Dependence of the relative retention of organic compounds on the nature and pressure of the carrier gas and on the thickness of the PEG-20M film in the capillary column

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The effects of the carrier gas nature and pressure on the relative retention values of organic compounds were studied using a series of capillary columns differing in the film thickness of the polar stationary phase (PEG-20M). Relative retention depends linearly on the carrier gas pressure. This dependence becomes more pronounced in the following order of carrier gases: helium < nitrogen < carbon dioxide. The limiting relative retention at a carrier gas pressure approaching zero rather than relative retention values measured experimentally (relative retention time, Kovats retention index, *etc.*) is an invariant characteristic of a compound subjected to chromatography. For the carrier gases studied, the limiting retention value almost does not depend on the nature of the carrier gas used. The limiting retention values depend on the thickness of the stationary liquid phase PEG-20M film, indicating the complex absorption—adsorption nature of these parameters. Dissolution of a carrier gas in the stationary liquid phase has an effect on the relative retention.

Key words: capillary gas chromatography, carrier gas, retention on PEG-20M, dependence of retention on the carrier gas pressure.

Relative retention values are chromatographic characteristics of compounds under analysis; they are used to identify the components of mixtures.[1,2] It has been shown in our studies[3,4] that, strictly speaking, relative retention values are not constant even at relatively low pressures (1—5 atm) of the carrier gas, which are normally used in routine capillary chromatography, but they depend on the nature of the carrier gas and on the average pressure in the capillary column. The limiting relative retention Rel(0) (relative retention time, Kovats retention index) calculated for a carrier gas pressure p approaching zero is a chromatographic constant of a compound under analysis.[3] These effects are especially pronounced in capillary chromatography, because it provides a higher accuracy of determination of the retention time of a chromatographic zone (than chromatography on packed columns) owing to the markedly higher efficiency of capillary columns.

Only few papers devoted to the experimental investigation of the dependence of relative retention values on the average pressure in the column have been published.

It appeared pertinent to study the dependence of the relative retention values of compounds subjected to chromatography on the nature of the carrier gas (He, N_2, CO_2) for a series of capillary columns containing a polar stationary phase (PEG-20M) and differing in the effective thickness of the layer of this phase (0.10, 0.22, 0.28, and 0.38 mm). Up to now, no experimental data of this sort have been published.

Experimental

Chromatographic measurements were carried out on an LKhM-8MD gas chromatograph (5th model) with a flame ionization detector ("Khromatograf" plant, Moscow, Russia) that we adapted for operating with capillary columns.

The retention times of sorbates were measured by a modified I-02 integrator with a resolution of 0.1 s. Capillary columns (25 m×0.16 mm) of fused silica with a layer of poly(ethylene glycol) PEG-20M (0.10—0.38 μm) were used. Helium, nitrogen, and carbon dioxide were used as carrier gases. The temperature of the detector and the column was 150 °C, and the temperature of the injector was 250 °C. The specific efficiency of the capillary columns was ~5000 theoretical plates per meter. The pressure at the inlet of the capillary column was measured by a standard manometer, and the average pressure in the column was calculated from the equation

$$p = p_0 \cdot J_3^4, \quad (1)$$

where $J_3^4 = (3/4)[(p_i/p_0)^3 - 1]/[(p_i/p_0)^4 - 1]$, p_i and p_0 are the carrier gas pressures at the inlet and the outlet of the column, respectively.

The mixture of test compounds contained n-C_7—C_{12} aliphatic alcohols, decan-2-ol, methyl pelargonate, naphthalene, 2,6-dimethylaniline, and 2,6-dimethylphenol (1—2% each of

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Table 1. Dependence of the capacity factors (*k*) for some organic compounds on the average pressure (p = 1.6—4.5 atm) in a capillary column with PEG-20M (SLP) for various carrier gases (helium, nitrogen, carbon dioxide)

Chromatographed compound	Helium				Nitrogen				Carbon dioxide			
	1.6*	2.3*	3.4*	4.5*	1.6*	2.3*	3.4*	4.5*	1.6*	2.3*	3.4*	4.5*
0.1-μm-thick SLP layer												
Heptan-1-ol	0.352	0.346	—	0.340	0.352	0.342	0.339	0.337	0.349	0.339	0.339	0.340
Methyl pelargonate	0.452	0.443	—	0.439	0.452	0.437	0.433	0.427	0.444	0.432	0.429	0.425
Octan-1-ol	0.550	0.540	—	0.530	0.550	0.533	0.525	0.520	0.542	0.527	0.521	0.517
Decan-2-ol	0.712	0.699	—	0.686	0.710	0.687	0.676	0.667	0.698	0.679	0.666	0.655
Nonan-1-ol	0.855	0.840	—	0.824	0.852	0.827	0.812	0.803	0.840	0.816	0.799	0.786
Naphthalene	1.326	1.300	—	1.274	1.318	1.278	1.252	1.230	1.296	1.257	1.227	1.197
Decan-1-ol	1.388	1.361	—	1.332	1.382	1.342	1.315	1.299	1.364	1.321	1.289	1.261
2,6-Dimethylaniline	1.968	1.927	—	1.887	1.958	1.902	1.861	1.837	1.930	1.866	1.816	1.771
Undecan-1-ol	2.048	2.006	—	1.967	2.030	1.969	1.922	1.885	1.997	1.932	1.873	1.812
2,6-Dimethylphenol	2.446	2.399	—	2.347	2.434	2.369	2.322	2.287	2.402	2.323	2.263	2.202
Dodecan-1-ol	3.155	3.088	—	3.023	3.119	3.025	2.948	2.894	3.068	2.961	2.867	2.773
0.22-μm-thick SLP layer												
Heptan-1-ol	0.797	0.778	0.760	0.751	0.780	0.765	0.755	0.736	0.776	0.766	0.741	0.730
Methyl pelargonate	1.033	0.990	0.987	0.976	1.008	0.987	0.967	0.941	1.000	0.983	0.946	0.928
Octan-1-ol	1.248	1.218	1.192	1.178	1.221	1.194	1.172	1.143	1.211	1.190	1.150	1.128
Decan-2-ol	1.611	1.573	1.540	1.545	1.575	1.536	1.504	1.465	1.557	1.525	1.471	1.438
Nonan-1-ol	1.942	1.896	1.858	1.838	1.899	1.852	1.813	1.769	1.878	1.839	1.775	1.734
Naphthalene	3.012	2.941	2.881	2.850	2.944	2.836	2.797	2.724	2.899	2.834	2.732	2.661
Decan-1-ol	3.215	3.141	3.075	3.043	3.157	3.071	3.003	2.929	3.111	3.038	2.936	2.863
2,6-Dimethylaniline	4.531	4.431	4.340	4.293	4.451	4.327	4.231	4.128	4.376	4.270	4.126	4.021
Undecan-1-ol	4.656	4.544	4.450	4.403	4.551	4.408	4.231	4.128	4.4465	4.354	4.126	4.021
2,6-Dimethylphenol	5.609	5.487	5.377	5.318	5.511	5.357	5.239	5.112	5.415	5.292	5.113	4.984
Dodecan-1-ol	7.166	6.996	6.858	6.785	7.001	6.777	6.603	6.415	6.857	6.683	6.424	6.227
0.28-μm-thick SLP layer												
Heptan-1-ol	1.039	1.019	1.004	0.992	1.032	1.009	0.975	0.960	1.021	0.997	0.959	0.932
Methyl pelargonate	1.307	1.280	1.263	1.249	1.293	1.260	1.217	1.195	2.275	1.240	1.190	1.152
Octan-1-ol	1.620	1.585	1.563	1.545	1.606	1.566	1.515	1.487	1.585	1.542	1.484	1.441
Decan-2-ol	2.068	2.024	1.996	1.973	2.047	1.993	1.928	1.890	2.016	1.957	1.880	1.818
Nonan-1-ol	2.509	2.453	2.418	2.390	2.482	2.417	2.342	2.295	2.447	2.377	2.285	2.216
Naphthalene	3.871	3.782	3.728	3.686	3.825	3.717	3.602	3.524	3.767	3.650	3.505	3.387
Decan-1-ol	4.132	4.041	3.984	3.935	4.096	3.983	3.863	3.788	4.039	3.916	3.770	3.656
2,6-Dimethylaniline	5.872	5.741	5.658	5.589	5.835	5.670	5.502	5.390	5.734	5.558	5.348	5.166
Undecan-1-ol	5.872	5.741	5.658	5.589	5.833	5.670	5.502	5.390	5.734	5.558	5.348	5.166
2,6-Dimethylphenol	7.279	7.112	7.007	6.925	7.226	7.026	6.822	6.684	7.110	6.895	6.635	6.417
Dodecan-1-ol	9.129	8.914	8.787	8.680	9.010	8.725	8.450	8.243	8.840	8.542	8.172	7.866
0.38-μm-thick SLP layer												
Heptan-1-ol	1.395	1.360	1.335	1.322	1.384	1.345	1.314	1.288	1.356	1.309	1.283	1.246
Methyl pelargonate	1.745	1.702	1.671	1.655	1.724	1.674	1.628	1.593	1.687	1.624	1.580	1.528
Octan-1-ol	2.170	2.116	2.077	2.057	2.149	2.086	2.035	1.992	2.108	2.030	1.981	1.922
Decan-2-ol	2.761	2.694	2.645	2.619	2.731	2.646	2.577	2.518	2.674	2.573	2.503	2.419
Nonan-1-ol	3.353	3.268	3.212	3.181	3.317	3.217	3.137	3.062	3.251	3.132	3.045	2.946
Naphthalene	5.164	5.035	4.944	4.897	5.097	4.944	4.813	4.695	4.997	4.807	4.663	4.505
Decan-1-ol	5.553	5.419	5.319	5.263	5.499	5.336	5.201	5.083	5.396	5.195	5.048	4.893
2,6-Dimethylaniline	7.896	7.690	7.548	7.473	7.810	7.576	7.385	7.210	7.659	7.368	7.143	6.908
Undecan-1-ol	7.896	7.690	7.548	7.473	7.810	7.576	7.385	7.210	7.659	7.368	7.143	6.908
2,6-Dimethylphenol	9.755	9.513	9.344	9.251	9.672	9.393	9.157	8.945	9.478	9.132	8.866	8.580
Dodecan-1-ol	12.132	11.834	11.611	11.494	11.946	11.585	11.259	10.947	11.693	11.237	10.853	10.423

