Solvation in Dipolar Aprotic Solvents. Ionic Enthalpies of Transfer

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Abstract: Enthalpies of solution have been determined for a series of alkali perchlorates and tetraethylammonium salts in sulfolane. Further measurements were carried out in propylene carbonate (PC), dimethylformamide, dimethyl sulfoxide, and methanol, to complement literature data. Cationic and anionic enthalpies of transfer (from water to solvent) were separated with the single extrathermodynamic assumption $\Delta H_t(\mathrm{AsPh_4^+}) = \Delta H_t(\mathrm{BPh_4^-})$. The behavior of ionic enthalpies of transfer from PC to the other dipolar aprotic solvents cannot be explained only in terms of coulombic interactions. Cationic solvation is related to solvent basicity whereas anionic solvation does not depend in a simple way on ionic radius. The order of solvation enthalpies is $\mathrm{Cl^-} > \mathrm{Br^-} > \mathrm{I^-} > \mathrm{ClO_4^-} > \mathrm{BPh_4^-}$, and is the same for the aprotic solvents, water, and methanol. Some comments are made on the protic–dipolar aprotic solvent effects on the enthalpy changes of some charged nucleophiles and transition states.

The energetics of ion solvation in nonaqueous media have recently become the subject of many investigations. The dipolar aprotic solvents are particularly interesting in that the solvents of this class have solvating properties toward anions very different from those of water and other protic solvents.[1] This is usually reflected in drastic changes in equilibrium constants and rates for reactions involving anions, when one compares values for both classes of solvents.[2] Free energies of transfer, which are possibly simpler to interpret, are somewhat difficult to attain, owing to the small number of reversible electrodes. Enthalpies of transfer, which are thought to reflect some solvent structural features,[3] are easier to determine, but existing data are limited and somewhat scattered.

During the course of a study of solvation in sulfolane (TMS), the enthalpies of solution of a series of alkali perchlorates and tetraethylammonium salts have been determined. Additional measurements have been made in propylene carbonate (PC), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) to supplement existing data, so that heats of transfer could be evaluated for a series of salts. Furthermore, solution enthalpies of $\mathrm{AsPh_4I}$ and $\mathrm{NaBPh_4}$ have been determined when necessary, so that single anion and cation transfer enthalpies could be put on the same scale by means of a single extrathermodynamic assumption.[4]

Results and Discussion

Results are given in Table I for the heats of solution measured in sulfolane and the additional determinations made in the other solvents. Selected literature values are also included for the enthalpies of solution in PC, DMF, DMSO, methanol, and water. Each of our values is the result of at least three experiments with salt concentrations ranging from 3×10^{-3} to 5×10^{-4} *M*. There is usually no concentration effect in this range. Using the dielectric constant and density data reported by Lamanna, *et al.*,[5] for TMS, the Debye–Hückel term for dilution was calculated[6] as $\Delta H_{\mathrm{dil}} = 0.74\sqrt{m}$ (kcal/mole), and in our concentration range this amounts to about 0.03 kcal/mole. For the other solvents, the literature values are corrected, and we took in account the Debye–Hückel term for our own values, corrections being minimal for PC. In DMF there is, however, a strong concentration effect for $\mathrm{NaBPh_4}$ below 10^{-3} *M*, similar to that found by Held and Criss[7] for LiBr, LiCl, and NaI. Conductance measurements indicate that ion pairing is negligible at these low concentrations,[8] and these concentration effects may be due to the presence of impurities in DMF. The values of the enthalpies of solution for $\mathrm{NaBPh_4}$ in DMF were therefore extrapolated to infinite dilution, as it was done by Weeda and Somsen[9] without accounting for this anomalous effect. From some recent results on MeOH–DMF transfers,[10] we calculated $\Delta H_t(\mathrm{Na^+}) = -1.25$ kcal/mole, with an extrathermodynamic assumption slightly different from ours; this is to be compared with our own value -1.1 (Table II). This agreement is in favor of our selected value for $\mathrm{NaBPh_4}$ in DMF. Attempts were made to determine directly the enthalpy of transfer of $\mathrm{AsPh_4BPh_4}$. Because of the very low solubility of this salt in water, its heat of precipitation had to be measured. The reproducibility was not good; the average value, -12.1 kcal/mole, combined with 10.1 kcal/mole for the heat of solution of $\mathrm{AsPh_4BPh_4}$ in TMS, leads to -2.0 kcal/mole for the transfer, to be compared with -5.7 kcal/mole, the calculated value. Similar difficulties were experienced when measuring the heat of precipitation of $\mathrm{NEt_4BPh_4}$ in water. It would seem that our microcalorimeter and cell are not suitable for precipitation measurements and the corresponding values were discarded. The internal consistency of the data in Table I was checked when possible. The agreement between experimental enthalpies of transfers and calculated values is usually

