

Thermodynamic Modeling of Adsorption Isotherms Using VST-UNIQUAC: A Novel Approach for Solid-Liquid Equilibrium

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ABSTRACT:

Based on the vacancy solution theory (VST) and using the UNIQUAC activity coefficient model, a new adsorption isotherm model (VST-UNIQUAC) is developed for solid-liquid equilibrium systems. Following VST, the solid-liquid equilibrium system is considered as a solution consisting of the adsorbate and adsorbent where the adsorbate is the solute and vacancies play the role of the solvent. The UNIQUAC equation is used to account for the non-ideality or the solute-solvent interaction in the vacancy solution. The parameters of the proposed model are calculated by using the optimization of experimental data for different single-component adsorption systems at various temperatures. The new isotherm is used to correlate the isotherms of 12 different organic compounds on activated carbon, each one at different temperatures. The accuracy of the present isotherm is presented by the coefficient of determination (R^2), average absolute deviation percent (AAD%), and root mean square error (RMSE) and compared with those results obtained using Wilson, Van Laar, and NRTL equations. It is shown that the proposed VST-UNIQUAC model correlates the adsorption equilibrium with significantly higher accuracy, achieving R^2 values consistently above 0.98 and AAD% values ranging from 2% to 17%, which is substantially better than the deviations obtained from other models. The VST-UNIQUAC isotherm demonstrates superior capability in describing adsorption behavior across different temperatures, making it a reliable tool for design and optimization of adsorption processes in industrial and environmental applications.

Keywords: Adsorption isotherm, Vacancy solution theory, Thermodynamics of adsorption, UNIQUAC, Activated carbon, Solid-liquid equilibrium

INTRODUCTION:

Adsorption underlies a number of important processes and has wide applications in chemical, environmental, and biotechnology industries [1][2]. Surface adsorption has emerged as an effective and economical method for removing pollutants from industrial wastewater and various chemical processes due to its simplicity, high efficiency, lower cost, ease of design and operation, minimal production of hazardous secondary materials, and the ability to modify adsorbents containing adsorbates [3][4]. Gas separation and purification using molecular sieves, selective membranes, and pressure swing adsorption have been widely used as adsorption processes and proven to be economical and viable unit operations for separation of mixtures [5]. Undoubtedly, to have a thorough representation of adsorption kinetics, it is necessary to use a suitable isotherm equation for description of single-component adsorption equilibrium [6].

There are several models for adsorption isotherms which have been developed over the years. The Langmuir theory [7], the most basic theory in adsorption, proposed a model for adsorption of gases onto a flat surface based on a kinetic viewpoint. According to this theory, there is a continual bombardment of molecules onto the surface and a

corresponding desorption of molecules from the surface to maintain zero rate of accumulation at the surface at equilibrium. It is clear that the Langmuir's approach is kinetic by nature, but adsorption equilibria can be described by using the thermodynamic approach as well. By assuming the adsorbed phase as a single entity, in the approach of Gibbs the classical thermodynamics was adopted for both the bulk and adsorbed phases [8]. The vacancy solution theory was originally proposed by Suwanayuen and Danner [9] that proposed a unified presentation of single as well as multicomponent isotherms within the same framework. The vacancy is an imaginary entity defined as a vacuum space which acts as the solvent of the system, and it has the same size as the adsorbate. Suwanayuen and Danner used the Wilson activity equation while Cochran et al. [10] used the Flory-Huggins equation that leads to one less parameter in comparison with the original vacancy solution model. Suwanayuen and Danner showed that the vacancy solution theory using the Wilson equation gives the most accurate prediction of adsorption, but Cochran et al. recommended that in order to predict the multicomponent adsorption it would be better to use the Flory-Huggins form of the VST [10]. The VST has been used to study the enthalpic effects accompanying mixed-gas adsorption equilibria [11], and the theory has

been applied to study the adsorption on heterogeneous solid surfaces [12].

However, there remains a need for more accurate thermodynamic models that can better account for the complexities of molecular interactions, temperature effects, and adsorbent characteristics. In particular, local composition models such as UNIQUAC have demonstrated superior performance in describing non-ideal liquid mixtures but have not been extensively applied to adsorption systems within the vacancy solution theory framework [13][14].

In this work, we follow the approach of vacancy solution theory to develop a new isotherm using the UNIQUAC activity coefficient equation. The UNIQUAC model combines combinatorial and residual contributions to the excess Gibbs energy, providing a more rigorous thermodynamic description of molecular interactions. The new isotherm is applied to correlation of the adsorption of different organic compounds including nitriles, alcohols, ketones, phenols, and aromatic compounds on activated carbon at various temperatures, and results are compared with those obtained from vacancy solution theory using Wilson, Van Laar, and NRTL activity coefficient models.

2. Thermodynamic Framework:

2.1. Vacancy Solution Representation of Solid-Liquid Adsorption:

In the present work, the solid-liquid adsorption equilibrium is described within the vacancy solution theory (VST), in which the adsorbed phase is treated as a binary "solution" composed of the adsorbate (component 1) and vacancies (v) occupying the adsorption sites on the solid surface. The liquid phase is considered as an ideal solution with activity coefficient $\gamma_1^l = 1$, while the non-ideality of the adsorbed phase is modeled explicitly through activity coefficients γ_1^s and γ_v^s . Vacancies are hypothetical entities with no real molecular size; therefore, in the parameterization they are assigned $q_v = 1$, $r_v = 1$, and the self-interaction parameters are set to $\tau_{vv} = \tau_{11} = 1$.

