

Article

Determination of Energy Interaction Parameters for the UNIFAC Model Based on Solvent Activity Coefficients in Benzene–D2EHPA and Toluene–D2EHPA Systems

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Abstract

This study examines the activity coefficients of benzene, toluene, and di-(2-ethylhexyl) phosphoric acid (D2EHPA) in binary benzene–D2EHPA and toluene–D2EHPA systems, as well as the ternary n-hexane–toluene–D2EHPA system, using gas chromatography at 293.0 K. The primary objective was to determine UNIFAC model interaction parameters and validate their accuracy for predicting thermodynamic behavior in these systems. Experimental measurements revealed activity coefficient maxima for benzene and toluene at mole fractions of 0.8–0.9, decreasing to 0.46–0.67 in dilute solutions. The UNIFAC interaction parameters were calculated as follows: ACH–HPO₄ (–334, 4605), ACCH₃–HPO₄ (680, 467), and refined CH₂–HPO₄ (54, 1199). The UNIFAC model achieved deviations of less than 2% from experimental data in both binary and ternary systems. A novel methodology incorporating intermediate standards for gas chromatography was developed to overcome challenges in measuring volatile solvent concentrations, enhancing measurement precision. These findings enable accurate prediction of activity coefficients in mixtures of alkanes, cycloalkanes, and monoaromatic hydrocarbons with D2EHPA, offering significant implications for optimizing metal liquid–liquid extraction processes.

Keywords: activity coefficients; D2EHPA; benzene; toluene; UNIFAC; gas chromatography; modelling; interaction parameters

1. Introduction

This study extends prior research on the binary n-hexane–di-(2-ethylhexyl)phosphoric acid (D2EHPA) system, where experimental activity coefficients of n-hexane were used to determine UNIFAC interaction parameters for the CH₂–HPO₄ group pair [1]. D2EHPA is a highly effective extractant widely employed in liquid–liquid extraction processes for separating rare earth elements [2,3], manganese [4], cadmium, nickel [5,6], aluminum, zinc, copper [7–9], and purifying metal-containing wastes [10,11]. Its efficacy stems from its ability to form stable complexes through cation-exchange and donor–acceptor mechanisms across diverse media, enhancing metal extraction efficiency [12–16].

Solvents play a pivotal role in liquid–liquid extraction by reducing extractant viscosity, improving phase separation, and influencing the extraction mechanism. Solvents affect metal complex formation [17–19], third-phase formation in extraction systems [20,21],



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and the solubility of D2EHPA in aqueous phases [14]. The influence of solvents is quantified through activity coefficients, which are critical for selecting optimal solvents [22,23], determining selectivity and distribution coefficients [24–26], and modeling phase equilibrium compositions [27–29].

The UNIFAC (UNIQUAC Functional-group Activity Coefficients) model was selected due to its group-contribution approach, which enables the prediction of activity coefficients in non-ideal liquid mixtures based on molecular structure. This method is widely used for systems composed of well-defined functional groups, such as CH₂, CH₃, ACH, ACCH₃, HPO₄. By accounting for both combinatorial (molecular size and shape) and residual (intergroup energy interactions) contributions to non-ideality, UNIFAC provides a reliable framework for extrapolating thermodynamic behavior to systems with limited experimental data [22,30]. A comprehensive description of the model can be found in standard references on thermodynamic modeling [31,32]. This study aims to measure the activity coefficients of benzene and toluene in binary benzene–D2EHPA and toluene–D2EHPA systems respectively, determine UNIFAC interaction parameters for ACH–HPO₄ and ACCH₃–HPO₄ group pairs, and validate their accuracy in the ternary n-hexane–toluene–D2EHPA system. These parameters enable reliable prediction of activity coefficients for all components in mixtures of alkanes, cycloalkanes, and monoaromatic hydrocarbons with D2EHPA, crucial for optimizing metal extraction processes.

This work presents experimental activity coefficient data for binary D2EHPA–benzene and D2EHPA–toluene systems, obtained via gas chromatography at 293.0 K, addressing challenges in measuring volatile components across a wide range of vapor pressures. A novel methodology incorporating intermediate standards enhances measurement precision. By refining UNIFAC parameters and validating them in ternary systems, this study advances the understanding of non-ideal solution behavior and supports the design of efficient liquid–liquid extraction processes involving D2EHPA.

2. Materials and Methods

2.1. Reagents

In this work, high-grade benzene (CAS 71-43-2), high-grade toluene (CAS 108-88-3) from EKOS-1, and high-grade n-hexane (CAS 110-54-3), D2EHPA (CAS 298-07-7) at 99% purity from LeapChemCo. (Hangzhou, China) were used.

Di-2-ethylhexylphosphoric acid, benzene, and toluene were stored under controlled conditions in their original sealed containers in a dry, temperature-controlled warehouse. Storage facilities were maintained away from heat sources and direct sunlight, with all chemicals remaining within their validated shelf life (through December 2027).

All vapor–liquid equilibrium measurements were performed at a constant temperature of 293.0 K. This temperature was chosen to maintain consistency with prior experimental studies on related systems, such as the n-hexane–D2EHPA binary system investigated in our earlier work [1], thereby ensuring methodological continuity and facilitating the comparison and refinement of UNIFAC parameters across different solvent–extractant combinations. Furthermore, operating near room temperature offers practical advantages: it simplifies thermal control, minimizes errors associated with the temperature sensitivity of vapor-pressure measurements for volatile aromatic solvents, and corresponds to standard reference conditions commonly used in thermodynamic studies of organic mixtures [33].

2.2. Gas Chromatography (GC) Method

Vapor-phase concentrations of benzene, toluene, and n-hexane, in binary (benzene–D2EHPA, toluene–D2EHPA) and ternary (n-hexane–toluene–D2EHPA) solutions were measured using an Agilent GC-6890 gas chromatograph (Agilent Technologies, Santa Clara,

CA, USA) equipped with a flame ionization detector (FID) and a 0.1 cm³ stainless steel dosing loop. Component separation was achieved on a Restek-QS-Bond capillary column (30 m length, 0.53 mm inner diameter, 20 µm phase thickness).

