Application of UNIFAC to Vegetable Oil–Alkane Mixtures

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The prediction of the vapor–liquid equilibria of vegetable oil–hexane mixtures is studied. Activity coefficients are calculated by the UNIFAC model. Different entropic contributions to activity coefficients from the literature are analyzed. These modifications improve the performance of the original UNIFAC model in vapor–liquid equilibrium calculations.

KEY WORDS: Hexane, UNIFAC, vapor–liquid equilibria, vegetable oil.

Hexane petroleum fractions are traditionally used in the extraction of vegetable oils from oilseeds. The recovery of the solvent from the oil–solvent mixture is accomplished by evaporation and steam stripping. The residual solvent content in the vegetable oil product should be only a few ppm. For this reason, an accurate knowledge of the vapor–liquid equilibriums (VLE) of vegetable oil–solvent mixtures is required for the design and operation of the separation process.

At the low pressures involved in the industrial process, the conditions for VLE can be stated as:

$$y_i P = \gamma_i x_i \, \phi_i^{sat} P_i^{sat} \quad i = 1, \ldots\ldots, N_c \qquad [1]$$

where P is the pressure, x_i and y_i are the molar fractions of component i in the liquid and vapor phase, respectively, γ_i is the activity coefficient, ϕ_i^{sat} and P_i^{sat} are the pure-component fugacity coefficient and pressure at saturation.

The solvents normally used in the extraction process are about seven orders of magnitude more volatile than the vegetable oils. For this reason, the vegetable oil can be considered a nonvolatile component, and the equilibrium criteria apply only to the solvent constituents.

Taking into account the moderate values of the saturation pressures at normal operating conditions (0.4–0.8 MPa), the pure-component fugacity coefficients at saturation (ϕ_i^{sat}) can be calculated by the virial equation of state. The Tsomopoulos (1) correlation for the computation of second virial coefficients of hydrocarbons was used in this work.

Vegetable oils are mixtures of triglycerides of saturated and unsaturated fatty acids, i.e., mixtures of long-chain, slightly polar molecules, with molecular weights in the order of 850. The solvent traditionally used in industry is a mixture of alkanes (a C_6 fraction) with a molecular weight of about 85. Therefore, the properties of a solvent–oil solution will be governed by the difference in the molecular size of its components, rather than by energy interactions between the molecules. A few functional groups (paraffin, olefin and ester groups) are present in the solvent–vegetable oil mixtures; therefore, a group contribution model for the calculation of activity coefficients is attractive. The UNIFAC (2) model was chosen for this work. In this model the activity coefficient is calculated by:

$$\ln\gamma = \ln\gamma^{comb} - \ln\gamma^{res} \qquad [2]$$

where γ^{comb} is the entropic contribution to the nonideality of the mixture (related to size and shape differences between molecules) and γ^{res} is the residual or energy-related contribution.

To determine the performance of the UNIFAC model for predicting the activity coefficients of these systems, experimental information on the VLE of alkane and vegetable oil mixtures is essential.

Previous experimental work on the VLE of alkanes and vegetable oils at low pressures are those of Pollard *et al.* (3), Smith and Wechter (4), and Lebert and Richon (5). Pollard *et al.* (3) studied mixtures of commercial hexane with cottonseed and peanut oils that covered a wide range of compositions (13.4 to 99.5 wt% oil). Smith and Wechter (4) present data on diluted commercial hexane in soybean oil (94.8 to 99.8 wt% of oil). Lebert and Richon (5) report infinite-dilution activity coefficients of *n*-alkanes in olive oil. The available experimental data cover temperatures from 298 to 413°K, and range from subatmospheric to atmospheric pressures.

Thermodynamic modelling of alkane–vegetable oil solutions. The compositions of the solvent and the oil have to be known to apply the equilibrium conditions (Eq. 1) for VLE calculations by the UNIFAC/virial model. Taking into account that different hexane fractions will differ only slightly in group composition, it is reasonable to presume that the solvent could be represented by *n*-hexane.

Table 1 shows a comparison between the calculated bubble pressures at 304.8°K for mixtures of cottonseed oil with three different solvents: A, commercial hexane (Skellysolve); B, normal hexane; and C, hypothetical solvent, which has the chemical structure of normal hexane and the vapor pressures of commercial hexane.

