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Density, Partial Molar Volume, and Excess Volume of Solutions of Acrylic Acid in Acetonitrile, 1,2-Dichloroethane, Hexane, and Benzene at 293 K

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Abstract—Using pycnometric method, we have measured density of the solutions of acrylic acid in acetonitrile, 1,2-dichloroethane, hexane, and benzene at 293 K and atmospheric pressure. The values of the excess molar volume for these systems and the values of the partial molar volumes of components were derived. In the whole concentration range the excess molar volume for binary mixtures of acrylic acid and either 1,2-dichloroethane, or benzene, or hexane has positive values, and in the system of acrylic acid–acetonitrile the value is negative.

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Mixing components of different nature leads to the formation of solutions, whose properties differ from the ideal ones. The deviation from ideality can be expressed with various thermodynamic functions, but the redundant functions demonstrate it most clearly. The redundant thermodynamic functions of solutions represent the difference between the thermodynamic function of the real and the ideal solution and are therefore useful in the study of molecular interactions in real systems. In particular, they reflect the interacttions that occur between homogeneous and heterogeneous molecules in solution. For example, the positive value of excess molar volume shows that the solution structure is a less compact compared to the pure components, while a negative value of the excess molar volume indicates the formation of a more compact structure compared to pure substances.

This work is a part of our program on the characterization of molecular interactions between solvents and commercially important monomers, in particular, the evaluation of the effect of the chemical structure of the solvent on the properties of the systems studied.

Acrylic acid and its esters are important industrial chemicals, used to produce a large number of different polymers. They are interesting chemically for they contain a carboxy group and a double bond in the α-position. Acetonitrile, 1,2-dichloroethane, hexane, and benzene are excellent solvents, which are often used for the polymerization processes and other chemical reactions.

To date, there are many publications on measuring the density and excess molar volumes of solutions of methacrylic acid and esters of acrylic and methacrylic acids [1–6]. But despite the great interest of researchers to this class of compounds, we have not found among the available publications papers describing the measurements of densities and excess molar volumes of acrylic acid solutions.

Table 1 lists the density and the refractive index of pure components, as well as the content of the main component in the tested compound.

For the investigated solutions, we calculated the values of excess molar volume V_m^E, using the values of density of pure components and mixtures according to Eq. (1).

$$V_\mathrm{m}^\mathrm{E} = [x_1M_1 + x_2M_2]/\rho - [x_1M_1/\rho_1 + x_2M_2/\rho_2]. \tag{1}$$

Here ρ, ρ_1, ρ_2 are the densities of the solutions and pure components 1 and 2, respectively, x_1, x_2 are the mole fractions of components 1 and 2, respectively; M_1 and M_2 are the molecular masses of the solution components.

The values of excess molar volumes V_m^E are given in Table 2, the concentration dependence of excess

Table 1. Physicochemical characteristics of the components of the investigated solutions

Substance	M, g mol^{-1}	n_D^{20}		ρ, g cm^{-3}		Content of main component, wt %
		published data	experiment	published data	experiment	
Acrylic acid	72.0627	1.4224 [8]	1.4210	1.0511 [8]	1.0508	99.9
Acetonitrile	41.0524	1.3437 [7]	1.3441	0.7828 [7]	0.7824	99.8
Benzene	78.1134	1.5011 [7]	1.5009	0.8790 [7]	0.8787	99.9
Hexane	86.1766	1.3750 [7]	1.3751	0.6594 [7]	0.6593	99.9
1,2-Dichloroethane	98.9596	1.4448 [8]	1.4445	1.2530 [8]	1.2533	99.8

Table 2. Density and excess molar volume of the studied systems at 293 K

x_1	ρ, g cm^{-3}	V_m^E, cm^3 mol^{-1}	x_1	ρ, g cm^{-3}	V_m^E, cm^3 mol^{-1}
	Benzene–acrylic acid			1,2-Dichloroethane–acrylic acid	
0.8999	0.8899	0.2333	0.7988	1.2114	0.3552
0.8010	0.9023	0.3810	0.6980	1.1911	0.4359
0.7000	0.9161	0.4858	0.6021	1.1722	0.4651
0.5997	0.9307	0.5617	0.5000	1.1520	0.4568
0.5022	0.9459	0.6125	0.4145	1.1353	0.4139
0.4004	0.9629	0.6410	0.3370	1.1200	0.3547
0.2999	0.9812	0.6235	0.3049	1.1127	0.3289
0.1991	1.0014	0.5411	0.2137	1.0954	0.2352
0.1032	1.0233	0.3553			
	Hexane–acrylic acid			Acetonitrile–acrylic acid	
0.8022	0.7021	0.3458	0.8014	0.8524	–0.2865
0.7014	0.7278	0.4572	0.7016	0.8837	–0.3529
0.5989	0.7573	0.5269	0.6032	0.9125	–0.3874
0.4993	0.7899	0.5520	0.5025	0.9400	–0.4008
0.4041	0.8253	0.5398	0.4084	0.9642	–0.3950
0.3063	0.8670	0.4946	0.3115	0.9875	–0.3666
0.2035	0.9181	0.3963	0.2242	1.0071	–0.3144

