



THE USE OF THE NRTLmKW MODEL FOR PREDICTING VLE DATA OF BINARY SYSTEMS FROM THE EXCESS ENTHALPY DATA

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A new local composition model NRTLmKW has been used for correlation of 15 binary excess enthalpy data. The data, binary systems formed by hydrocarbons and alkanols, have been selected to give a wide representation of various kinds molecular interactions in solution. Further the model, basing on the results of the correlation, has been used for prediction of excess enthalpy and VLE (vapour-liquid equilibria) in these systems.

The obtained results have been discussed from the point of view of intermolecular interactions and some recommendations have been made on the use of the NRTLmKW model for such calculation.

Keywords: excess enthalpy, NRTLmKW model, vapour-liquid equilibria

Introduction

The prediction of equilibrium behaviour of fluids and fluid mixtures belong nowadays to the most challenging and perhaps also most significant tasks at the boundary between physical chemistry and physics. An enormous amount of data has been collected and correlated over the years but the rapid advance of technology into new fields seems always to maintain a significant gap between demand and availability. Therefore, the construction of new thermodynamic models with deep theoretical background is absolutely necessary both for the better understanding of behaviour of fluids and the proper design in the modern technologies.

The NRTLmKW [1, 2] model can be treated as one of such new thermodynamic models. The model is based on the modified lattice theory [3] where interaction between the particles is not limited to the neighbours but is strictly dependent on the intermolecular potential of the particles and the particle can interact by so-called ‘active sides’ [3]. Such modification of the Guggenheim theory [4] and further application of the Scott ‘two-liquid theory’ [5] leads to the final form of the new local composition model – the NRTLmKW model [1, 2].

In this paper the applicability of the NRTLmKW model for correlation and prediction of binary excess enthalpy data and VLE data have been checked and discussed from the point of view of intermolecular interactions.

Correlation of excess enthalpy data

This model can be used directly for calculation of excess enthalpy. According to the general relation:

$$h^E = \left(\frac{\partial \left(\frac{g^E}{T} \right)}{\partial \left(\frac{1}{T} \right)} \right)_{x_i}$$

where T – temperature/K, x – mole fraction of component i .

The expression for excess enthalpy in the case of the NRTLmKW equation has the following form:

$$h^E = (h^E)_{\text{phys}} + (h^E)_{\text{chem}}$$

where:

$$\begin{aligned} (h^E)_{\text{phys}} = & \frac{x_i x_j^{1-\beta} A_{ji} \exp(-\alpha \tau_{ji})}{x_i + x_j^{1-\beta} A_{ji} \exp(-\alpha \tau_{ji})} (g_{ji} - g_{ii}) + \\ & + \frac{x_j x_i^{1+\beta} A_{ij} \exp(-\alpha \tau_{ij})}{x_j + x_i^{1+\beta} A_{ij} \exp(-\alpha \tau_{ij})} (g_{ij} - g_{jj}) + \\ & - \alpha \left(\frac{x_i^2 x_j^{1-\beta} A_{ji} \exp(-\alpha \tau_{ji})}{(x_i + x_j^{1-\beta} A_{ji} \exp(-\alpha \tau_{ji}))^2} \right) \tau_{ji} + \\ & + \left(\frac{x_j^2 x_i^{1-\beta} A_{ij} \exp(-\alpha \tau_{ij})}{(x_j + x_i^{1-\beta} A_{ij} \exp(-\alpha \tau_{ij}))^2} \right) \tau_{ij} \end{aligned}$$

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where

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT}, \quad \alpha = \beta = \frac{s}{150} \quad \text{or} \quad \alpha = -\beta = -\frac{s}{150}$$

$$A_{ij} = \frac{[(2+\beta)/\alpha]^{1+\beta/2}}{[(2-\beta)/\alpha]^{1-\beta/2}} \quad A_{ji} = \frac{[(2-\beta)/\alpha]^{1-\beta/2}}{[(2+\beta)/\alpha]^{1+\beta/2}}$$

$$s = |s_i - s_j + 1|$$

where g_{ij} – g_{jj} , g_{ji} – g_{ii} , – energetic parameters (adjustable); s_i , s_j – s -mers of component i and j , respectively, calculated from the following equation:

$$\ln K_i = \ln \frac{s_i}{s_j - 1} + (s_i - 1) \ln 2$$

where K_i – association constant of component i , and

$$(h^E)_{\text{chem}} = -\Delta H^0 K (\varphi_A^0 - \varphi_A) x_i$$

where x_i – molar fraction of associating component, φ_A – true molar fractions of monomers in mixture, φ_A^0 – true molar fractions of monomers in pure associating component i , ΔH – enthalpy of association,

$$\varphi_A = \frac{1 + 2K_A \varphi_i - \sqrt{1 + 4K_A \varphi_i}}{2K_A^2 \varphi_i}$$

$$\varphi_A^0 = \frac{1 + 2K_A - \sqrt{1 + 4K_A}}{2K_A^2}$$

$$\varphi_i = \frac{x_i}{x_i + r x_j} \quad r = \frac{V_j}{V_i}$$

where V_j , V_i – the molar volume of pure component j and i , respectively.

This model has been used for calculation of binary systems formed by hydrocarbons and alcohols. The experimental data have been taken from the Data Bank of Institute of Physical Chemistry PAS [6] after very careful selection and checking their thermodynamic consistency by three independent consistency tests [6]. This class of systems has been already widely studied [7–16] what gave a good possibility of comparison of the obtained results.

The calculations have been carried out for 12 excess enthalpy data sets [6]:

- ethanol – n -hexane at 298.15 K;
- ethanol – n -heptane at 298.15 K;
- ethanol – n -nonane at 298.15 K;
- propanol-1 – n -hexane at 298.15 K;
- propanol-1 – n -heptane at 303.15 K;
- propanol-1 – n -octane at 298.15 K;
- propanol-1 – n -nonane at 298.15 K;
- butanol-1 – n -hexane at 298.15 K;

- butanol-1 – n -octane at 288.15 K;
- butanol-1 – n -decane at 298.15 K;
- pentanol-1 – n -pentane at 298.15 K;
- pentanol-1 – n -hexane at 303.15 K;
- hexanol-1 – n -hexane at 298.15 K;
- octanol-1 – n -hexane at 298.15 K;
- decanol-1 – n -hexane at 298.15 K.

The minimization function (F) was defined as follows:

$$F = \min \sum_{i=1}^n (H_i^{E \text{ exp}} - H_i^{E \text{ cal}})^2$$

where $H_i^{E \text{ exp}}$, $H_i^{E \text{ cal}}$ – the experimental and calculated excess enthalpy, respectively, n – the number of experimental data points and for each data set the model parameters (g_{ij} – g_{ii} – energetic parameters) were adjusted using the Levenberg-Marquardt algorithm [17]. The association constant (K_i) was assumed to be equal to that obtained using the homomorph approach by Hofman and Nagata [18].

The association parameters for all investigated alcohol's: K and ΔH are given in Table 1.

Table 1 Association parameters for all alcohols investigated (ΔH – the enthalpy of association, K – association constant at 25°C)

Compound	K	$-\Delta H/\text{kJ mol}^{-1}$
methanol	119.2	23.16
ethanol	89.8	22.96
propanol-1	70.5	22.76
butanol-1	54.6	22.53
pentanol-1	43.8	22.34
hexanol-1	35.4	22.15
octanol-1	24.2	21.73
decanol-1	13.2	21.52

The results of correlation ($D(H^E)$ – relative deviation of excess enthalpy) as well as the obtained binary energetic parameters for all systems investigated are shown in Table 2.

$$D(H^E) = \frac{1}{n} \sum_{i=1}^n \left| \frac{H_i^{\text{Exp}} - H_i^{\text{cal}}}{H_i^{\text{Exp}}} \right| 100$$

where $H_i^{E \text{ exp}}$, $H_i^{E \text{ cal}}$ – the experimental and calculated excess enthalpy, respectively, n – the number of experimental data points.

