Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Possibility of chiral recognition by adsorption on enantiomorphous crystals: the impact of crystal surface polarity.

Vladimir Yu. Gus'kov,*[a] Gulshat A. Gallyamova,[a] Natalia I. Sairanova[a], Yulia F. Sharafutdinova[a], Leonard M. Khalilov[b], Timur A. Mukhametzyanov[c], Ilya M. Zinoviev[a] and Yulia Yu. Gainullina[a]

[a]Bashkir State University, 32 Zaki Validi str., Ufa, Russia.
[b]Institute of Petrochemistry and Catalysis RAS, 141 Oktyabrya av., Ufa, Russia
[c]A.M. Butlerov Chemical Institute, Kazan Federal University, Kremlevskaya Str. 18, Kazan 420008, Russia
*corresponding author, Email: guscov@mail.ru

Polarity calculations

The inverse gas chromatography was used to obtain polarity values. Two methods were applied: linear free energy relationship method (LFER) and Dong polarizability method.

LFER method

Hexane, heptane, octane, nonane, decane, undecane, benzene, toluene, ethanol, n-propanol, n-butanol, i-propanol, i-butanol and ethyl acetate (all chemically pure, Chimreactivsnab, Russia) were used as probes. The probes were injected as sample vapours at the minimum possible amount, which allowed us to consider adsorption processes in the column that were closer to ideal linear chromatography, making it possible to equate specific retention volume V_g with the adsorption-desorption equilibrium constants. From

$$\Delta F = - RTlnV_g \qquad (1)$$

differential isosteric free energies ($-\Delta F$, kJ/mol) of adsorption were calculated.

Contributions of intermolecular interactions to adsorption free energy and surface polarity were evaluated using the method of the linear free energy relationship (LSER):

$$-\Delta F = \Delta F^{disp} + \Delta F^{spec} + \Delta F^{da} \quad (2)$$

$$-\Delta F = K_1\alpha_B + K_2\left(\frac{2\mu_B^2}{3kT} + \alpha_B\right) + K_3 Wb^a + K_4 Wb^d + K_5 \quad (3)$$

where ΔF^{disp}, ΔF^{spec} and ΔF^{da} are free energies of dispersion, orientation and induction, and donor-acceptor interactions; K_1–K_5 are coefficients characterizing the sorbent surface properties: dispersion, induction and orientation, electron-donor and electron-acceptor, respectively; α_B, μ_B, $W_b{}^a$ and $W_b{}^d$ are, respectively, polarizability, dipole moment, and electron-acceptor and electron-donor constants of the adsorbate. k is the Boltzmann constant, and T is temperature, K. Eq. (3) coefficients were calculated by multiple regression analysis in REGRES 23 software (ENEK Group, Russia).

From coefficients K_1–K_5, ΔF^{disp}, ΔF^{spec} and ΔF^{da} were calculated. We used the average impact of ΔF^{spec} and ΔF^{da} in ΔF as parameter (P) to compare initial and modified sorbent polarities:

$$P = \frac{\sum\left(\frac{\Delta F_n^{spec} + \Delta F_n^{da}}{\Delta F_n}\right)}{n_{probes}} \cdot 100\% - P_{GCB} \quad (6)$$

where n_{probes} is the number of adsorbates. As a reference, the P_{GCB} graphitized carbon black was used.

Dong method

The second method is in using linear dependence of free energy of sorption of alkanes from the polarizability (Dong method). At this method, it is suggested, that the alkanes interacts with surface only by dispersion interactions. The energy of nonspecific interactions of other molecules considered as a sorption energy of hypothetic alkane with the same polarizability. The energy of specific interactions can be calculated as a difference between the total sorption energy and the energy of nonspecific interactions.