molar volumes of the studied systems is shown in the figure.

We approximated the values of excess molar volumes by the power polynomial [Eq. (2)].

$$V_m^E = x_1x_2(A_0 + A_1x + A_2x^2 + A_3x^3). \quad (2)$$

The function V_m^E/x_1x_2 is extremely sensitive to errors, especially in the range of dilute solutions, and this helps to detect possible experimental errors and to check the quality of experimental data for each system.

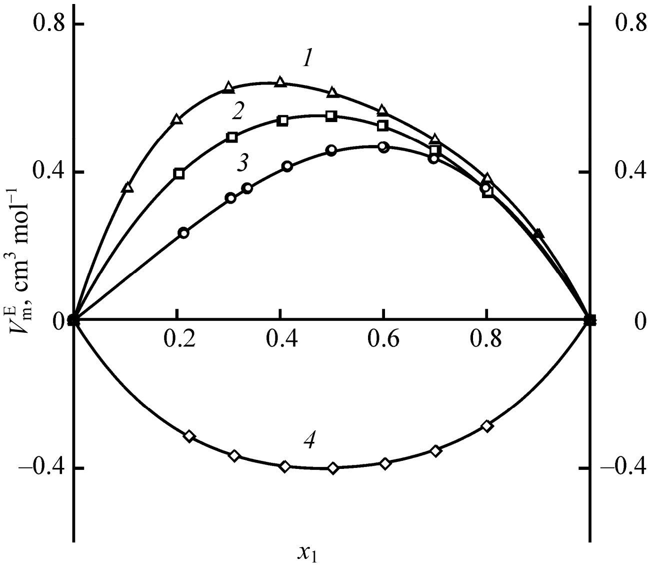
Table 3 lists the values of the coefficients of polynomials and the values of standard deviations of excess volumes from those determined with the polynomial, for the studied systems.

Using the dependence of the molar volume V_m of the studied systems on the concentration, we calculated the values of partial molar volumes of components, using Eqs. (3), (4) given in [5].

$$V_{m1} = V_m + x_2(dV_m/dx_1), \quad (3)$$

$$V_{m2} = V_m - x_1(dV_m/dx_1) \quad (4)$$

The values of partial molar volumes of components are shown in Table 4.



Concentration dependence of excess molar volume of the studied systems at 293 K: (*1*) benzene–acrylic acid, (*2*) hexane–acrylic acid, (*3*) 1,2-dichloroethane–acrylic acid, and (*4*) acetonitrile–acrylic acid.

The values given in Table 2 show that in the entire range of investigated concentrations the excess molar volume is positive for the binary systems of acrylic acid with hexane, benzene, and 1,2-dichloroethane, and for the system of acrylic acid–acetonitrile it takes negative values.

Function V_m^E is almost symmetric for the solutions of acrylic acid in hexane and acetonitrile. We can therefore assume that the specific interaction maximum corresponds to the equimolar composition. This corresponds to a low association of components of the solution, or, the association of components in these systems is absent totally.

The investigated solvents can be arranged by the values of the maximum excess molar volume in the series: benzene > hexane > 1,2-dichloroethane > acetonitrile.

Minimum and maximum values of excess molar volume for the mixtures are in the range from –0.40 to +0.65 cm^3 mol^{-1}.

