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

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Abstract. Densities and excess volumes of the binary systems of lauryl (dodecyl) methacrylate with hexane, benzene, 1,2-diclorethane and acetic acid have been measured as a function of concentration, at 293 K and atmospheric pressure by pycnometric methods. The calculated excess volumes were approximated by polynomials.

Keywords: solutions; densities; excess volumes; lauryl methacrylate; hexane; benzene; 1,2-diclorethane; acetic acid.

1. Introduction

Mixing of different compounds results in the creation of solutions that differ from the ideal ones. The deviation from idealness is expressed by many thermodynamic functions, particularly by excess functions. Excess thermodynamic functions of mixtures represent the difference between the functions of actual and ideal solutions, and thus are useful in the study of molecular interactions and arrangements. In particular, they reflect the interactions that take place between solute-solute, solute-solvent, and solvent-solvent. For example, a positive value of the excess volume represents an intercalation packing effect, that is, an expansion of the mixture.

This work is a part of our study of the characteristics of the molecular interactions between solvents and commercially important monomers, in particular, the influence of the chemical structure of the solute in the systems under consideration. Methacrylic esters and hexane, benzene, 1,2-diclorethane, and acetic acid are important industrial chemicals used in the large-scale preparation of useful polymers. The esters are also interesting because they contain both a double bond and an ester group.

N. Sastry and P. Dave [1, 2] measured the excess volumes and dielectric behavior of fifteen binary mixtures of alkyl (methyl, ethyl, and butyl) methacrylate with hexane, heptane, carbon tetrachloride, chlorobenzene, and *o*-dichlorobenzene at 308 K and found that in case of aliphatic hydrocarbons the result were controlled by dispersing interactions while for chlorinated solvents the controlling factors were specific interactions (O–Cl and *n-p* types).

N. Sastry and M. Valand [3] also measured the excess volumes of mixtures of alkyl (methyl, ethyl, and butyl) acrylates in several alcohols at 298 and 308 K, and found that they were always positive. These results were explained on the basis of nonspecific interactions between the components.

N. Sastry and S. Patel [4] measured the excess volumes of methylmethacrylate with ethylbenzene and other aromatic hydrocarbons such as benzene, toluene, and (*o-, m-, p-*)xylene, at 298 and 303 K and found that except for toluene all exhibited positive excess volumes. However, no literature data are available for excess volumes of lauryl methacrylate (LMA) with hexane, benzene, 1,2-diclorethane and acetic acid.

2. Experimental

2.1. Materials

The raw materials were of the commercial grade and 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 and refractive indexes. The contamination was kept below 0.2 wt %, as verified through chromatography. The densities of the purified reagents at 293 K were determined, and their values are reported in Table 1 along with values given in the literature.

Table 1

Purity, densities, and molar masses of pure components at 293 K

Component	M, g/mol	n_D^{20}		r, g/cm^3		Purity, mas %
		lit.	determ..	lit.	determ.	
Acetic acid	60.0324	1.3717 [5]	1.3716	1.0491 [5]	1.0491	99.9
Benzene	78.1134	1.5011 [5]	1.5009	0.8790 [5]	0.8787	99.9
Hexane	86.1766	1.3750 [5]	1.3751	0.6594 [5]	0.6593	99.9
1,2-Diclorethane	98.9596	1.4448 [6]	1.4445	1.2530 [6]	1.2533	99.8
Lauryl methacrylate	254.4118	1.4457 [6]	1.4455	0.8733 [6]	0.8731	99.8

2.2. Density Measurements

All liquids were boiled or heated to remove dissolved air. Solutions of different compositions were prepared by mass in a 15 cm^3 rubber-stopper vial to prevent evaporation with the weighting accuracy of $\pm 5 \cdot 10^{-5}$ g. To minimize the errors in composition, the heavier component (lauryl 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 the volume of 10 cm^3, which was precalibrated with double-distilled water at 277 K. The pycnometer was placed vertically in an electronically controlled thermostat with the temperature measuring accuracy of ±0.1 K.

3. Results and Discussion

The density measurements were performed for each binary system in the whole concentration range ($0 < x_1 < 1$).

