Adsorption Equilibrium Data of Binary Liquid Mixtures Containing *n*-Alkanes, Cycloalkanes, and 1-Alkanols on Activated Carbons

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Surface excess isotherms of seven binary liquid mixtures with hexane, 2,2,4-trimethylpentane (isooctane), cyclohexane, methylcyclohexane, ethanol, 1-propanol, and 2-ethylhexanol on several activated carbons at 298.15 K are presented. The surface excess depends on the accessibility of the pore system and on the interaction energies between adsorbate and adsorbent which can be extremely high due to superficial polar groups. For future modelling the characterization of the adsorbents is extended by Boehm titrations in order to determine the concentration of polar functional surface groups.

Introduction

Activated carbons are widely used in purification and separation processes of liquid mixtures, particularly in the environmental technology or for high-grade products. However, due to the lack of data an experimental investigation of the adsorption equilibrium has usually to be carried out in order to determine the calculation basics for engineering. On this account we present adsorption equilibrium data for binary liquid mixtures with *n*-alkanes, cycloalkanes and 1-alkanols on four activated carbons extending our previous work.[1]

The most meaningful presentation of the liquid-phase adsorption equilibrium is the surface excess Γ_1^e, which is defined as

$$\Gamma_1^e = \frac{n^\circ}{m_a}(x^\circ_1 - x_1^b) \qquad (1)$$

In eq 1 n° describes the amount of substance of the liquid mixture with its mole fraction x°_1, which is given onto the adsorbent, while x_1^b denotes the equilibrium molar fraction in the bulk phase. Γ_1^e is related to the mass of the adsorbent m_a. The surface excess data presented can be used for a thermodynamically consistent modeling[1] of surface excess isotherms using the Adsorbate Solid Solution Theory ASST.

Experimental Section

Materials. Four commercially available activated carbons were used as adsorbents, as characterized in Table 1. The activated carbons were selected from different raw materials and activation procedures in order to consider the influence of pore size distribution and polar functional groups. The activated carbons were dried and outgassed[2] for at least 4 h at 120 °C below 1 hPa.

To determine the polar (acidic and basic) surface groups, Boehm titrations[3] were carried out. The amount of the basic surface groups were determined by neutralization with HCl. The amount of the carboxylic functional groups is obtained by titration with $NaHCO_3$. The lactonic groups are determined by difference of the consumption of Na_2CO_3 and $NaHCO_3$ and the phenolic groups by the difference

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Table 1. Characterization of the Used Activated Carbons

	Carpolur W-S (LURGI)	ROTH (ROTH)	L3S (ELF)	CPL (ELF)
raw material	hard coal	peat	pine wood	pine wood
activation procedure	steam	steam	steam, acid washed	phosphoric acid
BET surface area/$m^2 \cdot g^{-1}$	500	750	1150	1700
pH	9−10	9−10	4	4−7
acid solubility/%	12.0	5.5	0.5	2.0
total pore volume (N_2 isotherm)/$cm^3 \cdot g^{-1}$	0.297	0.441	0.659	1.122
amount of acidic surface groups/mmol·g^{-1}				
carboxylic	0.000	0.000	0.005	0.430
lactonic	0.000	0.000	0.105	0.115
phenolic	0.290	0.400	0.200	0.425
amount of basic surface groups/mmol·g^{-1}	2.100	1.180	0.395	0.170

Table 2. Surface Excess Data of Hexane (1) + Isooctane (2) on Activated Carbons at 25 °C