A positive value of excess molar volume in the whole concentration range indicates the formation of less compact structure compared to the pure components. This effect increases from 1,2-dichloroethane to hexane and benzene, and the effect is caused by the insertion of nonpolar molecules, which break the association of the acrylic acid dimers. The maxima on the curves of the concentration dependence of excess molar volume for solutions of acrylic acid in benzene and 1,2-dichloroethane are at 40 and 60 mol %, which probably corresponds to the molecular association in these systems. The slight decrease in values of excess molar volume in going from benzene to hexane is due most likely to the geometric features of benzene and hexane, and their location between acrylic acid dimers. The dichloroethane molecule is capable of more intensive interaction with the molecules of acrylic acid, so the excess volume in the system with dichloroethane is less than in systems with benzene and hexane. Negative values of excess volume in the system with acetonitrile are due to its ability to form a hetero-conjugated hydrogen bonds with the molecules of acrylic acid and to the absence of such bonds between similar molecules of pure acetonitrile.

EXPERIMENTAL

The starting materials (Merck, Germany) were purified by distillation to remove possible impurities, benzene and acrylic acid were purified by recrystallization. The purity of substances was determined by chromatography and monitored by the values of density and refractive indices.

All the liquids before measuring density and preparing solutions were boiled to remove the dissolved air. Solutions of different concentrations (V = 11 cm^3) were prepared by weight in containers with ground glass stoppers to prevent evaporation. Solutions

Table 3. Coefficients of polynomials of the concentration dependence of excess molar volumes of the studied systems at 293 K

System	A_0	A_1	A_2	A_3	Sn×10^3
Benzene–acrylic acid	4.4222	–6.01278	3.82475	0.656307	6.32
1,2-Dichloroethane–acrylic acid	2.8877	–2.91739	4.07734	–1.922060	3.68
Hexane–acrylic acid	0.9473	2.52955	–2.22720	1.298770	5.22
Acetonitrile–acrylic acid	–2.2040	2.17980	–1.75054	–0.426300	1.29

Table 4. Molar volume of the studied systems and partial molar volume of components (cm^3 mol^{-1}) at 293 K

x_1	V_m	V_{m1}	V_{m2}	x_1	V_m	V_{m1}	V_{m2}
Benzene–acrylic acid				Hexane–acrylic acid			
0.000	68.673	91.325	68.673	0.000	68.596	132.933	68.596
0.100	70.914	90.859	68.698	0.100	75.007	132.510	68.618
0.200	73.105	90.442	68.771	0.200	81.374	132.132	68.685
0.300	75.248	90.074	68.894	0.300	87.697	131.798	68.796
0.400	77.341	89.755	69.065	0.400	93.975	131.509	68.952
0.500	79.386	89.486	69.286	0.500	100.208	131.264	69.152
0.600	81.381	89.265	69.556	0.600	106.397	131.064	69.396
0.700	83.328	89.093	69.875	0.700	112.542	130.908	69.686
0.800	85.225	88.971	70.243	0.800	118.642	130.797	70.019
0.900	87.073	88.897	70.660	0.900	124.697	130.730	70.398
1.000	88.872	88.872	71.126	1.000	130.708	130.708	70.820
1,2-Dichloroethane–acrylic acid				Acetonitrile–acrylic acid			
0.000	68.527	80.779	68.527	0.000	68.571	50.824	68.571
0.100	69.734	80.443	68.545	0.100	66.812	51.136	68.554
0.200	70.907	80.142	68.598	0.200	65.087	51.415	68.505
0.300	72.043	79.877	68.686	0.300	63.394	51.661	68.423
0.400	73.145	79.647	68.810	0.400	61.734	51.874	68.308
0.500	74.211	79.452	68.969	0.500	60.107	52.054	68.161
0.600	75.241	79.293	69.164	0.600	58.513	52.202	67.980
0.700	76.237	79.169	69.394	0.700	56.952	52.316	67.767
0.800	77.196	79.081	69.659	0.800	55.423	52.398	67.521
0.900	78.121	79.028	69.960	0.900	53.927	52.448	67.242
1.000	79.010	79.010	70.296	1.000	52.464	52.464	66.931

were weighed to within ±10^{-5} g. To minimize changes in the concentration at the preparation of solution, the less volatile component, in this case, acrylic acid, was poured first. The prepared solutions were gently stirred, and the samples to measure the density were taken with a syringe.

The density of solutions was determined using pycnometers of 10 cm^3 capacity, which were calibrated with bi-distilled degassed water at 4.0°C. Before weighing, the solutions were maintained at the desired temperature in a water thermostat at 293 K up to ±0.1 K. Weighing of the pycnometer was performed on an analytical balance with the accuracy ±10^{-5} g. The values of the density of the investigated solutions are shown in Table 2. The concentrations of the solutions are expressed in molar fractions (x_1) of a volatile substance, in this case the solvent.

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