DENSITIES, EXCESS VOLUMES, AND PARTIAL MOLAR VOLUMES OF BUTYL METHACRYLATE SOLUTIONS IN SOME ORGANIC SOLVENTS

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Abstract. Densities and excess volumes of the binary systems of butyl methacrylate with acetonitrile; acetic acid, benzene, 1,2-dichlorethane, and hexane have been measured as a function of composition at 293 K and atmospheric pressure by pycnometric method. The measured excess volumes were correlated by polynomials. The partial molar volumes were calculated by experimental data.

Key words: solutions, densities, excess volumes, partial molar volumes, butyl methacrylate.

1. Introduction

The mixing of compounds with different properties gives rise to solutions that generally do not behave ideally. The deviation from ideality is expressed by many thermodynamic variables, particularly by excess properties. Excess thermodynamic properties of mixtures correspond to the difference between the actual property and the property when the system behaves ideally. Thus, they are useful in the study of molecular interactions and arrangements. In particular, they reflect the different interactions that take place between solute-solute, solute-solvent, and solvent-solvent species. The geometric configuration of the molecules, which form the solution, also has a significant effect on the value of the excess molar volume. For example, a positive value of the excess volume represents an intercalation packing effect, that is, an expansion of the mixture. And the negative value is a consequence of formation of associates in solution and denser packaging of heterogeneous molecules compared to homogeneous ones.

Methacrylic acid and its esters are essential reagents for existing and promising technologies for the production of different polymers with a wide range of properties. Butyl methacrylate (BMA) is one of the most widely used esters of methacrylic acid in chemical technology. Acetonitrile, benzene, hexane, 1,2-dichloroethane, and acetic acid are solvents that are frequently used in industry for polymerization and other chemical processes.

Excess properties of solutions of methacrylic acid and its esters have been studied in numerous works. George *et al.*[1] determined the heats of mixing and excess volumes of mixtures for liquid binary mixtures of methyl methacrylate with benzene, toluene, *n*-xylene, cyclohexane, and ethers. The qualitative analysis of both excess molar functions was done taking into consideration the molecular size of ethers and the nature of the hydrocarbon. In the work of Peralta *et al.*,[2] the density and excess molar volume of tetrahydrofuran binary systems with ethenyl ethanoate (vinyl acetate), methacrylic acid, butyl methacrylate, and allyl methacrylate were determined. Wisniak *et al.*[3] determined the densities of cyclohexane binary systems with allyl methacrylate, butyl methacrylate, methacrylic acid, and vinyl acetate, which were also described by the Legendre polynomial. In articles,[4,5] the same authors determined the densities of binary systems of toluene and benzene with butyl methacrylate, allyl methacrylate, methacrylic acid, and vinyl acetate. The densities of three-component dimethylcarbon systems with butyl methacrylate and allyl methacrylate are described in Ref [6]. These studies show great scientific interest in the surplus properties of systems containing acrylic monomers.

However, the publications on the determination of the excess volume of solutions of the butyl ester of methacrylic acid in acetonitrile, hexane; 1,2-dichloroethane and acetic acid are absent in the literature available to us, so the study of these systems is relevant, both in terms of theoretical science and chemical technology.

This work is part of our research on the characteristics of intermolecular interactions between organic solvents and such commercially important monomers as acrylic acids and their esters.[7-14] These studies are necessary to determine the effect of the components chemical structure on the thermodynamic properties of solutions containing acids and esters of the acrylic series.

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2. Experimental

2.1. Materials

The commercial-grade raw materials were supplied by MERCK (Germany). The chemicals received were further purified through repeated evaporation and acetic acid additionally by recrystallization. The chemicals were then selected based on their unique densities, as well as the refractive index. The contamination was kept below 0.2 wt. %, as verified through chromatography. The densities (ρ) and the refractive index (n_D^{20}) of the purified reagents at 293 K were determined, and their values are reported in Table 1 along with the values given in the literature. Table 1 also shows the values of molecular weight (M), dipole moment (μ), and geometric size (L) of the studied substances, which were calculated by the Hyper Chem program at the extreme points of the molecule.