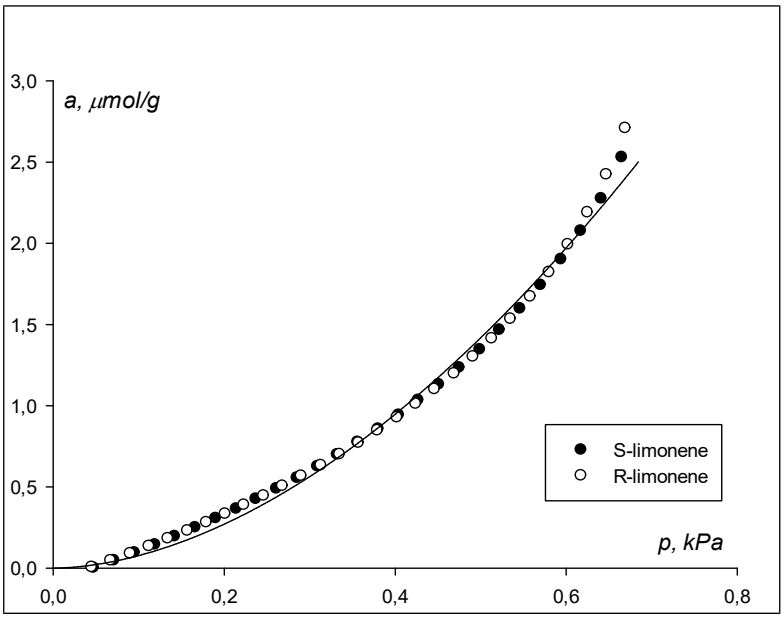

Figure 1S. Isotherms of limonene vapors adsorption at 50 °C by hippuric acid

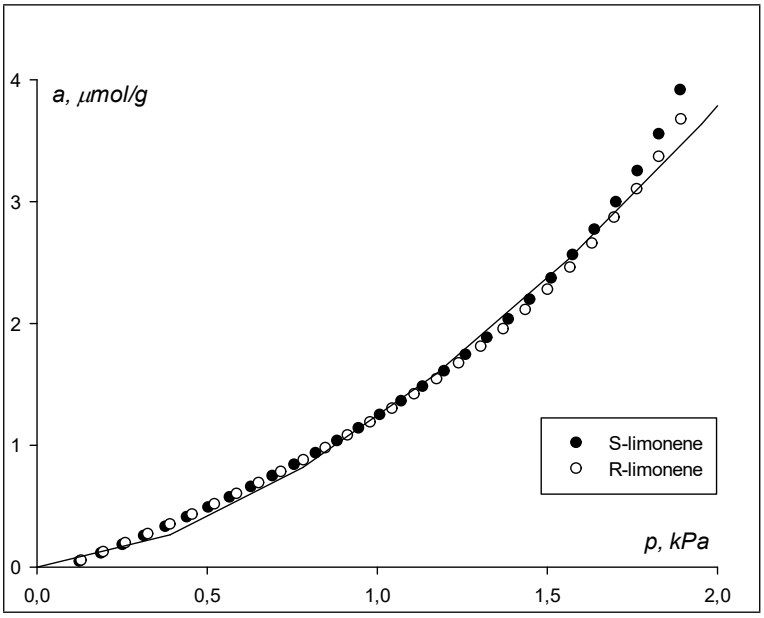

Figure 2S. Isotherms of limonene vapors adsorption at 70 °C by hippuric acid

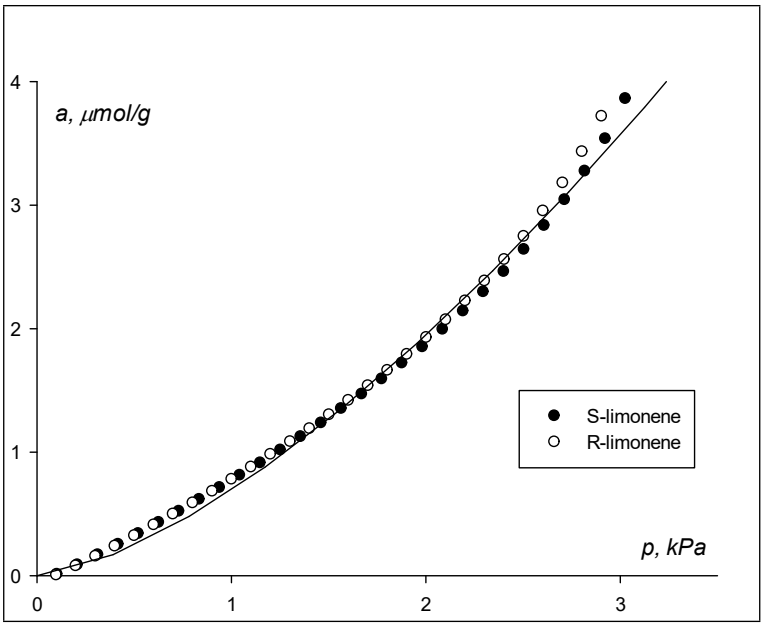

Figure 3S. Isotherms of limonene vapors adsorption at 80 °C by hippuric acid

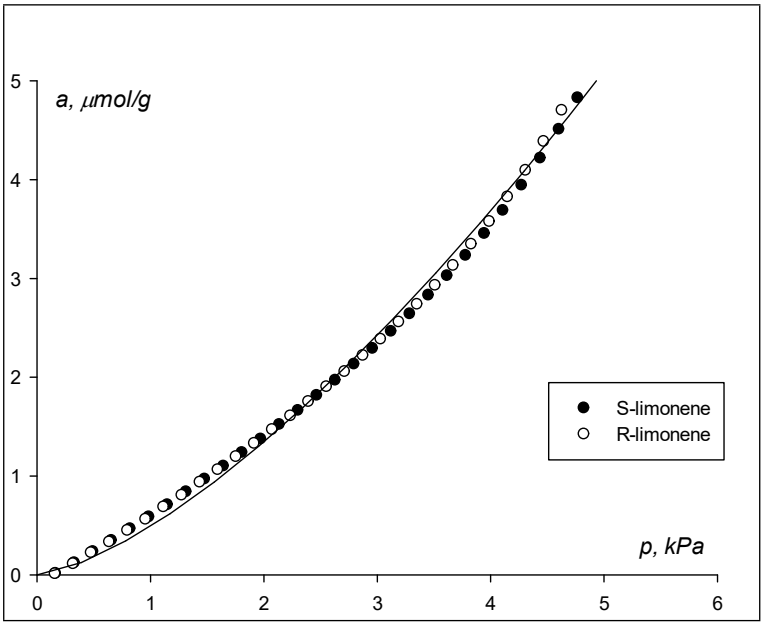

Figure 4S. Isotherms of limonene vapors adsorption at 90 °C by hippuric acid

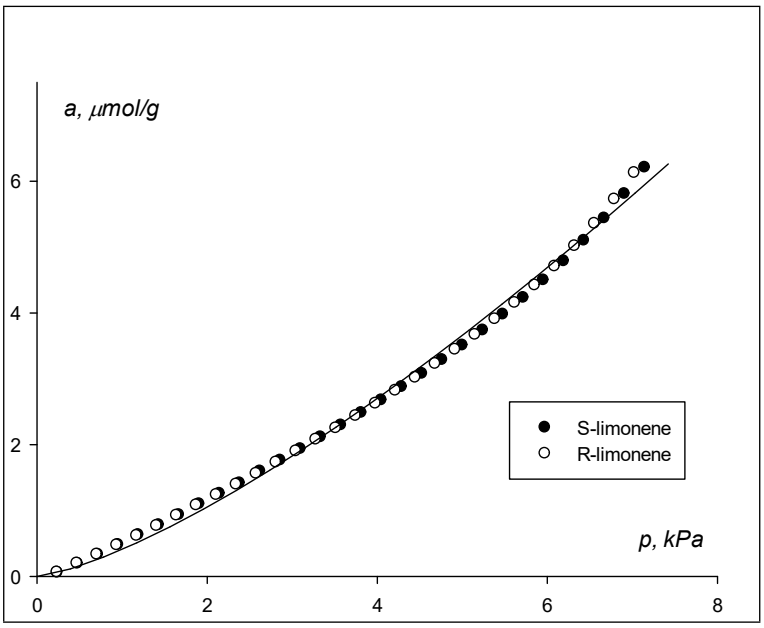

Figure 5S. Isotherms of limonene vapors adsorption at 100 °C by hippuric acid

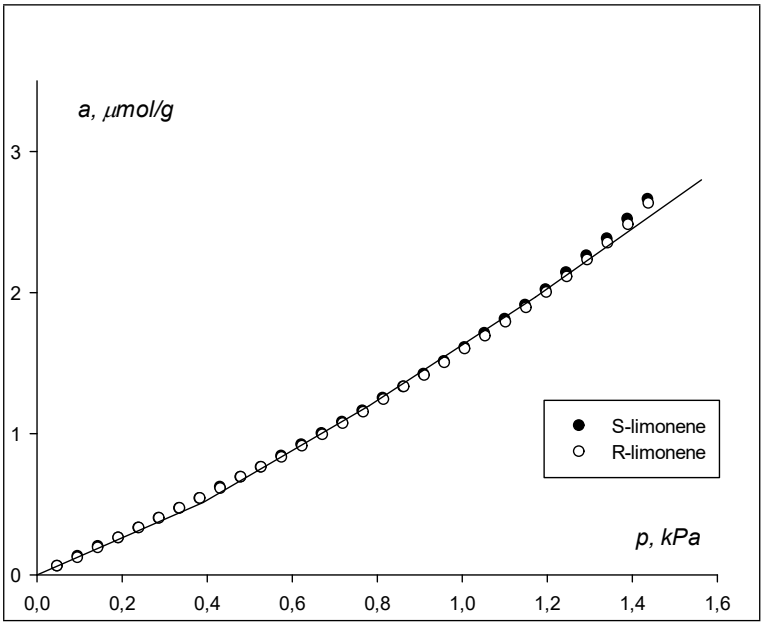

