Enthalpies of solution and partial molar volumes of magnesium perchlorate in alcohols and salt effect of acceleration of the Diels–Alder reaction

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ABSTRACT

Densities and enthalpies of solution at 25 °C were measured for dilute solutions of magnesium perchlorate (MP) in some alcohols using the Anton Paar DSA 5000M vibrating tube densimeter and differential calorimetric measurements. In all studied solvents the solution of MP was highly exothermic and large solvent volume contraction was observed. Maximum effect was obtained in methanol and ethanol solutions. Acceleration effect of the Diels–Alder reaction of 9,10-dimethylanthracene with acrylonitrile (in medium of acrylonitrile) in the presence of salts $LiClO_4$, $Mg(ClO_4)_2$ and $GaCl_3$ was as 18:160:59,000.

1. Introduction

Perchlorates of alkali and alkaline earth metals have high solubility in polar *n*-donor aprotic and protic mediums. Metal ions are stabilized by the strong interaction with the *n*-donor centers of the solvent molecules, and the large size perchlorate anion, possessing a high degree of delocalization of the charge, is stabilized by the interaction with polar solvent [1–3]. At present there is a large database on the heats of solution and partial molar volumes (PMV) of salts in water and some organic solvents [4–7]. Increased scatter of literature data on these parameters is more often observed for solvents with low dielectric constant, ε, and/or low donor numbers, *DN*. Since the limiting concentration of calorimetric measurements typically $\sim 10^{-3}$ mol L^{-1}, and in the measurements of the molar volume of $\sim 10^{-2}$ mol L^{-1}, the complete dissociation of salts in these conditions is not always observed, and extrapolation to zero concentration can lead to appreciable errors. For lithium [6] and magnesium [7] perchlorates it was showed that the dissolution of anhydrous salts in solvents, accompanied by a strong exothermic effect, and the values of PMV sharply decrease due to electrostriction and even may be negative. For magnesium perchlorate it was noted more dramatic change of these characteristics than for lithium perchlorate (LP) [7]. In relation to our systematic

study of the salt effects on reaction rate [8–10], partial molar volumes and enthalpies of solution of salts in organic solvents [6,7], the properties of magnesium perchlorate in alcohols (methanol, ethanol, propanol-1, propanol-2, butanol-1, 3-methylbutanol-1, and hexanol-1) were studied in this work. Acceleration effect of the Diels–Alder reaction in the presence of MP was estimated and compared with that of LP and gallium chloride.

2. Experimental part

2.1. Materials

Magnesium perchlorate "trihydrate" (Fisher Scientific), typically a sample of 7–10 g in a glass vessel, had an initial water content of about 15% and was dried in a glass tube at 240–245 °C for 20–25 h in vacuum ($\sim$50 Pa). The tube (50 cm) with freshly dried calcium chloride was connected between a sample with MP and vacuum pump. For a high efficiency of drying, the growth of the melting point of the sample MP should be higher than the elevation of temperature of the heater. Smooth elevation of the temperature up to 245 °C in the heater was carried out for about 6 h. The holding of the vessel with the MP sample under these conditions (240–245 °C, 50 Pa, 20–25 h) to the constant weight ($\pm$2 mg) is an accurate (>99.95%) testing method of the final dehydration.

Spectral purity of 9,10-dimethylanthracene (Aldrich, m.p. 182–183 °C, lit. 183–184 [11]) was obtained after column chromatography (eluent benzene:*n*-hexane, 1:5) and was confirmed

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by the complete disappearance of the initial absorption of diene (390–405 nm) in solution with a slight excess of maleic anhydride.

Acrylonitrile was purified as described [12]. Solvents were purified and dried by known methods [13].

2.2. Apparatus and procedures

2.2.1. Densities measurement

The vibration densimeter manufactured by Anton Paar, model DSA 5000M, was used for the measurements. The densimeter was calibrated with water and air following the instructions and requirements of the manufacturer. Calibrations were performed at temperature 25 °C. Very small differences (few ppm) of the densities between fresh prepared solution (MP) and after 1 day exclude the by-processes in studied alcohols. Molar volumes of MP were calculated from data on the density of their solutions. In all methods of calculation of the apparent molar volume (φ_A) of a solute (A) in solution the unchanged volume of the solvent in the formation of the solution is accepted. In terms of molar concentration (c_A), molal concentration (m_A), moles per kilogram of solution (w_A), or grams per milliliter of solution (T_A), the following Eqs. (1)–(4) can be obtained:

$$\frac{1000 - (1000, d - c_A \cdot M_A)}{d_0} = c_A \cdot \varphi_A \quad (1)$$

$$\frac{(1000 + m_A \cdot M_A)}{d} = \frac{1000}{d_0} + m_A \cdot \varphi_A \quad (2)$$

