

Chemicals	Purity (mass%)	Degree of hydrogenation (%)	Analysis method
Dibenzyltoluene (H0-DBT) ⁺	>99	0	GC-MS ^a
Hexahydro-dibenzyltoluene (H ₆ -DBT) ⁺	>99	33	GC-MS ^a
Dodecahydro-dibenzyltoluene (H ₁₂ -DBT) ⁺	>99	67	GC-MS ^a
Octadecahydro-dibenzyltoluene (H ₁₈ -DBT) ⁺	>99	100	GC-MS ^a
Acetone	>99	-	-

Table 1: Specifications of phenyl hexyl Silica provided by manufacturer.

Parameter	Value
Particle size	11-15 μm
Particle size distribution	1.8 (dp 90/10)
Pore diameter	100 ^a Å
Surface diameter	390 m ² /g
Bulk density	0.58 g/cm ³
Total carbon	16%
Metal contents	11 ppm

Table 2: Purity information of chemicals used.

distillation was performed in packed distillation column (Normag GmbH, Germany) equipped with Sulzer structured packing (L=2 m, DXP, SS 1.4404). Due to the overlapping range of boiling points, pure compounds were not obtained via distillation but fractions consisting of compounds with similar boiling points were obtained. The batch plot for vacuum distillation experiment and boiling point range of DBT-fractions is provided in the supporting information. Then in the second step, using those fractions as feed, single isomers representing each fraction of dibenzyltoluene were separated on semi-preparative scale column (250 mm (L) × 50 mm (I.D.)) using reversed phase liquid chromatography. The detailed procedure can be found somewhere else [7]. The GC analysis and NMR analysis of each isomer used in this work is given in the supporting information.

Measurement of adsorption isotherm: The adsorption isotherms were measured using a static method (shake-flask method) [13]. Solutions in acetone/water (96.4%, v/v) containing equal concentration of dibenzyltoluene (H0-DBT), hexahydro-dibenzyltoluene (H6-DBT), dodecahydro-dibenzyltoluene (H12-DBT), and octadecahydro-dibenzyltoluene (H18-DBT) were prepared in 10 ml bottles for the concentration range of 0.1-25 mg/ml. The upper threshold of concentration was determined on the basis of the least soluble compound, i.e., H18-DBT in acetone/water solvent. The uncertainty of the initial concentration was ± 0.01 mg/ml. Then a fixed amount (0.5 ± 0.003 g) of phenylhexyl silica was added to each bottle and the tightly closed bottles were kept for 24 hours under stirring. Preliminary experimental studies indicate that the adsorption equilibrium was reached after 18 hours for all components. The same procedure was repeated for the determination of the isotherms of dibenzyltoluene and octadecahydro-dibenzyltoluene fractions. It should be noted that fraction represents the isomeric mixture of components with same degree of hydrogenation. The initial and final concentrations were measured using Gas Chromatography (Agilent technology 7890 A system). The amount of solutes adsorbed on phenylhexyl silica were determined with initial and equilibrium concentrations using eq. (1).

$$q_e = \frac{(c_i - c_e) \cdot v}{m} \quad (1)$$

where C_i and C_e are initial and equilibrium concentrations of solutes, respectively; m is the mass of the phenylhexyl silica phase in gram and v is the volume of solution. Each measurement was repeated three times and the standard deviation was found to be less than 5%.

Results

The experimental data for the adsorption isotherm for fraction

of dibenzyltoluene and octadecahydro-dibenzyltoluene and single components of dibenzyltoluene, hexahydro-dibenzyltoluene, dodecahydro-dibenzyltoluene, and octadecahydro-dibenzyltoluene over phenylhexyl silica in acetone/water solvent (96/4, v/v%) at 22 ± 1°C are presented in Table 3 and 4. It was observed that adsorption to stationary phase increased with degree of hydrogenation of compounds i.e., phenylhexyl silica has three times more adsorption capacity for fully hydrogenated octadecahydro-dibenzyltoluene in comparison to fully dehydrogenated dibenzyltoluene at the same concentration. Moreover, the results show that within the studied concentration range (0 to 25 mg/ml), the adsorption isotherm for H0-DBT and H18-DBT were not influenced by other species as single component data were comparable with the competitive adsorption isotherms within deviation of only 1% as shown in Figure 1.

