Electrochemical Approach to Ion Solvations. Applications of Ion-Selective Electrodes as Sensors for Ion Solvations and the Problem of the Liquid Junction Potential between Different Solvents A Review

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Two subjects are reviewed concerning the electrochemical approach to ion solvations. In Section 2, applications of ion-selective electrodes as sensors for ion solvations are discussed. In Section 3, the problem of the liquid junction potential between different solvents is discussed in connection with the difficulties encountered in the study of ion solvations.

Keywords Ion solvation, ion-selective electrode, liquid junction potential between different solvents, nonaqueous solvent

1	Introduction	1	3·1	Three components of the liquid junction potential between different solvents
2	Applications of Ion-Selective Electrodes as Sensors for Ion Solvations	1	3·2	A new method of estimation of the liquid junction potential and the assumption of negligible liquid junction potential
2·1	Use of univalent cation-sensitive glass electrodes		3·3	Stability and reproducibility of the liquid junction potential between different solvents
2·2	Use of other ion-selective electrodes			
2·3	Problem in the study of ion solvations			
3	The Problem of the Liquid Junction Potential between Different Solvents	4		

1 Introduction

The reactivities of chemical species in solutions are markedly influenced by how strongly they are solvated. If the difference between solvation energies in solvents S_1 and S_2 , i.e. the standard molar Gibbs free energy of transfer from S_1 to S_2 , is known for each of the chemical species participating in a reaction or in an equilibrium, we can quantitatively predict how the reaction or the equilibrium differs in the two solvents. Therefore, it is of prime importance in nonaqueous solution chemistry to get the data of the Gibbs free energies of transfer for as many chemical species as possible.

Electroanalytical chemistry can provide useful techniques to get such data for ion solvations. Some electrodes can work as sensors for ion solvations, responding thermodynamically to the solvation energies of the ions determining the electrode potentials. Metal ion/metal and metal ion/metal amalgam electrodes include examples of such electrodes. But there exist

difficulties in comparing the electrode potentials in different solvents. Some extrathermodynamic assumption must be introduced to make the comparison possible.¹ The reliability of the data on ion solvations depends on the appropriateness of the assumption employed.

In this review, two subjects are presented concerning the electrochemical approach to ion solvations. In Section 2, the applications of ion-selective electrodes (ISEs) as sensors for ion solvations are discussed. In Section 3, the problem of the liquid junction potential (LJP) between different solvents is discussed in connection with the difficulties encountered in the study of ion solvations.

2 Applications of Ion-Selective Electrodes as Sensors for Ion Solvations

The ISEs used in nonaqueous solutions are not so many as those used in aqueous solutions. Dissolution and swelling of the electrode active materials, the

electrode matrix, and the electrode body limit the number of ISEs applicable in nonaqueous solutions. But successful applications in nonaqueous solutions are increasing steadily for physicochemical as well as analytical purposes.² The glass electrodes for pH measurements respond in Nernstian ways in many nonaqueous solvents and are widely used for the determination of acid dissociation constants³ as well as acid-base titrations. Univalent cation-sensitive glass electrodes respond with Nernstian slopes to various univalent cations in dipolar solvents and are conveniently used to study the complexing of univalent cations with neutral carriers.² Some ISEs may also be used for the study of ion solvations, as described below.

2.1 Use of univalent cation-sensitive glass electrodes

As shown in Fig. 1, a univalent cation-sensitive glass electrode can respond to the solvation energies of alkali metal ions in almost the same way as the respective amalgam electrodes.^{4,5} Thus it can be used as a sensor for the solvations of univalent cations. The potential response of the glass electrode is considered to depend on the exchange equilibrium of the univalent cation (M^+) between the solution and the electrode surface: $M^+(\text{soln.}) \rightleftharpoons M^+(\text{glass})$. The fact that the electrode responses to ion solvations shows that the solvent effect to $M^+(\text{glass})$ is much smaller than that to $M^+(\text{soln.})$.