$$\frac{1000}{d} = \frac{1000}{d_0} + w_A \cdot \left(\frac{\varphi_A - M_A}{d_0} \right) \quad (3)$$

$$d = d_0 + T_A \left(\frac{1 - \varphi_A d_0}{M_A} \right) \quad (4)$$

Here, d_0 and d are the densities of the solvent and solution, M_A is the molar mass of solute. Eqs. (1)–(4) can be transformed to direct calculation of the value φ_A for each concentration. In this way Eq. (2) can be converted to calculate φ_A:

$$\varphi_A = \frac{1000(d_0 - d)}{m_A d_0 d} + \frac{M_A}{d} \quad (5)$$

The value of partial molar volume $\overline{V}_{MP}$ was calculated as the limit of correlation φ_{MP} vs. $(m_{MP})^{1/2}$.

2.2.2. Calorimetric experiment

The enthalpies of solution of MP were measured at 25 °C in a differential calorimeter, as previously reported [7]. Samples were weighed in a small stainless steel cylinder, both polished sides of which were covered by thin (0.1 mm) rings of Teflon seals. Tightness of the containers was verified by the constancy of mass of cylinders with diethyl ether in a period of 24 h. The accuracy of the calorimetric measurements was verified by determining the enthalpy of dissolution of dry potassium chloride in water at 25 °C. The result (4.18 ± 0.01 kcal mol^{-1}) is in agreement with the published [14] value of (4.185 ± 0.002 kcal mol^{-1}). The calibration was made by the introduction of a certain amount of Joule heat. For all solutions 4–6 measurements of sequentially dissolving samples of MP were carried out. The total uncertainty of the measurements did not exceed ±2%. The data of sequential dissolution of MP samples in calorimetric cell allow us to calculate the values of differential and integral enthalpies of solution for each sample.

2.2.3. Kinetic measurements

For kinetic measurements double beam spectrophotometer Hitachi 2900 with temperature-controlled module was used. The temperature of the water around the optical cell was controlled to ±0.03 °C. Realizations of Beer's law as well as the absence of absorption in this region of acrylonitrile and adduct have been tested.
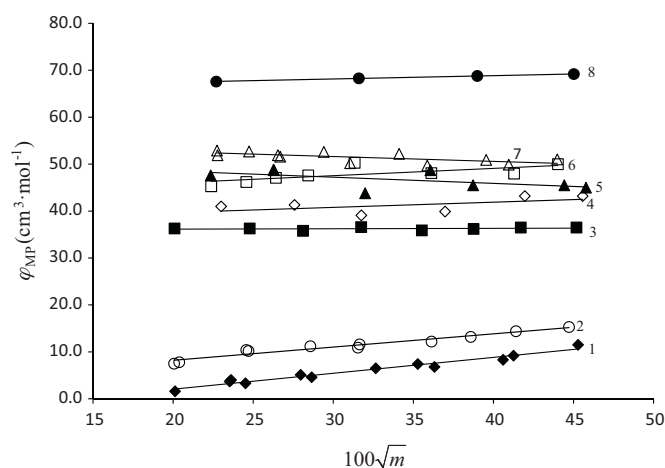

Fig. 1. Dependence of the apparent molar volume of solution (φ_{MP}) of Mg(ClO$_4$)$_2$ on the square root of its molal concentration ($100\sqrt{m}$) in alcohols (1)–(7) and in water (8) at 25 °C. The numbers refer to the serial numbers of the alcohols given in Table 3.

Kinetic measurements of the reaction of 9,10-dimethylantracene with acrylonitrile were carried out in the medium of dienophile at 20, 30 and 45 °C in the absence and the presence of MP. In such conditions, only molecules of acrylonitrile are surrounded by the cation Mg^{2+} which ensures more accurate calculation of the acceleration effect. Measurements of the reaction rate were carried out by changing the absorption of 9,10-dimethylantracene at 397–403 nm.

3. Results and discussion

3.1. Molar volumes

Concentration dependence of the enthalpy of solution and apparent molar volume are expressed very poorly [6] at dissolution of nonpolar and low polarity organic compounds whereas for the salt solutions, this dependence is often observed due to the incomplete dissociation [4–7]. The obtained values of apparent molar volumes of MP in the studied alcohols are presented in Table 1 and Fig. 1.