Carpolur W-S		ROTH		L3S		CPL	
x_1^b	Γ_1^e [a]	x_1^b	Γ_1^e [a]	x_1^b	Γ_1^e [a]	x_1^b	Γ_1^e [a]
0.035	0.53	0.028	0.68	0.215	0.26	0.052	0.13
0.096	0.44	0.088	0.62	0.256	0.24	0.106	0.12
0.246	0.53	0.197	0.61	0.309	0.25	0.217	0.14
0.299	0.40	0.244	0.58	0.462	0.26	0.261	0.08
0.408	0.34	0.297	0.58	0.528	0.24	0.310	0.18
0.453	0.40	0.399	0.55	0.568	0.22	0.415	0.13
0.523	0.32	0.455	0.46	0.628	0.19	0.465	0.18
0.564	0.27	0.507	0.56	0.683	0.21	0.528	0.24
0.626	0.24	0.561	0.38	0.735	0.13	0.571	0.09
0.684	0.12	0.622	0.34	0.847	0.08	0.629	0.19
0.734	0.14	0.679	0.29	0.892	0.08	0.686	0.05
0.788	0.04	0.734	0.14	0.945	0.03	0.736	0.12
0.845	0.11	0.784	0.18			0.787	0.07
0.891	0.10	0.843	0.18			0.847	0.04
0.944	0.04	0.889	0.11			0.893	0.04
		0.944	0.03			0.945	−0.01

[a] mmol·g^{-1}

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Table 3. Surface Excess Data of Hexane (1) + Methylcyclohexane (2) on Activated Carbons at 25 °C

Carpolur W-S		ROTH		L3S		CPL	
x_1^b	Γ_1^e [a]	x_1^b	Γ_1^e [a]	x_1^b	Γ_1^e [a]	x_1^b	Γ_1^e [a]
0.044	0.45	0.046	0.36	0.051	0.26	0.053	0.09
0.098	0.46	0.099	0.39	0.102	0.29	0.107	0.11
0.152	0.38	0.151	0.44	0.154	0.30	0.159	0.10
0.203	0.37	0.201	0.44	0.206	0.31	0.210	0.13
0.255	0.35	0.252	0.43	0.258	0.30	0.263	0.12
0.308	0.32	0.306	0.45	0.310	0.27	0.315	0.05
0.359	0.27	0.355	0.36	0.363	0.24	0.368	0.03
0.411	0.26	0.410	0.30	0.416	0.17	0.420	−0.04
0.464	0.25	0.462	0.26	0.470	0.18	0.474	−0.03
0.519	0.20	0.517	0.25	0.524	0.09	0.528	−0.11
0.573	0.18	0.571	0.21	0.578	0.12	0.583	−0.09
0.626	0.17	0.625	0.18	0.631	0.09	0.636	−0.10
0.784	0.07	0.684	0.04	0.685	0.07	0.689	−0.10
0.840	0.05	0.735	0.15	0.738	0.03	0.741	−0.10
0.893	0.02	0.784	0.07	0.791	0.00	0.793	−0.09
0.945	0.01	0.840	0.03	0.842	−0.02	0.844	−0.09
		0.892	0.03	0.893	−0.02	0.895	−0.08
		0.945	0.01	0.945	−0.01	0.946	−0.04

[a] mmol·g^{-1}.

Table 4. Surface Excess Data of Ethanol (1) + Isooctane (2) on Activated Carbons at 25 °C

Carpolur W-S		ROTH		L3S		CPL	
x_1^b	Γ_1^e [a]	x_1^b	Γ_1^e [a]	x_1^b	Γ_1^e [a]	x_1^b	Γ_1^e [a]
0.004	1.66	0.001	1.52	0.023	1.37	0.007	1.91
0.095	2.06	0.093	2.40	0.132	1.40	0.076	4.06
0.145	1.95	0.131	2.31	0.175	1.59	0.113	4.32
0.201	2.02	0.252	1.88	0.237	1.52	0.135	4.59
0.248	1.88	0.321	2.15	0.348	1.14	0.224	4.49
0.325	1.71	0.411	1.51	0.396	1.30	0.287	4.29
0.446	1.14	0.497	1.42	0.464	0.43	0.351	3.97
0.610	1.00	0.533	0.67	0.516	0.87	0.405	3.21
0.665	0.73	0.612	0.84	0.539	0.51	0.480	3.31
0.775	0.65	0.777	0.64	0.631	−0.02	0.510	2.18
0.842	0.19	0.842	0.24	0.792	−0.41	0.727	0.84
0.898	0.08	0.895	0.27	0.852	−0.51	0.778	0.72
0.946	0.03	0.947	−0.06	0.905	−0.47	0.843	0.22
				0.951	−0.44	0.901	−0.10

[a] mmol·g^{-1}.

