.0051
Propan-1-ol + chlorobenzene ¹²	156.60	26.1	8.53	0.0062
Butan-1-ol + chlorobenzene ¹²	249.09	32.8	15.18	0.0061
Butan-2-ol + chlorobenzene ¹²	229.09	36.5	6.72	0.0030
Pentan-1-ol + chlorobenzene ¹²	158.62	37.9	14.17	0.0063
Butan-1-ol + <i>n</i> -heptane ³⁰	45.45	20.9	9.87	0.0078
Butan-2-ol + <i>n</i> -heptane ³²	20.18	10.2	5.36	0.0160
Butan-1-ol + hexan-1-amine ¹¹	2.66	1.41	1.95	0.0129
Methanol + acetonitrile ⁷	26.11	15.4	3.03	0.0026
Ethanol + acetonitrile ²⁷	240.09	39.0	29.06	0.0037
Hexan-1-amine + <i>n</i> -heptane ⁹	20.90	8.95	3.16	0.0042

Two systems containing an alcohol (butan-1-ol and butan-2-ol) and *n*-heptane and one system of an amine (hexan-1-amine) and *n*-heptane were also analyzed. All systems exhibit positive V^E vs. x_1 trend. In these mixtures the unlike molecules are not capable to make heteroassociates due to hydrogen bonding. Con-

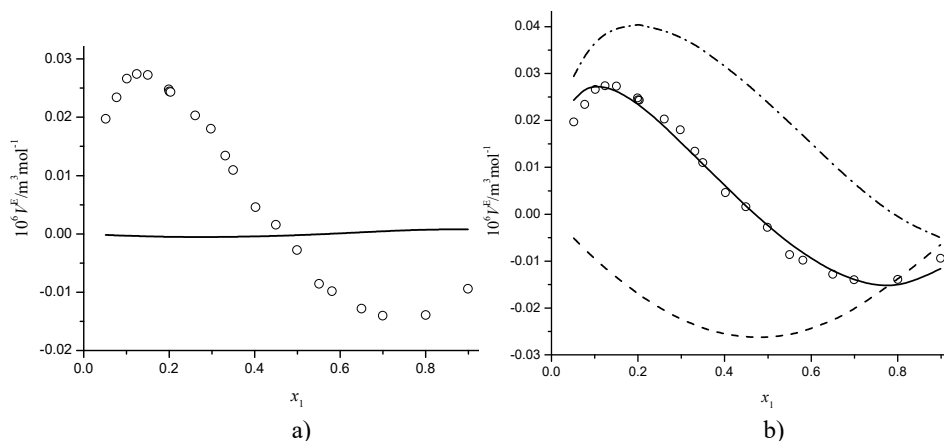


Fig. 1. The experimental excess molar volumes compared with the correlated values *via* PFP theory and ERAS model for binary mixture of methanol + benzene at 298.15K; a) PFP theory and b) ERAS model (---) physical contribution, (- · -) chemical contribution.

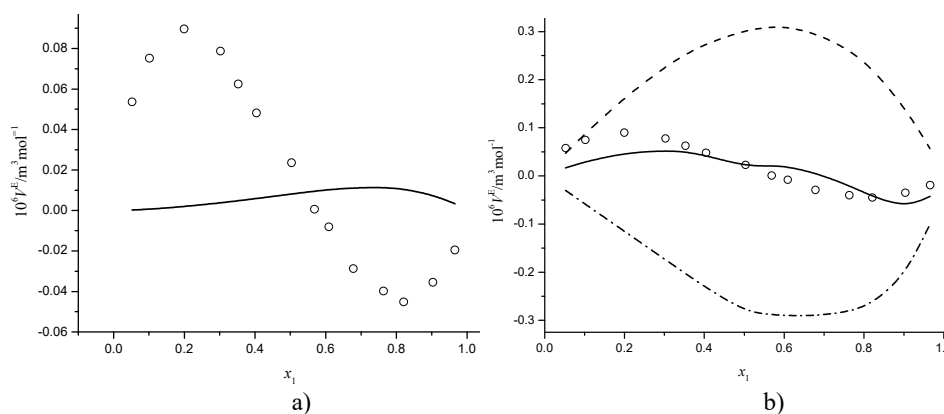


Fig. 2. The experimental excess molar volumes compared with the correlated values *via* PFP theory and ERAS model for binary mixture of ethanol + benzene at 298.15K; a) PFP theory and b) ERAS model (---) physical contribution, (- · -) chemical contribution.