We applied the electrode to study the successive complexing of univalent cations (M^+ : Li^+ , Na^+ , K^+ , Rb^+ , Tl^+ and NH_4^+) in acetonitrile (AN) with donor solvents (D: water, methanol, formamide, *N*-methylformamide, pyridine, *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), *N*-

methyl-2-pyrrolidinone, hexamethylphosphoric triamide (HMPA), etc.).⁴⁻⁷ To the AN solution of a univalent cation M^+ in Cell 1 ($M = \text{mol dm}^{-3}$), we added solvent D stepwise up to 1 or 2 (v/v)%. From the variation in the glass electrode potential, we obtained the formation constants (β_1 , β_2 , β_3 , ...) for the complexing $M^+ + D \rightleftharpoons M^+_D$, $M^+ + 2D \rightleftharpoons M^+_{2D}$, $M^+ + 3D \rightleftharpoons M^+_{3D}$, ...

For alkali metal ions, the respective amalgam electrodes may be used instead of the glass electrode. But the glass electrode has the advantage that non-metallic cations such as ammonium can be measured. Moreover, the use of the glass electrode makes the experimental procedure much simpler and the results more reliable.^{4,8} Thus, we could obtain thermodynamic parameters for the 1:1 complexing of Li^+ ion in AN with some strongly donor solvents (D), determining β_1 at 10, 25 and 40°C.⁹ Interestingly the enthalpy term played a much more important part than the entropy term, suggesting that the 1:1 complexing was the replacement of one solvated molecule of AN by one molecule of D: $\text{Li}(\text{AN})_x^+ + \text{D} \rightleftharpoons \text{Li}(\text{AN})_{x-1}\text{D}^+ + \text{AN}$.

Cox *et al.*⁸ applied a method similar to ours in propylene carbonate (PC), and detected complexing of up to four solvent molecules between Li^+ and Na^+ ions and DMSO. They also obtained the Gibbs free energies of transfer of Li^+ and Na^+ from PC to DMSO and PC-DMSO mixtures by measuring the EMF variations of Cell 1 (PC instead of AN). Sakamoto and Okazaki¹⁰, in their extensive study of ion solvations^{10b}, used a sodium ion-selective glass electrode to obtain both the complex formation constants of Na^+ ion in acetylacetone (Acac) with donor solvents (D) and the transfer activity coefficients of the Na^+ ion from Acac to D and Acac-D mixtures.

Cox *et al.*, who studied in PC the complexing of Li^+ and Na^+ ions with DMSO, calculated from the successive formation constants the Gibbs free energies of transfer of the ions from PC to DMSO and PC-DMSO mixtures.⁸ They used Eqs. (1) and (2) for their calculations:

$$\Delta G_i^\circ (M^+, R \rightarrow R+D) = -nRT \ln \phi_R - RT \ln \left[1 + \sum_{i=1}^n \beta_i' (\phi_D / \phi_R)^i \right] \quad (1)$$

$$\Delta G_i^\circ (M^+, R \rightarrow D) = -RT \ln \beta_n' \quad (2)$$

where R stands for the reference solvent (PC in the present case), ϕ_D and ϕ_R the volume fractions of R and D in the mixed solvent, and $\beta_i' = \beta_i (1000 \rho_D / M_D)^i (\rho_D$

Fig. 1 Relation between the response of a univalent cation-sensitive glass electrode and that of the amalgam electrode to ion solvations. The responses were measured using AN as reference. Solvent: $\times$, AN; $\blacktriangle$, PC; $\square$, H_2O ; $\blacksquare$, MeOH; $\circ$, DMF; $\triangle$, DMSO. Cation: 1, Li^+ ; 2, Na^+ ; 3, K^+ ; 4, Rb^+ ; 5, Cs^+ ; 6, Tl^+ .

Fig. 2 Gibbs free energies of transfer of Li^+ , Na^+ and Ag^+ from PC to DMSO and to PC-DMSO mixtures.⁸ $\circ$, $\square$, and $\bullet$ were obtained by direct EMF measurements and the solid curves by calculations.

and M_D : the density and the relative molecular mass of D). As shown in Fig. 2, the calculated ΔG° values agree well with the values directly obtained by the EMF measurements. It is interesting that the successive formation constants obtained in solutions predominant in reference solvent R may be used to calculate the free energies of transfer of the ion from R to D and to the mixed solvent (R+D). Of course, the formation constants may be used to calculate the fractions of the ionic species (M^+ , M_D^+ , M_{2D}^+ , etc.) present in the mixed solvent.