Activity coefficients of benzene, toluene and n-hexane were determined in a 0.27 L glass container thermostat at 293.0 K, equipped with a magnetic stirrer. The test solution filled approximately 20% of the container's volume. Vapor samples were drawn through a 0.1 mL dosing loop, with a steel syringe needle venting to the atmosphere, using a 3 mL gas-tight syringe. Samples were collected at 90-s intervals, with at least five replicates per sample, and the average chromatographic peak area was calculated. To address variations in FID sensitivity, particularly for volatile solvents like toluene, intern standards (mixtures of known concentrations) were employed, as detailed in [1] and further discussed in Section 4.2, ensuring high precision across a wide range of vapor pressures.

The activity (a_i) of component i (benzene, toluene and n-hexane) was calculated as the ratio of its vapor pressure above the solution to that above the pure component, per Equation (1):

$$a_i = \frac{P_i}{P_i^0} = \frac{C_i}{C_i^0}, \quad (1)$$

where a_i is the activity of component i ; P_i and P_i^0 are vapour pressures (Pa) above the solution and pure component; C_i is the vapor-phase concentration (mg/L) of component i in solution, and C_i^0 is the solvent concentration (mg/L) above the pure component at 293.0 K.

The activity coefficient (γ_i) was calculated using Equation (2):

$$\gamma_i = \frac{a_i}{x_i}, \quad (2)$$

where γ_i is solvent activity coefficient of component i and x_i is its mole fraction in the solution.

This method enabled accurate determination of activity coefficients for all volatile components in the ternary system.

2.3. UNIFAC Modelling

The UNIFAC model predicts solution properties by representing molecules as collections of functional groups, each characterized by volume (R_k), surface area (Q_k), and interaction parameters (a_{km}). In this study, di-(2-ethylhexyl)phosphoric acid comprises CH₂, CH₃, CH, and HPO₄ groups; n-hexane includes CH₂ and CH₃ groups; benzene contains ACH groups; and toluene consists of ACH and ACCH₃ groups. The structural parameters (r , q) for each functional group are standard UNIFAC values obtained from the literature [34,35], where they are derived from the Bondi group contribution method based on molecular geometry and physical properties [36]. Structural parameters (r , q) of groups are listed in Table 1. For the HPO₄ group of D2EHPA, the parameters were calculated from the geometry of the D2EHPA dimer using Bondi's atomic volumes and surfaces, consistent with the known association behavior of D2EHPA in nonpolar solvents [14,25]. Interaction parameters for CH₂-HPO₄, ACH-HPO₄, and ACCH₃-HPO₄ pairs were determined by modelling, based on experimental data. This allows activity coefficients predictions of all components, including D2EHPA.

The activity coefficient (γ_i) of component i is the product of combinatorial (γ_i^{comb}) and residual (γ_i^{res}) contributions, as shown in Equation (3):

$$\ln \gamma_i = \ln \gamma_i^{\text{comb}} + \ln \gamma_i^{\text{res}}, \quad (3)$$

Table 1. Structural parameters (r, q) of the Unifac model.

Group	r	q	Reference
HPO ₄ ¹	1.6978	1.752	[36]
CH ₃	0.9011	0.848	[34]
CH ₂	0.6744	0.540	[34]
CH	0.4469	0.228	[34]
ACH	0.5313	0.400	[35]
ACCH ₃	1.2663	0.968	[35]

¹ Calculated on the base D2EHPA dimer form data.

The combinatorial contribution (γ_i^{comb}), accounting for molecular size and shape, and the residual contribution (γ_i^{res}), accounting for energy interactions, are calculated using Equations (4) and (5):

$$\ln \gamma_i^{\text{comb}} = \ln \left(\frac{\varphi_i}{x_i} \right) + 10q_i \ln \frac{\theta_i}{\varphi_i} + l_i - \frac{\varphi_i}{x_i} \sum x_i l_i, \quad (4)$$

where $\varphi_i = \frac{r_i x_i}{\sum r_j x_j}$ and $\theta_i = q = \frac{q_i x_i}{\sum q_j x_j}$ are volume and surface fractions, $l_i = 5(r_i - q_i) - (r_i - 1)$ is the volume factor, $r_i = \sum n_{ik} \cdot R_k$ and $q_i = \sum n_{ik} \cdot Q_k$ are the Van der Waals volume and surface area of component i (relative units), n_{ik} is the number of group k in component i, and R_k and Q_k volumes and surface areas of individual groups.

$$\ln \gamma_i^{\text{res}} = \sum n_{is} (\ln G_{ks} - \ln G_{ki}), \quad (5)$$

where G_{ks} and G_{ki} are residual activity coefficients of group k in our solution and in solution of component i respectively, calculated via Equation (6):

$$\ln G_k = Q_k \left[1 - \ln \left(\sum_m \theta_m \Psi_{km} \right) - \sum_m \frac{\theta_m \Psi_{km}}{\sum_n \theta_n \Psi_{nm}} \right], \quad (6)$$

where θ_m is the surface fraction of group m, $\Psi_{km} = e^{-\frac{a_{km}}{T}}$ and a_{km} is the energy interaction parameter (non-zero for CH₂–HPO₄, ACH–HPO₄, and ACH₃–HPO₄ pairs).

The energy interaction parameters were calculated by minimizing the total deviation between the theoretical and experimental activity coefficients of the volatile components. The objective function, defined as the sum of the natural logarithms of the ratios of experimental (γ_i^{exp}) to theoretical (γ_i^{theor}) activity coefficients, was minimized according to Equation (7):

$$F = \sum \left| \ln \left(\frac{\gamma_{\text{exper}}}{\gamma_{\text{teor}}} \right) \right| \quad (7)$$

where γ_{exper} and γ_{teor} are experimental and theoretical values of solvent activity coefficients.