trary to that, both alcohol and amine molecules are making homoassociates. It is assumed that *n*-heptane added to a pure alcohol/amine causes disruption of alcohol or amine homoassociates and volume expansion, *i.e.*, positive V^E values. Increase in the volume in butan-2-ol + *n*-heptane mixture is higher, compared to butan-1-ol + *n*-heptane system, while both V^E curves are slightly skewed towards mixtures rich in *n*-heptane. The same trend, the V^E-x_1 shape, is also characteristic for the hexan-1-amine + *n*-heptane system. Both models work better for the system butan-2-ol + *n*-heptane, since the V^E curves are more symmetric. The average percentage deviation for the ERAS model and butan-1-ol + *n*-heptane system

goes up to 10 %, though ERAS model curve follows experimental data very well (see Figs. 3 and 4).

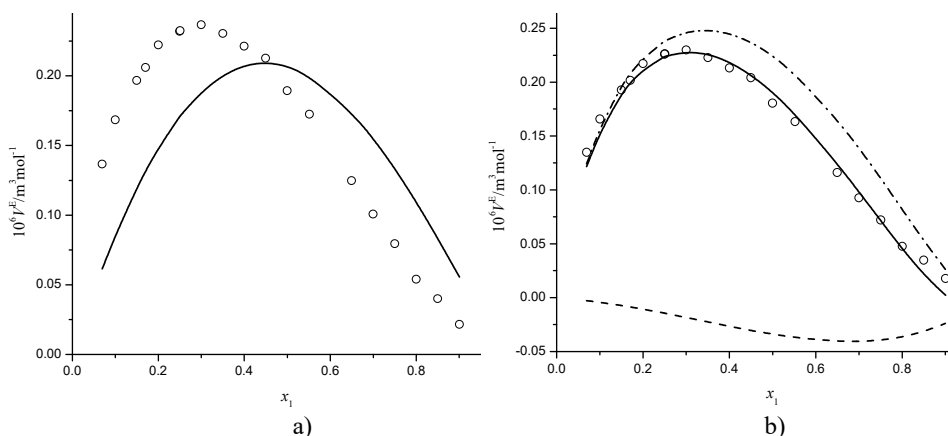


Fig. 3. The experimental excess molar volumes compared with the correlated values *via* PFP theory and ERAS model for binary mixture of butan-1-ol + *n*-heptane at 298.15K; a) PFP theory and b) ERAS model(- -) physical contribution, (- · -) chemical contribution.

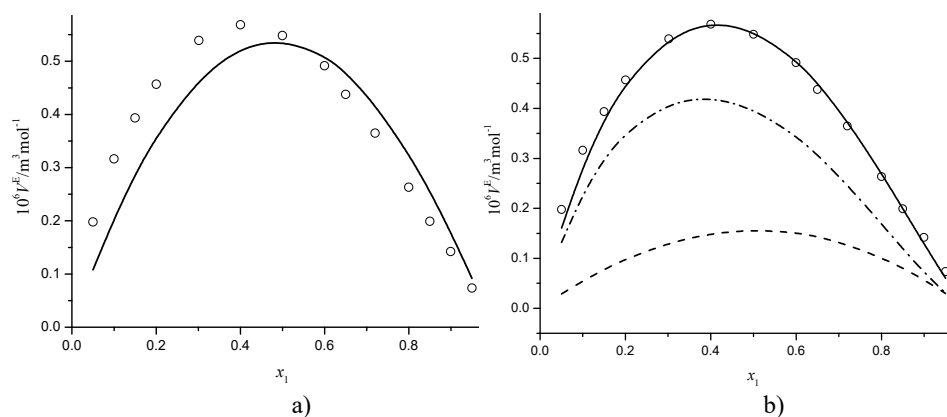


Fig. 4. The experimental excess molar volumes compared with the correlated values *via* PFP theory and ERAS model for binary mixture of butan-2-ol + *n*-heptane at 298.15K; a) PFP theory and b) ERAS model(- -) physical contribution, (- · -) chemical contribution.

In Figs. 5 and 6 two systems of methanol and ethanol with acetonitrile are shown. The excess molar volumes for the system with methanol show small negative values, while the V^E-x_1 curve for the system with ethanol is S-shaped, *i.e.*, positive for the mixtures rich in acetonitrile and negative for higher ethanol concentrations. From shown figures it is obvious that ERAS model succeeds to follow the S-shaped V^E curve, although with much higher average relative deviation, comparing to the system with ethanol. On the other hand PFP model com-

pletely fails to describe the complex V^E behaviour of ethanol + acetonitrile system. For the system with methanol the situation is better, however the PFP model still does not follow the asymmetric V^E vs. x_1 trend.

