

Solvent effect on the heat of solution and partial molar volume of magnesium perchlorate

V. D. Kiselev^{a*}, A. V. Bolotov^a, H. A. Kashaeva^a, I. Shakirova^a,
A. Averyanova^a, A. Satonin^a and A. I. Kononov^a

For magnesium perchlorate (MP), the solvent effect on the heat of solution and partial molar volumes (PMV) at 25 °C was studied. Since the complete dissociation of magnesium perchlorate is more difficult to achieve as compared with lithium perchlorate (LP), the concentration dependence of the values of the heat of solution and partial molar volume were noted. Only in highly polar solvents with large donor numbers (DN), such as water, dimethyl sulfoxide, *N,N*-dimethyl formamide, and formamide, the differential and integral values of the enthalpies of solution were the same in the range of concentrations studied. In all solvents studied, the values of the heat of solution of MP were highly exothermic and exceed that of LP by more than 30 kcal mol⁻¹. The values of the partial molar volume of MP were changed from 82.3 cm³ mol⁻¹ in formamide to -2.4 cm³ mol⁻¹ in acetone, and correlate linearly with that of LP ($R = 0.975$). Taking into account the significant change in the properties of molecules in the solvate shell of cation Mg²⁺, the large increase in the reactivity of reactants, activated by such interaction with Mg²⁺ cation is expected. Copyright © 2010 John Wiley & Sons, Ltd.

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INTRODUCTION

Many cycloaddition reactions are accelerated in the presence of Lewis acids. Usually, the acceleration of Diels–Alder reactions with normal electronic demand consists of 4, 5, and 6 orders of magnitude in the presence of gallium trichloride, aluminum trichloride, and aluminum tribromide, respectively.^[1] The influence of salt solutions on the rate of non-polar, polar, and ionic reactions was widely studied.^[2–4] Solutions of lithium perchlorate in organic solvents were suitable for these purposes, and their influence was studied quite thoroughly. There are also reports about the acceleration of solution reactions in the presence of magnesium perchlorate.^[3] A significant difference in the behavior of common soft Lewis acids (GaCl₃, AlCl₃, AlBr₃), compared with the influence of solutions of perchlorates of alkaline and alkaline-earth metals, has been noted. Catalytic processes in the presence of *n*-donor reagents and halides of gallium and aluminum are usually performed in inert media (benzene, toluene, dichloromethane, 1,2-dichloroethane), while lithium and magnesium perchlorates are extremely low soluble in these conditions. Therefore, the reactions should be carried out in *n*-donor solvents. Since the concentration of the solvent is much higher than that of *n*-donor reagent, the part of activated reagent in salt solutions is usually small. This usually explains the relatively weak total salt influence on the acceleration of reactions.^[3–5] It is interesting to note that at the transition of the Diels–Alder reaction of cyclopentadiene with acrylonitrile from diethyl ether solution to a 1 M solution of LP in diethyl ether, the rate of acceleration is even higher than that for the same reaction in the transition from the acrylonitrile to a 1 M solution of LP in acrylonitrile.^[4] On the other hand, the acceleration of the rate of reactions, catalyzed by gallium or aluminum trihalides in inert

media, practically coincides with the acceleration of reactions found in the dienophile medium.^[1,5] In *n*-donor solvents, the catalytic effect of gallium or aluminum trichloride is almost entirely suppressed.^[1,5]

For soft Lewis acids (SnCl₄, BBr₃, GaCl₃, AlBr₃), a significant decrease in PMV in the *n*-donor solvents has been observed, and the effect of acceleration of the Diels–Alder reactions in an inert media was proportional to the enthalpy of formation of *n,v*-complexes with dienophiles.^[1]

For LP, sufficient data are available on the heat of solution and partial molar volume \bar{V}_{LP} in some organic solvents,^[6–9] and the salt influence on the rate of reactions.^[2,4] Similar data for MP are very limited. There are data on the PMV of magnesium perchlorate, \bar{V}_{MP} , for solutions in dimethyl sulfoxide, obtained by the vibrating tube densimeter method,^[10] and for solutions in *N,N*-dimethyl formamide and propylene carbonate, obtained by the pycnometer method.^[11]

EXPERIMENTAL

Materials

Solvents were purified and dried by known methods,^[12–15] used for determining the conductivity of MP in these media.

* Correspondence to: V. Kiselev, Butlerov Institute of Chemistry, Kazan State University, Kremlevskaya Str. 18, Kazan 420008, Russia.
E-mail: Vladimir.Kiselev@ksu.ru

a V. D. Kiselev, A. V. Bolotov, H. A. Kashaeva, I. Shakirova, A. Averyanova, A. Satonin, A. I. Kononov
Butlerov Institute of Chemistry, Kazan State University, Kremlevskaya Str. 18, Kazan 420008, Russia

Nitromethane was dried over freshly calcined CaCl_2 , fractionally distilled, stored over molecular sieves (4 Å), and freshly distilled before use. The purity of solvents was checked by comparison of their densities at 25 °C with literature data. The determination of the heat of solution ($\Delta_{\text{sol}}H_{\text{MP}}$) and the PMV of magnesium perchlorate (\bar{V}_{MP}) were performed with solvents of the same quality.

