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Solid-Liquid Equilibrium for the System Activated Carbon and Aqueous Solution of both Phenol and Dinitro-o-Cresol.

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Water purification processes, based on rather severe chemical conditions, particularly oxidation, have a tendency to produce dangerous by-products. Among chemicals that undergo this transformation there are phenolic compounds which are quite usual contaminants in industrial wastewaters. Adsorption of phenolic compounds dissolved in aqueous solution by using industrial activated carbon is an interesting alternative since it makes possible to achieve a practically complete removal of the polluting compounds without any negative consequence.

To this purpose, new equilibrium data for two pseudo binary systems: a) activated carbon - aqueous solutions of phenol; b) activated carbon - aqueous solutions of dinitro-o-cresol, along with new experimental data for the pseudo ternary system: c) activated carbon - aqueous solutions of both phenol and dinitro-o-cresol, were measured at 298.15 K and 308.15 K, after a proper characterization of the adsorption material as received by SICAV (Italy).

All the pseudo binary SLE data are in good agreement with corresponding literature data, while for the pseudo ternary SLE is not possible any comparison. SLE data were satisfactorily correlated by a Freundlich based competitiv model.

1. Experimental section

1.1 Materials

The main characteristics of the activated carbon, as measured by us, are: total Surface Area: 327 m^2/g (N2 BET method); Single Point Total Pore Volume of pores less than 1272 Å at P/Po = 0.9845: 0.2214 cm^3/g; Average Pore Diameter (4V/A by Langmuir): 20.02 Å; Moisture Content: 3.10 %; Iodine Number: 800 mg/g; Apparent Density: 400 kg/m^3. The as-received powdered activated carbon was sieved and the 125÷150 μm fraction was used to perform the equilibrium experimental tests. Phenol (component A; MW=94.1) and 4,6-dinitro-o-cresol (DNOC; component B; MW=198.1) were bought from Aldrich. De-ionized water was obtained from a reverse osmosis laboratory device (ROS-50T).

1.2 Apparatus and Experimental Procedures

Adsorption quantification of phenol and/or DNOC dissolved in liquid phase was carried out in specially designed jacketed glass-stoppered flasks having a volume capacity of 250 ml. A known quantity (typically, 1 g) of activated carbon, having predetermined moisture content, was placed in several of these cells. According to experimental procedure followed by other Authors (e.g.: Edgehill and Lu, 1998) a constant quantity of organic aqueous solution (typically, 100 ml) with a predetermined composition was poured into the flasks. The cells content was kept at constant temperature by circulating in the jacket a stream of water coming from a controlled water bath (Heto Birkerød thermostat). The experimental equilibrium measurements were carried out at 298 ± 0.1 K and at 308 ± 0.1 K. Stirring of the solutions inside the flasks was obtained by magnetic stirring at controlled speed. To prevent photodecomposition of organic compounds, flasks were covered with aluminium foils. Preliminarily, it was verified that practical equilibrium is always reached in a time much lower than 30 hours. At the end of equilibration, stirring was stopped, activated carbon was allowed to settle and, to remove the finest solid particles, the recovered solution was filtered by Supelco filter (0.45μm pore diameter). The residual concentration of organic compound/s in the equilibrated aqueous solutions, C_{ej}, (g/l) were determined by means of a UV-VIS spectrophotometer (Perkin Elmer Lambda 2S), previously calibrated. The measured quantity was the typical assorbance of each organic compound, which is linearly related to the concentration. The concentration of each phenolic compound in the solid phase was calculated using the material balance equations:

$$q_{ej} = \frac{(C_{ij} - C_{ej})V}{m} \qquad j = A, B \tag{1}$$

where: C_{iA} and C_{iB} are the initial liquid phase concentrations (g/l) of A and B respectively; C_{eA} and C_{eB} are the equilibrium liquid phase concentrations (g/l) of A and B respectively; q_{eA} and q_{eB} are the equilibrium solid phase concentrations in grams of A for each gram of activated carbon (g/g); m is the mass of activated carbon (g), V is the volume of the solution in liters .