The results of correlation of excess enthalpy data are on the level of the experimental accuracy (average error about 3–4%). There are much better (almost twice) that results obtained by the use of other thermodynamic models both so called ‘ γ – φ ’ models (av-

Table 2 Results of correlation of the excess enthalpy data of binary systems by means of the NRTLmKW model

System	T/K	$\frac{g_{12}-g_{22}}{g_{21}-g_{11}}/$ $J\ mol^{-1}$	$\Delta(H^E)/\%$
ethanol – <i>n</i> -hexane	298.15	–10835.2 16335.3	3.98
ethanol – <i>n</i> -heptane	298.15	–12697.9 18580.0	3.71
ethanol – <i>n</i> -nonane	298.15	–9428.6 14752.8	4.87
propanol-1 – <i>n</i> -hexane	298.15	–3764.3 11056.9	3.46
propanol-1 – <i>n</i> -heptane	303.15	–2317.8 9212.1	5.43
propanol-1 – <i>n</i> -octane	298.15	–806.2 7231.8	4.30
propanol-1 – <i>n</i> -nonane	298.15	10217.9 –5510.2	4.19
butanol-1 – <i>n</i> -hexane	288.15	–6869.3 14774.9	3.22
butanol-1 – <i>n</i> -octane	298.15	765.7 4558.7	2.71
butanol-1 – <i>n</i> -decane	298.15	3592.4 1276.5	1.84
pentanol-1 – <i>n</i> -pentane	298.15	–9414.8 18132.1	6.78
pentanol-1 – <i>n</i> -hexane	303.15	–8299.3 16557.5	7.21
hexanol-1 – <i>n</i> -hexane	298.15	–9573.4 18234.7	4.36
octanol-1 – <i>n</i> -hexane	298.15	–10234.6 21564.9	3.11
decanol-1 – <i>n</i> -hexane	298.15	–11456.9 23861.1	1.21

erage error about 6–7%) [19, 20] and equations of state (average error about 10–12%) [21–23].

The best results of correlation have been obtained for decanol-1 where the association is much weaker than in the case of shorten 1-alcohols (ethanol). However the differences in correlation results between ‘short’ and ‘long’ 1-alcohols are very small and seem to be much more depended on the quality of the experimental data than the chain length of hydrocarbons and 1-alcohols.

The correlation results show the proper relation between the physical and chemical part of the NRTLmKW model.

The values of the adjusted energetic parameters differ from one system to other. It is impossible to find a tendency of behavior of those parameters both with the change of temperature and in homologous series of hydrocarbons and alcohols.

This can be cause by many reasons [24] but the main seems be the fact that the data originated from

various laboratories and the surface of minimization function (minimum of the sum of square deviations between experimental and calculated excess enthalpy) is very flat with many local minimums being often very close to the global one.

That is why no physical meaning should be given to the values of adjustable energetic parameters. They can be treated only as the model parameters which have to be calculated for every new system.

The predictive abilities the obtained model parameters have been checked on prediction of excess enthalpy data measured at different temperature than that at which the parameters were adjusted.

The adjusted energetic parameters have been used also for prediction of the excess enthalpy data at different (higher) than the correlated temperature for the following 5 systems [6]:

- ethanol – *n*-heptane at 348.15 K;
- hexanol-1 – *n*-octane at 328.15 K;
- butanol-1 – *n*-heptane at 318.15 K;

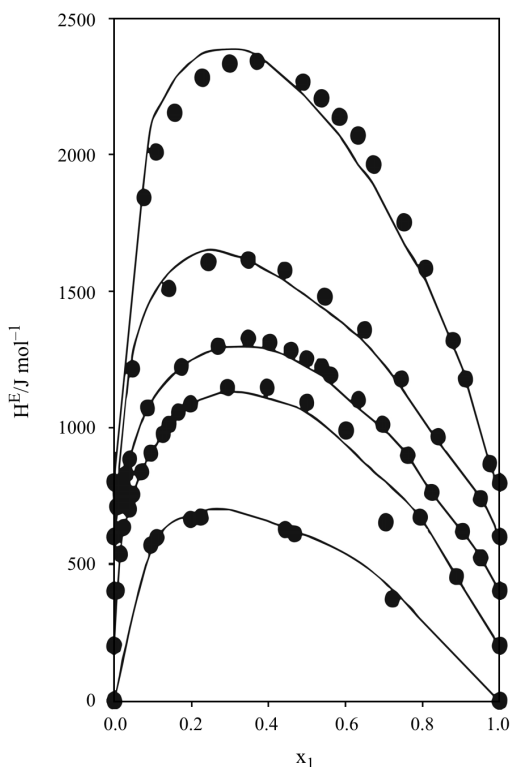


Fig. 1 Results of prediction of excess enthalpy (from the top): ethanol – *n*-heptane (348.15 K), hexanol-1 – *n*-octane (328.15 K), butanol-1 – *n*-heptane (318.15 K), propanol-1 – *n*-heptane (318.15 K), octanol-1 – *n*-hexane (318.15 K) ● – experimental points, — – NRTLmKW model (the values of higher curves were moved up: 200, 400, 600, 800 J mol⁻¹, respectively)