Figure 6S. Isotherms of limonene vapors adsorption at 80 °C by phloroglucinol

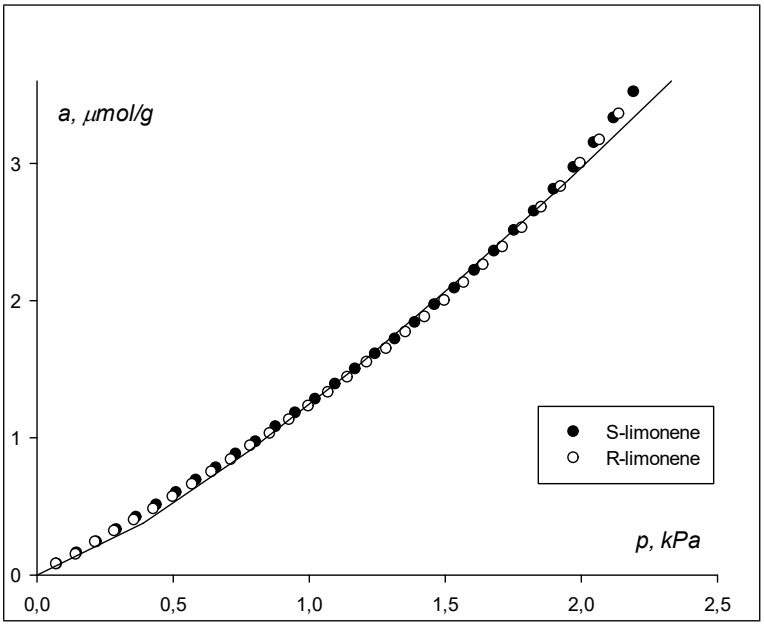

Figure 7S. Isotherms of limonene vapors adsorption at 90 °C by phloroglucinol

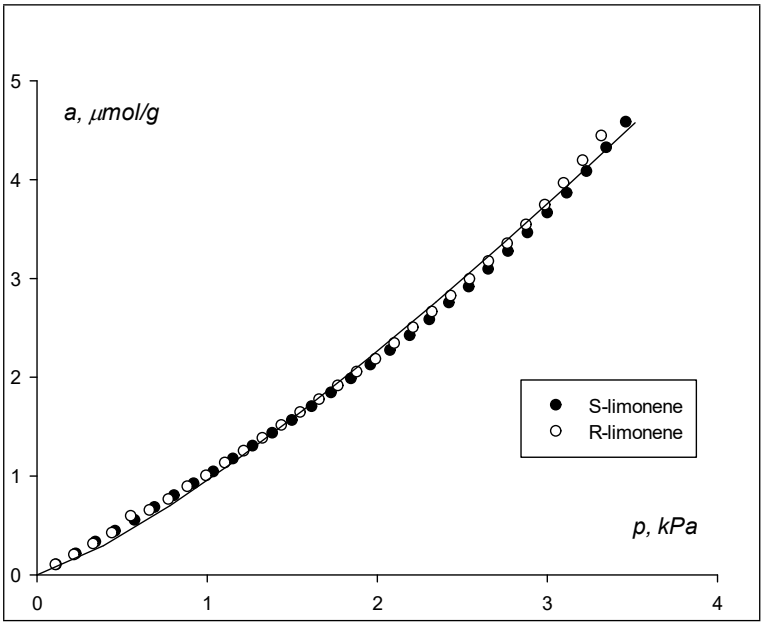

Figure 8S. Isotherms of limonene vapors adsorption at 100 °C by phloroglucinol

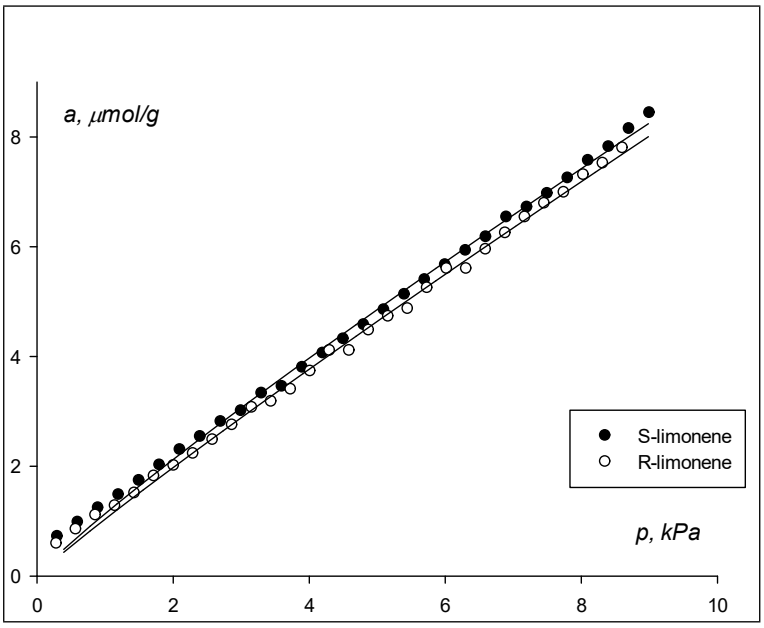

Figure 9S. Isotherms of limonene vapors adsorption at 120 °C by phloroglucinol

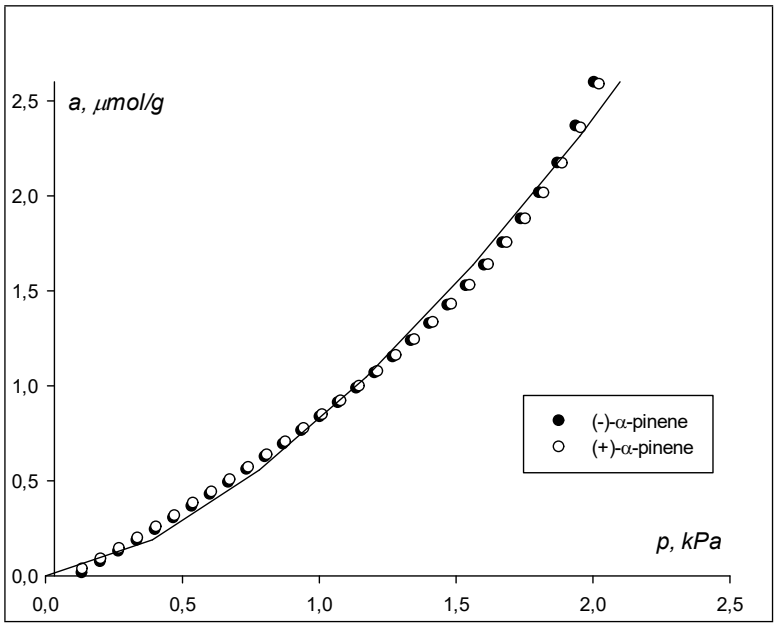

Figure 10S. Isotherms of α-pinenes vapors adsorption at 50 °C by hippuric acid

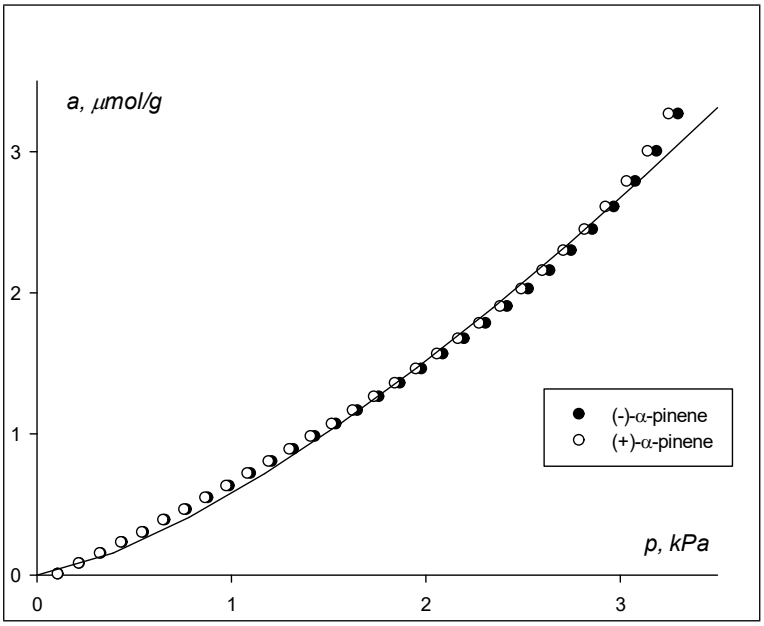

Figure 11S. Isotherms of α-pinenes vapors adsorption at 60 °C by hippuric acid