Table 1. Physico-chemical properties of Pure Components at 293 K

Component	M, g/mol	μ, D	L, nm	n_D^{20}		ρ, g/cm^3		Purity, wt. %
				literature	measured	literature	measured	
Acetonitrile	41.0524	3.94	0.319	1.3437[15]	1.3441	0.7828[15]	0.7821	99,8
Acetic acid	60.0324	1.70	0.401	1.3715[16]	1.3716	1.0492[16]	1.0493	99.9
Benzene	78.1134	0.00	0.499	1.5011[15]	1.5011	0.8790[15]	0.8787	99.9
1,2-Dichloroethane	98.9596	1.27	0.438	1.4448[17]	1.4445	1.2530[17]	1.2538	99.8
Hexane	86.1766	0.00	0.820	1.3750[15]	1.3751	0.6594[15]	0.6593	99.9
Butyl methacrylate	142.1974	2.33	1.043	1.4241[17]	1.4240	0.8948[17]	0.8941	99.9

2.2. Density Measurements

Before the experiment, all liquids were boiled or heated to remove dissolved air. Solutions of different compositions were prepared by weight in a 15 cm^3 rubber-stopper vial to prevent evaporation, using a balance accuracy of $\pm 5 \cdot 10^{-5}$ g. To minimize the errors in composition, the heavier component (butyl methacrylate) was loaded first. To prevent contact between the samples and the rubber stopper, each component was added with a syringe; the mixtures were agitated gently, and the samples for density measurements were also withdrawn with a syringe.

The densities of pure components and mixture were measured by pycnometer with volume of 10 cm^3, which was precalibrated with double-distilled water at the temperature of 277 K. The pycnometer was placed vertically in an electronically controlled thermostat maintained at a measuring temperature (± 0.1 K). Solutions in the pycnometer were poured above the mark, and their temperature was measured with a digital thermometer inside the pycnometer, the accuracy of temperature measurement was ± 0.1 K. At the time of reaching the required temperature, excess fluid was removed using a syringe. The pycnometers were then wiped to remove water and weighed.

3. Results and Discussion

The density measurements were performed for each binary system over the full concentration range.

The excess volumes V_M^E of the solutions of mole fraction of solvent (x_1) were calculated from the densities of the pure liquids and their mixtures according to the following equation:[17]

$$V_M^E = [x_1 M_1 + x_2 M_2]/\rho - [x_1 M_1/\rho_1 + x_2 M_2/\rho_2] \quad (1)$$

where ρ, ρ_1, and ρ_2 are the densities of the solution and pure components 1 and 2, respectively; M_1 and M_2 are the molar masses of the pure components.

The corresponding values of densities and excess volumes, calculated by Equation (1), are reported in Table 2 and their dependence on concentration is shown in Fig. 1.

The concentration dependence of the excess volume, for the convenience of calculations, was approximated by polynomials of the form:

$$V_M^E = a_0 + a_1 x_1 + a_2 x_1^2 + a_3 x_1^3 + a_4 x_1^4 \quad (2)$$

The obtained polynomials make it possible to calculate the values of excess molar volumes of the studied systems at any concentration.

To estimate the deviation of the values calculated by the polynomial from the experimental ones, the standard value of the variance was calculated. Standard dispersion Sn was calculated as the average difference between the experimental values and the values calculated by the polynomial:

$$Sn = [\Sigma(V_{i, \exp}^E - V_{i, calc}^E)^2/(N-1)]^{1/2} \quad (3)$$

The coefficients of polynomials and pertinent values of dispersion Sn appear in Table 3 and are necessarily consistent. The obtained values of the standard dispersion are commensurate with the error of the experiment, which indicates the absence of random errors in measuring the density of solutions.

