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Short communication

Solubility data for benzene in aqueous solutions of methyldiethanolamine (MDEA) and of diglycolamine (DGA)

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Abstract

Specially designed equipment based on a static-analytic method with Rolsi^{TM} pneumatic samplers for on line gas chromatograph analysis has been used for this work. Operating pressures and temperatures are between 0.3 and 10 MPa and between 293 and 393 K. Vapor pressures over liquid–liquid mixtures and benzene solubility data are reported herein for benzene with amine aqueous solutions (methyldiethanolamine (MDEA) and diglycolamine (DGA)). Modelling of solubility data is achieved using a simple model based on activity coefficients.

Keywords: Solubility data; Methyldiethanolamine; Diglycolamine; Water; Benzene; Methane; Modelling

1. Introduction

Aqueous alkanolamine solutions are used extensively for removal of acid gases in gas mixtures or liquefied petroleum gas (LPG). Some hydrocarbons particularly BTEX are absorbed in the amine solution and so industries need accurate hydrocarbon solubility data to develop new equation or correlations in order to design their absorption or liquid–liquid contactor units. BTEX quantities emissions have been specified by the Clean Air Act. Moreover, the benzene, toluene, ethylbenzene, xylene (BTEX) regulations obviously have considerable effect on most amine systems. Aromatics have particularly harmful effects in a sulfur plant feed. The amine treating units absorb appreciable quantities of aromatics from the feed gas. Aromatics are responsible of rapid loss of sulfur plant recovery efficiency, and consequently of frequent replacements of catalyst.

Key factors that affect sulfur catalyst deactivation are the amount of aromatics absorbed in the amine plant and the efficiency of aromatic destruction in the reaction furnace. This paper, first of a series, deals with benzene solubility in aqueous amine systems.

In this work, influence of various concentrations of MDEA and DGA (weight fractions from 0 to 0.5 and 0.7, respectively) on benzene solubility has been studied in presence of methane. DGA is a primary amine capable of removing not only hydrogen sulfide and carbon dioxide but also COS and mercaptans from gas and liquid stream [1]. MDEA is a tertiary amine which can be used to selectively remove H_2S. CO_2 hydrolyzes much slower than H_2S [1].

2. Thermodynamic of the system

Due to very low mutual solubilities in aqueous solvent–hydrocarbon systems, it is very easy to reach vapor–liquid–liquid equilibrium (VLLE) conditions. At high pressures the vapor phase in mainly composed of methane and benzene. The organic phase is composed mainly of benzene and methane. The aqueous phase is mainly composed of water and alkanolamine. Fig. 1 presents typical phase diagram of such a system. Consequently two hypotheses are done:

- There is no significant quantity of water or alkanolamine in organic phase.
- There is no significant quantity of water or alkanolamine in vapor phase.

Thus, for benzene, equilibrium thermodynamic equations are:

$$x_2^o \gamma_2^o = x_2^w \gamma_2^w \tag{1}$$

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Nomenclature

A, B, C, D, E	adjustable parameters
AAD	$\frac{1}{N}\sum\left\|\frac{U_{\mathrm{exp}}-U_{\mathrm{cal}}}{U_{\mathrm{exp}}}\right\|$
BIAS	$\frac{1}{N}\sum\frac{U_{\mathrm{exp}}-U_{\mathrm{cal}}}{U_{\mathrm{exp}}}$
N	number of experimental point
P	pressure (MPa)
T	temperature (K)
w	weight fraction
x	liquid mole fraction
y	vapor mole fraction

Superscript

o	organic phase
v	vapor phase
w	aqueous phase
*	pure property

Greek letters

Φ	fugacity coefficient
γ	activity coefficient

$$x_2^{\mathrm{o}}\Phi_2^{\mathrm{o}}(T, P, x_2^{\mathrm{o}}) = y_2\Phi_2^{\mathrm{v}}(T, P, y_2) \tag{2}$$

$$\text{with } \gamma_2^{\mathrm{o}} = \frac{\Phi_2^{\mathrm{o}}(T, P, x_2^{\mathrm{o}})}{\Phi_2^{\mathrm{o}*}(T, P)} \tag{3}$$

The PSRK model [2] is used to calculate the activity coefficient and the composition of benzene in the organic phase.

