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A multi-fluid nonrandom lattice fluid model for mixtures containing nonionic surfactants

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Abstract−Surfactant systems show highly non-ideal phase behavior because of the inter-association and intra-association hydrogen bond. We present a lattice fluid equation of state that combines the multi-fluid nonrandom lattice fluid model with modified Veytsman statistics for intra+inter molecular association to calculate phase behavior for mixture containing surfactant systems. The literatureresults fitted to this model show good accordance for mixtures containing nonionic surfactant systems.

Key words: Amphipiles, Lattice Model, Association Surfactants, Alkanes

INTRODUCTION

Thermodynamic properties and equations of states play a major role in separation operations, particularly with respect to energy requirements, phase equilibria, and sizing equipment. Many equations of state such as PR model [1] and SAFT model [2] were successfully capable of describing thermodynamic properties for non-associating systems and inter-molecular associating systems.

Surfactant systems play a very important role in many applications such as cosmetic, food, pharmaceutical, polymer process, semiconductor, and chemical processes. Phase behavior for mixtures containing surfactant systems has been needed in theseindustrial applications [3-5]. C_iE_j, an abbreviation of homologous series of nonionic amphiphiles $CH_3(CH2)_{i-1}$-$(OCH_2CH_2)_j$-OH, is a particularly interesting class of substances due to the presence of oxygen (O) and hydroxyl (OH) group in the same molecule. This OHO research is the so-called TOM project [6-8]. Inter- and intra-hydrogen bonds of this ethoxylated alcohol amphiphiles lead the phase behavior of the systems with these substances highly non-ideal.

Intra-molecular association has been investigated in lattice fluids [9,10] and its applications to equation of state (EOS) frameworks have been researchedby many groups. The non-random hydrogen-bonding (NRHB) EOS with intra-molecular association [11,12] and the non-random lattice fluid hydrogen-bonding EOS with intra- and inter-molecular association (NLFHBi) [13] as an application of Guggenheim's lattice fluid theory obtained a satisfactory agreement between experimental and calculated phase equilibria properties. However, A close look reveals that the precedent lattice fluid models with intra-molecular associating term have a combinatorial mismatching problem during the arrangement of donors and acceptors, which leads to the combination into not a H-bond but an original molecule itself.

In this study, we presented modified Veytsman statistics for inter- and intra-molecular association, combined it with the multi-fluid nonrandom lattice fluid (MLF) [14,15] as a physical description of fluids, and finally tested the present model with the literature data for mixtures containing surfactant systems.

THERMODYNAMIC MODEL

1. Configurational Partition Function

The configurational lattice-fluid partition function for systems with associating interactions can be approximated as a product of the physical and chemical contributions. The chemical contribution comes from the associating interaction. The associating part of the partition function is

$$\Omega_A=\left(\frac{\tilde{\rho}}{rN}\right)^{N_{11}+N_{12}} c^{N_{1B}}\,\Omega\exp\left(-\frac{\sum\limits_{ij} A_{ij}}{kT}\right) \tag{1}$$

where c is the flexibility parameter [10] that represents the probability that the intra-molecular bonding sites are adjacent to each other. And in the above expression, the first term means the coordination factor, Ω, is the number of arrangements, and the last term indicates the free energy marginal sum of association. Ω is derived from combinatorial calculation by adopting the argument of Veytsman, so that the partition function due to the hydrogen bonding was derived to count the number of arrangements of hydrogen bonding interaction.

Let us consider this with N_1 C_iE_j molecules and N_2 alkane molecules. N_1 C_iE_j surfactants have a hydroxyl group containing a type 1 proton donor and type 1 acceptor and x ether groups containing type 2 acceptor. Three types of associating interactions are possible, that is, inter-molecular OH···OH, inter-molecular OH···O-, and intra-molecular OH···O-. Let there be N_{11} inter-molecular hydrogen bonds of OH···OH, N_{12} inter-molecular hydrogen bonds of OH···O-, and N_{1B} intra-molecular hydrogen bonds of OH···O-. The total number of proton donor is N_1 and the non-interacting proton donor N_{10} is

$$N_{10}=N_1-N_{11}-N_{12}-N_{1B} \tag{2}$$

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[‡] This article is dedicated to Professor Chul Soo Lee in commemoration of his retirement from Department of Chemical and Biological Engineering of Korea University.