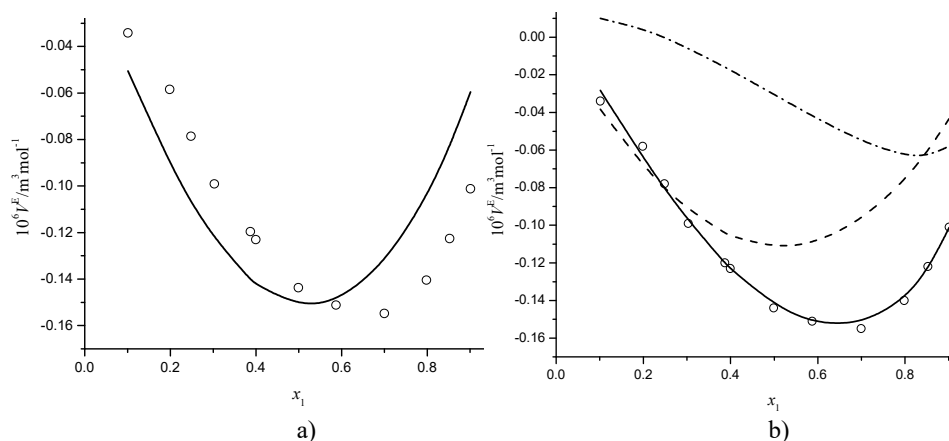


Fig. 5. The experimental excess molar volumes compared with the correlated values *via* PFP theory and ERAS model for binary mixture of methanol + acetonitrile at 298.15K; a) PFP theory and b) ERAS model (- -) physical contribution, (- · -) chemical contribution.

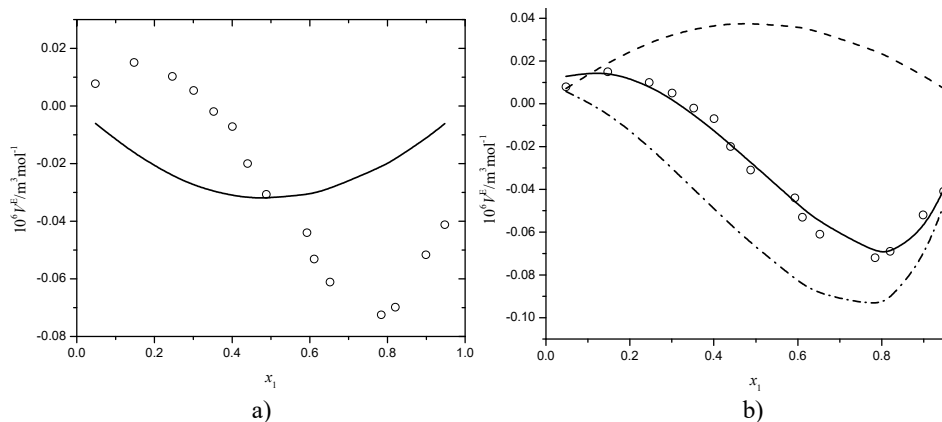


Fig. 6. The experimental excess molar volumes compared with the correlated values *via* PFP theory and ERAS model for binary mixture of ethanol + acetonitrile at 298.15K; a) PFP theory and b) ERAS model (- -) physical contribution, (- · -) chemical contribution.

The mixtures of alcohols and amines show highly negative excess molar volume data with the symmetric V^E vs. x_1 curve,⁹ due to the hydrogen bonding and hetero-association between alcohol and amine molecules. This type of non-ideal behaviour can be successfully fitted by both PFP and ERAS models, yet the ERAS model fits minimal region slightly better than PFP model. From the all mentioned above it is obvious that except for the alcohol + amine mixtures, the

PFP model was not able to describe the different V^E-x_1 curve shapes. The best results were achieved for the hexan-1-amine + *n*-heptane system (see Fig. 7).

