

Excess Molar Volume of Binary Systems Containing Mesitylene

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This paper presents a review of density measurements for binary systems containing 1,3,5-trimethylbenzene (mesitylene) with a variety of organic compounds at atmospheric pressure. Literature data of the binary systems were divided into nine basic groups by the type of contained organic compound with mesitylene. The excess molar volumes calculated from the experimental density values have been compared with literature data. Densities were measured by a few experimental methods, namely using a pycnometer, a dilatometer or a commercial apparatus. The overview of the experimental data and shape of the excess molar volume curve versus mole fraction is presented in this paper. The excess molar volumes were correlated by Redlich–Kister equation. The standard deviations for fitting of excess molar volume versus mole fraction are compared. Found literature data cover a huge temperature range from (288.15 to 343.15) K.

Key words: Mesitylene, 1,3,5-trimethylbenzene, comparison, density, excess molar volume

Introduction

The investigation of the physico-chemical behaviour of liquid systems, which includes also measurement of density and related excess properties, provides important and useful information focused on intermolecular interactions in liquids and their mixtures. Such volumetric data are significant both for formulating models and theories of solutions and testing the reliability of the existing methods for prediction of the system behaviour. It is obvious that compiling experimental data is valuable for industrial objectives as well as for theoretical and applied thermodynamics.

The aromatic compounds are used e.g. for extractions from refinery products in the petrochemical industry. For this reason, the systematic investigation of physical properties of pure liquids and liquid mixtures containing aromatic compounds and their dependence on composition and temperature as basic data is essential. Mesitylene is an important aromatic compound, because it plays a significant role in formation of urban ozone.¹ Moreover, mesitylene can be used in the soot model development for practical application to complex blended liquid fuels.² On the other hand, mesitylene is not only studied as an air pollutant but mesitylene can also be used as a solvent for nitration of biological samples³ and other syntheses^{4,5} or this compound has been used during the liquid–liquid equilibrium studying.⁶

This review represents a comparative study of excess molar volumes (V_m^E) at atmospheric pressure of binary systems containing aromatic compounds, namely mesitylene.

Significant concern about density measurements of binary mixtures containing mesitylene started in the seventies^{7,8} and has continued to the present day.^{9–11}

Experimental methods

The published V_m^E data of binary systems containing mesitylene^{7–43} have been determined using four experimental techniques (see Table 1) either for density measurements or directly for excess molar volume determination.

The first and the oldest experimental methods use a pycnometer; this method is described in ten papers. The most precise measurement using this method is reported by *Subach et al.*⁷ The pycnometer used had a volume 53 cm³ and reproducibility of density measurements agreed within $\pm 0.5 \cdot 10^{-4}$ g cm⁻³ and from an analysis of experimental uncertainties it can be concluded that the excess volume of mixing is determined with accuracy ± 0.009 cm³ mol⁻¹. However, the high precision is in contrast with the statement of other authors as will be discussed later. The worst experimental data are reported by *Absood et al.*,⁸ where a little pycnometer with volume of only 16 cm³ was used. The calculated excess molar volumes are in most cases lower than 0.20 cm³ mol⁻¹. However, it is obvious that $V_m^E - x$ curve is not smooth. Moreover, two experimental points are remote from the other data and the values of excess molar volumes are significantly higher, i.e. 1.11 cm³ mol⁻¹ and 0.60 cm³ mol⁻¹.

Dilatometry is the second experimental method, used in two papers.^{12,13} Data published by *Nath et al.*¹² are slightly smoother than data published by *Willis et al.*¹³ However, *Nath et al.* reported the second best accuracy of V_m^E measurement as ± 0.002 cm³ mol⁻¹.

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The third experimental method for studying binary systems containing mesitylene uses vibrating flow densimeter by *Suri et al.*¹⁴ The accuracy of this method is reported as $\pm 0.005 \text{ cm}^3 \text{ mol}^{-1}$.

The last experimental technique for density measurement uses commercial apparatuses such as density meter (abbreviated DMA) or density and sound velocity meter (abbreviated DSA). This method is nowadays used in most of the published papers. The precision of measurement is higher than with techniques described above. The differences between V_m^E will be discussed in detail below (the largest differences between published data were found for mesitylene + alcohol systems).

Discussion

The collected literature volumetric data^{7–43} of binary systems containing mesitylene are compared with each other and can be divided into nine basic groups of organic compounds as summarized in Table 1 and as discussed here.

