Modern Chemistry & Applications

Research Article — **Open Access**

Adsorption Isotherm of Dibenzyl Toluene and its Partially Hydrogenated Forms Over Phenyl Hexyl Silica

Rabya Aslam[1,2]* and Karsten Muller[1]

[1]*Institute of Separation Science and Technology, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*
[2]*Institute of Chemical Engineering and Technology, University of the Punjab, Lahore, Pakistan*

Abstract

Liquid organic hydrogen carriers (LOHC) are an interesting option for chemical energy storage and hydrogen transportation. Dibenzyltoluene (H0-DBT), heat transfer oil, is capable of reversibly storing hydrogen emerged as a feasible LOHC system. However, it is not available as a pure compound but consists of an isomeric mixture of 6 to 8 compounds. During the hydrogen storage process a high number of stable intermediate species is formed. These compounds can be categorized into four main classes according to their degree of hydrogenation. To implement H0-DBT as a LOHC system, thermophysical data of these intermediate compounds are required. In our previous work, a reversed phase HPLC method was developed using phenylhexyl silica stationary phase and acetone/water as eluent to separate these partially hydrogenated fractions with a purity >98%. For further designing a batch or continuous HPLC process, adsorption isotherm data are required. In this work, adsorption isotherms for dibenzyltoluene and its partial and fully hydrogenated forms namely hexahydro-dibenzyltoluene, dodecahydro-dibenzyltoluene, and octadecahydro-dibenzyltoluene are measured over phenylhexyl silica in acetone/water solvent using the static method. Sip's equation (Combined Langmuir-Freundlich isotherm) fits the data better as compared to simple Freundlich, Langmuir or competitive Langmuir adsorption isotherms.

Keywords: Adsorption isotherms; LOHC; RP-HPLC

Introduction

Liquid organic hydrogen carriers (LOHC) are a promising approach for hydrogen storage and transportation. This concept is based on the reversible cycle of hydrogenation and dehydrogenation for uptake and release of hydrogen [1-5]. The LOHC system consists of a pair of dehydrogenated and hydrogenated compounds representing the hydrogen lean and rich forms, respectively. Due to the chemical bonding of the hydrogen in the hydrogenated LOHC compound, the latter can store H_2 at ambient conditions over longer periods. Recent studies shows the potential of dibenzyltoluene (H0-DBT) as a competitive LOHC system due to its reasonable hydrogen storage capacity and thermal stability [5,6]. Each H0-DBT molecule can store 9 molecules of hydrogen in the form of octadecahydro-dibenzyltoluene (H18-DBT). However, to implement it as LOHC system, its thermophysical data are required. Since it is not available as pure compound and partial hydrogenation further produces a number of stable intermediate species. More than 24 compounds are observed in a partially hydrogenated reaction mixture which can be classified into four main fractions on the basis of their degree of hydrogenation namely dibenzyltoluene (H_0-DBT), hexahydro-dibenzyltoluene (H_6-DBT), dodecahydro-dibenzyltoluene (H_{12}-DBT), and octadecahydro-dibenzyltoluene (H_{18}-DBT). In our previous work, a reversed phase high pressure liquid chromatography method was developed and successfully scaled up to semi preparative scale for the separation of these partially hydrogenated derivatives of dibenzyltoluene with phenylhexyl silica as stationary phase and a acetone water mixture as mobile phase (96/4, *v/v*%) [7]. In order to simulate and design a linear or non-linear chromatographic processes, adsorption isotherm data over mobile and stationary phase are required which describe the distribution behavior of the DBT fractions in the chromatographic system [8-10]. Adsorption isotherms can experimentally be determined using static (shake-flask and adsorption-desorption methods) or dynamic methods (frontal analysis method, elution curve methods and minor perturbation methods) [8,11,12]. Moreover, for a mixture, competitive isotherms can be predicted using single solute adsorption isotherm but it often comes with limited applicability range and accuracy [8]. In this work, adsorption isotherm data of single isomers of dibenzyltoluene derivatives such as dibenzyltoluene, hexahydro-dibenzyltoluene, dodecahydro-dibenzyltoluene, and octadecahydro-dibenzyltoluene are determined using static method over phenylhexyl silica from a acetone/water solution (96/4, v/v%) within a concentration range of 0-25 mg/ml at 22 ± 1°C.