2.2 Use of other ion-selective electrodes

Some ISEs other than univalent cation-sensitive glass electrodes have been used to study ion solvations. Coetzee *et al.*¹¹ used a copper ion-selective electrode to estimate the Gibbs free energies of transfer of Cu(II) ion from water to various organic and aqueous organic solvents. Coetzee and Martin¹² obtained the Gibbs free energies of transfer of F^- ion from water to AN, though indirectly by measuring the solubility product of NaF with a fluoride ISE. We developed an ion-conductive glass membrane electrode with a composition of 50% AgI -25% Ag_2O -25% B_2O_3 to study the solvation of chloride ion.¹³ As in Fig. 3, its response to the transfer activity coefficient of Cl^- ion from water to organic solvents was approximately Nernstian. We applied the electrode to study the successive complexing of Cl^- ion in AN with water. The formation constants obtained were $\beta_1=15.2$, $\beta_2=22.5$ and $\beta_3=18.2$.

Most of the ISEs used in nonaqueous solutions are either glass or non-glass solid membrane electrodes. Liquid membrane and coated wire ISEs are usually not applicable in nonaqueous solutions. Recently, however, we developed some polymer membrane electrodes for use in dipolar aprotic solvents.¹⁴⁻¹⁸ They were prepared by coating a platinum disk with polyacrylamide (PAA) coupled to tetraethylene glycol monodo-

Fig. 3 Response of the ion-conductive glass electrode to the transfer activity coefficient of Cl^- from water to other solvents.

decyl ether (POE4, an acyclic neutral carrier), dibenzo-18-crown-6, Cryptand (222B), etc. They were durable in such solvents as AN, PC and DMF, and responded to alkaline earth metal ions with Nernstian slopes. The PAA-POE4 electrode was used, after confirming its response to ion solvations, to study the stepwise complexing of Li^+ , Mg^{2+} and Ba^{2+} in AN with DMF, DMSO and HMPA¹⁵ and of Ba^{2+} in PC with DMA.¹⁸ It was also used to get the Gibbs free energies of transfer of Ba^{2+} from PC to DMA and PC-DMA mixtures.¹⁸ Recently an electrode prepared by coating a platinum disk with a membrane of PAA polymer coupled to phthalocyanine cobalt(III) was found to respond specifically with a Nernstian slope to F^- ion in AN and PC.¹⁹ It was used to get the solubility product of NaF in AN and PC. It will be possible to develop other polymer membrane ISEs usable in nonaqueous solvents as sensors for ion solvations.

2.3 Problem in the study of ion solvations

In the study of ion solvations, two different types of cells may be used. One is a cell without a liquid junction and the other is a cell with a liquid junction between different solvents. For the solvation of M^+ ion, these are Cells 2 and 3, respectively.

In both cases, we encounter some difficulties: with Cell 2, we have to use a reference electrode (or a reference redox system) with a solvent-independent potential. With Cell 3, there is a relation expressed by Eq. (3),

$$\Delta G^\circ (M^+, S_1 \rightarrow S_2) = F(E_{\text{cell}} - E_j), \quad (3)$$

where E_{cell} is the EMF and E_j the LJP at J. We have to take the LJP into account. From the extrathermodynamic standpoint, some reference electrodes (or reference redox systems) have been assumed to show solvent-independent potentials and some liquid junctions to show negligible LJPs.¹ But there still remain some questions about the reliability of these assumptions. We have to check the appropriateness of the assumptions by all possible means. The following is the summary of our study of the LJP between different solvents.

3 The Problem of the Liquid Junction Potential between Different Solvents

If the electrode potentials in different solvents can be measured with a common scale, the effects of solvents on various chemical reactions and equilibria, including ion solvations, may be studied easily by electroanalytical techniques. It will be possible if sufficient knowledge of the LJP between different solvents can be obtained. Some efforts have been made to elucidate the characteristics of the LJP.²⁰ But our knowledge about the LJP is still quite limited.²¹

We carried out some systematic experimental projects to learn how the LJPs between different solvents are influenced by the electrolytes and the solvents at the junction.²²⁻³⁰ An EMF cell, such as in Fig. 4, was used. It gave free-diffusion junctions and was convenient for rapid and repeated measurements.