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 15–20 h in vacuum (~50 Pa). The tube (50 cm) with freshly dried calcium chloride was connected between a sample with MP and vacuum pump. Smooth elevation of the temperature up to 245 °C in the heater was carried out for about 4 h. Thereby, 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. The holding of the vessel with the MP sample under these conditions (240–245 °C, 50 Pa, 15–20 h) to the constant weight (± 2 mg) is an accurate (>99.95%) testing method of the final dehydration.

The reported value of the heat of solution of MP in acetone^[16] differs significantly from our results (Table 1), which indicates an incomplete drying of MP in the glove box with P_2O_5 .

Calorimetric experiment

The enthalpies of solution of MP were measured at 25 °C (Table 1) in a differential calorimeter, as previously reported for lithium perchlorate.^[17]

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 ($4.18 \pm 0.01 \text{ kcal mol}^{-1}$) is in agreement with the published^[18] value of ($4.185 \pm 0.002 \text{ kcal mol}^{-1}$). The calibration was made by the introduction of a certain amount of Joule heat.

For all solutions 4–7 measurements of sequentially dissolving samples of MP were carried out. The total uncertainty of the measurements did not exceed $\pm 2\%$. 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 (Table 1).

Densities measurement

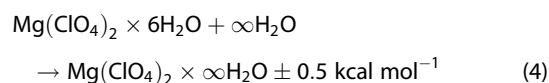
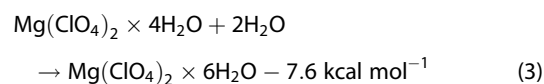
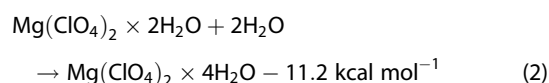
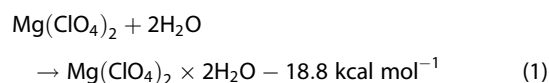
The partial molar volumes, \bar{V}_{MP} (Table 2), were calculated from the values of the density of solutions.

Density measurements ($\pm 2 \times 10^{-6} \text{ g cm}^{-3}$) were made with an Anton-Paar DMA 602 vibrating tube densimeter at 25 ± 0.002 °C. The apparatus was calibrated with bidistilled water and nitrogen, according to the manual instructions. Densities of solutions for each solvent were determined at least in two series of independent experiments. The dissolution of MP in diethyl ether held in long-term heating followed by an accurate determination of the weight of diethyl ether. The $\bar{V}_{\text{Mg}^{2+}}$ values were calculated from the equation $\bar{V}_{\text{Mg}^{2+}} = \bar{V}_{\text{MP}} - 2\bar{V}_{\text{ClO}_4^-}$, using literature data^[6,8,9] on the value of $\bar{V}_{\text{ClO}_4^-}$.

RESULTS AND DISCUSSION

Heat of solution of magnesium perchlorate

There are data on the heat of solution of MP in water, methanol, and some aqueous solutions.^[19–21] In all solvents studied (Table 1), the heat of solution of MP was exothermic and more than 30 kcal mol^{-1} larger than that of anhydrous LP. This explains the high stability of crystalline MP solvates not only with water but also with many other *n*-donor solvents.^[10,19,21] The values of the heat of solution of MP in water (Table 1) are in a good agreement with literature data. The following thermal effects of solution in water for crystalline magnesium perchlorate hydrates can be calculated from the selected data:^[20]



There are many factors affecting the experimental values of the thermal effects of dissolution.

(1) From Eqns (1) to (4) a very high affinity of MP to water, causing the problem of dehydration, should be expected. For this reason, the variation in the values of heat of solution within $\pm (0.5\text{--}1.0) \text{ kcal mol}^{-1}$ for different samples of dried MP is due to an experimental error.

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

$$\Delta_{\text{sol}}H_{\text{MP}} = \Delta_{\text{lat. en.}}H_{\text{MP}} + \Delta_{\text{hole}}H_{\text{S}} + \Delta_{\text{inter}}H_{\text{MP-S}} \quad (5)$$

The total heat of solution of MP in water and in formamide is in addition affected by the superposition of the higher energy of the cavity formation ($\Delta_{\text{hole}}H_{\text{S}}$) due to the breaking of the solvent's hydrogen-bond net.^[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.

