Solvent effect on the heat of solution and partial molar volume of some non-electrolytes and lithium perchlorate

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ABSTRACT: For several non-electrolytes and for lithium perchlorate the solvent effect on the heat of solution and partial molar volumes was studied. In the absence of the donor–acceptor and electrostatic interactions, clear proportionality can be seen only in the alkane solutions and these changes are defined by the non-alkane component. For solutions of π-acceptor (tetracyanoethylene) and ν-acceptor (gallium chloride) in the presence of π,π-, π,ν- and n,ν-complexes, the relation between the changes of interaction energy and the values of the partial molar volumes can be seen. The maximum change in the value of partial molar volumes (up to $50\,cm^3\,mol^{-1}$) was noted for lithium perchlorate in ten solvents. The volume change is proportional to the compressibility coefficients of the solvents and correlates less with the values of heat of solution and solvent permittivity. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: partial molar volume; solution enthalpy; electrostriction; electrolytes; non-electrolytes

INTRODUCTION

The application of high external pressure leads to a significant growth in the rate and equilibrium constants of reactions, accompanied by a volume decrease on going to the transition state ($\Delta V^{\neq}$) or the product (ΔV_0).[1–3]

$$(\partial \ln k/\partial p)_T = -1/RT(\partial G^{\neq}/\partial p)_T = -\Delta V^{\neq}/RT \quad (1)$$

$$(\partial \ln K/\partial p)_T = -1/RT(\partial G_0/\partial p)_T = -\Delta V_0/RT \quad (2)$$

The question of the solvent effect on the changes in the molar volumes of the reagents, activated complex and products is key to clarifying the reasons for the changes of rate and equilibrium in conditions of enhanced pressure. The volume of the diluted solution can be presented as:

$$V = V_A N_A + V_S N_S + (V_S^* - V_S)z N_A \quad (3)$$

where V_A, V_S and V_S* are the molar volumes of the dissolved compound, neat solvent in bulk and the solvent in the solvation shell, respectively, z is the number of

solvent molecules in the solvation shell of the dissolved compound (A) and N_A and N_S are the numbers of moles of the dissolved compound and the solvent, respectively. It follows from this expression that the partial molar volume (PMV) of the compound (V_A) in the diluted solution is determined by:

$$\partial V/\partial N_A = V_A + z(V_S^* - V_S) \quad (4)$$

The observable value of the PMV can be presented as the sum of contributions:

$$V_A = V_W^A + V_{el}^S + V_{str}^S + V_{disp}^S + V_{sp.}^S \quad (5)$$

Here V_W^A is van der Waals volume of the compound (A), V_{el}^S is the volume contribution caused by solvent electrostriction, V_{str}^S is the volume contribution of the structure and the packing changes, V_{disp}^S is the contribution caused by the difference in the dispersion interaction energy of the molecules S–S and A–S and V_{sp}^S is the contribution caused by formation or destruction of the complexes with the solvent.[1–7]

It is clear that for a mechanistic description of the degree of bond cleavage or formation in the transition state it is necessary to consider first of all the change in the V_W contribution. But the solvation contribution $z(V_S^* - V_S)$ may even exceed the value of the activation volume ($\Delta V_W^{\neq}$) or reaction volume ($\Delta V_{0,W}$), which may be reflected or not by the sign.[8,9] The maximum contribution of the solvent electrostriction can be seen in the electrolyte solutions.[4–7] Brower proposed considering the ratio of the difference in the activation volumes in two solvents of very different polarities to the difference in

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the molar volumes of similarly sized ions in the same solvents as a measure of the charge separation in the transition state of the reaction.[10] The change of volume or heat during the process of solution, related to the mole number of the dissolved compound, characterizes the change of these parameters for the whole system, both the dissolved compound and the solvent. From this point of view, when a correlated change of PMV and other parameters takes place it would be useful to predict the change of PMVs and the values of the activation volume ($\Delta V^{\neq}$) to choose the optimal conditions for carrying out the reaction. It should be mentioned that the experimental problems of thermodynamic parameter determination occur even in non-electrolyte solutions, such as alcohols in alkanes[11] and especially in electrolyte solutions.[7]

In this work the solvent effect on the PMV and solution enthalpy of several liquid and solid compounds (not capable and capable of forming the specific π,π-, n,π-, π,ν- and n,ν-interactions) and for 1:1 electrolyte—lithium perchlorate is considered. In addition, all studied non-polar, polar and ionic compounds can be represented as models of appropriate transition states. The solvent effect on the enthalpy level and molar volume of these kinds of transition states can be useful for prediction of the pressure effect on the rate and equilibrium. Lithium perchlorate was chosen because of its good solubility in a wide range of n-donor solvents (e.g. up to 6 M in diethyl ether[12]) and its high dissociation level.