Calculations with solvent A are based on the actual composition of the commercial hexane. Because this solvent is a mixture of various hydrocarbons, the bubble pressures are calculated from the following expression:

$$P = \Sigma_i \gamma_i x_i \phi_i^{sat} P_i^{sat} \qquad i = 1,2, \ldots\ldots, N_s \qquad [3]$$

where subscript i refers to each of the N_s solvent components.

TABLE 1

Equilibrium Pressures at 304.8°K for Different Solvent–Cottonseed Oil Mixtures

Solvent weight fraction	A	B	C
1.000	219.3	200.4	216.5
0.850	214.6	196.2	211.9
0.630	199.7	183.1	197.7
0.465	178.0	163.9	177.1
0.360	156.8	145.0	156.7
0.257	127.9	119.0	128.6
0.154	88.3	82.8	89.4
0.104	64.0	60.3	65.1
0.070	45.3	42.8	46.2
0.039	26.4	25.0	27.0

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If the real multicomponent solvent is assumed to be represented by one component, the VLE calculations can be simplified to:

$$P = \gamma_s x_s \phi_s^{sat} P_s^{sat} \quad [4]$$

When this equation is applied to mixtures of oils with solvents B and C, the P_s^{sat} value corresponds to the vapor pressure of pure *n*-hexane and commercial hexane, respectively. In both cases, γ_s is calculated *via* UNIFAC by using the group composition of normal hexane.

Comparison between the values in Table 1 indicates that the property that has the greatest effect in the VLE calculations of these systems is the vapor pressure of the solvent (differences between the first and second columns), rather than the solvent composition (differences between the first and third columns). As a result, the VLE calculations may be simplified by applying the equilibrium condition to one component (*n*-hexane) while keeping the vapor pressure of the real multicomponent solvent as the P_s^{sat} value.

Natural vegetable oils, on the other hand, differ from each other by the length and degree of unsaturation of the hydrocarbon chains bound to the triester nucleus. These differences can be taken into account through the oil molecular weight (MW), which gives a measurement of the lengths of the fatty acid chains; and the iodine number (I), which quantifies the amount of double bonds in the fatty acid chains.

Calculations of *n*-hexane activity coefficients on hypothetical oils of exactly known compositions were performed to study the effect of the vegetable oil composition on the VLE predictions by the UNIFAC model. The computations included: (i) Activity coefficients of *n*-hexane in solutions with triglycerides of the same MW and I values but with different compositions of various fatty acids. The γ_s values predicted were the same within the first four decimal figures in each case. These results are a consequence of the similar group compositions of the different triglycerides. (ii) Activity coefficients of *n*-hexane in solutions with three hypothetical oils (identified as A, B and C in Table 2) of the same MW but different I. Table 2 contains the composition, MW and I of each oil and shows the values of the solvent activity coefficient infinitely diluted in the oil (γ_s^∞), as well as the combinatorial and residual contributions to those values. The results in Table 2 show that the greater the I value, the greater the activity coefficient predicted by UNIFAC. This can be explained by the increase in the residual contribution to γ, produced by a higher number of olefin/paraffin (CH_2) group interactions. (iii) Activity coefficients of *n*-hexane in solutions with six hypothetical oils (A through F in Table 3) of the same I, but different MW. The results in Table 3 show that an increase in MW leads to lower γ values. This effect is due to the higher combinatorial contribution produced when the difference in size between solvent and oil molecules is greater. The results in Tables 2 and 3 also show that for alkane–vegetable oil mixtures, the UNIFAC-combinatorial contributions to the activity coefficients are greater than those of the residual contributions, as should be expected in these types of solutions.

Experimental data on VLE by Pollard *et al.* (3) were used to check the above UNIFAC results. Applying Equation 4 to Pollard *et al.*'s VLE experimental data (3) on mixtures of commercial hexane(s) with cottonseed oil (c) and peanut oil (p), at the same temperature and liquid-phase compositions, we have:

$$\frac{P^c}{P^p} = \frac{\gamma_s^c}{\gamma_s^p} \quad [5]$$

where γ_s^c, γ_s^p, P^c and P^p represent, respectively, the hexane activity coefficients and bubble pressures of the solvent–cottonseed oil and solvent–peanut oil mixtures.