Note. Experimental conditions: a fused silica capillary column (25 m×0.16 mm), 150 °C. * p/atm.

Table 2. Dependence of the relative retention time α for organic compounds on the average pressure (p = 1.6—4.5 atm) in a capillary column with PEG (SLP) for various carrier gases used (helium, nitrogen, carbon dioxide)

Chromato-graphed compound	Helium				Nitrogen				Carbon dioxide			
	1.6*	2.3*	3.4*	4.5*	1.6*	2.3*	3.4*	4.5*	1.6*	2.3*	3.4*	4.5*
					0.10-μm-thick SLP layer							
Methyl pelargonate	1.284	1.283	—	1.291	1.285	1.278	1.278	1.269	1.274	1.277	1.266	1.250
Octan-1-ol	1.562	1.561	—	1.562	1.562	1.560	1.552	1.546	1.555	1.558	1.537	1.519
Decan-2-ol	2.022	2.021	—	2.021	2.016	2.012	1.995	1.982	2.002	2.005	1.967	1.924
Nonan-1-ol	2.430	2.430	—	2.425	2.422	2.421	2.397	2.385	2.409	2.412	2.360	2.310
Naphthalene	3.767	3.760	—	3.753	3.744	3.742	3.697	3.655	3.718	3.712	3.623	3.516
Decan-1-ol	3.944	3.938	—	3.923	3.929	3.929	3.882	3.859	3.912	3.901	3.806	3.705
2,6-Dimethyl-aniline	5.590	5.575	—	5.557	5.565	5.567	5.495	5.457	5.533	5.511	5.364	5.203
Undecan-1-ol	5.819	5.803	—	5.791	5.769	5.762	5.676	5.598	5.726	5.707	5.533	5.322
2,6-Dimethyl-phenol	6.949	6.940	—	6.911	6.918	6.933	6.858	6.794	6.887	6.863	6.682	6.470
Dodecan-1-ol	8.964	8.934	—	8.902	8.864	8.853	8.706	8.597	8.797	8.746	8.467	8.147
					0.22-μm-thick SLP layer							
Methyl pelargonate	1.296	—	1.299	1.300	1.293	1.290	1.280	1.279	1.288	1.283	1.276	1.270
Octan-1-ol	1.565	1.566	1.568	1.568	1.566	1.560	1.552	1.554	1.560	1.552	1.551	1.544
Decan-2-ol	2.022	2.023	2.027	2.057	2.020	2.008	1.991	1.991	2.006	1.990	1.984	1.969
Nonan-1-ol	2.436	2.438	2.445	2.446	2.435	2.420	2.401	2.404	2.419	2.400	2.395	2.375
Naphthalene	3.778	3.782	3.791	3.794	3.775	3.741	3.703	3.702	3.734	3.698	3.686	3.644
Decan-1-ol	4.034	4.039	4.047	4.050	4.048	4.013	3.976	3.982	4.007	3.965	3.961	3.921
2,6-Dimethyl-aniline	5.685	5.698	5.711	5.714	5.707	5.654	5.602	5.611	5.637	5.572	5.567	5.508
Undecan-1-ol	5.841	5.844	5.856	5.860	5.835	5.760	5.602	5.611	5.751	5.682	5.567	5.508
2,6-Dimethyl-phenol	7.037	7.056	7.076	7.079	7.066	6.999	6.937	6.948	6.976	6.906	6.897	6.826
Dodecan-1-ol	8.991	8.996	9.025	9.032	8.977	8.855	8.742	8.720	8.832	8.720	8.666	8.529
					0.28-μm-thick SLP layer							
Methyl pelargonate	1.258	1.256	1.257	1.259	1.252	1.249	1.249	1.245	1.248	1.244	1.240	1.236
Octan-1-ol	1.559	1.555	1.556	1.557	1.556	1.553	1.554	1.550	1.552	1.546	1.547	1.545
Decan-2-ol	1.990	1.985	1.987	1.989	1.983	1.976	1.977	1.969	1.973	1.962	1.960	1.951
Nonan-1-ol	2.414	2.406	2.407	2.410	2.405	2.397	2.402	2.391	2.395	2.383	2.382	2.377
Naphthalene	3.724	3.711	3.712	3.716	3.706	3.686	3.694	3.672	3.688	3.659	3.654	3.633
Decan-1-ol	3.976	3.965	3.966	3.967	3.968	3.949	3.962	3.948	3.954	3.926	3.931	3.922
2,6-Dimethyl-aniline	5.649	5.632	5.632	5.634	5.653	5.622	5.642	5.616	5.614	5.572	5.576	5.542
Undecan-1-ol	5.649	5.632	5.632	5.634	5.651	5.622	5.642	5.616	5.614	5.572	5.576	5.542
2,6-Dimethyl-phenol	7.004	6.977	6.976	6.980	7.001	6.967	6.996	6.966	6.960	6.913	6.916	6.884
Dodecan-1-ol	8.784	8.745	8.748	8.750	8.730	8.651	8.666	8.590	8.654	8.564	8.519	8.438
					0.38-μm-thick SLP layer							
Methyl pelargonate	1.251	1.252	1.252	1.252	1.246	1.245	1.239	1.1.237	1.244	1.240	1.231	1.227
Octan-1-ol	1.556	1.556	1.556	1.556	1.552	1.551	1.549	1.546	1.554	1.551	1.544	1.543
Decan-2-ol	1.980	1.981	1.981	1.981	1.973	1.968	1.962	1.954	1.972	1.965	1.951	1.942
Nonan-1-ol	2.404	2.403	2.405	2.406	2.396	2.392	2.388	2.377	2.397	2.393	2.373	2.365
Naphthalene	3.703	3.702	3.703	3.704	3.683	3.677	3.664	3.644	3.685	3.672	3.633	3.616
Decan-1-ol	3.982	3.984	3.984	3.982	3.973	3.968	3.959	3.946	3.980	3.969	3.934	3.928
2,6-Dimethyl-aniline	5.662	5.654	5.654	5.653	5.643	5.635	5.621	5.596	5.649	5.628	5.556	5.545
Undecan-1-ol	5.662	5.654	5.654	5.653	5.643	5.635	5.621	5.596	5.649	5.628	5.556	5.545
2,6-Dimethyl-phenol	6.995	6.995	6.998	6.998	6.988	6.986	6.970	6.944	6.991	6.976	6.909	6.887
Dodecan-1-ol	8.699	8.701	8.697	8.695	8.631	8.616	8.570	8.497	8.624	8.584	8.457	8.367