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[3] D. Feakins in "Physico-chemical Processes in Mixed Aqueous Solvents," F. Franks, Ed., American Elsevier Publishing Co., Inc., New York, N. Y., 1967.

[4] A. J. Parker and R. Alexander, *J. Am. Chem. Soc.*, 90, 3313 (1968).

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[9] L. Weeda and G. Somsen, *Rec. Trav. Chim.*, 86, 893 (1967).

[10] P. Haberfield, L. Clayman, and J. S. Cooper, *J. Am. Chem. Soc.*, 91, 787 (1969).

Table I. Heats of Solution per Formula Weight (kcal/mole)

Solute	TMS	PC	DMF	DMSO	MeOH	H_2O[j]
$NaClO_4$	−5.40	−3.05[a]			−2.62[h]	3.32
NaCl					−2.00[i]	0.93
NaBr			−7.39[c]		−4.00[i]	−0.14
NaI	−7.41	−5.04[a]	−13.14[d]	−11.53[f]	−7.00[i]	−1.80
$NaBPh_4$	−10.90	−10.72[a]	−12.05	−14.23[f]	−8.02	−4.00,[k] −4.77[f]
$LiClO_4$	−5.62	−9.51[a]				−6.35
LiCl			−11.82[d]	−10.09[g]	−11.48[i]	−8.85
LiBr			−18.52[d]	−17.1[g]		−11.67
LiI		−15.06[a]	−19.10[d]	−24.2[g]		−15.13
$KClO_4$	1.10					12.20
KCl					1.08[i]	4.11
KBr			−3.89[c]	−2.7[g]	0.87[i]	4.75
KI			−8.04[d]	−6.15[f]	0.17[i]	4.86
$KBPh_4$		0.74[a]				9.41[a]
$RbClO_4$	2.02					13.56
RbCl					1.28[i]	4.13
RBI			−6.64[d]			6.00
$RbBPh_4$		2.41[a]				11.73[a]
$CsClO_4$	2.21					13.25
CsCl					1.86[i]	4.25
CsI			−4.25[d]	−2.84[f]	4.15[e]	7.97
$CsBPh_4$		2.38[a]				12.40[a]
NMe_4I		5.34[b]	4.01[e]		9.60[e]	10.06
NEt_4ClO_4	3.63		1.80	3.90	8.24[h]	8.10
NEt_4Cl	3.94	3.30[b]	1.34	2.42[f]	−0.31[h]	−3.02[f]
NEt_4Br	4.99	4.90[b]		3.27[f]	4.38[h]	1.38[f]
NEt_4I	5.53	6.08[b]	2.95	4.86[f]	7.99[e]	6.83[f]
$AsPh_4I$	3.87	5.74	0.69	3.44[f]	8.65	8.28[f]

[a] Reference 11. [b] Y. C. Wu and H. L. Friedman, *J. Phys. Chem.*, **70**, 2020 (1966). [c] Reference 7. [d] Reference 9. [e] Reference 18. [f] Reference 12. [g] Reference 19. [h] F. A. Asken, E. Bullock, H. T. Smith, R. K. Tinkler, O. Gatty, and J. H. Wolfenden, *J. Chem. Soc.*, 1368 (1934). [i] C. M. Slansky, *J. Am. Chem. Soc.*, **62**, 2430 (1940). [j] Most values for heats of solutions have been selected from V. B. Parker, "Thermal Properties of Aqueous Uni-Univalent Electrolytes," U. S. National Bureau of Standards NSRDS-NBS2, Washington, D. C., 1965. [k] The value at 30° for solution in water, −4.00, has been calculated from S. Subramanian and J. C. Ahluwalin, *J. Phys. Chem.*, **72**, 2528 (1968). As heats of solution of $NaBPh_4$ in TMS, DMF, and MeOH were measured at 30°, this value was used to calculate the enthalpy of transfer. When considering measurements at 25° (PC, DMSO), the value for solution in water at 25°, −4.77, was used.

within 0.2 kcal/mole except for methanol where the enthalpies of solution come from various sources and appear less reliable.