Only density data were found in some papers and excess molar volume, V_m^E , had to be calculated from literature data as the difference between real mixture volume, $V_m^{\text{real,mix}}$, and ideal mixture volume, $V_m^{\text{ideal,mix}}$. It is calculated using experimental densities, ρ_i , of individual compounds,¹⁵

$$V_m^E = V_m^{\text{real,mix}} - V_m^{\text{ideal,mix}} = \left(\sum_{i=1}^N x_i M_i \right) / \rho - \sum_{i=1}^N (x_i M_i / \rho_i), \quad (1)$$

where x_i is mole fraction, M_i is molar mass of components, ρ is density of mixture, and N is number of components in a mixture.

All excess molar volumes were correlated by the Redlich–Kister type equation as follows¹⁵

$$V_m^E = x_1 x_2 \sum_{k=0}^n A_k (x_1 - x_2)^k, \quad (2)$$

where A_k are adjustable parameters. The number of parameters A_k (usually $n = 3$ or 5) is determined by the least squares method (see Table 2 with standard deviations for the fitting by Redlich–Kister equation).

Table 1 – Investigated binary systems containing mesitylene with organic compounds. Ref. denotes literature reference.

Tablica 1 – Istraživanja binarnih sustava koji sadrže mezitilen s organskim spojevima. Ref. označava literaturnu referenciju.

Compound Spoj	Published data Objavljeni podaci	Experimental technique Eksperimentalna metoda	T / K	Shape of V_m^E vs. x curve Oblik krivulje $V_m^E - x$	Ref.
<i>Alkanes and their derivatives</i> <i>Alkani i derivati</i>					
heptane heptan	x, ρ, V_m^E	10 cm ³ pycnometer piknometar 10 cm ³	303.15 – 323.15	convex konveksni	11
octane oktan	x, ρ, V_m^E	DMA 58	298.15 – 328.15	S-shape, ^a concave S-oblik, ^a konkavni	15
tetrachloromethane tetraklometan	x, V_m^E	53 cm ³ pycnometer piknometar 53 cm ³	300.15, 313.15	S-shape S-oblik	7
tetrachloromethane tetraklometan	x, V_m^E	DMA 4500	298.15		16
<i>Cycloalkanes</i> <i>Cikloalkani</i>					
cyclopentane, cyclohexane, methylcyclohexane, cyclooctane ciklopentan, cikloheksan, metilcikloheksan, ciklooktan	x, ρ, V_m^E	DSA-48	298.15, 313.15	concave konkavni	9
methylcyclohexane metilcikloheksan	x, ρ	DMA 4500	298.15 – 308.15	concave konkavni	17
<i>Aromatics and their derivatives</i> <i>Aromati i derivati</i>					
benzene benzen	x, V_m^E	53 cm ³ pycnometer piknometar 53 cm ³	300.15, 313.15	S-shape S-oblik	7
benzene benzen	x, ρ, V_m^E	DMA 58	298.15 – 328.15	concave konkavni	18

Compound Spoj	Published data Objavljeni podaci	Experimental technique Eksperimentalna metoda	T / K	Shape of V_m^E vs. x curve Oblik krivulje $V_m^E - x$	Ref.
1-chloronaphthalene 1-klornaftalen	x, ρ	15 cm ³ pycnometer piknometar 15 cm ³	298.15 – 308.15	convex konveksni	19
<i>Alcohols</i> <i>Alkoholi</i>					
methanol, ethanol, propan-1-ol, propan-2-ol metanol, etanol, propan-1-ol, propan-2-ol	x, V_m^E	DMA 601	298.15	concave konkavni	20
ethanol, propan-1-ol, propan-2-ol, butan-1-ol, pentan-1-ol, 3-methylbutan-1-ol etanol, propan-1-ol, propan-2-ol, butan-1-ol, pentan-1-ol, 3-metilbutan-1-ol	x, ρ	DMA 4500	298.15 – 308.15	concave konkavni	21
butan-1-ol, 2-methylpropan-1-ol, butan-2-ol, 2-methylpropan-2-ol butan-1-ol, 2-metilpropan-1-ol, butan-2-ol, 2-metilpropan-2-ol	x, V_m^E	DMA 4500	298.15	concave konkavni	22
decan-1-ol dekan-1-ol	x, ρ	DSA 5000	298.15, 308.15	S-shape S-oblik	10
<i>Ketones</i> <i>Ketoni</i>					
acetone aceton	x, V_m^E	dilatometry technique dilatometrijski	298.15, 308.15	concave konkavni	12
acetophenone acetofenon	x, ρ, V_m^E	DMA 58	298.15, 328.15	convex konveksni	23
cyclohexanone cikloheksanon	x, ρ	15 cm ³ pycnometer piknometar 15 cm ³	298.15 – 308.15	concave konkavni	24
<i>Carboxylic acids and their derivatives</i> <i>Karboksilne kiseline i derivati</i>					
propionic acid propanska kiselina	x, ρ, V_m^E	Anton Paar 60/602	313.15	concave konkavni	25
ethyl acetate etil-acetat	x, ρ, V_m^E	DMA 58	298.15	concave konkavni	26
propyl acetate, butyl acetate propil-acetat, butil-acetat	x, ρ, V_m^E	DMA 4500	298.15 – 313.15	concave konkavni	27
isopropyl acetate, isobutyl acetate izopropil-acetat, izobutil-acetat	x, V_m^E	DMA 4500	298.15 – 313.15	concave konkavni	28
vinyl acetate vinyl-acetat	x, ρ, V_m^E	DMA 58	298.15	concave konkavni	29
methyl acetoacetate metil-acetoacetat	x, ρ	10 cm ³ pycnometer piknometar 10 cm ³	298.15 – 308.15	concave konkavni	30
ethyl chloracetate etil-kloracetat	x, ρ	10 cm ³ pycnometer piknometar 10 cm ³	298.15 – 308.15	concave konkavni	31
methyl acrylate metil-akrilat	x, ρ, V_m^E	10 cm ³ pycnometer piknometar 10 cm ³	293.15 – 318.15	concave konkavni	32
γ -butyrolactone γ -butirolakton	x, ρ, V_m^E	DMA 4500	288.15 – 308.15	concave konkavni	33

