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PROPERTIES OF BINARY STATIONARY PHASES IN GAS–LIQUID PARTITION CHROMATOGRAPHY

III. APPLICATION OF ASSOCIATION CONSTANTS FOR THE DETERMINATION OF THE ADSORPTIVE PROPERTIES OF THE SUPPORT

TERESA CZAJKOWSKA*
Department of Physical Chemistry, Institute of Chemistry, Marie Curie-Sklodowska University, 20031 Lublin (Poland)

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SUMMARY

Association constants were used to determine the effective concentration of bis(ethylhexyl) tetrachlorophthalate (EHTCP) in the system EHTCP–squalane on a diatomite support with a specific surface area of 0.5 m^2/g (Polsorb B NAW) at different coverages of the support by the stationary phase. It was shown that, even with relatively large amounts of the stationary phase (10%), the effective concentration of the polar component is lower than the original concentration. Retention data of aromatic and aliphatic oxygen-containing compounds, measured at different temperatures, were used.

INTRODUCTION

In a previous study[1] it was demonstrated that in the system tetradecylamine (TDA)–*n*-octadecane (OD), the association constants calculated from the bulk partition coefficients, K_L, differ considerably from those calculated on the basis of the partition coefficients observed with different coverages of the support by the stationary phase. The effective concentration of the complexing agent in the stationary phase for various coverages of the support by that phase were also calculated on the basis of association constants determined from the bulk data.

In this study we applied the measurement of association constants to the determination of the adsorptive properties of the support and the adsorption contribution to the overall retention mechanism. To this end, a less active (*i.e.*, white instead of pink) diatomite support (Polsorb B NAW[2]) with a specific surface area nearly seven times smaller and less active than the hexadecylamine complexing agent bis(ethylhexyl) tetrachlorophthalate (EHTCP) was used. Aromatic hydrocarbons and polar aliphatic compounds were used as solutes.

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* Present address: Macromolecular Chemistry Section, Gerontology Research Center, National Institute on Aging, Baltimore City Hospitals, Baltimore, MD 21224, U.S.A.

The equations of Purnell[3] were used to determine association constants despite the fact that, as described by these equations, they do not constitute the absolute thermodynamic equilibrium constants[4]. However, the main purpose of the work was the determination of the adsorptive properties of the support, by defining the effective concentration, C_{eff}, for various coverages, and not the determination of association constants.

The bulk partition coefficients were determined using the method of Conder *et al.*[5].

EXPERIMENTAL

Measurements were made with a Perkin-Elmer Model 116E instrument equipped with a katarometer with nitrogen as the carrier gas at a flow-rate of 60 ml/min. A silanized glass column (1 m × 4 mm I.D.) was used. The measurements were made at 67.6, 76.7, 83.4 and 95.6°C. The size of the samples was held constant at 0.1 µl.

The Polsorb B NAW[2] support, with a particle size of 0.2–0.3 mm, was dried for 4 h at 200°C before coating. The support was coated in amounts of 3, 6 and 10% (w/w) with EHTCP and its mixtures with squalane in ratios of 3:1, 1:1 and 1:3 (w/w) by means of the fluidization method. The columns were conditioned overnight at 120°C with the carrier gas at the stated flow-rate. The column packings were prepared, then the volume of the stationary phase was calculated from the previously measured[6] density of these liquids at the specified temperature.

RESULTS AND DISCUSSION

The ratios of the observed (K_R) and bulk (K_L) partition coefficients for 1-butanol and ethylbenzene in the mixed stationary phase to the partition coefficients in the inert component of the stationary phase (K_R°, K_L°), as a function of the concentration of EHTCP in the mixed stationary phase at various coverages of the support, are shown graphically in Figs. 1, 2 and 3. The slope increases as the amount of stationary phase increases and, even at 10% coverage, it is clearly smaller than the slope of the line representing the pure partition.

The above observations suggest that for each different amount of the stationary phase, the concentration of the complexing agent originally introduced is higher than that of its effective concentration, that is, in the stationary phase there are fewer polar groups able to interact with the solutes than might appear judging from the composition of the mixed stationary phase.

At 67.6°C the dependence of the ratio K_R/K_R° takes a parabolic shape and two types of complexes (1:1 and 2:1) are formed[3].

Table I lists the association constants calculated on the basis of the bulk partition coefficients for the compounds presented in Fig. 1 and for other solutes analyzed in this system. The so-called effective concentrations that were calculated for these solutes, with different coverages of the support at different temperatures, are given in Table II.