This function emphasizes relative deviations, aligning with excess chemical potential differences, unlike the sum-of-squares function, $S = \sum (\gamma_i^{\text{exp}} - \gamma_i^{\text{theor}})^2$, which prioritizes absolute differences. For example, an F value of 0.2 for 10 data points indicates an average deviation of 0.02 per point, or approximately 2% error in activity coefficients, as $\ln(1 \pm x) \approx \pm x$ for $x \leq 0.1$.

Primary minimization was conducted by evaluating the function F at the nodes of a two-dimensional grid defined by the two energy interaction parameters under investigation (Figure 1a). These parameters ranged from −1000 to 5000 in increments of 10, expressed in units of the gas constant ($R = 8.31 \text{ J}/(\text{mol} \cdot \text{K})$). The range and step size were adjusted when necessary to refine the calculations. Contour lines representing equal F values

were plotted based on the results, providing a visual representation of the parameter space. While this grid-based approach is visually compelling, it may introduce errors in accurately determining the optimal parameters. The dependencies observed were consistent across all three systems studied (hexane–D2EHPA, benzene–D2EHPA, and toluene–D2EHPA), as illustrated for the hexane–D2EHPA system in Figure 1a.

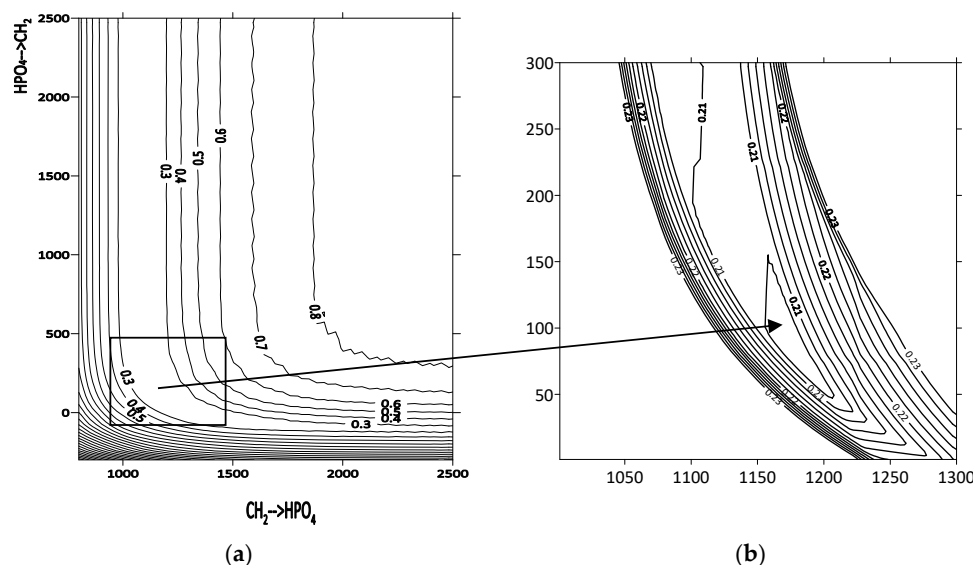


Figure 1. Contour lines of the function F for the hexane–D2EHPA system: (a) contour lines of relative deviations between theoretical and experimental values of activity coefficients of volatile component; (b) sequential descent method for minimum deviation determination.

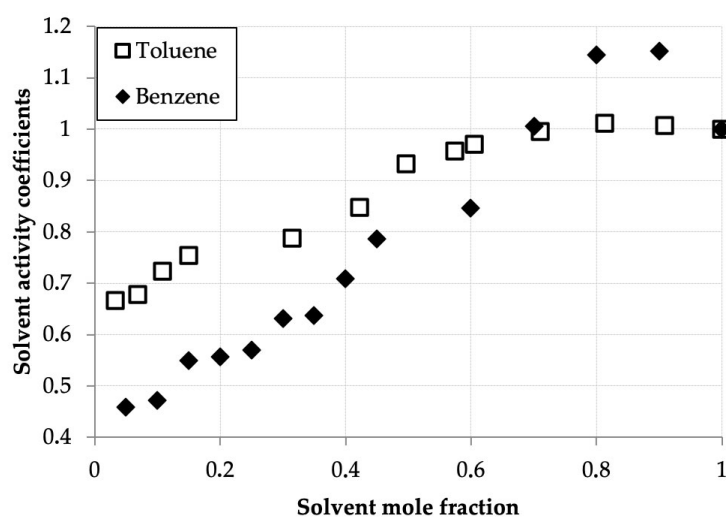
The region of minimum F values exhibits an elongated shape along the coordinate axes, resembling a hyperbolic dependence. Consequently, the error in determining one of the two energy interaction parameters is greater than that for the other. Notably, both parameter sets describe the experimental activity coefficients of hexane in the D2EHPA–hexane system with a deviation of no more than 2%, corresponding to an objective function value of $F = 0.2$ for 14 data points. In order to overcome such errors, the secondary sequential descent method was applied (Figure 1b). For the hexane–D2EHPA system, this algorithm refined the UNIFAC energy interaction parameters for the CH_2 – HPO_4 pair, specifically for $\text{CH}_2 \rightarrow \text{HPO}_4$ from 1144 to 1199 and for $\text{HPO}_4 \rightarrow \text{CH}_2$ from 228 to 54. The modeling of group energy parameters and the issue of error accumulation without applying the sequential descent method are further discussed in Section 4.1.

