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Enthalpies of solution of lithium perchlorate and Reichardt′ dye in some organic solvents

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Abstract

Enthalpies of a solution, at 298 K, of lithium perchlorate and Reichardt′ dye were determined in diethyl ether (−26.0; 23), acetonitrile (−38.3; 10), acetone (−66.3; 0), dimethyl sulfoxide (−75.3; −16), tetrahydrofurane (−49.0; 7.5), nitromethane (−62.0; 0), ethyl acetate (−37.2; 13) and methanol (−51.9; −33 kJ mol^{-1}), respectively. For lithium perchlorate, a sharp dependence on integral enthalpy of solution was observed in diethyl ether and nitromethane in the range of low concentration.

Keywords: Enthalpy of solution; Calorimetry; Lithium perchlorate; Reichardt′ dye

1. Introduction

For the Diels–Alder reaction with normal electronic demand (diene – donor, dienophile – acceptor), the acceleration effects in the presence of $AlBr_3$, $AlCl_3$, $GaCl_3$ and BCl_3 were nearly independent of the structure of reagents, and 10^6, 10^5, 10^4 and 10^3 times, respectively [1]. However, some reagents (cyclopentadiene, furan, vinyl ethers etc.) are unstable in the presence of even trace quantity of these Lewis acids, but are stable in solution of lithium perchlorate in diethyl ether (LPDE) [2]. Large promotion effect for a number of reactions in LPDE medium has been intensively studied during the last decade [3]. Our kinetic data for the (4 + 2)-, (3 + 2)- and (2 + 2)-cycloaddition reactions in LPDE medium showed that rate constants can be increased up to 10^3–10^4 times for some reactions, unchanged or even decreased for others [4]. The acceleration effect is usually larger in solution of $LiClO_4$ in diethyl ether, and in polar solution this effect, as a rule, reduces with the exception of nitromethane [5].

2. Experimental

The enthalpies of solution were measured at 298 K in differential calorimeter, as previously reported [6]. Samples were weighed in a small cylinder made of stainless steel, both sides of which were covered by thin (0.1 mm) ring of Teflon seal. Zero effect of cutting Teflon seal was obtained when sample of the solvent was dissolved in the same solvent (working volume 180 cm^3), but cutting of the empty container gave the endo-effect, the greatest for diethyl ether, determined

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by solvent evaporation in the free volume of the container. These values were taken into account in calculations. For all solutions 3–5 measurements of sequentially dissolving of the samples were carried out.

Lithium perchlorate was obtained from lithium hydroxide and perchloric acid, twice recrystallized from water, and dried at 460 K and 10 Pa up to m.p. 511–513 K (not corrected), 519.8 K [7]. Reichardt′ dye (RD) [2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate] was kindly supplied by Reichardt and used without purifying. Solvents were purified by known methods [8] and dried over 4 Å molecular sieves for 20–30 h.

3. Results and discussion

Exothermic effect of the lithium perchlorate when dissolved was observed in all solutions (Table 1). The concentration dependence of LP integral enthalpy of solutions was observed for only solvents – diethyl ether and nitromethane (Fig. 1). For LPDE solution this behavior can be conditioned by the decrease of free ions fraction in the range of low concentration according to molar conductivity data in low polar solutions [9].

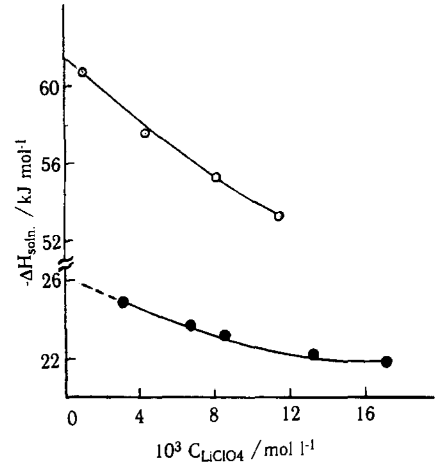

Fig. 1. Concentration dependence of integral enthalpy of solution for lithium perchlorate in diethyl ether (●) and in nitromethane (○) in the range of low concentration.

Correlation between the enthalpies of LP solutions and solvent E_T parameters shows (Fig. 2) that in an aprotic solvents exo-effect of solution increase with increase of solvent polarity. In the protic solvents the large increase of the E_T value depends on the hydrogen bond formation with anionic part of dyes [10]. For LP, the strong solvation of Li^+ cation does not result from the hydrogen bond formation, and exo-effect of LP solution decrease in these solvents (Fig. 2). From this point of view, such a deflection is not associated with the enthalpies of solution of Reichardt′ dye. In spite of the large molar mass of RD (551.7 g), the values of

Table 1
Solution enthalpies (in kJ mol^{-1}) of lithium perchlorate and 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate, polarity scale (E_T), donor numbers (DN) and acceptor numbers (AN) of solvents