- propanol-1 – *n*-heptane at 318.15 K;
- octanol-1 – *n*-hexane at 318.15 K.

The obtained results, summarized in Fig. 1, confirm proper work of the model with these set of parameters and allow for its recommendation for such calculations.

Prediction of VLE data

Further, the applicability of the proposed model has been checked on prediction of isothermal vapour-liquid equilibria for binary systems formed by hydrocarbons and alcohols.

The selected experimental data [6] fulfilled two conditions: good thermodynamic consistency and wide representation of strong molecular interactions in solution:

- ethanol – *n*-hexane at 298.15 K;
- ethanol-1 – *n*-heptane at 303.27 K, 323.15 K, 343.15 K;
- ethanol – *n*-nonane at 343.21 K;
- propanol-1 – *n*-hexane at 313.15 K;

- propanol-1 – *n*-heptane at 303.15 K, 333.15 K;
- propanol-1 – *n*-octane at 313.15 K;
- propanol-1 – *n*-nonane at 333.15, 363.15 K;
- butanol-1 – *n*-hexane at 332.15 K;
- butanol-1 – *n*-octane at 373.15 K, 383.15 K;
- butanol-1 – *n*-decane at 383.15 K;
- pentanol-1 – *n*-pentane at 383.15 K;
- pentanol-1 – *n*-hexane at 303.15 K, 323 K;
- hexanol-1 – *n*-hexane at 293.15 K, 308.15 K;
- octanol-1 – *n*-hexane at 313.15 K;
- decanol-1 – *n*-hexane at 298.15 K, 313.15 K, 333.15 K.

We have performed our calculations using the NRTLmKWA model with the model parameters (the energetic parameters – Table 2) obtained from the binary excess enthalpy data at the temperature equal to 298.15 K or in the case of lack of such experimental data at the closest temperature to that. The association parameters for all investigated alcohols: K and ΔH (Table 1), as previously, were assumed to be equal to those obtained by Hofman and Nagata [18].

The obtained results of prediction of the vapour – liquid equilibrium isothermal data ($D(P)$ – relative deviation of vapour pressure) for all systems investigated are given in Table 3.

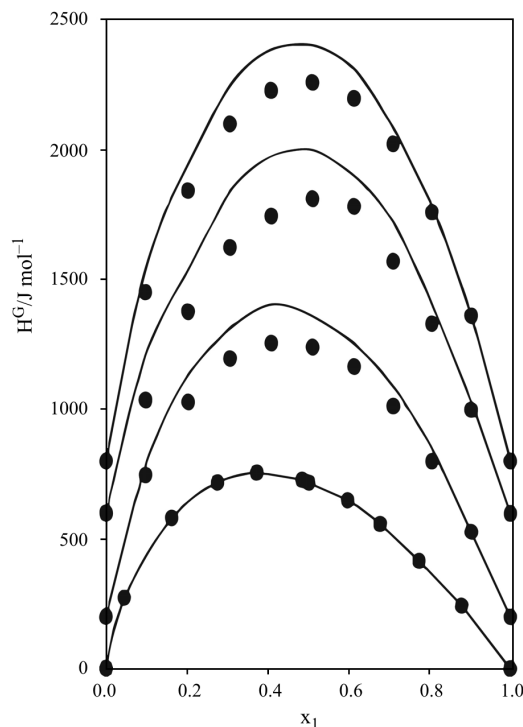


Fig. 2 Results of prediction of excess Gibbs energy (from the top): ethanol – *n*-heptane (323.15 K), butanol-1 – *n*-octane (383.15 K), pentanol-1 – *n*-hexane (303.15 K), decanol-1 – *n*-hexane (313.15 K), ● – experimental points, — – NRTLmKW model (the values of higher curves were moved up: 200, 600, 800 J mol⁻¹, respectively)