RESULTS AND DISCUSSION

The values of PMVs were determined for water and several alcohols in organic solvents[11] and for numerous reagents and products when calculations of the reaction volumes were made.[1–3] It was shown using numerous examples that the enthalpy of the intermolecular interaction of the different organic compounds is minimal in the media of alkanes and cycloalkanes.[13,14] As follows from the data in Table 1, the value of the PMV for compounds **2–5** in cyclohexane is always greater than in neat liquids, and the PMV for cyclohexane (**1**) in solutions **2–8** is also greater than in cyclohexane itself. The value of the slope (0.604) of the correlation (Fig. 1) of the solution enthalpy for compounds **1–8** in cyclohexane and for cyclohexane in solvents **1–8** is in agreement with the proposal that during the solution of cyclohexane solvents **2–8** provide cyclohexane with their fragments, which have the weakest energy of the intermolecular interactions.[13,14]

On a qualitative level, the intermolecular interaction energy of any organic compound will lessen with its dissolution in alkane or with the dissolvation of alkane in it, and the loss always takes place due to the second component (non-alkane). According to the aforesaid, all the volume effects of solutions containing cyclohexane are caused by the increase of the intermolecular distance for compounds **2–8**. This is confirmed by the clear

Table 1. Partial molar volumes (V, cm³ mol⁻¹), solution enthalpies[a] ($\Delta_{sol}H.$, kcal mol⁻¹) and relative enthalpies of solvent evaporation ($\delta^2 = \Delta_{vap}H/V$, cal cm⁻³) of the compounds at 25°C

Solvent (δ^2)	(1)		(2)		(3)		(4)		(5)	
	V	$\Delta_{sol}H$	V	$\Delta_{sol}H$	V	$\Delta_{sol}H$	V	$\Delta_{sol}H$	V	$\Delta_{sol}H$
Cyclohexane (**1**) (72.7)	108.74	0	83.68	0.66	90.56	2.00	57.89	3.60	104.53 / 104.38^c	1.74
Chloroform (**2**) (90.5)	110.92	0.57	80.68	0	84.20	−2.40	51.40	−1.05	98.96	−2.10
1,4-Dioxane (**3**) (104.4)	111.94	1.60	80.68	−1.15	85.80	0	52.16	—	97.54	0.12
Acetonitrile (**4**) (148.2)	112.27	2.16	80.01	−0.33	84.23 / 84.26^c	—	52.85	0	97.28	0.03
Ethyl acetate (**5**) (85.3)	113.23 / 113.56^c	1.22	81.15 / 80.94^c	−1.40	85.59 / 85.29^c	0.12	51.99 / 52.24^c	—	98.49	0
Tetrachloromethane[b] (**6**) (79.8)	109.84	0.16	81.56	0.22	85.28	−0.17	53.05	1.50 / 1.35^c	99.42	0.01
Benzene[b] (**7**) (90.5)	111.41	0.81	81.45	−0.29	85.22	−0.11	51.82	0.60	99.17	0.10
Toluene[b] (**8**) (85.0)	110.93	0.53	80.82 / 80.97^c	−0.64	85.51	—	51.32	—	98.66	0.12