Correlation of experimental data

Due to the negligible difference between the single and competitive adsorption isotherms (Figure 1), it was assumed that components do not influence each other during adsorption within concentration range studied. Several equations for correlating single component adsorption data such as Freundlich, Langmuir and combined Langmuir-Freundlich (also known as Sip's equation) were evaluated for the correlation of the experimental data. The Freundlich isotherm with two parameters is given by eq (2) [14,15].

$$q_e = q_{sat} \cdot \frac{b \cdot c_i}{1 + b \cdot c_i} \quad (2)$$

Where q_e is the amount of solute adsorbed on the stationary phase, k and n are Freundlich parameters. The Langmuir adsorption isotherm with two parameters is described by eq (3) [14,15].

$$q_e = q_{sat} \cdot \frac{b \cdot c_i}{1 + b \cdot c_i} \quad (3)$$

Where q_{sat} is the saturation capacity of monolayer and b is second Langmuir parameter which quantifies the adsorption energy H_{ads} using eq (4) [14].

$$q_e = q_{sat} \cdot \frac{(b \cdot c_i)^n}{1 + (b \cdot c_i)^n} \quad (4)$$

The parameters for the Freundlich equation, Langmuir equation, and Sip's equation are presented in Table 4. The Freundlich correlation did not fit the experimental data satisfactorily (with 13 data points for each compound), especially at low concentrations. The average relative error for the Freundlich model was 11.6% with a maximum deviation of 18.4% observed at low concentrations. For the Langmuir model, the fitting results were better in comparison to the Freundlich

H ₀ -DBT		H ₆ -DBT		H ₁₂ -DBT		H ₁₈ -DBT	
C _e	q _e	C _e	q _e	C _e	q _e	C _e	q _e
mg·ml ⁻¹	mg·g ⁻¹	mg·ml ⁻¹	mg·g ⁻¹	mg·ml ⁻¹	mg·g ⁻¹	mg·ml ⁻¹	mg·g ⁻¹
0.25	17.9	0.25	36.5	0.24	41.8	0.24	47.9
0.38	27.2	0.39	59.7	0.37	69.7	0.38	84.9
0.56	39.7	0.57	92.2	0.54	109.1	0.57	143.1
1.00	70.5	0.98	169.6	0.93	206.9	0.98	283.2
1.92	133.3	1.92	357.9	1.84	450.3	1.92	656.0
2.87	195.8	2.89	553.6	2.77	704.8	2.86	1055.4
3.64	244.2	4.61	928.0	4.86	1264.8	4.52	1760.9
4.98	325.1	5.27	1025.8	6.88	1754.4	4.92	1927.4
8.81	533.4	7.52	1435.4	9.24	2260.5	7.04	2749.7
10.61	620.5	10.08	1856.8	11.73	2721.7	9.55	3602.3
14.58	793.2	14.45	2470.3	14.40	2960.0	14.06	4814.8
26.55	1190.4	25.38	3564.0	23.42	4160.4	23.98	6484.8

Table 3: Experimental competitive adsorption isotherm data for dibenzyl toluene derivatives from acetone/water (96/4, v/v) solution over phenylhexyl silica.