3. Results

Table 2 and Figure 2 present the measured solvent vapor concentrations and calculated experimental activity coefficient values of benzene and toluene in their binary solutions with D2EHPA as a function of the mole fraction of the volatile component. Both systems exhibit similar behavior, distinct from the hexane–D2EHPA system [1]. In contrast to hexane, for benzene and toluene, the activity coefficient maxima occur at mole fractions, equal 0.9 for benzene and 0.8 for toluene, shifted toward the pure solvents. A key distinction from the hexane system is the lower activity coefficient values (ranging from 0.5 to 0.9) at solvent mole fractions below 0.5. Notably, at equivalent mole fractions in this region, benzene’s activity coefficients are generally lower than those of toluene, with benzene exhibiting a more pronounced maximum. These findings align closely with published data for the toluene–D2EHPA system in [33].

Table 2. Activity coefficients of benzene and toluene in the solvent–D2EHPA system at 293.0 K.

Benzene				Toluene			
x_{benzene}	C (mg/L)	a_{benzene}	γ_{benzene}	x_{toluene}	C (mg/L)	a_{toluene}	γ_{toluene}
1.000	322.7	1.000	1.000	1.000	128.4	1.000	1.000
0.90	335.0	1.038	1.152	0.90	116.7	0.909	1.007
0.80	295.6	0.916	1.145	0.80	104.5	0.814	1.012
0.70	226.9	0.703	1.005	0.71	91.3	0.711	0.996
0.60	163.6	0.507	0.845	0.62	77.7	0.605	0.970
0.45	114.2	0.354	0.786	0.60	73.7	0.574	0.957
0.40	91.3	0.283	0.708	0.53	63.8	0.497	0.932
0.35	72.0	0.223	0.637	0.50	54.3	0.423	0.847
0.30	61.0	0.189	0.632	0.40	40.4	0.315	0.787
0.25	46.8	0.145	0.570	0.20	19.3	0.150	0.754
0.20	36.1	0.112	0.556	0.15	13.9	0.108	0.724
0.15	26.8	0.083	0.549	0.10	8.7	0.068	0.679
0.10	15.5	0.048	0.472	0.05	4.2	0.033	0.667
0.05	7.7	0.024	0.458				

**Figure 2.** Benzene and toluene activity coefficients (γ_i) versus mole fraction (x_i) in D2EHPA solutions at 293.0 K.

The low activity coefficients of benzene and toluene in dilute solutions with D2EHPA can be attributed to their affinity for polar solvents, as the polar D2EHPA molecules effectively retain these compounds in solution. This effect is less pronounced for toluene compared to benzene, which is expected because the addition of a methyl group to toluene's aromatic ring shifts its properties toward those of alkanes, which exhibit lower solubility in polar solvents. Explaining the presence of activity coefficient maxima in the benzene–D2EHPA and toluene–D2EHPA systems is more challenging, yet these maxima are consistently reproduced in experimental data.

The activity coefficient maxima observed for benzene and toluene arise from the competition between solvent–solvent and solvent–D2EHPA interactions. The shift in the maximum from $x \approx 0.9$ (benzene) to $x \approx 0.8$ (toluene) is attributed to the presence of a methyl group in toluene, which imparts partial aliphatic character. This results in toluene behaving as an intermediate between benzene and n-hexane, thereby modifying the balance of interactions with D2EHPA and shifting the maximum toward a lower solvent mole fraction. It should be noted that this interpretation, while consistent with the observed

trends and molecular reasoning, remains a plausible explanation, as direct measurement of the specific intermolecular interactions was beyond the scope of this thermodynamic study.

4. Discussion

4.1. Determination of UNIFAC Energy Interaction Parameters Using Experimental Data

D2EHPA–benzene and D2EHPA–toluene solutions were modelled as mixtures of CH_2 , CH_3 , CH , ACH , ACCH_3 and HPO_4 groups, with structural parameters listed in Table 1.

In a previous study [1], the energy interaction parameters for the CH_2 – HPO_4 pair were established for the hexane–D2EHPA system. Substituting hexane with benzene introduces the ACH group, for which ACH – HPO_4 interaction parameters remain unknown. Using the known CH_2 – HPO_4 parameters, the ACH – HPO_4 interaction parameters can be calculated. Similarly, in D2EHPA–toluene solutions, the ACCH_3 group is introduced, necessitating the determination of ACCH_3 – HPO_4 interaction parameters based on data from prior hexane and benzene systems.

Energy parameters (a_{km}) for ACH – HPO_4 and HPO_4 – ACH , ACCH_3 – HPO_4 and HPO_4 – ACCH_3 interactions were optimized to minimize deviations between experimental and theoretical γ_i values using Equation (7) and subsequent descent method [37,38]. The UNIFAC energy interaction parameters for benzene and toluene are $\text{ACH} \rightarrow \text{HPO}_4 = 4605$, $\text{HPO}_4 \rightarrow \text{ACH} = -334$, $\text{ACCH}_3 \rightarrow \text{HPO}_4 = 467$, and $\text{HPO}_4 \rightarrow \text{ACCH}_3 = 680$.

The relative positioning of the energy interaction parameters in the parameter space defined by $E(\text{X} \rightarrow \text{HPO}_4)$ and $E(\text{HPO}_4 \rightarrow \text{X})$ is illustrated in Figure 3. The ACH group, representing benzene, is positioned at a significant distance from the ACCH_3 and CH_2 groups, underscoring their distinct interaction characteristics in the UNIFAC model.