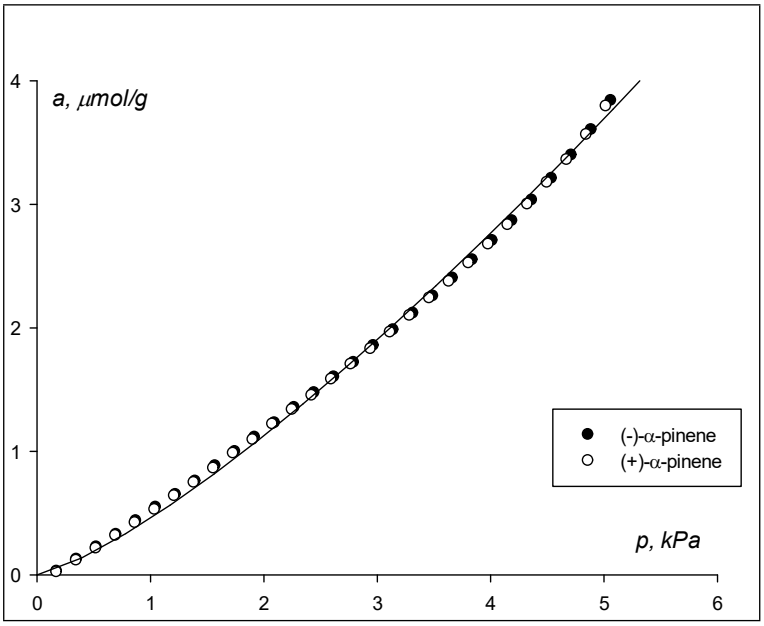

Figure 12S. Isotherms of α-pinenes vapors adsorption at 70 °C by hippuric acid

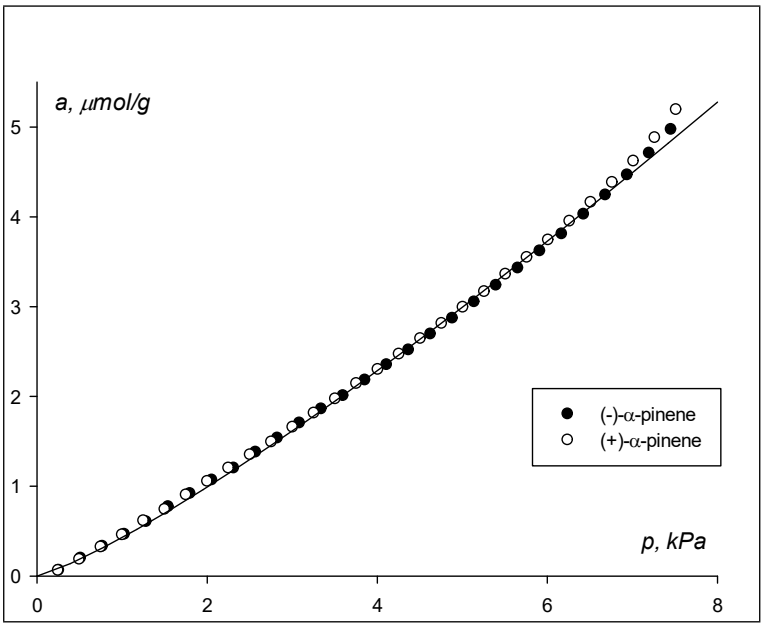

Figure 13S. Isotherms of α-pinenes vapors adsorption at 80 °C by hippuric acid

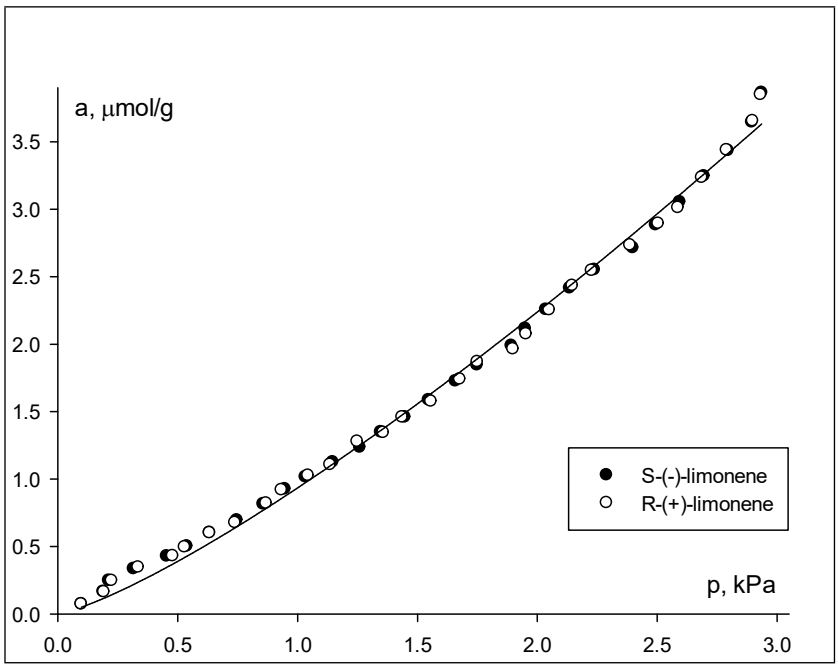

Figure 14S. Isotherms of limonenes vapors adsorption at 60 °C by hippuric acid N-crystals

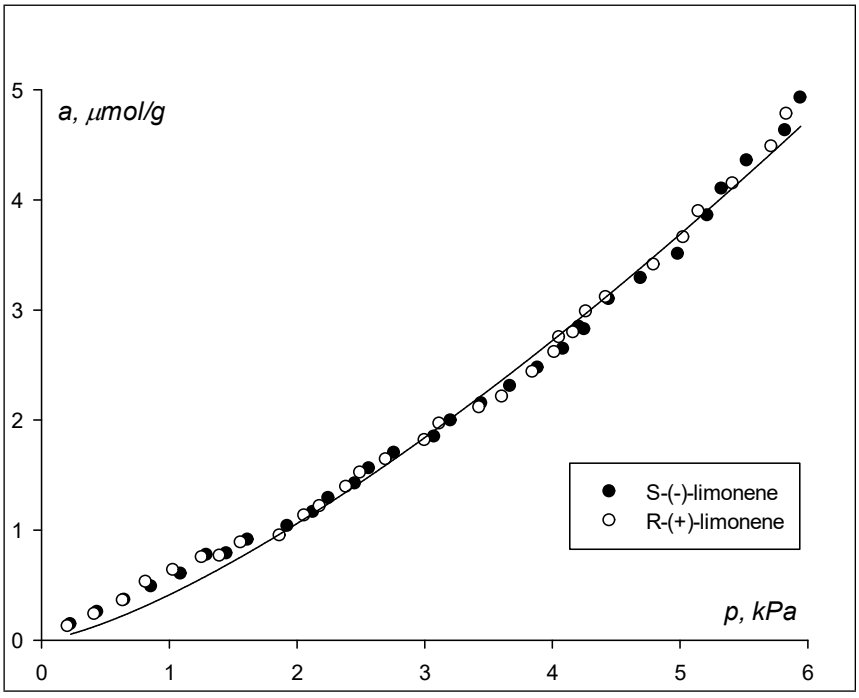

Figure 15S. Isotherms of limonenes vapors adsorption at 70 °C by phloroglucinol Ncrystals

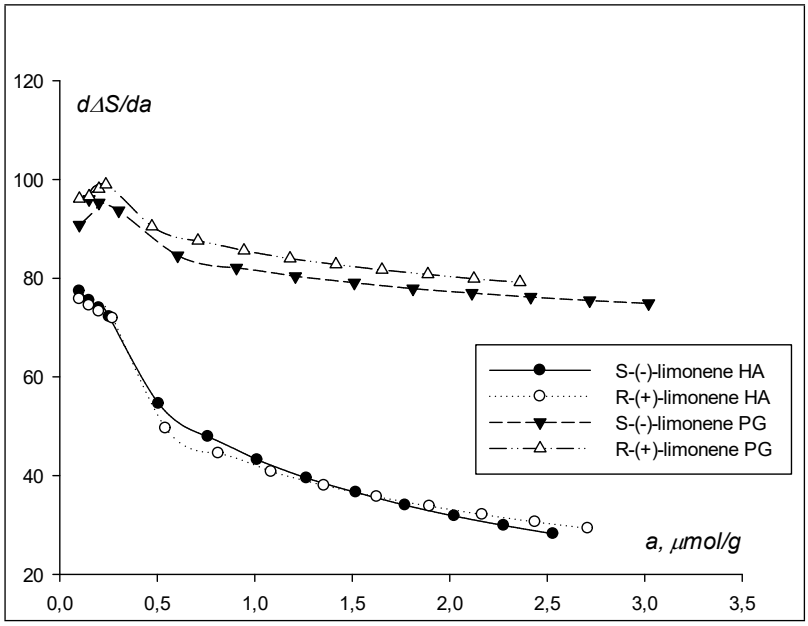

Figure 16S. Differential entropies of limonenes adsorption on hippuric acid (HA) and phloroglucinol (PG) crystals at 90 °C