It is evident that when the amount of the stationary phase is 3% only about 40% of the functional groups of the polar component are involved in the complexation process, but when the coverage is 10% the amount of these groups does not exceed 65%. The remaining groups are probably linked with the support surface or oriented towards its surface and present on the gas–liquid surface.

Fig. 1 and the data in Table I show the different behaviors of aromatic and aliphatic polar compounds in the system investigated. Although weak complexes are

TABLE I

ASSOCIATION CONSTANTS AT 95.6, 83.4, 76.7 AND 67.6°C FOR THE COMPLEXATION REACTIONS BETWEEN EHTCP AND VARIOUS SOLUTES

Solute	*95.6°C (K_1)*	*83.4°C (K_1)*	*76.7°C (K_1)*	*67.6 C*	
				K_1	K_2
1-Butanol	0.196	0.107	0.090	0.087	0.275
Diethyl ketone	0.246	0.115	0.096	0.089	0.218
Isoamyl acetate	0.245	0.096	0.065	0.042	0.272
Benzene	0.259	0.346	0.624	0.351	0.390
Toluene	0.225	0.334	0.476	0.299	0.066
Ethylbenzene	0.207	0.22	0.328	0.301	0.403

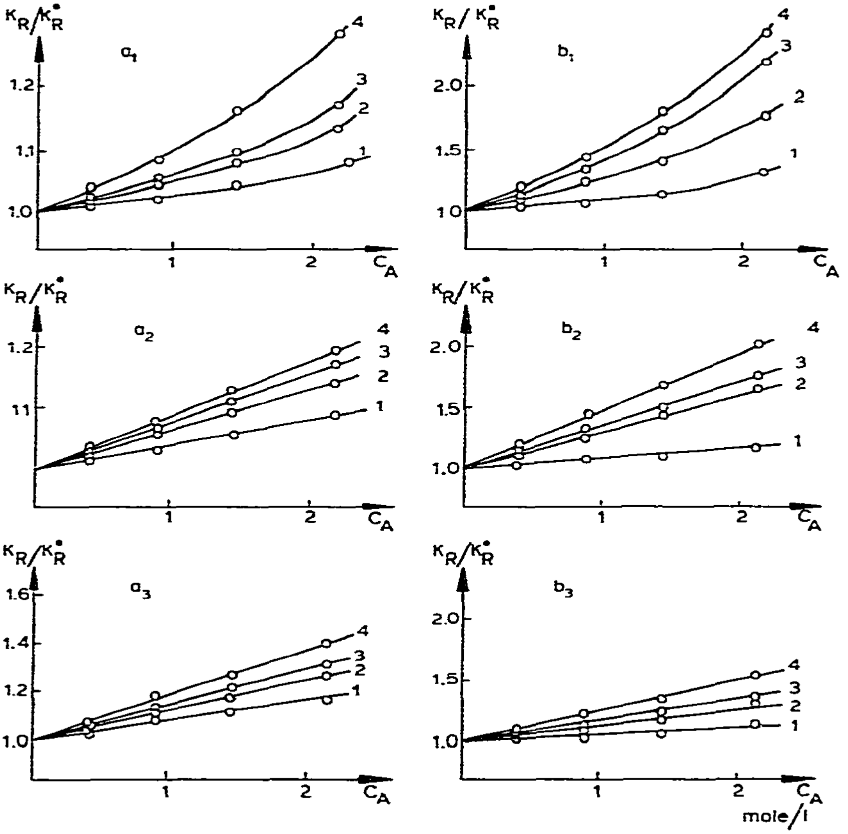
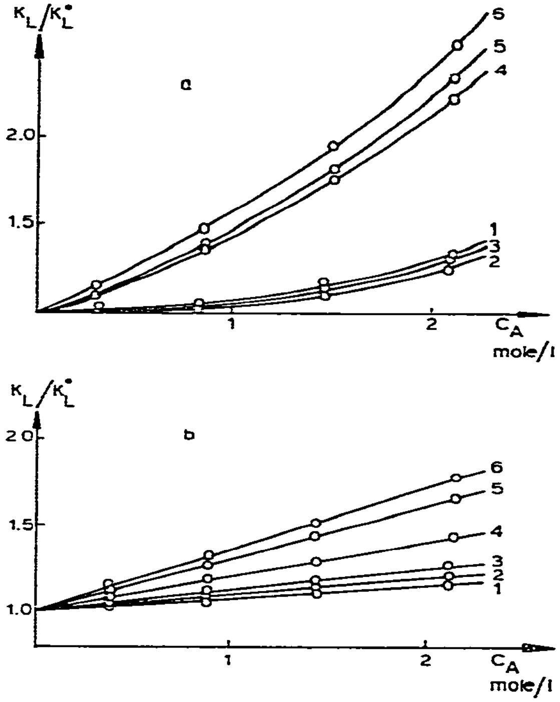