The number of arrangements available is counted by three steps.

i) Selecting proton donor and acceptor

ii) Counting the arrangements between the interacting species

iii) Eliminating over-count

Step i, ii are the same as Missopolinou and Panayiotou's Veytsman statistics [10], but step iii has mathematical difference which originates from the overcount problem during the combinatorial calculation. Classical Veytsman statistics assumed that the combinatorial arrangement does not have any mismatch such as a molecule itself, not hydrogen bonding. But during the arrangement, the proton donor and acceptor from the same molecule do not form the hydrogen bonding, but the original molecule itself. This can happen in the middle of an arrangement with a certain possibility. So this overcount from the combinatorial should be removed. Let the equivalent term that indicates the possibility of overcount be Ω_{iii}, then the term is expressed by the subtraction of the possibility from 1. The summation of the possibility from the overcount that has to be subtracted can be simplified as follows.

$$1-\left(1-\frac{1}{\mathrm{N}_1}\right)^{N_{11}} \tag{3}$$

This term can be replaced by an exponential term because the number of donors and acceptors is Avogadro's scale, that is, the limiting case of the definition of e. The resulting expression from iii is

$$\Omega_{iii}=\exp\left(-\frac{\mathrm{N}_{11}}{\mathrm{N}_1}\right)\exp\left(-\frac{\mathrm{xN}_{12}}{\mathrm{xN}_1-\mathrm{N}_{1B}}\right) \tag{4}$$

The resulting equation Ω is

$$\Omega=\frac{\mathrm{x}^{N_{1B}}(\mathrm{N}_1!)^2(\mathrm{xN}_1-\mathrm{N}_{1B})!\exp\left(-\frac{\mathrm{N}_{11}}{\mathrm{N}_1}\right)\exp\left(-\frac{\mathrm{xN}_{12}}{\mathrm{xN}_1-\mathrm{N}_{1B}}\right)}{\mathrm{N}_{1B}!\mathrm{N}_{11}!\mathrm{N}_{12}!\mathrm{N}_{10}!(\mathrm{N}_1-\mathrm{N}_{11})!(\mathrm{xN}_1-\mathrm{N}_{1B}-\mathrm{N}_{12})!} \tag{5}$$

The exponential terms which are obtained by simple calculation of its probability are representing the elimination of the over-counting mentioned above.

Combining Eqs. (1) and (5) provides the resulting expression of associating partition function.

$$\Omega_A=\frac{\mathrm{x}^{N_{1B}}(\mathrm{N}_1!)^2(\mathrm{xN}_1-\mathrm{N}_{1B})!\exp\left(-\frac{\mathrm{N}_{11}}{\mathrm{N}_1}\right)\exp\left(-\frac{\mathrm{xN}_{12}}{\mathrm{xN}_1-\mathrm{N}_{1B}}\right)}{\mathrm{N}_{1B}!\mathrm{N}_{11}!\mathrm{N}_{12}!\mathrm{N}_{10}!(\mathrm{N}_1-\mathrm{N}_{11})!(\mathrm{xN}_1-\mathrm{N}_{1B}-\mathrm{N}_{12})!} \cdot \mathrm{c}^{N_{1B}}\left(\frac{\tilde{\rho}}{\mathrm{rN}}\right)^{N_{11}+N_{12}}\exp\left(-\frac{\sum \mathrm{N}_{ij}\mathrm{A}_{ij}}{\mathrm{kT}}\right) \tag{6}$$

2. Helmholtz Energy

The associating contribution of Helmholtz free energy, A_A^c is written as follows.

$$\mathrm{A}_A^c=-\mathrm{kT}\ln\Omega_A \tag{7}$$

Where Ω_A is expressed in Eq. (6). And the Helmholtz free energy consists of a physical and chemical part. Omitting details in the derivation, the resulting expression for the configurational Helmholtz freeenergy is written as

$$\mathrm{A}^c=\mathrm{A}_P^c+\mathrm{A}_A^c \tag{8}$$

The physical contribution A_P^c was given by Shin et al. [14,15].