Table 3 Results of prediction of the VLE isothermal data of binary systems by means of the NRTLmKW model

System	<i>T</i> /K	<i>D</i> (<i>P</i>)/%
ethanol – <i>n</i> -hexane	298.15	5.90
	303.27	6.01
	323.15	6.82
ethanol – <i>n</i> -heptane	343.15	5.23
	343.21	3.02
	343.15	3.02
ethanol – <i>n</i> -nonane	343.21	3.02
	343.15	3.02
propanol-1 – <i>n</i> -hexane	313.15	9.32
	313.15	9.32
propanol-1 – <i>n</i> -heptane	303.15	8.43
	333.15	7.96
propanol-1 – <i>n</i> -octane	331.15	8.96
	331.15	8.96
propanol-1 – <i>n</i> -nonane	333.15	4.13
	363.15	6.70
butanol-1 – <i>n</i> -hexane	332.57	7.15
	332.57	7.15
butanol-1 – <i>n</i> -octane	373.15	7.21
	383.15	6.23
butanol-1 – <i>n</i> -decane	383.15	5.11
	383.15	5.11
pentanol-1 – <i>n</i> -pentane	303.15	5.47
	303.15	5.47
pentanol-1 – <i>n</i> -hexane	303.15	7.28
	323.15	7.12
hexanol-1 – <i>n</i> -hexane	293.15	6.34
	308.15	6.56
octanol-1 – <i>n</i> -hexane	313.15	6.94
	313.15	6.94
decanol-1 – <i>n</i> -hexane	298.15	1.92
	313.15	1.34
	333.15	1.56

$$D(P) = \frac{1}{n} \sum_{i=1}^n \left| \frac{P_i^{\text{exp}} - P_i^{\text{cal}}}{P_i^{\text{exp}}} \right| 100$$

where P_i^{exp} , P_i^{cal} – the experimental and calculated vapour pressure, respectively, n – the number of experimental data points.

Additionally Fig. 2 shows a comparison of calculated and experimental values of excess Gibbs energies (G^E) for four of these systems.

The prediction of VLE data from excess enthalpy data with accuracy about 6% can be fully accepted and appreciated as very good. The accuracy of correlation of excess enthalpy for systems formed by 1-alkanols and n -alkanes is about 3–7% (Table 2).

Moreover, in most cases prediction have been done at the different temperatures than those of the adjusted binary parameters (298.15 K), which proves the proper temperature dependence of the model. In some cases, the extrapolation of temperature was more than 50 K, and the prediction was still very accurate.

Conclusions

The results of correlation of excess enthalpy data are on the level of the experimental accuracy and prove the proper relation between the physical and chemical part of the NRTLmKW model.

The prediction results of VLE data, obtained basing on the energetic parameters adjusted from the excess enthalpy data, indicate that in all cases the NRTLmKWA model ensure very good description of isothermal vapour-liquid equilibria on the level of correlation of the excess enthalpy data.

It is necessary to point out that the NRTLmKWA model gave very good prediction irrespectively of the kind of the alcohol and length of the hydrocarbon chain as well as irrespectively of the character of intermolecular interaction (strong, intermediate, weak).

The prediction results obtained for the associating systems confirm not only the proper work and relation between the physical and chemical part of the NRTLmKWA model but especially its appropriate temperature dependence.

The NRTLmKWA model has only two energetic parameters for binary mixtures, which have to be adjusted from experimental data. The third parameter (K – association constant) can be calculated for every associating compound using the homomorph approach.

Moreover, for some systems which are low correlative, the description (flexibility of the equation) can be improved by the adjusting of the association parameters (K and ΔH^0) but in this case we can loose the predictive power of the NRTLmKWA model.

It is worth noticing also that if we are interested in the very precise description of the particular phase equilibrium in the associating system and we know that for this system the different association model gives the best result, we can easily replace the chemical part of the NRTLmKWA equation with the proper one but we have to remember that in this case it is necessary also to change the way of adjusting of s parameter.

The good prediction results obtained using the NRTLmKWA model allow us to recommend this model for accurate calculation of VLE data and excess enthalpy data in binary systems formed by 1-alkohols and hydrocarbons.