Fig. 1. Variation of K_R/K_R° with concentration of EHTCP in squalane at different loadings of the stationary phase. (a) 1-Butanol; (b) benzene. a_1, b_1, 67.6°C; a_2, b_2, 76.7°C; a_3, b_3, 95.6°C. Graphs: 1, 3%; 2, 6%, 3, 10%; 4, values obtained from K_L.

TABLE II

EFFECTIVE CONCENTRATION OF EHTCP IN EHTCP SQUALANE POLSORB B NAW SOLUTE SYSTEMS AT VARIOUS TEMPERATURES AND LOADINGS OF THE STATIONARY PHASE

Solute	*Concentration of liquid stationary phase on the support (%, w/w)*	*Temperature (°C)*															
		95.6				*83.4*				*76.7*				*67.6*			
		Concentration of EHTCP in squalane introduced (mole/l)															
		2.14	*1.42*	*0.86*	*0.38*	*2.16*	*1.43*	*0.86*	*0.39*	*2.17*	*1.43*	*0.87*	*0.39*	*2.18*	*1.44*	*0.87*	*0.40*
1-Butanol	3	0.923	0.586	0.382	0.178	0.962	0.610	0.250	0.173	1.027	0.748	0.379	0.245	0.736	0.458	0.276	0.140
	6	1.403	0.892	0.556	0.244	1.551	1.009	0.731	0.268	1.608	1.050	0.736	0.312	1.251	0.770	0.479	0.187
	10	1.596	1.102	0.658	0.259	1.851	1.231	0.826	0.351	1.929	1.284	0.910	0.357	1.468	0.960	0.578	0.203
Diethyl ketone	3	1.126	0.776	0.434	0.170	1.065	0.672	0.535	0.139	1.046	0.711	0.356	0.156	0.987	0.653	0.397	0.110
	6	1.386	0.914	0.565	0.256	1.484	0.908	0.620	0.270	1.642	1.130	0.607	0.271	1.489	0.987	0.617	0.233
	10	1.593	1.032	0.599	0.313	1.791	1.231	0.812	0.314	1.932	1.297	0.910	0.376	2.064	1.230	0.748	0.320
Isoamyl acetate	3	1.114	0.775	0.428	0.195	0.906	0.645	0.395	0.250	0.775	0.527	0.341	0.108	0.704	0.512	0.228	0.083
	6	1.189	1.106	0.669	0.302	1.541	1.093	0.562	0.320	1.333	0.759	0.480	0.115	1.125	0.700	0.478	0.204
	10	1.804	0.934	0.730	0.318	1.842	1.229	0.656	0.384	1.689	0.945	0.680	0.344	1.543	0.832	0.521	0.317
Benzene	3	0.532	0.324	0.200	0.088	0.473	0.303	0.196	0.101	0.314	0.189	0.131	0.072	0.647	0.309	0.170	0.054
	6	1.127	0.718	0.463	0.189	1.239	0.823	0.537	0.176	1.049	0.690	0.447	0.113	1.345	0.854	0.309	0.218
	10	1.463	0.969	0.548	0.362	1.375	0.956	0.552	0.179	1.225	0.882	0.496	0.150	1.894	1.269	0.730	0.356
Toluene	3	0.542	0.355	0.182	0.093	0.832	0.538	0.338	0.134	0.661	0.420	0.246	0.113	0.837	0.425	0.287	0.107
	6	1.413	0.964	0.560	0.231	1.383	0.907	0.505	0.290	1.303	0.862	0.527	0.214	1.576	0.912	0.587	0.237
	10	1.804	1.161	0.702	0.315	1.676	1.119	0.673	0.305	1.859	1.003	0.729	0.340	2.000	1.300	0.812	0.312
Ethylbenzene	3	0.565	0.376	0.236	0.072	0.540	0.319	0.220	0.216	0.546	0.311	0.226	0.186	0.665	0.443	0.288	0.144
	6	1.149	0.724	0.371	0.207	1.144	0.729	0.436	0.238	1.126	0.769	0.448	0.299	1.572	0.962	0.588	0.165
	10	1.521	0.980	0.589	0.289	1.858	1.454	0.882	0.300	1.474	0.980	0.613	0.183	1.833	1.148	0.674	0.271