2. Results and Discussion

2.1 Pseudo Binary Systems

All the measured SLE data (q_e, C_e) are reported in Table 1. Freundlich equation ($q_e = K_F C_e^n$) was used to fit the experimental data where K_F has been expressed as a linear function of temperature in the range between 298.15 K and 398.15 K.

$$q_{e,j} = \left(K_{1j} + K_{2j} \cdot T\right) \cdot C_{ej}^{n_j} \qquad j = A, B \tag{2}$$

The following Objective Function (OF) was minimized in order to find the numerical values of the model parameters: K_{1j}, K_2j, and n_j for each component.

$$OF\left(K_{1j}, K_{2j}, n_j\right) = \sum_{i=1}^{N_j} \left(\frac{q_{ej}^{\exp} - q_{ej}^{cal}}{q_{ej}^{\exp}} \right)_i^2 \qquad j = A, B \tag{3}$$

Table 1. Experimental SLE Data for the Pseudo Binary Systems.

Test N.	T (K)	Activated carbon–aqueous solutions of Phenol		Activated carbon-aqueous solutions of DNOC	
		C_{eA} (g/l)	q_{eA} (g/g)	C_{eB} (g/l)	q_{eB} (g/g)
1	298.15	0.0034	0.015	0.00073	0.064
2	298.15	0.0045	0.023	0.00077	0.061
3	298.15	0.0050	0.015	0.00083	0.058
4	298.15	0.0067	0.023	0.00096	0.058
5	298.15	0.0073	0.033	0.00162	0.072
6	298.15	0.0077	0.033	0.00164	0.072
7	298.15	0.0120	0.027	0.00213	0.079
8	298.15	0.0120	0.027	0.00223	0.079
9	298.15	0.0148	0.042	0.00566	0.099
10	298.15	0.0164	0.033	0.00576	0.105
11	298.15	0.0170	0.042	0.00600	0.094
12	298.15	0.0186	0.033	0.00930	0.104
13	298.15	0.0300	0.054	0.01046	0.100
14	298.15	0.0310	0.054	0.01316	0.133
15	298.15	0.0401	0.051	0.02060	0.106
16	298.15	0.1070	0.055	0.02168	0.130
17	298.15	0.1072	0.055	0.02199	0.108
18	298.15	0.1210	0.066	0.02588	0.118
19	298.15	0.1262	0.076	0.03854	0.132
20	298.15	0.1270	0.075	0.04157	0.142
21	298.15	0.1283	0.064	-	-
22	308.15	0.0051	0.016	0.00018	0.055
23	308.15	0.0056	0.016	0.00019	0.054
24	308.15	0.0060	0.018	0.00034	0.043
25	308.15	0.0088	0.020	0.00035	0.043
26	308.15	0.0089	0.021	0.00085	0.052
27	308.15	0.0140	0.021	0.00087	0.052
28	308.15	0.1540	0.038	0.00251	0.067
29	308.15	0.0160	0.021	0.00263	0.069
30	308.15	0.0290	0.027	0.00665	0.079
31	308.15	0.0290	0.027	0.00994	0.079
32	308.15	0.0350	0.031	0.01891	0.091
33	308.15	0.0360	0.031	0.01903	0.091
34	308.15	0.0710	0.035	0.02584	0.100
35	308.15	0.0790	0.033	0.02606	0.106
36	308.15	0.0790	0.033	0.02606	0.110
37	308.15	0.0860	0.032	0.02611	0.108
38	308.15	0.0880	0.033	0.02621	0.098
39	308.15	0.1150	0.039	0.03537	0.092
40	308.15	0.1190	0.039	0.03537	0.095
41	308.15	0.1350	0.042	0.04397	0.106
42	308.15	0.1370	0.041	0.04397	0.109

The results are summarized in Table 2 along with the per cent Absolute Average Deviation (AAD) defined as:

$$AAD_j = \frac{100}{N_j} \sum_{i=1}^{N_j} \left(\frac{\left| q_{ej}^{\exp} - q_{ej}^{cal} \right|}{q_{ej}^{\exp}} \right)_i \qquad j = A, B \qquad (4)$$

Table 2. Results obtained by fitting Pseudo Binary SLE experimental data.

Organic Component	OF_j	K_{1j}	K_{2j}	n_j	AAD_j
Phenol (A)	1,3	1.647	-0.0051064	0.3	12.16
DNOC (B)	0.28	1.8585	-0.0053595	0.2	6.86

Where N_j is the number of experimental measurements for each component. When comparable, our SLE data are in good agreement with literature data (Edgehill and Lu, 1998; Khan, et al. 1999; Ravi, et al. 1998). Figure 1 shows the comparison between experimental and calculated SLE data as function of phenol (a) and DNOC (b) composition in the aqueous solution, at 298.15 K and 308.15 K. As can be seen, in both cases, the agreement is satisfactory and, consequently, the Freundlich model can be confidently used, in combination with the parameters reported in Table 2, to predict SLE for the pseudo binary systems.