Table 2. Densities and Excess Volumes for all systems at 293 K

x_1	ρ, g/cm^3	V_M^E, cm^3/mol	x_1	ρ, g/cm^3	V_M^E, cm^3/mol
	Acetonitrile – BMA			1,2-Dichloroethane – BMA	
0.0000	0.8941	0.0000	0.0000	0.8941	0.0000
0.2034	0.8862	-0.1170	0.2078	0.9302	0.8280
0.3420	0.8789	-0.1694	0.3407	0.9601	1.0215
0.5081	0.8672	-0.1902	0.5006	1.0045	1.0795
0.6073	0.8579	-0.1800	0.7000	1.0770	0.9687
0.8031	0.8311	-0.1142	0.7986	1.1231	0.8061
1.0000	0.7821	0.0000	1.0000	1.2538	0.0000
	Acetic acid – BMA			Hexane – BMA	
0.0000	0.8941	0.0000	0.0000	0.8941	0.0000
0.1956	0.9055	0.1665	0.2280	0.8483	-0.0090
0.3245	0.9147	0.3126	0.2894	0.8355	-0.0419
0.5111	0.9326	0.4491	0.4618	0.7978	-0.1470
0.7021	0.9605	0.4379	0.5140	0.7859	-0.1774
0.8323	0.9895	0.3063	0.6021	0.7651	-0.2109
1.0000	1.0493	0.0000	0.7013	0.7406	-0.2128
	Benzene – BMA		0.7923	0.7171	-0.1844
0.0000	0.8941	0.0000	1.0000	0.6593	0.0000
0.1113	0.8928	0.0496			
0.3054	0.8903	0.1179			
0.5035	0.8875	0.1434			
0.7082	0.8843	0.1155			
0.9010	0.8808	0.0467			
1.0000	0.8787	0.0000			

Table 3. Coefficients of polynomials of concentrations dependencies excess volumes at 293 K

System	a_0	a_1	a_2	a_3	a_4	Sn, cm^3/mol
Acetonitrile – BMA	0.0001	-0.6553	0.2289	0.8550	-0.4287	0.0003
Acetic acid – BMA	-0.0002	0.4357	3.1498	-5.3449	1.7595	0.0019
Benzene – BMA	-0.0001	0.4646	-0.0479	-0.8130	0.3966	0.0003
1,2-Dichloroethane – BMA	-0.0002	6.3831	-14.5278	16.1817	-8.0367	0.0011
Hexane – BMA	-0.0002	0.6566	-4.0508	4.8333	-1.4386	0.0019
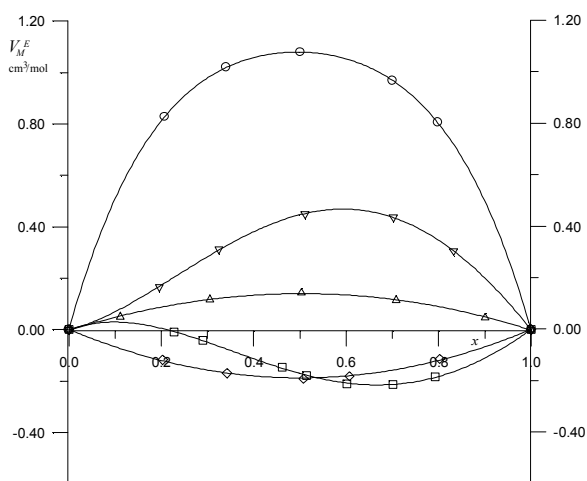
Fig. 1. Excess volumes of investigated solutions at 293 K (◊-Acetonitrile – BMA; Δ -Benzene – BMA; □-Hexane – BMA; ○-1,2-Dichloroethane – BMA; ∇-Acetic acid – BMA)

The determined values of excess molar volumes allow to calculate the molar volumes (V_M) for the studied systems:

$$V_M=(x_1 M_1/\rho_1+x_2 M_2/\rho_2) + V_M^E \qquad (4)$$

Partial molar volumes of the components were calculated from the molar volumes of the solutions. Partial molar volumes are an important thermodynamic parameter because they demonstrate how the addition of an infinitesimal amount of each component affects the properties of the solution. The determined values of excess molar volumes made it possible to calculate the partial molar volumes of the components for the studied systems. Partial molar volumes of components ($\overline{V}_{M1}$, $\overline{V}_{M2}$) of the investigated systems are calculated using the following dependencies:[18]

$$\overline{V}_{M1} = V_{M1} + x_2 \left(\frac{dV_M}{dx_1}\right) \qquad (5)$$

$$\overline{V}_{M2} = V_{M2} + x_1 \left(\frac{dV_M}{dx_1}\right) \qquad (6)$$

The values of solutions molar volume and the values of partial molar volumes of the investigated systems components, calculated by Equations (5) and (6), are shown in Table 4.