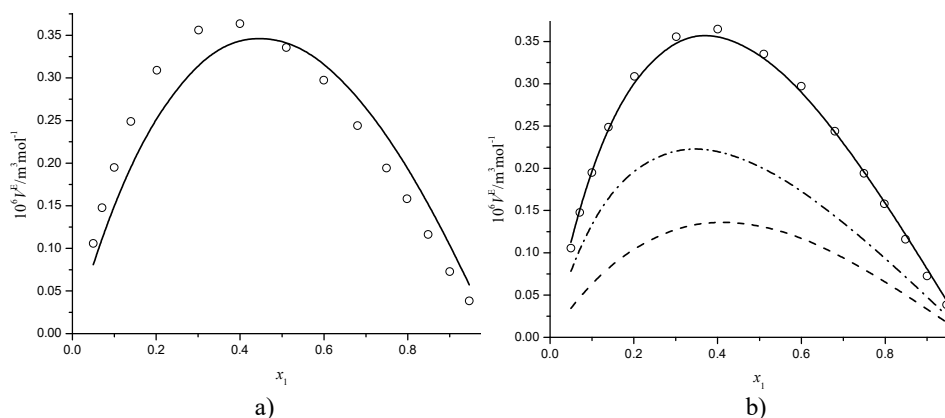


Fig. 7. The experimental excess molar volumes compared with the correlated values *via* PFP theory and ERAS model for binary mixture of hexan-1-amine + *n*-heptane at 298.15K; a) PFP theory and b) ERAS model (---) physical contribution, (- · -) chemical contribution.

CONCLUSIONS

In this paper, two theoretical models, the Prigogine–Flory–Patterson (PFP) and the extended real association solution (ERAS) for the excess molar volume correlation were tested on 17 binary mixture systems divided into five groups: alcohols + aromates, alcohols + *n*-alkane, alcohols + amine, alcohols + acetonitrile and amine + *n*-alkane. The excess molar volumes for binary mixtures are described qualitatively for all ranges of mole fractions by the PFP and the ERAS model. Both models can be applied on the systems that have only positive or negative excess molar volume values over the whole range of mole fractions, where the ERAS model gives better results. Also, the ERAS model was much better comparing to the PFP for systems that have both, positive and negative excess molar volume values, over the whole range of mole fractions. The PFP theory is able to describe the systems with only negative or only positive excess molar volume values over the whole range of mole fractions. However, if the V^E-x_1 curve is asymmetric and tends to shift towards higher or lower concentration than an equimolar point, the errors are getting higher. The comparison of calculated and experimental excess properties of binary systems shows that the ERAS model is able to describe all the excess functions ranging from positive values to strong negative values, as well as the S-shaped V^E-x_1 curves, which cannot be completed for the PFP model.

SUPPLEMENTARY MATERIAL

Tables S-I–S-III are available electronically at the pages of journal website: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД

ОДРЕЂИВАЊЕ ДОПУНСКЕ МОЛАРНЕ ЗАПРЕМИНЕ БИНАРНИХ СИСТЕМА ПОМОЋУ PRIGOGINE–FLORY–PATTERSON (PFP) И EXTENDED REAL ASSOCIATION SOLUTION (ERAS) МОДЕЛА

ИВОНА Р. РАДОВИЋ, НИКОЛА Д. ГРОЗДАНИЋ, БОЈАН Д. ЂОРЂЕВИЋ, СЛОБОДАН П. ШЕРБАНОВИЋ
И МИРЈАНА Љ. КИЈЕВЧАНИН

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У овом раду је извршено израчунавање допунских моларних запремина 17 бинарних система алкохола (метанол, етанол, пропан-1-ол, бутан-1-ол, бутан-2-ол и пентан-1-ол) са бензеном, хлорбензеном, ацетонитрилом, хексан-1-амином и *n*-хептаном на температури од 298,15 К и на атмосферском притиску, коришћењем теоријских модела: Prigogine–Flory–Patterson (PFP) и Extended Real Association Solution (ERAS). Бинарни системи садржали су 333 експерименталне тачке за 11 различитих једињења. ERAS модел показао је боље корелативне карактеристике за бинарне смеше у поређењу са PFP моделом. ERAS модел успешно је примењен на свим бинарним системима, осим на смеше етанол + бензен и пропан-1-ол + бензен. PFP модел генерално даје лошије резултате за све системе, осим за систем бутан-1-ол + хексан-1-амин, за који су добијени прихватљиви резултати.

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A tribute to Professor Bojan Djordjević in honour of his 80th birthday



Journal of the Serbian Chemical Society wishes to draw attention to Professor Djordjević's rich legacy and superior contribution to the field of thermodynamics in general and to *JSCS* in particular.

Prof. Dr. Bojan D. Djordjević was born in 1937 in Belgrade where he graduated from the Faculty of Technology, University of Belgrade in 1961 and commenced his career as Research Fellow in IHTM, Belgrade. He stayed in IHTM for the period from 1961 to 1964. He received his PhD in 1970 from the Institute of Nuclear Sciences "Vinča" and the Faculty of Technology where in 1971 he was promoted to the position of the Assistant Professor and in 1976 to the position of the Associate Professor.