Taking into account that the I of cottonseed oil is greater than that of peanut oil, while the MW of cottonseed oil is lower than that of peanut oil, the ratio γ_s^c/γ_s^p should be greater than one, following UNIFAC predictions. This is confirmed by the results in Table 4, where the experimental values obtained with Equation 5 are compared to UNIFAC predictions. Though UNIFAC predictions are not quantitatively correct, they follow the experimental results qualitatively.

Comparison between UNIFAC predictions and experimental data. The experimental data of Pollard (3) for cottonseed and peanut oils were used to verify the UNIFAC predictions of activity coefficients. Due to the high relative volatilities of these systems, the vapor-phase mole fraction of the solvent is nearly unity over the whole concentration range. Thus, no reliable thermodynamic consistency test can be applied to the VLE experimental data of Pollard *et al.* (3). A consistency test (6) was applied to the isothermal P-x data, however, with the aim of checking the quality of the fit to the total pressure. The result of the test indicates mean deviations in the order of 1–10 mmHg.

The data of Smith and Wechter (4) on soybean oil were not used, due to the lack of information on the vapor

TABLE 2

Activity Coefficient of Normal Hexane Infinitely Diluted in Oils with Different Iodine numbers

Triglyceride[a]	A	B	C
Tripalmitin	9.9	7.1	5.4
Tristearin	32.7	7.2	27.2
Triolein	33.5	48.0	15.4
Trilinolin	10.7	27.2	13.2
Trilinolein	13.2	10.5	38.8
MW oil	876	876	876
I oil	82.2	116.4	137.6
γ_s^∞	0.322	0.328	0.333
ln (γ_s^{comb})	−1.242	−1.237	−1.235
ln (γ_s^{res})	0.108	0.124	0.134

[a] MW, molecular weight; I, iodine number.

TABLE 3

Activity Coefficients of Normal Hexane Infinitely Diluted in Oils with Different Molecular Weights[a]

	A	B	C	D	E	F
Oleic acid	1.0	3.0	5.0	7.0	9.0	11.0
Tripalmitin	5.9	5.9	5.9	5.9	5.9	5.9
Tristearin	7.5	7.5	7.5	7.5	7.5	7.5
Triolein	28.5	26.5	24.5	22.5	20.5	18.5
Trilinolin	50.7	50.7	50.7	50.7	50.7	50.7
Trilinolein	6.4	6.4	6.4	6.4	6.4	6.4
MW oil	870.0	858.0	845.9	835.3	821.9	809.8
I oil	130.4	130.4	130.4	130.4	130.4	130.4
γ_s^∞	0.333	0.338	0.342	0.347	0.351	0.356
ln (γ_s^{comb})	−1.230	−1.217	−1.205	−1.193	−1.180	−1.167
ln (γ_s^{res})	0.131	0.132	0.132	0.133	0.134	0.135

[a] Abbreviations as in Table 2.

TABLE 4

Comparison Between the Experimental γ_s^c/γ_s^p Ratio and UNIFAC Predictions

T (°C)	Solvent weight fraction	Experimental	UNIFAC
114.17	0.036	1.273	1.070
80.53	0.080	1.237	1.059
25.13	0.858	1.006	1.001

pressures and composition of the commercial hexane used in their experiments.

Even though Pollard *et al.* (3) do not report the specific MW of the cottonseed and peanut oils, they report the I and free fatty acid contents of the oils. This information, together with typical MW values given by Bailey (7), was used to obtain the MW of the cottonseed and peanut oils.

Figure 1 shows the absolute errors in the boiling temperatures, predicted by the UNIFAC/virial model, for ten experimental isobars ranging from 160 to 760 mmHg, as measured by Pollard *et al.* (3) for mixtures of commercial hexane [Skellysolve (Ghetty Petroleum Corps. Skelly Oil Co., Jericho, NY)] with peanut and cottonseed oils. Throughout the concentration range, the calculated boiling temperatures are greater than the experimental ones. The absolute errors are lower than 10°C in the composition range from pure solvent to solutions with 90 wt% of oil; in the dilute region of the solvent, the errors increase to values as high as 60°C.