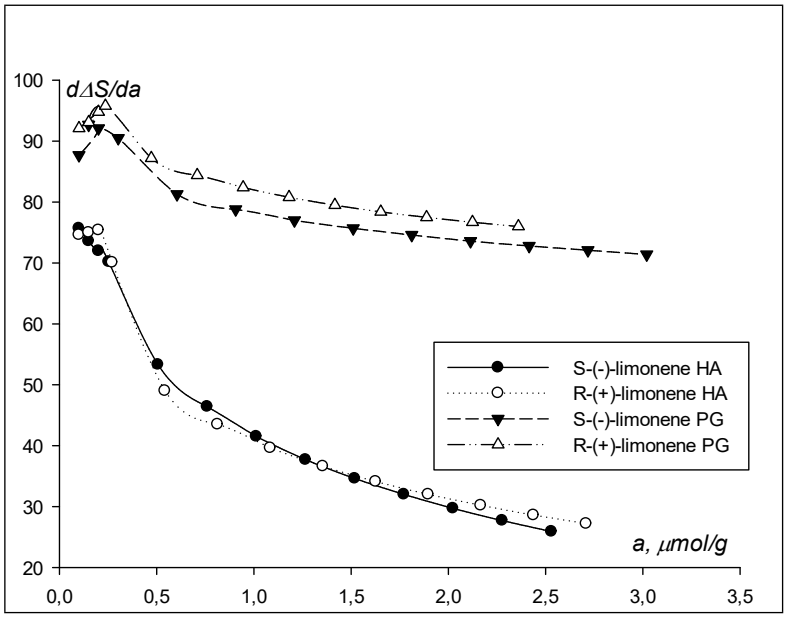

Figure 17S. Differential entropies of limonenes adsorption on hippuric acid (HA) and phloroglucinol (PG) crystals at 100 °C

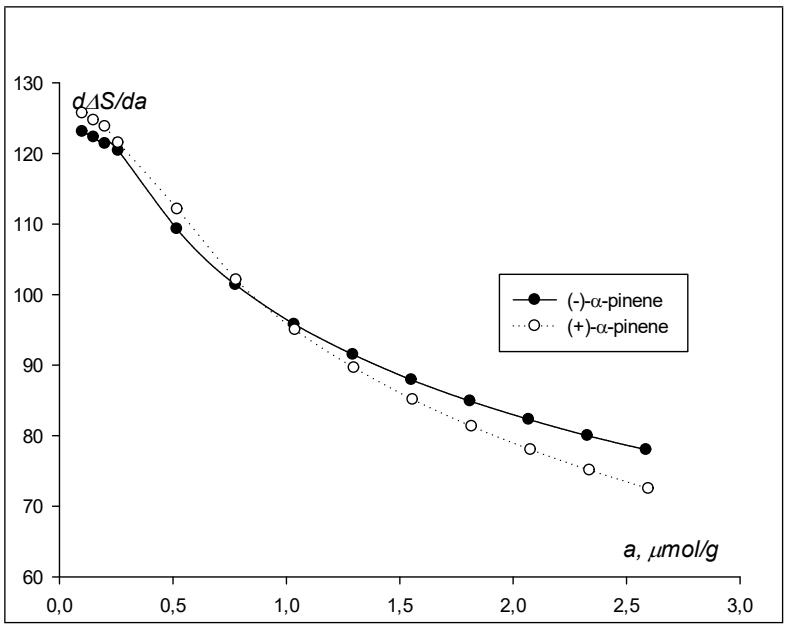

Figure 18S. Differential entropies of α-pinenes adsorption on hippuric acid crystals at 50 °C

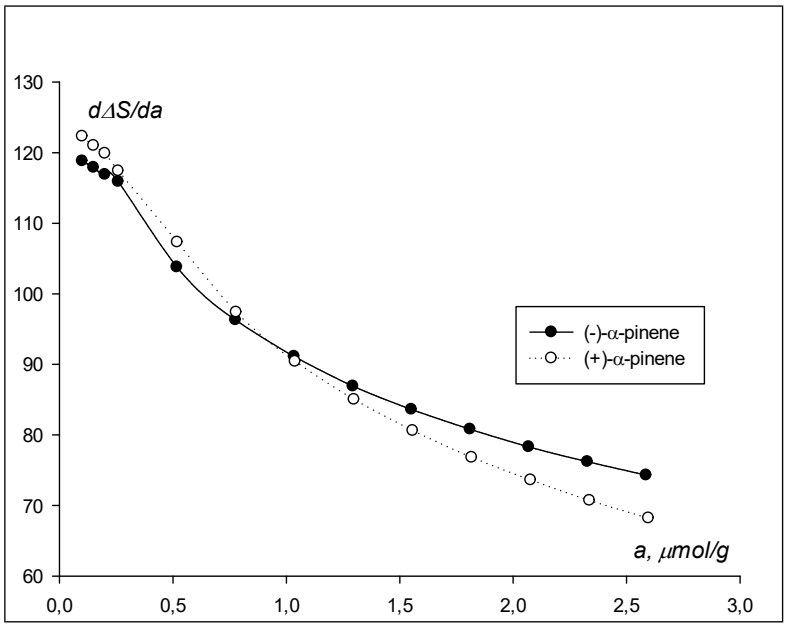

Figure 19S. Differential entropies of α-pinenes adsorption on hippuric acid crystals at 60 °C

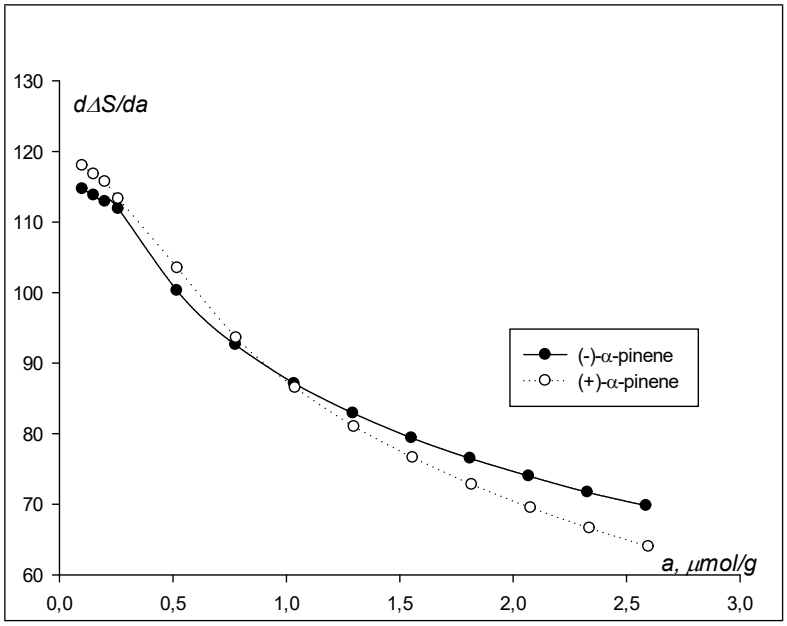

Figure 20S. Differential entropies of α-pinenes adsorption on hippuric acid crystals at 70 °C