Repeated measurements of the density of MP solutions in methanol with freshly prepared salt and solvent confirm the existence of a clear dependence φ_{MP} vs. $m^{1/2}$ with extrapolated values to zero concentration $\overline{V}_{MP} = -4.7 \pm 0.7$ cm^3 mol^{-1}. In other studied alcohols the values of $\overline{V}_{MP}$ is positive. Using the value of van der Waals volume of Mg^{2+} ion (1.1 cm^3 mol^{-1}), perchlorate ion (33.1 cm^3 mol^{-1}) [15], and crystal volume of MP (85.4 cm^3 mol^{-1}) [16] the calculated value of the packing coefficient ($V_W/V_{cryst} = 67.3/85.4$) of crystalline MP (0.788) is almost the same as for LP (0.783). PMVs of MP, like that of LP in all studied media, are significantly lower than V_{cryst} and V_W. From the obtained data follows that electrostriction is observed in all studied solvents, but particularly sharply – in methanol and ethanol.

It is interesting to note that the sharp growth of $\overline{V}_{MP}$ and decreasing of the solvent electrostriction is observed on passing from ethanol to propanol-1. Decisive influence of the volume of solvent molecules (V_S) to be quantitatively fit into the first solvation shell of the ion was observed in some works [1–3,17]. In a series of alcohols from propanol-1 to hexanol-1 it is observed only a slight increase in the $\overline{V}_{MP}$. Previously it was assumed [18] that complete dissociation of LP at a concentration of 10^{-2}–10^{-3} mol L^{-1} occurs only in polar solvents with a dielectric constant greater than 20. In the less polar media, $\varepsilon < 20$, even with high donor numbers, the dissolution is accompanied by the formation of conglomerates with a

Table 1

Experimental values of the solvent density (d_0, g cm^{-3}), magnesium perchlorate solutions (d, g cm^{-3}) for different molal concentrations (m, mol kg^{-1}), calculated values of apparent volume (φ_{MP}), and partial molar volume ($\overline{V}_{MP}$, cm^3 mol^{-1}), at 25 °C.

Solvent	m	D	d_0	φ_{MP}
Methanol	0.04048	0.793582	0.786517	1.6
	0.05578	0.796170	0.786517	4.0
	0.06013	0.796948	0.786517	3.3
	0.08212	0.800696	0.786517	4.6
	0.05535	0.796157	0.786568	3.7
	0.07818	0.800042	0.786568	5.1
	0.10661	0.804844	0.786567	6.5
	0.12447	0.807835	0.786568	7.4
	0.13191	0.809155	0.786567	6.8
	0.16486	0.814636	0.786568	8.3
	0.17023	0.815445	0.786567	9.2
	0.20513	0.821061	0.786570	11.5
	$\overline{V}_{MP} = -4.7 \pm 0.7$[a]			
Ethanol	0.04023	0.79195	0.785087	7.5
	0.04153	0.792163	0.785087	7.8
	0.06034	0.79527	0.785087	10.4
	0.06104	0.795415	0.785108	10.2
	0.08161	0.798837	0.785108	11.2
	0.09948	0.801859	0.785108	10.9
	0.10012	0.801899	0.785087	11.6
	0.13057	0.806957	0.785084	12.2
	0.14886	0.809918	0.785084	13.2
	0.17145	0.813547	0.785084	14.4
	0.19997	0.818166	0.785084	15.3
	$\overline{V}_{MP} = 2.5 \pm 0.7$[a]			
Propanol-1	0.04035	0.805921	0.799662	36.3
	0.06141	0.809180	0.799662	36.3
	0.07899	0.811926	0.799662	35.8
	0.10073	0.815239	0.799662	36.6
	0.12624	0.819195	0.799635	35.9
	0.15024	0.822871	0.799635	36.2
	0.17394	0.826481	0.799635	36.5
	0.20417	0.831125	0.799635	36.5
	$\overline{V}_{MP} = 36.3 \pm 0.3$[b]			
Propanol-2	0.05290	0.788927	0.781040	41.0
	0.07606	0.792334	0.781018	41.3
	0.10084	0.796153	0.781027	39.1
	0.13679	0.801411	0.780984	39.9
	0.17606	0.806939	0.781040	43.2
	0.20770	0.811506	0.780989	43.2
	$\overline{V}_{MP} = 41.3 \pm 1.7$[b]			
Butanol-1	0.04994	0.813233	0.805807	47.6
	0.06901	0.815984	0.805788	48.8
	0.06915	0.816031	0.805809	48.7
	0.10234	0.821237	0.805799	43.8
	0.13006	0.824995	0.805809	48.7
	0.15005	0.828233	0.805802	45.5
	0.19734	0.835267	0.805814	45.5
	0.20957	0.837144	0.805811	45.0
	$\overline{V}_{MP} = 46.7 \pm 1.9$[b]			
3-Methylbutanol-1	0.05006	0.815547	0.808013	45.3
	0.06037	0.817060	0.808013	46.2
	0.06978	0.818425	0.808013	47.1
	0.08086	0.820045	0.808013	47.6
	0.09817	0.822438	0.808013	50.3
	0.13049	0.827356	0.808013	48.1
	0.17048	0.833246	0.808013	48.0
	0.19386	0.836426	0.808013	50.0
	$\overline{V}_{MP} = 47.8 \pm 1.7$[b]			
Hexanol-1	0.05170	0.823047	0.815473	52.9
	0.05186	0.823107	0.815473	51.9
	0.06122	0.824424	0.815450	52.7
	0.07046	0.825812	0.815450	51.9
	0.07123	0.825963	0.815473	51.6
	0.08650	0.828120	0.815450	52.6
	0.09643	0.829718	0.815444	50.2
	0.11635	0.832526	0.815473	52.2
	0.12865	0.834511	0.815444	49.7
	0.15640	0.838493	0.815473	50.9