We showed already that, for alkane–vegetable oil mixtures, the combinatorial contribution to the activity coefficient is more important than the residual term. For example, in mixtures where the solvent is infinitely diluted in the oil, the combinatorial part of the solvent activity coefficient represents about 90% of the total value. Therefore, from here on, we will only analyze the effects of different combinatorial expressions (8) and the addition of a free volume term (9) to the UNIFAC model, while keeping the original UNIFAC residual contribution.

Table 5 shows the different combinatorial expressions studied. The Staverman and Guggenheim (SG) form corresponds to the original UNIFAC model. Figure 2 compares the experimental boiling temperatures of commercial hexane–cottonseed oil mixtures (3) at 310 mmHg with the values predicted by some of the combinatorial expressions in Table 5. Also included in the figure is the ideal-solution boiling curve. The hexane–oil system presents negative deviation to Raoult's law throughout the composition range. The results in Figure 2 show that the predictions are not so much affected by the definition of the fractions (φ_i, ψ_i, τ_i) as by the value of the exponent ($p_i = 1$ or $p_i = 2/3$) used with those fractions. As expected, the use of an exponent equal to one in the volume or surface fractions, equivalent to the original Flory-Huggins model, overpredicts the nonideality of the hexane–vegetable oil mixtures; but the use of an exponent equal to 2/3, as suggested by Kikic *et al.* (8) for mixtures of aliphatic hydrocarbons, gives activity coefficient values higher than the experimental ones. For this reason, an intermediate value of $p_i = 3/4$ for the volume fraction φ_i was adopted in this work. The combinatorial contribution to the activity coefficients (identified here as SG, r3/4) has the form:

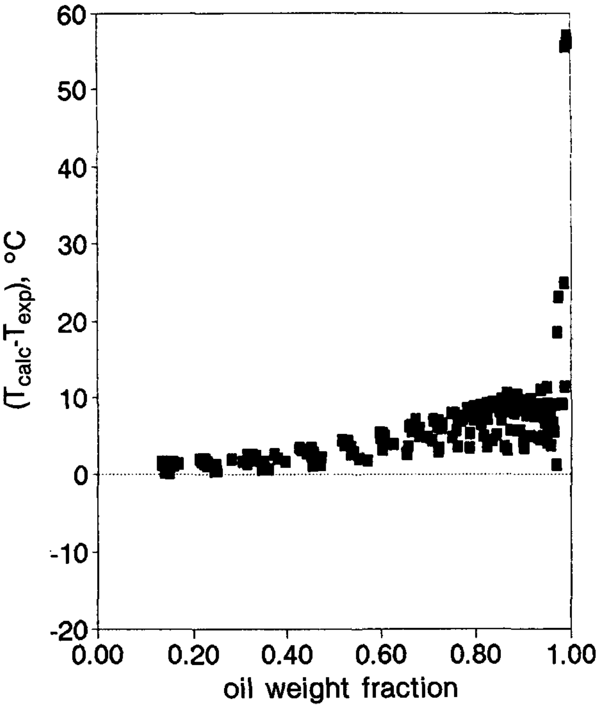

FIG. 1. Absolute errors in the boiling temperatures as predicted by the UNIFAC/virial model for mixtures of commercial hexane with cottonseed and peanut oils. T_{calc}, calculated temperature; T_{exp} experimental temperature.

$$ln\gamma_i^{comb} = (ln\frac{\psi_i}{x_i} + 1 - \frac{\psi_i}{x_i}) - \frac{z}{2}\, q_i\,(ln\frac{\psi_i}{\varphi_i} + 1 - \frac{\psi_i}{\varphi_i}) \qquad [6]$$

$$\psi_i = \frac{x_i r_i^{3/4}}{\sum x_j r_j^{3/4}} \qquad [7]$$

Figure 3 shows the absolute errors in the boiling temperatures, as predicted by the UNIFAC-SG, r3/4 model, for the same VLE data set used in the evaluation of the original UNIFAC model (Fig. 1). Compared to the original UNIFAC model, the errors are lower up to solutions with 90% of oil by weight (absolute errors lower than −5°C), although they continue to be large in the infinite diluted region.