We can obtain the minimizationof Helmholtz energy from these three partial differentiations of Eq. (6). Let there be β=1/kT hereafter.

$$\frac{\partial\beta\mathrm{A}_A^c}{\partial\mathrm{N}_{11}}=0 \tag{9}$$

$$\frac{\partial\beta\mathrm{A}_A^c}{\partial\mathrm{N}_{12}}=0 \tag{10}$$

$$\frac{\partial\beta\mathrm{A}_A^c}{\partial\mathrm{N}_{1B}}=0 \tag{11}$$

By using Stirling's approximation, the maximum term condition is obtained. Rearranging and solving the equations gives the number of N_{11}, N_{12}, N_{1B}.

3. EOS and Chemical Potential

The EOS and the chemical potential expression due to the associating interaction is derived from the configurational partition function.

$$\mathrm{P}_A=\mathrm{P}_A^{\mathrm{c}}=-\left(\frac{\partial\mathrm{A}_A^c}{\partial\mathrm{V}}\right)_{T,N_i}==-\frac{1}{\upsilon^*}\left(\frac{\partial\mathrm{A}_A^c}{\partial\mathrm{N}_0}\right)_{T,N_i} \tag{12}$$

To obtain the pressure term from association, the Helmholtz free energy should be differentiated with regard to N_0. The resulting expression is as follows:

$$\mathrm{P}_A=-\frac{1}{\beta\upsilon^*}(\nu_{11}+\nu_{12})\tilde{\rho} \tag{13}$$

where ν_{11}, ν_{12} is defined by

$$\nu_{11}=\mathrm{N}_{11}/\mathrm{rN},\ \nu_{12}=\mathrm{N}_{12}/\mathrm{rN} \tag{14}$$

The EOS is rearranged into the reduced variable type, and the resulting equation is as follows:

$$\left(\frac{\tilde{\mathrm{P}}}{\tilde{\mathrm{T}}}\right)_A=-(\nu_{11}+\nu_{12})\tilde{\rho} \tag{15}$$

The chemical potential was obtained by differentiation of the free energy with regard to the number of i-th component's mole fraction. In this case, the contribution from associating interaction is derived from A_A^c.

$$\mu_{A,i}=\left(\frac{\partial\mathrm{A}_A^c}{\partial\mathrm{n}_1}\right)_{T,V,n_j}=\mathrm{N}_a\left(\frac{\partial\mathrm{A}_A^c}{\partial\mathrm{N}_1}\right)_{T,V,N_j} \tag{16}$$

Where N_a is Avogadro's number. After some mathematical steps, the resulting chemical potential is expressed as follows:

$$\frac{\mu_{A,1}}{\mathrm{RT}}=\ln\frac{(\mathrm{N}_1-\mathrm{N}_{1B}-\mathrm{N}_{11}-\mathrm{N}_{12})(\mathrm{N}_1-\mathrm{N}_{11})}{\mathrm{N}_1^2}+\mathrm{x}\ln\frac{\mathrm{xN}_1-\mathrm{N}_{1B}-\mathrm{N}_{12}}{\mathrm{xN}_1-\mathrm{N}_{1B}}-\frac{\mathrm{N}_{11}}{\mathrm{N}_1^2}-\frac{\mathrm{x}^2\mathrm{N}_{12}}{(\mathrm{xN}_1-\mathrm{N}_{1B})^2} \tag{17}$$

After normalization of the partition function due to association [16], we can obtain the exact expression of the associating contribution for EOS and chemical potential without physical part.

$$\left(\frac{\tilde{\mathrm{P}}}{\tilde{\mathrm{T}}}\right)_A=-(\nu_{11}+\nu_{12}-\nu_{11}^o-\nu_{12}^o)\tilde{\rho} \tag{18}$$

$$\frac{\mu_{A,1}}{\mathrm{RT}}=\ln\frac{(\mathrm{N}_1-\mathrm{N}_{1B}-\mathrm{N}_{11}-\mathrm{N}_{12})(\mathrm{N}_1-\mathrm{N}_{11})}{(\mathrm{N}_1-\mathrm{N}_{1B}^o-\mathrm{N}_{11}^o-\mathrm{N}_{12}^o)(\mathrm{N}_1-\mathrm{N}_{11}^o)}$$

$$+x\ln\frac{(xN_1-N_{1B}-N_{12})(xN_1-N_{1B}^o)}{(xN_1-N_{1B}^o-N_{12}^o)(xN_1-N_{1B})} -\frac{N_{11}}{N_1^2}+\frac{N_{11}^o}{N_1^2}-\frac{x^2N_{12}}{(xN_1-N_{1B})^2}+\frac{x^2N_{12}^o}{(xN_1-N_{1B}^o)^2} \tag{19}$$