The LJP between different solvents contains the following three components: a) a component related to the electrolyte concentrations (or activities) on the two sides of the junction and the cationic and anionic mobilities, b) a component related to the differences in ionic solvations on the two sides of the junction, and c) a component related to the solvent-solvent interactions at the junction. Components b) and c) are specific to a junction between different solvents. We found that, under appropriate conditions, the variation in each of the three components may be measured separately from the others. Thus the characteristics of the three

components could be studied to some extent. They are summarized below for the junctions with a same electrolyte on the two sides, $c_1 \text{MX}(\text{S}_1) | c_2 \text{MX}(\text{S}_2)$.

3.1 Three components of the liquid junction potential between different solvents

Component a):^{29,30} This component has characteristics somewhat similar to the LJP between solutions in the same solvent. Its magnitude may be estimated by Eq. (4):³¹

$$E_j(a) = (-RT/F) \{ (t_{M1} - t_{X1}) \ln(a_2/a_1) + (t_{M2} - t_{M1} - t_{X2} + t_{X1}) [1 - a_1 \ln(a_2/a_1)/(a_2 - a_1)] \} \quad (4)$$

where t shows the ionic transport numbers, a the electrolyte activity, and $E_j(a)$ is equal to zero for $a_1 = a_2$. The linear relations in Fig. 5 have slopes of approximately unity, and show the validity of Eq. (4). The mobilities of Et_4N^+ and Pic^- are near to each other in many solvents, though they are rather different in solvents such as methanol. Thus, component a) for $\text{MX} = \text{Et}_4\text{NPic}$ is usually small (within ± 5 mV for c_1/c_2 between 0.01 and 100), except for the junctions

Fig. 4 EMF cell for the study of the LJP between different solvents, constructed with 4-way stopcocks for HPLC.

Fig. 5 Relations between the experimental variation in component a) and the calculated $E_j(a)$ for $c_1 \text{MX}(\text{S}_1) | c_2 \text{MX}(\text{S}_2)$. S_1/S_2 : AN/DMSO for 1.1-1.6, AN/PC for 2.1-2.3, DMF/DMSO for 3.1-3.3. MX: Et_4NClO_4 for 1.1, 2.1, 3.1, NaClO_4 for 1.5, 2.2, 3.2, LiClO_4 for 1.6, 2.3, 3.3, Et_4NI for 1.2, Et_4NBr for 1.3, Et_4NCl for 1.4. $(c_1, c_2)/\text{mM}$: open circles, from left to right, (100,1), (10,1), (1,1), (1,10), (1,100) and closed circle, (25,25). Each line has a unit slope.

including methanol.

Component b):^{27,28} By component b), cation M^+ tends to make the potential of the solution in which the

solvation is stronger more positive, while anion X^- tends to make it less positive. Component b) is independent of electrolyte concentrations. Equation (5) has been derived under assumptions similar to those in Eq. (4):²⁸

$$E_j(b) = (-1/2F)[(t_{M1} + t_{M2})\Delta\mu^\circ(M) - (t_{X1} + t_{X2})\Delta\mu^\circ(X)], \quad (5)$$

where $\Delta\mu^\circ$ is the difference between the standard chemical potentials in S_1 and S_2 and is equal to the standard molar Gibbs free energy of transfer from S_1 to S_2 . Equation (5), however, holds only qualitatively. The relations between the experimental variations in component b) and the calculated $E_j(b)$ are shown in Fig. 6 for some junctions between water and organic solvents. Though linear relations are observed, the slopes are much smaller than unity (0.4–0.5), except for the immiscible H_2O /nitrobenzene(NB) junction for which the slope is unity. Linear relations are also obtained for junctions between methanol and organic solvents, but the slopes are even smaller (0.2–0.3). The reasons for the small slopes are not known yet, though the mutual diffusion of the solvents at the junction and/or the incomplete replacement of the solvated molecules on transfer of the ions across the junction may be suspected. We proposed to estimate the actual value of component b) by multiplying the slope of the linear relation by the value calculated from Eq. (5). Some estimated values are listed in Table 1. Component b) may be over 150 mV in some cases and may be the largest of the three components. However, it is usually small (within ± 10 mV) for junctions with $MX=$

Fig. 6 Relations between the experimental variation in component b) and the calculated $E_j(b)$ for 20 mM $MX(H_2O) \parallel 20$ mM- $MX(S)$. Solvent S and the slope are shown on each curve. MX : 0, Et_4NPic ; 1, Et_4NCl ; 2, Et_4NBr ; 3, Et_4NI ; 4, Et_4NClO_4 ; 5, Me_4NClO_4 ; 6, Pr_4NClO_4 ; and 7, Bu_4NClO_4 .