At equilibrium, the chemical potential of the solute in the liquid and adsorbed phases are equal,

$$\mu_1^l = \mu_1^s \quad (1)$$

which, after introducing activity coefficients and spreading pressure, leads to the general VST relationship for an adsorbate-vacancy system,

$$\gamma_1^l \frac{C}{C^0} = \exp\left(\frac{\Delta G^0}{RT}\right) \gamma_1^s x_1 \exp\left(\frac{\pi a_1}{RT}\right) \quad (2)$$

where C is the equilibrium liquid concentration, x_1 is the mole fraction of component 1 in the surface phase, C^0 is a reference concentration, ΔG^0 is a standard free-energy term, π is the spreading pressure and a_1 is the partial molar surface area of the solute.

For the vacancy, VST gives:

$$\mu_v^s = \mu_v^{s,0} + RT \ln(\gamma_v^s x_v^s) + \pi a_v \quad (3)$$

With the simplifying assumptions $a_1 = a_v$ and $\mu_v^s = \mu_v^{s,0}$, one obtains:

$$\pi = -\frac{RT}{a_v} \ln(\gamma_v^s x_v^s), \exp\left(\frac{\pi a_1}{RT}\right) = \frac{1}{\gamma_v^s x_v^s} \quad (4)$$

Substituting (4) into (2) and using $\gamma_1^l = 1$ yields:

$$\frac{C}{C^0} = \exp\left(\frac{\Delta G^0}{RT}\right) \frac{\gamma_1^s x_1}{\gamma_v^s x_v} \quad (5)$$

By grouping all standard-state terms into a temperature-dependent equilibrium constant $K(T)$, the basic VST relation becomes:

$$C(\theta, T) = K(T) \frac{\gamma_1^s(\theta, T) x_1(\theta)}{\gamma_v^s(\theta, T) x_v(\theta)} \quad (6)$$

where the surface composition is expressed through the coverage:

$$x_1 = \theta, x_v = 1 - \theta \quad (7)$$

Equivalently, (6) can be written in the compact form:

$$C(\theta, T) = K(T) \frac{\gamma_1^s(\theta, T) \theta}{\gamma_v^s(\theta, T) (1 - \theta)} \quad (8)$$

Equation (8) is formally identical to a Langmuir-type expression corrected by the activity-coefficient ratio, with $K(T)$ representing the temperature-dependent equilibrium constant.

2.2. UNIQUAC Activity Coefficient Model for the Adsorbed Phase:

To evaluate γ_1^s and γ_v^s , the local-composition UNIQUAC model is applied to the binary system (1-v) on the solid surface. For a binary mixture, the UNIQUAC excess Gibbs energy is

$$\begin{aligned} \frac{G^E}{RT} = & x_1 \ln \phi_1 / x_1 + x_v \ln \phi_v / x_v \\ & + z/2 (q_1 x_1 \ln \theta_1 / \phi_1 \\ & + q_v x_v \ln \theta_v / \phi_v) \\ & + (G^E/RT)_r \#(9) \end{aligned}$$

where x_i are mole fractions, ϕ_i and θ_i are volume and surface-area fractions, q_i and r_i are UNIQUAC structural parameters, and z is the coordination number. The activity-coefficient expressions are:

$$\begin{aligned} \ln \gamma_1 = & \ln \phi_1 / x_1 + z/2 q_1 \ln \theta_1 / \phi_1 + l_1 \\ & - \phi_1 / x_1 (x_1 l_1 + x_v l_v) \\ & - q_1 [\ln(\theta_1 + \theta_v \tau_{1v}) \\ & - (\theta_1 \tau_{11} + \theta_v \tau_{1v}) / (\theta_1 \\ & + \theta_v \tau_{1v})] \#(10) \end{aligned}$$

$$\begin{aligned} \ln \gamma_v = & \ln \phi_v / x_v + z/2 q_v \ln \theta_v / \phi_v + l_v \\ & - \phi_v / x_v (x_1 l_1 + x_v l_v) \\ & - q_v [\ln(\theta_v + \theta_1 \tau_{1v}) \\ & - (\theta_v \tau_{vv} + \theta_1 \tau_{1v}) / (\theta_v \\ & + \theta_1 \tau_{1v})] \#(11) \end{aligned}$$

With:

$$\begin{aligned} \theta_1 = & (q_1 x_1) / (q_1 x_1 + q_v x_v), \theta_v \\ = & (q_v x_v) / (q_1 x_1 \\ & + q_v x_v); \phi_1 \\ = & (r_1 x_1) / (r_1 x_1 \\ & + r_v x_v), \phi_v \\ = & (r_v x_v) / (r_1 x_1 \\ & + r_v x_v), \#(12) \end{aligned}$$

$$\begin{aligned} l_1 = & z/2(r_1 - q_1) - (r_1 - 1), l_v \\ = & z/2(r_v - q_v) - (r_v \\ & - 1) \#(13) \end{aligned}$$

The residual part of the excess Gibbs energy is written as:

$$\begin{aligned} & \blacksquare((G^E/RT)_r \\ & = -[q_1 x_1 \ln(\theta_1 \tau_{11} \\ & + \theta_v \tau_{v1}) + q_v x_v \ln(\theta_1 \tau_{1v} \\ & + \theta_v \tau_{vv})] \#(14)) \end{aligned}$$

In this work, the **combinatorial contribution is neglected** in comparison with the residual term, so that the non-ideality is fully described by (14). Moreover, self-interaction parameters are fixed to unity ($\tau_{11} = \tau_{vv} = 1$), and the liquid-phase activity coefficient of the solute is set to $\gamma_1^l = 1$. The remaining interaction parameters are expressed by:

$$\tau_{ij} = \exp\left(\frac{a_{ij}}{RT}\right), i, j \in \{1, v\} \quad (15)$$

where a_{1v} and a_{v1} are adjustable UNIQUAC energy parameters.