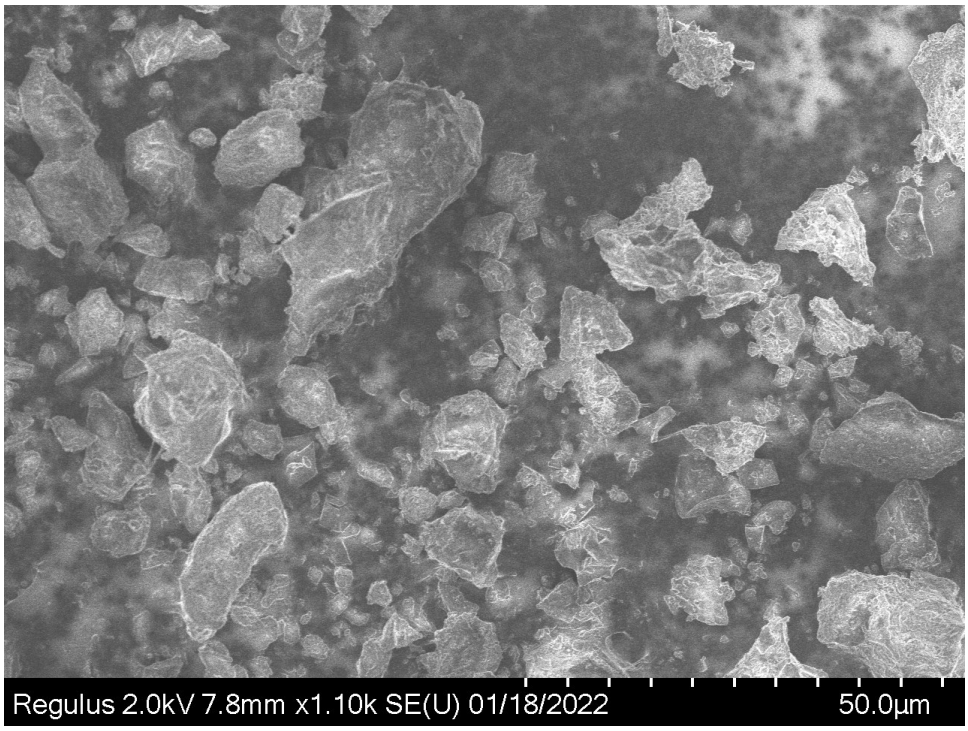

Figure 21S. SEM images of phloroglucinol crystals, obtained from acetonitrile

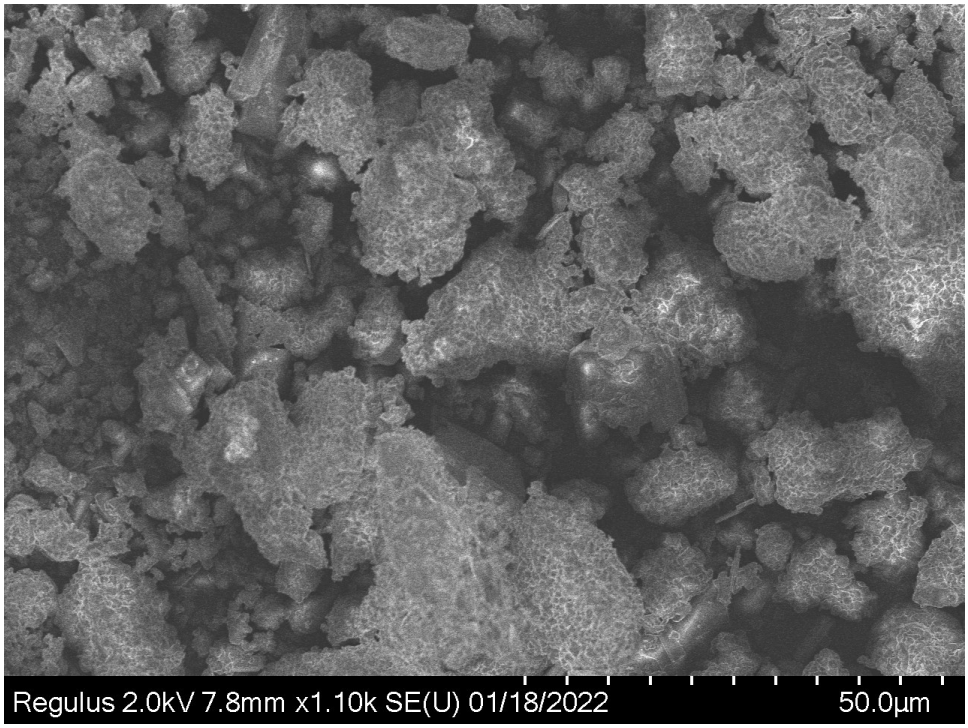

Figure 22S. SEM images of phloroglucinol crystals, obtained from water

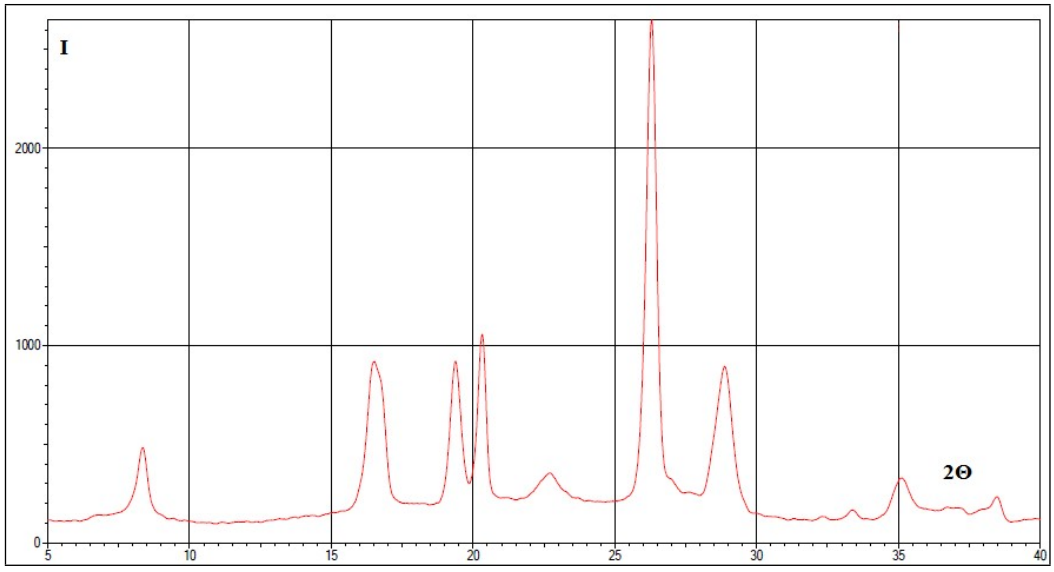

Figure 23S. Powder XRD of phloroglucinol crystals, obtained from acetonitrile

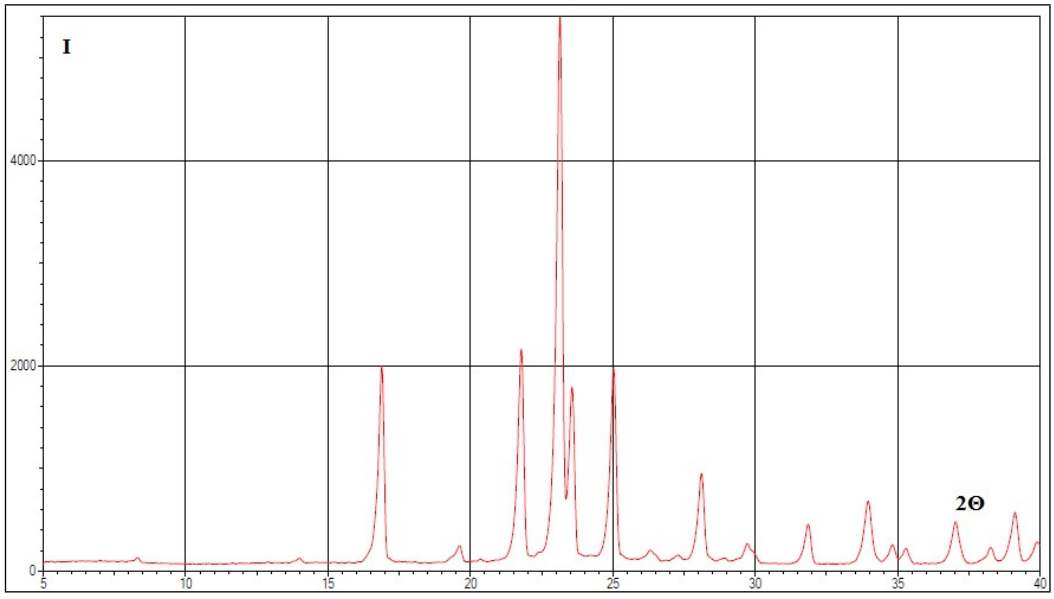

Figure 24S. Powder XRD of phloroglucinol crystals, obtained from water

Table 1S. P-values for pairs of points of of limonene vapours adsorption at 100 °C on phloroglucinol crystals (α = 0.05).