In order to compare ionic enthalpies of transfer, an extrathermodynamic assumption is needed to separate anionic and cationic contributions. Na^+ has been used as a reference cation to evaluate transfers from water to PC, with the somewhat fortuitous result that Cs^+ and I^- have the same ΔH_t value.[11] This procedure is adequate when considering the shapes of the curves ΔH_t *vs.* ionic radii, as the result of a different assumption would only be to alter the respective positions of the anionic and cationic curves. However, the use of Na^+ as a reference cannot be extended to other solvents in order to compare solvation effects, as this would imply that Na^+ has the same solvation enthalpy in all solvents. On the other hand, the assumption $\Delta H_t(Cs^+) = \Delta H_t(I^-)$ is somewhat arbitrary and yields the unlikely conclusion that differences in anionic and cationic enthalpies of transfer increase with increasing ionic size.

Arnett and McKelvey[12] used the assumption previously discussed by Grunwald, *et al.*,[13] *i.e.*, that $\Delta H_t(AsPh_4^+) = \Delta H_t(BPh_4^-)$. This implies identical enthalpy of transfer for large cations and large anions and seems reasonable. To test the validity of this assumption,[13] attempts were made to determine ΔH_t for $SnPh_4$, but the solubility of this compound in the aprotic solvents is lower than 5×10^{-3} *M*, except in DMF, and the rate of solution is low so that measurements could not be made with our calorimeter. Cationic and anionic enthalpies of transfer from water to solvents have been separated according to this assumption and are given in Table II. When more than one salt could be used for the calculation, an average value was taken; this procedure was only significant for methanol where the uncertainty on the enthalpies of solution is larger.

Table II. Single Ion Enthalpies of Transfer from Water to Solvents (kcal/mole)

	TMS	PC	DMF	DMSO	MeOH
Li^+	5.4	−0.05	1.5	−6.5	−3.7
Na^+	−4.05	−3.3	−5.9	−7.2	−4.8
K^+	−6.4	−6.0	−7.5	−8.45	−4.7
Rb^+	−6.8	−6.7	−7.2		−4.7
Cs^+	−6.3	−7.4	−6.8	−8.25	−3.8
NMe_4^+		−4.8	−0.6		−0.05
NEt_4^+	0.3	−0.8	1.6	0.6	1.4
$AsPh_4^+$	−2.85	−2.6	−2.15	−2.3	0.8
Cl^-	6.7	7.45	2.8	5.1	1.9
Br^-	3.35	4.35	−1.35	1.1	0.9
I^-	−1.6	0.1	−5.4	−2.6	−0.4
ClO_4^-	−4.7	−3.05	−7.9	−4.8	−1.1
BPh_4^-	−2.85	−2.6	−2.15	−2.3	0.8

As our main interest is in dipolar aprotic solvents, and that the peculiar structure of water may lead to some distorsion of the values, it was thought preferable to

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(11) Y. C. Wu and H. L. Friedman, *J. Phys. Chem.*, **70**, 501 (1966).

(12) E. M. Arnett and D. R. McKelvey, *J. Am. Chem. Soc.*, **88**, 2598 (1966).

(13) E. Grunwald, G. Baughman, and G. Kohnstam, *ibid.*, **82**, 5801 (1960).