Compound Spoj	Published data Objavljeni podaci	Experimental technique Eksperimentalna metoda	T / K	Shape of V_m^E vs. x curve Oblik krivulje $V_m^E - x$	Ref.
<i>Other oxygen compounds</i> <i>Drugi spojevi s kisikom</i>					
ethylene glycol monomethyl ether, ethylene glycol dimethyl ether etilen-glikol-monometil-eter, etilen-glikol-dimetil-eter	x, V_m^E	DMA 4500	298.15, 313.15	concave konkavni	34
dimethyl carbonate, diethyl carbonate dimetil-karbonat, dietil-karbonat	x, V_m^E	DMA 4500	298.15, 313.15	concave konkavni	35
anisole anisol	x, ρ, V_m^E	DMA 4500	288.15 – 303.15	concave konkavni	36
1,1-diethoxyethane, ^b 2,2-dimethoxypropane ^c 1,1-dietoksietan, ^b 2,2-dimetoksipropan ^c	x, V_m^E	DMA 4500	298.15 – 313.15	convex, ^b concave ^c konveksni, ^b konkavni ^c	37
1,4-dioxane 1,4-dioksan	x, ρ, V_m^E	10 cm ³ pycnometer piknometar 10 cm ³	288.15 – 318.15	concave konkavni	38
tetrahydrofurane tetrahidrofuran	x, V_m^E	DMA 4500	298.15	concave konkavni	16
<i>Nitrogen compounds</i> <i>Spojevi s dušikom</i>					
triethylamine trietilamin	x, V_m^E	flow densimeter protočni denzimetar	313.15	convex konveksni	14
acetonitrile acetonitril	x, ρ	16 cm ³ pycnometer piknometar 16 cm ³	303.15	concave konkavni	8
benzonitrile benzonitril	x, ρ, V_m^E	densimeter 02D, 03DCss denzimetar 02D, 03DCss	298.15, 308.15	convex konveksni	39
<i>N,N</i> -dimethylformamide, ^b hexamethylphosphortriamide ^c <i>N,N</i> -dimetilformamid, ^b heksametil-fosfotriamid ^c	x, V_m^E	continuous dilatometer kontinuirani dilatometar	298.15	convex, ^b concave ^c konveksni, ^b konkavni ^c	13
<i>N,N</i> -dimethylformamide <i>N,N</i> -dimetilformamid	x, V_m^E	densimeter Sodev 02D denzimetar Sodev 02D	298.15	convex konveksni	40
nitromethane, nitroethane, 2-nitropropane nitrometan, nitroetan, 2-nitropropan	x, ρ, V_m^E	capillary pycnometer kapilarni piknometar	293.15	concave konveksni	41
1,3-dimethyl-2-imidazolidinone 1,3-dimetil-2-imidazolidinon	x, V_m^E	DMA 601	298.15	convex konveksni	42
<i>N</i> -acetylmorpholine <i>N</i> -acetilmorfolin	x, ρ	DMA 60/602	293.15 – 343.15	convex konveksni	43
<i>Sulphur compounds</i> <i>Spojevi sa sumporom</i>					
dimethyl sulphoxide dimetil-sulfoksid	x, ρ	16 cm ³ pycnometer piknometar 16 cm ³	303.15	concave konkavni	8
dimethyl sulphoxide dimetil-sulfoksid	x, V_m^E	DMA 4500	298.15	concave konkavni	16

^a S-shaped excess molar volume curve at 298.15 K
S-oblik krivulje ekscenog molarnog obujma pri 298,15 K

^b Convex shape for excess molar volume curve
Konveksna krivulja ekscenog molarnog obujma

^c Concave shape for excess molar volume curve
Konkavna krivulja ekscenog molarnog obujma

Table 2 – Standard deviations σ of the Redlich–Kister equation. Ref. denotes literature reference.Tablica 2 – Standardna devijacija, σ , Redlich-Kisterove jednačbe. Ref. označava literaturnu referenciju.