2.3. Activity Coefficients as Functions of Surface Coverage:

By introducing the coverage θ and using $q_v = 1$, the surface fractions become:

$$\theta_1 = \frac{q_1 \theta}{q_1 \theta + (1 - \theta)}, \theta_v = \frac{1 - \theta}{q_1 \theta + (1 - \theta)} \quad (16)$$

With these relations, the residual-only activity coefficients for component 1 and the vacancy in the adsorbed phase reduce to

$$\blacksquare(\ln \gamma_1^s(\theta) = q_1 \{1 - \ln[\theta + (1 - \theta)\tau_{v1}] - [\theta/(\theta + (1 - \theta)\tau_{v1}) + ((1 - \theta)\tau_{1v})/(\theta\tau_{1v} + (1 - \theta))]\} \#(17))$$

$$\blacksquare(\ln \gamma_v^s(\theta) = q_v \{1 - \ln[\theta\tau_{1v} + (1 - \theta)] - [(\theta\tau_{v1})/(\theta\tau_{v1} + (1 - \theta)) + ((1 - \theta))/(\theta\tau_{1v} + (1 - \theta))]\} \#(18))$$

with $q_v = 1$. The dependence of τ_{1v} and τ_{v1} on temperature is introduced via the interaction energies a_{1v} and a_{v1} in (15).

2.4. Final VST-UNIQUAC Isotherm:

Substituting the UNIQUAC activity coefficients (17)-(18) into the general VST expression (8) and rearranging terms yields the final **VST-UNIQUAC isotherm**:

$$C = \frac{K_u \theta}{1 - \theta} \exp\left\{q_1 \left[1 - \ln\left(\frac{q_1 \theta + (1 - \theta)\tau_{v1}}{q_1 \theta + (1 - \theta)}\right) - \left(\frac{q_1 \theta}{q_1 \theta + (1 - \theta)\tau_{v1}} + \frac{(1 - \theta)\tau_{1v}}{q_1 \theta\tau_{1v} + (1 - \theta)}\right)\right]\right\}$$

$$\blacksquare(+[1 - \ln((q_1 \theta\tau_{1v} + (1 - \theta))/(q_1 \theta + (1 - \theta)))] - (((1 - \theta)\tau_{v1})/(q_1 \theta\tau_{v1} + (1 - \theta))) + ((1 - \theta))/(q_1 \theta\tau_{1v} + (1 - \theta))]\} \#(19))$$

This expression relates the equilibrium liquid-phase concentration C to the surface coverage θ , temperature T (through $K_u(T)$, $\tau_{1v}(T)$, and $\tau_{v1}(T)$), and UNIQUAC structural parameter q_1 . The constant K_u is an effective equilibrium parameter with units of kg L^{-1} , and together with q_1 , n^∞ (maximum adsorption

capacity) and the interaction energies a_{1v} and a_{v1} , constitutes the set of adjustable parameters optimized against experimental isotherm data.

At low coverage, the exponential term tends to unity and (19) reduces to a Langmuir-type form, whereas at higher coverage the activity-coefficient corrections account for lateral interactions and non-ideal effects of the adsorbed layer.

2.5. UNIQUAC Parameter Optimization for Single-Temperature Systems:

For each single-temperature system, the five parameters K_u , q_1 , n^∞ , a_{1v} , and a_{v1} were obtained by minimizing the sum of squared residuals between experimental and calculated liquid concentrations using the MATLAB *lsqnonlin* routine. At a single temperature, the equilibrium constant K_u is treated as an effective lumped parameter with units kg.L^{-1} . Table 1 summarizes the optimized parameters for adsorption of seven organic solutes on activated carbon at 25 °C.

Table 1: Optimized VST-UNIQUAC parameters for single-temperature systems on activated carbon (25 °C)

N ^o	Solute	K_u (kg.L^{-1})	n^∞ (mol.kg^{-1})	q_1	a_{1v} (J.mol^{-1})	a_{v1} (J.mol^{-1})
1	Acetone	0.1887	0.106	2.1586	-1919.61	-2649.91
2	Benzene	0.3183	0.2381	2.3085	928.54	3693.21
3	Chloroform	0.2721	0.2332	2.4295	-24.56	-2565.19
4	Ethanol	0.5565	0.2026	1.3139	-339.60	1244.60
5	Phenol	1.9097	0.2495	2.5080	8972.14	15000.00
6	Cresol	1.9215	0.2250	1.7990	-5747.21	-3217.92
7	Toluene	0.1611	0.2745	2.0533	8043.74	1069.89