Materials and Methods

Materials

The stationary phase phenylhexyl silica (Luna 15 μm, 100°A) was purchased from Phenomenex, Germany. The specifications of the adsorbent provided by the supplier are summarized in Table 1. The single isomers of dibenzyltoluene, hexahydro-dibenzyltoluene, dodecahydro-dibenzyltoluene and octadecahydro-dibenzyltoluene were separated and purified via vacuum distillation and reversed phase high pressure liquid chromatography with >99% purity. The details of the separation process are described in section 2.2.1. The HPLC grade acetone was purchased from VWR Germany and 18 MΩ water produced by a Milli Q integral-3 system (Merck Millipore) was used in the experimental work. The details of the chemicals used are given in Table 2.

Methods

Separation of dibenzyltoluene derivatives: Single isomers of dibenzyltoluene derivatives representing each fraction of dibenzyltoluene were separated in two steps. Firstly, vacuum distillation was used to separate a partially hydrogenated reaction mixture. The

Chemicals	Purity (mass%)	Degree of hydrogenation (%)	Analysis method
Dibenzyltoulene (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
Surface diameter	390 m²/g
Bulk density	0.58 g/cm³
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).

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

where Ci and Ce 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].

$$q_e = q_{sat} \cdot \frac{b.c_i}{1 + b.c_i} \tag{2}$$

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].

$$q_e = q_{sat} \cdot \frac{b.c_i}{1 + b.c_i} \tag{3}$$

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].

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

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
$mg \cdot ml^{-1}$	$mg \cdot g^{-1}$	$mg \cdot ml^{-1}$	$mg \cdot g^{-1}$	$mg \cdot ml^{-1}$	$mg \cdot g^{-1}$	$mg \cdot ml^{-1}$	$mg \cdot g^{-1}$
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
$mg \cdot ml^{-1}$	$mg \cdot g^{-1}$	$mg \cdot ml^{-1}$	$mg \cdot g^{-1}$
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.

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

Although the number of parameters (three instead of two) increases, higher values of adj. R^2 (adjusted determination coefficient) and Q^2 (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].

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

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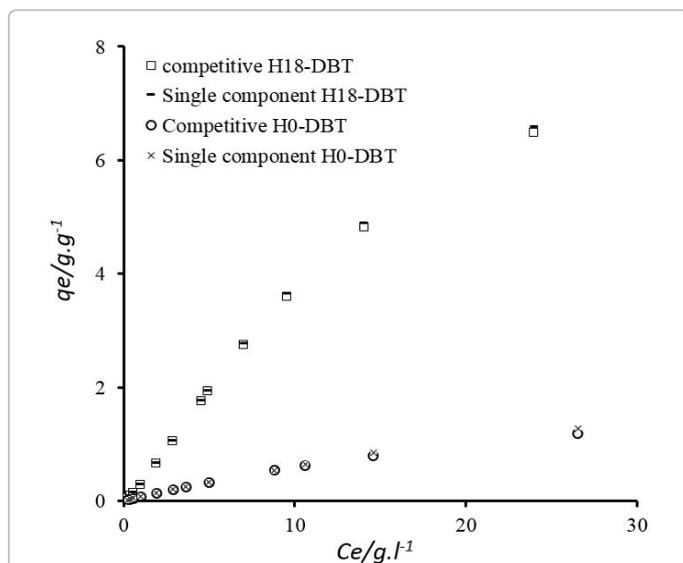
Figure 1: Comparison of single component isotherm with competitive isotherm for H0-DBT and H18-DBT.
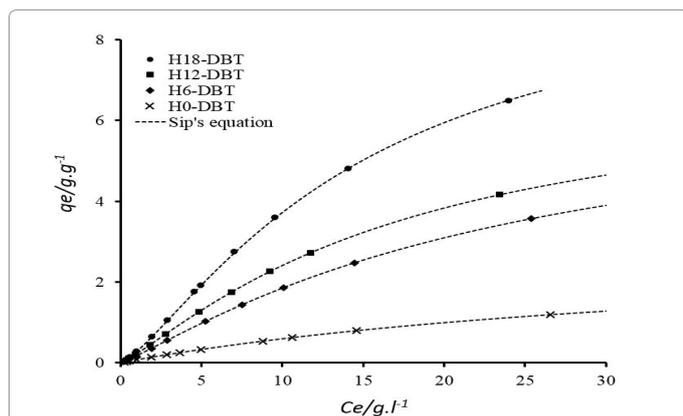

