CONCENTRATION-DEPENDENT LIQUID DENSITY CHANGES IN LIQUID – SOLID EMULSIONS

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A study was undertaken into the effects of the properties of the liquid and solid phase on the density change of the dispersion medium.

Measurements have been made of the density of dehydrated absorbents using liquids of various chemical natures as the dispersion medium.

The materials considered comprised KSM, coarse-grained silica gel (0.25 mm fraction), Crimean kil in the Al or Ba form, Chasov Yar monothermite clay in the Na form, and glass spheres of diameter 0.1 mm. The densities of the adsorbents were measured by immersion for powder masses of 30, 25, 20, 15, 10, 5, 3, 2, 1, and 0.5 g; the material was dried in the weighing bottles at 473°K under vacuum. The specimens were weighed after drying and the relevant liquid was added in an amount sufficient to cover the adsorbent with a layer of 10–15 mm; the volume of liquid added to bottles without adsorbent was exactly the same as that used in measuring the density.

The air in the pores was displaced by leaving the specimens for 1–2 days under normal conditions, with the bottles connected to a vacuum system having a residual gas pressure of 400–500 N/m^2. After the end of the pumping, which ranged from 1–2 to 30–40 min depending on the adsorbent, the bottles were filled with the liquid under investigation and placed in a Khopler ultrathermostat bath, where the water was stirred continuously. This produced a uniform temperature in the water bath, which was usually kept at about 293°K, with fluctuations of not more than 0.01°.

The materials were left in the thermostat for 3–4 h, and the liquid levels were set exactly at the marks. The density of the dehydrated adsorbent was determined as follows:

$$d = \frac{m}{V - \frac{m_1}{\rho}}. \tag{1}$$

In Fig. 1 the change in the density of the dehydrated silica-gel powder and the kil in the Al and Ba forms is shown as a function of their content in the volume of the dispersion system formed by the various liquids.

We found a smooth reduction in the density of the silica gel in butanol, toluene, thiophen, butyl bromide, o-dichlorobenzene, and carbon tetrachloride; there was a density increase in water and ethanol, while the density of silica gel in propanol and butyl acetate was close to constant at 2.2170 g/cm^3 without relation to the content of solid phase. Curves 1–9 of Fig. 1 converge for $m/V \to 0$ to $d_0 = 2.2170$ g/cm^3.

For Crimean kil in the Al form we found a density reduction in toluene and an increase in butanol; in p-cymene, the density was nearly constant at 2.6170 g/cm^3. The density of the dehydrated Ba form increased with the content in butanol and isobutanol, but it remained constant at 2.8576 g/cm^3 in toluene. The glass spheres gave densities close to the constant value 2.9650 g/cm^3 in water, toluene, and carbon tetrachloride for any m/V.

This can be explained if we suppose that when CCl_4, $C_6H_4Cl_2$, $SCH=CHCH=CH$, $(CH_3)_3CBr$, $C_6H_5CH_3$, $H-C_4H_9OH$, or $C_6H_5CH_3$ in the Al form wet the surface of the silica gel there is a reduction in the density

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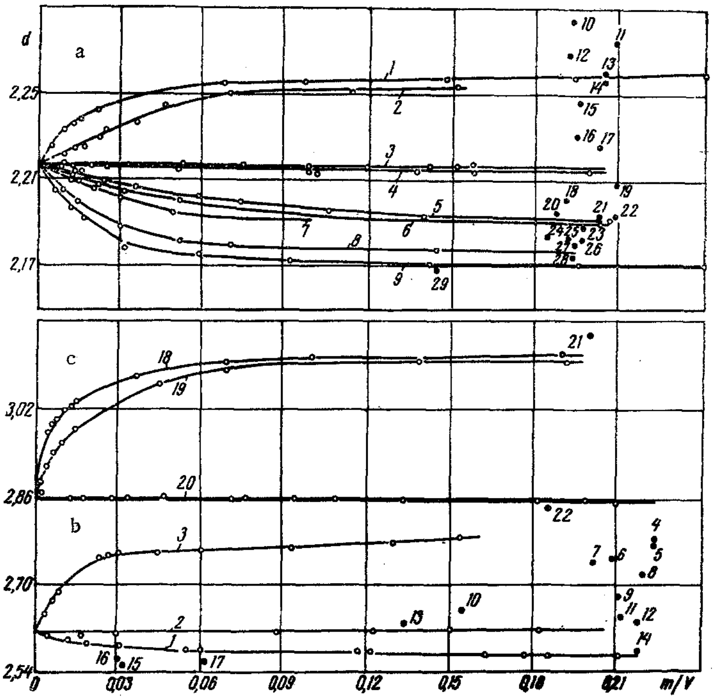