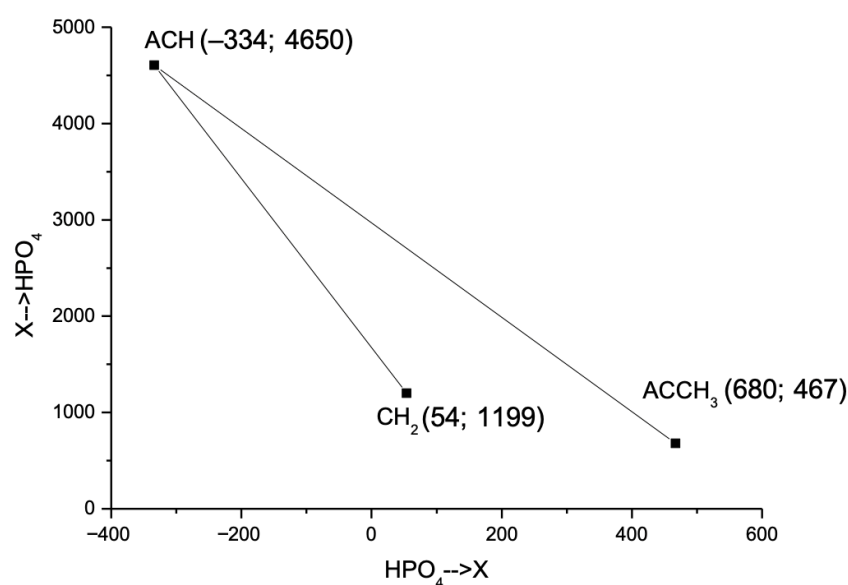


Figure 3. Intergroup energy interaction parameters for X – HPO_4 pairs ($\text{X} = \text{CH}_2$, ACH , ACCH_3).

The need to refine the UNIFAC energy interaction parameters emerged during data analysis for the D2EHPA–benzene system, where the interaction parameters for the HPO_4 – CH_2 pair were assumed to be known from prior studies. In the D2EHPA–toluene system, the discrepancy between calculated and experimental activity coefficients increased significantly, resulting in deviations exceeding 20% per experimental data point for the observed dependency. For ternary systems, such as D2EHPA–hexane–benzene, this discrepancy escalated to 30% or greater, highlighting challenges in accurately modeling these complex mixtures.

The observed discrepancies were not attributed to fundamental limitations in the UNIFAC model but rather to inaccuracies in the determination of the energy interaction parameters and the cumulative effect of errors. To accurately model all three systems studied (D2EHPA–hexane, D2EHPA–benzene, and D2EHPA–toluene), the energy interaction parameters must be determined with an accuracy of at least 1%.

The activity coefficients for the D2EHPA, benzene, and toluene were calculated using the UNIFAC model. Figures 4 and 5 compare experimental γ_i values with UNIFAC predictions at these parameters, showing strong agreement across compositions. Results of calculations are presented in Table 3

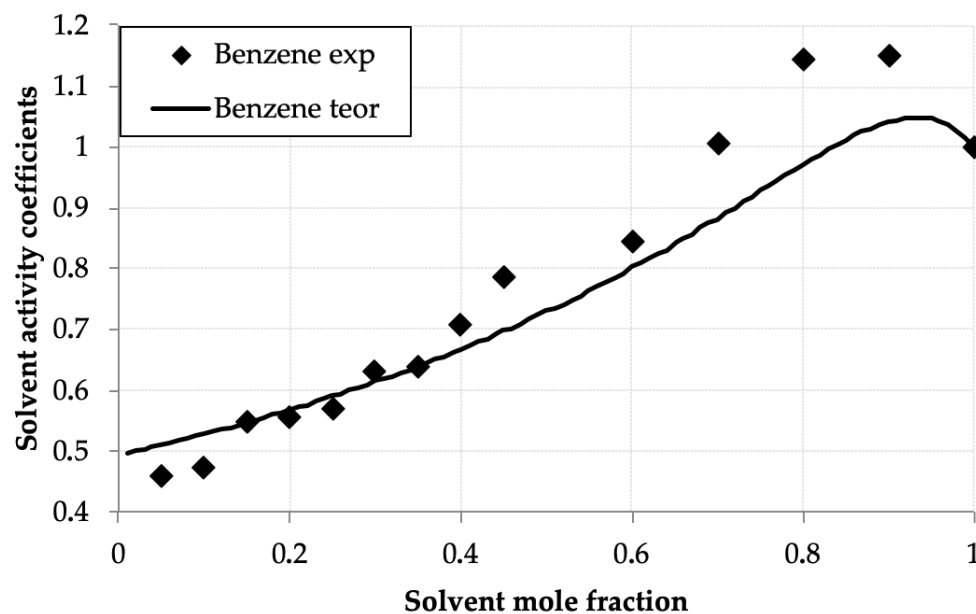


Figure 4. Benzene activity coefficients (γ_{benz}) versus mole fraction (x_{benz}) in the benzene–D2EHPA system at 293.0 K: experimental (points) and UNIFAC calculations (line).

