

Valentyn Serheyev

THE ENTHALPY OF MIXING OF THE LAURYL METHACRYLATE WITH SOME ORGANIC SOLVENTS

*Lviv Polytechnic National University
12 Bandery str., 790013 Lviv, Ukraine; vsergeev@lp.edu.ua*

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Abstract. The enthalpy of mixing for the binary systems of the laurylmethacrylate with hexane, benzene, 1,2-dichloroethane and acetic acid have been measured as a function of their concentration, the temperature of 293 K and at the atmospheric pressure, by the calorimetric methods. The concentration dependences of the enthalpies of mixing were correlated by polynomials. For the system acetic acid–laurylmethacrylate the enthalpies of mixing were positive for all concentrations, while for other systems the enthalpies of mixing takes were positive only when the solvent concentration was greater than 25 mol %.

Key words: solution, calorimetric method, enthalpy of mixing, laurylmethacrylate, hexane, benzene, 1,2-dichloroethane, acetic acid.

1. Introduction

The mixing of different compounds gives rise to solutions that generally do not behave as the ideal solutions. These deviations are expressed by many thermodynamic variables, particularly by excess properties. The excess thermodynamic properties of mixtures correspond to the difference between the actual property and the property of the system that behaves ideally, and thus are useful in the study of the molecular interactions and arrangements. In particular, they reflect the interactions that take place between the solute–solute, the solute–solvent, and the solvent–solvent species. For example, a negative value of the enthalpies of mixing indicates that the molecular interactions in the solution state are stronger than those of the individual components.

This article is a continuation of a series of the recent publications [1-5] on the general characterization of the molecular interactions between solvents and acrylic monomers, and in particular, on the influence of the chemical structure of the solutes. The methacrylic esters and hexane, benzene, 1,2-dichloroethane and acetic acid are important industrial chemicals used in the large-scale

preparation of engineering and performance polymers. Chemical properties of esters of methacrylic acid are also interesting because they contain both a double bond and the carboxyl group.

The properties of the solutions of the esters based on the acrylic acids have been studied extensively. J. George, N. Sastry *et al.* [6, 7] determined the heat of mixing and the excess volumes of the methylmethacrylate solutions with benzene, toluene, *p*-xylene, cyclohexane, aliphatic diethers and the alkanes. In works by R. Peralta, J. Wisniak *et al.* [8, 9] the excess volumes of the solutions of the methylmethacrylate, ethylacrylate and butylmethacrylate in styrene and toluene were determined. A. K. Nain *et al.* [10] studied the density and the excess volumes of the solutions of the ethylacrylate in butyl alcohols.

It is known that among the existing methods for determination of the thermal effects, a calorimetric method is considered as the most reliable [11, 12]. At the same time, there is no information in the literature on the utility of the calorimetric method for determination of the enthalpies of mixing of laurylmethacrylate (LMA) with organic solvents. Therefore the goal of the present work is to study these thermal interactions.

2. Experimental

2.1. Materials

The raw materials, used in our measurements were supplied by MERCK (Germany). The chemicals received were purified through the repeated evaporation while the benzene and the acetic acid were additionally purified by the recrystallization method. The chemicals were then selected based on their unique densities as well and the refractive index. The chemicals purity was greater than 99.8 %, as was determined by the permeation chromatography. Table 1 shows the densities and the refractive indices of the purified reagents at 293 K along with the reported literature values.

Table 1

Purity, densities and refractive indexes of pure components at 293 K

Component	n_D^{20}		$r, \text{g/cm}^3$		Purity, mas %
	literature	measured	literature	measured	
Benzene	1.5011 [13]	1.5009	0.8790 [13]	0.8787	99.9
Hexane	1.3750 [13]	1.3751	0.6594 [13]	0.6593	99.9
1,2-Dichlorethane	1.4448 [14]	1.4445	1.2530 [14]	1.2533	99.8
Acetic acid	1.3717 [13]	1.3716	1.0491 [13]	1.0491	99.9
Laurylmethacrylate	1.4450 [15]	1.4455	0.8735 [15]	0.8731	99.8

2.2. Determination of the Enthalpy of Mixing

The enthalpies of mixing were measured by differential microcalorimeter MID-200 according to the ampoules methodology. The mixing cell and the firing pin were made from glass, and the compacting gasket was made from Teflon®. The cell volume was 15.870 cm^3 . The first component was introduced directly into the cell, while the second one was placed into the glass ampoule that was sealed through welding. The mass of both the test cell and the ampoule was determined with the accuracy of $5 \cdot 10^{-5} \text{ g}$. The test cell and the ampoule were loaded in the microcalorimeter and were conditioned at the temperature of 293 K, with the accuracy of 0.1 K. After the thermal equilibrium had been established, the ampoule was broken up through by the glass firing-pin. The magnitudes of the thermal transport between the microcalorimeter cells were captured by the voltmeter, with the accuracy of $1 \mu\text{V}$, which corresponded to $8 \cdot 10^{-6} \text{ W}$. After every measurement the calorimeter was undergone the internal calibration.