(3) A low water content in dipolar aprotic solvent leads to a significant increase of the water activity due to the loss of the hydrogen-bond net. For this reason, the dissolution of MP in such water-organic solvent mixtures is often accompanied by a high exothermic effect, exceeding the values of the heat of solution in each of the individual solvent. The quota of water molecules in the ion solvation shell can be substantially higher than the part of water molecules in the bulk of the mixed solvent.^[21,22]

(4) The sequential dissolution of portions of MP in non-aqueous solvents can be accompanied by a decrease of the salt dissociation, and in the case of low-polarity solvents ($\epsilon_r < 20$) the heat of dissolution results mainly from the formation of solvated contact ion pairs.^[23] The last two factors do not occur at low

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

Solvent	W (mg)	$1000 \times m$	$-\Delta_{\text{sol}}H_{\text{dif}}$	$-\Delta_{\text{sol}}H_{\text{int}}$
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	10.6	36.8	36.8
	82.7	13.1	36.9	36.8
			36.7 ± 0.1^a	36.6 ± 0.1^b 38.2; ^c 37.5 ^d
Ethyl acetate	36.4	1.22	34.0	34.0
	46.3	2.76	33.4	33.7
	104.1	6.25	31.7	32.6
	79.0	8.90	31.2	32.2
	67.8	11.2	31.2	32.0
	55.6	13.0	31.6	31.9
	62.2	15.1	30.8	31.8
			32.0 ± 1.0^a	34.0 ± 0.2^b
Acetone	83.7	3.19	45.0	45.0
	48.0	5.02	44.2	44.7
	43.1	6.67	43.5	44.4
	68.4 ^e	2.60	45.1	45.1
			44.5 ± 0.6^a	45.6 ± 0.1^b
Formamide	80.5	2.13	45.7	45.7
	63.3	3.80	44.9	45.4
	125.0	7.12	45.1	45.3
	101.2	9.80	45.5	45.3
	110.4	12.7	45.3	45.3
	64.5	14.4	45.1	45.3
	69.3 ^e	1.83	45.0	45.0
	49.0 ^e	3.13	45.6	45.3
	53.6 ^e	4.55	45.5	45.3
	93.4 ^e	7.03	46.2	45.6
	86.5 ^e	9.33	43.6	45.1
	61.0 ^e	10.9	44.0	45.0
	68.4 ^e	12.8	43.6	44.8
				45.4 ± 0.2^a
Dimethyl sulfoxide	30.0	0.822	56.7	56.7
	96.7	3.45	56.4	56.5
	56.8	5.01	57.0	56.6
	58.1	6.60	58.5	57.1
	45.2	7.84	58.0	57.2
			57.3 ± 0.7^a	56.8 ± 0.3
<i>N,N</i> -Dimethyl formamide	83.9	2.66	59.2	59.2
	30.5	3.62	56.6	58.5
	46.2	5.09	60.4	59.1
	24.0	5.84	57.4	58.9
	36.8	7.01	58.9	58.9
	48.7	8.56	60.8	59.2
	36.9	9.74	59.9	59.3
			59.0 ± 1.2^a	58.7 ± 0.3^b
Propylene carbonate	114.1	2.83	43.2	43.2
	57.4	4.25	39.7	42.0
	74.2	6.09	38.3	40.9
	79.4	8.06	34.4	39.3
			38.9 ± 2.6^a	45.2 ± 0.2^b

(Continues)

Table 1. (Continued)

Solvent	W (mg)	1000 × m	−Δ _{sol} H _{dif.}	−Δ _{sol} H _{int.}
Nitromethane	71.9	1.90	38.1	38.1
	72.6	3.83	22.8	30.4
	82.0	6.00	18.8	24.7
	92.3	8.45	16.3	22.3
	76.9	10.5	12.3	20.4
	78.3	12.6	11.4	18.9
	61.2 ^e	1.62	41.5	41.5
	109.0 ^e	4.50	22.6	29.4
	125.1 ^e	7.83	16.0	23.8
	102.1 ^e	10.5	13.7	21.2
	211.1 ^e	16.1	9.9	17.3
	157.9 ^e	23.0	8.3	14.6
	294.3 ^e	30.9	7.0	12.7
				64.5 ± 3.0 ^g
Acetonitrile	52.2	2.01	46.4	46.4
	46.8	3.81	46.1	46.3
	53.9	5.89	44.2	45.5
	97.6	9.66	42.1	44.2
	59.2 ^e	2.28	46.7	46.7
	75.2 ^e	5.18	44.5	45.5
	74.0 ^e	8.03	42.8	44.5
	46.1 ^e	9.82	41.0	43.9
			44.2 ± 1.5 ^a	47.3 ± 0.2 ^b
			44.3 ± 1.5 ^h	

^a Average value Δ_{sol}H_{dif.}; ^b Limited value Δ_{sol}H_{int.}⁰ of the dependence Δ_{sol}H_{int.} versus m^{0.5} at m → 0; ^cRef. [19]; ^dRef. [20]; ^eRepeated measurements with different samples of dried Mg(ClO₄)₂ and solvent; ^fRef. [16]; ^gLimited value Δ_{sol}H_{int.}⁰ of the dependence Δ_{sol}H_{int.} = a × m^{0.5} + b × m at m → 0; ^hRef. [21].

concentrations of MP in strong polar media such as water, formamide, DMSO, and DMF; the values of differential and integral enthalpies of solution were the same within the accuracy of experimental measurements (Table 1).