Since 1982 he had been Full Professor at the Faculty of Technology and Metallurgy, where he had been extensively involved in curricula development and teaching of various subjects of thermodynamics, including but not limited to chemical engineering thermodynamics, energy of process industry, and molecular thermodynamics. During his fruitful carrier he also mentored hundreds of graduate students supporting them selflessly to commence their own academic paths. Further, Professor Djordjević lectured different subjects of thermodynamics at many other university centers (Novi Sad, Podgorica, Priština, The Military–Technical Academy, Belgrade, Higher Technical School, Kosovska Mitrovica, *etc.*). He is the author of 27 text-books and monographs including Thermodynamics and Thermotechnics, Thermodynamics of Fluids, Chemical Engineering Thermodynamics, and Heat Transfer.

Professor Djordjević was a foundational member of the Laboratory for chemical engineering parameters. In two terms he was the Head of Fundamental Technical Science Department and, also, led a national research projects and sub-projects. He contributed to over 50 technical studies and projects, many of which have been applied in chemical industry (Mineloprema, Pančevo; Oil Refinery,

Beograd; Oil Refinery, Pančevo; HIP, Pančevo; Miloje Zakić, Kruševac, Železara, Smederevo, *etc.*) and he also established cooperation with Imperial Chemical Industries, United Kingdom and University of Berkley, USA. His research has incorporated a wide range of fundamental areas, with a focus on equations of state, vapour–liquid equilibria, excess properties of solution and thermo-hydraulic design of heat equipment. Professor Djordjevic has also been very active in the Yugoslav Association of Chemists and Technologists. He is a member of Serbian Scientific Society, Serbian Chemical Society and American Chemical Society. He received a number of national and international acknowledgments, awards, plaques and certificates: Men of Achievement for Distinguished Achievement, Cambridge, England, 1982.; 5.000 Personalities of the Word, American Biographical Institute; The International Who' S Who of Intellectuals, Cambridge, England, 1983; Certificate of Merit for Distinguished Service to the Community, Cambridge, England, 1984.; Who's Who in the World 1980/1981; Who's Who in the World 1982/1983; Medal for outstanding and long-lasting contribution to science (for development of chemical engineering thermodynamics), Serbian Chemical Society, 2000; Honorary diploma on the 25th anniversary of the Faculty of Technology, University of Novi Sad, for a significant contribution to the work and development of the Faculty of Technology, University of Novi Sad, 1984; Certificate as a sign of acknowledgment and gratitude for the great contribution to the work and development of the Serbian Chemical Society on the occasion of 100th anniversary 1997.

Professor Djordjević authored and contributed to over 100 scientific articles, more than hundred scientific papers presented on international and national congresses and symposia and over 30 professional papers. His articles were published in international journals, such as: *Journal of Chemical Thermodynamic*, *Fluid Phase Equilibria*, *Journal of Chemical Engineering Data*, *Chemical Engineering Science*, *AIChE Journal*, *Canadian Journal of Chemical Engineering*, *Industrial & Engineering Chemistry Process Design and Development*, *Industrial & Engineering Chemistry Research*, *Thermochimica Acta*, *Physics and Chemistry of Liquids*, *Chemie Ingenieur Technik*, *Korean Journal of Chemical Engineering*, *Journal of Applied Polymer Science*, *Hungarian Journal of Industrial Chemistry*, *Chemische Technik*, *Journal of Chemical Education*, *etc.*

Being internationally recognized and respected, Professor Djordjević was cited over 500 times in the international journals, university textbooks and monographs. He was a referee in the leading international and national journals and congresses and was a member of Editorial Boards of *the Journal of the Serbian Chemical Society* and *Chemical Industry*.

Professor Djordjević has made an exceptional contribution to the field of thermodynamics throughout his career, and has also been graciously involved in supporting the *Journal of the Serbian Chemical Society*.

Being a member of Editorial Board of the *Journal of the Serbian Chemical Society* (more than 30 years) and publishing more than 40 scientific papers in this journal*, professor Djordjević provided an outstanding contribution to *Journal of the Serbian Chemical Society* development and reputation as well. It is therefore great pleasure to honour him in this tribute, on the celebration of his 80th birthday.

We join in wishing him well in the future and thanking him for all the work and the high standards he set for all of us.

Mirjana Kiječćanin
Ivona Radović
Slobodan Šerbanović

*The paper JSCS–5048 in this issue is dedicated to Professor Djordjević on the occasion of his jubilee.