Compound in the mixture with mesitylene Spoj u smjesi s mezitilenom	Ref.	T / K										
		288.15	293.15	298.15	300.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15
		$\sigma / 10^{-2} \text{ cm}^3 \text{ mol}^{-1}$										
<i>Alkanes and their derivatives</i> <i>Alkani i derivati</i>												
heptane heptan	11					0.75	1.35	1.35	1.54	1.35		
octane oktan	15		0.10				0.14		0.13		0.12	
tetrachloromethane tetraklormetan	7				6.17			6.17				
tetrachloromethane tetraklormetan	16		0.44									
<i>Cycloalkanes</i> <i>Cikloalkani</i>												
cyclopentane ciklopentan	9		1.00					0.60				
cyclohexane cikloheksan	9		1.20					0.80				
methylcyclohexane metilcikloheksan	9		0.50					0.70				
cyclooctane ciklooktan	9		0.50					0.40				
methylcyclohexane metilcikloheksan	17		0.90		0.80	0.90						
<i>Aromatics and their derivatives</i> <i>Aromati i derivati</i>												
benzene benzen	7				3.84			2.14				
benzene benzen	18		0.14				0.12		0.11		0.12	
1-chloronaphthalene 1-klornaftalen	19		2.30		2.90	8.70						
<i>Alcohols</i> <i>Alkoholi</i>												
methanol metanol	20		0.35									
ethanol etanol	20		0.38									
propan-1-ol propan-1-ol	20		0.40									
propan-2-ol propan-2-ol	21		0.50									
ethanol etanol	21		1.42		1.71	1.42						
propan-1-ol propan-1-ol	21		3.50		3.61	3.55						
propan-2-ol propan-2-ol	21		1.69		1.75	1.89						

Compound in the mixture with mesitylene Spoj u smjesi s mezitilenom	Ref.	T / K											
		288.15	293.15	298.15	300.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	343.15
		$\sigma / 10^{-2} \text{ cm}^3 \text{ mol}^{-1}$											
butan-1-ol butan-1-ol	21			5.89			5.54		5.39				
pentan-1-ol pentan-1-ol	21			7.17			16.48		15.38				
3-methylbutan-1-ol 3-metilbutan-1-ol	21			6.85			6.87		7.86				
butan-1-ol butan-1-ol	22			0.15									
2-methylpropan-1-ol 2-metilpropan-1-ol	22			0.33									
butan-2-ol butan-2-ol	22			0.33									
2-methylpropan-2-ol 2-metilpropan-2-ol	22			0.34									
decan-1-ol dekan-1-ol	10			0.30				0.30					
<i>Ketones</i> <i>Ketoni</i>													
acetone aceton	12			0.51				0.27					
acetophenone acetofenon	23			0.08						0.11			
cyclohexanone cikloheksanon	24			0.40			0.80	0.90					
<i>Carboxylic acids and their derivatives</i> <i>Karboksilne kiseline i derivati</i>													
propionic acid propanska kiselina	25								0.12				
ethyl acetate etil-acetat	26			0.67									
propyl acetate propil-acetat	27			0.13			0.41	0.22	0.46				
butyl acetate butil-acetat	27			0.17			0.13	0.06	0.18				
isopropyl acetate izopropil-acetat	28			0.14				0.11	0.11				
isobutyl acetate izobutil-acetat	28			0.09				0.18	0.15				
vinyl acetate vinyl-acetat	29			0.30									
methyl acetoacetate metil-acetoacetat	30			1.40			1.30	2.10					
ethyl chloracetate etil-kloracetat	31			3.60			5.80	3.50					
methyl acrylate metil-akrilat	32		0.12	0.14			0.16	0.18	0.16	0.15			
γ -butyrolactone γ -butirolakton	33	0.10	0.20	0.30			0.10	0.40					

Alkanes and their derivatives

Excess molar volumes of binary systems containing mesitylene with either heptane¹¹ or octane¹⁵ slightly depend on temperature. The deviations from the ideal volumetric behaviour are asymmetric and positive for the binary system containing octane while negative deviations occur for the binary system containing heptane (see Fig. 1). V_m^E for the system containing tetrachloromethane is S-shaped⁷ and decreases with temperature. In contrast to the data,⁷ literature data¹⁶ shows concave shape of excess molar volume versus concentration. The newer data¹⁶ are published 30 years after the previous one⁷ and it could be concluded that the rapid progress in precise density measurement is evident from these differences. The highest precision of newer data is also obvious from Table 2 where lower deviations after fitting by Redlich–Kister equation were obtained.