To minimize the heat released as a result of the partial condensation of the component in the cell and the heat evolved as a result of the evaporation of the component in the ampoule upon its breakage, the component with lower vapour pressure (LMA) was placed in the ampoule.

The measurement methodology was validated by conducting a series of the experiments whereby the enthalpies of the equimolar benzene-hexane mixtures were determined. A good agreement between the experimentally measured value of $884.3 \pm 3.4 \text{ J/mol}$ and the value ($883.4 \pm 1.5 \text{ J/mol}$) published in the literature [12] was found.

3. Results and Discussion

The enthalpies of mixing $\Delta_m H$, the heat evolved during the experiment Q , the mass of the ester m_e , and the

solvent m_s , as well as the mole fraction of the solvent x are reported in Table 2.

The enthalpies of mixing for the investigated solutions were fit using the polynomials:

$$\Delta_m H = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + a_4 x^4$$

The standard deviation S was calculated as:

$$S = [\sum (\Delta_m H_i^{\text{exp}} - \Delta_m H_i^{\text{calc}})^2 / (N-1)]^{1/2}$$

The coefficients of the polynomials and the corresponding values of S are shown in Table 3. The value of the standard dispersion is comparable to the experimental error, therefore the polynomials may be used for calculation of the enthalpies of mixing of the investigated solutions at any concentration.

The dependence of the enthalpies of mixing for the investigated solutions on the concentration of the first component is shown in the Fig. As can be seen from the figure, the excess enthalpies of mixing for the binary system acetic acid–LMA are positive for all solvent concentrations, however, for the systems benzene–LMA, hexane–LMA and 1,2-dichlorethane–LMA the excess enthalpies of mixing are negative for solvent concentrations below 25 mol % but become positive above this concentration. The magnitude of enthalpies of mixing for equimolar solution of the investigated system values showed the following trend:

$$\text{Hexane} < \text{Benzene} < \text{1,2-Dichlorethane} < \text{Acetic acid}$$

For the system acetic acid–LMA the maximum of the enthalpy of mixing corresponds to the solvent concentration of 60 mol %. The systems benzene–LMA, hexane–LMA and 1,2-dichlorethane–LMA also exhibit the maxima of the heat of mixing in the range of 60–70 mol % by the solvent, and the minima that correspond to about 10 mol %. The presence of the maxima and the minima indicate potential inter-molecular associations in these systems.

Table 2

The enthalpies of mixing for investigated solutions at 293 K

m_e , g	m_s , g	x	Q , J	$\Delta_m H$, J/mol
Benzene–LMA				
1.59760	0.06140	0.1112	-0.512	-72.5
3.36575	0.18900	0.1546	-0.943	-60.2
3.37725	0.47430	0.3138	1.357	70.1
1.97605	0.60320	0.4985	3.746	241.8
1.75510	1.27115	0.7023	6.525	281.6
1.98710	2.51375	0.8047	9.388	234.7
Hexane–LMA				
3.14540	0.13510	0.1125	-0.532	-38.2
3.23205	0.48235	0.3058	1.005	54.9
3.14755	1.07860	0.5029	4.942	198.6
1.97775	1.02755	0.6053	4.779	242.6
1.91805	1.52435	0.7012	6.415	254.3
1.70925	5.25690	0.9008	10.179	150.3
1,2-Dichloroethane–LMA				
3.28830	0.31130	0.1957	-1.079	-67.2
2.10050	0.37640	0.3154	0.892	73.9
1.94080	0.82020	0.5207	5.803	364.6
1.91300	1.73950	0.7004	11.486	457.6
1.05610	1.95470	0.8263	8.753	366.2
Acetic acid–LMA				
4.53685	0.25345	0.1914	3.522	159.7
2.19840	0.24915	0.3245	4.025	314.6
2.16915	0.58850	0.5348	8.889	485.0
1.74980	1.01255	0.7103	10.547	444.2
1.05470	1.07570	0.8121	7.157	324.4