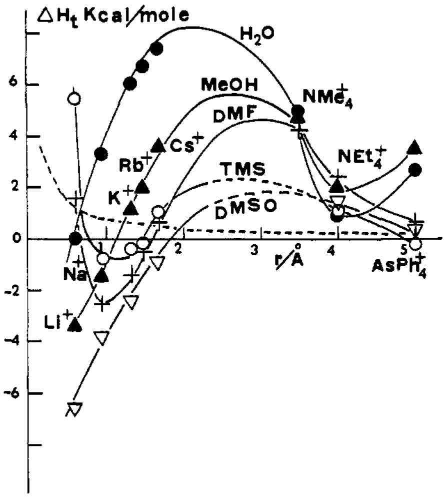

Figure 1. Cationic enthalpies of transfer from PC to (○) TMS, (▽) DMSO, (+) DMF, (▲) MeOH, and (●) water. Dashed lines represent the calculated Born term for transfer from PC to TMS.

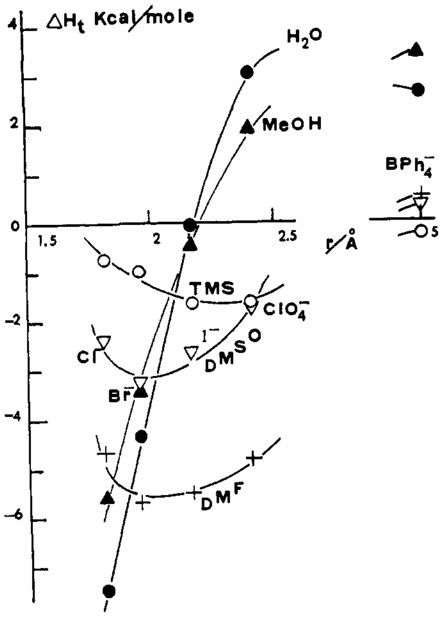

Figure 2. Anionic enthalpies of transfer from PC to (○) TMS, (▽) DMSO, (+) DMF, (▲) MeOH, and (●) water.

consider ionic transfers with a dipolar aprotic solvent as a reference. Propylene carbonate was selected for that purpose; according to Friedman, it is a nearly ideal solvent because of its weaker basicity.[14] Ionic enthalpies of transfer from PC to solvents cannot be calculated from heats of solution of salts in PC and solvent, as only some of them are known in PC. Values were therefore deduced from the data presented in Table II according to

$$\Delta H_t(\text{PC}\rightarrow\text{S}) = \Delta H_t(\text{H}_2\text{O}\rightarrow\text{S}) - \Delta H_t(\text{H}_2\text{O}\rightarrow\text{PC})$$

The uncertainty on $\Delta H_t(\text{PC}\rightarrow\text{S})$ amounts to 0.2 kcal/mole for aprotic solvents and is larger for methanol; the values are plotted against ionic radii in Figure 1 for cations and in Figure 2 for anions. The choice of radii values is not crucial, as the same ions are to be compared in different solvents, requiring only a semiquantitative scale of ion size. Pauling crystal radii have been used for simple ions, and radii of complex ions have been evaluated according to Robinson and Stokes.[15]

The Born equation, $\Delta G = (-e^2/2r)[1 - (1/D)]$, gives the electrostatic free energy of solvation of an ion with radius r in a medium of uniform dielectric constant D. In PC, TMS, DMF, DMSO, MeOH, and water, where D values are 65.1, 41.3, 36.7, 46.7, 31.5, and 78.5, respectively, values of $-r\Delta G$ are 161.28, 159.83, 159.34, 160.29, 158.60, and 161.71 kcal/mole. The derivative of the Born equation

$$\Delta H = -\frac{e^2}{2r}\left(1 - \frac{1}{D}\right)\left[1 - \frac{T\partial D/\partial T}{D(D-1)} + \frac{T}{r}\frac{\partial r}{\partial T}\right] \quad (1)$$

would give the corresponding enthalpy of solvation. Assuming that $(T/r)(\partial r/\partial T)$ can be neglected,[7,11] values of $-r\Delta H$ for each solvent are 164.05, 163.27, 165.35, 162.64, 167.16, and 164.56 kcal/mole. Considering the ionic enthalpies of transfer from PC to solvents TMS, DMF, DMSO, MeOH, and water, the calculated values for $r\Delta H_t$ are 0.78, −1.30, 1.41, −3.11, and −0.51 kcal/mole. These values can explain neither the shapes nor the respective positions of the curves in Figures 1 and 2. The experimental enthalpies of transfer from PC to solvents are larger than predicted by eq 1, and anions and cations do not follow the same pattern. It appears therefore that these enthalpies of transfer are not mainly governed by coulombic interactions, and in the following discussion cationic and anionic solvation are considered separately.