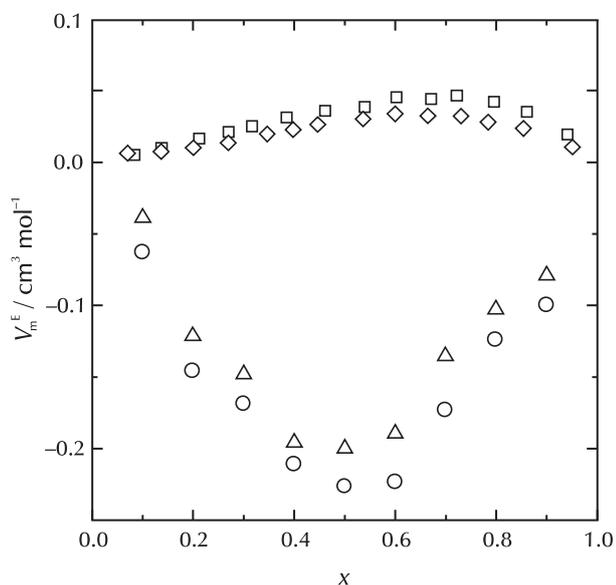


Fig. 1 – Excess molar volumes of binary systems (heptane + mesitylene)¹¹ and (octane + mesitylene);¹⁵ x denotes mole fraction of either heptane or octane.

Δ – heptane + mesitylene at 308 K; \circ – heptane + mesitylene at 318 K; \square – octane + mesitylene at 308 K; \diamond – octane + mesitylene at 318 K.

Slika 1 – Ekscesni molarni obujmi binarnih sustava (heptan + mezitilen)¹¹ i (oktan + mezitilen);¹⁵ x označava molni udjel heptana odnosno oktana.

Δ – heptan + mezitilen pri 308 K; \circ – heptan + mezitilen pri 318 K; \square – oktan + mezitilen pri 308 K; \diamond – oktan + mezitilen pri 318 K.

Cycloalkanes

The volumetric data for binary system containing mesitylene with methylcyclohexane are reported by two authors;^{9,17} the data are very close to each other within experimental errors. González *et al.*⁹ reported the comparison of binary systems containing mesitylene with cycloalkanes. It is interesting that V_m^E does not increase with the length of carbon chain. The highest V_m^E is for the binary system mesitylene with cyclohexane. Only a single substituent as methyl on cyclohexane causes a significant

V_m^E decrease. Very small influence of temperature is observed. The increase of V_m^E with temperature is found in systems containing cyclopentane or cyclohexane while the decrease is reported for binary systems containing methylcyclohexane or cyclooctane.

The lowest standard deviation after the fitting by Redlich–Kister equation was obtained for cyclooctane⁹ and the other standard deviations for systems containing mesitylene with a cycloalkane are comparable values.

Aromatics and their derivatives

Only two compounds from the aromatic homologous series are found in the literature, namely benzene^{7,18} and 1-chloronaphthalene.¹⁹ However, the data for the benzene + mesitylene system are in conflict. The data measured by Subach *et al.*⁷ yield S-shaped V_m^E vs. composition (x) curve with a small temperature influence on the curve, while the data published by Morávková *et al.*¹⁸ are positive in the whole concentration region without obvious temperature effect on the volumetric properties. This great difference in volumetric data could be caused by the different method of density measurement. Authors⁷ report density values with four decimal places, which was excellent precision in the past. However, nowadays requirements are to have density values determined more precisely, preferably with five decimal places.¹⁸ The higher precision is also obvious from the lowest deviations after fitting by Redlich–Kister equation (see Table 2).

The second studied system is mesitylene with 1-chloronaphthalene.¹⁹ The V_m^E calculated from published density data is negative but scattered, and only slightly depends on temperature.

Alcohols

Systems containing mesitylene with alcohols are reported by four authors.^{10,20–22} All V_m^E data are positive^{20–22} except for the binary system mesitylene with decan-1-ol.¹⁰ The positions of maxima on the $V_m^E - x$ curve are approximately in the same part of the concentration region except for methanol;²⁰ it is not surprising that the first member of a homologous series behaves atypically. The publication²⁰ deals with methanol, ethanol, propan-1-ol or propan-2-ol systems, which show increasing V_m^E with the length of carbon chain. A very significant increase is reported for the propan-2-ol system.