Finally the multi-fluid nonrandom (intra+inter) molecular associating lattice fluid [MiALF] EOS and the chemical potential due to physical and chemical contribution are as follows, respectively:

$$\frac{\tilde{P}}{\tilde{T}}=-\ln(1-\tilde{\rho})+\frac{z}{2}\ln\left[1+\left(\frac{q}{r}-1\right)\tilde{\rho}\right] -(\nu_{11}+\nu_{12}-\nu_{11}^o-\nu_{12}^o)\tilde{\rho}-\frac{\theta^2}{\tilde{T}} \tag{20}$$

$$\beta\mu_i^c=\gamma_i(T)+r_i\frac{\tilde{P}}{\tilde{T}}+Z\frac{r_i}{r}\left(\frac{v_i^*}{v^*}-1\right)+\ln\left(\frac{\theta_i}{q_i}\right)+r_i\left(1-\frac{z}{2}\right)\ln\left(1+\left(\frac{q}{r}-1\right)\tilde{\rho}\right) +\frac{r_i\theta^2}{\tilde{T}}+(1-r_i)\theta-\frac{zq_i}{2}\Bigg[\ln\sum_{k=0}\theta_k\tau_{ki}+\beta\varepsilon_{ii} +\sum_{l=1}\frac{\theta_l(\tau_{il}-\tau_{0l}(r_i/q_i))}{\sum_{m=0}\theta_m\tau_{ml}}\Bigg]-\beta\mu_{A,1} \tag{21}$$

Here, all the quantities with the tilde (~) denote the reduced variables defined by

$$\tilde{P}=\frac{P}{P^*},\ \tilde{T}=\frac{T}{T^*},\ \tilde{\rho}=\frac{\rho}{\rho^*},\ \rho^*=\frac{1}{r\upsilon^*} \tag{22}$$

where the reducing parameters are defined by

$$P^*\upsilon^*=kT^*=\frac{z}{2}\varepsilon_M \tag{23}$$

and ε_M, θ are defined by

$$\varepsilon_M=\frac{1}{\beta\theta^2}\left[\sum_{i=1}\theta_i\left(1-\frac{\tau_{0i}}{\sum_{k=0}\theta_k\tau_{ki}}\right)\right] \tag{24}$$

$$\theta=\frac{\sum N_iq_i}{N_q}=\frac{(q/r)\tilde{\rho}}{1+(q/r-1)\tilde{\rho}}=1-\theta_0 \tag{25}$$

where τ_{ji}, ε_{ij} are defined by

$$\tau_{ji}=\exp[\beta(\varepsilon_{ji}-\varepsilon_{ii})] \tag{26}$$

$$\varepsilon_{ij}=\sqrt{\varepsilon_{ii}\varepsilon_{jj}}(1-k_{ij}) \tag{27}$$

and $\gamma_i(T)$ is the reference chemical potential, which depends only on temperature.

RESULTS AND DISCUSSION

In this study the MiALF model was tested for mixtures containing surfactant systems and was compared with the multi-fluid nonrandom molecular associating lattice fluid (MALF) model [17], PR EOS and SAFT EOS. The MALF EOS has three molecular parameters for pure fluids: v_i^*, r_i, ε_{ii}, and the MiALF EOS has four molecular parameters: v_i^*, r_i, ε_{ii}, c. Pure parameters are fitted to liquid density and vapor pressure data from the Korea thermophysical properties Databank (KDB) [18]. Pure parameters for the MALF and MiALF EOS are listed in Table 1. We use the inter-molecular associating energy parameters for alkoxyethanol, U_{11}^A=−25.1 kJ/mol of Renon and Prausnitz [19], S_{11}^A=−26.5 J/(mol K) as given by Panayiotou [20] and U_{12}^A=−22.0 kJ/mol, S_{12}^A=−52.0 J/(mol K) of Nagata and Tamura [21].We set the intra-molecular associating energy parameters $U_{int\,ra}^A$=−10.47 kJ/mol, $S_{int\,ra}^A$=−16.0 J/(mol K) as given by Missopolinou et al. [11].