The measured values of excess volumes for systems with 1,2-dichloroethane, benzene, and acetic acid are positive for all concentrations; for the acetonitrile system are negative for all concentrations. For solutions of hexane with butyl methacrylate, the excess volume assumes positive values in the concentration range from 0 to 25 mol % and negative values at higher concentration values. For the convenience of comparing the excess molar volumes of the studied systems, we compare their values for equimolar solutions, calculated by polynomials (2) (Table 5).

As the value of excess volumes for equimolar solutions increases, the investigated solvents are arranged in the following order:

Acetonitrile < Hexane < Benzene < < Acetic acid < 1,2-Dichloroethane

Table 4. Molar Volumes and Partial Molar Volumes of components for all systems at 293 K

x_1	V_M, cm³/mol	$\overline{V}_{M1}$, cm³/mol	$\overline{V}_{M2}$, cm³/mol	x_1	V_M, cm³/mol	$\overline{V}_{M1}$, cm³/mol	$\overline{V}_{M2}$, cm³/mol
	Acetonitrile – BMA				1,2-Dichlorethane – BMA		
0.00	159.04	51.83	159.04	0.00	159.04	85.31	159.04
0.10	148.32	51.90	159.04	0.10	151.98	82.97	159.16
0.20	137.61	51.99	159.02	0.20	144.61	81.55	159.40
0.30	126.92	52.10	158.99	0.30	137.01	80.72	159.67
0.40	116.24	52.20	158.93	0.40	129.22	80.27	159.91
0.50	105.57	52.30	158.85	0.50	121.28	79.99	160.13
0.60	94.93	52.38	158.76	0.60	113.19	79.77	160.40
0.70	84.30	52.43	158.65	0.70	104.95	79.54	160.85
0.80	73.68	52.47	158.55	0.80	96.53	79.28	161.64
0.90	63.08	52.49	158.46	0.90	87.88	79.04	163.03
1.00	52.49	52.49	158.39	1.00	78.93	78.93	165.31
	Acetic acid – BMA				Hexane – BMA		
0.00	159.04	57.65	159.04	0.00	159.04	131.37	159.04
0.10	148.93	58.10	159.02	0.10	156.24	130.73	159.07
0.20	138.85	58.28	158.99	0.20	153.38	130.37	159.13
0.30	128.77	58.25	159.00	0.30	150.49	130.22	159.18
0.40	118.69	58.10	159.08	0.40	147.59	130.22	159.18
0.50	108.57	57.89	159.25	0.50	144.70	130.30	159.11
0.60	98.41	57.68	159.51	0.60	141.84	130.41	158.97
0.70	88.20	57.48	159.86	0.70	139.00	130.53	158.74
0.80	77.92	57.33	160.28	0.80	136.19	130.63	158.45
0.90	67.59	57.25	160.74	0.90	133.43	130.69	158.11
1.00	57.21	57.21	161.18	1.00	130.71	130.71	157.74
	Benzene – BMA						
0.00	159.04	89.36	159.04				
0.10	152.07	89.33	159.04				
0.20	145.10	89.27	159.05				
0.30	138.11	89.20	159.08				
0.40	131.12	89.12	159.12				
0.50	124.11	89.05	159.18				
0.60	117.09	88.99	159.25				
0.70	110.06	88.94	159.34				
0.80	103.02	88.92	159.42				
0.90	95.96	88.90	159.48				
1.00	88.90	88.90	159.52				