Fig. 1. Density of solid phase as a function of system content: a) liquid + KSM silica gel: 1) water; 2) ethanol; 3) propanol, butyl acetate; 4) butanol; 5) toluene; 6) butyl bromide; 7) thiophen; 8) o-dichlorobenzene; 9) CCl_4; 10) alylamine; 11) triethylamine; 12) butyric anhydride; 13) acetone; 14) isopropyl acetate; 15) pynikalin; 16) butyl formate; 17) isoamyl acetate; 18) isopropyl bromide; 19) butyl butyrate; 20) propyl bromide; 21) toluidine; 22) benzyl butyrate; 23) amyl bromide; 24) ethylbenzene; 25) butylbenzene; 26) mesitylene; 27) o-bromotoluene; 28) bromobenzene; 29) octane; b) liquid + Crimean kil in Al form: 1) toluene; 2) p-cymol; 3) butanol; 4) benzyl alcohol; 5) heptyl alcohol; 6) amyl alcohol; 7) o-toluidine; 8) butyl formate; 9) butyl acetate; 10) butyl methacrylate; 11) amyl acetate; 12, 13) butyl butyrate; 14) benzoyl chloride; 15) benzene; 16) cumene; 17) p-xylene; c) liquid + Crimean kil in Ba form: 18) butanol; 19) isobutanol; 20) toluene; 21) water; 22) CCl_4 d, g/cm^3; m/V, g/cm^3.

and an expansion of these liquids, together with compression of water or ethanol on silica gel, and of butanol and isobutanol on the Al and Ba forms of Crimean kil.

Figure 2 shows the density change $\Delta\rho$ of these liquids, calculated as follows:

$$\Delta\rho = -\rho + \frac{m_1}{V - \frac{m}{d_0}}, \tag{2}$$

where d_0 is the true density of the dehydrated adsorbent (represented in Fig. 2 by the point of intersection of the curves for m/V → 0).

The density change for water in contact with silica gel at m/V = 0.42 g/cm^3 is 0.0039 g/cm^3, i.e., 0.39% of the density of normal water; in [1] the estimated value is 0.12%.

Some of the density measurements on the adsorbents and the corresponding calculations of $\Delta\rho$ were made for set values of m/V; these are shown by black points in Fig. 2, and the calculations were performed as for a dispersion medium showing no density effect, which enabled us to examine the effects of the liquid properties on the exact magnitude of the effect.