3. Experimental work

3.1. Materials

The liquids chemicals have been used after distillation and careful degassing under a vacuum. The origin and purity of compounds are given in Table 1.

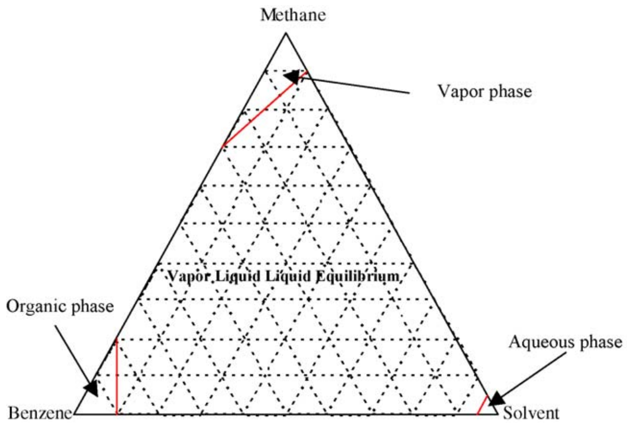

Fig. 1. Example of thermodynamic diagram in conditions close to described study.

3.2. Apparatus and experimental procedures

The apparatus used for the study is based on a static-analytic method with liquid and vapor phase sampling. This apparatus was described by Valtz et al. [3].

Three pressure transducers have been used for this work (Druck, model PTX 611) (nominal loads: 0.6, 4 and 6 MPa). They can be used up to 0.7, 5 and 7 MPa, respectively. They are thermo regulated at fixed temperature (higher than the working temperature to avoid any condensation phenomenon).

Below 0.6 MPa, the calibration is performed against a pressure calibration device (Desgranges et Huot, model 24610). Between 0.3 and 7 MPa, it is done against a dead weight balance (Desgranges et Huot, model 5202 S CP). Uncertainty between 1.4×10^3 Pa and 0.6 MPa is ±0.0001 MPa. Uncertainty between 0.7 and 7 MPa is ±0.002 MPa.

Analytic methods are described in previous paper [3]. According to calibrations, uncertainty on benzene mole fraction is less than 2%.

3.3. Preparation of the aqueous amine solutions

The compositions of aqueous solutions were prepared gravimetrically as described in Ref. [3].

3.4. Experimental procedure for benzene solubility measurements

The evacuated equilibrium cell is loaded with about 5 cm^3 of solvent (distilled water or aqueous amine solution). About 2 cm^3 of benzene are added. In these conditions two liquid phases are present in the cell. At equilibrium, the total pressure is measured. Then the total pressure is increased up to about 0.5 MPa when necessary using methane. The solution is stirred vigorously for a long time, more than 1 h to achieve phase equilibrium. Steering speed is reduced for 1 h and samples of aqueous phase are withdrawn and analyzed by gas chromatography [4]. Several samples are analyzed to evaluate the repeatability of measurements.

4. Results

4.1. Solubility in water

After loading the equilibrium cell, vapor pressure of the liquid–liquid mixture has been measured as a function of temperature. The results are presented in Ref. [3]. Anderson and Prausnitz [5] have measured the vapor pressure at seven temperatures. A very good agreement was found with our data. Methane is used to pressurize the system when sampling is not possible. The influence of methane on the benzene solubility has been studied and already presented in Ref. [3]. Increasing methane pressure leads to decreasing benzene solubility. Consequently, extrapolation must be done to obtain the benzene solubility in the free of methane aqueous solution (see Fig. 2). Up to 0.5 MPa, methane has low influence on benzene

Table 1
Origin and purity of compounds

Compound	Formula	CAS number	Furnisher	Purity
Methane	CH_4	74-82-8	Messer Griesheim	>99.995% vol
Benzene	C_6H_6	71-43-2	Prolabo	>99.8% GC
Methyldiethanolamine (MDEA)	$C_5H_{13}NO_2$	105-59-9	Fluka	>98% GC
Diglycolamine (DGA)	$C_4H_{11}NO_2$	929-6-6	Merck	>99% GC

Table 2
Vapor pressure over benzene—(MDEA (1) + water (2)) for different amine concentrations