The excess volumes V^E of the solutions of mole fraction x_1 were calculated from the densities of the pure liquids and their mixtures according to the following equation [7]:

$$V_m^E = [x_1M_1 + x_2M_2]/r - [x_1M_1/r_1 + x_2M_2/r_2] \quad (1)$$

where r, r_1 and r_2 are the densities of the solution and pure components 1 and 2, respectively; M_1 and M_2 are molar masses of the pure components.

The corresponding values of densities and excess volumes are reported in Table 2 and Fig. 1.

The excess volumes calculated by the Eq. (1) were approximated using the polynomials [8]:

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

The standard deviation S was calculated as

$$S = [S(V^E_{i,\,\mathrm{exp}} - V^E_{i,\,\mathrm{calc}})^2/(N-1)]^{1/2} \quad (3)$$

The coefficients of polynomials and corresponding values of S are presented in Table 3. A plot of the function V_m^E/x_1x_2 against composition was used in every case to verify the quality of the data; this function is extremely sensitive to experimental errors, particularly in the small concentrations range and helps detecting possible errors.

The values of the measured molar volumes were used to calculate the partial volumes of the components. Partial molar volumes for binary systems were calculated using the relations [9]:

$$V_{m1} = V_m + x_2(dV_m/dx_1) \quad (4)$$

$$V_{m2} = V_m - x_1(dV_m/dx_1) \quad (5)$$

The calculated values are reported in Table 4.

Table 2

Densities and excess volumes for all systems at 293 K

x_1	r, g/cm^3	V_m^E, cm^3/mol	x_1	r, g/cm^3	V_m^E, cm^3/mol
Acetic acid–LMA			1,2-Diclorethane-LMA		
0.1030	0.8766	0.1293	0.1957	0.8955	0.3286
0.3245	0.8865	0.4231	0.3154	0.9131	0.5519
0.5348	0.9020	0.6468	0.5207	0.9552	0.8371
0.7103	0.9251	0.7086	0.7004	1.0144	0.8859
0.8995	0.9802	0.4248	0.9002	1.1378	0.4824
Hexane-LMA			Benzene-LMA		
0.1137	0.8624	-0.3033	0.1113	0.8736	-0.1040
0.3058	0.8402	-0.6883	0.1546	0.8737	-0.0982
0.5029	0.8099	-0.9154	0.3139	0.8737	0.0291
0.6053	0.7898	-0.9461	0.4986	0.8735	0.1940
0.7012	0.7674	-0.9088	0.7023	0.8741	0.2300
0.9008	0.7038	-0.4873	0.9011	0.8763	0.1080

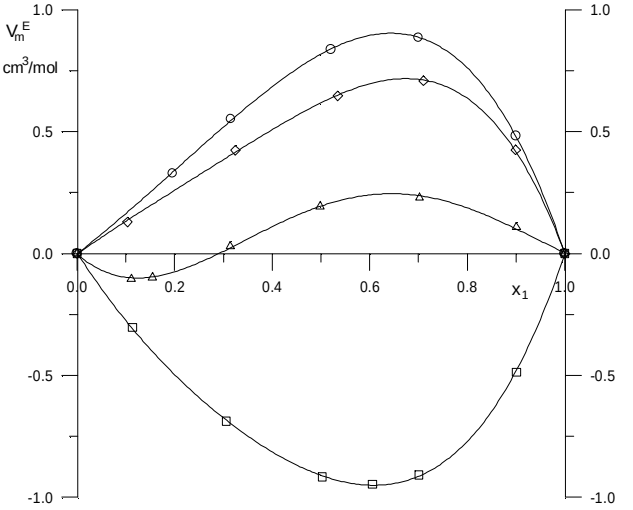

Fig. 1. Excess volumes at 293 K: 1,2-diclorethane-LMA (○); acetic acid-LMA (◊);-benzene-LMA (Δ) and hexane-LMA (□)

Table 3

Coefficients of Eq. (2) and standard deviations

System	A_0	A_1	A_2	A_3	$S{\cdot}10^3$
Acetic acid-LMA	1.1757	2.2279	-0.6687	2.8340	1.52
1,2-Diclorethane-LMA	1.3356	4.0487	-1.3193	2.0028	2.48
Hexane-LMA	-2.8906	-1.0513	0.4387	-2.6945	1.42
Benzene-LMA	-1.9869	9.3675	-9.2387	3.0867	0.92