Note. Experimental conditions: a fused silica capillary column (25 m×0.16 mm), 150 °C, heptan-1-ol as the standard. * p/atm.

the components in dichloromethane). The volume of the sample being analyzed was 0.1—0.5 μL of the test mixture and 0.5 μL of methane as a non-sorbing substance used in the calculation of the capacity factor. Each retention value was found as the average of 3—5 injections.

Results and Discussion

Table 1 shows the dependence of the capacity factor *k* on the average pressure of the carrier gas (He, N_2, and CO_2) in a capillary column with PEG-20M, and Tables 2 and 3 present the corresponding dependences for the relative retention time α and retention index *I* for all the sorbates. Analysis of the data presented in the tables allows one to identify the following characteristic features of the dependences under study. First, the capacity factor is the parameter most dependent on the carrier gas pressure. Second, the effect of the carrier gas nature on the retention increases in the following series: He < N_2 < CO_2. Third, the dependences of the relative retention time and retention index on the average carrier-gas pressure are the least clear-cut in the case of He.

When the experimental results obtained for He are described by a linear correlation, the correlation coefficients *r* for the relative retention values vary from 0.10 to 0.98, and those for the retention index vary from 0.18 to 0.98. For the "most ideal" carrier gas (He), which is the least soluble in organic liquids,[5] the difference be-

Table 3. Dependence of the retention indices *I* for organic compounds on the average pressure (p = 1.6—4.5 atm) in a capillary column with PEG-20M (SLP) for various carrier gases used (helium, nitrogen, carbon dioxide)

Chromatographed compound	Helium				Nitrogen				Carbon dioxide			
	1.6*	2.3*	3.4*	4.5*	1.6*	2.3*	3.4*	4.5*	1.6*	2.3*	3.4*	4.5*
0.10-μm-thick SLP layer												
Methyl pelargonate	756.00	755.90	756.67	757.32	756.26	755.14	755.80	754.64	754.80	755.15	754.82	753.27
Decan-2-ol	858.37	858.34	858.58	858.52	858.24	857.89	857.76	857.28	857.66	857.75	857.44	856.36
Naphthalene	990.51	990.41	990.67	990.78	990.06	989.94	989.86	988.73	989.53	898.68	989.66	988.91
2,6-Dimethylaniline	1089.66	1089.67	1089.57	1089.39	1090.65	1091.01	1091.45	1093.12	1091.03	1090.83	1091.70	1093.74
2,6-Dimethylphenol	1141.08	1141.46	1141.39	1141.12	1142.31	1143.07	1144.20	1145.11	1142.99	1143.19	1144.35	1145.85
0.22-μm-thick SLP layer												
Methyl pelargonate	757.81	790.84	758.17	758.20	757.26	757.20	756.21	755.85	756.88	756.71	755.53	755.08
Decan-2-ol	857.83	857.79	857.71	860.98	857.67	857.46	857.17	856.76	857.31	857.07	856.66	856.49
Naphthalene	987.04	986.95	987.02	987.04	986.27	986.14	985.90	985.59	986.01	986.14	985.71	985.40
2,6-Dimethylaniline	1092.69	1093.14	1093.21	1093.18	1098.93	1094.89	1100.00	1100.00	1094.43	1094.56	1100.00	1100.00
2,6-Dimethylphenol	1143.19	1143.67	1143.74	1143.67	1144.44	1145.33	1148.03	1148.50	1145.00	1145.55	1148.42	1149.07
0.28-μm-thick SLP layer												
Methyl pelargonate	751.69	751.57	751.74	751.95	750.94	750.55	750.37	749.99	750.44	750.07	749.38	748.73
Decan-2-ol	855.83	855.94	856.05	856.07	855.69	855.48	855.31	855.24	855.36	855.10	854.82	854.08
Naphthalene	986.93	986.73	986.73	986.86	986.32	986.17	986.01	985.59	986.11	985.91	985.43	984.74
2,6-Dimethylaniline	1100.00	1100.00	1100.00	1100.00	1100.10	1100.00	1100.00	1100.00	1100.00	1100.00	1100.00	1100.00
2,6-Dimethylphenol	1148.69	1148.68	1148.59	1148.68	1149.24	1149.76	1150.12	1150.67	1149.67	1150.18	1150.83	1151.60
0.38-μm-thick SLP layer												
Methyl pelargonate	750.68	750.81	750.85	750.79	749.90	749.96	749.03	748.76	749.53	749.06	747.84	747.11
Decan-2-ol	855.39	855.56	855.45	855.41	855.21	854.93	854.59	854.46	854.94	854.60	854.45	853.82
Naphthalene	985.60	985.48	985.52	985.67	985.01	984.94	984.65	984.32	984.82	984.63	984.28	983.68
2,6-Dimethylaniline	1100.00	1100.00	1100.00	1100.00	1100.00	1100.00	1100.00	1100.00	1100.00	1100.00	1100.00	1100.00
2,6-Dimethylphenol	1149.24	1149.35	1149.56	1149.58	1150.31	1150.62	1151.01	1151.65	1150.38	1150.86	1151.66	1152.70

Note. Experimental conditions: a fused silica capillary column (25 m×0.16 mm), 150 °C, representatives of the homologous series of *n*-alcohols as standards. * p/atm.

