

Phase Separation in Carboxylated Polysulfone/Solvent/Water Systems[†]

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SYNOPSIS

The cloud point curves for the ternary systems carboxylated polysulfones/solvent/water were determined by a titration method. Membrane-forming solvents used were NMP, DMAc, DMF, DMSO, TMU, and DMPU. Four modified polysulfones containing 0.43, 0.93, 1.38, and 1.93 carboxyl groups per repeat unit were synthesized for this study. Water/solvent theta-compositions and solubility parameters for these polymers were also estimated.

INTRODUCTION

Aromatic polysulfones are extensively used as ultrafiltration (UF) membrane materials due to their excellent mechanical strength, thermal stability, and membrane forming qualities. Utility of these polysulfones can be extended when polar functional groups are attached to the polymer chain, for example, through sulfonation.^{1,2} A process of lithiation followed by treatment of the reactive lithiated intermediate with various electrophiles has been reported as a versatile general method of introducing functional groups on polysulfone.³⁻⁵ A series of Udel® polysulfones containing increasing amounts of carboxyl groups, almost up to two per repeat unit, has been prepared by this process.⁶ In this case, the reaction electrophile was carbon dioxide. Solubility and other properties of these modified polysulfones were also investigated.⁶ The presence of polar carboxyl functionality on polysulfone broadens the scope of membranes produced from these materials, for example, by extending the separation range from UF to reverse osmosis through increased hydrophilicity,⁷ or by altering solubility characteristics and solvent resistance. Carboxyl groups also provide the potential for charged membranes and an at-

tachment point for immobilization of enzymes or other molecules.

In this paper we report the phase separation behaviour of a series of carboxylated polysulfones with degree of substitution (DS) from 0.00 to 1.93 in the form of cloud point curves in ternary phase diagrams. This information is pertinent to understanding the characteristics of these polymers during the phase inversion step in making asymmetric membranes. During this step, a polymer solution cast upon a support is brought in contact with water (nonsolvent), causing phase separation by replacement of the solvent with the nonsolvent within the polymer matrix being formed. Polysulfone (PSf) cloud point curves for DMF/H₂O,^{8,9} DMAc/H₂O,¹⁰ and NMP/H₂O⁹ have been reported. Cloud point curves for the related polymer polyethersulfone (PES)/solvent/H₂O systems have also been reported.^{9,11}

We also report the solubility parameters δ of the solvents and the modified polysulfones. The calculated δ values were generally in good agreement with the experimental results.

EXPERIMENTAL

Materials and Method

Carboxylated polysulfones of various DS were prepared by lithiation of PSf, followed by treatment with carbon dioxide.⁶ The carboxylate polymers were acidified to the carboxylic acid form by treatment with hydrochloric acid. The starting material for the

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carboxylated polymers was Udel® P-3500 polysulfone from Amoco Performance Products. The following polymers were used in this study:

Polymer	DS
A Udel polysulfone	0.00
B Carboxylated PSf	0.43
C Carboxylated PSf	0.93
D Carboxylated PSf	1.38
E Carboxylated PSf	1.93

The polymers were dissolved at various concentrations at room temperature in the following solvents: *N*-methylpyrrolidinone (NMP) and dimethylformamide (DMF) from Anachemia Ltd. were both distilled under vacuum before use; dimethylacetamide (DMAc) containing 0.001% water and dimethylsulfoxide (DMSO) containing 0.002% water, both from J. T. Baker Chemical Co.; tetramethylurea (TMU) from Sigma Chemical Co.; and *N,N*-dimethylpropyleneurea (DMPU) from Aldrich Chemical Co. The last four solvents were used as supplied. Distilled water was the nonsolvent.