Table 5. Surface Excess Data of Ethanol (1) + Methylcyclohexane (2) on Activated Carbons at 25 °C

Carpolur W-S		ROTH		L3S		CPL	
x_1^b	Γ_1^e [a]	x_1^b	Γ_1^e [a]	x_1^b	Γ_1^e [a]	x_1^b	Γ_1^e [a]
0.004	1.31	0.079	1.02	0.006	1.42	0.010	2.16
0.067	1.51	0.134	1.18	0.058	1.86	0.040	3.21
0.101	1.57	0.188	1.28	0.107	1.70	0.092	3.75
0.172	1.63	0.247	1.15	0.169	1.95	0.143	4.33
0.231	1.48	0.303	0.95	0.231	1.61	0.192	4.21
0.281	1.52	0.357	0.78	0.283	1.51	0.243	4.09
0.339	1.31	0.411	0.43	0.339	1.36	0.302	3.49
0.407	1.13	0.526	−0.04	0.412	1.20	0.362	3.29
0.501	0.75	0.581	−0.20	0.500	0.74	0.430	2.75
0.513	0.71	0.634	−0.46	0.515	0.55	0.493	1.91
0.592	0.36	0.691	−0.62	0.596	0.19	0.557	1.54
0.630	0.42	0.747	−0.87	0.633	0.30	0.613	1.06
0.681	0.28	0.801	−0.98	0.686	0.04	0.677	0.52
0.747	0.07	0.852	−0.93	0.750	−0.15	0.736	−0.05
0.776	0.10	0.910	−0.83	0.780	−0.13	0.794	−0.40
0.844	−0.01	0.953	−0.58	0.846	−0.17	0.849	−0.55
0.898	−0.23			0.900	−0.42	0.907	−0.54
0.948	−0.10			0.950	−0.27	0.951	−0.39

[a] mmol·g^{-1}.

of the consumption of NaOH and Na_2CO_3. 0.05 mol/L solutions were used. The samples were stored in a shaking water bath for 24 h at 25 °C.

Table 6. Surface Excess Data of 1-Propanol (1) + Cyclohexane (2) on Activated Carbons at 25 °C

Carpolur W-S		ROTH		L3S		CPL	
x_1^b	Γ_1^e [a]	x_1^b	Γ_1^e [a]	x_1^b	Γ_1^e [a]	x_1^b	Γ_1^e [a]
0.026	1.40	0.020	1.59	0.034	1.16	0.017	2.42
0.074	1.31	0.129	1.66	0.072	1.36	0.062	2.65
0.134	1.32	0.181	1.46	0.140	1.43	0.126	2.86
0.186	1.18	0.243	1.62	0.254	1.29	0.168	2.66
0.294	0.90	0.286	1.28	0.360	0.83	0.337	2.45
0.351	0.96	0.349	1.19	0.408	0.73	0.455	1.66
0.400	0.80	0.398	1.05	0.467	0.52	0.514	0.99
0.459	0.92	0.453	0.89	0.522	0.18	0.564	1.04
0.516	0.50	0.566	0.64	0.574	0.39	0.623	0.70
0.569	0.55	0.624	0.49	0.630	0.08	0.676	0.55
0.625	0.43	0.676	0.43	0.684	−0.07	0.735	0.29
0.677	0.39	0.735	0.26	0.741	−0.13	0.789	0.12
0.734	0.28	0.786	0.28	0.793	−0.12	0.845	−0.02
0.787	0.28	0.893	0.13	0.846	−0.11	0.895	0.02
0.844	0.10			0.895	0.05	0.948	−0.07
0.894	0.10			0.947	−0.06		
0.946	0.03						

[a] mmol·g^{-1}.