Another paper²¹ deals with ethanol, propan-1-ol, propan-2-ol, butan-1-ol, pentan-1-ol or 3-methylbutan-1-ol but density data provide rather scattered V_m^E data. Despite the authors' claim that data on mesitylene with ethanol, propan-1-ol, propan-2-ol, butan-1-ol, and 3-methylbutan-1-ol were not published before, it is true only for the latter alcohol, the other were published elsewhere earlier.^{20,22} The maximum on $V_m^E - x$ curve for the system mesitylene with propan-1-ol is higher by 1 $\text{cm}^3 \text{mol}^{-1}$ in comparison with the other source²¹ that is the least accurate data due to the highest deviation in Table 2. Moreover, the concentration dependence for the mesitylene + 3-methylbutan-1-ol system is not smooth although authors declare that density data were determined within $\pm 10^{-5} \text{ g cm}^{-3}$ and that published data were sup-

posedly correlated by Redlich–Kister equation achieving good agreement with experimental data. A magnitude of scatter of experimental V_m^E from correlated values is an indicator of poor quality of data; the worst V_m^E value was as low as $-6.5 \text{ cm}^3 \text{ mol}^{-1}$ for the mesitylene + butan-1-ol system at 308.15 K which is difficult to believe because excess molar volumes rarely exceed $1 \text{ cm}^3 \text{ mol}^{-1}$.^{7–43}

The paper²² reports data on systems containing butan-1-ol, 2-methylpropan-1-ol, butan-2-ol or 2-methylpropan-2-ol. The V_m^E are almost twice as high as for butan-1-ol or 2-methylpropan-1-ol in comparison with butan-2-ol or 2-methylpropan-2-ol.

Ketones

Three systems with ketones are reported in the literature^{12,23,24} (see Figure 2). However, it is impossible to compare ketone systems mutually because they are not from the same homologous series. The binary systems containing mesitylene with aliphatic ketone¹² and a ketone group on the cyclic alkane²⁴ show positive deviation on $V_m^E - x$ curve. Acetophenone²³ interacts with mesitylene, which results in negative excess molar volume. Temperature does not play a significant role in all systems containing ketones.

The lowest deviation after fitting by Redlich–Kister equation is for the literature data²³ while the other literature data^{12,24} are comparable.

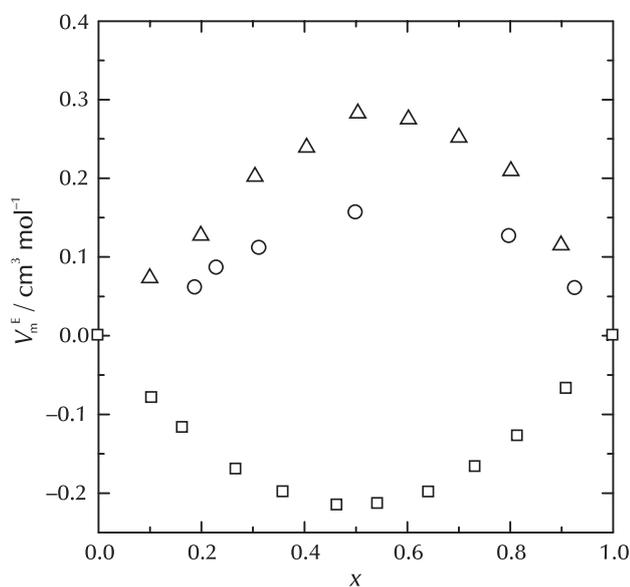


Fig. 2 – Excess molar volumes of binary systems (acetone + mesitylene),¹² (acetophenone + mesitylene),²³ and (cyclohexanone + mesitylene)²⁴ at 298 K; x denotes mole fraction of either acetone, acetophenone or cyclohexanone.

○ – acetone + mesitylene; □ – acetophenone + mesitylene; △ – cyclohexanone + mesitylene.

Slika 2 – Ekscesni molarni obujmi binarnih sustava (acetona + mezitilen),¹² (acetofenona + mezitilen)²³ i (cikloheksanona + mezitilen)²⁴, pri 298 K; x označava molni udjel acetona, acetofenona odnosno cikloheksanona.

○ – acetona + mezitilen; □ – acetofenona + mezitilen; △ – cikloheksanona + mezitilen.