Cloud Point Curve

Cloud points were determined by titrating polymer solutions with water at 25°C. Quantities of materials used were determined by weight, using an electronic balance capable of reading to 0.0001 g. For polymer solution of 10 wt % or less, the solution viscosity was low enough to allow agitation by a magnetic

bar. Polymer was weighed into a 50 mL Erlenmeyer flask containing a Teflon-coated magnetic bar. The flask was capped tightly with a rubber septum stopper. The required quantity of solvent was added through the septum by means of a syringe. The clear polymer solution was then titrated with distilled water injected through the septum by a microsyringe until turbidity was observed. The cloudy mixture was placed in a water bath thermostatically controlled at $25 \pm 0.1^\circ\text{C}$ for several hours. More distilled water was added if turbidity disappeared at 25°C. For solutions of higher than 10 wt % polymer, mixing by a magnetic bar was either inefficient or impossible. Polymer was weighed into a dry glass sample bottle of about 25 mL capacity which was capped with a rubber septum stopper through which a stainless steel stirring rod was inserted. Again, addition of solvent and water was via syringe. After mixing by the stirring rod, the samples were placed in a temperature regulated bath set at 50°C. Mixing was quite effective by this combination of thermal treatment and mechanical agitation. The bath temperature was then lowered to 25°C. More water would be added if turbidity was not observed at 25°C. A fast-acting thermostat bath was very helpful in bringing about this thermal swing. Since the addition of water was incremental, this titration method was somewhat tedious, but its simplicity allowed a large number of samples to be treated systematically.

The use of a rubber septum isolated each sample, reducing loss of material and solvent evaporation to a negligible amount. Experimental error occurred mainly in the weight of water added in small incre-

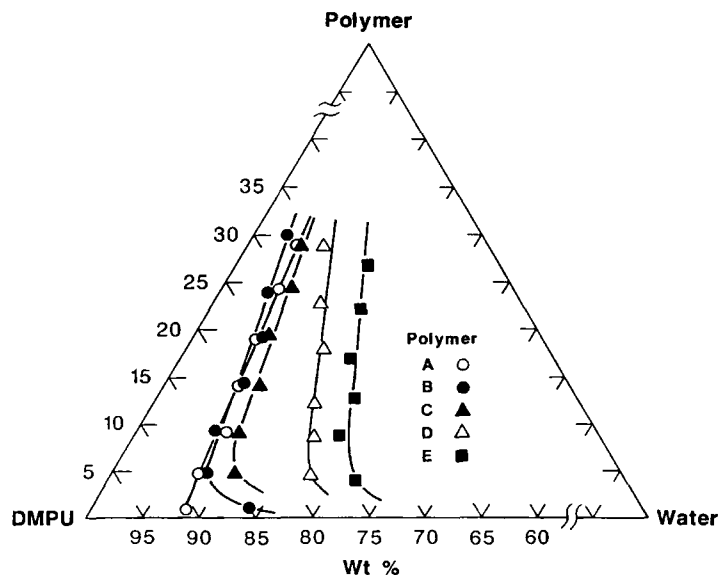


Figure 1 Cloud point curves of carboxylated polysulfones/DMPU/water at 25°C.

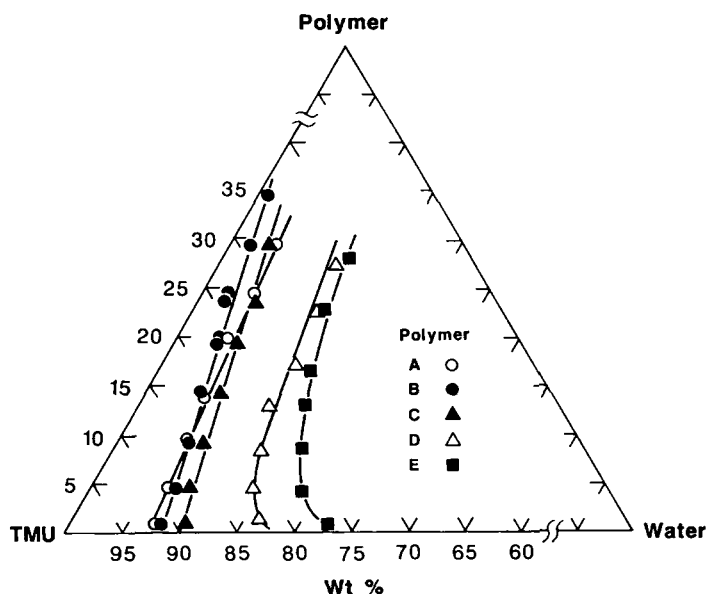


Figure 2 Cloud point curves of carboxylated polysulfones/TMU/water at 25°C.

ments, which overshoot the end point. About 30 g of materials were used in one titration flask and the error was estimated to be 0.3%. About 5 g of materials were used in one sample bottle and the error was estimated to be 0.5%.