Concluding, we can say that the NRTLmKWA model can be easily extended for multicomponent systems and fruitfully use for any non-associating and associating binary and ternary systems independently of the concentration range.

The model can be recommended also for common correlation of all these types data what should still improve the accuracy of description.

Appendix

g^E	excess Gibbs energy
h^E	excess enthalpy
$(h^E)_{\text{phys}}$	physical contribution to excess enthalpy
$(h^E)_{\text{chem}}$	chemical contribution to excess enthalpy
T	temperature in K
R	gas constant
$g_{ij}-g_{jj}, g_{ji}-g_{ii}$	energetic parameters (adjustable)
x_i	mole fraction of component i
A_{ij}, A_{ji}	entropy parameters
s_i, s_j	s -mers of component i and j , respectively
K_i	association constant of component i
φ_i	volume fraction of component i
φ_A	true molar fractions of monomers in mixture
φ_A^0	true molar fractions of monomers in pure associating component i
ΔH	enthalpy of association
V_j, V_i	the molar volume of pure component j and i , respectively
$P_i^{\text{exp}}, P_i^{\text{cal}}$	the experimental and calculated vapour pressure, respectively
$H_i^{\text{Exp}}, H_i^{\text{Ecal}}$	the experimental and calculated excess enthalpy, respectively
n	the number of experimental data points
$D(P)$	relative deviation of vapour pressure
$D(H^E)$	relative deviation of excess enthalpy

References

- 1 P. Gierycz, Polish J. Chem., 70 (1996) 498.
- 2 P. Gierycz, Polish J. Chem., 70 (1996) 1193.
- 3 P. Gierycz, Phys. Chem, Liq., 22 (1990) 177.
- 4 E. A. Guggenheim, 'Mixtures', Clarendon Press, Oxford (1952).
- 5 R. L. Scott, J. Chem. Phys., 25 (1956) 193.
- 6 A. Mączyński and A. Skrzecz, Thermodynamic Data Bank of the Institute of Physical Chemistry, Polish Academy of Sciences, Warszawa, Poland.
- 7 G. C. Savini, D. R. Winterhalter and H. C. Van Ness, J. Chem. Eng. Data, 10 (1965) 168.
- 8 R. H. Stokes and C. Burfitt, J. Chem. Thermodyn., 5 (1973) 623.
- 9 J. Brown, W. Fock and F. Smith, Austr. J. Chem., 17 (1964) 1106.
- 10 H. D. Pflug, A. E. Pope, B. Dacre and G. C. Benson, J. Chem. Eng. Data, 13 (1968) 435.
- 11 A. E. Pope, H. D. Pflug, B. Dacre and G. C. Benson, Can. J. Chem., 45 (1967) 2665.
- 12 H. H. Sun, J. J. Christensen, R. M. Izatt and R. W. Hanks, J. Chem. Thermodyn., 12 (1980) 95.
- 13 M. I. Paz-Andrade, L. Rornani and F. Gonzales, An. Quim., 70 (1974) 314.
- 14 F. Vesely, V. Hynek, V. Svoboda and R. Holub, Collect. Czech. Chem. Commun., 39 (1974) 355.
- 15 R. H. Stokes and C. Burfitt, J. Chem. Thermodyn., 5 (1973) 623.
- 16 R. V. Mrazek and H. C. Van Ness, AIChE J., 11 (1965) 924.
- 17 T. Hofman and I. Nagata, Fluid Phase Equilibria, 28 (1986) 233.
- 18 D. Marquardt, SIAM J. Appl. Math., 11 (1963) 431.
- 19 V. Brandani and F. Evangelista, Ind. Eng. Chem. Res., 26 (1987) 2423.
- 20 K. Moorthi, P. Gierycz and I. Nagata, Fluid Phase Equilibria, 64 (1991) 13.
- 21 A. Anderko, Fluid Phase Equilibria, 45 (1989) 39.
- 22 M. Baumgartner, Ph.D. Thesis, Erlangen University, Erlangen (1981).
- 23 W. Peschel, Ph.D. Thesis, Erlangen University, Erlangen (1986).
- 24 P. Gierycz, 'Thermodynamics of Fluids: Measurement and Correlation', World Scientific Publishing Company, Singapore, 370–414 (1990).

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