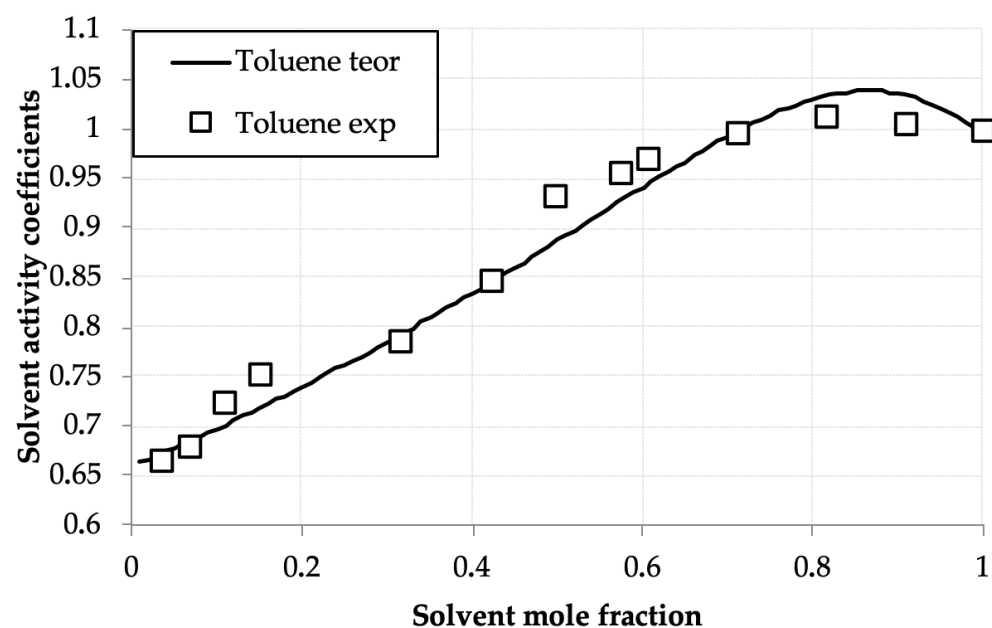


Figure 5. Toluene activity coefficients (γ_{tol}) versus mole fraction (x_{tol}) in the toluene–D2EHPA system at 293.0 K: experimental (points) and UNIFAC calculations (line).

Table 3. UNIFAC-calculated activity coefficients of benzene (γ_{benz}) and toluene (γ_{tol}) and D2EHPA (γ_{D2EHPA}) at 293.0 K.

Benzene			Toluene		
x_{benz}	γ_{benz}	γ_{D2EHPA}	x_{tol}	γ_{tol}	γ_{D2EHPA}
0.01	0.4966	1.0000	0.01	0.6631	1.0000
0.02	0.4999	0.9999	0.02	0.6668	0.9999
0.03	0.5033	0.9997	0.03	0.6705	0.9998
0.04	0.5067	0.9995	0.04	0.6743	0.9995
0.05	0.5101	0.9991	0.05	0.6780	0.9993
0.1	0.5281	0.9963	0.1	0.6975	0.9970
0.2	0.5680	0.9834	0.2	0.7392	0.9867
0.3	0.6140	0.9580	0.3	0.7848	0.9671
0.4	0.6673	0.9157	0.4	0.8342	0.9356
0.5	0.7293	0.8510	0.5	0.8868	0.8897
0.6	0.8013	0.7577	0.6	0.9407	0.8275
0.7	0.8835	0.6307	0.7	0.9914	0.7503
0.8	0.9711	0.4731	0.8	1.0295	0.6707
0.9	1.0412	0.3190	0.9	1.0361	0.6572
0.95	1.0467	0.3063	0.95	1.0199	0.8136
0.96	1.0428	0.3321	0.96	1.0152	0.8980
0.97	1.0365	0.3930	0.97	1.0103	1.0269
0.98	1.0276	0.5553	0.98	1.0056	1.2340
0.99	1.0156	1.2570	0.99	1.0017	1.5946
1	1.0000	2.2754	1	1.0000	2.3034

4.2. Validation of the UNIFAC Model for the Ternary Hexane–Toluene–D2EHPA System

To validate the performance of the UNIFAC model by comparing calculated activity coefficients with experimental values, the ternary hexane–toluene–D2EHPA system was investigated, as it comprises only the studied groups (CH_2 , ACH , ACCH_3 , HPO_4), enabling the model to reliably predict the activity coefficients of both volatile components (n-hexane and toluene).

Despite the high sensitivity of the flame ionization detector (FID) and optimized chromatographic separation conditions, simultaneous measurement of the activity coefficients of both volatile components is often challenging. At varying concentrations of the volatile components in solution, the areas of their chromatographic peaks can differ by a factor of 20 to 100. This significant variation necessitates switching the detector's sensitivity ranges to accurately determine the concentrations and activity coefficients of each component.

The use of intermediate compositions (interim standard) in place of pure solvents (standard solution) addresses the challenge of varying detector sensitivity for each component in the mixture, such as in the hexane–toluene–D2EHPA ternary system. These interim standard composition is selected to minimize measurement errors in component activity coefficients and must meet two conditions: (1) the detector (FID) maintains identical sensitivity settings during gas chromatography of both standard and interim standard solutions; (2) the chromatographic peak areas of the standard and interim standard solutions differ by less than a factor of 10. Under these conditions, the calculation of activity coefficients, as described by Equation (8), is expressed as follows:

$$a_i = \frac{C_1}{C_1^{\text{int}}} \cdot \frac{C_2^{\text{int}}}{C_2^{\text{st}}} = \frac{C_1}{C_1^{\text{int}}} \cdot a_i^{\text{int}}, \quad (8)$$

where C —solvent concentration in vapour phase (mg/L); the indices 1 and 2 designate sensitivity FID ranges; the index st means standard solution (pure solvent); the index int

means interim standard; the ratio $C_2^{\text{int}}/C_2^{\text{st}}$ is the activity of the volatile component in the intermediate standard (a_1^{int}).

To measure the activity coefficients in the ternary n-hexane–toluene–D2EHPA system, a binary solution of toluene in n-hexane was prepared, consisting of 80% n-hexane and 20% toluene by mole fraction. The activity coefficients of n-hexane and toluene were determined using the gas chromatography method outlined previously. Subsequently, D2EHPA was added to the binary mixture, and the activity coefficient measurements were repeated for the resulting ternary composition. A total of four distinct compositions were investigated. The results are presented in Figure 6, demonstrating excellent agreement between the UNIFAC model predictions and experimental data for the ternary system.