The increase in the exothermicity of the MP dissolution in damp solvents^[21,22] and the reduction of the degree of dissociation of MP with increase in MP concentration^[12–14,22] were thoroughly considered. There is evidence that the complete MP dissociation in many non-aqueous solvents is rather complicated. Although the first step of the MP dissociation with the formation of MgClO₄⁺ and ClO₄⁻ runs in diluted solutions quite easily, the next-step dissociation of MgClO₄⁺ was estimated^[13] at 17 and 45% for 0.1 and 0.01 M solutions of MP, respectively, in acetonitrile at 25 °C.

It should be noted that between the change in the solubility of LP and MP in nine solvents^[24,25] a mutual proportionality has not been observed ($R = -0.45$). The solubility of LP in diethyl ether at 25 °C corresponds to a maximum value of 6.06 M, whereas the solubility of MP in diethyl ether amounts only to (6–9) × 10⁻³ M.^[24,25] There is also a considerable difference concerning the solvent influence on the enthalpy of solution of MP and LP ($R = 0.79$). Also, reliable correlations have not been noted between the values of enthalpy of solution of MP and a set of other physical characteristics of solvents, such as the relative permittivity, ε_r ($R = 0.018$), the donor number, DN, ($R = 0.47$), the solvatochromic parameter, E_T^N, ($R = -0.22$), analogous to that of LP.^[6] In acetone, ethyl acetate, acetonitrile, propylene carbonate, and nitromethane the sequential addition of MP to these

solutions in a calorimetric vessel leads to a substantial reduction of the exothermic effect of dissolution (Fig. 1).

The poor reproducibility of the heat of MP solution in acetonitrile (−44.3 ± 1.5 kcal mol⁻¹)^[21] is in agreement with our data of the average value of differential heat of solution (−44.2 ± 1.5 kcal mol⁻¹, Table 1). However, two independent series of measurements of the heat of solution in acetonitrile with different samples of repeatedly dried MP and solvent show a smooth common curvature (Table 1, Fig. 1) of the integral enthalpy of solution, with a limiting value of −47.3 ± 0.2 kcal mol⁻¹. An especially sharp influence of the salt concentration on the heat of solution of MP was observed for nitromethane (Fig. 2), which has the lowest normalized value of DN, equal to 0.07.

Previously, a significant concentration influence on the decrease of the exothermicity of LP solution in nitromethane and diethyl ether was noted,^[17] for which a sharp disbalance between the relative permittivity, ε_r, and normalized donor properties, DN, was observed. We were not able to determine the heat of solution of MP in ethylene glycol, because of the very slow rate of dissolution, and in diethyl ether because of the very low solubility.

Partial molar volumes

The partial molar volume of MP was calculated from the experimental densities of the solutions (Table 2).

Table 2. Experimental values of the solvent density (d_o , 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 (\bar{V}_{MP} , cm³ mole⁻¹), at 25 °C

Solvent	m	d	d_o	φ_{MP}
Water	0.01698	0.998000	0.997039	67.7
	0.02080	1.000134	0.997039	67.3
	0.05148	0.998602	0.997039	67.6
	0.09984	0.999678	0.997039	68.3
	0.15205	0.998309	0.997039	68.8
	0.2027	1.001985	0.997039	69.2
$\bar{V}_{MP} = 67.3 \pm 0.5; 67.0^a$				
Ethyl acetate	0.01306	0.896490	0.894371	46.7
	0.02055	0.897699	0.894370	46.8
	0.02579	0.898558	0.894371	46.4
	0.05221	0.902825	0.894370	46.7
	0.1097	0.912107	0.894341	46.2
	0.1514	0.918748	0.894370	46.9
0.2011	0.926810	0.894341	46.0	
$\bar{V}_{MP} = 46.6 \pm 0.3$				
Acetone	0.01968	0.787729	0.784273	-0.9
	0.05658	0.794222	0.784270	-1.3
	0.09857	0.801471	0.784273	0.9
	0.1325	0.807197	0.784273	3.2
	0.2034	0.819216	0.784273	5.1
	0.2161	0.821334	0.784270	5.5
$\bar{V}_{MP} = -2.4 \pm 0.6$				
Formamide	0.00925	1.130424	1.129064	82.3
	0.01012	1.130552	1.129064	82.2
	0.02087	1.132136	1.129064	82.0
	0.04015	1.134957	1.129064	82.1
	0.06135	1.138102	1.129064	81.5
	0.1028	1.145192	1.130063	81.2
	0.1480	1.151754	1.130061	81.2
	0.2062	1.160043	1.130056	81.5
$\bar{V}_{MP} = 82.3 \pm 0.3; 86^b$				
Ethylene glycol	0.03103	1.114897	1.110067	74.4
	0.07640	1.121885	1.110067	74.8
	0.1004	1.125656	1.110067	74.1
	0.1309	1.130233	1.110067	74.7
	0.1741	1.136382	1.110067	76.6
	0.1790	1.137043	1.110067	76.9
	0.2183	1.142910	1.110067	76.7
$\bar{V}_{MP} = 73.4 \pm 0.6$				
Diethyl ether	0.00464	0.708299	0.707625	25.3
	0.00525	0.708403	0.707625	21.1
	0.00528	0.708391	0.707625	25.7
$\bar{V}_{MP} = 24 \pm 3$				
Propylene carbonate	0.04688	1.208200	1.199524	57.0
	0.07732	1.213754	1.199524	57.5
	0.1083	1.219278	1.199524	58.3
	0.1522	1.227084	1.199524	58.9
	0.1772	1.231558	1.199524	58.9
	0.2691	1.247495	1.199524	59.8
$\bar{V}_{MP} = 56.7 \pm 0.3; 56.9^c$				