The order DMSO > DMF > TMS > PC found in Table II for the solvating strength of the aprotic solvents toward Na^+, K^+, Rb^+ is also found from phenol or iodine adducts[16] or from Ag^+ solvation activity coefficients.[4,17] Strong specific interactions in DMSO and weaker ones in DMF probably account for the different position of Li^+, although the Li^+ value in DMF is somewhat in doubt as it was calculated from the heat of solution of LiI, and values from LiCl and LiBr are at variance. Water and, to some extent, methanol do not solvate the larger cations as well as the aprotic solvents. NEt_4^+ may be specifically solvated by both protic solvents possibly because it enhances their structure.[18] The fairly constant value of $AsPh_4^+$ for all aprotic solvents implies a small and nearly constant enthalpy of transfer for $AsPh_4BPh_4$.

The anionic solvations in PC and DMSO were previously compared,[14] and it was concluded that the anionic enthalpies of transfer from water to PC and to DMSO were similar, but anions and cations were separated in each case with different assumptions $\Delta H_t(Cs^+) = \Delta H_t(I^-)$ in PC and $\Delta H_t(AsPh_4^+) = \Delta H_t(BPh_4^-)$ in DMSO. The present use of the single assumption, $\Delta H_t(AsPh_4^+) = \Delta H_t(BPh_4^-)$ for all solvents, leads to the conclusion that differences of several kcal/mole may appear in the anionic enthalpies of transfer from PC to solvents as is shown in Figure 2. The order of solvating strength of solvents toward anions is DMF > DMSO > TMS > PC. The largest changes

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[14] H. L. Friedman, *J. Phys. Chem.*, **71**, 1723 (1967).

[15] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth and Co. Ltd., London, 1955, Table 6.2.

[16] R. S. Drago, B. Wayland, and R. L. Carlson, *J. Am. Chem. Soc.*, **85**, 3125 (1963).

[17] R. L. Benoit, *Inorg. Nucl. Chem. Letters*, **4**, 723 (1968).

[18] O. N. Bhatnagar and C. M. Criss, *J. Phys. Chem.*, **73**, 174 (1969).

appear for I^- whose solvation enthalpy may differ by up to 5.5 kcal/mole from one dipolar aprotic solvent to another. With increasing anion size, these changes vanish, so that BPh_4^- has nearly the same enthalpy of solvation in all the aprotic solvents studied. However, the solvent effect is smaller on chloride than on bromide or iodide; it would have been of value to obtain enthalpies of transfer for the small anions F^- or OH^-, but either the low solubility of the salts or the difficulty in obtaining anhydrous compounds does not allow simple heats of solution measurements. As expected, the shape of the curve ΔH_t *vs.* ionic radii for anions is quite different when considering transfers to protic solvents, where the smaller ions are more strongly solvated because of hydrogen bonding. However, Fuchs, *et al.*,[19] showed recently that the enthalpies of solvation, ΔH_{solv}, of halide ions lie in the order $Cl^- > Br^- > I^-$ for DMSO and water. Our results indicate that the order can be extended, $Cl^- > Br^- > I^- > ClO_4^- > BPh_4^-$, and is common to the aprotic solvents water and methanol. The single ion solvation enthalpies ΔH_{solv} were calculated from references[20,21] and are presented in Table III. It is apparent that although small anions are less solvated and large anions more solvated in aprotic solvents than in water or methanol, the differences are not sufficient to reverse the solvation order. Turning to the relative positions of the protic–dipolar aprotic curves for anions given in Figure 2, the enthalpy changes of small and large anions on going from protic to dipolar aprotic solvents depend strongly upon the aprotic solvent nature. Such changes are of value in understanding protic–dipolar aprotic effects on rates of some bimolecular reactions of anions X^- with molecules RY, as these effects are usually reflected more strongly in the enthalpy rather than in the entropy of activation.[2] On one hand, the large transition state XRY^- is likely to be more solvated in all dipolar aprotic media, but to an extent depending somewhat on the solvent; CP is, for example, probably less effective than DMF. On the other hand, as recently pointed out by Haberfield, *et al.*,[10] who compared MeOH and DMF, the nucleophile X^- can be either better solvated by the protic or the dipolar aprotic solvent; for instance, Cl^- is slightly better solvated by MeOH, while I^- is much more strongly solvated by DMF. The influence of the solvent nature is also brought to light when replacing DMF by TMS in the previous example.