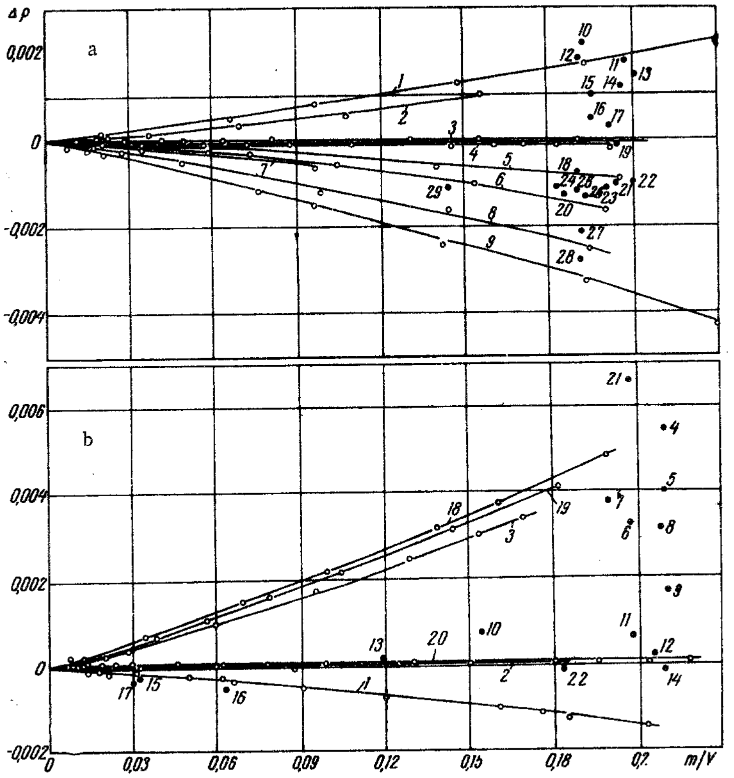

Fig. 2. Density change $\Delta\rho$ in dispersion medium in relation to content of solid phase: a) liquid + KSM silica gel (symbols as in Fig. 1a); b) liquid + Crimean kil in Al form and liquid + Crimean kil in Ba form (symbols as in Fig. 1b, c). $\Delta\rho$, g/cm^3; m/V, g/cm^3.

Table 1 compares the calculated density change $\Delta\rho$ for the liquid–silica gel system with the shift in the frequencies of the stretching vibrations for the free hydroxyl groups $\Delta\nu_{OH}$, together with the differences of the differential heats of adsorption for the hydroxylated and dehydroxylated surfaces ΔQ, as derived for various silica adsorbents in various papers. The + sign in front of $\Delta\rho$ corresponds to compression of the dispersion medium.

It is readily seen that the decrease in positive $\Delta\rho$ and the increase in negative $\Delta\rho$ are caused by the reduction in the absolute values of the adsorption energies, structure of the chemical bond, and esters.

We know that the adsorption of amines, water, alcohols and esters (i.e., compounds containing oxygen and nitrogen) on surfaces with localized positive charges (cations of small radius, protonated hydrogen atoms of hydroxyl groups, uncompensated charges in crystal lattice defects) is a result of the formation of donor–acceptor bonds and in some cases hydrogen bonds, representing in the main the interaction of electron pairs of oxygen and nitrogen atoms of the adsorbate molecule with protonated hydroxyl groups, exchange cations, or other active centers of the surface. The main role in this interaction is played, on the one hand, by local concentrations of electron density at the periphery of the corresponding links and bonds in the molecule and, on the other hand, the formation of mutual hydrogen bonds, i.e., compensating the adsorbate–adsorbate interaction.

We consider now the systems silica gel–water and silica gel–triethylamine.

In our experiments $\Delta\rho_{H_2O} = +0.00188$ g/cm^3, $\Delta\rho_{[(C_2H_5)_3N]} = 0.00179$ g/cm^3 for m/V = 0.206 g/cm^3.

The density increase in the dispersion medium can be evaluated as an increase in the concentration of liquid molecules on unit volume of the surface layer relative to the concentration in the normal liquid.

TABLE 1. Calculated Density Change $\Delta\rho$ for Liquid + Silica Gel and Frequency Shifts in Surface Free OH Stretching $\Delta\nu_{OH}$ or Differences in Heats of Adsorption ΔQ for Hydroxylated and Dehydroxylated Surfaces for Various Silica Adsorbents from Various Sources