H ₀ -DBT		H ₁₈ -DBT	
C _e	q _e	C _e	q _e
mg·ml ⁻¹	mg·g ⁻¹	mg·ml ⁻¹	mg·g ⁻¹
0.24	17.7	0.24	48.0
0.36	27.1	0.37	84.7
0.54	39.5	0.58	143.0
0.95	70.5	0.99	283.0
1.88	133.0	1.95	656.3
2.85	195.8	2.80	1054.0
3.6	244.2	4.50	1760.2
4.92	325.3	4.88	1925.4
8.9	533.4	7.10	2749.7
10.58	620.5	9.56	3602.3
14.55	793.3	14.10	4814.8
25.98	1190.2	24.05	6487.8

Table 4: Single component adsorption isotherm data for dibenzyltoluene and octadecahydro-dibenzyltoluene from acetone/water (96/4, v/v) solution over phenylhexyl silica.

correlations. However, the Langmuir model fits the H0-DBT and H6-DBT data satisfactorily but gives poor fitting for H12-DBT and H18-DBT data. The average relative error for the Langmuir isotherm was 6.2% with a maximum error of 13%. The relative error was high at low concentrations while the fit was observed to be better at high concentrations. A comparison of the Langmuir and Freundlich isotherms with experimental data is presented in Figure 2.

The Sip's equation with three parameters (eq (5)) correlates the experimental data within the working concentration range better compared to the other correlations.

$$q_e = q_{sat} \frac{(b \cdot c_i)^n}{1 + (b \cdot c_i)^n} \quad (5)$$

Although the number of parameters (three instead of two) increases, higher values of adj. R² (adjusted determination coefficient) and Q² (cross validated determination coefficient) show the better fit quality (compare Table 5). Additionally, the calculated average relative deviation was only 0.5% with a maximum value of 0.6%. The comparison of the Sip's equation data with the experimental data is presented in Figure 3.

Additionally, the bi-Langmuir adsorption isotherm (eq (6)) was used to correlate the experimental data by assuming the maximum loadability equal for all components in the system [14,15].

$$q_{i,e} = q_{i,sat} \cdot \frac{b_j \cdot c_i}{1 + \sum_{j=1}^n b_j \cdot c_j} \quad (6)$$

As expected, the model based on this assumption did not fit the data well because the loadability for various hydrogenated fractions is fairly different for the different compounds. If maximum loadability is considered to be different for all compounds, 8 parameters would be needed to fit eq (6) to 13 experimental data points. Such a high number of parameters do not seem to be reasonable. Thus, within the studied concentration range, Sip's equation was found to be the best suited correlation for the adsorption isotherms of all partially hydrogenated derivatives of dibenzyltoluene.

Conclusion

In this work, adsorption isotherm data for single isomers of dibenzyltoluene, hexahydro-dibenzyltoluene, dodecahydro-dibenzyltoluene and octadecahydro-dibenzyltoluene are presented. The distribution of these components has been investigated between a acetone/water (96/4, v/v) liquid phase and a phenylhexyl silica (stationary phase) at 22 ± 1°C within the concentration range from 0 to 25 mg/ml. Langmuir and Freundlich isotherms with 2 parameters and Sip's equation (combined Langmuir-Freundlich equation) with 3 parameters and multicomponent isotherm based on the Langmuir

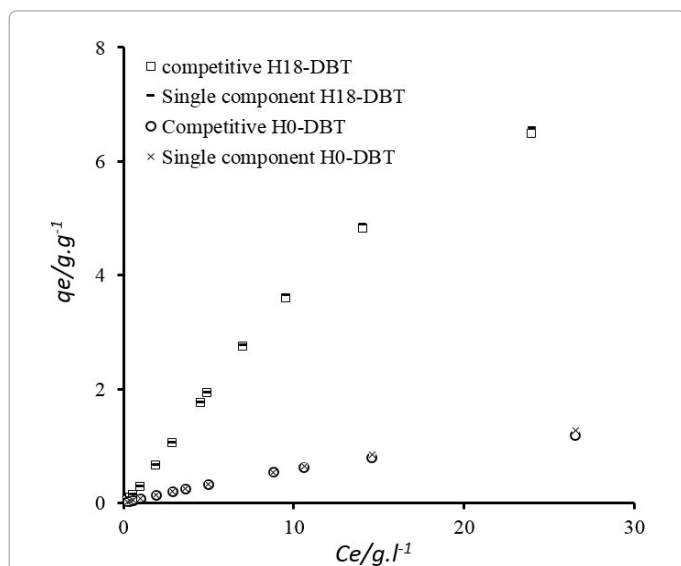


Figure 1: Comparison of single component isotherm with competitive isotherm for H0-DBT and H18-DBT.