(Continues)

Table 2. (Continued)

Solvent	m	d	d_0	φ_{MP}
Acetonitrile	0.02009	0.779942	0.776718	21.3
	0.05140	0.784969	0.776699	20.7
	0.1058	0.793480	0.776668	23.7
	0.1238	0.796268	0.776615	23.5
	0.1486	0.800165	0.776615	23.6
	0.1946	0.807253	0.776674	25.9
	0.2102	0.809618	0.776615	25.9
	0.2646	0.817827	0.776615	27.3
	0.2750	0.795285	0.776615	27.2
		$\bar{V}_{MP} = 20.3 \pm 0.5$		
Nitromethane	0.00828	1.131884	1.130481	64.8
	0.03159	1.135733	1.130481	67.0
	0.04150	1.137338	1.130481	67.7
	0.05165	1.138958	1.130481	68.5
	0.05987	1.140265	1.130481	69.0
	0.07064	1.141970	1.130481	69.5
		$\bar{V}_{MP} = 63.9 \pm 0.3^d$		
Dimethyl sulfoxide	0.00961	1.097012	1.095381	62.1
	0.02023	1.098783	1.095366	62.8
	0.03547	1.101377	1.095366	62.2
	0.04964	1.103748	1.095366	62.6
	0.09760	1.111732	1.095366	63.1
	0.1021	1.112530	1.095366	62.8
	0.1531	1.120960	1.095366	63.0
	0.2059	1.129599	1.095366	63.2
		$\bar{V}_{MP} = 62.3 \pm 0.2; 63.0^e$		
<i>N,N</i> -Dimethyl formamide	0.04154	0.951005	0.943886	43.8
	0.1022	0.961296	0.943985	45.5
	0.1526	0.969498	0.943985	47.6
	0.2045	0.977918	0.943985	48.5
		$\bar{V}_{MP} = 42.6 \pm 0.5; 43.1^c$		

^a Ref. [9], ^b Ref. [8], ^c Ref. [11], ^d Limit value was calculated from: $\varphi_{MP} = \bar{V}_{MP} + a \times m^{0.5} + b \times m$; ^e Ref. [10].

It should be noted that the experimental measurements of the enthalpy of solution and the PMV values cover different concentration ranges: 1–10 and 10–250 mmol L⁻¹, respectively. For non-polar molecules, it is often easier to determine the value of PMV of a solute from the slope of linear dependence of the density on the concentration of solution. 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), Eqns (6)–(9) can be obtained:

$$1000 - (1000/c - c_A M_A)/d_0 = c_A \varphi_A \quad (6)$$

$$(1000 + m_A M_A)/d = 1000/d_0 + m_A \varphi_A \quad (7)$$

$$1000/d = 1000/d_0 + w_A (\varphi_A - M_A/d_0) \quad (8)$$

$$d = d_0 + T_A (1 - \varphi_A d_0/M_A) \quad (9)$$

Here d_0 and d are the densities of the solvent and solution, and M_A is the molar mass of the solute. Eqns (6)–(9) can be transformed to direct calculation of the value φ_A for each concentration. In this work, clear linear relationships between φ_A

and $m_A^{0.5}$ were observed for all solutions of MP in the range of concentrations studied (Fig. 3). The limit values \bar{V}_{MP} were calculated at $m_A \rightarrow 0$ (Table 2).

The data obtained for \bar{V}_{MP} in water, formamide, DMSO, propylene carbonate and DMF are in a good agreement with the literature data (Table 2).