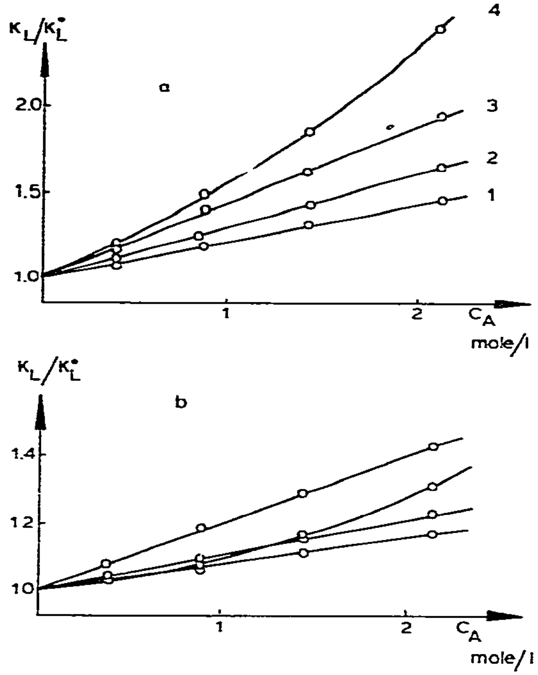


Fig. 2. Variation of $K_L/K_L^{\bullet}$ with concentration of EHTCP in squalane for various solutes at (a) 67.6°C and (b) 83.4°C. Graphs: 1, isoamyl acetate; 2, 1-butanol; 3, diethyl ketone; 4, ethylbenzene; 5, toluene; 6, benzene.

Fig. 3. Variation of $K_L/K_L^{\bullet}$ with concentration of EHTCP in squalane at various temperatures. (a) Toluene; (b) diethyl ketone. Graphs: 1, 95.6°C; 2, 83.4°C; 3, 76.7°C; 4, 67.6°C.

usually formed in this system the more stable complexes are formed by aromatic compounds, especially at lower temperatures (Figs. 2 and 3).

The ratio of the effective concentration of the complexing agent to the concentration originally introduced had been previously suggested[1] to be treated as the activity coefficient (Fig. 4) of the complexing agent in the system mixed stationary phase–support–solute. Table III presents such values for different coverages of the support at different temperatures. The values of the activity coefficients are less than unity in nearly all instances, and are essentially identical within the limits of experimental error, for different compositions of the mixed stationary phase at a given coverage (Fig. 5), and they all increase with increase in the amount of stationary phase on the support. At higher temperatures (83.4 and 95.6°C), the activity coefficients calculated from the retention data of aromatic compounds are lower than those calculated from the retentions of 1-butanol, diethyl ketone, and isoamyl acetate (Table III, Fig. 5a). A decrease in temperature reduces the differences, whereas at 67.6°C a reverse process is observed, even for higher coverages (Fig. 5b).

The above observation agrees with the reverse dependence of the association constants of aromatic and aliphatic compounds on temperature. The activity coefficients do not reach unity with any amount of the stationary phase (except for two

TABLE III

ACTIVITY COEFFICIENTS OF EHTCP IN EHTCP SQUALANE POLSORB B NAW SOLUTE SYSTEMS AT VARIOUS TEMPERATURES AND LOADINGS OF THE STATIONARY PHASE