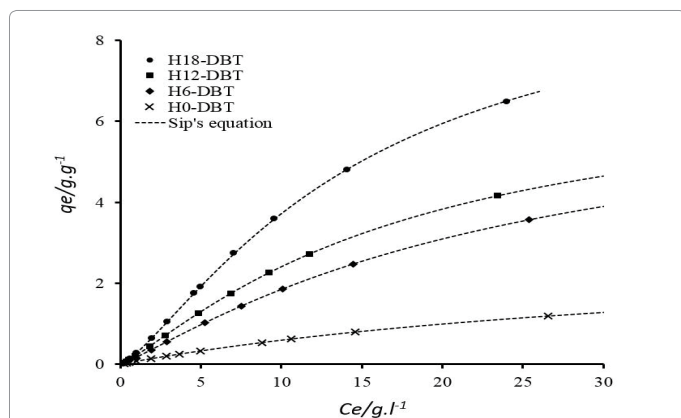


Figure 2: Comparison of experimental and modelled data using Langmuir and Freundlich isotherms.

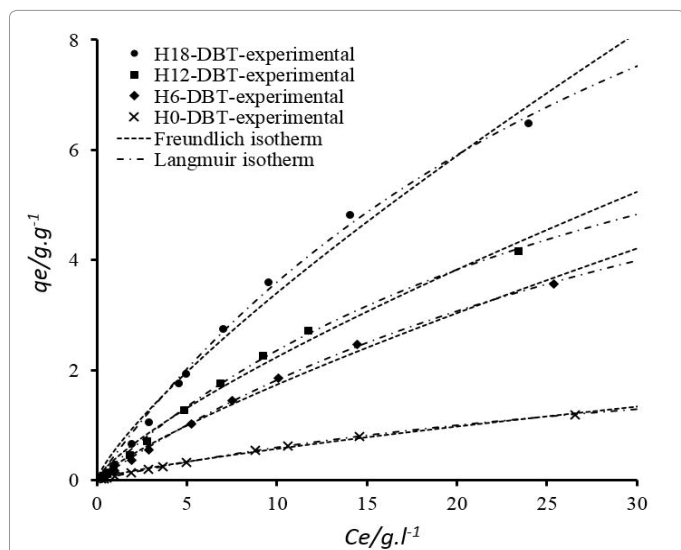


Figure 3: Comparison of experimental and modelled data using Sip's equation.

Parameters	H ₁₈ -DBT	H ₁₂ -DBT	H ₆ -DBT	H ₀ -DBT
Langmuir equation				
q _{sat}	14.215	10.207	9.883	3.068
b	0.034	0.029	0.023	0.024
Adj. R ²	0.996	0.998	0.999	0.999
Q ²	0.995	0.977	0.995	0.999
ARD/%	13.5	6.21	3.89	1.01
Freundlich equation				
k	0.55	0.37	0.293	0.099
n	0.79	0.78	0.779	0.752
Adj. R ²	0.979	0.988	0.961	0.996
Q ²	0.945	0.920	0.942	0.991
ARD/%	14.5	16.4	9.8	5.8
Sip's equation				
q _{sat}	9.92	7.042	6.915	2.991
b	0.068	0.058	0.042	0.025
n	1.32	1.2	1.15	1.01
Adj. R ²	0.999	0.999	0.999	0.999
Q ²	0.999	0.999	0.999	0.999
ARD/%	0.0023	0.0078	0.0003	0.0001

Table 5: Model parameters for adsorption isotherms with statistical parameters.

model (with 8 parameters) were used to correlate the experimental data. Good agreement with experimental data was found for Sip's equation as compared to the other models. Moreover, adsorption isotherms data for single components of dibenzyltoluene and octadecahydro-dibenzyltoluene were comparable with their competitive adsorption isotherms. Thus, influence of the individual components on each other were found to be negligible within the studied concentration range.

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