Table 1 (Continued)

Solvent	m	D	d_0	φ_{MP}
	0.16777	0.840242	0.815444	49.9
	0.19347	0.843869	0.815444	51.0
	$\overline{V}_{MP} = 51.5 \pm 1.1$[b]			
Water	0.05148	0.998602	0.997039	67.6
	0.09984	0.999678	0.997039	68.3
	0.15205	0.998309	0.997039	68.8
	0.20270	1.001985	0.997039	69.2
	$\overline{V}_{MP} = 67.3 \pm 0.5$[c]			

[a] $\overline{V}_{MP}$ was calculated from: $\varphi_{MP} = \overline{V}_{MP} + a \times m^{0.5}$.

[b] $\overline{V}_{MP}$ was calculated from: $\overline{V}_{MP} = \sum_i \frac{\varphi_{i(MP)}}{i}$.

[c] Ref. [7].

high degree of contact ion pairs [18,19]. Sharp break of the dependence $\overline{V}_{MP}$. vs. V_S from ethanol to higher alcohols for which the dielectric constant is less than 20 is observed. Additionally a smaller volume of CH$_3$OH and C$_2$H$_5$OH allows arranging greater number of molecules in the solvation shell of the Mg^{2+} cation.

The value of PMV of ClO$_4^-$-anion in alcohols was determined only in methanol [5,6,20]. The value $\overline{V}_{ClO_4^-} = 42$ cm^3 mol^{-1} was calculated from PMV of sodium perchlorate, assuming $\overline{V}_{Ph_4P^+} = \overline{V}_{BPh_4^-}$ [20]. Similar value of PMV for the perchlorate anion ($\overline{V}_{ClO_4^-} = 43.6$ cm^3 mol^{-1}) follows from the PMV of LP in methanol (24.6 cm^3 mol^{-1} [6]) and PMV of Li$^+$ cation in methanol (−19 cm^3 mol^{-1} [5]). Taking into account that $\overline{V}_{MP} = -4.7$ cm^3 mol^{-1} and $\overline{V}_{ClO_4^-} = 43$ cm^3 mol^{-1} in methanol the calculated value of PMV of magnesium cation $\overline{V}_{Mg^{2+}}$ is −91 cm^3 mol^{-1}. For the previously studied of MP in 12 solvents [7] the negative value of PMVs of MP is defined only in acetone, −2.4 cm^3 mol^{-1}. With the value $\overline{V}_{ClO_4^-} = 20$ cm^3 mol^{-1} [5] the calculated value of $\overline{V}_{Mg^{2+}} = -42.4$ cm^3 mol^{-1} in acetone is much larger than in methanol. From these data follow very strong electrostriction of methanol at solvation of the Mg^{2+} cation, and the weak electrostriction at solvation of ClO$_4^-$ anion in methanol.

3.2. Enthalpies of solution

Values of the differential and integral enthalpies of solution are collected in Table 2. Concentration dependence is presented in Fig. 2.

Large values of the heats of solution allow carrying out the measurements at low concentrations of MP. Therefore, the
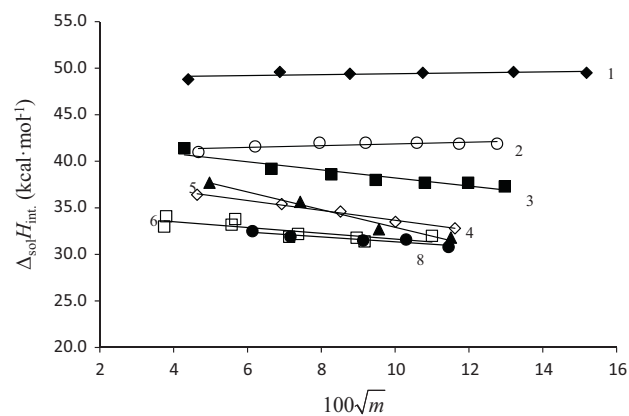

Fig. 2. Dependence of the integral enthalpy of solution ($\Delta_{sol}H_{int.}$) of Mg(ClO$_4$)$_2$ on the square root of its molal concentration ($100\sqrt{m}$) in alcohols (1)–(6) and in water (8) at 25 °C. The numbers refer to the serial numbers of the alcohols given in Table 3.