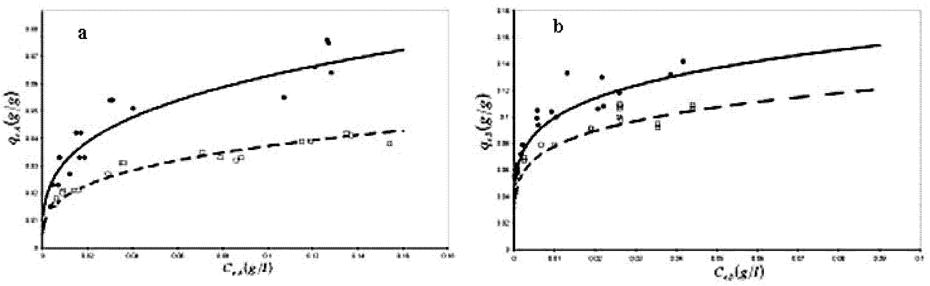

Figure 1. Comparison between measured and calculated SLE compositions for the Pseudo Binary Systems: a) activated carbon - aqueous solutions of Phenol and, b) activated carbon - aqueous solutions of DNOC. —— Calculated at 298.15 K; ● Measured at 298.15 K; — — Calculated at 308.15 K; □ Measured at 308.15 K.

2.2 Pseudo Ternary System

All the measured SLE data (qe, Ce) are reported in Table 3. The values of the activities in the aqueous solutions of phenol and DNOC, a_A and a_B, respectively, were calculated using equations (5) and were compared with the values of the fractions on water free bases, X_A and X_B, respectively.

$$a_J = \frac{q_{eJ}}{\left(K_{1J} + K_{2J} \cdot T\right) \cdot C_{eJ}^{n_J}} \qquad j = A, B \qquad (5)$$

a_A differs significantly from X_A and a_B differs significantly from X_B, as a consequence of the non negligible interactions existing between molecules of phenol and molecules of DNOC when both these compounds are dissolved in the aqueous solutions. For this reason it is not possible to predict SLE related to the pseudo ternary systems by only using pseudo binary model parameters.

Table 3. Experimental SLE Data for the Pseudo Ternary System: activated carbon – aqueous solutions of Phenol and 4,6 Dinitro-o-Cresol at 298.15 K and 308.15 K.

Test N.	C_{eA} (g/l)	q_{eA} (g/g)	C_{eB} (g/l)	q_{eB} (g/g)	X_A	a_A	a_B	T (K)
1	0.020	0.050	0.008	0.085	0.714	1.290872	0.869078	298.15
2	0.023	0.048	0.007	0.088	0.766	1.188352	0.924104	298.15
3	0.041	0.095	0.049	0.149	0.455	1.977474	1.060242	298.15
4	0.043	0.091	0.049	0.151	0.467	1.867339	1.074473	298.15
5	0.044	0.029	0.013	0.089	0.772	0.590996	0.825770	298.15
6	0.044	0.029	0.013	0.089	0.772	0.590996	0.825770	298.15
7	0.050	0.049	0.023	0.096	0.685	0.961009	0.794664	298.15
8	0.050	0.050	0.023	0.101	0.685	0.980621	0.836053	298.15
9	0.051	0.049	0.023	0.100	0.689	0.955317	0.827775	298.15
10	0.052	0.047	0.021	0.104	0.712	0.911002	0.876693	298.15
11	0.056	0.030	0.037	0.116	0.602	0.568705	0.873123	298.15
12	0.139	0.088	0.040	0.094	0.776	1.269991	0.696584	298.15
13	0.142	0.070	0.025	0.089	0.850	1.003769	0.724536	298.15
14	0.170	0.072	0.052	0.103	0.765	0.978183	0.724260	298.15
15	0.171	0.069	0.053	0.099	0.763	0.925777	0.693486	298.15
16	0.037	0.026	0.015	0.058	0.711	0.942304	0.646655	308.15
17	0.038	0.026	0.015	0.057	0.717	0.934795	0.635506	308.15
18	0.050	0.033	0.024	0.110	0.675	1.092700	1.116384	308.15
19	0.052	0.029	0.024	0.106	0.684	0.949019	1.075788	308.15
20	0.058	0.041	0.018	0.106	0.763	1.298475	1.139500	308.15
21	0.059	0.023	0,034	0.120	0.634	0.724687	1.135922	308.15
22	0.060	0.037	0.026	0.106	0.697	1.159937	1.058703	308.15
23	0.062	0.034	0.020	0.109	0.756	1.055454	1.147318	308.15
24	0.063	0.032	0,026	0.107	0.708	0.988612	1.068691	308.15
25	0.096	0.038	0.073	0.151	0.568	1.034619	1.226805	308.15
26	0.097	0.036	0.073	0.151	0.570	0.977123	1.226805	308.15
27	0.105	0.033	0.083	0.220	0.558	0.874652	1.742088	308.15
28	0.108	0.023	0.087	0.201	0.554	0.604476	1.576723	308.15