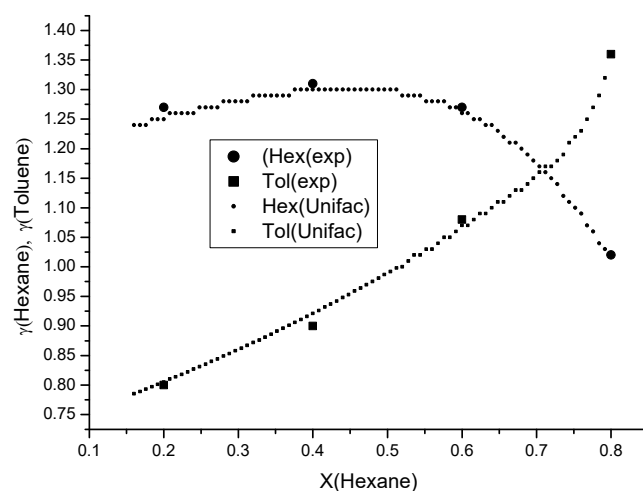


Figure 6. Experimental and UNIFAC–predicted activity coefficients of n-hexane and toluene in the ternary D2EHPA–Toluene–n-Hexane system. Large markers denote experimental values obtained via gas chromatography.

4.3. Modeling of Component Activity Coefficients in Ternary Liquid Systems

The activity coefficients of the components in the ternary n-hexane–toluene–D2EHPA system were analyzed. The UNIFAC model, utilizing known geometric and energy interaction parameters for groups CH_2 , ACH , ACCH_3 , HPO_4 , enables the calculation of contour lines within the corresponding composition triangle. These ternary diagrams are presented in Figures 7–9. Each side of the diagram corresponds to the composition of the binary mixture (n-hexane–toluene, n-hexane–D2EHPA, and toluene–D2EHPA) and each vertex corresponds to a pure component (n-hexane, toluene, or D2EHPA).

Firstly, the activity coefficients of n-hexane were examined across the composition space, as illustrated in the ternary diagram in Figure 7. The activity coefficient of n-hexane at a mole fraction of $x_{\text{C}_6\text{H}_{14}} = 1$ is $\gamma_{\text{C}_6\text{H}_{14}} = 1$. In the binary n-hexane–D2EHPA mixture, at $x_{\text{D2EHPA}} = 1$, the activity coefficient is $\gamma_{\text{C}_6\text{H}_{14}} = 1.2$, while in the binary n-hexane–toluene mixture, at $x_{\text{C}_7\text{H}_8} = 1$, it is $\gamma_{\text{C}_6\text{H}_{14}} = 1.6$. Thus, starting from n-hexane vertex, at least one composition exists for which activity coefficient of n-hexane is a specified value between 1.2 and 1.6.

In the ternary n-hexane–toluene–D2EHPA system, various compositions with identical n-hexane activity coefficients but differing mole fraction ratios of toluene to D2EHPA define a contour line of constant n-hexane activity coefficients within the triangle. By varying the activity coefficient of n-hexane within its permissible range (e.g., 1.2 to 1.6) at discrete intervals, a family of contour lines representing constant n-hexane activity coefficients can be constructed. These contour lines are illustrated in Figure 7.

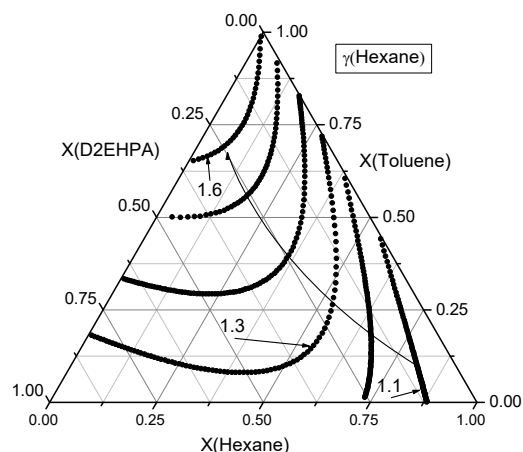


Figure 7. Contour lines of n-hexane activity coefficients in the ternary n-Hexane–Toluene–D2EHPA system. A curved line with an arrow denotes the direction of increasing activity coefficients for n-hexane. The isoclines are plotted with an increment of $\Delta\gamma = 0.1$.

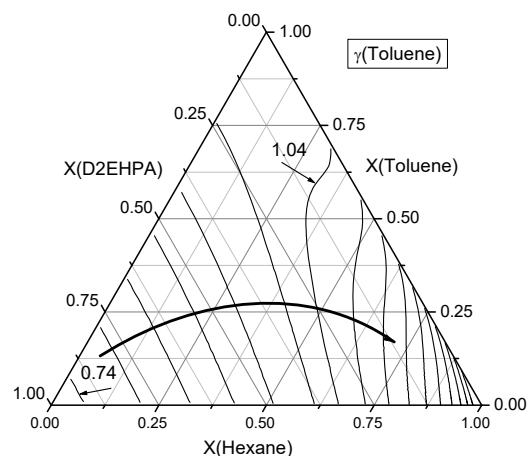


Figure 8. Contour lines of toluene activity coefficients in the ternary n-Hexane–Toluene–D2EHPA system. A curved line with an arrow denotes the direction of increasing toluene activity coefficients (γ_{tol}). The contour lines are plotted with an increment of $\Delta\gamma = 0.05$.

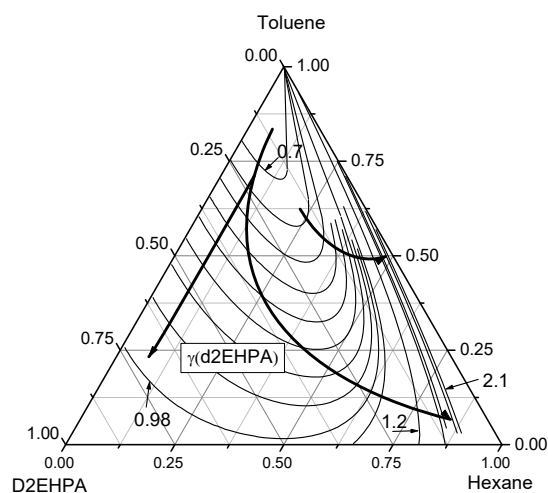


Figure 9. Contour lines of D2EHPA activity coefficients in the ternary n-Hexane–Toluene–D2EHPA system. The curved lines with arrows denote the directions of increasing D2EHPA activity coefficients (γ_{D2EHPA}). The contour lines are plotted with an increment of $\Delta\gamma = 0.1$ near the n-hexane vertex and $\Delta\gamma = 0.03$ when the mole fraction of n-hexane is less than 0.7.