Taking into account the rather large negative deviations to Raoult's law, predicted by UNIFAC for the hexane–vegetable oil systems, the modification originally proposed by Oishi and Prausnitz (9) for solvent and polymer mixtures was also studied. This model includes an independent free-volume term. The expression for the activity coefficient now takes the form:

$$ln\gamma_i = ln\gamma_i^{comb} + ln\gamma_i^{res} + ln\gamma_i^{fv} \qquad [8]$$

TABLE 5

Different Combinatorial Expressions for the UNIFAC Model

Source	Expression[a]	p_i
Flory	$\ln\varphi_i/x_i + 1 - \varphi_i/x_i$	1
Scheller	$\ln\tau_i/x_i + 1 - \tau_i/x_i$	1
Donohue	$\ln\varphi_i/x_i + 1 - \varphi_i/x_i$	2/3
SG	$\ln\varphi_i/x_i + 1 - \varphi_i/x_i - (z/2)q_i\,(\ln\psi_i/\varphi_i + 1 - \psi_i/\varphi_i)$	1
SG,V	$\ln\tau_i/x_i + 1 - \tau_i/x_i - (z/2)q_i\,(\ln\psi_i/\varphi_i + 1 - \psi_i/\varphi_i)$	1
SG,q	$\ln\psi_i/x_i + 1 - \psi_i/x_i - (z/2)q_i\,(\ln\psi_i/\varphi_i + 1 - \psi_i/\varphi_i)$	1
SG,r2/3	$\ln\varphi_i/x_i + 1 - \varphi_i/x_i - (z/2)q_i\,(\ln\psi_i/\varphi_i + 1 - \psi_i/\varphi_i)$	2/3
SG,V2/3	$\ln\tau/x_i + 1 - \tau_i/x_i - (z/2)q_i\,(\ln\psi_i/\varphi_i + 1 -\psi_i/\varphi_i)$	2/3

[a] Where

$$\tau_i = \frac{x_i V_i^{p_i}}{\sum x_j r_j^{p_j}}, \qquad \varphi_i = \frac{x_i q_i^{p_i}}{\sum x_j q_j^{p_j}}, \qquad \psi_i = \frac{x_i r_i^{p_i}}{\sum x_j r_j^{p_j}},$$

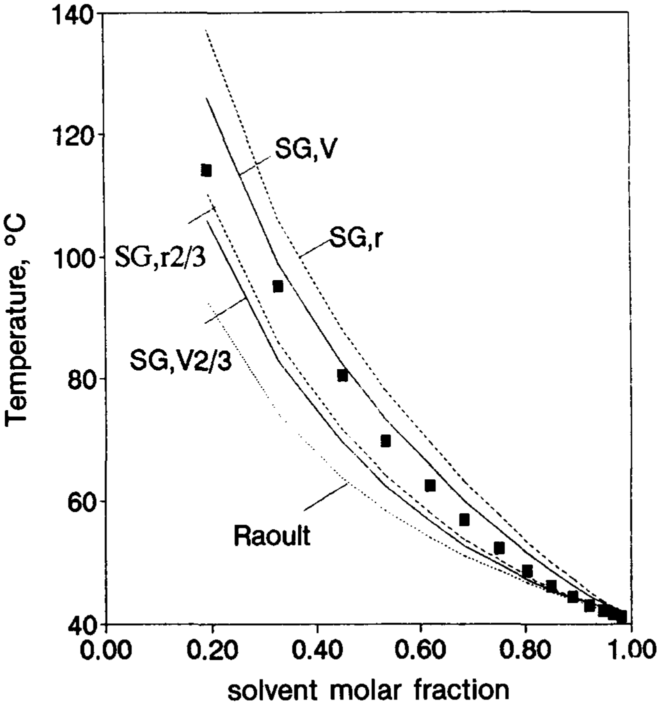

FIG. 2. Comparison between experimental boiling temperatures of commercial hexane–cottonseed oil mixtures and values predicted by different combinatorial models.