Table 4. Characteristics of linear equation (2)

Compo-und*	k_0			b_k		
	He	N_2	CO_2	He	N_2	CO_2
				0.10-μm-thick SLP layer		
1	0.357±0.009	0.347±0.001	0.353±0.006	−0.0045±0.0026	−0.0023±0.0008	−0.0033±0.0017
2	0.458±0.004	0.465±0.005	0.454±0.001	−0.0054±0.0015	−0.0088±0.0014	−0.0058±0.0024
3	0.557±0.007	0.560±0.008	0.554±0.007	−0.0062±0.0023	−0.0096±0.0031	−0.0089±0.0022
4	0.722±0.009	0.726±0.011	0.716±0.007	−0.0089±0.0030	−0.0138±0.0031	−0.0140±0.0028
5	0.869±0.009	0.871±0.012	0.863±0.010	−0.0111±0.0030	−0.0160±0.0042	−0.0178±0.0031
6	1.346±0.016	1.355±0.016	1.341±0.010	−0.0176±0.0050	−0.0288±0.0054	−0.0327±0.0040
7	1.410±0.016	1.415±0.020	1.409±0.015	−0.0187±0.0054	−0.0273±0.058	−0.0340±0.0053
8	1.999±0.024	2.008±0.025	2.002±0.022	−0.0269±0.0082	−0.0400±0.0081	−0.0527±0.0074
9	2.079±0.024	2.094±0.023	2.086±0.017	−0.0272±0.012	−0.0480±0.0071	−0.0614±0.0058
10	2.486±0.027	2.497±0.026	2.493±0.025	−0.0337±0.0089	−0.0485±0.0080	−0.0660±0.0082
11	3.208±0.037	3.218±0.037	3.208±0.034	−0.0447±0.0112	−0.0749±0.0111	−0.0983±0.0094
				0.22-μm-thick SLP layer		
1	0.818±0.007	0.801±0.004	0.802±0.006	−0.0158±0.0024	−0.0140±0.0014	−0.0166±0.0020
2	1.062±0.014	1.042±0.004	1.040±0.008	−0.0201±0.0024	−0.0220±0.0010	−0.0257±0.0031
3	1.278±0.013	1.259±0.007	1.256±0.008	−0.0235±0.0040	−0.0258±0.0022	−0.0291±0.0026
4	1.634±0.027	1.628±0.010	1.621±0.010	−0.0203±0.0081	−0.0361±0.0032	−0.0416±0.0031
5	1.986±0.021	1.961±0.013	1.955±0.012	−0.0348±0.0065	−0.0432±0.0040	−0.0502±0.0043
6	3.082±0.032	3.048±0.023	3.026±0.017	−0.0540±0.0101	−0.0729±0.0073	−0.0826±0.0054
7	3.290±0.030	3.263±0.025	3.240±0.020	−0.0578±0.0110	−0.0754±0.0081	−0.0855±0.0059
8	4.636±0.044	4.600±0.037	4.560±0.028	−0.0800±0.0140	−0.1070±0.0122	−0.1221±0.0870
9	4.763±0.050	4.759±0.050	4.709±0.055	−0.0847±0.0160	−0.1451±0.0173	−0.1583±0.0179
10	5.737±0.053	5.695±0.047	5.642±0.030	−0.0979±0.0168	−0.1324±0.0153	−0.1489±0.0098
11	7.328±0.077	7.272±0.067	7.192±0.041	−0.1270±0.0240	−0.1937±0.0222	−0.2176±0.0122
				0.28-μm-thick SLP layer		
1	1.060±0.008	1.068±0.011	1.069±0.006	−0.0155±0.0020	−0.0250±0.0030	−0.0310±0.0022
2	1.331±0.011	1.341±0.013	1.340±0.008	−0.0189±0.0035	−0.0338±0.0039	−0.424±0.0025
3	1.651±0.014	1.665±0.016	1.659±0.010	−0.0245±0.0046	−0.0410±0.0051	−0.0490±0.0031
4	2.107±0.018	2.124±0.020	2.118±0.013	−0.0311±0.0057	−0.0540±0.0063	−0.0678±0.0042
5	2.557±0.023	2.573±0.023	2.566±0.018	−0.0389±0.0071	−0.0642±0.0071	−0.0791±0.006
6	3.945±0.038	3.969±0.037	3.961±0.027	−0.0603±0.0111	−0.1020±0.0121	−0.1297±0.0086
7	4.213±0.037	4.242±0.041	4.232±0.032	−0.0643±0.0122	−0.1050±0.0133	−0.1310±0.010
9	5.989±0.054	6.043±0.058	6.024±0.038	−0.0925±0.0170	−0.1500±0.0190	−0.1932±0.0124
10	7.363±0.095	7.480±0.071	7.463±0.049	−0.1170±0.0870	−0.1830±0.0219	−0.2360±0.0154
11	9.310±0.090	9.371±0.095	9.339±0.067	−0.1460±0.0290	−0.2580±0.0304	−0.3320±0.0210
				0.38-μm-thick SLP layer		
1	1.424±0.016	1.427±0.014	1.404±0.016	−0.0240±0.0050	−0.0319±0.0041	−0.0355±0.0051
2	1.781±0.020	1.785±0.017	1.759±0.020	−0.0298±0.0062	−0.0441±0.0052	−0.0522±0.0759
3	2.216±0.025	2.220±0.021	2.190±0.027	−0.0374±0.0081	−0.0522±0.0069	−0.0610±0.0810
4	2.819±0.032	2.827±0.029	2.790±0.030	−0.0470±0.0100	−0.0714±0.0093	−0.0836±0.0100
5	3.421±0.040	3.434±0.032	3.391±0.036	−0.0565±0.0130	−0.0851±0.0100	−0.1004±0.0119
6	5.271±0.061	5.284±0.046	5.224±0.058	−0.0882±0.0191	−0.1331±0.0154	−0.1621±0.0181
7	5.673±0.064	5.689±0.052	5.623±0.065	−0.0960±0.0194	−0.1379±0.0171	−0.1659±0.0210
8	8.064±0.097	8.085±0.076	8.004±0.090	−0.1390±0.0311	−0.1991±0.0240	−0.2481±0.0282
9	8.064±0.097	8.085±0.076	8.004±0.090	−0.1390±0.0311	−0.1991±0.0240	−0.2481±0.0282
10	9.958±0.0117	10.008±0.089	9.892±0.103	−0.1671±0.0374	−0.2420±0.0283	−0.2949±0.0332
11	12.394±0.138	12.422±0.101	12.300±0.120	−0.2116±0.0412	−0.3337±0.0319	−0.4220±0.0380

Note. Characteristics were obtained using Eq. (2) to describe the experimental data on the dependence of the capacity factor (k) on the average carrier-gas pressure (p) in a capillary column (25 m×0.16 mm) with poly(ethylene glycol) PEG-20M using various carrier gases (He, N_2, CO_2) at 150 °C. r is the correlation coefficient, MV is multiple variance. * **1** is heptanol, **2** is methyl pelargonate, **3** is octan-1-ol, **4** is decan-2-ol, **5** is nonan-1-ol, **6** is naphthalene, **7** is decan-1-ol, **8** is 2,6-dimethylaniline, **9** is undecan-1-ol, **10** is 2,6-dimethylphenol, **11** is dodecan-1-ol.