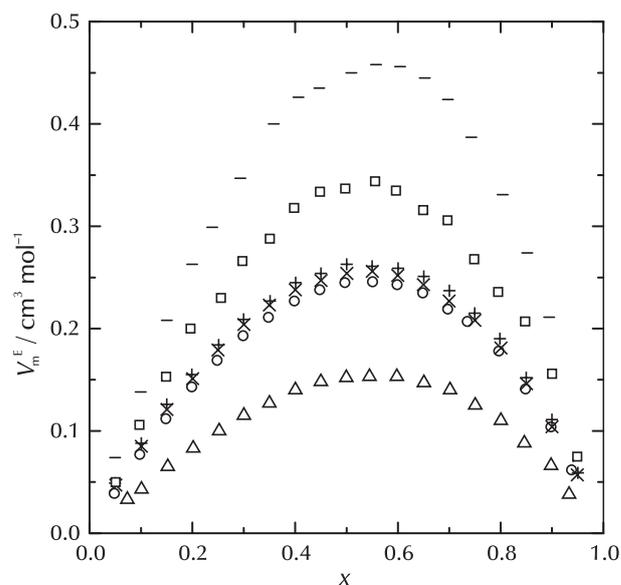


Fig. 3 – Excess molar volumes of binary systems (ethyl acetate + mesitylene),²⁶ (propyl acetate + mesitylene),²⁷ (butyl acetate + mesitylene),²⁷ (isopropyl acetate + mesitylene),²⁸ (isobutyl acetate + mesitylene),²⁸ (vinyl acetate + mesitylene)²⁹ at 298 K; x denotes mole fraction of acetate ester.

□ – ethyl acetate + mesitylene; ○ – propyl acetate + mesitylene; △ – butyl acetate + mesitylene; + – isopropyl acetate + mesitylene; × – isobutyl acetate + mesitylene; — – vinyl acetate + mesitylene.

Slika 3 – Ekscesni molarni obujmi binarnih sustava (etil-acetat/mezitilen),²⁶ (propil-acetat/mezitilen),²⁷ (butil-acetat/mezitilen),²⁷ (izopropil-acetat/mezitilen),²⁸ (izobutil-acetat/mezitilen)²⁸ i (vinil-acetat/mezitilen),²⁹ pri 298 K; x označava molni udjel acetatnog estera.

□ – etil-acetat + mezitilen; ○ – propil-acetat + mezitilen; △ – butil-acetat + mezitilen; + – izopropil-acetat + mezitilen; × – izobutil-acetat + mezitilen; — – vinil-acetat + mezitilen.

Carboxylic acids and their derivatives

All the found literature data on binary systems containing mesitylene with either fatty acids or their derivatives show positive deviations from the ideal volumetric behavior.^{25–33} It is possible to compare systems with acetates^{26–29} using compiled literature data (see Fig. 3). It is obvious that the V_m^E is decreasing in the homologous series from ethyl acetate to butyl acetate. The system with vinyl acetate exhibits the highest values. It is interesting that data for systems containing isopropyl acetate or isobutyl acetate are very close and similar to the system containing butyl acetate. In this group, V_m^E increases with temperature for all systems except for these two similar systems containing isopropyl or isobutyl acetate.

The highest deviation after fitting by Redlich–Kister equation is for the literature data³¹ while the other literature data^{25–30,32,33} are comparable.

Other oxygen compounds

Volumetric data are reported in the literature in five papers.^{16,34–38} The greatest V_m^E was found for binary system containing dimethyl carbonate³⁵ (approximately twice as high as for diethyl carbonate³⁵). The smallest V_m^E is for the system containing tetrahydrofurane.¹⁶

Excess molar volumes increase with temperature for mesitylene systems with dimethyl carbonate,³⁵ diethyl carbonate,³⁵ and 1,4-dioxane³⁸ while decrease for systems with anisole,³⁶ 1,1-diethoxyethane,³⁷ and 2,2-dimethoxypropane.³⁷ However, temperature does not have a great influence on V_m^E in these systems. It is worth mentioning that the data are completely different for 1,1-diethoxyethane (convex curve) and 2,2-dimethoxypropane (concave curve).

The excess molar volume is approximately twice higher for the system containing ethylene glycol monomethyl ether³⁴ in comparison to the system containing ethylene glycol dimethyl ether.³⁴ The excess molar volume increase with temperature for the system with ethylene glycol monomethyl ether³⁴ while the excess molar volume are almost independent of temperature for the system containing ethylene glycol dimethyl ether.³⁴

All found data were successfully correlated by Redlich–Kister equation.^{16,34–38}

Nitrogen compounds

Nitrogen derivatives with mesitylene are studied in a number of publications.^{8,13,14,39–43} Nevertheless, V_m^E data are very scattered around correlated curve for acetonitrile.⁸ Triethylamine system has the lowest V_m^E of all the nitrogen derivatives systems.¹⁴ Excess molar volumes are increasing with temperature for benzonitrile³⁹ while they decrease for system with *N*-acetylmorpholine.⁴³ Other volumetric data are published for one temperature only. The system with *N,N*-dimethylformamide was published by two authors^{13,40} and data are in good mutual agreement. Pronounced deviations from ideal behaviour were found for systems with triethylamine,¹⁴ benzonitrile,³⁹ nitromethane,⁴¹ nitroethane,⁴¹ 2-nitropropane,⁴¹ 1,3-dimethyl-2-imidazolidinone,⁴² and hexamethylphosphotriamide.¹³ Nitrogen derivatives are the only one family where V_m^E are often negative due to associations in the liquid mixture.