To account for the above mentioned molecular interactions, it is used the Wilson Equation (Wilson, 1964) previously parametrized by fitting all the SLE experimental data reported on Table 3. To this purpose, it was minimized the following OF:

$$OF\left(\Lambda_{AB},\Lambda_{BA}\right)=\sum_{i=1}^{N_j}\left(\frac{q_{eA}^{\exp}-q_{eA}^{cal}}{q_{eA}^{\exp}}\right)_i^2+\sum_{i=1}^{N_j}\left(\frac{q_{eB}^{\exp}-q_{eB}^{cal}}{q_{eB}^{\exp}}\right)_i^2+\sum_{i=1}^{N_j}\left(\frac{q_{eT}^{\exp}-q_{eT}^{cal}}{q_{eT}^{\exp}}\right)_i^2 \qquad (6)$$

Where: q_{eA}^{exp} and q_{eB}^{exp} are the experimental data, $q_{eT} = q_{eA} + q_{eB}$, whlile q_{eA}^{cal} and q_{eB}^{cal} are the corresponding quantities calculated by using the activity of phenol and the activity of DNOC obtained with the Wilson model (a_{Amod} and a_{Bmod}). The ratio between molar volumes of A and B which appears inside Λ_{AB} and Λ_{BA} is 0.708.

Table 4 shows the results obtained by fitting pseudo ternary SLE experimental data. A comparison between experimental and calculated values of q_{eA} and q_{eB} are reported on Figure 2. Comparison of the values of AADj reported on Table 2 with the corresponding values reported on Table 4 show that, in any case, simulation of pseudo ternary SLE behaviour is more difficult than simulation of pseudo binary SLE behaviour. In fact, the values of AADj reported on Table 2 are about 50% of the corresponding values reported in Table 4. However, Figures 1 and 2 shows that deviation between calculated and experimental equilibrium adsorbate concentration in the solid phase are always well distributed. This result is the direct consequence of the introduction of the Wilson model for simulating pseudo ternary SLE since, the simple prediction, gives rise to completely undistributed deviations for the calculated equilibrium adsorbate concentration in the solid phase along with higher values (up to almost 400%) for the two AADj.

Table 4. Results obtained by fitting Pseudo Ternary SLE experimental data.

Organic Component	OF	$-\frac{\lambda_{AB}-\lambda_{AA}}{R}$ (K)	$-\frac{\lambda_{BA}-\lambda_{BB}}{R}$ (K)	AAD$_j$
Phenol (A)	4.5	6635.1800	466.6467	20.6
DNOC (B)				16.8

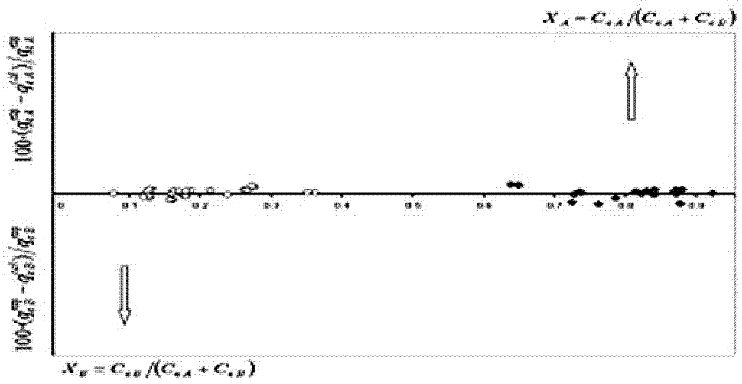

Figure 2. Per cent Relative Deviation between exp. and calc. $q_{e,A}$ and $q_{e,B}$ for the Pseudo Ternary System at 298.15 K and 308.15 K. ◆ Phenol; ○ DNOC.

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