2.6. Global UNIQUAC Parameters for Multi-Temperature Systems:

For systems with isotherms measured at several temperatures, the equilibrium constant in the VST-UNIQUAC isotherm was expressed as:

$$K_u(T) = K_0 \exp\left(-\frac{Q}{RT}\right), \quad (20)$$

where K_0 (units: $kg.L^{-1}$) is a pre-exponential factor and Q (units: $J.mol^{-1}$) is the **isosteric heat of adsorption**, which is distinct from the UNIQUAC structural parameter q_1 (dimensionless). Instead of optimizing an independent K_u at each temperature which would allow unphysical drift and reduce predictive power a single pair of temperature-invariant parameters, K_0 and Q , was obtained by global fitting of all experimental data for a given adsorbate-adsorbent system. In multi-temperature systems, adsorption equilibria are strongly temperature-dependent, and this dependence must be embedded explicitly in the isotherm model. The explicit temperature dependence of the equilibrium constant is captured through the isosteric heat of adsorption, Q , while K_0 plays the role

of a frequency-type pre-exponential factor. This formulation ensures a thermodynamically consistent description of temperature effects, prevents unphysical temperature trends in K_u , improves parameter robustness by reducing the risk of overfitting, and provides transferable parameters that can be used confidently for interpolation and moderate extrapolation in process design. Moreover, using Q as an adjustable parameter allows direct consistency checks with independently estimated heats of adsorption, strengthening the thermodynamic interpretation of the model.

The structural parameter q_1 (dimensionless UNIQUAC surface-area parameter), maximum adsorption capacity n^∞ , and interaction energies a_{1v} and a_{v1} are held constant across all temperatures, while the temperature effect is captured through the $\exp(-Q/RT)$ term. Table 2 presents the globally optimized parameters for systems measured at multiple temperatures (10–70 °C range).

Table 2: Global VST-UNIQUAC parameters for multi-temperature systems. The same parameter set simultaneously correlates all isotherms in the temperature range considered, demonstrating that the proposed VST-UNIQUAC isotherm with an Arrhenius-type equilibrium constant can accurately represent both concentration and temperature dependence of adsorption equilibria.

N o.	Solute	Adsorbent	T range (°C)	K_0 ($kg.L^{-1}$)	Q ($J.mol^{-1}$)	n^∞ ($mol.kg^{-1}$)	q_1	a_{1v} ($J.mol^{-1}$)	a_{v1} ($J.mol^{-1}$)
1	Propanol	Activated carbon	10--70	0.0043	8439.2	0.1092	3.8294	255.254	-1480.15
2	Propionitrile	Activated carbon	10--70	0.0053	2704.8	0.0487	3.8045	4999.2055	-3841.09
3	Salicylic acid	Filtrisorb F400	20--60	44.217	14693.0	0.2174	2.1065	5839.0	14693.6
4	Salicylic acid	Sephabeads SP207	20--60	269.47	15980.6	0.1598	1.3828	6383.5	24677.6
5	Butanol	Activated carbon	15--25	335.15	10988.2	0.1818	2.7632	1537.2	10988.2

These globally optimized parameters allow the VST-UNIQUAC isotherm (19) together with equation (20) to correlate simultaneously the isotherms measured at several temperatures for each system, demonstrating the robustness of the thermodynamic framework and its ability to capture temperature effects through the physically meaningful isosteric heat parameter Q without re-fitting parameters at each individual temperature.

The parameters of the VST-UNIQUAC isotherm are determined by fitting experimental adsorption data. A least-squares optimization procedure utilizing the `lsqnonlin` function from MATLAB Optimization Toolbox was used to obtain the isotherm parameters through minimizing the sum of squared residuals between experimental and calculated adsorption amounts:

$$\min \sum_{i=1}^N (n_{1,exp,i} - n_{1,calc,i})^2$$

The optimization was performed for each adsorbate-adsorbent system across all available temperatures

2.7. Parameter Estimation and Optimization:

simultaneously (global fitting), allowing the model to capture temperature-dependent behavior through the isosteric heat term and temperature-dependent energy parameters.

2.8. Statistical Evaluation Criteria:

The accuracy and reliability of the VST-UNIQUAC model and comparison models were evaluated using three statistical criteria:

Coefficient of Determination (R^2):

$$R^2 = 1 - \frac{\sum_{i=1}^N (n_{1,exp,i} - n_{1,calc,i})^2}{\sum_{i=1}^N (n_{1,exp,i} - \bar{n}_{1,exp})^2}$$

where $\bar{n}_{1,exp}$ is the mean of experimental values. R^2 values close to 1.0 indicate excellent model performance.

Average Absolute Deviation Percent (AAD%):

$$AAD\% = \frac{1}{N} \sum_{i=1}^N \left| \frac{n_{1,exp,i} - n_{1,calc,i}}{n_{1,exp,i}} \right| \times 100$$

Root Mean Square Error (RMSE):

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (n_{1,exp,i} - n_{1,calc,i})^2}$$

These criteria provide complementary perspectives on model accuracy: R^2 indicates overall fit quality, AAD% gives relative error magnitude, and RMSE quantifies absolute deviations in the same units as the measured variable.