[a] Solution enthalpies values are taken from Refs 13–16.
[b] The values of solution enthalpy for tetrachloromethane (0.60), benzene (0.95) and toluene (0.72 kcal mol⁻¹) in cyclohexane are taken from Ref. 15.
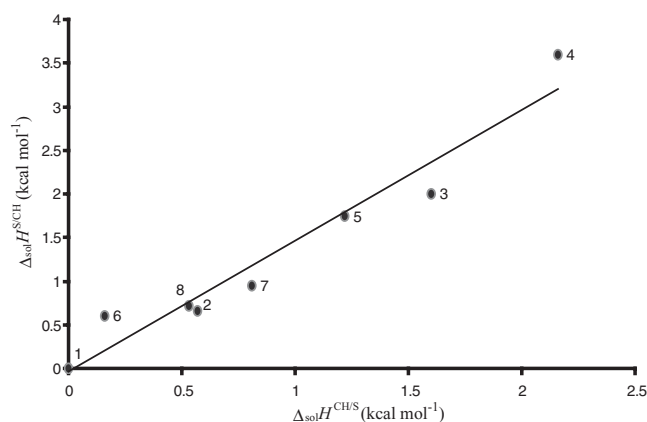[c] The results of the check measurements with freshly re-purified solutions.

Figure 1. Relation between solution enthalpy of cyclohexane in **1**–**8** ($\Delta_{sol}H^{CH/S}$, kcal mol^{-1}) and solution enthalpy of **1**–**8** in cyclohexane ($\Delta_{sol}H^{S/CH}$, kcal mol^{-1}). Numbers correspond to Table 1

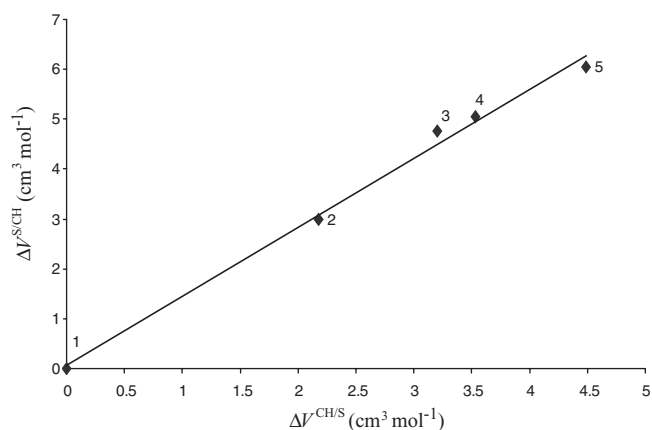**Figure 2.** Relation between the changes of partial molar volumes of cyclohexane in **1**–**5** ($\Delta V^{CH/S}$, cm^3 mol^{-1}) and **1**–**5** in cyclohexane ($\Delta V^{S/CH}$, cm^3 mol^{-1}). Numbers of compounds correspond to Table 1

Figure 3. Relation between the change of the relative volume [$(V - V_S)/V_S$] on the formation of solutions containing cyclohexane and the enthalpy of these solution processes ($\Delta_{sol}H$, kcal mol^{-1}). Points 1–8 correspond to cyclohexane solutions in solvents **1**–**8** from Table 1. Points 9–12 correspond to solutions of **2**,**3**,**4** and **5** (Table 1) in cyclohexane

proportionality ($r = 0.994$, Fig. 2) in the changes of the PMV of the compounds in these solutions.

For all the solutions containing cyclohexane the correlation between solution enthalpy ($\Delta_{sol}H$) and the relative change of volume ($\Delta V_A/V_A$) can be seen (Fig. 3). For the other studied solutions (Table 1) the relationship between the heat and volume effects cannot be seen. The solution of chloroform, capable of forming a hydrogen bond with n-donors, is accompanied by heat emission in the studied solvents (except cyclohexane and tetrachloromethane) but a small decrease of PMV can be seen only in acetonitrile. In spite of the significant *exo*-effect of the process of solution of ethyl acetate in chloroform ($\Delta_{sol}H = -2.10$ kcal mol^{-1}), its PMV still grows ($\Delta V = 0.47$ cm^3 mol^{-1}). On the other hand, the heat of solution for ethyl acetate in solvents **3**–**8** is less than 0.12 kcal mol^{-1} but the volume changes in these media differ by 2 cm^3 mol^{-1}. All these volume changes may be
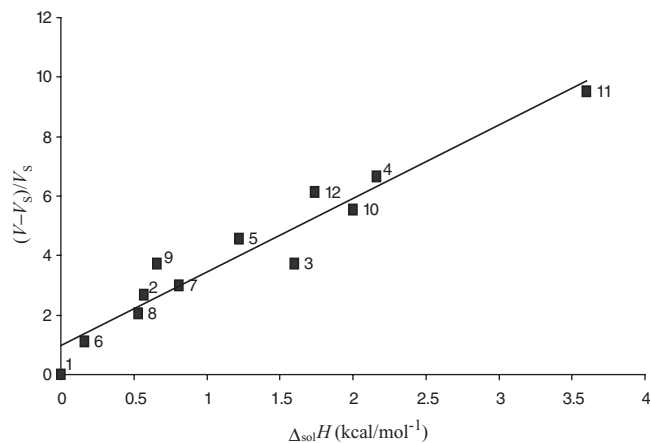
ascribed to the differences in the dispersion interaction energy (V_{disp}^S) and probably also to the changes of the solvent packing density (V_{str}^S) on the solution formation.