Note the absence of a linear correlation between the values of $\Delta_{sol}H_{MP}$ and \bar{V}_{MP} for MP in the studied media ($R = -0.02$), which is analogous to that of LP ($R = 0.07$).^[6] On the other hand, the changes of \bar{V}_{MP} in the solvents studied (Table 1) and \bar{V}_{LP} ^[6] are largely proportional (Fig. 4, $R = 0.975$, $n = 11$):

$$\bar{V}_{MP} = (-1.86 \pm 4.10) + (1.70 \pm 0.12) \times \bar{V}_{LP} \quad (10)$$

The change in the values of \bar{V}_{MP} in the solvents studied, with the exception of ethyl acetate ($\epsilon_r = 6.08$) and diethyl ether ($\epsilon_r = 4.33$), is proportional to the coefficient of the electrostriction of the solvent [$\partial(1/\epsilon_r)/\partial p$, $R = 0.91$]. A similar dependence ($R = 0.94$) was observed previously for the solutions of LP in the polar solvents with high relative permittivity ($\epsilon_r > 20$).^[23] It should be noted that the slope of the dependence of the volume

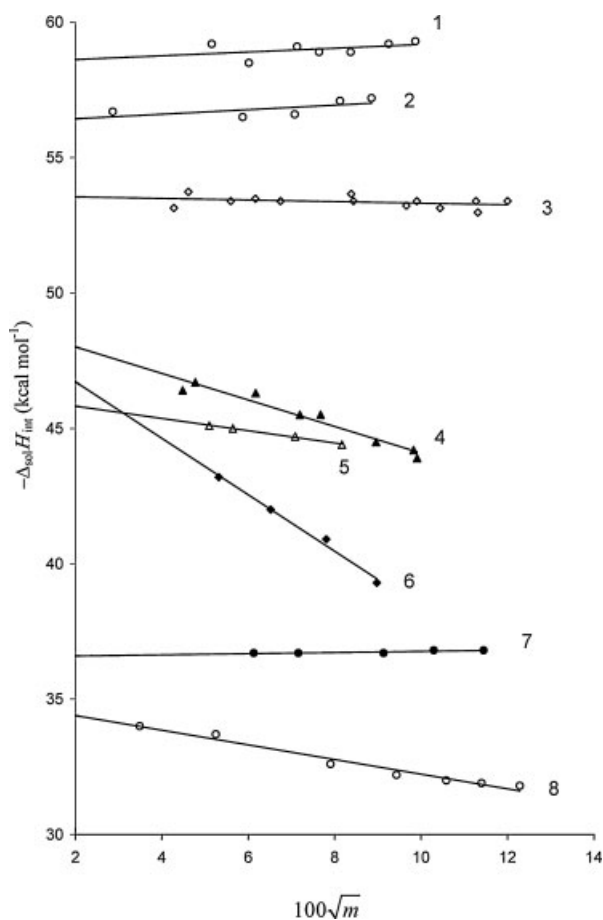


Figure 1. Dependence of the integral enthalpy of solution ($\Delta_{\text{sol}}H_{\text{int}}$) of $\text{Mg}(\text{ClO}_4)_2$ on the square root of its molal concentration ($100\sqrt{m}$) in: (1) *N,N*-dimethyl formamide; (2) dimethyl sulfoxide; (3) formamide; (4) acetonitrile; (5) acetone; (6) propylene carbonate; (7) water; (8) ethyl acetate, at 25 °C

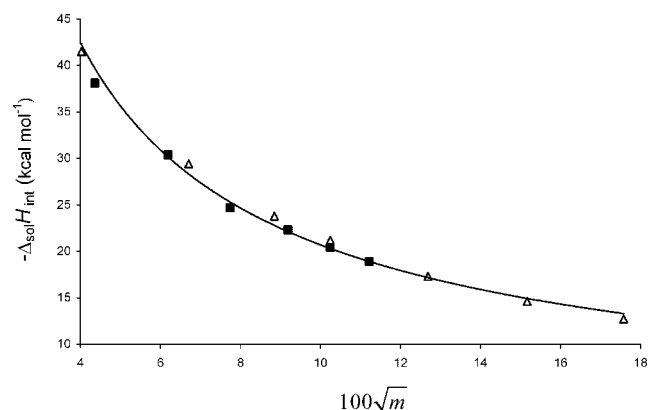


Figure 2. Dependence of the integral enthalpy of solution of $\text{Mg}(\text{ClO}_4)_2$ in nitromethane ($\Delta_{\text{sol}}H_{\text{int}}$) on the square root of its molal concentration ($100\sqrt{m}$). The points (■) and (Δ) correspond to data of repeated measurements of this work at 25 °C

of electrostriction on the pressure coefficient of the relative permittivity (\bar{V}_{LP} vs. $\partial(1/\epsilon_r)/\partial p$, Table 3) is almost 20 times higher for solvent-separated ions of LP than for contact ion pairs.^[23] Mg^{2+} and Li^+ cations have nearly the same crystallographic radii (0.078 nm), but substantially different electronic structures.^[26] It