tween the pressure dependences of the values characterizing relative retention are minor at this particular experimental accuracy. Therefore, to study these dependences in detail in the case of He, the accuracy of measurements needs to be substantially increased (compared to that attained in this study). Hence, in the subsequent discussion of the results obtained for the relative retention times α and the retention indices I, we

r			MV		
He	N_2	CO_2	He	N_2	CO_2
0.87	0.99	0.89	0.005	0.000	0.004
0.96	0.99	0.98	0.003	0.003	0.003
0.94	0.93	0.97	0.005	0.005	0.005
0.92	0.95	0.97	0.006	0.007	0.005
0.94	0.95	0.97	0.006	0.008	0.007
0.93	0.97	0.99	0.011	0.011	0.009
0.93	0.96	0.98	0.011	0.013	0.010
0.93	0.96	0.98	0.017	0.017	0.015
0.93	0.98	0.99	0.017	0.016	0.011
0.94	0.97	0.99	0.019	0.018	0.018
0.94	0.98	0.99	0.026	0.025	0.021
0.98	0.99	0.99	0.005	0.003	0.004
0.98	0.99	0.99	0.009	0.003	0.006
0.97	0.99	0.99	0.009	0.005	0.006
0.93	0.99	0.99	0.017	0.007	0.007
0.97	0.99	0.99	0.014	0.009	0.008
0.97	0.99	0.99	0.02	0.016	0.012
0.97	0.99	0.99	0.024	0.018	0.013
0.97	0.99	0.99	0.031	0.026	0.019
0.97	0.99	0.99	0.036	0.037	0.039
0.97	0.99	0.99	0.037	0.033	0.022
0.97	0.99	0.99	0.053	0.047	0.027
0.98	0.98	0.99	0.005	0.007	0.004
0.97	0.98	0.99	0.008	0.009	0.006
0.97	0.99	0.99	0.010	0.011	0.008
0.97	0.99	0.99	0.013	0.014	0.009
0.97	0.99	0.99	0.016	0.016	0.012
0.97	0.99	0.99	0.027	0.026	0.019
0.97	0.99	0.9	0.025	0.029	0.023
0.97	0.99	0.99	0.037	0.041	0.027
0.94	0.99	0.99	0.191	0.049	0.034
0.96	0.99	0.99	0.063	0.066	0.047
0.96	0.98	0.98	0.011	0.010	0.011
0.96	0.99	0.99	0.014	0.044	0.014
0.96	0.98	0.98	0.018	0.015	0.019
0.96	0.98	0.99	0.022	0.020	0.022
0.95	0.99	0.99	0.028	0.023	0.026
0.96	0.99	0.99	0.042	0.032	0.040
0.96	0.99	0.99	0.042	0.038	0.045
0.96	0.99	0.99	0.068	0.053	0.062
0.96	0.99	0.99	0.068	0.053	0.062
0.96	0.99	0.99	0.082	0.062	0.063
0.96	0.99	0.99	0.096	0.071	0.065

used only the data for N_2 and CO_2. In our opinion, the dependence of the relative retention on the pressure and on the nature of the carrier-gas for all of the columns and all of the compounds should also be observed in the case of He.

Previously[3] we have derived theoretically the linear dependence

$$k(p) = k_0 + b_k p, \quad (2)$$

Table 5. Comparison of the capacity factors* of compounds subjected to chromatography with various carrier gases (helium, nitrogen, carbon dioxide) on capillary columns with PEG-20M (SLP) layers of various thicknesses

Compound**	$k_0(He)/k_0(N_2)$	$k_0(CO_2)/k_0(N_2)$	$k_{4.5}(He)/k_{4.5}(N_2)$	$k_{4.5}(CO_2)/k_{4.5}(N_2)$	$k_{4.5}/k_0$ He	$k_{4.5}/k_0$ N_2	$k_{4.5}/k_0$ CO_2
			0.10-μm-thick SLP layer				
1	1.03	1.02	1.01	1.01	0.95	0.97	0.96
2	0.98	0.98	1.03	0.99	0.96	0.92	0.94
3	0.99	0.99	1.02	0.99	0.95	0.93	0.93
4	0.99	0.99	1.03	0.98	0.95	0.92	0.91
5	0.99	0.99	1.03	0.98	0.95	0.92	0.91
6	0.99	0.99	1.01	0.97	0.95	0.91	0.89
7	0.99	0.99	1.03	0.97	0.94	0.92	0.89
8	0.99	0.99	1.03	0.96	0.94	0.91	0.88
9	0.99	0.99	1.04	0.96	0.95	0.90	0.87
10	0.99	0.99	1.03	0.96	0.94	0.92	0.88
11	0.99	0.99	1.04	0.96	0.94	0.90	0.86
AV***	0.99	0.99	1.03	0.98	0.95	0.92	0.90
			0.22-μm-thick SLP layer				
1	1.02	1.00	1.02	0.99	0.92	0.92	0.91
2	1.02	1.00	1.04	0.99	0.92	0.90	0.89
3	1.02	1.00	1.03	0.99	0.92	0.91	0.90
4	1.00	1.00	1.05	0.98	0.95	0.90	0.89
5	1.01	1.00	1.04	0.98	0.93	0.90	0.89
6	1.01	0.99	1.05	0.98	0.92	0.89	0.88
7	1.01	0.99	1.04	0.98	0.92	0.90	0.88
8	1.01	0.99	1.04	0.97	0.93	0.90	0.88
9	1.01	0.99	1.07	0.97	0.92	0.87	0.85
10	1.01	0.99	1.04	0.97	0.93	0.90	0.88
11	1.01	0.99	1.06	0.97	0.93	0.88	0.97
AV***	1.01	0.99	1.05	0.98	0.93	0.89	0.88
			0.28-μm-thick SLP layer				
1	0.99	1.00	1.03	0.97	0.94	0.90	0.87
2	0.99	1.00	1.05	0.96	0.94	0.89	0.86
3	0.99	1.00	1.04	0.97	0.94	0.89	0.87
4	0.99	1.00	1.04	0.96	0.94	0.89	0.86
5	0.99	1.00	1.04	0.97	0.94	0.89	0.86
6	0.99	1.00	1.05	0.97	0.93	0.89	0.86
7	0.99	1.00	1.04	0.96	0.93	0.89	0.86
8	0.99	1.00	1.04	0.96	0.93	0.89	0.86
9	0.99	1.00	1.04	0.96	0.93	0.89	0.86
10	1.05	1.00	1.04	0.96	0.88	0.89	0.86
11	0.99	1.00	1.05	0.95	0.93	0.88	0.84
AV***	0.99	1.00	1.04	0.96	0.93	0.89	0.86
			0.38-μm-thick SLP layer				
1	1.00	0.98	1.03	0.97	0.93	0.90	0.89
2	1.00	0.99	1.04	0.96	0.93	0.89	0.87
3	1.00	0.99	1.03	0.96	0.93	0.90	0.88
4	1.00	0.99	1.04	0.96	0.93	0.89	0.87
5	1.00	0.99	1.04	0.96	0.93	0.89	0.87
6	1.00	0.99	1.04	0.96	0.93	0.89	0.86
7	1.00	0.99	1.04	0.96	0.93	0.89	0.87
8	1.00	0.99	1.04	0.96	0.93	0.89	0.86
9	1.00	0.99	1.04	0.96	0.93	0.89	0.86
10	1.00	0.99	1.03	0.96	0.93	0.89	0.87
11	1.00	0.99	1.05	0.95	0.93	0.88	0.85
AV***	1.00	0.99	1.04	0.96	0.93	0.89	0.87

* k_0 is the limiting capacity factor, $k_{4.5}$ is the capacity factor at a pressure of 4.5 atm. ** **1** is heptan-1-ol, **2** is methyl pelargonate, **3** is octan-1-ol, **4** is decan-2-ol, **5** is nonan-1-ol, **6** is decan-1-ol, **7** is naphthalene, **8** is 2,6-dimethylaniline, **9** is undecan-1-ol, **10** is 2,6-dimethylphenol, **11** is dodecan-1-ol. ***AV is the average value.