Figure 2: Comparison of experimental and modelled data using Langmuir and Freundlich isotherms.
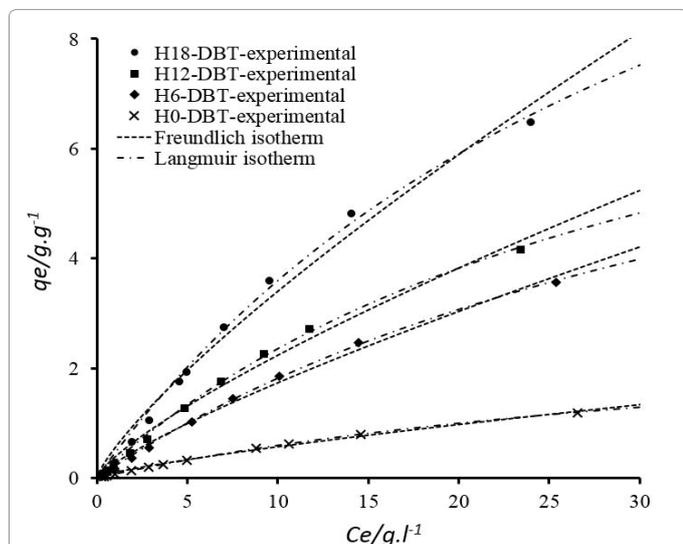

Figure 3: Comparison of experimental and modelled data using Sip's equation.

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.

Acknowledgements

References

1. Muller K, Arlt W (2013) Status and Development in Hydrogen Transport and Storage for Energy Applications. Energy Technology 1: 501-511.

2. Muller K (2012) Amine Borane Based Hydrogen Carriers: An Evaluation. Energy & Fuels 26: 3691-3696.

3. Usman MR (2011) The Catalytic Dehydrogenation of Methylcyclohexane over Monometallic Catalysts for On-board Hydrogen Storage Production and Utilization. Energy Sources Part A: Recovery Utilization and Environmental Effects 33: 2231-2238.

4. Teichmann D, Arlt W, Wasserscheid P (2012) Liquid Organic Hydrogen Carriers as an efficient vector for the transport and storage of renewable energy. International Journal of Hydrogen Energy 37: 18118-18132.

5. Markiewicz M (2015) Environmental and health impact assessment of Liquid Organic Hydrogen Carrier (LOHC) systems - challenges and preliminary results. Energy & Environmental Science 8: 1035-1045.

6. Bruckner N (2014) Evaluation of Industrially Applied Heat-Transfer Fluids as Liquid Organic Hydrogen Carrier Systems. Chem Sus Chem 7: 229-235.

7. Aslam R (2016) Development of a liquid chromatographic method for the separation of a liquid organic hydrogen carrier mixture Separation and Purification Technology. Separation and Purification Technology 163: 140-144.

8. Lisec OP, Hugo, Seidel AM (2001) Frontal analysis method to determine competitive adsorption isotherms. Journal of Chromatography A 908: 19-34.

9. Schmidt TH (2005) Preparative Chromatography of Fine Chemicals and Pharmaceutical Agents, p: 485.

10. Ching CB, Chu KH, Ruthven DM (1990) A study of multicomponent adsorption equilibria by liquid chromatography. AICHE Journal 36: 275-281.

11. Knoerzer K (2011) Innovative Food Processing Technologies. Advances in Multiphysics Simulation.

12. Myers AL, Prausnitz JM (1965) Thermodynamics of mixed-gas adsorption. AICHE Journal 11: 121-127.

13. Bonomo R (2003) Multicomponent adsorption of whey proteins by ion exchanger. Braz J Food Technol 6: 323-326.

14. Hindarso H (2001) Adsorption of Benzene and Toluene from Aqueous Solution onto Granular Activated Carbon. Journal of Chemical & Engineering Data 46: 788-791.

15. Wan X, Lee J, Row K (2009) Nonlinear isotherm of benzene and its derivatives by frontal analysis. Korean Journal of Chemical Engineering 26: 182-188.