Preferential Ion Transport in Electrodialysis through Ion-exchange Resin Membranes

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In electrodialysis through ion-exchange resin membranes, different ionic species of the same charge sign are usually transported at different rates.1-4) Even early in the development of practical permselective membranes, suggestions were made for ion separations by means of electrodialysis.5) In electrodialytic water treatment, the preferential ion transport has implications with respect to meeting the product specifications (the desired product being either the partially-desalted water or the simultaneously-produced concentrated brine), e. g., with respect to the maximum allowable concentration of precipitate-forming ions in the brine.

Preferential ion transport through permselective membranes can be described from first principles,6-10) but, as will be shown, the inherent difficulties allow only qualitative conclusions and predictions to be made, particularly in practical systems.

Theoretical Considerations

The migrating counterions are transported consecutively (Fig. 1) through the bulk solution being electrodialysed by electric and convective transport, through the diffusion layer on the respective membrane by electric and diffusional transport, across the solution/membrane interface, through the membrane and across a second membrane/solution interface, and through a second diffusion layer into the bulk of the brine.

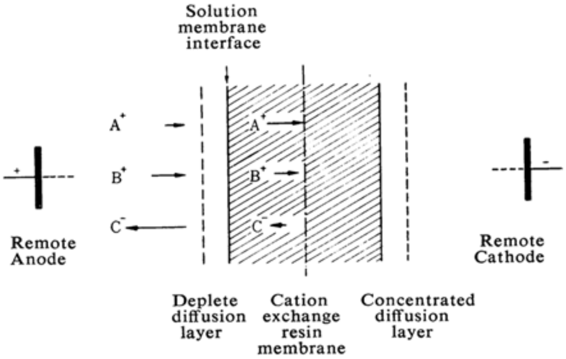

Fig. 1. Preferential ion transport through a single (cation) exchange membrane.

Transport through the Membrane.—The electrical transport ratio of two counterions, *i* and *j*, in an ion-exchange resin membrane is given by:

$$\frac{\bar{t}_i}{\bar{t}_j}=\frac{\bar{u}_i\bar{X}_i}{\bar{u}_j\bar{X}_j} \tag{1}$$

in which *t* is the transport number, *u*, the electrical mobility, and *X*, the fractional contribution of one counterion to the total counterion content; the barred symbols refer to the resin phase.

The mobility of each counterion in the membrane phase is determined by the restricting forces acting on that (hydrated) counterion, by the electrostatic and other binding forces exerted by the fixed ionic groups in the resin, and by the frictional forces encountered. Equation 1 holds for local values; however, ion-exchange resins are known to have some heterogeneity in their crosslinking or pore structure,11-14) and only average values for $\bar{u}$ and $\bar{X}$ can be measured.

Furthermore, the mobilities of the counterions in the resin are not independent,15) there occurs some interaction, which can be detected from the non-linearity of a plot of the resin conductance versus the equivalent counterion

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composition in the resin.[16-19] The deviation from linearity is sometimes negligible;[1,20] it can be expected, that the interaction will be strong in highly-crosslinked ion-exchange resins with a high concentration of fixed ions.

From published data,[21-26] it is apparent that the electrical mobilities of the counterions are governed by much the same factors as those which play an important part in ion-exchange equilibria, namely, the charge and size of the hydrated counterion and the nature and concentration of the fixed ions. Consequently, when a pressure-volume effect is not determining, the preferentially-absorbed counterion often has a relatively low mobility in the resin. It is, therefore, not surprising that some ion-exchange resin membranes specially prepared to have a specific affinity for a certain counterion[27,28] show little specific transport of that ion *across* that membrane. The effect of the preferential absorption of the counterion is then counteracted by the strong binding of that ion. This counteraction can be so strong that, for example, very little Ba^{2+} is transported across a sulphonic acid resin membrane placed in a mixed sodium chloride/barium chloride solution.[29]

When the preferential absoption of one counterion in the resin is caused by the specific exclusion of the other counterion, then the preferentially-absorbed ion may have a relatively high mobility in the resin which enhances the preferential transport of that ion across the membrane.