P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p
0.06	0,055	0.46	0.026	0.86	0,054	1.26	0,066	1.66	0.060
0.13	0,230	0.53	0.206	0.93	0,066	1.33	0,068	1.72	0.051
0.19	0,013	0.59	0.061	0.99	0,089	1.39	0,071	1.79	0.053
0.26	0,092	0.66	0.069	1.06	0,096	1.46	0,072	1.86	0.049
0.33	0,596	0.73	0.075	1.13	0,072	1.52	0,063	1.92	0.047
0.39	0,017	0.79	0.050	1.19	0,062	1.59	0,057	1.99	0.031

Table 2S. P-values for pairs of points of of limonene vapours adsorption at 120 °C on phloroglucinol crystals (α = 0.05).

P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p
0.16	0.268	1.14	0.103	2.12	0.073	3.10	0.063	4.08	0.199
0.32	0.251	1.30	0.094	2.29	0.124	3.27	0.117	4.25	0.174
0.49	0.331	1.47	0.085	2.45	0.424	3.43	0.280	4.41	0.086
0.65	0.164	1.63	0.133	2.61	0.066	3.59	0.060	4.58	0.129
0.81	0.139	1.79	0.142	2.78	0.117	3.76	0.063	4.74	0.083
0.98	0.154	1.96	0.357	2.94	0.238	3.92	0.108	4.90	0.086

Table 3S. P-values for pairs of points of of limonene vapours adsorption at 160 °C on phloroglucinol crystals (α = 0.05).

P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p
0.23	0.871	1.64	0.013	3.04	0.149	4.45	0.019	5.86	0.021
0.46	0.116	1.87	0.042	3.28	0.053	4.69	0.105	6.09	0.073
0.70	0.210	2.11	0.017	3.51	0.118	4.92	0.109	6.33	0.059
0.93	0.150	2.34	0.061	3.75	0.004	5.16	0.010	6.56	0.058
1.17	0.044	2.58	0.021	3.98	0.069	5.39	0.135	6.80	0.068
1.40	0.132	2.81	0.102	4.22	0.009	5.63	0.056	7.03	0.069

Table 4S. P-values for pairs of points of of limonene vapours adsorption at 170 °C on phloroglucinol crystals (α = 0.05).

P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p
0.33	0.055	2.36	0.223	4.38	0.129	6.41	0.400	8.43	0.904
0.67	0.052	2.70	0.116	4.72	0.340	6.75	0.894	8.77	0.738
1.01	0.433	3.03	0.163	5.06	0.457	7.08	0.957	9.11	0.794
1.35	0.071	3.37	0.216	5.40	0.631	7.76	0.803	9.45	0.929
1.68	0.090	3.71	0.261	5.73	0.800	8.10	0.135	9.78	0.982
2.02	0.091	4.05	0.219	6.07	0.440	8,27	0.056	10.12	0.962

Table 5S. P-values for pairs of points of of limonene vapours adsorption at 175 °C on phloroglucinol crystals (α = 0.05).

P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p
0.45	0.940	3.17	0,050	5.90	0.154	8.62	0.049	11.35	0.115
0.90	0.108	3.63	0.122	6.35	0.037	9.08	0.129	11.80	0.109
1.36	0.063	4.08	0.167	6.81	0.051	9.53	0.116	12.26	0.066
1.81	0.160	4.54	0.036	7.26	0.070	9.99	0.107	12.71	0.069
2.27	0.085	4.99	0.144	7.72	0.055	10.44	0.061	13.17	0.075
2.72	0.083	5.45	0.107	8.17	0.044	10.90	0.105	13.62	0.079

Table 6S. P-values for pairs of points of of limonene vapours adsorption at 180 °C on phloroglucinol crystals (α = 0.05).

P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p
0.42	0.108	2.99	0,455	5.56	0.97	8.13	0.334	10.69	0.411
0.85	0.175	3.42	0.179	5.99	0.461	8.55	0.444	11.12	0.152
1.28	0.161	3.85	0.003	6.41	0.549	8.98	0.232	11.55	0.391
1.71	0.315	4.27	0.133	6.84	0.853	9.41	0.593	11.98	0.710
2.13	0.337	4.70	0.050	7.27	0.560	9.84	0.504	12.41	0.463
2.56	0.112	5.13	0.509	7.70	0.563	10.27	0.429	12.83	0.506

Table 7S. P-values for pairs of points of of limonene vapours adsorption at 50 °C on hippuric acid crystals (α = 0.05).

P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p
0.14	0.048	1.01	0.242	1.87	0.512	2.73	0.779	3.59	0.898
0.29	0.169	1.15	0.128	2.01	0.669	2.87	0.350	3.74	0.882
0.43	0.113	1.29	0.392	2.16	0.544	3.02	0.799	3.88	0.918
0.57	0.320	1.44	0.404	2.30	0.618	3.16	0.908	4.02	0.857
0.72	0.187	1.58	0.534	2.44	0.553	3.30	0.818	4.17	0.943
0.86	0.119	1.72	0.453	2.59	0.760	3.45	0.888	4.31	0.916

Table 8S. P-values for pairs of points of of limonene vapours adsorption at 60 °C on hippuric acid crystals (α = 0.05).

P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p
0.24	0.595	1.65	0.438	3.07	0.699	4.49	0.617	5.90	0.594
0.47	0.318	1.89	0.562	3.31	0.442	4.72	0.622	6.14	0.624
0.71	0.608	2.13	0.644	3.54	0.442	4.96	0.797	6.38	0.639
0.94	0.239	2.36	0.747	3.78	0.817	5.19	0.707	6.61	0.601
1.18	0.483	2.60	0.758	4.01	0.856	5.43	0.652	6.85	0.595
1.42	0.619	2.83	0.875	4.25	0.872	5.67	0.625	7.08	0.646

Table 9S. P-values for pairs of points of of limonene vapours adsorption at 70 °C on hippuric acid crystals (α = 0.05).

P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p
0.38	0.815	2.65	0.012	4.91	$1.34*10^{-3}$	7.18	$1.55*10^{-3}$	9.45	$4.50*10^{-4}$
0.76	0.303	3.02	0.006	5.29	$1.33*10^{-3}$	7.56	$6.68*10^{-4}$	9.83	$6.76*10^{-4}$
1.13	0.039	3.40	0.003	5.67	$1.24*10^{-3}$	7.94	$2.80*10^{-4}$	10.20	$6.14*10^{-4}$
1.51	0.355	3.78	0.002	6.05	$4.67*10^{-4}$	8.31	$7.82*10^{-4}$	10.58	$7.38*10^{-4}$
1.89	0.007	4.16	0.004	6.42	$7.51*10^{-4}$	8.69	$3.15*10^{-4}$	10.96	$7.17*10^{-4}$
2.27	0.003	4.54	0.003	6.80	$8.19*10^{-4}$	9.07	$7.29*10^{-4}$	11.34	$7.48*10^{-4}$

Table 10S. P-values for pairs of points of of limonene vapours adsorption at 80 °C on hippuric acid crystals (α = 0.05).

P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p
0.62	0.032	4.33	0.383	8.04	0.903	11.75	0.889	15.46	0.753
1.23	0.052	4.94	0.598	8.65	0.854	1237	0.833	16.08	0.765
1.85	0.186	5.56	0.192	9.27	0.614	12.98	0.869	16.69	0.719
2.47	0.146	6.18	0.281	9.89	0.751	13.60	0.863	17.31	0.714
3.09	0.763	6.80	0.569	10.51	0.803	14.22	0.756	17.93	0.705
3.71	0.705	7.42	0.985	11.13	0.878	14.84	0.770	18.55	0.715

Table 11S. P-values for pairs of points of of limonene vapours adsorption at 90 °C on hippuric acid crystals (α = 0.05).