The highest deviation after fitting by Redlich–Kister equation is for the literature data⁸ and data⁴³ at 293.15 K while the others literature data^{13,14,39–42} are comparable.

Sulphur compounds

All published data are measured at one temperature only.^{8,16} Dimethyl sulphoxide is reported by two authors^{8,16} and the data published later¹⁶ give smoother curve than older ones.⁸ Excess molar volumes are positive in the whole concentration region. The fitting by Redlich–Kister equation of data¹⁶ is significantly better than for data.⁸

Conclusions

The excess molar volumes of binary systems containing mesitylene are available in the literature in many publications.^{7–43} Literature data are frequently in qualitative agreement, but they differ quantitatively. Moreover, V_m^E calculated from density data occasionally differ in comparison with the data from publications where only densities are reported. Accuracies of density values are usually published with five decimals. Then, the excess molar

volumes calculated from density data are reported with three decimals only. Concave shape (positive values) of $V_m^E - x$ curve occurs more frequently than convex shape (negative values); concave shape of the curve indicates that the liquid system does not exhibit more organised structure in comparison to the pure compounds before mixing. Convex curves are typical only for nitrogen-containing compounds with mesitylene which is a consequence of associate formation in liquid mixtures.

The largest differences between published volumetric data are found for the mesitylene + alcohol systems. This is due to difficulties during measurements with highly hygroscopic alcohols. The increasing amount of water in an alcohol changes the density considerably and thus the excess molar volume. It is not possible to compare all collected data because measurements are rarely at the same temperature or there are no available data for at least three members of a homologous series.

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List of symbols and abbreviations

Popis simbola i kratica

A_k	– parameter – parametar
M	– molar mass, g mol ⁻¹ – molarna masa, g mol ⁻¹
N	– number of components – broj sastojaka smjese
n	– number of parameters A – broj parametara A
V_m^E	– excess molar volume, cm ³ mol ⁻¹ – ekscresni molarni obujam, cm ³ mol ⁻¹
$V_m^{\text{ideal,mix}}$	– ideal mixture molar volume, cm ³ mol ⁻¹ – molarni obujam idealne smjese, cm ³ mol ⁻¹
$V_m^{\text{real,mix}}$	– real mixture molar volume, cm ³ mol ⁻¹ – molarni stvarni obujam smjese, cm ³ mol ⁻¹
x	– mole fraction, 1 – molni udjel, 1
T	– temperature, K – temperatura, K
ρ	– mixture density, g cm ⁻³ – gustoća smjese, g cm ⁻³
ρ_i	– mixture component density, g cm ⁻³ – gustoća sastojka smjese, g cm ⁻³
σ	– standard deviation of excess molar volume, cm ³ mol ⁻¹ – standardna devijacija ekscresnog molarnog volumena, cm ³ mol ⁻¹
DMA	– density meter – mjerač gustoće
DSA	– density and sound velocity meter – mjerač gustoće i brzine zvuka

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SAŽETAK

Ekscesni molarni obujam binarnih sustava koji sadrže mezitilen

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U ovom je radu dan pregled izmjerenih gustoća binarnih sustava koji sadrže 1,3,5-trimetilbenzen (mezitilen) s različitim organskim spojevima pri atmosferskom tlaku. Literaturni podaci o binarnim sustavima razvrstani su u devet osnovnih skupina prema vrsti organskog spoja u smjesi s mezitilenom. Ekscesni molarni obujmi izračunati su iz eksperimentalno određenih vrijednosti gustoće i uspoređeni s literaturnim podacima. Gustoće su izmjerene pomoću nekoliko eksperimentalnih metoda: piknometrom, dilatometrom ili nekom od komercijalnih aparatura. Prikazani su eksperimentalni podaci i oblik krivulje ekscesnog molarnog obujma u ovisnosti o molnom udjelu. Procijenjene vrijednosti ekscesnih molarnih obujama u ovisnosti o molnom udjelu korelirane su Redlich-Kisterovom jednadžbom, a prikladnost odabrane funkcije izražena je usporedbom standardnih devijacija. Literaturni podaci pokrivaju široko temperaturno područje (od 288,15 do 343,15 K).

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