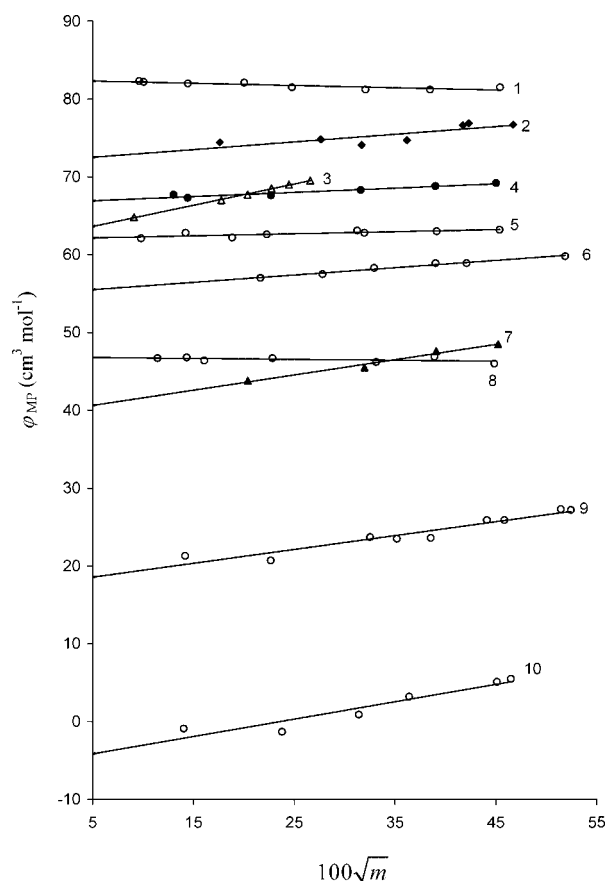


Figure 3. Dependence of the apparent molar volume of solution (ϕ_{MP}) of $\text{Mg}(\text{ClO}_4)_2$ on the square root of its molal concentration ($100\sqrt{m}$) in: (1) formamide; (2) ethylene glycol; (3) nitromethane; (4) water; (5) dimethyl sulfoxide; (6) propylene carbonate; (7) *N,N*-dimethyl formamide; (8) ethyl acetate; (9) acetonitrile; (10) acetone, at 25 °C

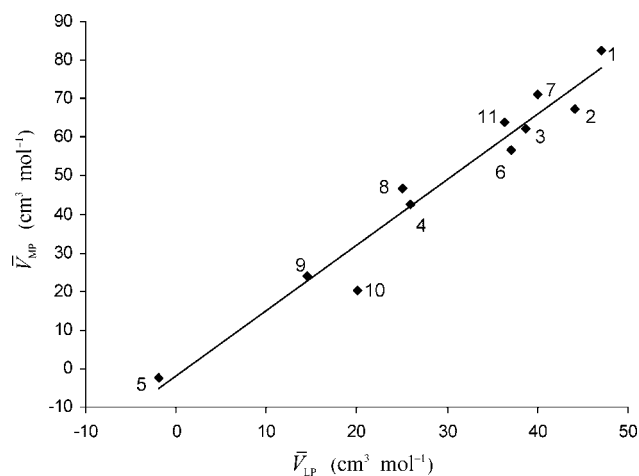


Figure 4. Solvent effect on the values of \bar{V}_{MP} and \bar{V}_{LP} at 25 °C. The numbers refer to the serial numbers of the solvents given in Table 3

follows from the data obtained that the electrostriction of solvent in MP solutions is significantly larger than that for LP (Table 3).

This can be explained by the greater charge density of the cation ($26.8 \times 10^{-20} \text{ C} \text{ \AA}^{-3}$ for Mg^{2+} and $12.1 \times 10^{-20} \text{ C} \text{ \AA}^{-3}$ for Li^+),^[31] and by the larger number of solvent molecules in the first

Table 3. Values of partial molar volumes of magnesium perchlorate, \bar{V}_{MP} , and lithium perchlorate, \bar{V}_{Li^+} , and magnesium cation, $\bar{V}_{Mg^{2+}}$ ($\text{cm}^3 \text{mol}^{-1}$), in 12 solvents, the enthalpies of solution of these salts ($\Delta_{\text{sol}}h_{\text{mp}}$ and $\Delta_{\text{sol}}h_{\text{lp}}$, kcal mol^{-1}), the isothermal compressibility coefficient of solvent, β_T (bar^{-1}), the electrostriction parameter $\partial(1/\epsilon_r)/\partial p$, the relative permittivity, ϵ_r , the normalized donor number, DN, and solvatochromic parameter E_{T}^{N} at 25 °C