Transport Across the Solution/Membrane Interface. — The concentration ratio, $\bar{X}_i/\bar{X}_j$, inside the membrane depends on the uptake of the ions from the solution on the membrane surface, which has a different composition from the bulk solution because of polarisation, which is caused by the fact that the transport number in the membrane of the joint counterions is close to 1. It has been pointed out by Dibenedetto[9] that the ion-exchange equilibrium on the interface is hardly affected at all by the current density because the (electrical) transport velocities of the ions are small in comparison with their velocities because of Brownian motion.

If we define the relative affinity coefficient, K_j^i, by:

$$K_j^i \equiv \left(\frac{X^*_j}{\bar{X}_j}\right)^{z_i}\left(\frac{\bar{X}_i}{X^*_i}\right)^{z_j} \tag{2}$$

in which z is the electrovalency of each counterion and * refers to the solution on the membrane surface, then:

$$\frac{\bar{X}_i}{\bar{X}_j} = \bar{X}_j^{(z_i/z_j-1)} \cdot (K_j^i)^{1/z_j} \cdot \frac{X^*_i}{(X^*_j)^{z_i/z_j}} \tag{3}$$

It has been shown[19] that K_j^i is the sum of a number of terms and is far from constant when i and j are of unequal valency; K_j^i is, then, dependent on the total external electrolyte concentration and on $\bar{X}_j$ (or X_j). In electrodialytic processes, both the total electrolyte concentration and X_j change with either time or place.

An interesting development is the layered membranes in which a highly conductive ion-exchange resin membrane has been covered on both sides with a thin layer of a less conductive but very highly crosslinked ion-exchange resin,[30] the special properties of this thin layer of resin determining the uptake of counterions from the adjacent solution. The thin layer on the other side of these membranes has been applied for mechanical reasons, but it may simultaneously serve to eliminate the effect of possible polarisation at the first resin/resin interface.

Transport Across the Depleted Diffusion Layer. —If only one electrolyte is present, the system can be described in terms of a diffusion layer with a linear concentration gradient.[8,31,32] In systems with two electrolytes sharing the ion which has the same sign as the fixed ions in the resin membrane, it has been assumed[6-8] that two systems, each with one electrolyte and a linear concentration gradient, can be superimposed (Fig. 2) to arrive at a relation between X^*_i/X^*_j and X_i/X_j. This leads, however, to an inconsistency. With two superimposed linear gradients, t_i/t_j varies in

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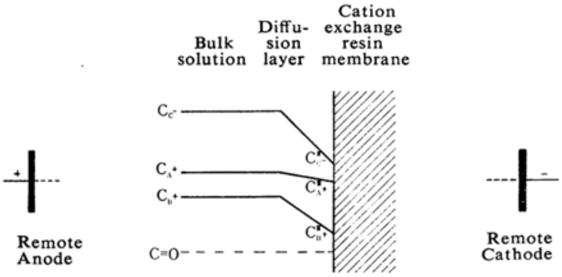

Fig. 2. Concentration gradients across a diffusion layer in a dialysate compartment.

the diffusion layer with the distance from the membrane, because the ratio of the concentrations of the two ions varies (anywhere: $t_i/t_j = u_iC_i/u_jC_j$). Therefore the diffusion fluxes of i and j should also vary across the diffusion layer, but this requires non-linear concentration gradients.

In practical electrodialysis, the effect of polarisation is counteracted by the forced convection of the electrolyte solution towards the membrane surface through the use of convection-inducing devices placed in the path of the solution.[33-36] This makes it virtually impossible to relate X and X^*. The limit to preferential transport for the zero current density may, however, be estimated from

$$\frac{\bar{t}_i}{\bar{t}_j} = \bar{X}_j^{(z_i/z_j-1)} \cdot (K^i{}_j)^{1/z_j} \cdot \frac{\bar{u}_i X_i}{\bar{u}_j (X_j)^{z_i/z_j}} \tag{4}$$

while at high current density $\bar{t}_i/\bar{t}_j$ approaches t_i/t_j.

Overall Transport. — More complicating factors are introduced in practical electrodialysis because a number of processes occur simultaneously (Fig. 3). The membranes are not ideally (charge-) selective, and co-ion transport takes place, together with a certain amount of salt diffusion and also osmosis in the opposite direction. The preferential ion transport measured by the analysis of the desalting or the concentrating stream is the total effect of all the processes taking place.