The binary interaction parameter, k_{ij}, is determined in this calculation such that the deviation of calculated values from experimental data is minimal. The Marquardt algorithm was used to minimize the following objective function, the root mean square deviations (RMSD) for pressure:

$$\text{RMSD}=\left\{\frac{1}{N_{exp}}\sum_i^{N_{exp}}\left[\frac{P_{exp}-P_{cal}}{P_{exp}}\right]^2\right\}^{1/2} \tag{21}$$

where N_{exp} is the number of experimental data points and P_{exp} and P_{cal} are the experimental and the calculated pressures, respectively.

The published data [22-24] for alkoxyethanol+alkane systems were correlated with the MALF, MiALF, and PR EOS. Binary parameters and the RMSD for alkoxyethanol+alkane systems are shown in Table 2. In Figs. 1 and 2, the calculated P-x equilibria of the MALF, MiALF EOF for the C_1E_1+cyclohexane, the C_2E_1+n-heptane systems are compared with the literature data. The present MiALF EOS, which considers a contribution from intra-molecular associations, represented better calculated results than the MALF EOS in alkoxyethanol+alkane systems. The PR EOS showed fewer calculated

Table 1. Molecular parameters of pure fluids for the MALF and MiALF EOS

MALF EOS	v_i^*, cm^3/mol	r_i	ε_{ii}/k, K		AADP*	AADρ*
C_1E_1	20.219	3.703	149.19		0.019	0.011
C_2E_1	20.126	4.524	141.62		0.023	0.010
C_3E_1	19.790	5.421	138.70		0.019	0.008
MiALF EOS	v_i^*, cm^3/mol	r_i	ε_{ii}/k, K	c	AADP*	AADρ*
C_1E_1	14.892	4.980	145.29	0.071	0.017	0.007
C_2E_1	15.627	5.787	138.64	0.070	0.017	0.006
C_3E_1	15.828	6.747	136.81	0.090	0.018	0.006

*: $\text{AADP}=\frac{1}{n_T}\sum_i^N\left|\frac{P^{cal}-P^{exp}}{P^{exp}}\right|$, n_T: number of experiment

**: $\text{AAD}\rho=\frac{1}{n_T}\sum_i^N\left|\frac{P^{cal}-P^{exp}}{P^{exp}}\right|$, n_T: number of experiment

Table 2. Binary parameters and RMSD of the MALF, MiALF, and PR EOS for C_iE_j+alkane systems

	T/K	MALF EOS		MiALF EOS		PR EOS	
		k_{ij}	RMSD	k_{ij}	RMSD	k_{ij}	RMSD
C_1E_1+n-hexane	313.15	0.010	0.066	0.044	0.060	0.058	0.119
	323.15	0.010	0.048	0.044	0.048	0.066	0.114
C_1E_1+cyclohexane	303.15	0.018	0.042	0.049	0.029	0.086	0.071
	323.15	0.017	0.045	0.050	0.022	0.099	0.080
C_1E_1+n-heptane	323.15	0.012	0.059	0.045	0.066	0.061	0.135
C_2E_1+n-hexane	303.15	0.005	0.032	0.029	0.031	0.052	0.098
	323.15	0.005	0.018	0.031	0.013	0.062	0.089
C_2E_1+cyclohexane	303.15	0.008	0.026	0.030	0.019	0.076	0.057
	323.15	0.009	0.012	0.032	0.012	0.086	0.060
C_2E_1+n-heptane	303.15	0.007	0.031	0.031	0.012	0.048	0.110
	323.15	0.008	0.014	0.033	0.012	0.060	0.103
C_3E_1+n-hexane	303.15	0.001	0.020	0.018	0.017	0.062	0.076
	313.15	−0.001	0.018	0.018	0.012	0.066	0.062
	323.15	−0.003	0.024	0.019	0.010	0.067	0.068
C_3E_1+n-heptane	303.15	0.003	0.026	0.021	0.011	0.070	0.091
	313.15	0.003	0.030	0.021	0.012	0.073	0.074
	323.15	0.001	0.017	0.022	0.012	0.074	0.062