Table 5. Excess molar volumes for equimolar solutions

System	V_M^E, cm³/mol
Acetonitrile – BMA	-0.190
Acetic acid – BMA	0.447
Benzene – BMA	0.143
1,2-Dichloroethane – BMA	1.080
Hexane – BMA	-0.170

The concentration-dependent form of the excess volume for the systems containing acetonitrile, benzene, and 1,2-dichloroethane is a symmetric parabola with a maximum or minimum corresponding to the equimolar composition of the solution. For solutions with acetic acid, the maxima on the curves correspond to a solvent concentration of 60 mol. %. For the hexane – BMA system, the maximum value corresponds to a concentration of 10 mol. %, and the minimum – a concentration of 66 mol. %. The maxima and minima on the curves of the excess molar volume versus concentration correspond to the possible associations of heterogeneous molecules in the studied systems.

For the studied polar solvents, the value of the excess molar volume of equimolar butyl methacrylate solutions increases in the following raw:

Acetonitrile < Acetic acid < 1,2-Dichlorethane

In this series of solvents, the magnitude of the dipole moment of their molecules decreases. That is, the increase in the dipole moment of solvent molecules makes the solutions more compact, which indicates the determining influence of orientational dipole interactions on the properties of their solutions.
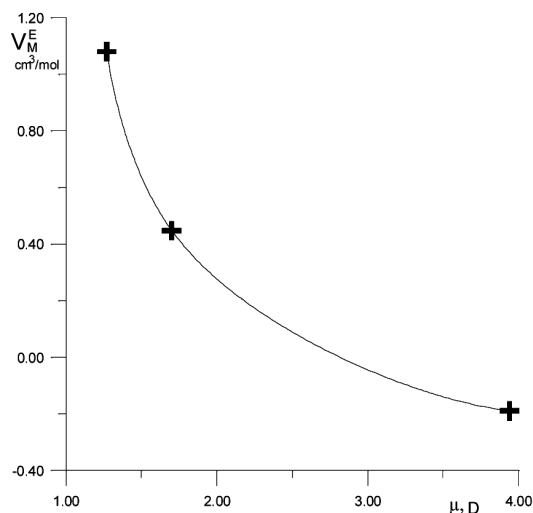
Fig. 2. Dependence of values of excess molar volume of equimolar butyl methacrylate solutions on dipole moment of investigated solvents

The dependence of the excess molar volume of equimolar solutions of acetonitrile, acetic acid, and 1,2-dichloroethane on the dipole moment of the solvents is shown in Fig. 2.

If we analyze the dependence of the excess molar volume on the size of the solvent molecules, the closer the size of the solvent molecules to the size of the butyl methacrylate molecules, the smaller the value of the excess volume and the denser the packing of molecules in solution.
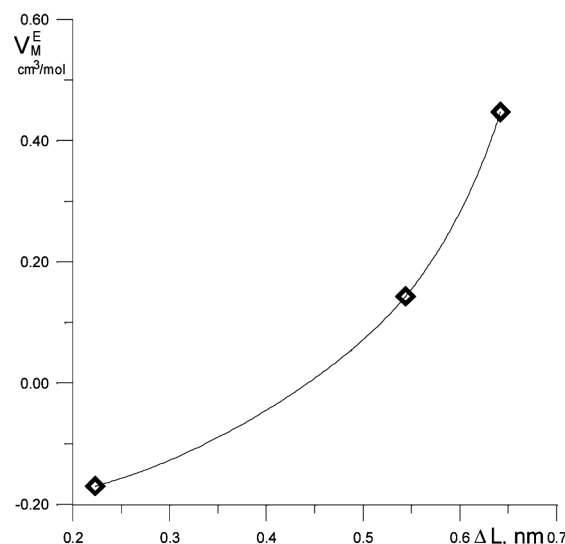
Fig. 3. Dependence of the values of the excess molar volume of equimolar solutions on the difference in the size of the molecules of butyl methacrylate and the corresponding solvent

The exceptions are acetonitrile dipole moment and, accordingly, its polarity, much higher than other studied solvents, and 1,2-dichloroethane, the molecule of which is geometrically "uncomfortable" for BMA due to the presence of two chlorine atoms with a negative charge. Fig. 3 shows the dependence of the excess molar volume of equimolar solutions of butyl methacrylate in benzene, hexane, and acetic acid on the size of the solvent molecules.