Point or curve in Fig. 1	Dispersion medium	m/V, g/m^3	$\Delta_\rho \cdot 10^3$ g/cm^3	$\frac{\Delta\rho}{\rho}\cdot 10^2$	$\Delta\nu_{OH}$	ΔQ, kcal/mole
10	alylamine	0,19	+2,221	0,826		
12	butric anhydride	0,19	+1,797	0,221		
11	triethylamine	0,206	+1,787	0,248	990 [2]	8,0 [2]
1	water	0,210	+1,920	0,192	330 [4]	
13	acetone	0,210	+1,512	0,192	330 [2]	6,2 [2]
14	isopropyl acetane	0,204	+1,22	0,14		
	ethyl acetate				280 [2]	6 [2]
15	pynikalin	0,194	+1,04	0,125		
16	butyl formate	0,194	+0,54	0,06		
17	isoamyl acetate	0,202	+0,34	0,04		
3	propanol	0,200	0,000	0,000		
4	butyl acetate	0,200	0,000	0,000		
19	butyl butyrate	0,206	—0,118	0,014		
18	isopropyl bromide	0,190	—0,745	0,057		
30	p-cymene	0,190	—0,750	0,09		
5	toluene	0,190	—0,800	0,093	120 [3]	
22	benzyl butyrate	0,210	—0,948	0,094		
21	p-toluidine	0,203	—1,04	0,105		
23	amyl bromide	0,201	—1,116	0,096		
24	ethylbenzene	0,183	—1,11	0,129	120 [3]	
25	butylbenzene	0,191	—1,23	0,139	110 [2]	1,9 [2]
26	mesitylene	0,194	—1,304	0,150	156 [8]	
20	propyl bromide	0,186	—1,295	0,0960		
6	butyl bromide	0,186	—1,400	0,123		
7	thiophen	0,1	—0,6	0,07		
17	o-bromotoluene	0,192	—2,100	0,15		
8	o-dichlorobenzene	0,195	—2,390	0,18		
	chlorobenzene				100 [5]	
28	bromobenzene	0,195	—2,72	0,18		
9	carbon tetrachloride	0,195	—3,20	0,21	40 [5]	

The dimensions of the triethylamine and water molecules are such that the areas taken up by them in a close-packed monolayer are close to the areas required for free hydroxyl groups on the surface [2]; the surface layers of these dispersed systems are almost free from overlap or screening of the free active centers by adsorbed molecules, while the structure of the normal liquid is disrupted (the structure in terms of polyhedra with five-cornered faces as described by Bernal and Pauling), with production of a closer packing of bonded molecules.

The oxygen atom of the OH group is responsible for the adsorption on the solid in systems consisting of silica gel with water or lower aliphatic alcohols (C_2H_5OH, C_3H_7OH, C_4H_9OH, $C_5H_{11}OH$); it is clear that the area ω available to a molecule per active center increases in series $\omega_{H_2O} < \omega_{C_2H_5OH} < \omega_{C_3H_7OH} < \omega_{C_4H_9OH}$, and in the same sequence there increases the capacity for screening of the free active centers in the adsorbed molecules, which is responsible for the increase in the hydrogen bonds, the reduction in the molecule concentration in the surface layer, and the variation in $\Delta\rho$ in the series $\Delta\rho_{H_2O} > \Delta\rho_{C_2H_5OH} > \Delta\rho_{C_3H_7OH} > \Delta\rho_{C_4H_9OH}$.

In Fig. 2b the calculated density change for the dispersion medium in liquid–Crimean kil systems in the Al and Ba form is shown; the specific surface of the Al form was 703 m^2/g, while that of the Ba form was 682 m^2/g, and that of the silica gel 187 m^2/g.

There is a marked increase in the positive values of $\Delta\rho$ in the main for all the nitrogen- and oxygen-bearing compounds on the Ba and Al forms of the kil relative to the silica gel, which is due to the increased surface area of the solid per unit volume of dispersion medium for a given m/V, which means an increase in the concentration of the adsorbate molecule at the solid–liquid interface.

A somewhat different situation occurs in systems where the liquid is an aromatic hydrocarbon (benzene, toluene, p-xylene, mesitylene, ethylbenzene, cumene, butylbenzene, and p-cymene), and the same applies to aromatic amines (p-toluidine), aromatic halides (o-bromotoluene, o-dichlorobenzene), alkyl halides (amyl bromide, propyl bromide, isopropyl bromide), alkanes (octane), and polyhalides (carbon tetrachloride).