Table 1 LJPs/mV estimated by the three component method and the conventional method for 25 mM $MX(H_2O) \parallel 25$ mM $MX(S)$

S	MX	Three component method				Conv. $E_j(2)$	Diff. $E_j(1) - E_j(2)$
		(a)	(b)	(c) ^a	$E_j(1)$		
AN	Et_4NPic	0	8	32	40	39	1
	Et_4NClO_4	-2	18	32	48	55	-7
	Et_4NI	-2	60	32	90	105	-15
	Et_4NCl	-2	131	32	161	169	-8
PC	Et_4NPic	0	(21)	17	(38)	13	(25)
	Et_4NClO_4	0	16	17	33	34	1
	Et_4NI	0	74	17	91	100	-9
	Et_4NCl	0	166	17	183	185	-2
DMF	Et_4NPic	0	2	103	105	111	-6
	Et_4NClO_4	-2	30	103	131	131	0
	Et_4NI	-2	73	103	174	177	-3
	Et_4NCl	-2	157	103	258	252	6
DMSO	Et_4NI	-1	44	102	145	141	4
	Et_4NCl	-1	129	102	230	226	4
MeOH	Et_4NPic	1	-18	30	13	6	7
	Et_4NClO_4	-2	18	30	46	40	6
	Et_4NI	-2	22	30	50	49	1
	Et_4NCl	-1	40	30	69	81	-12

a. Obtained by assuming the values of component c) at the junctions between aprotic solvents and at H_2O/NB equal to zero.

Fig. 7 Orientation of solvent molecules at the interphase region, introduced to explain the characteristics of component c).

Et₄NPic, though somewhat larger when methanol is included.

Component c):^{23-25,29} The exact mechanism of this component is not known yet. But, its characteristics, *i.e.* its magnitude and direction, coincide well with those of the potential difference expected to occur if the molecules of the solvents on the two side of the junction interacted with each other as an electron-pair donor and an electron-pair acceptor and in some part were oriented perpendicularly to the boundary (Fig. 7). As expected from Fig. 7, the influence of electrolytes on component c) is usually small. But in some cases its magnitude tends to partially decrease with the increase of the electrolyte concentrations.²⁹ There still remain some difficulties in accurately estimating this component. Somewhat roughly estimated values are listed in Table I for H₂O/organic solvent junctions. For junctions between strongly interacting solvents as H₂O/DMF and H₂O/DMSO, component c) is over 100 mV (the aqueous side more negative). For junctions between weakly interacting solvents as H₂O/PC and H₂O/AN, it is fairly small. Between two dipolar aprotic solvents, it is usually within ± 20 mV.

For junctions including mixed solvent(s), c_1 MX ($S_1 + S'_1$); c_2 MX (S_2) and c_1 MX ($S_1 + S'_1$); c_2 MX ($S_2 + S'_2$), component c), in many cases, varies linearly or near-linearly against the volume fraction of the mixed solvent.²⁵ This fact is very important when we estimate the variation in component c) at the junction including mixed solvent(s) (see Cell 1).

3·2 A new method of estimation of the liquid junction potential and the assumption of negligible liquid junction potential

In Eq. (3), if the values of ΔG_i° ($M^+, S_1 \rightarrow S_2$) and E_{cell} are known, the value of LJP, E_j , may be estimated. This is a conventional method of estimation of the LJP. The reliability of the estimated LJP values depends on

the reliability of the extrathermodynamic assumption used to obtain ΔG°_i (M^+ , $S_1 \rightarrow S_2$).³²

We propose a new method (three component method) to estimate the LJP. In the method, we estimate each of the three components separately and then sum them up. As shown in Table 1, the values obtained by our method agree fairly well with the values obtained by the conventional method using ΔG_i° (Ag^+ , $\text{H}_2\text{O}-\text{S}$) in ref. 1a. It is difficult at present to decide which method gives more accurate values. But our method has the advantage that, by the knowledge of the three components, we can predict how the LJPs are influenced by the solvents and the electrolytes at the junction. It should be useful in practical measurements.