Solvent No.	Solvent	ΔH_{soln} ($LiClO_4$)	ΔH_{soln} (RD)	E_T [a]	DN [a]	AN [a]
1	Diethyl ether	−26.0	23 [b]	0.117	0.49	0.039
2	Tetrahydrofurane	−49.0	7.5	0.207	0.52	0.080
3	Ethyl acetate	−37.2	13	0.228	0.44	0.093
4	Acetone	−66.3	0	0.355	0.44	0.125
5	Dimethylsulfoxide	−75.3 [c]	−16	0.444	0.77	0.193
6	Acetonitrile	−38.3	10	0.460	0.36	0.189
7	Nitromethane	−62.0	0	0.481	0.07	0.205
8	Propylene carbonate	−39.7 [d]	—	0.491	0.39	0.183
9	N-Methylformamide	−56.5 [d]	—	0.799	—	0.398
10	Methanol	−51.9	−33	0.762	0.66	0.415
11	Formamide	−43.9 [d]	—	0.799	—	0.398
12	Water	−26.4 [d]	—	1.000	—	0.548

[a] Normalized values E_T, DN and AN taken from Ref. [9];
[b] Calculated value (see text);
[c] −72.0 from Ref. [7];
[d] From Ref. [7]. Accuracy of ΔH_{soln} values for lithium perchlorate equals ±0.8 kJ mol^{-1} and for Reichardt′ dye ±2 kJ mol^{-1}.

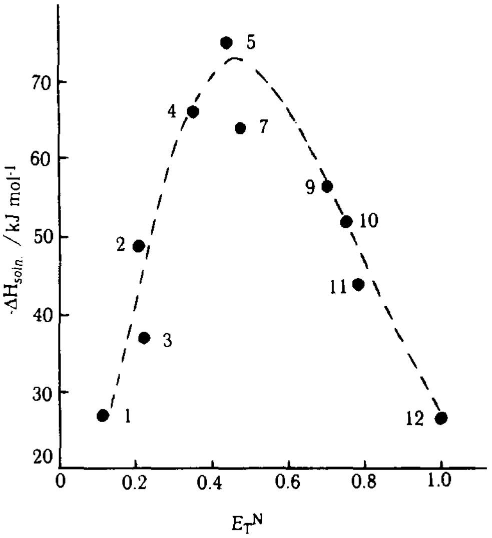

Fig. 2. Correlation between the values of solution enthalpies for lithium perchlorate and solvent polarity scale in aprotic and protic solvents. Numeration of the solvents is as in the table. (Points of acetonitrile and propylene carbonate withdrawn from consideration).

enthalpies of solution are small (Table 1). Exo-effect of RD solution was observed only in DMSO and in methanol. From the correlation between the heats of solution for LP and RD in aprotic solvents ($\Delta H^{\rm LP}_{\rm soln} = 1.39\Delta H^{\rm RD}_{\rm soln} - 58.2$ kJ mol^{-1}, $R = 0.928$, $N = 6$), the value of enthalpy of solution for RD in diethyl ether was estimated as 23 ± 4 kJ mol^{-1}.

There is no clear correlation between the heats of solution of LP or RD with donor numbers (DN), acceptor numbers (AN) or with polarity scale (E_T) of the solvents. Correlation between E_T values and the enthalpies of Reichardt′ dye solutions shows that exothermic effect increases in protic solvent in contrast to lithium perchlorate (Fig. 2), but that correlation is very poor ($R = 0.88$). For the heats of LP solutions the correlation with donor numbers of solvents could be expected. But $SbCl_5$ and $GaCl_3$ are more soft Lewis acids than Li^+ cation. Therefore covalent binding is more important for the interaction energy of the first salt pair with solvent, and an electrostatic binding is more important for the interaction energy of lithium perchlorate [11]. This difference in the nature of interaction energy reflects the variation of acceleration effects of cycloaddition reactions in the presence of $GaCl_3$ and $LiClO_4$ solutions [4].

Enthalpy of solution reflects the energy changes for both solute and solvent in the dissolving process. The values of the energy of appropriate hole formation in the solvents for Reichardt′ dye can be large and different. On the other hand, the value of E_T according to the Franck–Condon principle reflects the charge transfer energy depending only on the solute energy levels.

Nitromethane and diethyl ether stand apart from other solvents due to their concentration dependence of the enthalpies of solution (Fig. 1). The raised acceleration effect for cycloaddition reactions was noted in the solution of lithium perchlorate in diethyl ether [2–4] and nitromethane [5]. Diethyl ether has large donor number (DN = 0.49), but low dielectric constant ($\varepsilon = 4.22$). Nitromethane, on the other hand, has very low donor number (DN = 0.07), but high dielectric constant ($\varepsilon = 35.9$). Lithium perchlorate in diethyl ether may stabilize polar states because of the low shell dielectric constant. Lithium perchlorate in nitromethane shell has the possibility to form new coordination with more donor center in reagent or in transition state. Lithium-7 and chlorine-35 NMR studies have shown [12], that the formation of contact ion pairs for $LiClO_4$ in nitromethane is nearly the same as in tetrahydrofurane (DN = 0.52, $\varepsilon = 7.6$).

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