All these compounds show negative values of $\Delta\rho$ with silica gel (expansion of the liquid), but nearly zero $\Delta\rho$ are found for toluene with Ba kil, toluene with the Na form of Chasov Yar clay, and p-cymene with the Al form of kil, and we find positive values for p-toluidine with the Al form of kil, as well as for p-cymene with the Ba form of kil.

It can be shown that the density change for the dispersion medium in such a system is determined by the concentration of active centers on the adsorbents, as well as by the surface area and the geometrical and electronic structures of the adsorbed molecules, or else of individual parts of them (symmetry of the electron shells, presence or absence of σ or π bonds).

The interactions of aromatic hydrocarbons, aromatic amines, and aromatic halides are determined by the association or dissociation of the materials in π-complex adsorption [6, 7].

The following are some results for the constant value $m/V = 0.20$ g/cm^3: silica gel + toluene 0.00094 g/cm^3, Al kil with toluene – 0.00129, Ba kil with toluene zero, and Na Chasov Yar clay with toluene zero.

The concentration C of active centers on these adsorbents decrease in the sequence: C [Al form of kil] > C [silica gel], C [Ba form of kil] > C [Na form of Chasov Yar clay].

The adsorption of toluene on the Al form of kil and on silica gel occurs via an associative mechanism, where two or more active centers react with one toluene molecule. In this case, the molecule has the plane of its ring parallel to the surface. This orientation produces overlap or screening of unused nearby active centers, which presents an obstacle to the access of free liquid molecules, which results in a reduction in the concentration in the surface layer.

Toluene on the Ba form of kil and on the Na form of Chasov Yar clay is adsorbed by a dissociative mechanism, with the molecules rotated through 90° and taking up vertical positions [6], a π bond becoming a σ bond, and the conditions providing for more ready access of free liquid molecules to the surface, which results in an increase in the concentration in the surface layer.

Various substituents in the aromatic rings affect the strength of the adsorption, and also the orientation relative to the surface, which affects the concentration in the surface layer. For such compounds we found that $\Delta\rho$ decreases in the following order:

$$\Delta\rho\,\underbrace{[\mathrm{pCH_3 - C_6H_4 - CH\,(CH_3)_2}]}_{\text{p-cymene}} > \Delta\rho\,\underbrace{[\mathrm{C_6H_5 - CH_3}]}_{\text{toluene}}, > \Delta\rho\,\underbrace{[\mathrm{C_6H_3 - (CH_3)_3}]}_{\text{mesitylene}} > \Delta\rho\,\underbrace{[\mathrm{C_6H_5 - C_2H_5}]}_{\text{ethylbenzene}}$$

$$> \Delta\rho\,\underbrace{[\mathrm{C_6H_5 - C_4H_9}]}_{\text{butylbenzene}} > \Delta\rho\,\underbrace{[o - \mathrm{CH_3C_4H_4Br}]}_{\text{o-bromotoluene}} > \Delta\rho\,\underbrace{[\mathrm{C_6H_4Cl_2}]}_{\text{o-dichlorobenzene}} > \Delta\rho\,\underbrace{[\mathrm{C_6H_5Br}]}_{\text{bromobenzene}},$$

which accords with the changes in the heats of adsorption for these liquids.

These results show that the density of the dispersion medium may be somewhat more or less than that of the normal liquid at the same temperature and pressure when a solid with extensive free surface is in contact with it. The changes are determined by the concentration of the dispersed phase, the chemical nature of the liquid molecules, and the surface properties of the adsorbent.

Subsequent studies will deal with the effects of temperature on this phenomenon.

NOTATION

d	is the apparent density of the dehydrated adsorbent;
m	is the mass of adsorbent;
V	is the volume of the vessel with the adsorbent and the investigated liquid (the volume of the disperse medium);
m_1	is the mass of liquid in the vessel;
ρ	is the density of the liquid, determined in the absence of adsorbent;
α	is the true density of the dehydrated adsorbent.

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