Table 6. Characteristics of the linear dependence of the β_k coefficient (Eq. (5)) on the limiting capacity factor (k_0) for organic compounds on capillary columns with the PEG-20M SLP at 150 °C

Thickness of the SLP layer/μm	A_β			B_β			r			MV		
	He	N_2	CO_2	He	N_2	CO_2	He	N_2	CO_2	He	N_2	CO_2
0.10	−0.0118	−0.0177	−0.0144	−0.0007	−0.0015	−0.0057	0.81	0.72	0.91	0.0005	0.0014	0.0025
0.22	−0.0188	−0.0204	−0.0241	0.0003	−0.0007	−0.0008	0.78	0.89	0.95	0.0005	0.0009	0.0006
0.28	−0.0147	−0.0240	−0.0295	−0.0001	−0.0004	−0.0006	0.92	0.86	0.82	0.0001	0.0006	0.0011
0.38	−0.0168	−0.0238	−0.0269	0.0000	−0.0002	−0.0006	0.77	0.70	0.86	0.0001	0.0007	0.0014

Note. r is the correlation coefficient, MV is multiple variance.

where $k(p)$ and k_0 are the capacity factors of a sorbate at the gas pressure p and at a pressure equal to zero, respectively, and b_k is a coefficient depending on the properties of the sorbate, the carrier gas, and the stationary liquid phase, and we have confirmed this dependence using limited experimental material. We used the same dependence (2) to describe the experimental results obtained in the present study (Table 4). The use of expression (2) is quite justified, because the correlation coefficients r are 0.87—0.97 for He and ~0.99 for N_2 and CO_2. The correlation coefficients (especially in the case of He) increase on going from a column with a thin film of PEG-20M (0.10 μm) to columns with thicker layers (0.22—0.38 μm).

An examination of the variation of $k(p)$, which is characterized quantitatively by the $b_k = dk/dp$ value, in terms of Eq. (2) demonstrates that, first, $k(p)$ decreases as the pressure increases (see Table 1) and, second, the magnitudes of b_k for the compounds studied vary in the following order: $b_k(\mathrm{He}) < b_k(\mathrm{N_2}) < b_k(\mathrm{CO_2})$.

We also evaluated the possibility of describing the experimental results by a three-term equation that can be obtained by a method reported previously,[3] if three rather than the first two terms of the expansion of the initial function into the Maclaurin series are used:

$$k(p) = k_0 + b_{k_1}p + b_{k_2}p^2, \quad (3)$$

where b_{k_1} and b_{k_2} are constant coefficients.

Our estimate has shown that the correlation coefficient r for Eq. (2) varies in the 0.94—0.99 range, while that for Eq. (3) is 0.96—0.99. Although the correlation coefficient for Eq. (3) is somewhat larger, we used in our discussion linear equation (2), because the correlation coefficient for this equation is still relatively large, and the qualitative interpretation of the results in terms of this equation is simpler.

To describe the dependence of the capacity factor of the column on the average carrier-gas pressure, it is also expedient to use the following equation:

$$\ln k(p) = \ln k_0 + \beta p, \quad (4)$$

where β is a constant coefficient, whose magnitude depends on characteristics of the sorbate, carrier gas, and the stationary liquid phase (SLP).

The correlation coefficient r for Eq. (4) applied to the experimental data obtained in this study for capillary columns containing PEG-20M films of various thicknesses lies in the 0.89—0.99 range; it increases for capillary columns containing thicker layers of the SLP. It should also be noted that the limiting k_0 values found from Eqs. (2) and (4) differ only slightly from each other.

It may be expected that the limiting (invariant) capacity factors for the compounds analyzed in this study and for the carrier gases under consideration would be close to one another. To verify this assumption, we calculated the following ratios: $k_0(\mathrm{He})/k_0(\mathrm{N_2})$ and $k_0(\mathrm{CO_2})/k_0(\mathrm{N_2})$. In conformity with the theory, these ratios should be close to 1.0, *i.e.*, $k_0(\mathrm{He}) \approx k_0(\mathrm{N_2}) \approx k_0(\mathrm{CO_2})$. It follows from Table 5 that the average values for these ratios calculated from experimental data are in the 0.99—1.01 range for all the capillary columns with SLP films of various thicknesses.

Comparison of similar ratios of the capacity factors measured at a carrier-gas pressure of 4.5 atm $[k_{4.5}(\mathrm{He})/k_{4.5}(\mathrm{N_2}), k_{4.5}(\mathrm{CO_2})/k_{4.5}(\mathrm{N_2})]$ shows that these ratios differ by 2—5%, *i.e.*, in this case, the difference is several times larger (see Tables 1 and 5). These ratios tend to increase on going to columns with thicker SLP films; this indicates that the SLP has an effect on the variation of the capacity factor as a function of the carrier gas pressure. Apparently, this is due to the fact that the characteristics of a SLP change somewhat when a carrier gas is dissolved in it.

Table 5 presents the $k_{4.5}/k_0$ values for the three carrier gases characterizing the difference between the limiting capacity values and those measured at an average carrier-gas pressure in the capillary column equal to 4.5 atm for all the compounds under study. This difference varies from 5 to 13%. The $k_{4.5}/k_0$ ratio increases in the following series of carrier gases: He < N_2 < CO_2 (see Table 5).

Note that the $\beta_k = b_k/k_0$ value follows a linear dependence on the k_0 values characterizing the compounds under analysis:

$$\beta_k = A_\beta + B_\beta k_0, \quad (5)$$

where $\beta_k = (2B_{12} - V_1^\infty)/(RT)$ (B_{12} is the second mixed virial coefficient characterizing the interaction between

Table 7. Characteristics of linear equation (6) obtained by applying this equation to the description of experimental data using the dependence of the relative retention (α) on the average carrier-gas pressure (p)