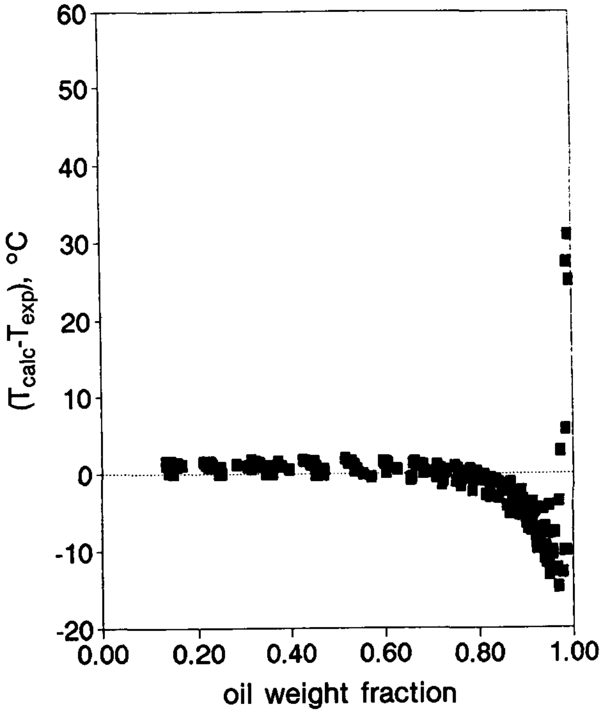

FIG. 3. Absolute errors in the boiling temperatures as predicted by the UNIFAC-SGr3/4 model for the same mixtures of Figure 1. Abbreviations as in Figure 1.

where γ_i^{fv} represent the free-volume contributions, and the first two terms are as the original UNIFAC model. The characteristic parameter in the free-volume term is Cs, one-third the total number of external degrees of freedom per solvent molecule. This parameter can be correlated with the acentric factor of the solvent, as is shown by Beret and Prausnitz (10). Following this approach, a value of Cs = 1.91 was used in this work, corresponding to an acentric factor of 0.296 for normal hexane.

Elbro *et al.* (11) developed a new equation for an entropic activity coefficient (UNIFAC-ELBRO), which includes combinatorial and free-volume contributions:

$$ln\gamma_i^{ent} = ln\gamma_i^{comb} + ln\gamma_i^{res} \qquad [9]$$

where:

$$ln\gamma_i^{ent} = ln\frac{\Phi_i^{fv}}{x_i} + 1 - \frac{\Phi_i^{fv}}{x_i} \qquad [10]$$

and

$$\Phi_i^{fv} = \frac{x_i\,[v_i - v_i^*]}{\sum x_i[v_i - v_j^*]} \qquad [11]$$

v_i^* is the molar hardcore volume of component i, calculated from the van der Waals volumes (12), and v_i represents the molar volume. The absolute errors in the prediction of boiling temperatures by these two last models (UNIFAC-FV and UNIFAC-ELBRO) are similar to the ones shown in Figure 3 for the UNIFAC-SGr3/4 method.

TABLE 6

Comparison Between Experimental and Predicted Infinite-Dilution Activity Coefficients of Alkane–Olive Oil Mixtures

	γ_s^∞				
Solvent	Exp.	UNIFAC	UNIFAC-SGr3/4	UNIFAC-FV	UNIFAC-ELBRO
n-Pentane	0.632	0.2829	0.4657	0.4802	0.4108
n-Hexane	0.709	0.3303	0.5193	0.5174	0.4465
n-Heptane	0.759	0.3777	0.5708	0.5761	0.4918
n-Octane	0.797	0.4251	0.6206	0.5939	0.5297
n-Nonane	0.824	0.4725	0.6691	0.6322	0.5706
n-Decane	0.846	0.5199	0.7163	0.6828	0.6164

The comparison between Figures 1 and 3 shows that UNIFAC–SG,r3/4 improves the capacity of the UNIFAC model for predicting the activity coefficients of hexane in hexane–vegetable oil mixtures. The performances of the UNIFAC–SG,r3/4, UNIFAC–FV and UNIFAC–ELBRO models are similar, and they seem to fail in the solvent-diluted region. Table 6 shows a comparison between the infinite-dilution activity coefficients predicted by UNIFAC, UNIFAC–SG,r3/4, UNIFAC–FV and UNIFAC–ELBRO and the experimental data reported by Lebert and Richon (5) for six different alkane–olive oil mixtures. These authors report uncertainties of 0.014 to 0.054 in the experimental infinite-dilution activity coefficient values. The differences between predicted and experimental data are in the order of 0.15 for UNIFAC–SGr3/4 and UNIFAC–FV, and 0.25 for UNIFAC–ELBRO. Additional reliable equilibrium data, especially in the diluted region, would be necessary to complete the present analysis.

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