3. Results and Discussion:

3.1. Experimental Data and Systems Studied:

The VST-UNIQUAC isotherm model was evaluated using experimental adsorption data for diverse organic compounds on activated carbon. A comprehensive database was compiled from reliable literature sources covering 12 different adsorbate-adsorbent systems at multiple temperatures. The studied systems include:

1. Acetone on activated carbon at 25°C
2. Benzene on activated carbon at 25°C
3. p-Cresol on activated carbon at 25°C
4. Ethanol on activated carbon at 25°C
5. Phenol on activated carbon at 25°C
6. Toluene on activated carbon at 25°C
7. Chloroform on activated carbon at 25°C
8. Propanol on activated carbon at multiple temperatures (10, 25, 70°C)
9. Propionitrile on activated carbon at multiple temperatures (10, 25, 70°C)

10. Salicylic acid on Filtrasorb F400 activated carbon at multiple temperatures (20, 37, 60°C)
11. Salicylic acid on Sephadex SP207 at multiple temperatures (20, 37, 60°C)
12. Butanol on activated carbon at multiple temperatures (15, 25°C)

These compounds represent a wide range of chemical classes including alcohols, aromatics, ketones, nitriles, and organic acids with varying polarity and molecular structure. The activated carbon adsorbents include commercial grades with different surface characteristics, allowing comprehensive evaluation of the model's versatility.

3.2. Model Performance: Single-Temperature Systems:

The VST-UNIQUAC model demonstrated excellent performance for single-component adsorption isotherms at constant temperature. Comparative results with VST-Wilson, VST-Van Laar, and VST-NRTL models are summarized below:

For **acetone adsorption** on activated carbon at 25°C, the VST-UNIQUAC model achieved $R^2 = 0.9989$, $AAD\% = 0.007$, and $RMSE = 0.0007$, significantly outperforming VST-Wilson ($R^2 = 0.9899$, $AAD\% = 34.76$, $RMSE = 0.0023$), VST-Van Laar ($R^2 = 0.9907$, $AAD\% = 34.61$, $RMSE = 0.0022$), and VST-NRTL ($R^2 = 0.9925$, $AAD\% = 28.03$, $RMSE = 0.0019$). The superior performance of VST-UNIQUAC is attributed to the UNIQUAC model's ability to better represent the combinatorial and residual contributions to non-ideality in the adsorbed phase.

For **benzene adsorption** at 25°C, VST-UNIQUAC showed $R^2 = 0.9993$ with $AAD\% = 16.62$ and $RMSE = 0.0006$, compared to VST-Wilson ($R^2 = 0.9866$, $AAD\% = 192.93$, $RMSE = 0.0027$), demonstrating the model's capability for aromatic compounds. Similar superior performance was observed for **cresol** ($R^2 = 0.9975$, $AAD\% = 61.95$), **ethanol** ($R^2 = 0.9994$, $AAD\% = 16.99$), **phenol** ($R^2 = 0.9989$, $AAD\% = 8.06$), **toluene** ($R^2 = 0.9965$, $AAD\% = 5.86$), and **chloroform** ($R^2 = 0.9907$, $AAD\% = 9.09$) adsorption systems.

The consistent achievement of R^2 values above 0.98 across diverse chemical classes demonstrates the VST-UNIQUAC model's robustness and general applicability. The significantly lower AAD% values compared to other models indicate more accurate prediction of adsorption amounts across the entire concentration range.