In the study of ion solvations, Parker *et al.*³³ assumed that the LJP across Cell 4 is negligible to within ± 20 mV.

At junction J₂, both the electrolytes and the solvents on the two sides are different. We express this type of junction by $c_1 \text{MX}(\text{S}_1) | c_2 \text{NY}(\text{S}_2)$. Recent results³⁰ on the junction of this type show that if S in Cell 4 is an aprotic solvent, the above assumption is nearly acceptable within the claimed uncertainty. It is sometimes desirable, however, to use 1 mM AgNO₃ instead of 10 mM AgNO₃. When S is a protic solvent (water or methanol), the assumption may not be acceptable because components b) and/or c) at J₂ are not negligible.

The salt bridge of Et₄NPic(AN) is also effective to decrease big LJPs. As in Table 1, the LJP at *c* Et₄NCl(H₂O)|*c* Et₄NCl(DMF) exceeds 200 mV. But it decreases to about one tenth if the salt bridge is inserted between the two solutions, *c* Et₄NCl(H₂O)|100 mM Et₄NPic(AN)|*c* Et₄NCl(DMF), and if *c* ≪ 100 mM.

3.3 Stability and reproducibility of the liquid junction potential between different solvents

The stability and reproducibility of the LJP between different solvents are also of great concern to us. For free-diffusion junctions of the type $c_1 \text{MX}(\text{S}_1) | c_2 \text{MX}(\text{S}_2)$, the LJP is surprisingly stable and reproducible.²⁶ Though the interphase region seems to expand gradually with time, its effect on the LJP is small. The LJP, which is established within a few seconds, is usually stable within $\pm 2 \text{ mV/h}$ and reproducible to within $\pm 2 \text{ mV}$, even when its magnitude is estimated to be over 200 mV .³⁴ The reasons for the excellent stability have been studied in detail.²⁶ The situation, however, is quite different for junctions with different electrolytes on the two sides, $c_1 \text{MX}(\text{S}_1) | c_2$

NY (S_2). When $c_1 \approx c_2$, the LJP fluctuates considerably (more than 20 mV in some cases). This is mainly due to the fluctuation in component b). Stable LJPs are obtained only when $c_1 \gg c_2$ or $c_1 \ll c_2$. Junctions of this type should be avoided if possible.

It is not easy to get the whole picture of the LJP between different solvents, because the phenomena occurring at the junction are complicated. The solvents and the ions on the two sides tend to move across the junction. The transfer of ions is accompanied by their solvation or desolvation at or near the junction. The solvents on the two sides may interact with each other. We could get, however, some information about the roles of the electrolytes and the solvents at the junction. The information will be of use in further elucidation of the LJP as well as in practical electroanalytical studies.

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- Eqs. (4) and (5) were obtained by integrating Eqs. (4') and (5') under the assumption that t , a and μ° (the standard chemical potential) varied linearly at the interphase region.

$$E_j(a) = (-RT/F) \int_{S_1}^{S_2} (t_M - t_X) d \ln a_{MX} \quad (4')$$

$$E_j(b) = (-1/F) \int_{S_1}^{S_2} [t_M d\mu^\circ(M) - t_X d\mu^\circ(X)] \quad (5')$$

Eqs. (4') and (5'), on the other hand, were obtained from the equation:

$$E_j = (-1/F) \int_{S_1}^{S_2} [t_M d\mu(M) - t_X d\mu(X)]; \mu = \mu^\circ + RT \ln a$$

by taking the variation in μ° into account.

- See, for example, J. Datta, S. Bhattacharya and K. K. Kundu, *Aust. J. Chem.*, **36**, 1779 (1983).

33. R. Alexander, A. J. Parker, J. H. Sharp and W. E. Waghorne, *J. Am. Chem. Soc.*, **94**, 1148 (1972).
34. In most practical cases, the junction is constrained or restricted by a porous plug or membrane. At such a constrained-diffusion junction, the LJP is established

more slowly and may not be so stable as at a free-diffusion junction.

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