Benzene—(MDEA (1) + water (2)) [with $w_1 = 0$]		Benzene—(MDEA (1) + water (2)) [with $w_1 = 0.25$]				Benzene—(MDEA (1) + water (2)) [with $w_1 = 0.5$]		Benzene—(DGA (1) – water (2)) [with $w_1 = 0.35$]		Benzene—(DGA (1) – water (2)) [with $w_1 = 0.7$]	
T (K)	*P* (MPa)	*T* (K)	*P* (MPa)	*T* (K)	*P* (MPa)	*T* (K)	*P* (MPa)	*T* (K)	*P* (MPa)	*T* (K)	*P* (MPa)
298.03	0.0160	294.85	0.0140	357.63	0.1689	291.80	0.0145	292.16	0.0127	293.14	0.0150
313.21	0.0316	297.54	0.0159	357.64	0.1693	293.33	0.0155	292.64	0.0129	294.36	0.0157
373.25	0.2815	300.07	0.0178	362.63	0.1986	298.12	0.0187	292.72	0.0130	297.79	0.0177
393.09	0.4960	302.57	0.0200	362.63	0.1987	303.14	0.0229	297.75	0.0163	302.81	0.0212
374.15[a]	0.287	302.58	0.0201	367.67	0.2319	313.22	0.0341	302.77	0.0203	312.85	0.0304
397.95[a]	0.577	307.57	0.0250	372.68	0.2710	322.89	0.0496	312.64	0.0307	322.68	0.0433
420.85[a]	1.053	312.64	0.0309	372.69	0.2714	332.91	0.0714	322.30	0.0455	332.82	0.0628
422.95[a]	1.073	317.63	0.0381	377.71	0.3144	342.93	0.1002	332.78	0.0681	342.87	0.0900
447.95[a]	1.901	317.63	0.0381	377.71	0.3142	352.87	0.1382	342.86	0.0992	352.89	0.1273
448.55[a]	1.859	322.62	0.0468	382.72	0.3634	363.00	0.1934	352.81	0.1406	362.89	0.1764
476.95[a]	3.218	327.66	0.0573	387.81	0.4196	372.94	0.2630	362.81	0.1958	372.92	0.2400
		327.68	0.0574	392.82	0.4812	383.10	0.3540	372.83	0.2672	382.95	0.3191
		332.74	0.0700	392.83	0.4818	393.35	0.4526	382.87	0.3590	392.99	0.4139
		337.75	0.0846	397.66	0.5480			392.91	0.4727	393.99	0.4239
		342.73	0.1007	397.82	0.5502			393.92	0.4854		
		347.61	0.1199	402.84	0.6265						
		347.61	0.1201	402.86	0.6272						
		352.63	0.1420								

[a] Anderson and Prausnitz [5].

solubility (deviation less than 1% between benzene mole fractions calculated by taking or not into account the methane contents). Several authors have studied the solubility of benzene in pure water [5–14]. As pointed out in Ref. [3] literature data appear a little dispersed, but close to the new data presented in Ref. [3].

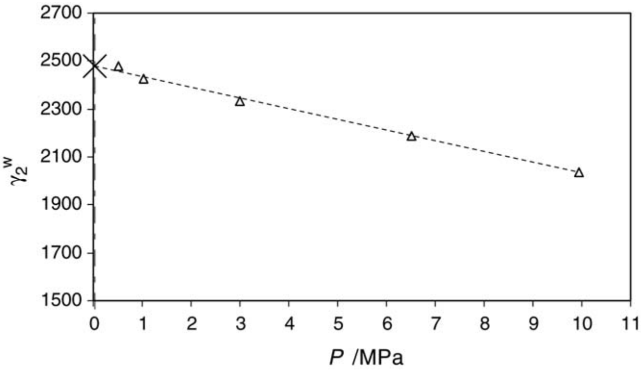

Fig. 2. Determination of the benzene activity coefficient in water from measurement containing methane at 298.10 K. The vertical dashed line corresponds to the vapor pressure of the system without methane. (×) Extrapolated value for free of methane solution.