P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p
0.86	0.058	6.05	0.348	11.23	0.899	16.42	0.215	21.60	0.145
1.73	0.188	6.91	0.682	12.10	0.773	17.28	0.600	22.47	0.084
2.59	0.231	7.78	0.628	12.96	0.780	18.15	0.490	23.33	0.121
3.46	0.563	8.64	0.959	13.83	0.857	19.01	0.249	24.19	0.102
4.32	0.242	9.50	0.629	14.69	0.851	19.87	0.074	25.06	0.119
5.18	0.970	10.37	0.763	15.55	0.378	20.74	0.195	25.92	0.103

Table 12S. P-values for pairs of points of of limonene vapours adsorption at 100 °C on hippuric acid crystals (α = 0.05).

P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p
1.26	0.214	8.81	0.940	16.36	0.229	23.92	0.022	31.47	0.094
2.52	0.382	10.07	0.939	17.62	0.417	25.17	0.285	32.73	0.160
3.78	0.310	11.33	0.456	18.88	0.086	26.43	0.343	33.98	0.103
5.03	0.213	12.59	0.361	20.14	0.945	27.69	0.322	35.24	0.125
6.29	0.634	13.85	0.516	21.40	0.956	28.95	0.207	36.50	0.112
7.55	0.910	15.10	0.717	22.66	0.496	30.21	0.204	37.76	0. 156

Table 13S. P-values for pairs of points of of α-pinenes vapours adsorption at 50 °C on hippuric acid crystals (α = 0.05).

P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p
0.35	0.190	2.46	0.407	4.56	0.795	6.67	0.571	8.78	0.543
0.70	0.265	2.81	0.488	4.91	0.367	7.02	0.472	9.13	0.246
1.05	0.070	3.16	0.502	5.27	0.628	7.37	0.634	9.48	0.482
1.40	0.360	3.51	0.127	5.62	0.070	7.72	0.423	9.83	0.345
1.76	0.151	3.86	0.346	5.97	0.060	8.07	0.673	10.18	0.242
2.11	0.464	4.21	0.437	6.32	0.736	8.43	0.675	10.53	0.146

Table 14S. P-values for pairs of points of of α-pinenes vapours adsorption at 60 °C on hippuric acid crystals (α = 0.05).

P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p
0.56	0.050	3.91	0.867	7.26	0.782	10.61	0.007	13.96	0.034
1.12	0.404	4.47	0.633	7.82	0.460	11.17	0.042	14.52	0.097
1.68	0.225	5.03	0.420	8.38	0.840	11.73	0.033	15.08	0.061
2.23	0.159	5.58	0.932	8.93	0.203	12.29	0.018	15,64	0.042
2.79	0.606	6.14	0.113	9.49	0.259	12.84	0.141	16.19	0.057
3.35	0.921	6.70	0.117	10.05	0.024	13.40	0.066	16.75	0.034

Table 15S. P-values for pairs of points of of α-pinenes vapours adsorption at 70 °C on hippuric acid crystals (α = 0.05).

P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p
0.85	0.992	5.92	0.730	10.99	0.044	16.05	0.042	21.12	0.012
1.69	0.833	6.76	0.003	11.83	0.019	16.90	0.012	21.97	0.042
2.54	0.213	7.61	0.032	12.67	0.057	17.74	0.031	22.81	0.012
3.38	0.235	8.45	0.021	13.52	0.066	18.59	0.012	23.66	0.041
4.23	0.094	9.30	0.023	14.36	0.088	19.43	0.024	24.50	0.031
5.07	0.222	10.14	0.044	15.21	0.052	20.28	0.034	25.35	0.042

Table 16S. P-values for pairs of points of of α-pinenes vapours adsorption at 80 °C on hippuric acid crystals (α = 0.05).

P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p
1.24	0.488	8.71	0.386	16.18	0.472	23.65	0.581	31.12	0.324
2.49	0.055	9.96	0.514	17.43	0.218	24.89	0.032	32.36	0.238
3.73	0.074	11.20	0.162	18.67	0.559	26.14	0.632	33.61	0.438
4.98	0.026	12.45	0.318	19.92	0.587	27.38	0.254	34.85	0.214
6.22	0.578	13.69	0.070	21.16	0.979	28.63	0.411	36.10	0.215
7.47	0.630	14.94	0.874	22.40	0.012	29.87	0.125	37.34	0.143

Table 17S. P-values for pairs of points of of α-pinenes vapours adsorption at 90 °C on hippuric acid crystals (α = 0.05)

P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p	P, kPa	p
1.79	0.048	12.51	0.497	23.23	0.006	33.95	0.086	44.67	0.004
3.57	0.086	14.29	0.560	25.02	0.321	35.74	0.035	46.46	0.002
5.36	0.808	16.08	0.017	26.80	0.863	37.52	0.043	48.24	0.003
7.15	0.453	17.87	0.011	28.59	0.169	39.31	0.015	50.03	0.004
8.93	0.221	19.65	0.669	30.38	0.084	41.10	0.001	51.82	0.003
10.72	0.732	21.44	0.561	32.16	0.021	42.88	0.002	53.60	0.004

Table 18S. The Freundlich equation parameters and degree of significance values *p* for limonene enantiomers adsorption isotherms on hippuric acid crystals (α = 0.05)

T, °C	K_F*10^3		p	n		p
	S-(−)	R-(+)		S-(−)	R-(+)	
50	2.5	3.7	**0.008**	0.495	0.526	**0.01**
60	2.3	2.0	**0.02**	0.562	0.545	**0.0005**
70	1.8	1.8	0.62	0.590	0.587	0.40
80	1.8	1.8	0.60	0.650	0.646	0.30
90	2.0	1.9	0.20	0.693	0.688	0.11
100	2.3	2.2	0.68	0.738	0.735	0.54

Table 19S. The Freundlich equation parameters and degree of significance values *p* for α-pinene enantiomers adsorption isotherms on hippuric acid crystals (α = 0.05)

T, °C	K_F*10^3		p	n		p
	(−)-α	(+)-α		(−)-α	(+)-α	
50	3.0	2.7	**0.002**	0.657	0.643	**0.003**
60	3.1	3.2	0.400	0.713	0.717	0.500
70	3.5	3.6	0.640	0.770	0.772	0.770
80	4.2	4.1	0.560	0.817	0.818	0.610

Table 20S. Dispersion and specific components of ΔF (kJ/mol) of adsorption on hippuric acid and phloroglucinol crystals, calculated by the Dong method

Adsorbate	phloroglucinol		hippuric acid	
	$-\Delta F_{disp}$	$-\Delta F_{spec}$	$-\Delta F_{disp}$	$-\Delta F_{spec}$
Ethanol	-10.1	9.8	-6.5	10.5
n-Propanol	-8.5	9.5	-5.1	11.0
i-Propanol	-8.7	7.9	-5.2	9.4
n-Butanol	-6.9	9.6	-3.6	11.8
i-Butanol	-7.0	8.3	-3.7	10.5
Benzene	-5.9	2.7	-2.6	5.2
Toluene	-4.2	2.4	-1.0	5.5
Ethylacetate	-6.6	4.5	-3.3	6.3

Table 21S. The impacts of intermolecular interactions in ΔF, by LFER calculations

Adsorbate	phloroglucinol			hippuric acid		
	$-\Delta F_{disp}$	$-\Delta F_{io}$	$-\Delta F_{da}$	$-\Delta F_{disp}$	$-\Delta F_{io}$	$-\Delta F_{da}$
n-Nonane	2.8	0.6	0.0	0.2	0.0	0.0
n-Decane	3.9	0.8	0.0	2.1	0.2	0.0
n-Undecane	5.4	1.2	0.0	3.9	0.4	0.0
Ethanol	1.3	1.0	1.7	-0.2	-0.1	-0.1
n-Propanol	2.2	1.5	2.3	0.5	0.1	0.3
i-Propanol	1.5	1.1	1.6	-0.4	-0.1	-0.3
n-Butanol	3.1	2.0	3.1	1.4	0.4	0.9
i-Butanol	2.6	1.7	2.5	0.7	0.2	0.4
Benzene	1.9	0.3	0.5	-2.6	-0.2	-0.4
Toluene	3.0	0.7	0.8	-1.5	-0.2	-0.2
Ethylacetate	1.2	0.8	1.0	-1.1	-0.4	-0.5