The activity coefficient of n-hexane increases smoothly and, in most regions, monotonically as pure n-hexane ($\gamma_{\text{C}_6\text{H}_{14}} = 1$) is diluted with a binary mixture of toluene and D2EHPA. Notably, the influence of toluene on the activity coefficient of n-hexane is more pronounced than that of D2EHPA.

Secondly, the behavior of toluene in the ternary n-hexane–toluene–D2EHPA system was examined and results are presented in Figure 8. Experimental measurements indicate that the minimum values of toluene activity coefficients occur near the D2EHPA vertex in the ternary composition space. As the composition moves away from the D2EHPA vertex, the activity coefficient of toluene (γ_{tol}) increases, reaching unity ($\gamma_{\text{tol}} = 1$) at a D2EHPA:n-hexane mole ratio of approximately 2:3. Notably, the mole fraction of toluene itself has a limited influence on its activity coefficient. Furthermore, a region surrounding this ray exists where the activity coefficient of toluene remains close to 1, largely independent of the toluene mole fraction.

Thirdly, the behavior of D2EHPA activity coefficients in the ternary n-hexane–toluene–D2EHPA system is depicted through contour lines in the ternary diagram shown in Figure 9. The activity coefficients of D2EHPA (γ_{D2EHPA}) increase from the toluene vertex ($x_{\text{tol}} = 1$) toward the D2EHPA vertex ($x_{\text{D2EHPA}} = 1$) and the n-hexane vertex ($x_{\text{hex}} = 1$). Along the toluene–D2EHPA binary edge, γ_{D2EHPA} rises from 0.7 to 1.0, a notably smaller increase compared to the toluene–n-hexane binary edge, where γ_{D2EHPA} ranges from 0.7 to 2.1. As the mole fraction of n-hexane increases along the toluene–n-hexane edge, the rate of increase in γ_{D2EHPA} diminishes, though the activity coefficient itself continues to rise. The contour lines of γ_{D2EHPA} converge as they approach the toluene vertex, indicating that the reduction in γ_{D2EHPA} caused by increasing the toluene mole fraction can be offset by decreasing the mole fraction of D2EHPA. These findings, derived from UNIFAC model predictions and validated by gas chromatography measurements, underscore the non-ideal interactions within the ternary n-Hexane–Toluene–D2EHPA system.

5. Conclusions

The main objective of this study was to implement the proposed methodology for activity coefficients calculations of components of D2EHPA and multicomponent solvent. This approach includes experimental determination of volatile components activity coefficients, calculation of group energy interaction parameters and UNIFAC modeling.

The following steps were implemented to achieve this objective:

- Firstly, initial experimental determination of the activity coefficient for benzene and toluene in binary systems with D2EHPA was performed by gas chromatography at 293.0 K.
- Secondly, the energy interaction parameters were calculated by minimizing the total deviation between the experimental and modeled via UNIFAC activity coefficients using sequential descent method. The resulting values for the energy interaction parameters are: $\text{ACH-HPO4} = 4650$, $\text{HPO4-ACH} = -334$, $\text{ACCH3-HPO4} = 467$, and $\text{HPO4-ACCH3} = 680$. The refined energy interaction parameters for the aliphatic group are $\text{CH2-HPO4} = 1199$ and $\text{HPO4-CH2} = 54$.
- Thirdly, the parameterized UNIFAC model was applied to calculate activity coefficient of the components of the ternary n-Hexane–Toluene–D2EHPA system, which contains all previously investigated groups. The calculated values were compared with the experimental data for the same system. The significant difference in saturated vapor pressures of n-hexane and toluene necessitated the application of an interim standard. The implementation of the interim standard improved measurement accuracy in systems where the vapor concentration of analytes varied by more than

20 times. The activity coefficient of the volatile components, as calculated by the model, demonstrated good agreement with experimental data.

- The final step involved calculating the activity coefficient contour lines for each component in the ternary n-Hexane–Toluene–D2EHPA system. The aliphatic n-hexane acts as a strong driver of non-ideality, significantly increasing the activity coefficients of both toluene and D2EHPA, especially the latter. In contrast, toluene is the primary agent affecting n-hexane's activity, but also stabilizes the activity coefficient of toluene itself and mitigates the strong non-ideal interactions between n-hexane and D2EHPA. This asymmetric interplay underscores the complexity of multicomponent systems and is critical for optimizing processes like liquid–liquid extraction where such mixtures are encountered.

The methodology developed in this study demonstrates broad applicability for investigating the thermodynamic behavior of organic phosphoric acid esters, such as D2EHPA, and aliphatic, aromatic and cyclic hydrocarbons.

The next phase of research will extend this approach to examine a D2EHPA complex coordinated with a rare earth metal cation. Due to the low solubility of such complexes in n-hexane, direct measurement of n-hexane activity coefficients using the previously employed gas chromatography methods may not be feasible. Similarly, this limited solubility precluded the determination of UNIFAC group interaction parameters for the H₂O–HPO₄ pair specific to D2EHPA in this study. Consequently, a shift from liquid–vapor equilibrium to liquid–liquid equilibrium is proposed, focusing on the measurement of distribution coefficients rather than activity coefficients. The distribution coefficient, defined as the ratio of a component's activity coefficients in coexisting liquid phases, can be reliably predicted using the UNIFAC model, offering a robust alternative for characterizing the thermodynamic properties of these complexes.

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Abbreviations

The following abbreviations are used in this manuscript:

D2EHPA	Di-(2-ethylhexyl)phosphoric acid
GC	Gas Chromatography
FID	Flame Ionization Detector

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