Compound*	α_0		b_α		r		MV	
	N_2	CO_2	N_2	CO_2	N_2	CO_2	N_2	CO_2
			0.10-μm-thick SLP layer					
1	1.292±0.004	1.293±0.008	−0.0048±0.0011	−0.0088±0.0030	0.94	0.93	0.003	0.006
2	1.572±0.002	1.593±0.003	−0.0058±0.0005	−0.0163±0.0010	0.99	0.99	0.001	0.002
3	2.038±0.004	2.059±0.018	−0.0123±0.0010	−0.0285±0.0059	0.99	0.96	0.002	0.013
4	2.448±0.007	2.481±0.020	−0.0140±0.0021	−0.0365±0.0070	0.97	0.97	0.005	0.015
5	3.806±0.016	3.857±0.040	−0.0325±0.0049	−0.0725±0.0104	0.98	0.98	0.011	0.025
6	3.979±0.015	4.051±0.030	−0.0267±0.0051	−0.0744±0.0115	0.97	0.98	0.011	0.022
7	5.643±0.024	5.752±0.049	−0.0412±0.0080	−0.1180±0.0152	0.97	0.98	0.017	0.034
8	5.885±0.027	5.999±0.069	−0.0622±0.0050	−0.1442±0.0200	0.98	0.98	0.019	0.048
9	7.015±0.036	7.166±0.066	−0.0469±0.0111	−0.1491±0.0210	0.95	0.98	0.025	0.046
10	9.053±0.044	9.223±0.091	−0.1015±0.0143	−0.2310±0.0289	0.98	0.99	0.031	0.063
			0.22-μm-thick SLP layer					
1	1.301±0.004	1.298±0.000	−0.0053±0.0012	−0.0062±0.0010	0.95	0.99	0.003	0.001
2	1.564±0.005	1.566±0.004	—	−0.0049±0.0037	1.00	0.95	0.003	0.003
3	2.033±0.009	2.022±0.006	−0.0103±0.0029	−0.0117±0.0019	0.93	0.97	0.006	0.004
4	2.448±0.013	2.438±0.008	−0.0110±0.0040	−0.0137±0.0026	0.89	0.97	0.009	0.006
5	3.805±0.020	3.774±0.015	−0.0250±0.0069	−0.0284±0.0050	0.93	0.97	0.016	0.010
6	4.073±0.027	4.041±0.020	−0.0230±0.0086	−0.0259±0.0061	0.89	0.95	0.019	0.014
7	5.742±0.040	5.686±0.029	−0.0332±0.0130	−0.0390±0.0099	0.88	0.94	0.028	0.022
8	5.947±0.078	5.879±0.028	−0.0828±0.0247	−0.0852±0.0090	0.92	0.99	0.055	0.020
9	7.107±0.049	7.037±0.033	−0.0405±0.0157	−0.0458±0.0099	0.87	0.95	0.035	0.023
10	9.082±0.071	8.974±0.041	−0.0870±0.0199	−0.0969±0.0129	0.94	0.98	0.049	0.028
			0.28-μm-thick SLP layer					
1	1.255±0.002	1.254±0.001	−0.0021±0.0006	−0.0040±0.0003	0.94	0.99	0.001	0.001
2	1.557±0.002	1.553±0.003	−0.0017±0.0059	−0.0037±0.0014	0.87	0.93	0.002	0.002
3	1.988±0.004	1.981±0.005	−0.0041±0.0011	−0.0068±0.0015	0.91	0.95	0.003	0.003
4	2.410±0.007	2.400±0.006	−0.0037±0.0019	−0.0053±0.0019	0.77	0.89	0.005	0.004
5	3.717±0.014	3.708±0.013	−0.0093±0.0039	−0.0168±0.0039	0.83	0.95	0.010	0.009
6	3.970±0.014	3.959±0.016	−0.0044±0.0048	−0.0086±0.0051	0.57	0.77	0.010	0.011
7	5.659±0.023	5.638±0.022	−0.0087±0.0073	−0.0210±0.0069	0.64	0.90	0.016	0.016
8	5.657±0.020	5.638±0.022	−0.0082±0.0070	−0.0210±0.0069	0.63	0.90	0.016	0.016
9	7.004±0.028	6.983±0.024	−0.0091±0.0093	−0.0220±0.0077	0.70	0.90	0.020	0.017
10	8.778±0.046	8.749±0.030	−0.0401±0.0150	−0.0693±0.0098	0.89	0.98	0.032	0.021
			0.38-μm-thick SLP layer					
1	1.252±0.002	1.254±0.002	−0.0034±0.0006	−0.0061±0.0007	0.97	0.99	0.001	0.002
2	1.556±0.001	1.560±0.003	−0.0021±0.0002	−0.0040±0.0010	0.99	0.96	0.000	0.002
3	1.983±0.001	1.989±0.002	−0.0064±0.0002	−0.0106±0.0007	0.99	0.99	0.000	0.002
4	2.407±0.003	2.417±0.005	−0.0063±0.0010	−0.0119±0.0021	0.98	0.98	0.002	0.004
5	3.707±0.004	3.726±0.009	−0.0134±0.0014	−0.0250±0.0090	0.99	0.99	0.003	0.007
6	3.989±0.002	4.010±0.012	−0.0092±0.0007	−0.0193±0.0040	0.99	0.96	0.002	0.009
7	5.671±0.006	5.709±0.017	−0.0160±0.0018	−0.0380±0.0171	0.99	0.98	0.004	0.012
8	5.671±0.006	5.709±0.017	−0.0160±0.0018	−0.0380±0.0171	0.99	0.98	0.004	0.012
9	7.018±0.009	7.055±0.019	−0.0155±0.0028	−0.0389±0.0061	0.97	0.98	0.006	0.013
10	8.719±0.020	8.780±0.019	−0.0464±0.0063	−0.0923±0.0069	0.98	0.99	0.014	0.015

Note. Experimental conditions: a capillary column (25 m×0.16 mm) with poly(ethylene glycol) PEG-20M, nitrogen and carbon dioxide as carrier gases, 150 °C. r is the correlation coefficient, MV is multiple variance. * **1** is methyl pelargonate, **2** is octan-1-ol, **3** is decan-2-ol, **4** is nonan-1-ol, **5** is naphthalene, **6** is decan-1-ol, **7** is 2,6-dimethylaniline, **8** is undecan-1-ol, **9** is 2,6-dimethylphenol, **10** is dodecan-1-ol.

a sorbate and a carrier gas, V_1^∞ is the partial molar volume of the dissolved substance at infinite dilution, R is the characteristic gas constant, T is the absolute temperature, and A_β and B_β are constants that depend on the characteristics of the chromatographic system and on the experimental conditions). Characteristics of Eq. (5) are given in Table 6, from which it follows that Eq. (5) provides a satisfactory description of the experimental data. The largest correlation coefficient r was obtained for CO_2. Note that the A_β value increases with an increase in the thickness of the SLP film in the capillary column, whereas the B_β value simultaneously

Table 8. Characteristics of linear equation (6) obtained by applying this equation to the description of experimental data using the dependence of the retention index (*I*) for organic compounds on the average carrier-gas pressure (*p*)

Compound*	I_0		b_I		*r*		*MV*	
	N_2	CO_2	N_2	CO_2	N_2	CO_2	N_2	CO_2
			0.10-μm-thick SLP layer					
1	756.68±0.85	757.32±1.10	−0.529±0.210	−0.853±0.312	0.93	0.94	0.43	0.49
2	858.69±0.15	—	−0.304±0.049	—	0.98	—	0.11	—
3	990.91±0.51	990.06±0.33	−0.428±0.160	−0.246±0.109	0.88	0.91	0.35	0.23
4	1089.15±0.59	1088.99±0.94	0.815±0.190	0.955±0.297	0.95	0.92	0.41	0.66
5	1140.81±0.14	1141.10±0.45	0.966±0.045	1.012±0.140	0.99	0.98	0.10	0.31
			0.22-μm-thick SLP layer					
1	758.99±0.05	758.50±0.34	−0.538±0.099	−0.676±0.107	0.97	0.98	0.22	0.24
2	858.18±0.05	857.74±0.12	−0.309±0.016	−0.289±0.038	0.99	0.98	0.04	0.08
3	986.66±0.04	986.53±0.22	−0.232±0.013	−0.240±0.070	0.93	0.93	0.03	0.15
4	1090.21±2.14	1090.53±2.31	2.364±0.679	2.269±0.732	0.93	0.91	1.49	1.62
5	1142.12±0.95	1142.46±0.94	1.505±0.302	1.539±0.299	0.96	0.96	0.67	0.66
			0.28-μm-thick SLP layer					
1	751.36±0.14	751.41±0.04	−0.304±0.040	−0.594±0.037	0.98	0.99	0.10	0.03
2	855.88±0.10	856.09±0.20	−0.150±0.029	−0.424±0.059	0.96	0.98	0.07	0.14
3	986.74±0.12	986.95±0.15	−0.242±0.036	−0.473±0.047	0.98	0.99	0.08	0.10
4	1100.11±0.06	1100.00±0.00	−0.028±0.019	0	1.00	1.00	0.00	0.00
5	1148.56±0.14	1148.63±0.049	0.469±0.043	0.655±0.016	0.99	0.99	0.10	0.03
			0.38-μm-thick SLP layer					
1	750.75±0.35	750.95±0.22	−0.452±0.11	−0.865±0.069	0.95	0.99	0.24	0.15
2	855.56±0.14	855.51±0.19	−0.259±0.040	−0.358±0.060	0.97	0.97	0.10	0.14
3	985.45±0.08	985.50±0.14	−0.244±0.026	−0.388±0.038	0.99	0.98	0.06	0.09
4	1100.00±0.00	1100.00±0.00	0	0	1.00	1.00	0.00	0.00
5	1149.56±0.10	1149.05±0.12	0.451±0.029	0.794±0.039	0.99	0.99	0.07	0.09