RESULTS AND DISCUSSION

Membrane performance in separation applications depends very much on polymer morphology in the

membrane. The final polymer morphology is the result of its history, a series of steps that involve mixing and demixing of components under a given set of environmental conditions. To understand a membrane forming process, both its thermodynamic and kinetic factors have to be considered. Cloud point curves presented in a ternary phase diagram can provide useful thermodynamic and kinetic in-

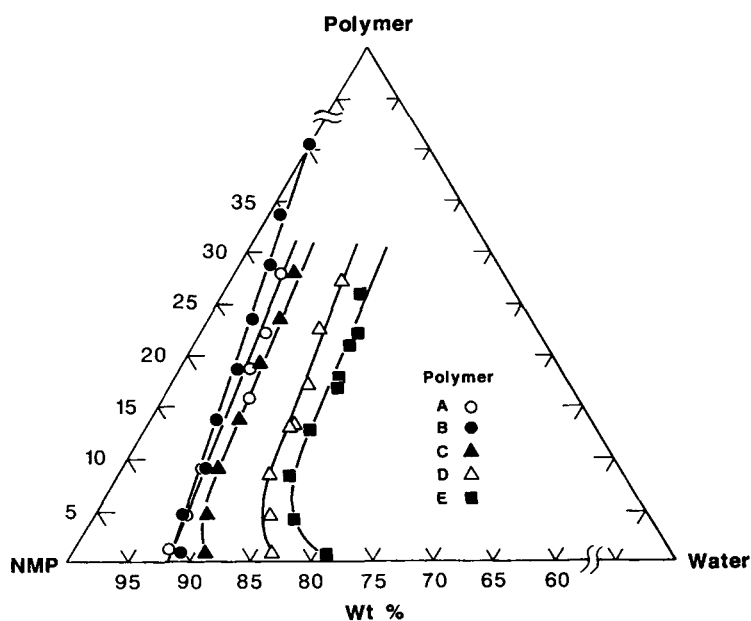


Figure 3 Cloud point curves of carboxylated polysulfones/NMP/water at 25°C.

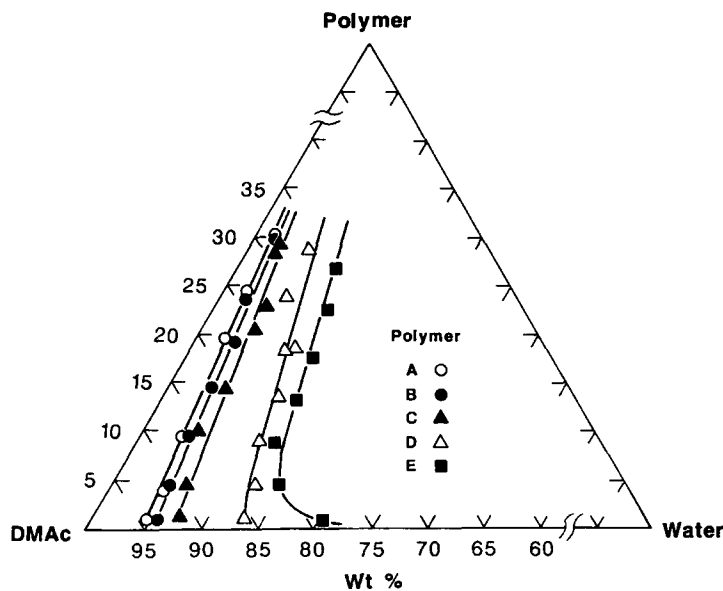


Figure 4 Cloud point curves of carboxylated polysulfones/DMAc/water at 25°C.

Cloud point curves of the five polymers in six solvents are presented in form of ternary phase diagrams in Figures 1–6 which show that both water and the polymers are miscible with the solvents. One obvious general observation in these figures is that wt % water at the cloud point increases with the DS of the polysulfones, that is, hydrophilicity of carboxylated polysulfones increases with DS. Another observation is that these water wt % values also reflect the dissolution power of these solvents for the

polymers and they rank in the following order: DMPU > TMU > NMP > DMAc > DMF > DMSO.