Table 7. Surface Excess Data of 2-Ethylhexanol (1) + Cyclohexane (2) on Activated Carbons at 25 °C

Carpolur W-S		ROTH		L3S		CPL	
x_1^b	Γ_1^e [a]	x_1^b	Γ_1^e [a]	x_1^b	Γ_1^e [a]	x_1^b	Γ_1^e [a]
0.046	0.49	0.039	0.71	0.039	1.02	0.027	1.87
0.092	0.48	0.086	0.80	0.093	0.91	0.074	1.81
0.148	0.33	0.144	0.62	0.249	0.73	0.178	1.68
0.253	0.30	0.250	0.51	0.293	0.71	0.238	1.20
0.303	0.24	0.295	0.52	0.348	0.69	0.281	1.20
0.469	0.12	0.351	0.33	0.480	0.61	0.343	0.84
0.573	0.09	0.464	0.30	0.790	0.13	0.458	0.82
0.733	0.04	0.628	0.24	0.837	0.12	0.474	0.86
0.792	0.03	0.680	0.21			0.620	0.65
0.839	0.01	0.791	0.03			0.680	0.37
		0.837	0.07			0.721	0.53
						0.786	0.33
						0.931	0.01

[a] mmol·g^{-1}.

Table 8. Surface Excess Data of Ethanol (1) + 2-Ethylhexanol (2) on Activated Carbons at 25 °C

Carpolur W-S		ROTH		L3S		CPL	
x_1^b	Γ_1^e [a]	x_1^b	Γ_1^e [a]	x_1^b	Γ_1^e [a]	x_1^b	Γ_1^e [a]
0.069	0.74	0.024	0.71	0.052	0.27	0.054	0.13
0.183	0.72	0.077	0.86	0.098	0.25	0.097	0.20
0.284	0.69	0.290	0.80	0.168	0.13	0.309	0.13
0.402	0.50	0.396	0.57	0.272	0.09	0.522	−0.09
0.514	0.26	0.466	0.36	0.404	−0.00	0.584	−0.11
0.579	0.19	0.516	0.24	0.415	−0.09	0.687	−0.23
0.623	0.29	0.627	0.12	0.523	−0.15	0.804	−0.34
0.684	−0.01	0.684	0.01	0.632	−0.25	0.948	−0.37
0.800	0.01	0.718	−0.09	0.687	−0.28		
0.846	−0.06	0.847	−0.16	0.719	−0.25		
0.897	−0.01	0.948	−0.17	0.848	−0.36		
0.947	−0.12			0.949	−0.40		

[a] mmol·g^{-1}.

The liquids used were of analytical grade, which was verified by GC: hexane, 2,2,4-trimethylpentane (isooctane), cyclohexane, methylcyclohexane, ethanol, 1-propanol, and 2-ethylhexanol. The purities were better than 99.0% (GC). The water content was below 200 ppm (mass).

Procedure. The experimental arrangement for the static adsorption equilibrium measurement was previously described in detail.[1] Adsorptions from binary mixtures were

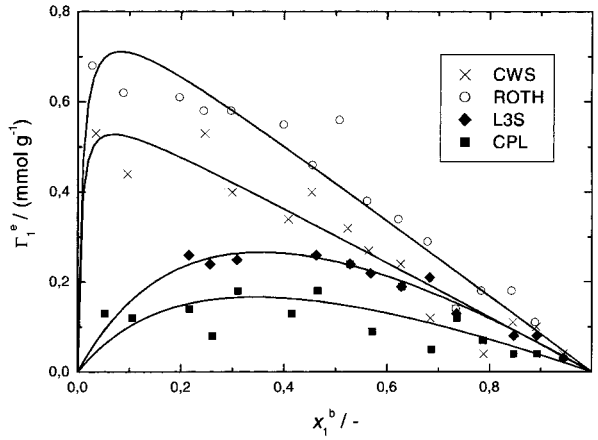

Figure 1. Surface excess of hexane (1) + isooctane (2) on activated carbons at 25 °C.