Solute	*Concentration of liquid stationary phase on the support (%, w/w)*	*Temperature (°C)*															
		95.6				*83.4*				*76.7*				*67.6*			
		Concentration of EHTCP in squalane introduced (mole/l)															
		2.14	*1.42*	*0.86*	*0.38*	*2.16*	*1.43*	*0.86*	*0.39*	*2.17*	*1.43*	*0.87*	*0.39*	*2.18*	*1.44*	*0.87*	*0.40*
1-Butanol	3	0.431	0.411	0.444	0.458	0.445	0.426	0.428	0.446	0.473	0.519	0.433	0.621	0.337	0.318	0.313	0.350
	6	0.655	0.628	0.646	0.577	0.711	0.705	0.841	0.683	0.741	0.729	0.842	0.791	0.575	0.534	0.544	0.467
	10	0.745	0.776	0.765	0.760	0.866	0.860	0.948	0.895	0.896	0.892	0.926	0.910	0.673	0.666	0.656	0.507
Diethyl ketone	3	0.526	0.546	0.504	0.447	0.394	0.469	0.322	0.356	0.482	0.497	0.409	0.390	0.452	0.453	0.451	0.275
	6	0.647	0.643	0.655	0.656	0.687	0.634	0.720	0.692	0.756	0.789	0.690	0.695	0.683	0.685	0.701	0.582
	10	0.744	0.726	0.694	0.802	0.829	0.860	0.944	0.805	0.885	0.890	1.045	0.964	0.946	0.854	0.850	0.800
Isoamyl acetate	3	0.520	0.545	0.497	0.500	0.419	0.451	0.459	0.441	0.341	0.454	0.368	0.391	0.322	0.355	0.259	0.207
	6	0.695	0.658	0.777	0.744	0.713	0.764	0.653	0.620	0.614	0.530	0.551	0.625	0.516	0.486	0.543	0.510
	10	0.842	0.778	0.848	0.815	0.852	0.859	0.762	0.820	0.778	0.660	0.712	0.940	0.707	0.577	0.592	0.792
Benzene	3	0.248	0.228	0.232	0.225	0.218	0.211	0.227	0.256	0.144	0.132	0.150	0.180	0.296	0.214	0.193	0.135
	6	0.526	0.505	0.484	0.573	0.575	0.575	0.624	0.451	0.482	0.482	0.514	0.289	0.616	0.593	0.355	0.545
	10	0.683	0.682	0.637	0.632	0.636	0.636	0.668	0.641	0.652	0.679	0.574	0.570	0.868	0.881	0.829	0.890
Toluene	3	0.253	0.250	0.211	0.238	0.385	0.376	0.393	0.343	0.304	0.291	0.282	0.283	0.384	0.295	0.326	0.250
	6	0.660	0.678	0.651	0.592	0.640	0.634	0.587	0.592	0.595	0.607	0.605	0.535	0.722	0.633	0.667	0.592
	10	0.842	0.817	0.816	0.807	0.775	0.855	0.782	0.743	0.586	0.706	0.837	0.850	0.954	0.902	0.922	0.720
Ethylbenzene	3	0.264	0.258	0.274	0.184	0.250	0.223	0.255	0.253	0.251	0.217	0.198	0.272	0.305	0.307	0.327	0.360
	6	0.536	0.509	0.431	0.530	0.529	0.509	0.506	0.610	0.553	0.518	0.537	0.514	0.457	0.721	0.668	0.412
	10	0.710	0.690	0.684	0.741	0.868	1.016	1.025	0.923	0.679	0.686	0.685	0.704	0.839	0.797	0.774	0.677

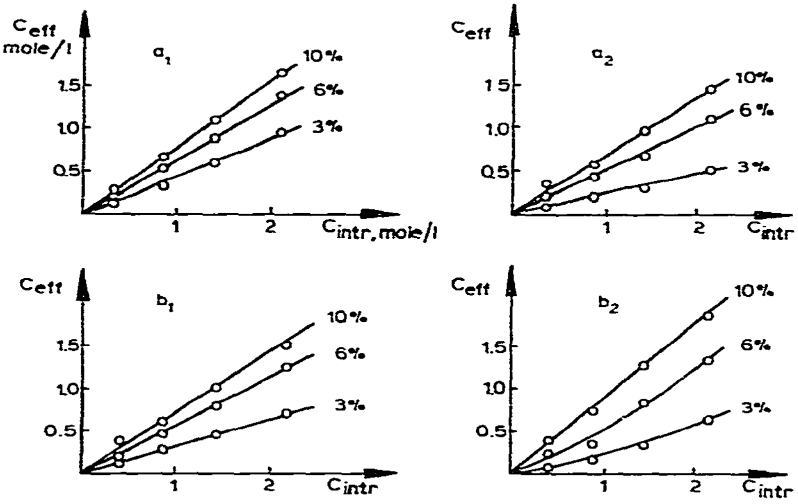


Fig. 4. Relationship between C_{eff} and C_{intr} for different loadings of the stationary phase. (a) 1-butanol; (b) benzene. a_1, b_1, 95.6°C; a_2, b_2, 67.6°C.