The homogeneous liquid phase region, which is largely defined by the space between the polymer–solvent axis and the cloud point curve, constitutes the miscibility region through which a membrane forming process by the phase inversion method must travel. The bigger is this region the larger would be the process resistance to precipitation by a nonsolvent. This resistance to polymer precipitation by

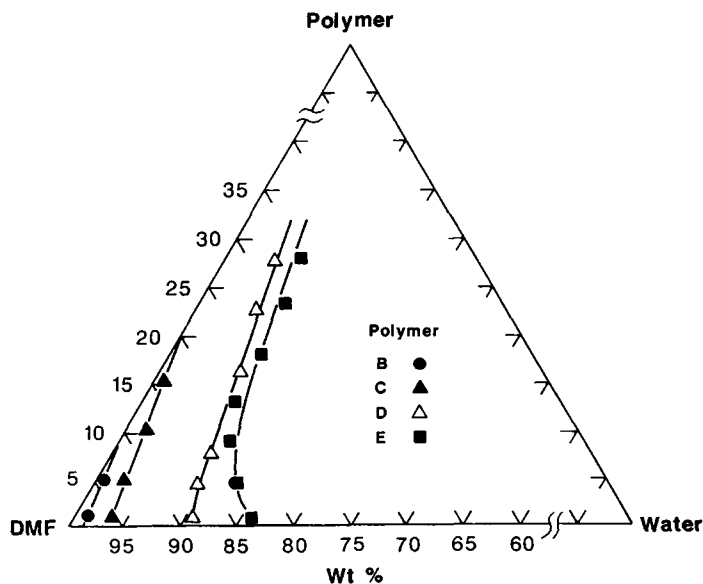


Figure 5 Cloud point curves of carboxylated polysulfones/DMF/water at 25°C.

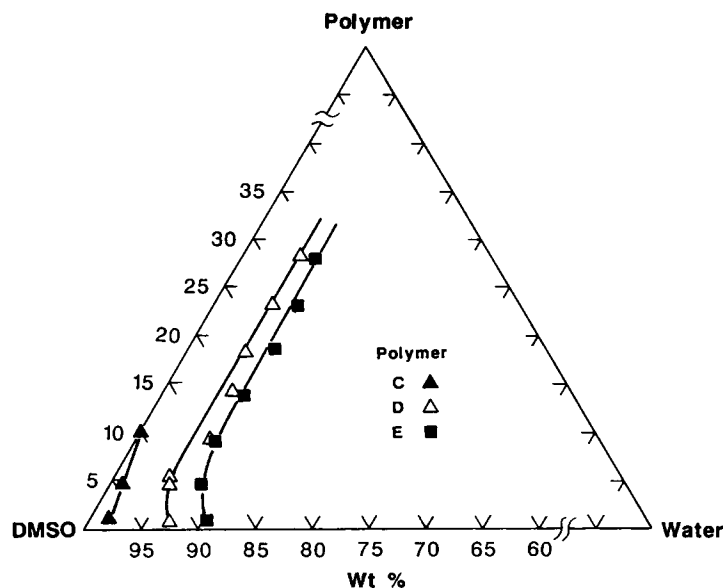


Figure 6 Cloud point curves of carboxylated polysulfones/DMSO/water at 25°C.

water also appears in the same order as stated above. Larger resistance to precipitation by water means longer time has to be allowed for the membrane to form. Attempts to model kinetically this water quench process have been made to trace the path through this miscibility region and to predict the time taken by going along this path from a given initial polymer concentration up to near the cloud point curve.¹²⁻¹⁴ A complete quench model, however, is still lacking.

During the water quench step in a membrane-making process, component molecules have to go through a series of rearrangement. One may visualize that polymer molecules in the initial polymer solution may assume an extended conformation in a good solvent. As the solvent power is lessened by the addition of water, the polymer molecules assume a less extended form. Park and Lee¹⁵ studied the conformational characteristics of PES in mixed solvents under theta-condition and concluded that the chain molecules of polyethersulfone can exist predominantly with trans-trans conformational sequence separated intermittently with trans-gauche and gauche-gauche conformers. It is a possibility that the polysulfones in our study may behave similarly in theta-solvents.