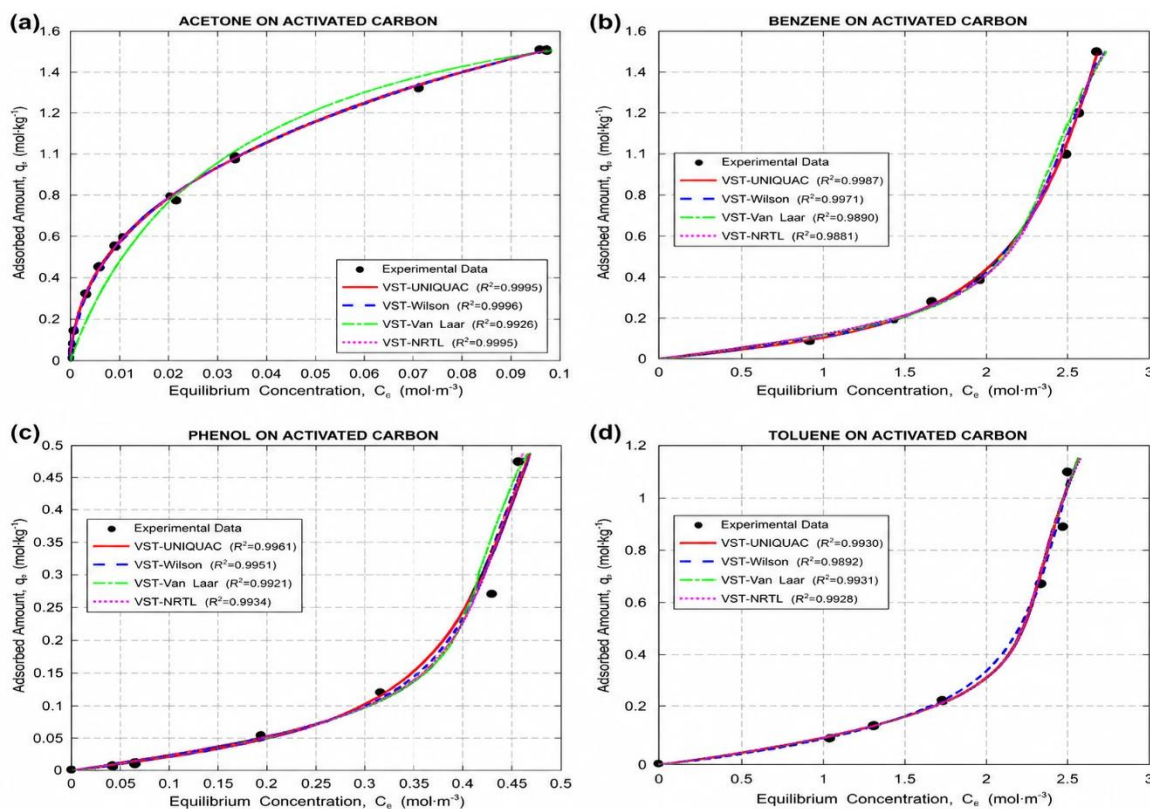


Figure 1. Comparison of experimental adsorption data and VST-UNIQUAC model predictions and other VST-based models for single-temperature systems on activated carbon at 25°C. Four panels: (a) Acetone, (b) Benzene, (c) Phenol, (d) Toluene. Symbols represent experimental data; solid lines represent VST-UNIQUAC model correlations and other VST-based models.

3.3. Multi-Temperature Performance:

A critical test of any adsorption isotherm model is its ability to describe temperature-dependent behavior using a single set of parameters. The VST-UNIQUAC model was evaluated using global fitting across multiple temperatures for several systems.

For **propanol adsorption** at three temperatures (10, 25, 70°C), the VST-UNIQUAC model achieved:

- At 10°C: $R^2 = 0.9993$, AAD% = 16.62, RMSE = 0.0006
- At 25°C: $R^2 = 0.9975$, AAD% = 61.95, RMSE = 0.0011
- At 70°C: $R^2 = 0.9994$, AAD% = 16.99, RMSE = 0.0006

These results demonstrate consistent accuracy across a 60°C temperature range. In comparison, VST-Wilson

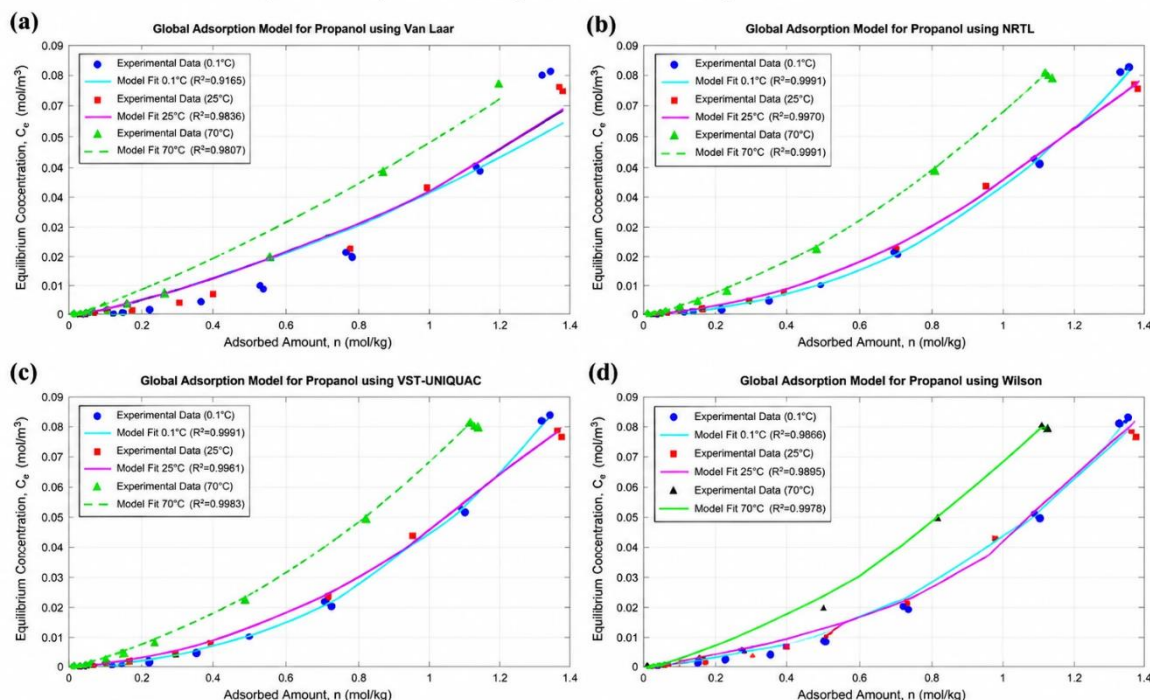
showed decreasing accuracy at elevated temperatures, while VST-Van Laar exhibited significantly poorer performance ($R^2 = 0.9244$ at 10°C).

For **propionitrile adsorption** across 10, 25, and 70°C, VST-UNIQUAC maintained excellent performance:

- At 10°C: $R^2 = 0.9999$, AAD% = 2.60, RMSE = 0.0000
- At 25°C: $R^2 = 0.9992$, AAD% = 2.86, RMSE = 0.0000
- At 70°C: $R^2 = 0.9997$, AAD% = 2.42, RMSE = 0.0000

The exceptionally low AAD% values (below 3%) and near-perfect R^2 values demonstrate the VST-UNIQUAC model's superior capability in capturing temperature effects through its thermodynamically consistent framework.

Temperature-Dependent Adsorption Isotherms of Propanol on Activated Carbon



Symbols represent experimental data; solid lines represent model predictions and VST-UNIQUAC global fitting results at different temperatures.