Table 2
Weights of the samples of magnesium perchlorate (W, mg) at sequential dissolution, salt concentration (m, mol kg^{-1} solvent), calculated values of differential ($\Delta_{sol}H_{dif.}$, kcal mol^{-1}), and integral ($\Delta_{sol}H_{int.}$, kcal mol^{-1}) enthalpies of solution at 25 °C.

Solvent	W	$1000 \times m$	$-\Delta_{sol}H_{dif.}$ [a]	$-\Delta_{sol}H_{int.}$ [b]
Methanol	50.8	1.93	48.8	48.8
	73.8	4.73	50.2	49.6
	78.3	7.7	49.1	49.4
	101.4	11.55	49.7	49.5
	154.9	17.44	49.7	49.6
	148.2	23.06	49.3	49.5
			49.5 ± 0.5	49.0 ± 0.2
Ethanol	57.3	2.18	41.0	41.0
	43.8	3.85	42.4	41.6
	64.9	6.32	42.6	42.0
	56.3	8.46	42.1	42.0
	72.3	11.21	41.9	42.0
	67.0	13.76	41.7	41.9
	66.4	16.28	41.6	41.9
			41.9 ± 0.5	40.9 ± 0.3
Propanol-1	49.3	1.84	41.4	41.4
	69.0	4.42	37.6	39.2
	64.9	6.84	37.4	38.6
	56.9	8.97	36.4	38.0
	72.4	11.67	36.4	37.7
	71.4	14.34	37.7	37.7
	66.5	16.82	35.2	37.3
			37.4 ± 1.4	42.5 ± 0.6
Propanol-2	56.1	2.15	36.3	36.4
	69.3	4.80	34.6	35.4
	64.5	7.26	32.9	34.6
	72.1	10.02	30.5	33.5
	90.9	13.50	30.9	32.8
			33.0 ± 2.5	39.0 ± 0.2
Butanol-1	66.6	2.47	37.9	37.7
	82.3	5.52	36.8	35.6
	97.8	9.14	33.6	32.7
	110.7	13.25	27.4	31.8
			33.9 ± 4.7	42.4 ± 0.9
3-Methylbutanol-1	37.9	1.40	33.0	33.0
	46.0	3.10	33.4	33.2
	63.1	5.43	30.8	32.2
	80.4	8.41	30.0	31.4
	38.9	1.44	32.5	34.1
	47.9	3.21	31.3	33.8
	50.7	5.08	30.9	31.9
	79.7	8.02	31.7	31.8
	98.1	12.09	29.2	32.0
			31.4 ± 1.4	34.8 ± 0.6
Water	125.8	3.76	36.7	36.7
	46.1	5.13	36.7	36.7
	107.5	8.34	36.8	36.7
	75.3	10.60	36.8	36.8
	82.7	13.10	36.9	36.8
			36.7 ± 0.1	36.6 ± 0.1 [c]

[a] $\Delta_{sol}H_{dif.}$ was calculated from: $\sum_i \frac{\Delta_{sol}H_{dif.}}{i}$.

[b] $\Delta_{sol}H_{int.}$ was calculated from: $\Delta_{sol}H_{int.}$ *vs.* $m^{0.5}$ at $m \to 0$.

[c] Ref. [7].

concentrations in all calorimetric measurements (Table 2) were lower than the concentrations in volumetric measurements (Table 1). Enthalpies of solution in water, methanol, ethanol and propanol-1 are almost independent of the concentration of MP (Fig. 2). Solution rate of sequent portions of MP in calorimetric cell for other alcohols substantially decreases, which results in increasing of measurement errors. In spite of the rather high solubility of MP in hexanol-1 (more than 0.2 M) we were not able to determine the heat of solution of MP in hexanol-1 because of the very low rate of dissolution.

The value of the enthalpy of solution ($\Delta_{sol}H_{MP}$) in strong polar solvent up to separated ions can be regarded as the sum of the lattice energy of bond breaking in the dissolved substance ($\Delta_{lat.en.}H_{MP}$), the energy of the creation of cavities for the accommodation of the solute ($\Delta_{hole}H_S$), and the energy of interaction ($\Delta_{inter}H_{ions-S}$) of dissolved ions with the solvent:

$$\Delta_{sol}H_{MP} = \Delta_{lat.en.}H_{MP} + \Delta_{hole}H_E + \Delta_{inter}H_{MP,ions-S} \quad (6)$$

In the case of solution up to the contact ion pairs we can write:

$$\Delta_{sol}H_{MP} = \Delta_{cryst.en.}H_{MP} + \Delta_{hole}H_S + \Delta_{inter}H_{MP,ion\ pair-S} \quad (7)$$

The total heat of solution of MP in water, formamide and in alcohols is in addition affected by superposition of the high energy of the cavity formation ($\Delta_{hole}H_S$) due to the breaking of the solvent's hydrogen-bond net [7,21,22]. It is clear that the difference in the experimental values of the enthalpy of solution does not always correspond to the difference in the energy of interaction.