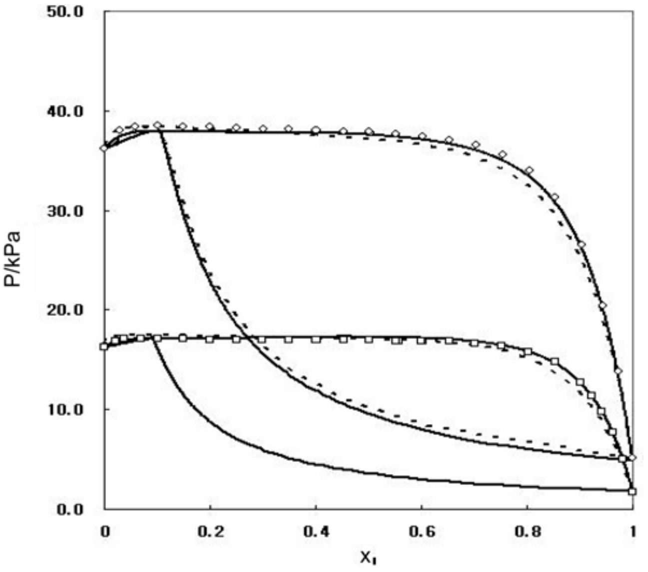

Fig. 1. Vapor-liquid equilibria of the C_1E_1 (1)+cyclohexane (2) system: Experimental data at (□) 303.15 K; (○) 323.15 K dotted lines: MALF EOS, solid lines: MiALF EOS.

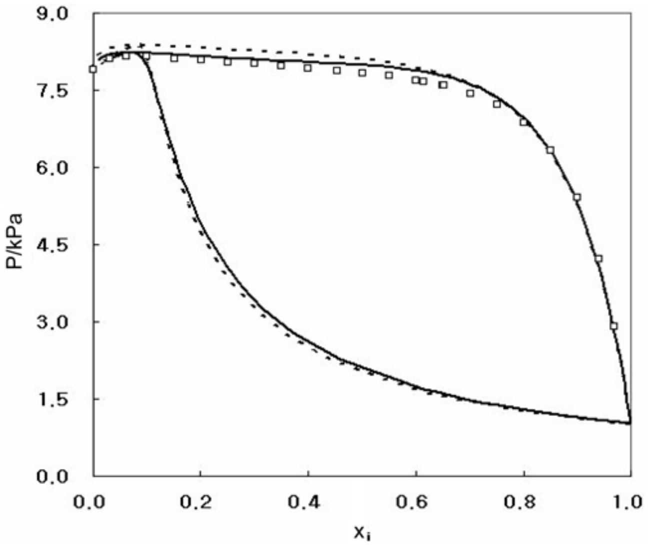

Fig. 2. Vapor-liquid equilibria of the C_2E_1 (1)+n-heptane (2) system: Experimental data at (□) 303.15 K dotted lines: MALF EOS, solid lines: MiALF EOS.

results than the MiALF and MALF model, because it had no associating contribution.

CONCLUSION

We have presented modified Veytsman statistics for inter- and intra-molecular association and combined it with the multi-fluid nonrandom lattice fluid model. The over-counting in the course of the combinatorial calculation was removed from the lattice model including the associating interaction term. The present EOS could correlate the literature data well for mixtures containing nonionic surfactant systems.

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NOMENCLATURE

A : Helmholtz free energy [J/mol]
c : flexibility parameter
N : number of molecule

N_{ij} : the number of associating pair
Q : canonical partition function
q : surface area parameter
r : number of segments per molecule
T : temperature [K]
V : volume [cm^3]
v : molar volume [cm^3/mol]
v^* : close packed volume of a mer [cm^3/mol]
x : liquid mole fraction
z : lattice coordination number
Z : compressibility factor

Greek Letters

β : reciprocal temperature [1/kT]
ε_{ij} : molecular interaction energy [J/mol]
ε_M : defined by Eq. (24) [J/mol]
φ : fugacity coefficient
ρ : molar density [mol/cm^3]
ρ^* : close packed molar density [mol/cm^3]
θ : surface area fraction

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