One may visualize possible conformational changes in the polysulfone molecules during a titration process. Initially the macromolecules in the polymer solution may exist as expanded chains, especially so when they are in a good solvent. As more and more water is added, the mixed solvent becomes

poorer and the polymer molecules would become less extended. At the point when the mixed solvent reaches its theta-composition, the polymer chains would be at an unperturbed conformation, possibly in a mainly trans-trans form. As more water is added, many polymer-solvent contacts will be replaced by water-solvent contacts and the polymer molecules are forced to seek self-association. At the cloud point, so many polymer-polymer contacts are created by the water addition that some polymer aggregates have to come out of solution. The first sight of turbidity indicates that the system has now reached a metastable state. Upon standing in a temperature regulated bath at 25°C for over a week, our cloud point samples decomposed into two clear liquid phases, whose composition would be related by tie lines in a ternary phase diagram. In a case when the titration was overshoot by too much water, too much polymer precipitated and the system could no longer resolve to two liquid layers, a situation which would result in the water quench step in the membrane making process.

Theta-Composition of Mixed Solvents

More information can be obtained when cloud point data are treated according to the method of Elias¹⁶ as demonstrated by Park and Lee.¹⁵ In this treatment of cloud point data the volume fraction of nonsolvent, in this case water ϕ_w is plotted versus the logarithm of the volume fraction of the polymer, ϕ_p , according to the following linear relationship:

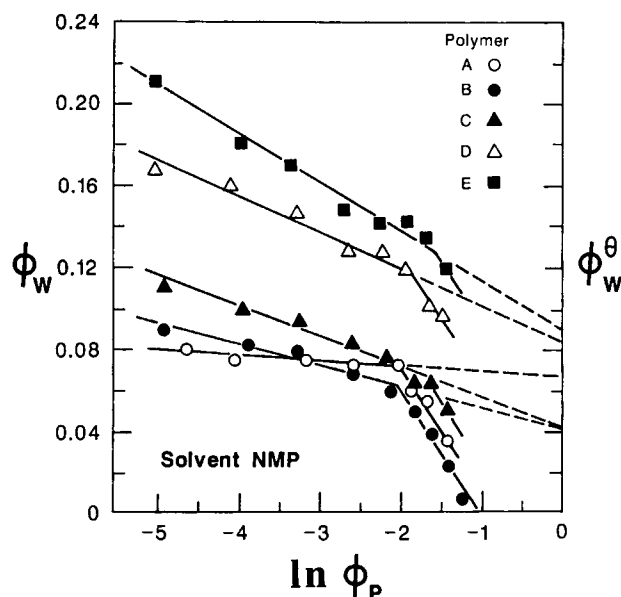


Figure 7 Volume fraction of water, ϕ_w , vs. $\ln \phi_p$, volume fraction of polymer at the cloud point.

$$\phi_w = \phi_w^\theta - B \ln \phi_p \quad (1)$$

where ϕ_w^θ is the theta-composition of the nonsolvent in the water/solvent mixture and B is a constant for the ternary system at a given temperature. The volume fraction of polymer was calculated based on the assumption that carboxylated PSf had the same density as PSf (1.24 g cm^{-3}).

All cloud point data collected in this study have been treated by this method and an example is shown in Figure 7. ϕ_w^θ values obtained by extrapolation to 100% polymer are summarized in Table I. For each polymer the ϕ_w^θ values corresponding to the individual solvents rank in about the same general order as the dissolution power of the solvents. For each solvent the polymer lines do not extrapolate to a single ϕ_w^θ , indicating that these carboxylated

Table I Volume Fractions of Water in the Nonsolvent/Solvent Mixture at Theta-Condition ϕ_w^θ , for Polymers A, B, C, D, and E

Solvent	Polymer				
	A	B	C	D	E
DMPU	0.071	0.017	0.047	0.064	0.064
NMP	0.067	0.044	0.044	0.084	0.090
TMU	0.036	0.036	0.036	0.082	0.088
DMAc	0.020	0.020	0.020	0.060	0.060
DMF	—	—	0.000	0.055	0.032
DMSO	—	—	—	0.052	0.052

polysulfones behave as individual distinct polymers and not as homologues.

Figure 7 shows that eq. (1) holds for dilute polymer solutions. The straight lines start to deviate from linearity at polymer concentration higher than 10 wt % polymer. This point of deviation marks a state in the polymer solution in which polymer-polymer association is strong and the macromolecules are highly perturbed.