The value of partial molar volume is also affected by the balance of solvent–solvent and solvent–solute intermolecular interactions, but, in addition, very sensitive to the solvent compressibility. Due to almost the same H-bond energy in studied alcohols, negative value of $\overline{V}_{MP}$ in methanol can be defined by the highest compressibility of this solvent (Table 3).

It was noted earlier [6,7] the absence of proportionality in the change of PMVs and the enthalpies of solution in a wide range of solvents for MP ($R = -0.02$) and LP ($R = 0.07$). In a series of alcohols, in contrast, such tendency is observed (Table 3). Existence of proportionality between the changes in molecular parameters, such as dielectric constant (ε), isothermal compressibility (β_T), molar volume (V_S) for all studied solvents can be explained by belonging to one class. The general tendency of increasing of exothermicity of MP solution and electrostriction with decreasing of molar volume of alcohols is in accord with higher values of relative permittivity, ε, and isothermal compressibility, β_T (Table 3). It is known [1,3] that the complete dissociation of 2:1 electrolyte Mg(ClO$_4$)$_2$ on the ions Mg^{2+} and ClO$_4^-$ is considerably more difficult than for 1:1 electrolytes. Comparison of the experimental data for solutions of MP in alcohols (Tables 1 and 2) with obtained previously data in n-donor solvents [7] reveals the interesting tendency. The enthalpies of solution of MP remain almost constant in the region $(1–15) \times 10^{-3}\ m$ in highly polar n-donor solvents: water, formamide, dimethyl sulfoxide, dimethyl formamide, propylene carbonate, methanol and ethanol. It can be explained by the complete dissociation of MP in these solvents in this concentration range. The combination of high dielectric constant with low n-donor properties leads to changing of enthalpies of solution in the experimental range of concentrations of MP in acetonitrile ($\varepsilon = 36.6$, $DN_{rel.} = 0.36$) by almost 15%, and in nitromethane ($\varepsilon = 37.3$, $DN_{rel.} = 0.07$) more than 5 times [7]. On the other hand in ethyl acetate ($\varepsilon = 6.1$, $DN_{rel.} = 0.44$) a weak dependence of the enthalpy of solution in the interval $(0.12–1.5) \times 10^{-2}\ m$ and the total absence of dependence φ_{MP} at higher concentrations $(1.3–20) \times 10^{-2}\ m$ [7] was observed. Such behavior of MP in ethyl acetate can be attributed to a small fraction of free ions in comparison with the ion pairs. Similarly we can explain the change in the properties of MP solutions in studied alcohols (Tables 1 and 2). A weak dependence of the enthalpy of solution of MP in methanol and ethanol in the experimental concentration range $(0.2–2.0) \times 10^{-2}\ m$ (Table 2) and strong concentration dependence of φ_{MP} in the range $(4.0–20.5) \times 10^{-2}\ m$ (Table 1) are observed. For the same reason calorimetric measurements at low concentrations $(0.2–1.6) \times 10^{-2}\ m$ in alcohols, except methanol and ethanol, show the concentration dependence of the enthalpy of solution of MP and the values of φ_{MP}, defined at higher concentrations $(2–20) \times 10^{-2}\ m$, for these alcohols remain constant.

Table 3
Values of partial molar volumes of magnesium perchlorate, $\overline{V}_{MP}$, solvent molar volume, V_S (cm^3 mol^{-1}) the enthalpies of solution ($\Delta_{sol}H_{dif.}$ and $\Delta_{sol}H_{int.}$, kcal mol^{-1}), the relative permittivity, ε_r, the isothermal compressibility coefficient of solvent, β_T (bar^{-1}), the electrostriction parameter $\partial(1/\varepsilon_r)/\partial P$ (bar^{-1}) at 25 °C.