For solutions of anthracene (**9**), 9,10-dihydroanthracene (**10**), *trans,trans*-1,4-diphenylbutadiene (**11**) and maleic anhydride (**12**) in a series of solvents (Table 2) there are no specific interactions, therefore a small and irregular change in the values of PMVs and solution enthalpy takes place. Similar conclusions were obtained for numerous reagents and adducts of the Diels–Alder reaction.[1–3]

For tetracyanoethylene solutions the formation of donor–acceptor π,π-complexes with aromatic solvents leads to similar PMV changes, as in the case of the formation of π,ν-complexes of gallium chloride with these solvents (Table 2). The formation of the weaker n,π-complexes between n-donor solvents and tetracyanoethylene leads to irregular changes of the analyzed parameters. For gallium chloride the transfer from π-donor to n-donor solvents is accompanied by a strong *exo*-effect of solution but a relatively small additional decrease of PMV value (Table 2). The last fact may be explained by the limiting approach of the molecules in 1:1 n,ν-complex, with the formation of a strong chemical bond. The unusually high PMV value of gallium chloride in ethyl acetate (Table 2) is probably caused by the conformation mobility of the molecules of this solvent.[18] The PMV value of tetracyanoethylene in π-donor solvents is close to its molar volume in the crystal, but the PMV of gallium chloride in π- and especially in n-donor solvents is sufficiently less than its molar volume in the crystal (Table 2).

It can be concluded from the data collected in the literature[1–3,12] and in Tables 1 and 2 that the PMV values of non-electrolytes in the absence of specific interactions

Table 2. Partial molar volumes (V, cm³ mol⁻¹) and solution enthalpies ($\Delta_{sol}H$, kcal mol⁻¹) for anthracene (9), 9,10-dihydroanthracene (10), trans,trans-1,4-diphenylbutadiene (11), maleic anhydride (12), tetracyanoethylene (13) and gallium chloride (14) at 25 °C

Solvent	(9)		(10)		(11)		(12)		(13)		(14)	
	V	$\Delta_{sol}H$	V	$\Delta_{sol}H$	V	$\Delta_{sol}H$	V	$\Delta_{sol}H$	V	$\Delta_{sol}H$	V	$\Delta_{sol}H$
Benzene	—	5.90	—	—	199.3	5.76	72.2	4.01	108.4	3.56	74.8	2.29
Toluene	158.0	5.92	163.8	4.66	199.8	5.71	71.1	3.92	104.6	2.31	68.7	0.60
o-Xylene	—	5.73	—	—	199.8	5.83	71.5	3.61	102.1	0.33	67.1	-0.19
Mesitylene	—	—	—	—	199.7	6.07	70.8	—	98.1	-0.65	64.8	-1.70
1,2-Dichloroethane	—	5.95	—	4.78	202.7	5.11	71.1	3.80	107.8	5.09	73.4	1.22
Ethyl acetate	153.7	6.00	160.9	6.00	195.2	5.38	—	2.72	112.1	2.20	70.7[b]	-15.7
Acetonitrile	158.2	6.69	164.8	4.59	200.0	7.65	70.4	3.13	110.0	3.63	61.9	-17.0
1,4-Dioxane	159.5	5.40	165.6		200.4	5.11	—	2.48	105.7	1.03	61.5	-17.7
$V_{cryst.}$[a]	141.6		147.1		179.2		65.4		97.5		71.3	
$\Delta V_{av.}/V_{cryst.}$	0.11		0.11		0.11		0.09		0.12		—	