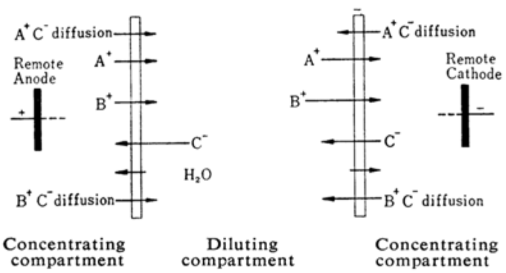

Fig. 3. Transport processes occurring simultaneously in a dialysate compartment.

From the considerations given above, it will be clear that a description of the preferential ion transport from first principles is very unattractive and that an empirical approach is to be preferred. Fortunately, the process can be described, under certain conditions, as a separation process with a constant separation factor[6,37] denoted s:

$$\frac{dC_i}{dC_j} = s\frac{C_i}{C_j} \tag{5}$$

When an amount of saline water is demineralised from concentrations C_i' and C_j' to concentrations C_i'' and C_j'', the integration of Eq. 5 gives:

$$\ln\frac{C_i''}{C_i'} = s \ln\frac{C_j''}{C_j'} \tag{6}$$

Experimental

A batch of 10 l. mixed electrolyte solution, contained in an aspirator with a calibrated-level glass for volume measurements, was circulated by a pump through the parallel desalting (or "dialysate") compartments of a membrane pack containing ten such compartments alternating with eleven concentrating (or "brine") compartments (Fig. 4). Samples

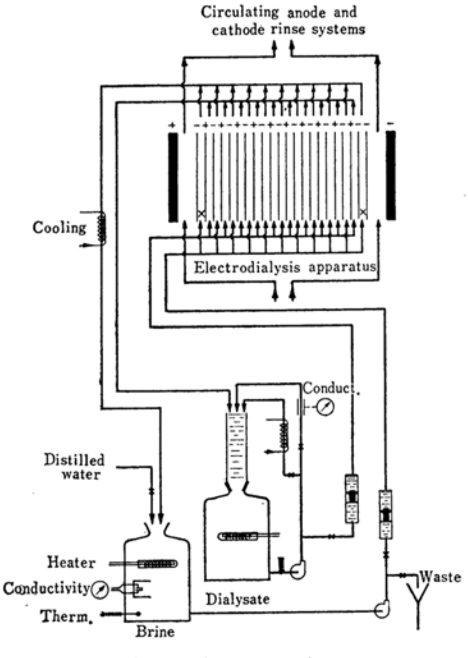

Fig. 4. Experimental set-up; the compartments marked X are connected to calomel electrodes.

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of the batch, which was thoroughly mixed by a fast flow through a by-pass of the membrane pack, were analyzed at regular intervals, while the total electrolyte content was indicated by a conductivity meter. The vertical compartments with upward flow were formed by the cut-away rectangular centre section of asbestos "steam-jointing" gaskets, 1/32 inch thick, which were filled with perforated corrugated spacers, each compartment having a surface area of 128 cm^2. The first and last brine compartments were connected to calomel electrodes, so that the voltage drop across the membrane pack could be measured by a vacuum-tube voltmeter with a high input resistance. The voltage on these electrodes was kept constant in each experiment. The current-carrying electrodes, having the same surface area as the compartments in the pack, were placed in electrode compartments adjacent to the end brine compartments. A separate electrode rinse solution was circulated through the electrode compartments.

A batch of brine, with the same initial composition as the initial dialysate, though usually double the concentration, was circulated through the brine compartments in parallel. The total electrolyte concentration of the brine, measured with a conductivity cell, was kept approximately constant during each experiment by continuous dilution with distilled water. The flow velocities in the brine and dialysate compartments were 10 cm./sec. All the solutions were thermostatically controlled. Further details on the experimental set-up are given elsewhere.38)