Note. Experimental conditions: a capillary column (25 m×0.16 mm) with polydimethylsiloxane SE-30, nitrogen and carbon dioxide as carrier gases, 100 °C. *r* is the correlation coefficient, *MV* is multiple variance. * **1** is methyl pelargonate, **2** is decan-2-ol, **3** is naphthalene, **4** is 2,6-dimethylaniline, **5** is 2,6-dimethylphenol.

decreases. Thus, the β_k values depend on the thickness of the SLP film in the capillary column, which implies that SLP plays a certain role in the variation of the capacity values.

In practice, relative retention times and retention indices are used more frequently than capacity factors. Generally, experimental data fit in the following linear equation:

$$\mathrm{Rel}(p) = \mathrm{Rel}(0) + b_{\mathrm{Rel}}p, \qquad (6)$$

where Rel(*p*) and Rel(0) are relative retention values at the average pressure in the column *p* and at a pressure approaching zero, respectively, b_{Rel} is a coefficient depending on the properties of the chromatographic system and on the experimental conditions.

Experimental data characterizing the applicability of Eq. (6) to the description of the pressure dependence of the relative retention time are presented in Table 7. It can be seen that Eq. (6) provides quite a satisfactory description of experimental data.

Similar dependences are observed for the Kovats retention index (Table 8); in this case, better correlation was found for capillary columns with thicker SLP (SE-30) films. For example, for a capillary column with a 0.38-μm-thick SLP layer, the average value $\Delta I_0 = [I_0(CO_2) - I_0(N_2)] = 0.17$ iu, while for a column with a 0.22-μm-thick layer, $\Delta I_0 = 0.30$ iu. For the retention indices measured at an average pressure of 4.5 atm, the ΔI values are much larger. Thus for a column in which the thickness of the SLP layer is 0.38 μm, $\Delta I = 0.8$ iu. Thus, the limiting retention indices I_0 for the sorbates and the carrier gases studied in this work can be regarded as invariant values and as true chromatographic constants of the sorbates. It is also noteworthy that the difference between the retention indices found at $\bar{p} = 4.5$ atm and the I_0 values for compounds under analysis and for all the columns increases in the following order: He < N_2 < CO_2.

Analysis of the dependence of the limiting retention index on the thickness of the SLP layer shows that this value markedly changes as the thickness of the layer increases, and that the difference can be both positive (for example, for 2,6-dimethylphenol) and negative (for example, for methyl pelargonate). This can be explained by adsorption effects, *i.e.*, retention is caused not only by the absorption of the analyzed compounds by the SLP layer but also by their adsorption at the SLP interfaces (the gas—SLP and SLP—solid support inter-

Table 9. Coefficients of equation (7) and correlation (*r*) and multiple variance (*MV*) coefficients for a series of organic compounds

Chromatographed compound	Invariant value I_{00}		b_{I_0} coefficient		*r*		*MV*	
	N_2	CO_2	N_2	CO_2	N_2	CO_2	N_2	CO_2
Methyl pelargonate	748.69±0.04	748.64±0.19	4.49	4.82	0.99	0.99	0.04	0.18
Decan-2-ol	854.47±0.02	852.33±0.82	2.37	2.66	0.99	0.98	0.02	0.31
Naphthalene	983.86±0.46	984.29±0.43	3.94	3.22	0.99	0.99	0.04	0.40
2,6-Dimethylphenol	1152.54±0.02	1152.04±0.36	−6.59	−6.06	0.99	0.99	0.02	0.34

faces). The adsorption effects and methods of their quantitative estimation were discussed in a monograph devoted to this topic.[7]

Using the methods developed previously,[7] we evaluated the correspondence of the following equation to experimental data:

$$I_0 = I_{00} + b_{I_0}/k_{st}, \qquad (7)$$

where I_{00} is the invariant value of the limiting index I_0, which is caused only by the absorption of the analyzed compounds by the SLP film, b_{I_0} is a coefficient determined by the adsorption interaction in the system, and k_{st} is the capacity factor for octan-1-ol chosen as the standard compound for which the adsorption at the SLP interfaces can be neglected.

Table 9 presents characteristics of the Eq. (7) in question and the correlation coefficients *r*. These results make it possible to conclude that Eq. (7) provides an adequate description of the experimental data. Thus, invariant I_{00} values take into account two groups of factors: first, the nature of the carrier gas and its pressure and, second, adsorption of the compounds under analysis at both interfaces of the SLP.

Thus, our results indicate that the effect of the carrier gas on the retention values should be taken into account in precise studies.

The following conclusions can be drawn. 1. Relative retention values (relative retention time, Kovats index) depend linearly on the average carrier-gas pressure in the chromatographic column. 2. The effect of the nature of the carrier gas on the retention values increases in the following order: He < N_2 < CO_2. 3. The limiting relative retention at a carrier gas pressure approaching zero rather than the relative retention measured experimentally should be used as an invariant characteristic of retention. 4. The nature of the stationary liquid phase has a noticeable effect on the relative retention values.

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References

1. M. S. Vigdergauz, L. V. Semenchenko, V. A. Ezrets, and Yu. N. Bogoslovskii, *Kachestvennyi gazokhromatograficheskii analiz* [*Qualitative Gas-Chromatographic Analysis*], Nauka, Moscow, 1978, 244 pp. (in Russian).
2. G. Guiochon and C. L. Guillemin, *Quantitative Gas Chromatography*, Elsevier, Amsterdam, 1988.
3. V. G. Berezkin, A. A. Korolev, and I. V. Malyukova, *J. Microcolumn Separation*, 1996, **8**, 389.
4. V. G. Berezkin, A. A. Korolev, and I. V. Malyukova, *Zh. Anal. Khim.*, 1997, **52**, 164 [*J. Anal. Chem.*, 1997, **52** (Engl. Transl.)].
5. P. J. Hesse, R. Battino, P. Scharlin, and E. Wilhelm, *J. Chem. Eng. Data*, 1996, **41**, 195.
6. J. R. Conder and C. L. Young, *Physico-Chemical Measurement by Gas Chromatography*, J. Wiley, Chichester, 1978.
7. V. G. Berezkin, *Gas-Liquid-Solid Chromatography*, Marcel Dekker, New York, 1990, 232 pp.

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