[a] Calculated according to the data of Ref. 17.
[b] Possible reasons for the unusually high PMV value of gallium chloride are discussed in Ref. 18.

with the solvent change by less than 5% because of the differences in the packing density (V_{str}^S) and in the dispersion interaction energy (V_{disp}^S). The dissolution of the crystal compounds 9–12 (Table 2) is accompanied by *endo*-effects and enlargement of the molar volume. It should be noted that in the absence of the specific interactions the average value of the ratio of the molar volume in solution to the molar volume in the crystal ($V/V_{cryst.}$) is relatively constant (1.09–1.12, Table 2). The results (presented in Tables 1 and 2) do not agree with Parker's supposition[4,19] that the PMV of non-electrolytes changes in proportion to the solvent compressibility. The data for tetracyanoethylene and especially for gallium chloride in the studied solutions show that complex formation or destruction during the reaction leads to significant differences in the volume parameters of activation and reaction depending on the solvent properties.[20] For solutions of alkali metal halides in water and especially in organic solvents a significant decrease of PMV of these salts in comparison with their molar volume in crystals, caused by the solvent electrostriction, was observed.[4,7,21] But the row of organic solvents available for such salt solutions is limited by their low solubility. The proposal that extrapolation of the measured molar parameters to a zero concentration of the solute corresponds to the partial parameters at complete salt dissociation needs to be verified.[21] In *n*-donor organic solvents strong stabilization of the small cation and sufficient stabilization of the large size anion takes place.[4,19,21–23] In Table 3 the results of PMV measurements and heats of solution for lithium perchlorate in the row of solvents are collected.

As follows from the Table 3 data, the solution of lithium perchlorate in all the studied solvents is accompanied by heat emission and a significant decrease of PMV. The absence of a correlation ($R = 0.158$) between the solution enthalpy and the donor numbers of the solvents corresponds to the fact that lithium perchlorate in the studied solutions does not behave as a typical Lewis acid.[27] For complexes with Lewis acids such as halides of Al, Fe, B, Ga or Sb, the contribution of the donor–acceptor bonding with *n*-donor centers of the solvents is dominant, whereas for lithium perchlorate the main contribution to the stabilization energy is brought about by the electrostatic contribution of the interaction energy of Li⁺ cation with the solvent.[4,7,21–23,27,28]

The change of the PMV values of lithium perchlorate does not correlate with the change in solution enthalpy ($R = 0.35$). A trend in the growth of PMV value together with the growth of media permittivity takes place ($R = 0.89$). More definite proportionality ($R = 0.95$) can be seen between the change of lithium perchlorate PMV in solution and the change in the compressibility coefficient of the solvent. The data obtained may be considered as experimental confirmation of the fact that the change of lithium perchlorate PMV value in the studied solutions

Table 3. Partial molar volumes (V, $cm^3 mol^{-1}$) and their changes (ΔV), solution enthalpies ($\Delta_{sol}H$, $kcal\,mol^{-1}$) of lithium perchlorate in a series of solvents, permittivity (ε), donor numbers (DN) and compressibility coefficients (β_T, bar^{-1}) at 25 °C

Solvent	V^a	ΔV	$\Delta_{sol}H$	ε^b	DN^b	$10^6\,\beta_T{}^b$
Diethyl ether	14.5	33.8	−6.2	4.33	0.49	186.5; 190[c]
Tetrahydrofuran	23.6	24.7	−11.7	7.52	0.52	116[c]
Ethyl acetate	25.1	23.2	−8.9	6.08	0.44	113.2; 112[c]
Dimethylsulfoxide	38.7	9.2	−18.0	47.2	0.77	49.0[d]
Acetonitrile	20.1	28.2	−9.2	36.6	0.36	113[c]
Nitromethane	36.4	11.9	−14.8	37.3	0.07	71[c]
Methanol	24.6	23.7	−12.4	33.0	0.66	121.4; 125[c]
Formamide	48.3	0	−10.8	100.5	—	40.0[c]
Water	44.2	4.1	−6.3[e]	80.1	—	45.8; 46.6[c]