Table 4

Molar volumes and partial molar volumes of components for all systems at 293 K

x_1	V_m, cm^3/mol	V_{m1}, cm^3/mol	V_{m2}, cm^3/mol	x_1	V_m, cm^3/mol	V_{m1}, cm^3/mol	V_{m2}, cm^3/mol
Acetic acid-LMA				1,2-Diclorethane-LMA			
0.000	291.613	57.650	291.613	0.000	291.278	82.292	291.278
0.100	268.227	57.840	291.603	0.100	270.347	81.677	291.310
0.200	244.860	58.010	291.573	0.200	249.351	81.128	291.407
0.300	221.514	58.160	291.523	0.300	228.291	80.642	291.569
0.400	198.188	58.290	291.453	0.400	207.166	80.222	291.796
0.500	174.882	58.400	291.363	0.500	185.976	79.866	292.087
0.600	151.595	58.490	291.253	0.600	164.722	79.575	292.442
0.700	128.329	58.560	291.123	0.700	143.403	79.349	292.863
0.800	105.083	58.610	290.973	0.800	122.019	79.187	293.348
0.900	81.856	58.640	290.803	0.900	100.571	79.090	293.898
1.000	58.650	58.650	290.613	1.000	79.057	79.057	294.513
Hexane-LMA				Benzene-LMA			
0.000	291.450	126.893	291.450	0.000	291.354	89.035	291.354
0.100	275.032	127.600	291.413	0.100	271.132	89.225	291.344
0.200	258.687	128.233	291.301	0.200	250.930	89.395	291.314
0.300	242.418	128.791	291.115	0.300	230.748	89.545	291.264
0.400	226.223	129.275	290.854	0.400	210.586	89.675	291.194
0.500	210.102	129.685	290.519	0.500	190.445	89.785	291.104
0.600	194.056	130.020	290.110	0.600	170.323	89.875	290.994
0.700	178.084	130.280	289.626	0.700	150.221	89.945	290.864
0.800	162.187	130.466	289.068	0.800	130.139	89.995	290.714
0.900	146.364	130.578	288.435	0.900	110.077	90.025	290.544
1.000	130.615	130.615	287.728	1.000	90.035	90.035	290.354

Excess volumes for 1,2-diclorethane-LMA and acetic acid-LMA systems are positive for all concentrations; for benzene-LMA system excess volumes are negative for solvent concentrations below 0.3 mol fraction and positive above this concentration; for hexane-LMA system excess volumes are negative for all concentrations. The magnitude of equimolar excess volumes showed the following trend:

1,2-Diclorethane > Acetic acid > Benzene> Hexane

4. Conclusions

The magnitude and the sign of excess volume reflect the type of interactions taking place in the mixture. This is very well demonstrated by minimum and maximum excess volumes values of the mixtures studied herein, ranging from about −0.946 to +0.886 $cm^3 \cdot mol^{-1}$.

The overall positive magnitude of excess volumes for 1,2-diclorethane-LMA and acetic acid-LMA systems indicates a net dislocation effect that increases as the structure of solutions becomes more branched.

The negative values of excess volumes for benzene-LMA system in the range $0 < x_1 < 0.3$ indicate that specific interactions between its esters and *p*-electrons of the aromatic ring are much stronger than in case of 1,2-diclorethane and acetic acid. As the concentration of benzene increases, the excess volumes turns positive due to the same reasons as for the solutions in 1,2-diclorethane and acetic acid.

The overall negative magnitude of excess volumes for hexane-LMA system indicates a creation of a more compact solution structure. The highest negative value for hexane-LMA system indicates strong interaction between the molecule of hexane and non polar hydrocarbon radical of ester.

The minimum and maximum values of excess volumes reflect the possible complexations between the compounds of the binary systems: 1,2-diclorethane-LMA (66 mol %); acetic acid-LMA(66 mol %); benzene-LMA (10.66 mol %); and hexane-LMA(60 mol %).

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

Анотація. *Визначено концентраційну залежність густини і надлишкового об'єму бінарних систем лаурил (додецил) метакрилату с гексаном, бензеном, 1,2-дихлоретаном і оцтовою кислотою при 293 K і атмосферному тиску, з використанням пікнометричного методу. Розраховані значення надлишкового об'єму були апроксимовані поліномами.*

Ключові слова: *розчини, густина, надлишковий об'єм, лаурилметакрилат, гексан, бензен, 1,2-дихлоретан, оцтова кислота.*