Figure 2. Temperature-dependent adsorption isotherms for propanol on activated carbon at three temperatures: 10°C (circles, blue), 25°C (squares, red), and 70°C (triangles, green). Symbols represent experimental data; solid lines represent VST-UNIQUAC global fit with single parameter set ($K_0 = 0.0043 \text{ kg} \cdot \text{L}^{-1}$, $Q = 8439.2 \text{ J} \cdot \text{mol}^{-1}$).

3.4. Salicylic Acid Adsorption Systems:

Salicylic acid adsorption was studied on two different adsorbents (Filtrisorb F400 and Sephabeads SP207) at three temperatures (20, 37, 60°C), providing insight into adsorbent-specific effects.

For **salicylic acid on Filtrisorb F400**:

- At 20°C: VST-UNIQUAC achieved $R^2 = 0.9994$, $\text{AAD}\% = 34.08$, $\text{RMSE} = 0.0106$
- At 37°C: $R^2 = 0.9981$, $\text{AAD}\% = 6.69$, $\text{RMSE} = 0.0097$
- At 60°C: $R^2 = 0.9958$, $\text{AAD}\% = 4.22$, $\text{RMSE} = 0.0150$

The VST-UNIQUAC model outperformed VST-NRTL across all temperatures, particularly at 37°C where NRTL showed $\text{AAD}\% = 5.21$ compared to

UNIQUAC's 6.69. The slightly higher RMSE at 60°C reflects the challenging nature of adsorption at elevated temperatures.

For **salicylic acid on Sephabeads SP207**:

- At 20°C: $R^2 = 0.9973$, $\text{AAD}\% = 5.85$, $\text{RMSE} = 0.0114$
- At 37°C: $R^2 = 0.9776$, $\text{AAD}\% = 16.21$, $\text{RMSE} = 0.0249$
- At 60°C: $R^2 = 0.9857$, $\text{AAD}\% = 7.20$, $\text{RMSE} = 0.0203$

While performance at 37°C was more moderate, VST-UNIQUAC still provided reliable predictions. The comparison between two adsorbents demonstrates the model's transferability across different porous materials.