[a] Molar volume of lithium perchlorate in crystals is $43.8\,cm^3\,mol^{-1}$ (from Ref. 17).
[b] According to the data of Ref. 24.
[c] Calculated using the data on the sound velocity in these media at 25 °C (from Ref. 25).
[d] According to the data of Ref. 26.
[e] According to the data of Ref. 7.

is controlled by the electrostriction of the solvent in the solvation shell.

$$V_{LiClO_4} = (52.6 \pm 2.8) - (0.228 \pm 0.028)\beta_T;$$
$$R = 0.948; N = 9; \beta_T \text{ in M bar}^{-1} \tag{6}$$

The enthalpy of the electrolyte transfer from one solvent to another allows calculation of the enthalpies of the ions transfer, commonly relatively to water.[23,29] A similar approach was proposed for determination of the PMV values of the ions.[4,7,21] It is clear that the solution enthalpy values of ion or the PMV of ion should be constant in the selected solvent independent of the source salt of this ion. This 'consensus technique'[4,7,23] allows the validity of experimental data determination to be checked. As an example, the changes in the solution enthalpy in the solvent row for lithium perchlorate (Table 3) and for sodium iodide[23] were found to be proportional:

$$\Delta_{sol}H_{LiClO_4} = -3.47 + 1.51\Delta_{sol}H_{NaI};$$
$$R = 0.977 \tag{7}$$

A similar solvent effect on the change of PMV values of lithium perchlorate (Table 3), sodium iodide and potassium iodide should be noted:[4,7,21]

$$V_{LiClO_4} = (8.6 \pm 1.2) + (0.774 \pm 0.052)V_{KI};$$
$$R = 0.997 \tag{8}$$

$$V_{LiClO_4} = (15.2 \pm 0.8) + (0.817 \pm 0.030)V\text{NaI};$$
$$R = 0.992 \tag{9}$$

The density, viscosity and conductivity of lithium perchlorate solutions in diethyl ether were determined in a wide range of concentrations (up to 6 M).[12] Over the

whole range the slope $\partial d/\partial C$ increases smoothly with dilution, giving a limiting value (0.096) that corresponds to the PMV value in ether, equal to $15\,cm^3\,mol^{-1}$. The PMV values obtained over the range of diluted solutions in ether ($14.5\,cm^3\,mol^{-1}$, Table 3) are in good accordance. The concentration dependence of the apparent molar volume (φ) of lithium perchlorate in dilute solutions was found only in acetone in this work (Table 3). The calculated PMV value from the dependence of $\varphi - m^{1/2}$ in acetone is $-2.0\,cm^3\,mol^{-1}$. The values for the PMV of Li^+ (-62) and ClO_4^- ($20\,cm^3\,mol^{-1}$) in acetone picked out in a review[7] were calculated on the basis of PMV data for LiJ (lithium iodide) ($-31\,cm^3\,mol^{-1}$, Ref. 30) and $NaClO_4$ ($4\,cm^3\,mol^{-1}$, Ref. 5) in acetone. From these PMV values of ions in acetone the calculated value for the PMV of lithium perchlorate in acetone ($-22\,cm^3\,mol^{-1}$) is $20\,cm^3\,mol^{-1}$ less than the value obtained in our work ($-2\,cm^3\,mol^{-1}$, Table 3). On the other hand, the difference in the values for the PMV of $NaClO_4$ ($4\,cm^3\,mol^{-1}$, Ref. 5) and $LiClO_4$ in acetone ($-2\,cm^3\,mol^{-1}$, Table 3) closely correspond[7] to the difference in the PMV of Na^+ and Li^+ cations in the big series of the solvents ($6 \pm 2\,cm^3\,mol^{-1}$).