No.	Solvent	ϵ_r^a	DN ^a	$E_{\text{T}}^{\text{N}a}$	$10^6 \beta_T^b$	$10^6 \partial(1/\epsilon_r)/\partial p^c$	\bar{V}_{MP}^d	\bar{V}_{LP}^e	$\bar{V}_{ClO_4^-}$	$\bar{V}_{Li^+}^f$	$\bar{V}_{Mg^{2+}}^d$	$\Delta_{\text{sol}}H_{\text{MP}}^g$	$\Delta_{\text{sol}}H_{\text{LP}}^h$
1	Formamide	111	—	0.775	40.3	0.45; (0.36)	82.3; (86, 104) ^f	47; 48.3 ^f	54 ^e	-7	-25.7	-45.5	-10.8
2	Water	80.1	—	1.00	45.7	0.57; (0.57)	67.3; 67.0 ^g	44.2; 43.2 ^g	50.6 ^f ; 49.6 ^g	-6	-33.9; -32.1 ^g	-36.6; -37.5 ^g	-6.3
3	Dimethyl sulfoxide	47.2	0.77	0.444	52.6	—; (1.1)	62.3; 63.0 ^h	38.7; (41; 92) ^f	44 ^f	-4	-25.7; -25 ^f	-56.8	-18.0
4	<i>N,N</i> -Dimethylformamide	36.7	0.80	0.386	64.0	—; (1.7)	42.6; 43.1 ⁱ	26.0	35 ^f	-10	-27.4; -26.9 ^f	-58.7	—
5	Acetone	20.5	0.44	0.552	129.3	5.6; (6.4)	-2.4	-2.0 ^e	20 ^e	-22	-42.4	-45.6	-15.8
6	Propylene carbonate	56.9	0.39	0.55	51.2	—; (0.87)	56.7 56.9 ^j	37.1 ^f	44 ^f	-7	-31.3; -31.1 ^f	-45.2	—
7	<i>N</i> -Methylformamide	182	—	0.722	59.4	—; (0.33)	71 ^f	40 ^f	50 ^f	-10	-29 ^f	—	—
8	Ethyl Acetate	6.08	0.44	0.228	113.2	19.3 (18.8)	46.6	25.1	—	—	—	-34.0	-8.9
9	Diethyl ether	4.20	0.49	0.117	194.5	47; (44)	24	14.5	—	—	—	insoluble	-6.2
10	Acetonitrile	36.6	0.36	0.460	113	3.1; (3.1)	20.3	20.1	24 ^e	-20	-27.7	-47.3	-9.2
11	Nitromethane	37.3	0.07	0.481	71.7	2.4 (1.9)	63.9	36.4	46 ^e	-18	-28.1	-64.5	-14.8
12	Ethylene glycol	37.7	—	0.790	36.7	—; (1.0)	73.4	—	—	-8	—	—	—
	Standard state	—	—	—	—	—	85.4 ^j	43.8 ^j	57.5 ^k	—	—	—	—

^a Ref. [27], ^b Ref. [28], ^c Ref. [29], ^d This work; ^e Ref. [6], ^f Ref. [8], ^g Ref. [9], ^h Ref. [10], ⁱ Ref. [11], ^j Calculated from the data^[30] on the density of the crystals of MP and LP; ^k Calculated from the data^[30] for 100% HClO₄ (25 °C).

solvation shell (6 and 4, respectively).^[9] Using the value of van der Waals volume of perchlorate ion ($33.1 \text{ cm}^3 \text{ mol}^{-1}$),^[26] the calculated value of the packing coefficient (V_w/V) of crystalline MP (0.788) is almost the same as for LP (0.783). PMV values of MP, like that of LP in all studied media, are significantly lower than in the crystal (Table 3). The changes of \bar{V}_{MP} in the solvents studied (Table 3) for MP ($84.7 \text{ cm}^3 \text{ mol}^{-1}$) are significantly higher than that for LP ($50.3 \text{ cm}^3 \text{ mol}^{-1}$). All these results are in accordance with the larger catalytic activity of MP solutions as compared to solutions of LP.^[2,3]

CONCLUSIONS

A proportionality between the solvent influence on the change of partial molar volume of magnesium perchlorate, \bar{V}_{MP} , and lithium perchlorate, \bar{V}_{LP} , was observed (linear correlation coefficient $R=0.975$). On the other hand, correlations between enthalpies of solution and the PMV values are absent for magnesium perchlorate ($R=-0.02$), as well as for lithium perchlorate ($R=0.07$). The calculated values of $\bar{V}_{Mg^{2+}}$ are more negative as compared to \bar{V}_{Li^+} . This corresponds to a significantly greater disturbance of molecules in the solvation shell of the magnesium cation, which explains the higher catalytic activity of solutions of magnesium perchlorate.

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