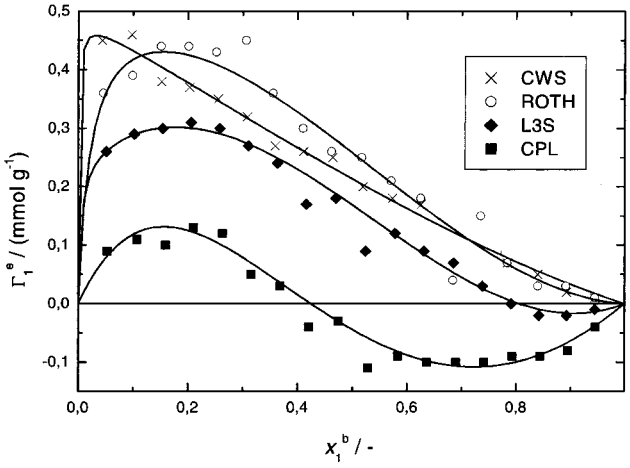

Figure 2. Surface excess of hexane (1) + methylcyclohexane (2) on activated carbons at 25 °C.

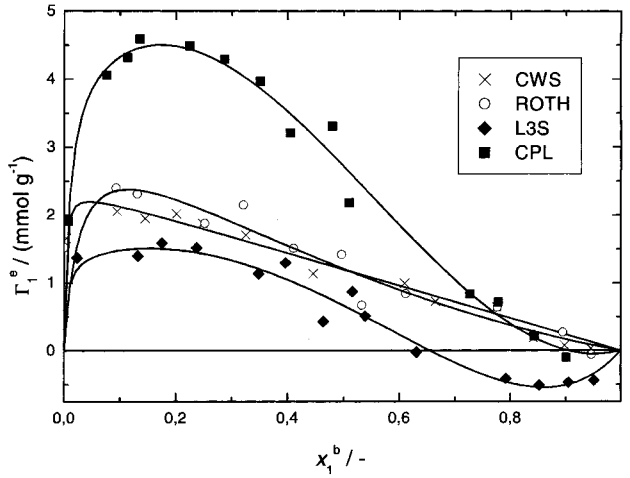

Figure 3. Surface excess of ethanol (1) + isooctane (2) on activated carbons at 25 °C.

carried out by the immersion method. The vials were stored for equilibration in an incubator for 7 days. The samples were analyzed using a Hewlett-Packard GC system consisting of a HP5890A gas chromatograph with a FID detector and a fused silica capillary column Optima 1 from Macheray & Nagel, Germany, in combination with a HP7673 autosampler.

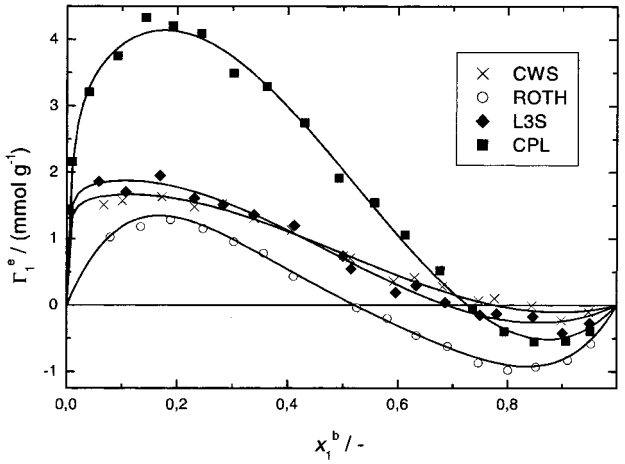

Figure 4. Surface excess of ethanol (1) + methylcyclohexane (2) on activated carbons at 25 °C.