The changes in the PMV of potassium iodide and sodium iodide,[4,7] as well as lithium perchlorate (Table 3), correlate better with the compressibility coefficient change ($R \geq 0.96$). As follows from the Table 2 data, in the absence of specific interactions the crystal volume increases approximately by 10% during the solution process. This allows an estimate to be made of the overall decrease of the solvent volume in a dilute solution (ΔV_S) that contains one mole of lithium perchlorate (Table 3). If we consider a PMV decrease of the salt as a result of compression of only one mole of the solvent in the solvation shell, as in the usual n,v-complex of an n-donor solvent with a Lewis acid (ratio 1:1), then the volume of the compressed solvent should be much less than its van der Waals volume, which seems unrealistic. Thus, the value of the coordination number z (in Eqn (4)) should be

more than unity. Hence lithium perchlorate in solution differs sharply from *n,v*-complexes with soft Lewis acids, where *z* is equal to unity.[27]

CONCLUSION

It follows from the data obtained, that for non-electrolytes the clear relationship between PMV change and solution enthalpy can be seen only for solutions containing alkanes and for molecular complex formation. From the comparisons made, it can be seen that the contribution of electrostriction of the media on the value of the lithium perchlorate PMV is determined not only by the value of the solvent permittivity but also (and more significantly) by its compressibility.

Available data on the free energy, enthalpy and entropy of electrolyte solvation have been collected in several reviews.[19,22,23] From the data obtained in this work it follows that the change of solution enthalpy corresponds qualitatively to the PMV change only in those cases when the enthalpy change controls the change of the free energy of solvation.

EXPERIMENTAL

All solvents were purified by known methods[31] and distilled just before measurement. Anthracene, 9,10-dihydroanthracene and *trans,trans*-1,4-diphenylbutadiene (Aldrich) were purified by column chromatography with neutral alumina oxide in a benzene–hexane (1:6) eluent. Maleic anhydride was purified by distillation. Tetracyanoethylene (Aldrich) was sublimed in a vacuum (100 °C, 20 Pa). Gallium chloride was obtained by chlorination of the metallic gallium in a flow of dry hydrogen chloride at 170 °C, with subsequent vacuum distillation.

The pure lithium perchlorate was dried continuously (150–180 °C, 50 Pa) until the melting point was no lower than 233 °C.

The apparent molar volume (φ) of the dissolved compound (A) in the solvent (S) can be calculated by the additivity assumption:

$$\varphi = 1000 \cdot (d_0 - d)/(m_A \cdot d_0 \cdot d) + M_A/d \quad (10)$$

Here d_0 and d are the densities of the solvent and solution, M_A is the molar weight of the dissolved compound and m_A is the molality of the solution. Similar relations can be obtained for the concentration expressed in molarity units, molar fraction or weight percent. The experimental values of φ and the limiting values of V_A are independent of the concentration scales. Equation (10) is more convenient in the following form:

$$(1000 + M_A \cdot m_A)/d = 1000/d_0 + m_A \cdot \varphi \quad (11)$$

The slope of dependence $(1000 + M_A \cdot m_A)/d$ from (m_A) at $m_A \rightarrow 0$ corresponds to the value of the PMV (V_A). Calibration of the densitometer (PAAR, DMA-602) was made using data on the vibration of the tube filled with dry nitrogen and then degassed with twice-distilled water. The triple system of maintaining the temperature in the densitometer was described earlier.[20] Deviation of the temperature during the experiment did not exceed ± 0.002 °C and the required correction was made according to data on the temperature coefficient of the solvent expansion. The experimental conditions of PMV determination for lithium perchlorate in the row of solvents are shown in Table 4.

For electrolytes (1:1) the problem of precise determination of the limit values of PMV and solution enthalpy in organic solvents is related to the reliability of extrapolation of experimental data to the state of complete salt

Table 4. Experimental interval of the concentrations (m_A, mol kg^{-1}), the number of measurements (N) and the correlation coefficient of linear regression (R, Eqn (11)) used for determination of PMV values (V, cm^3 mol^{-1}) for lithium perchlorate in a series of solvents at 25 °C

Solvent	m_A	R (N)	V
Diethyl ether	0.0577–0.2984	0.9966 (5)	14.5; 15[a]
Acetone	0.0508–0.3092	0.9998 (11)[b]	−2.0[b]
Tetrahydrofuran	0.0603–0.3382	0.9995 (5)	23.6; 23[c]
Ethyl acetate	0.0525–0.3519	0.9998 (5)	25.1
Dimethylsulfoxide	0.0492–0.3335	0.9999 (6)	38.7; 92[d]; 39[e]
Acetonitrile	0.0176–0.1592	0.9982 (9)	20.1; 20.8[f]; 14[c]
Nitromethane	0.0483–0.3206	0.9999 (5)	36.4
Methanol	0.0517–0.3395	0.9997 (6)	24.6; 22[e]
Formamide	0.0445–0.2898	0.9999 (5)	48.3; 49.6[g]; 47[e]
Water	0–0.3240	0.9999 (6)	44.2; 43.2[e]