No.	Solvent	ε_r [a]	V_m [a]	$10^6\beta_T$	$10^6\partial(1/\varepsilon_r)/\partial P$	$\overline{V}_{MP}$	$-\Delta_{sol}H_{dif.}$	$-\Delta_{sol}H_{int.}$
1	Methanol	32.6	40.7	123.2[b]	3.7[d]	−4.7	49.5	49.0
2	Ethanol	24.3	58.7	112.2[b]	3.8[d]	2.5	41.9	40.9
3	Propanol-1	20.1	75.1	97.8[b]	3.8[d]	36.3	37.4	42.5
4	Propanol-2	18.3	76.9	112.3[c]	4.0[d]	41.3	33.0	39.0
5	Butanol-1	17.1	91.5	91.4[b]	4.4[e]	46.7	33.9	42.4
6	3-Methyl-butanol-1	14.7	109.4	92.0[c]	6.0[e]	47.8	31.4	34.8
7	Hexanol-1	13.3	125.3	90.5[b]	5.5 (30 °C)[d]	51.5	–	–
8	Water	80.8	18.0	45.2[a]	0.58[d]	67.3	36.7	36.6

[a] Ref. [13].
[b] Ref. [23].
[c] Ref. [24].
[d] Ref. [25].
[e] Ref. [26].
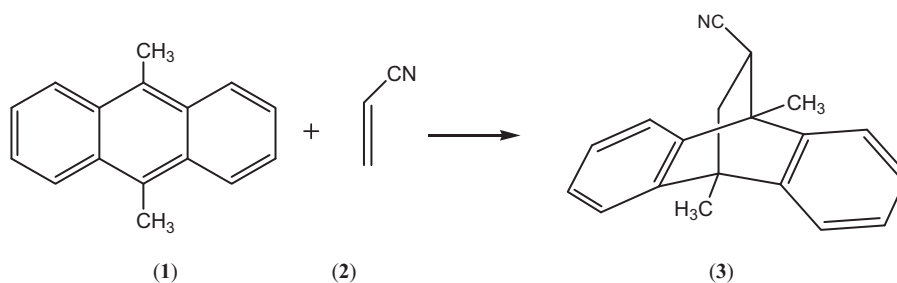
Scheme 1. Dimethylantracene (**1**) + acrylonitrile (**2**) → adduct (**3**).

Table 4
Apparent ($k_{2,app}$, L mol^{-1} s^{-1}), noncatalytic ($k_{2,noncat}$, L mol^{-1} s^{-1}) and catalytic ($k_{2,cat}$, L mol^{-1} s^{-1}) rate constants of the Diels–Alder reaction of 9,10-dimethylanthracene with acrylonitrile in dienophile medium in the presence of MP.

| T, °C	C_{MP}, mol L^{-1}	$k_{2,app}$	$k_{2,noncat}$	$k_{2,cat}$ [a]	$k_{2,cat}/k_{2,noncat}$
20.0	0	8.92×10^{-7}	8.92×10^{-7}	–	
	0.1029	1.88×10^{-6}	8.92×10^{-7}	1.45×10^{-4}	160
30.0	0	2.30×10^{-6}	2.30×10^{-6}	–	
	0.1015	4.81×10^{-6}	2.30×10^{-6}	3.72×10^{-4}	160
45.0	0	8.72×10^{-6}	8.72×10^{-6}	–	
	0.0952	1.55×10^{-5}	8.72×10^{-6}	1.07×10^{-3}	125

[a] The values of $k_{2,cat}$ were calculated from equation: $k_{2,app} = \ln(D_{01}/D_1)/t = k_{2,cat} C_{MP} + k_{2,noncat} C_2$, where D, C_{MP} and C_2 are optical absorption of 9,10-dimethylanthracene, molarities of magnesium perchlorate and acrylonitrile, respectively.

3.3. Kinetic measurements

The increased activity of molecules of n-donor reagent in the solvation shell of magnesium cation was determined from the change in the rate of Diels–Alder reaction between 9,10-dimethylanthracene and n-donor acrylonitrile (Scheme 1).

We have studied the reaction of 9,10-dimethylanthracene (**1**) with acrylonitrile (**2**) without cosolvent (in medium of acrylonitrile) in the presence of MP, where solvate shell of Mg^{2+} contents only dienophile molecules (Table 4). The possibility of complex formation of n-donor solvents with LP and MP was thoroughly investigated [27–33]. The structure of solvate shell of dilute
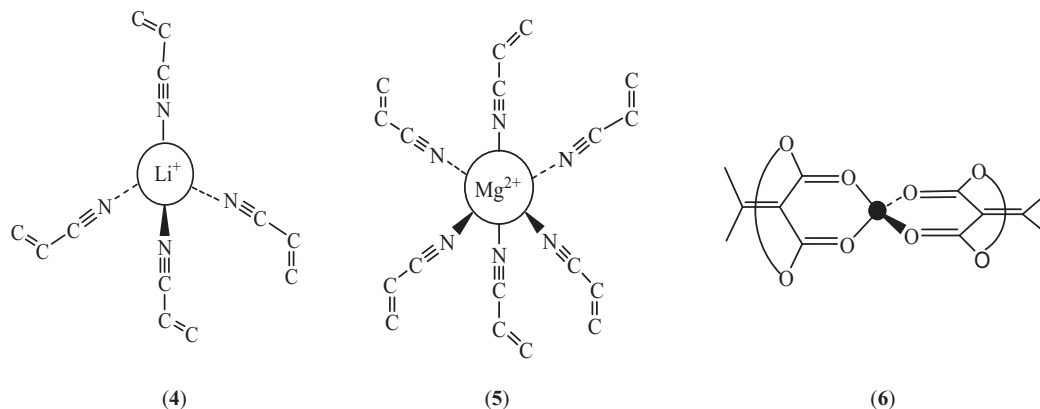
Scheme 2. [10].