Table III. Solvation Enthalpies, ΔH_{solv} (kcal/mole)

	H_2O[a]	TMS	PC	DMF	DMSO	MeOH
Cl^-	86.8	80.1	79.3	84.0	81.7	84.9
Br^-	80.3	77.0	76.0	81.6	79.2	79.4
I^-	70.5	72.1	70.4	75.9	73.1	70.9
ClO_4^-	57	61.7	60.1	64.9	61.8	58.1

[a] Reference 21.

Attempts have been made to correlate ΔH_{solv} for DMF and PC with ionic radii.[7,14] As ΔH_{solv} values are deduced by subtracting small transfer enthalpies from large hydration enthalpies, the linear relationships obtained between ΔH_{solv} and $1/(r + \delta)$,where δ is an adjustable parameter, clearly result from the known proportionality of ΔG_{hyd} or ΔH_{hyd} to $1/(r + \delta)$.[20] All the aprotic solvents considered here lead to the same cationic δ values which depend somewhat on whether Li^+ is kept or not in the series. On the other hand, if the cationic enthalpies of transfer are used to calculate δ values, in the manner described by Strehlow[22] for the free energies of transfer, it is found that δ is not constant for a given solvent. It would seem that such a treatment does not further our understanding of solvation effects in dipolar aprotic solvents.

Experimental Section

Reagents. Reagent alkali perchlorates were vacuum dried at 120°. Tetraethylammonium salts were dried under vacuum at 80° after recrystallization from aqueous ethanol. Tetraphenylarsonium iodide was prepared from the chloride; sodium iodide was recrystallized from acetone–water and vacuum dried at 80°. Reagent sodium tetraphenylborate was vacuum dried at 80°.

Sulfolane, kindly supplied by Shell Canada Ltd., was heated to 200° under a stream of air during 12 hr. It was then agitated under vacuum, treated with Norit A charcoal, filtered, and finally distilled under vacuum at a temperature of 80°. The product was uv clear from 240 mμ, had a melting point of 28.4°, and had the same refractive index as reported previously.[5]

Reagent propylene carbonate was purified by distillation under reduced pressure. Reagent dimethyl sulfoxide was dried on $CaCl_2$ and distilled under reduced pressure. Reagent dimethylformamide was dried by vigorous stirring on CaH_2 and distilled under reduced pressure. Reagent methanol was used without further purification. All solvents were kept on 3A or 4A molecular sieves. Karl Fischer titrations indicated the water content to be less than 0.01 %.

Calorimetry. The Tian-Calvet microcalorimeter[23] can be moved around an horizontal axis. Calibration is made by Joule effect. For solution measurements with low vapor pressure solvents, such as sulfolane, the cell is a glass cylinder inside which is a small plate on top of a rod. The liquid volume below the plate is about 10 ml. The salt to be dissolved is placed inside the cell on the plate and accurately weighed with a precision of ±0.02 mg. Once the solvent is added, the cell is closed and introduced in the calorimeter. After thermal equilibrium is reached, the calorimeter is overturned, allowing contact between solute and solvent. For measurements with more volatile solvents such as DMF, methanol or water, the cell used is made of two glass cylinders, one inside the other. The salt is placed in the central tubing and accurately weighed. A glass piston is introduced in this tubing and covered with mercury. The solvent is added in the outside part of the cell. The cell is closed and placed inside the microcalorimeter. When thermal equilibrium is reached, the calorimeter is overturned and mercury and piston are expelled from the central cylinder of the cell, allowing solution of the salt in the solvent. This procedure was tested by measuring the heat of solution of $KClO_4$ in water, and the value found, 12.2 kcal/mole, is in good agreement with literature data. Values of the heat of solution were reproducible within 2% and the uncertainty is no more than 3%. All measurements were carried out at 30°.

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