4.2. Solubility in aqueous MDEA solutions

Vapor pressure over the liquid–liquid mixture (without methane) measured as a function of temperature is reported in Table 2. Solubility of benzene (see Tables 3 and 4) has been

Table 3
Benzene solubility in MDEA (1) + water (2) [with $w_1 = 0.25$] mixture at various temperatures

T (K)	*P* (MPa)	x_2 ($\times 10^4$)	*n*	σ ($\times 10^5$)
298.04	0.5009	9.06	7	2
298.06	2.532	8.44	6	2
298.14	8.045	8.35	16	2
307.98	0.4486	9.82	6	3
332.96	0.4997	14.60	10	5
332.95	2.488	13.90	11	4
332.98	7.992	13.10	9	4
363.10	0.5066	25.90	35	8
375.25	8.156	36.50	16	9
393.21	0.5145	42.50	38	10
393.21	2.482	40.40	13	10

n: number of samples analysed. $\sigma = \left(\frac{n \times \sum x^2 - \left(\sum x \right)^2}{n \times (n-1)} \right)^{1/2}$.

Table 4
Benzene solubility in MDEA (1) + water (2) [with $w_1 = 0.5$] mixture at various temperatures

T (K)	P (MPa)	x_2 ($\times 10^4$)	n	σ ($\times 10^4$)
298.10	0.5035	38	12	2
298.14	2.501	31.9	8	1
333.09	0.4992	69.1	12	3
333.06	2.504	56.1	8	0.8
363.19	0.5036	113	8	6
393.32	0.5158	172	8	8
393.27	2.456	163	10	8

n: number of samples analysed. $\sigma = \left(\frac{n\times\sum x^2-\left(\sum x\right)^2}{n\times(n-1)}\right)^{1/2}$.

studied in two aqueous MDEA solutions (i.e. MDEA (1) + water (2) with $w_1 = 0.25$ and 0.5).

4.3. Solubility in aqueous DGA solutions

Vapor pressure over the liquid–liquid mixture (without methane) measured as a function of temperature is reported in Table 2. The solubility of benzene (see Tables 5 and 6) has been studied in two aqueous DGA solutions (i.e. DGA (1) + water (2) with $w_1 = 0.35$ and 0.7).

Table 5
Benzene solubility in (DGA (1) − water (2)) [with $w_1 = 0.35$] mixture at various temperatures

T (K)	P (MPa)	x_2 ($\times 10^4$)	n	σ ($\times 10^4$)
298.22	0.5015	19.3	9	1
298.21	2.486	15.6	10	0.5
333.14	0.5041	31.4	8	2
363.20	0.5052	47.3	9	2
393.22	0.5025	75.5	8	3

n: number of samples analysed. $\sigma = \left(\frac{n\times\sum x^2-\left(\sum x\right)^2}{n\times(n-1)}\right)^{1/2}$.

Table 6
Benzene solubility in (DGA (1) − water (2)) [with $w_1 = 0.7$] mixture at various temperatures

T (K)	P (MPa)	x_2 ($\times 10^4$)	n	σ ($\times 10^4$)
298.22	0.5049	240	10	10
298.22	4.995	222	9	8
333.11	0.5181	422	11	20
333.11	4.995	370	11	20
363.23	0.507	666	10	20
363.23	5.047	634	9	20
393.24	0.5283	1080	8	60

n: number of samples analysed. $\sigma = \left(\frac{n\times\sum x^2-\left(\sum x\right)^2}{n\times(n-1)}\right)^{1/2}$.