solution of LP (**4**) and MP (**5**) in acrylonitrile medium can be assumed [10]. For higher salt concentrations some acrylonitrile molecules can be replaced here by perchlorate anions (Scheme 2).

The calculated values of enthalpy and entropy of activation for the Diels–Alder reaction between 9,10-dimethylanthracene and acrylonitrile in the medium dienophile in the absence ($\Delta H^{\neq} = 16.3\,\mathrm{kcal\,mol^{-1}}$, $\Delta S^{\neq} = -30.4\,\mathrm{cal\,mol^{-1}\,K^{-1}}$) and in the presence ($\Delta H^{\neq} = 14.0\,\mathrm{kcal\,mol^{-1}}$, $\Delta S^{\neq} = -28.0\,\mathrm{cal\,mol^{-1}\,K^{-1}}$) of magnesium perchlorate indicate that the availability of the double bonds in the dienophile complex (**5**) for the reaction with 9,10-DMA in the catalytic process do not change, while the observed acceleration of the reaction with activated dienophile due to the decrease of activation enthalpy. The measurements of the catalytic effect of the same reaction in the presence of lithium perchlorate showed [9] that the activation of dienophile in the presence of magnesium perchlorate (**5**) (Table 4) on one order of magnitude higher than that in the presence of lithium perchlorate (**4**). Previously [8] it was discovered a simple relation between the effect of acceleration the Diels–Alder reaction and the enthalpy of formation of n,v-complexes (MC) between dienophiles and Lewis acids $\{Al(Hal)_3, Gal(Hal)_3, B(Hal)_3\}$:

$$\ln\left(\frac{k_{cat}}{k_{noncat}}\right) = 0.79 \times \Delta H_{MC}, \tag{8}$$

where ΔH_{MC} in kcal mol^{-1}.

Taking the close n-donor properties of acetonitrile and acrylonitrile it may be noted that the *exo*-effect of solution of lithium perchlorate crystals ($-9.2\,\mathrm{kcal\,mol^{-1}}$ [6]) are comparable, and magnesium perchlorate ($-47.3\,\mathrm{kcal\,mol^{-1}}$ [7]) in acetonitrile is much higher than the value of enthalpy of solution of gallium chloride in acetonitrile ($-17.0\,\mathrm{kcal\,mol^{-1}}$ [6]) and the formation of a complex between gallium chloride and acrylonitrile ($-12.2\,\mathrm{kcal\,mol^{-1}}$ [8]). Though, the ratio of the acceleration effects in the presence LiClO$_4$, Mg(ClO$_4$)$_2$ and GaCl$_3$ is 18:160:59,000. All possible modes of complex formation and aggregation of LP and MP with a solvent should be considered as the rapid exchange equilibrium, where position of solvent in solvate shell of Li$^+$ or Mg^{2+} can occupy other n-donor admixture, e.g., dienophile. It should be noted very small values (from 0.7 to about $10\,\mathrm{M^{-1}}$) of calculated equilibrium constants between LP and different n-donor molecules in diethyl ether [30]. Magnesium perchlorate demonstrates some stronger complex formation. In acetone and acetonitrile solutions the complex (**6**) formation of macrocyclic-yliden malonates with metal cation could be assumed from the data of UV–VIS and NMR spectroscopic investigations [32,33]. The large difference of the acceleration effects due to the activation of acrylonitrile in Diels–Alder reaction in the presence of LP, MP and gallium chloride can be explained by different contributions of electrostatic and covalent interaction in these complexes [8].

4. Conclusion

Due to the superposition of processes with the energy consumption for the restructuring of the solvent, for the dissociation of the MP and energy release in the solvation of ions, the experimentally observed differences in the enthalpy of dissolution is not so great. Assuming that the electrostriction of the solvent at the solvation of ions is much larger than at the solvation of the contact ion pair, the sharp differences in PMVs of MP from methanol and ethanol to higher alcohols can be considered as incomplete dissociation of MP in higher alcohols.

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