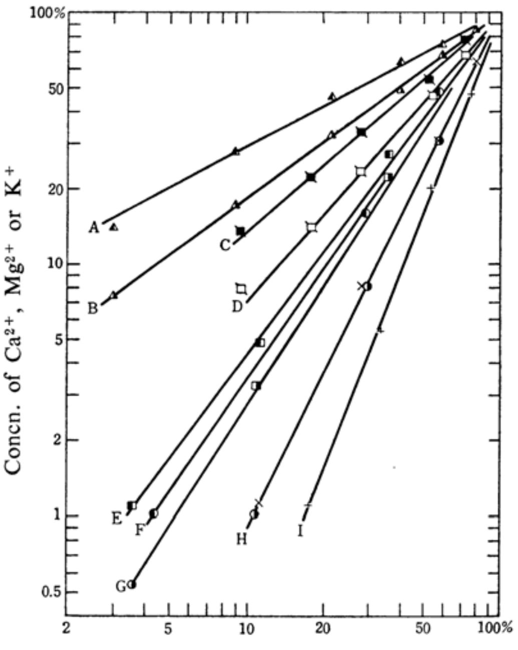
The following membrane pairs were used:

C. S. I. R. parchment-base-type PS (cation exchange) and G (anion exchange)
Permaplex39)—C20 and A20
T. N. O.40)—C60 and A60
A. M. F.41)—3129 B56 and 96

Results and Discussion

The reasonably general validity of Eq. 6 is illustrated for cation transfer and anion transfer in Figs. 5 and 6 respectively, in which results obtained with a variety of membrane combinations and on different initial water compositions have been brought together. The results of the investigation of the effect of compartmental voltage with T. N. O. membranes and Permaplex membranes are shown in Figs. 7 and 9 respectively.

The results obtained with parchment-base membranes (lines A and in Fig. 5 and line K



Concn. of reference ion Na^+

Fig. 5. Preferential cation transport according to Eq. 6, expressed in terms of the % residual concentration of an ion in the dialysate; details in Table I.

TABLE I. DETAILS OF DATA IN FIGS. 5 AND 6

Line	Symbol	Counter ion	Membranes	Initial dialysate
A	◭	Mg^{2+}	C. S. I. R. parchment base membranes	Synthetic sea water
B	◮	Ca^{2+}		
K	△	SO_4^{2-}		
C	■	$Ca^{2+}+Mg^{2+}$	T. N. O. A22 and C21 heterogeneous membranes	Brackish well water43)
D	□	K^+		
L	■	CO_3^{2-}		
N	□	SO_4^{2-}		
E	◧	Mg^{2+}	Mainly T. N. O. A22 and C21 heterogeneous membranes	Sea water42)
G	◨	Ca^{2+}		
M	□	SO_4^{2-}		
J	○	SO_4^{2-}	A. M. F. 3129 B56 and 96 homogeneous membranes	Synthetic sea water
F	◐	Mg^{2+}		
H	◑	Ca^{2+}		
H	×	Ca^{2+}		0.25 N $CaCl_2$/0.25 N NaCl
I	+	Ca^{2+}		

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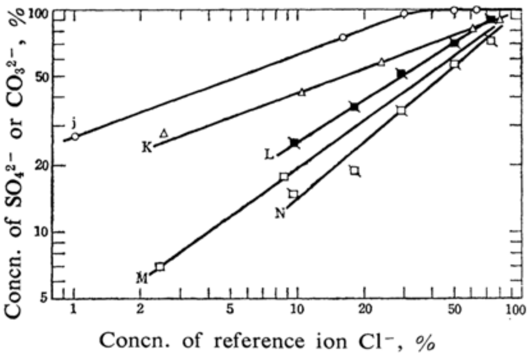

Fig. 6. Preferential anion transport according to Eq. 6, expressed in terms of the % residual concentration of an ion in the dialysate; details in Table I.

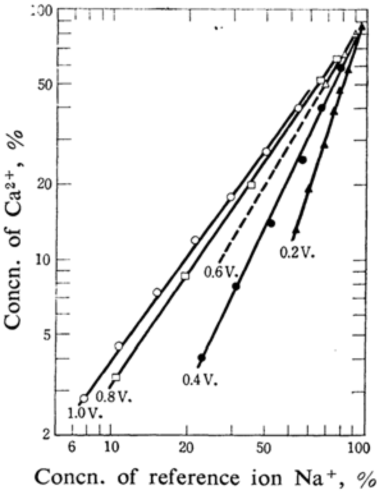

Fig. 7. Preferential cation transport through T.N.O. A 60 and C 60 membranes at various compartmental voltages.