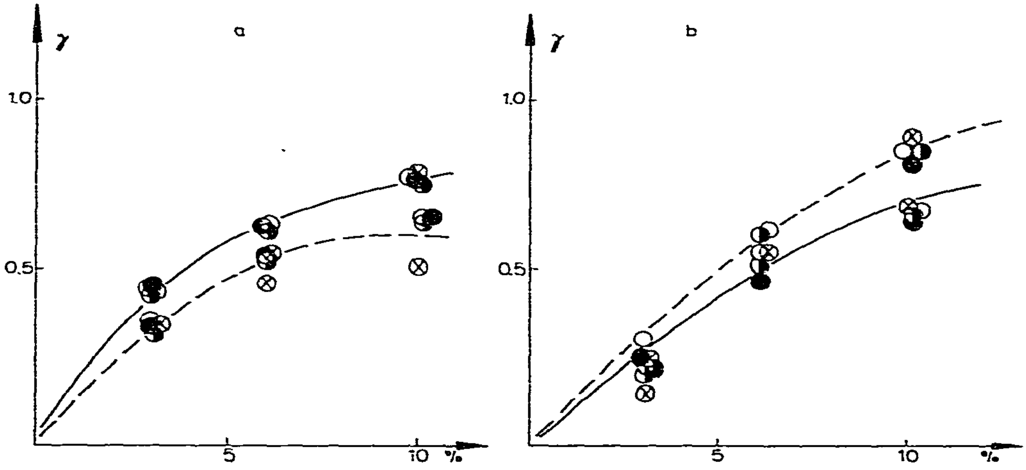


Fig. 5. Dependence of $\gamma = C_{eff}/C_{intr}$ on percentage of stationary phase on the support at 67.6 and 95.6°C. (a) 1-butanol; (b) benzene. Solid line, 95.6°C; broken line, 67.6°C. Concentration of complexing agent: ○, 2.14; ◑, 1.42; ●, 0.86; ⊗, 0.38 mole/l.

instances with ethylbenzene, Table III), whereas the effective concentrations, regardless of the degree of coverage, are always lower than the concentration originally introduced (Fig. 6).

CONCLUSIONS

Using the complexation constants in the systems with mixed stationary phases, one can establish the influence of the support on the observed retention data and

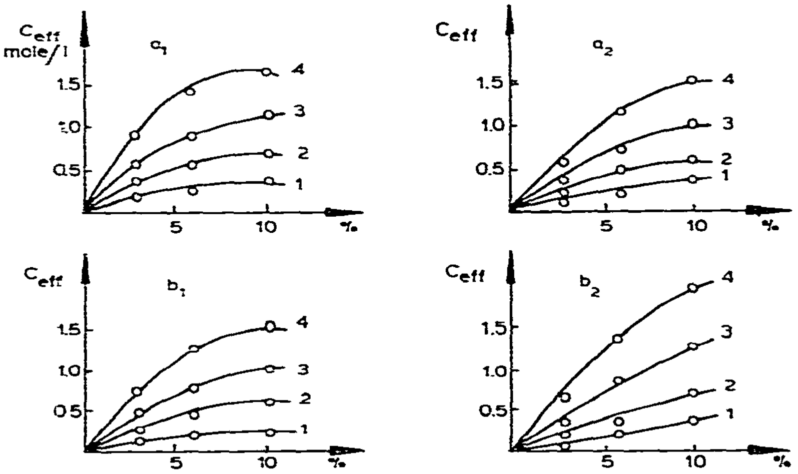


Fig. 6. Dependence of the effective concentration of complexing agent on liquid stationary phase loading. (a) 1-butanol; (b) benzene. a_1, b_1, 95.6°C; a_2, b_2, 67.6°C. Concentrations of complexing agent introduced: 1, 0.40; 2, 0.87; 3, 1.42; 4, 2.14 mole/l.

calculate the effective concentration of the polar component of the stationary phase with different coverages of the support. This concentration is lower than the original (also at 10% of the liquid stationary phase) even when the specific surface area of the support is as small as 0.5 m^2/g.

Because the complexing agent EHTCP is a polyfunctional compound, the interpretation of the observed temperature dependence may require that the mode in which these molecules orient themselves on to the liquid–solid and gas–liquid surfaces be defined, as well as determining the specificity of this interaction with solutes.

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