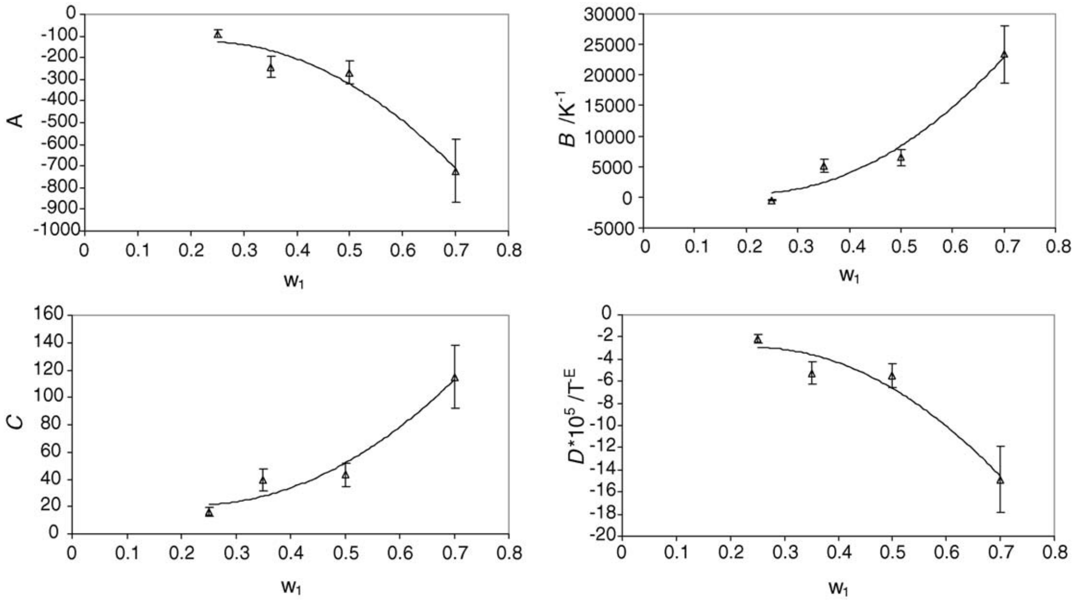

Fig. 3. Vapor pressure parameters as a function of amine weight fraction.

Table 7
Vapor pressures parameters and deviations

Solvent	ΔT	A	B (K^{-1})	C	D ($\times 10^5 T^{-E}$)	E	BIAS (%)	AAD (%)
MDEA (1) + water (2) ($w_1 = 0.25$)	294.85–402.86	−91.021	−522.4	15.8965	−2.1604	2	0.27	0.36
MDEA (1) + water (2) ($w_1 = 0.5$)	291.80–393.35	−268.194	6460	43.4264	−5.4759	2	0.30	0.77
DGA (1) + water (2) ($w_1 = 0.35$)	292.16–393.92	−243.460	5177	39.7816	−5.2494	2	0.11	0.19
DGA (1) + water (2) ($w_1 = 0.7$)	293.14–393.99	−723.763	23338.1	114.8912	−14.8608	2	0.58	0.68

Table 8
Calculated solubility data for benzene in aqueous amine solutions

T (K)	P (MPa)	γ_2^{w} ($\times 10^2$)	x_2 ($\times 10^4$)	Solvent
298.10	0.016	25	4	Water
313.19	0.0316	22	5	
373.11	0.2815	11	9	
393.10	0.496	8.6	1_2	
298.10	0.0163	11	9	MDEA (1) + water (2) ($w_1 = 0.25$)
307.98	0.0254	10	1_0	
332.97	0.0704	6.9	1_5	
363.10	0.2014	3.8	2_6	
375.25	0.2932	2.4	4_2	
393.21	0.4873	2.3	4_3	
298.12	0.0188	2.5	4_0	MDEA (1) + water (2) ($w_1 = 0.5$)
333.08	0.0713	1.4	7_3	
363.19	0.1946	0.88	11_4	
393.30	0.4562	0.58	17_2	
298.22	0.0164	4.9	2_0	DGA (1) + water (2) ($w_1 = 0.35$)
333.14	0.0684	3.2	3_2	
363.20	0.1958	2.1	4_8	
393.22	0.4716	1.32	7_6	
298.22	0.0181	0.413	24_4	DGA (1) + water (2) ($w_1 = 0.7$)
333.11	0.0645	0.234	43_5	
363.23	0.1818	0.149	66_7	
393.24	0.4273	0.092	111_1	

Vapor pressures can be represented with the following equation:

$$\ln(P) = A + \frac{B}{T} + C\ln(T) + D \times T^{E} \tag{4}$$

where A, B, C, D and E are parameters fitted on experimental data; they are reported in Table 7. These parameters appear as a function of amine weight fraction (see Fig. 3).

5. Discussion

Eqs. (1)–(3) were used to determine benzene activity coefficients in solvents. When enough isothermal experimental data are available, the activity coefficient can be calculated by extrapolation of the relationship between benzene activity coefficient and pressure (Fig. 2). Then, the solubility is determined with the following equation:

$$x_2^{w} = \frac{1}{\gamma_2^{w}} \tag{5}$$

The results are presented in Table 8. Fig. 4 presents the benzene activity coefficient as a function of temperature for all studied solutions. The first conclusion is that amine is a good solvent of benzene with solvent power increasing with temperature. Fig. 5 shows that the amine composition has more influence than the nature of the amine on benzene solubility. With respect to the previous conclusions, a simple model is developed in order to represent the activity coefficient of benzene in the aqueous solution. This model (see Eq. (6)) has a temperature second order polynomial form with parameters function of amine concentration.