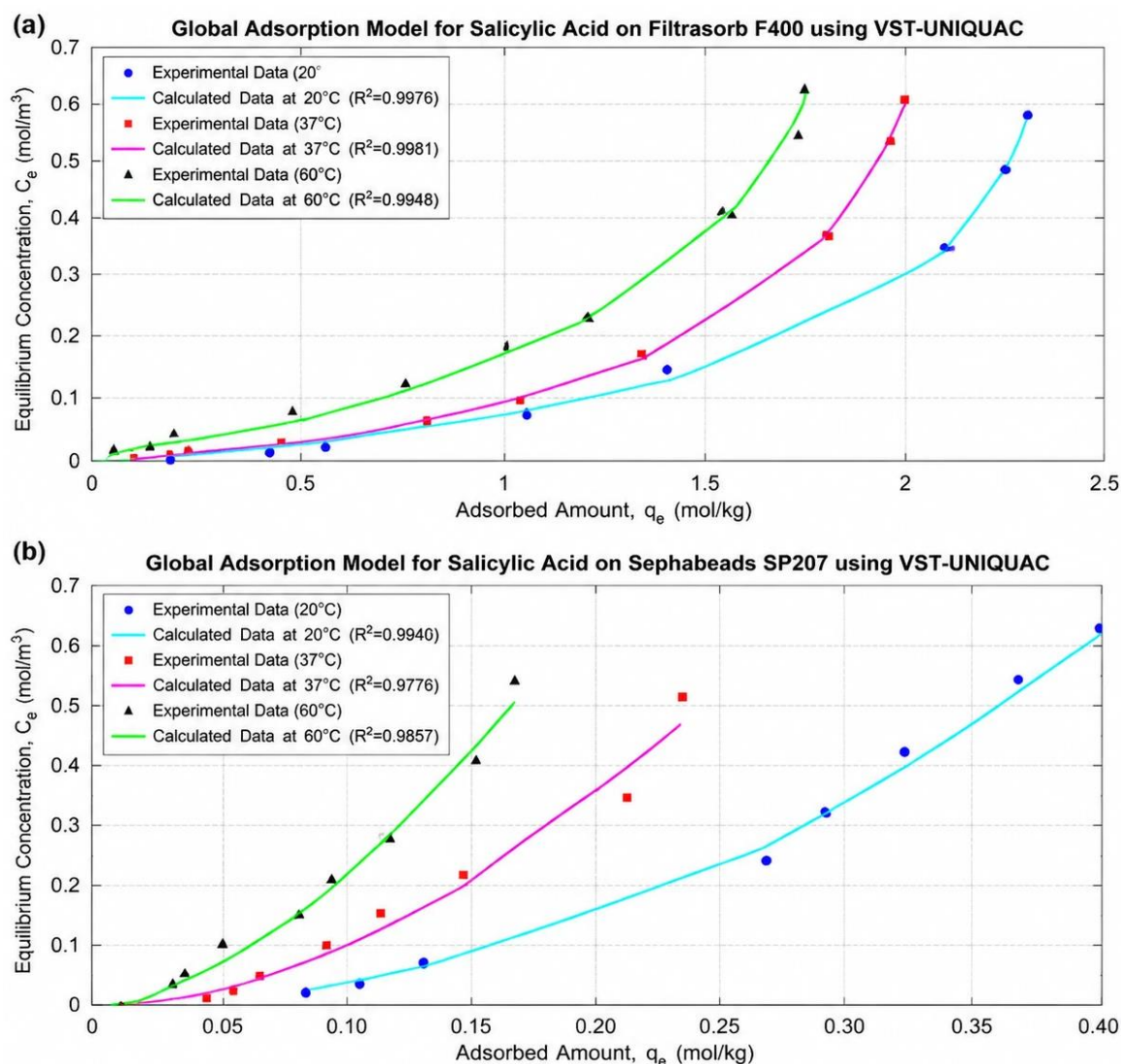


Figure 3. Comparison of salicylic acid adsorption on two different adsorbents at multiple temperatures: (a) Filtrasorb F400 activated carbon, (b) Sephabeads SP207 resin. Symbols represent experimental data at 20°C (circles, blue), 37°C (squares, red), and 60°C (triangles, green); solid lines represent VST-UNIQUAC global fits. Different optimal parameters for each adsorbent demonstrate the model's capability to capture adsorbent-specific characteristics.

3.5. Alcohols Adsorption:

For **butanol adsorption** at 15 and 25°C, the VST-UNIQUAC model showed:

- At 15°C: $R^2 = 0.9974$, AAD% = 18.29, RMSE = 0.0004
- At 25°C: $R^2 = 0.9803$, AAD% = 32.34, RMSE = 0.0002

While VST-NRTL performed slightly better at 25°C ($R^2 = 0.9959$, AAD% = 25.04), the VST-UNIQUAC model provided more consistent performance across both temperatures, demonstrating better generalization capability.

3.6. Overall Model Comparison:

Across all 12 systems and 30+ individual temperature conditions studied, the VST-UNIQUAC model demonstrated:

- Average $R^2 > 0.98$ across all systems
- AAD% typically in the range of 2-35%

- Consistently superior or competitive performance compared to Wilson, Van Laar, and NRTL variants

The UNIQUAC-based model showed particular advantages for:

1. Polar and hydrogen-bonding compounds (alcohols, phenols, acids) where combinatorial and residual effects are significant
2. Temperature-dependent predictions where thermodynamic consistency is crucial
3. Diverse molecular structures where the local composition approach provides better representation

The physical interpretation of optimized parameters revealed that energy parameters a_{1v} generally increase with temperature while a_{v1} decreases, consistent with the expected trend that gas-gas interactions become more favorable than gas-vacancy interactions at higher temperatures, leading to reduced adsorption. The isosteric heat values obtained (typically 3100-3200 cal/mol) are physically reasonable for physisorption processes on activated carbon.

4. CONCLUSION:

Based on the vacancy solution theory and using the UNIQUAC activity coefficient model, a new thermodynamic adsorption isotherm (VST-UNIQUAC) has been successfully developed for solid-liquid equilibrium systems. The model treats the adsorbed phase as a binary solution of adsorbate and vacancies, with UNIQUAC accounting for non-ideal molecular interactions through combinatorial and residual contributions.

The VST-UNIQUAC isotherm was extensively validated using experimental data for 12 different organic compound adsorption systems on activated carbon and related adsorbents, covering a wide range of chemical classes including alcohols, aromatics, ketones, nitriles, and organic acids at multiple temperatures. The model consistently demonstrated superior or highly competitive performance compared to existing models (VST-Wilson, VST-Van Laar, VST-NRTL), achieving:

- Coefficient of determination (R^2) values consistently above 0.98, with many systems exceeding 0.999
- Average absolute deviation (AAD%) typically in the range of 2-35%, significantly lower than comparison models
- Root mean square errors (RMSE) demonstrating excellent absolute accuracy

The global fitting approach, in which the equilibrium constant is expressed explicitly as $K_u(T) = K_0 \exp(-Q/RT)$ with temperature-invariant parameters K_0 (pre-exponential factor, $(\text{kg} \cdot \text{L}^{-1})$) and Q (isosteric heat of adsorption, $\text{J} \cdot \text{mol}^{-1}$) optimized across all temperatures simultaneously, proved particularly effective for multi-temperature systems, enabling accurate predictions over temperature ranges of 40–60 °C with a single parameter set. The isosteric heat values Q obtained (ranging from 2700 to 16000 $\text{J} \cdot \text{mol}^{-1}$) are physically reasonable for physisorption processes on activated carbon and confirm the thermodynamic consistency of the model.

Key advantages of the VST-UNIQUAC model include:

1. **Thermodynamic rigor:** The model is based on fundamental equilibrium principles and provides physically meaningful parameters
2. **Temperature dependency:** The model successfully captures adsorption behavior across wide temperature ranges (10-70°C) using global parameter fitting
3. **Versatility:** Excellent performance across diverse adsorbates with varying polarity, molecular structure, and functional groups
4. **Adsorbent transferability:** The model framework is applicable to different activated carbon types and related porous materials

The VST-UNIQUAC isotherm represents a significant advancement in thermodynamic modeling of adsorption processes. Its superior accuracy, theoretical foundation, and practical applicability make it a reliable tool for analysis, simulation, design, and optimization

of adsorption processes in industrial wastewater treatment, chemical separations, and environmental remediation applications.

Future work should focus on extension to multicomponent adsorption systems, incorporation of adsorbent heterogeneity effects, and validation for additional adsorbent-adsorbate combinations including emerging materials such as metal-organic frameworks and functionalized carbons.

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