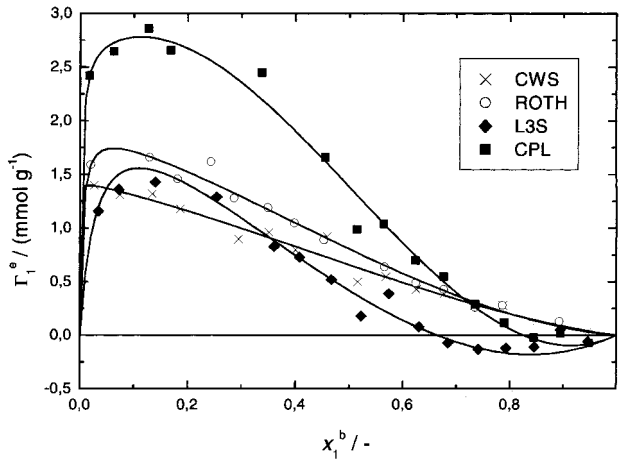

Figure 5. Surface excess of 1-propanol (1) + cyclohexane (2) on activated carbons at 25 °C.

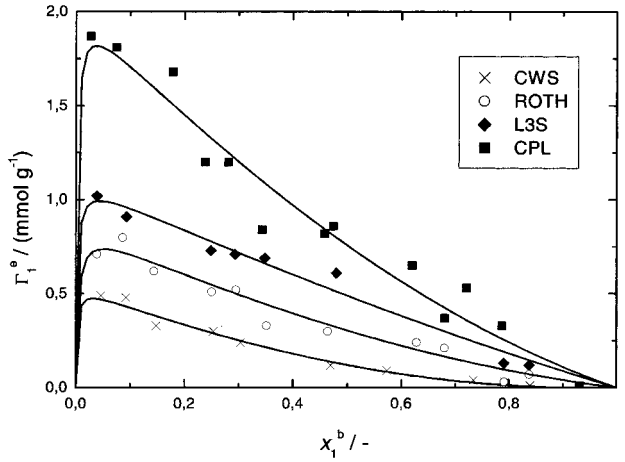

Figure 6. Surface excess of 2-ethylhexanol (1) + cyclohexane (2) on activated carbons at 25 °C.

Results

The surface excess isotherms shown in Figures 1−7 and the data shown in Tables 2−8 comply with isotherm types I−V of the classification of Schay and Nagy.[4]

As far as fluids are nonpolar, the maxima of the surface excess is below 1 mmol·g^{-1} (Figures 1 and 2). The striking factors are the interaction energies between adsorbate and

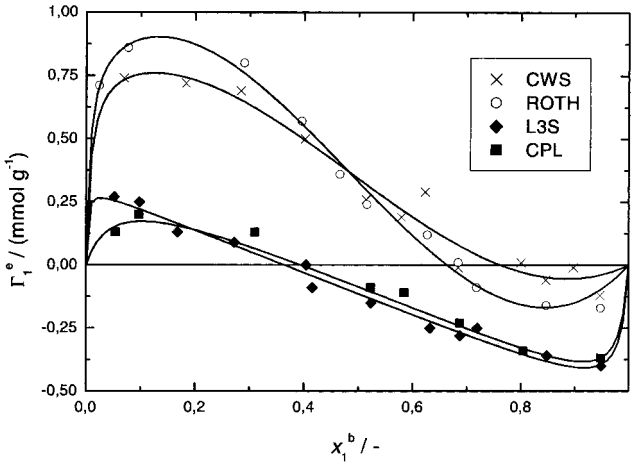

Figure 7. Surface excess of ethanol (1) + 2-ethylhexanol (2) on activated carbons at 25 °C.

adsorbent and the accessibility of the pore system: hexane is the preferentially adsorbed component in these systems because of its smaller size and showing higher enthalpies of wetting.[2]

Mixtures with a polar and an nonpolar component show significantly higher surface excess maxima (Figures 3−6). In this case, the polar molecule is generally preferentially adsorbed due to stronger − polar − interactions. Especially the activated carbon CPL shows very high surface excess maxima up to 5 mmol·g^{-1}. This can be explained by a strong interaction between the strongest acidic surface groups (the carboxylic groups) and the hydroxyl group.

With two polar components, the surface excess is much smaller (Figure 7) due to mutual competition for the polar surface sites.

The surface excess isotherms have a mean deviation of ∼0.05 mmol·g^{-1}. This uncertainty results mainly from the GC analyses.

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