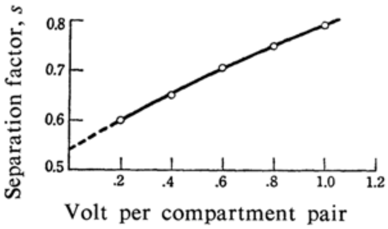

Fig. 8. The separation factors (from Fig. 7) versus compartmental voltage.

in Fig. 6), which were of an early type not highly efficient in sea water, indicate that Eq. 6 holds well even if the detrimental transfer processes indicated in Fig. 3 constitute a considerable portion of total ion transfer.

That the separation factor is independent of the initial composition is indicated by line H in Fig. 5, which represents two experiments with the same membrane pair, the same electric potential drop per compartment pair, and the same flow velocity in the compartments, but on water with a completely different composition, namely, synthetic sea water with a sodium : calcium equivalent ratio of 45 : 2, and a total electrolyte concentration 0.6 N, and a mixed sodium chloride/calcium chloride solution, 0.5 N in Cl^-, with a sodium : calcium equivalent ratio of 1 : 1.

That Eq. 6 holds even when a very small amount of one ion is present is demonstrated by line D in Fig. 5, which represents the removal of a small amount of K^+ from a natural brackish well water. A strong deviation from linearity was found for the separation of Cl^- and SO_4^{2-}, as is indicated in line J in Fig. 6. This will be discussed separately.

The Effect of Compartmental Voltage (Current Density).—This effect is illustrated by the different slopes of lines H and I in Fig. 5, representing identical experiments but run at 1.0 V. and 0.75 V. per compartment pair respectively. It should be noted that during the runs the current density, *i*, decreases with the electrolyte concentration in the dialysate *C*, approximately according to[38] $i=\dfrac{E}{a+b/C}$, in which *E* is the compartmental voltage and *a* and *b* are constants.

The effect of the compartmental voltage drop, which is a measure of the degree of polarisation at a constant flow velocity, was investigated in more detail, using T. N. O. C60 and A60 membranes at 30°C with initial electrolyte concentrations in the dialysate of 0.25 N Cl^- (0.125 N Na^+ and 0.125 N Ca^{2+}), a constant total brine concentration of 0.5 N, and compartmental voltage drops, constant in each run, from 0.2 to 1.0 V. The separation factors derived from the slopes of the lines in Fig. 7 are plotted in Fig. 8 versus the voltage.

Similar experiments have been carried out with Permaplex membranes, but the range of voltages used was higher (0.2 to 1.5 V. per compartment pair) because the higher resistance of these membranes caused the current densities to be 10~20% lower at equal voltages. The non-linearity of the preferential ion transport data, as given in Fig. 9, can be attributed to polarisation, which increases with a decrease in the electrolyte concentration in the dialysate. It is interesting that the lines in Fig. 9 tend to approach the same slope at low concentrations. It was not possible to measure the polarisation in terms of an increase in the electric resistance of the membrane pack. Preferential ion transfer could thus be used as a very sensitive, though rather impractical, measure of the degree of polarisation. Because of the curved lines in Fig. 9, only the separation factors corresponding to the *initial* slopes

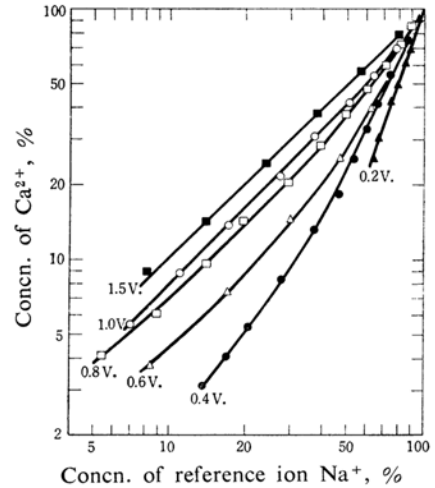

Fig. 9. Preferential cation transport through Permaplex A 20 and C 20 membranes at various compartmental voltages.