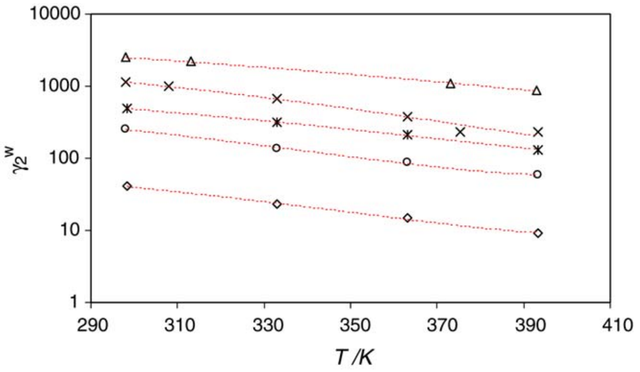

Fig. 4. Benzene activity coefficient as a function of temperature. (△) Water, (×) MDEA water (25/75) wt.% mixture, (*) DGA water (35/65) wt.% mixture, (○) MDEA water (50/50) wt.% mixture, (◇) DGA water (70/30) wt.% mixture.

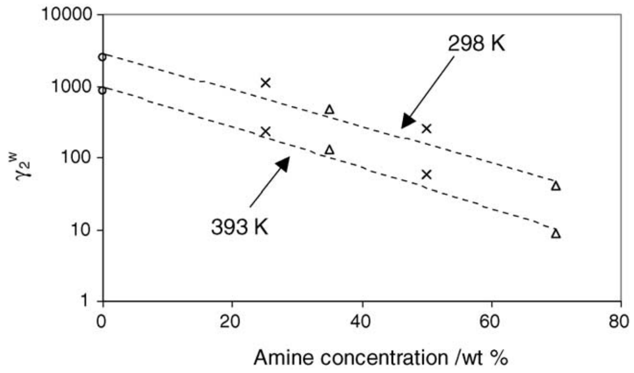

Fig. 5. Benzene activity coefficient as a function of Amine concentration. (○) Pure water, (△) DGA, (×) MDEA.

$$\gamma_2^{w}(T, X_{\text{amine}}) = A \times T^2 + B \times T + C \tag{6}$$

The corresponding parameters reported in Table 9. Combining Eqs. (5) and (6), allows calculating benzene solubility in any aqueous amine solution for the amine (1) + water (2) system in the 0–0.7 weight fraction range.

Table 9
Parameters of Eq. (4) and corresponding deviations

Solvent	A (K^{-2})	B (K^{-1})	C	BIAS (%)	AAD (%)
Pure water	−59.925	0.0616	14888.42	0.00	1.24
MDEA (1) + water (2) ($w_1 = 0.25$)	0.0591	−50.399	10905.76	−5.73	7.59
MDEA (1) + water (2) ($w_1 = 0.5$)	0.0182	−14.563	2976.83	−0.02	2.48
DGA (1) + water (2) ($w_1 = 0.35$)	0.0193	−17.063	3863.60	−0.01	0.66
DGA (1) + water (2) ($w_1 = 0.7$)	0.0026	−2.124	443.70	0.11	3.15

6. Conclusion

The specially designed equipment based on a static-analytic method with Rolsi^{TM} pneumatic samplers for on line gas chromatograph analysis has been operated to get benzene solubility data between 0.3 and 10 MPa and between 293 and 393 K. Vapor pressures over liquid–liquid mixtures are reported herein for benzene with amine aqueous solutions (methyldiethanolamine (MDEA) and diglycolamine (DGA)). They are successfully represented using DIPPR type equation (deviations less than 1%). Modelling of solubility data has been achieved using a simple model based on activity coefficients. Amine has been found as a good solvent of benzene with solvent power increasing with temperature. Amine composition has much more influence than the nature of the amine on benzene solubility.

Acknowledgments

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