Table 3

Coefficients of polynomials of concentrations dependencies enthalpies of mixing at 293 K

System	a_0	a_1	$a_2 \cdot 10^2$	$a_3 \cdot 10^4$	$a_4 \cdot 10^6$	S , J/mol
Benzene–LMA	-1.16	-1386.52	8033.73	-10506.20	3860.91	3.30
Hexane–LMA	-1.39	-718.59	4217.01	-4510.62	1015.93	3.46
1,2-Dichloroethane–LMA	0.15	-1933.96	10288.10	-11893.30	3538.87	0.85
Acetic acid–LMA	0.71	149.63	4910.05	-8249.37	3188.22	3.79

Table 4

Properties of solvents and enthalpies of mixing of equimolar solutions

Solvent	m , D	RM, cm ³ /mol	$\Delta_m H$, J/mol
Hexane	0	29.93	193
Benzene	0	26.19	242
1,2-Dichloroethane	1.27	21.01	340
Acetic acid	1.70	12.99	471

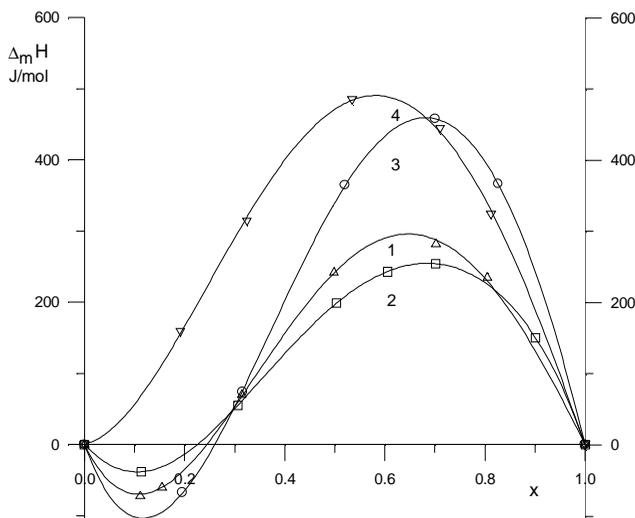


Fig. Concentration dependence of the enthalpies of mixing of the investigated systems at 293 K: benzene–LMA (1); hexane–LMA (2); 1,2-dichloroethane–LMA (3) and acetic acid–LMA (4)

4. Conclusions

The sign and the magnitude of the enthalpy of mixing are determined by the energy balance between the intermolecular attraction of the molecules in the solution and that of the pure components. For the systems benzene–LMA, hexane–LMA and 1,2-dichloroethane–LMA the enthalpies of mixing are positive for the solvent concentrations of 25 mol % and greater, and for the system acetic acid–LMA they are positive in the whole range of concentrations. The positive values of enthalpies of mixing can be explained by the lower level of the intermolecular interaction of the heterogeneous molecules compared to the strength of the homogeneous interactions within the pure components.

The magnitude of the enthalpies of mixing of equimolar solutions for the investigated systems decreases with the increase in the molecular refraction (RM) of the solvents, and increases with the dipole moment m . This suggests that the deviation from the ideal behavior becomes greater as the solvent polarity increases. The curves maxima in the Fig. exhibit a shift toward greater concentrations of the solvent, which can be related to the substantially larger size of LMA molecules in comparison to those of the solvents.

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ЕНТАЛЬПІ ЗМІШУВАННЯ ЛАУРИЛМЕТАКРИЛАТУ З ДЕЯКИМИ ОРГАНІЧНИМИ РОЗЧИННИКАМИ

Анотація. Калориметричним методом визначені ентальпії змішування бінарних систем лаурилметакрилату з гексаном, бенzenом, 1,2-дихлоретаном та оцтовою кислотою за температури 293 K та атмосферного тиску. Концентраційні залежності ентальпії змішування апроксимовані степеневими поліномами. Для системи оцтова кислота - лаурилметакрилат ентальпія змішування набуває додатних значень у всьому дослідженому діапазоні концентрацій, а для решти досліджених систем ентальпія додатна для концентрацій розчинника вищих за 25 % мол.

Ключові слова: розчин, калориметрія, ентальпія змішування, лаурилметакрилат, гексан, бензен, 1,2-дихлоретан, оцтова кислота.