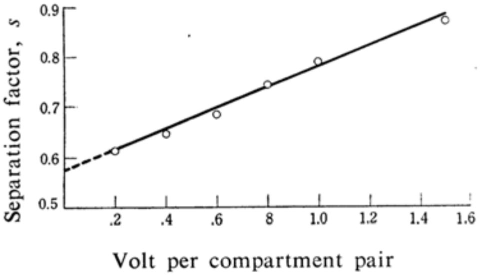

Fig. 10. The separation factors (from initial slopes in Fig. 9) versus compartmental voltage.

have been plotted versus the voltage in Fig. 10. The separation factors in Fig. 10 are approximately the same as in Fig. 9. The values for $K^{\mathrm{Na}}_{\mathrm{Ca}}$ were also reasonably close for the two types of membranes.[19]

The Effect of the Nature of the Membrane.—Heterogeneous membranes (ground ion-exchange resin embedded in a sheet-forming binder) appear to cause less separation than homogeneous membranes when used under comparable conditions, as is evident from the results shown in Figs. 5 and 6 and in Figs. 7 and 9. This can be explained by the fact that a portion of the ion transport through the heterogeneous membranes is through a liquid path;[44,45] moreover, as has been mentioned in the previous section, the polarisation on these membranes is stronger.[46]

A comparison of the data in Fig. 7 with lines H (1.0 V.) and I (0.75 V.) in Fig. 5 shows that the preferential transport of Ca^{2+} through the homogeneous AMF membranes, which have a high internal concentration of fixed ions, is much more marked than through the T. N. O. membranes, which have a relatively low internal concentration.[19] This can be attributed to the higher affinity of the AMF membranes for calcium ions at intermediate loadings.[19]

The Cl$^-$/SO$_4$$^{2-}$ Separation. — In Fig. 6 a strong deviation from linearity is found for the Cl/SO$_4$ separation using AMF membranes (line J). At high concentrations there is hardly any SO$_4^{2-}$ transport. It increases considerably, however, below a total electrolyte concentration of 0.15 N. This is a reflection of the strong increase in affinity for SO$_4^{2-}$ relative to Cl$^-$ at concentrations below 0.15N;[19] later experiments have shown that this phenomenon is quite general with membranes which are efficient at concentrations above 0.15 N, particularly if the membranes are highly crosslinked.

The Order of Preference.—The order of the preferential transport of common ions at total electrolyte concentrations below 1 N, using highly efficient ion-exchange resin membranes and preventing serious polarisation, as found by us agrees well with most data reported by other workers.[2,16,29,37,41,42,47-54] For cations the general order is $\mathrm{Ca^{2+}>Mg^{2+}>K^+>Na^+>Li^+}$, and for anions, $\mathrm{Cl^->SO_4^{2-}>CO_3^{2-}\cdot(HCO_3^-)}$ and $\mathrm{NO_3^->Cl^->F^-}$. These orders compare very well with those observed in ion exchange equilibria; the relative affinity coefficient, K_j^i, appears to be the determining factor unless the mobility in the membrane of one counterion is greatly reduced by very strong binding forces (e. g., ionpair formation).

Summary

Because of the great difficulties encountered when describing preferential ion transport in

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electrodialytic demineralisation from first principles, an empirical approach is more attractive. Preferential ion transport can be described as a simple separation process with a separation factor which is constant for a certain membrane pair under certain conditions, namely, a constant voltage drop per compartment pair at a constant flow velocity in the compartments, high enough to avoid any serious polarisation. Exceptions occur when one counterion is immobilised to a great extent in the resin, when specific strong binding forces are operative (e. g., ionpair formation), and also when the preferential absorption of a counterion is based on the preferential exclusion of the other counterion. The latter appears to be the case in the separation of Cl^- and SO_4^{2-} at high total electrolyte concentrations.

The order and magnitude of preference are, in the first instance, governed by the same factors which govern ion-exchange equilibrium. The separation of ions has been shown to decrease with an increase in the applied electric potential (current density). It has been demonstrated that heterogeneous membranes cause a concentration polarisation at lower current densities than homogeneous membranes and that this early polarisation can be detected from the preferential ion transport data before it can be measured in terms of the resistance of the membrane pack.

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