Solubility Parameters

The solubility parameter δ offers a scale for the capacity of solvents to dissolve a given polymer. When there is a reasonable match between solubility parameters of a polymer and a solvent, then that solvent is capable of dissolving the particular polymer. Hence, solubility parameters were calculated for each solvent involved in this study using the additivity rule to determine the contribution from each structural component of the solvent molecule.¹⁷ The results were TMU (18.24), NMP (18.70), DMPU (19.89), DMAc (21.68), DMF (21.74), and DMSO (23.15), respectively. The unit of the solubility parameter is $\text{J}^{0.5}/\text{cm}^{1.5}$.

The dissolution power can also be given by the mole fraction of water in the solvent/water mixture at the cloud point. The mole fraction was calculated corresponding to carboxylated polymer with DS of 1.93 at a polymer concentration of 20 wt %. This polymer concentration was chosen since it is typical for a membrane casting solution. For each of the six solvents, the water content at the cloud point versus the solvent solubility parameter is illustrated in Figure 8. The mole fraction of water decreases with an increase in solubility parameter. The same trend was found for the modified polymers with DS other than 1.93.

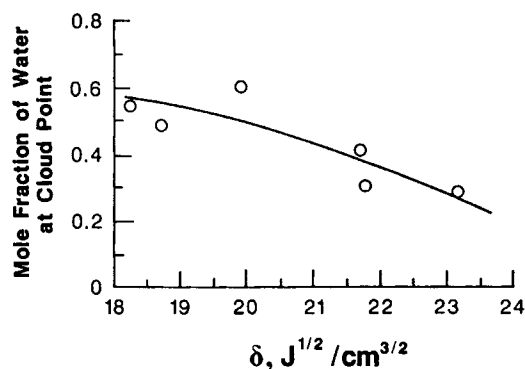


Figure 8 Solubility parameter of solvent/water mixture.

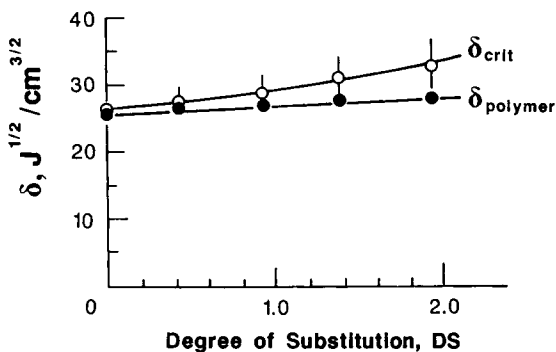


Figure 9 Solubility parameters of the polysulfones at various degrees of carboxylation.

Solubility parameters of solvent mixtures can be calculated as the sum of solubility parameters of each component weighed by its mole fraction. Therefore, using the results illustrated in Figure 8, it is possible to calculate the solubility parameter of the solvent/water mixture for different solvents. This solubility parameter is considered to be a critical value at which the cloud point of modified polymer (DS 1.93) appears and is called δ_{crit} . The result of the calculation was $32.9 \pm 3.3 \text{ J}^{0.5}/\text{cm}^{1.5}$. δ_{crit} values were the average of all the calculated values corresponding to the solvent/water composition at the cloud point for each polymer at 20 wt % concentration. The δ_{crit} calculation was extended to other polymers in the DS series and the results versus the DS value of the modified polymer are illustrated in Figure 9. δ_{crit} increases with an increase in DS. Solubility parameters were also calculated for polymers of different DS by applying the additivity rule to the repeat unit of the polymer. These values, illustrated in Figure 9, show that δ_{crit} is slightly higher than δ of the polymers.

CONCLUSIONS

We have experimentally obtained cloud point curves for the ternary system carboxylated polysulfones/solvent/water for PSf of DS from 0.43 to 1.93. For these polymers the dissolving power of the solvents used rank $\text{DMPU} > \text{TMU} > \text{NMP} > \text{DMAc} > \text{DMF} > \text{DMSO}$, in good agreement with their calculated solubility parameters except in the case of DMPU. Hydrophilicity of the carboxylated polysulfones increases with their degree of carboxylation. The water contents in the nonsolvent/solvent theta-composition for these polymers, as estimated from the

cloud point data, rank in about the same general order as the solvents above.

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