[a] According to the data of Ref. 12.
[b] From the correlation $\varphi - m_A^{1/2}$ (see text).
[c] According to the data of Ref. 7.
[d] According to the data of Ref. 32.
[e] Calculated using the optimization of PMV values of Li$^+$ and ClO$_4^-$ ions using the data on the PMV of the other salts (Ref. 7).
[f] According to the data of Ref. 33.
[g] According to the data of Ref. 34.

dissociation. Lithium perchlorate has very high solubility in selected solvents, along with heat evolution. The PMV values obtained (Tables 3 and 4) are in good agreement with data on the other measurements in water, methanol, formamide, tetrahydrofuran and ether. It should be noted that the linear dependence (Eqn (11)) is good ($R \geq 0.9999$) for the lithium perchlorate solutions in water, formamide, nitromethane and DMSO. Only in acetone is there a significant decrease of the apparent molar volume (φ) of lithium perchlorate in the diluted solutions. From the dependence $\varphi - m_A^{1/2}$, the two sets of measurements gave values for lithium perchlorate PMV in acetone of -2.1 ± 0.2 ($R = 0.9999$) and $-1.8 \pm 0.2\,cm^3\,mol^{-1}$ ($R = 0.9998$). The negative PMV values in acetone were obtained for lithium and sodium halides.[30] The PMV value of lithium cation ($-22\,cm^3\,mol^{-1}$) in acetone obtained in this work is in good agreement with the PMV values of the alkali metal ions in non-water media.[7]

The PMV value for lithium perchlorate in dimethyl-sulfoxide ($38.7\,cm^3\,mol^{-1}$, Table 3) differs sharply from the data of Ref. 32 ($92\,cm^3\,mol^{-1}$). The 'consensus technique'[4,7,23] predicts the PMV value of lithium perchlorate in DMSO to be $39 \pm 1\,cm^3\,mol^{-1}$.[7] The PMV value of lithium perchlorate in acetonitrile ($20.1\,cm^3\,mol^{-1}$, Table 3) is in agreement with the value of $20.8\,cm^3\,mol^{-1}$ from Ref. 33 but differs significantly from the results of another works.[7] For several solutions the check measurements were done with newly re-purified compounds. The errors in PMV determination of compounds did not exceed ± 0.3 (Table 1), ± 0.5 (Table 2) and $\pm 1.0\,cm^3\,mol^{-1}$ (Table 3).

The values of the heats of solution for more than 2000 diluted solutions were calculated earlier in our laboratory[15,16] using data from the literature on the heat of mixing of organic solvents. Data on direct measurements of the heats of solution of cyclohexane and compounds in cyclohexane have been collected in Refs 13 and 14. The values of the heats of solution of the other compounds listed in Tables 1–3 were determined with the help of a differential calorimeter. The solvent volume in the calorimeter cell was 160 ml and the weights of the samples of compounds were in the range 30–60 mg. Error in the determination of heats of solution did not exceed 2%. In the calculations 1 calorie was taken to be equal to 4.184 J. The procedure of measurements was described earlier.[35] The filling of the containers with gallium chloride and lithium perchlorate was performed in a glove-box with phosphorus pentoxide. It can be noted that between the heats of solution of sodium[4,23] and lithium (Table 3) perchlorates in the row of solvents a reliable correlation exists:

$$\Delta_{sol}H_{NaClO_4} = (9.92 \pm 0.17)$$
$$+ (1.052 \pm 0.013) \cdot \Delta_{sol}H_{LiClO_4}; \quad (12)$$
$$R = 0.9998$$

Table 3 lists experimental values[17,36] of the isothermal coefficients of solvent compressibility (β_T). Some β_T values were calculated from adiabatic data (β_S) based on the ultrasonic velocity[25] in these solvents.

Acknowledgments

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