4. Conclusions

The magnitude and sign of the excess volume reflect the types of interactions that take place in the mixture. The investigated ester, as well as the corresponding acid, are polar substances with large values of dipole moments of molecules. However, the value of the excess molar volume of solutions is influenced not only by the polarity of the solvents but also by the corresponding geometric configuration and dimensions of their molecules.

Excess molar volume of acetonitrile solutions takes negative values throughout the studied concentration range, indicating a more compact packaging of molecules in solutions compared to pure substances, which may be due to the strong orientation dipole interaction between the components of the solution.

Solutions with benzene, 1,2-dichloroethane, and acetic acid have positive values of excess molar volume, which indicates that the resulting systems are less compact structures compared to pure substances.

Solutions of hexane with butyl methacrylate have a variable nature of the concentration dependence of the excess molar volume, which is a consequence of the possible formation of associations between dissimilar molecules in this solution at hexane concentrations above 22 mol. %.

The fact that the maximum and minimum values of excess free volume for solutions of acetonitrile, benzene, and hexane are quite small values ($V_M < 0.21$ cm³/mol), and solutions of acetic acid and 1,2-dichloroethane are much larger (0.45 cm³/mol and 1.08 cm³/mol, respectively) is also important. This indicates a significant deviation of the properties of these solutions from ideal one.

References

[1] George, J.; Sastry, N.V.; Prasad, D.H.L. Excess Molar Enthalpies and Excess Molar Volumes of Methyl Methacrylate + Benzene, + Toluene, + p-Xylene, + Cyclohexane and + Aliphatic Diethers (Diethyl, Diisopropyl and Dibutyl). *Fluid Phase Equilib.* **2003**, *214*, 39-51. https://doi.org/10.1016/S0378-3812(03)00312-1

[2] Peralta, R.D.; Infante, R.; Cortez, G.; Wisniak, J. Density and other Thermodynamic Properties of the Binary Systems of tetrahydrofuran + Ethenyl Ethanoate, Methacrylic Acid, Butyl Methacrylate, and Allyl Methacrylate at 298.15 K. *Phys. Chem. Liquids* **2005**, *43*, 249-259. https://doi.org/10.1080/00319100500061274

[3] Wisniak, J.; Peralta, R.D.; Infante, R.; Cortez, G.; López, R.G. Densities, Isobaric Thermal Compressibilities and Derived Thermodynamic Properties of the Binary Systems of Cyclohexane with allyl Methacrylate, Butyl Methacrylate, Methacrylic Acid, and Vinyl Acetate at T = (298.15 and 308.15) K. *Thermochim. Acta* **2005**, *437*, 1-6. https://doi.org/10.1016/j.tca.2005.06.007

[4] Wisniak, J.; Cortez, G.; Peralta, R.D.; Infante, R.; Elizalde, L.E. Some Thermodynamic Properties of the Binary Systems of Toluene with Butyl Methacrylate, Allyl Methacrylate, Methacrylic Acid and Vinyl Acetate at 20, 30 and 40°C. *J. Solution Chem.* **2007**, *36*, 997-1022. https://doi.org/10.1007/s10953-007-9165-y

[5] Peralta, R.D.; Infante, R.; Cortez, G.; Wisniak, J. Densities and Derived Thermodynamic Properties of the Binary Systems of Benzene with Butyl Methacrylate, Allyl Methacrylate, Methacrylic Acid, and Vinyl Acetate at 298.15 K. *Chem. Eng. Commun.* **2007**, *194*, 635-647. https://doi.org/10.1080/00986440600992701

[6] Wisniak, J.; Cortez, G.; Peralta, R.D.; Infante, R.; Elizalde, L.E.; Amaro, T.A.; García, O.; Soto, H. Volumetric Properties of the Ternary System Dimethyl Carbonate + Butyl Methacrylate + Allyl Methacrylate and Its Binary Butyl Methacrylate + Allyl Methacrylate at 293.15 K and p=101.325 kPa. *J Solut. Chem.* **2012,** 41, 1631-1648. https://doi.org/10.1007/s10953-012-9892-6

[7] Sergeev, V.V.; Dibrivnyi, V.N.; Van-Chin-Syan, Yu.Ya. Heat of Mixing of Acrylic Acid with Certain Organic Solvents. *Russ. J. Appl. Chem.* **2011**, *84*, 898-901. https://doi.org/10.1134/S1070427211050284

[8] Sergeev, V.V.; Van-Chin-Syan, Yu.Ya. Heats of Mixing Butylacrylate with Certain Organic Solvents. *Russ. J. Appl. Chem.* **2012**, *85*, 689-691. https://doi.org/10.1134/S107042721204028

[9] Sergeev, V. V.; Dibrivnyi, V.N.; Van- Chin-Syan, Yu.Ya. Density, Partial Molar Volume, and Excess Volume of Solutions of Acrylic Acid in Acetonitrile, 1,2-Dichloroethane, Hexane, and Benzene at 293 K. *Russ. J. Gen. Chem.* **2012**, *82*, 202-205. https://doi.org/10.1134/S1070363212020065

[10] Serheyev, V. Enthalpies of Mixing Methylmethacrylate with Some Organic Solvents. *Chem. Chem. Technol.* **2012**, *6*, 15-18. https://doi.org/10.23939/chcht06.01.015

[11] Sergeev, V.V.; Van-Chin-Syan, Yu.Ya. Density, Partial, and Excess Volumes of Solutions of Methacrylic Acid in Organic Solvents at 293 K. *Russ. J. Phys. Chem.* A. **2015**, *89*, 406-410. https://doi.org/10.1134/S0036024415030279

[12] Serheyev, V. Enthalpies of Mixing of the Laurylmethacrylate with Some Organic Solvents. *Chem. Chem. Technol.* **2015**, *9*, 1-4. https://doi.org/10.23939/chcht09.01.001

[13] Sergeev, V.V. Enthalpy of Mixing of Methacrylic Acid with Organic Solvents at 293 K. *Russ. J. Phys. Chem. A.* **2016**, *90*, 575-578. https://doi.org/10.1134/S0036024416030274

[14] Sergeev, V.V. Enthalpies of Mixing of Butyl Methacrylate with Organic Solvents at 293 K. *Russ. J. Phys. Chem. A,* **2021,** *95*, 2177-2180. https://doi.org/10.1134/s0036024421100228

[15] *Spravochnik khimika, T 2*; Nikolskii, B.P., Ed.; Khimiya: Leningrad, 1966.

[16] *Svojstva organicheskikh soedinenii. Spravochnik*; Potekhin, A.A., Ed.; Khimiya: Leningrad, 1984.

[17] *Khimicheskii entsiklopedicheskii slovar*; Knuyants, I.L., Ed.; Sov. Entsiklopediya: Moskva, 1983.

[18] Van Ness, H.C.; Abbott, M.M. *Classical Thermodynamics of Nonelectrolyte Solutions*; McGraw-Hill: New York, 1982.

ГУСТИНА, НАДЛИШКОВИЙ ОБ'ЄМ І ПАРЦІАЛЬНІ МОЛЬНІ ОБ'ЄМИ РОЗЧИНІВ БУТИЛМЕТАКРИЛАТУ В ДЕЯКИХ ОРГАНІЧНИХ РОЗЧИННИКАХ

Анотація. *Визначено концентраційну залежність густини і надлишкового об'єму бінарних систем бутилметакрилату в ацетонітрилі, гексані, бензені, 1,2-дихлоретані й оцтовій кислоті за 293 К й атмосферного тиску з використанням пікнометричного методу. Визначені значення надлишкового об'єму апроксимовані поліномами. Розраховано значення парціальних мольних об'ємів досліджених розчинів.*

Ключові слова: *розчини, густина, надлишковий об'єм, парціальні мольні об'єми, бутилметакрилат.*