200. *The Sorption of Vapours by Ferric Oxide Gel. Part III.* Aliphatic Amines.*

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Sorption isothermals of the primary aliphatic amines, from ethyl to *n*-heptyl, and some related substances have been determined on ferric oxide gel. All show large hysteresis loops, and the general quantitative relations closely resemble those found previously with the aliphatic alcohols. The amounts (in mg./g.) of the various straight-chain amines required to form a monolayer are proportional to their molecular weights, whilst the amounts held at saturation correspond to the filling of a constant pore volume. The capillary radii, calculated by application of the Kelvin equation, are reasonably constant.

IN Part I (Foster, *Proc. Roy. Soc.*, 1934, *A*, **147**, 128) sorption isothermals of the aliphatic alcohols, from methyl to *n*-butyl, on ferric oxide gel were described. It was thought that an investigation of the aliphatic amines might be of interest since these compounds are considerably more volatile than the corresponding alcohols and it should therefore be possible to examine a wider range of molecular size. In the present work, isothermals of the primary aliphatic amines, from ethyl to *n*-heptyl, and some related substances, *viz.*, ethylenediamine, *tert.*-butylamine, *cyclo*hexylamine, and pyridine, have been determined. All show large hysteresis loops, and the general quantitative relations closely resemble those found with the alcohols, *e.g.*, the amounts held at saturation correspond to the filling of a constant pore volume, the amounts required to form a complete monolayer correspond to a constant number of molecules, and the capillary radii calculated by means of the Kelvin equation are reasonably constant.

EXPERIMENTAL

The technique described in Part I was used except with ethylamine, for which a modification of Goldmann and Polanyi's method (*Z. physikal. Chem.*, 1928, *A*, **132**, 313) was employed. The ethylamine was distilled from sodium in a Claisen flask, through a Quickfit condenser with joints lubricated with Silicone grease, into tube *A* (Fig. 1A) containing fresh sodium. The condenser and guard tube were then sealed off at *B* whilst *A* was cooled in liquid air and the system thoroughly evacuated; *A* was then left at room temperature until effervescence due to reaction of moisture with sodium had ceased. The ethylamine was again frozen, and the gas pumped off. This treatment was repeated until no further gas was evolved and the dry amine was then distilled into another bulb *C*. After the apparatus had been sealed at *D*, a first fraction of ethylamine was condensed in *E* and removed by sealing. The middle fraction was then condensed in a series of small bulbs *F*, which were then sealed and stored in a refrigerator. One of these bulbs was then weighed and placed in the tube *G* (Fig. 1B), where it could be broken *in vacuo* by means of the iron-cored tube *H* and an external magnet ; *G* was connected *via* the mercury-actuated sintered-glass cut-offs J_1, J_2, J_3, and J_4 to a bulb *K*, mercury manometer *L*, a set of small tubes *M*, and finally to the mercury-vapour pump and McLeod gauge. Since the sintered-glass disc reduced the rate of pumping considerably, a by-pass *N* of wide bore tubing was used to evacuate the left-hand side of the system.

A known weight of previously evacuated gel was placed in the bulb *K*, which was then sealed on to the apparatus and evacuated at 150°. After prolonged evacuation and heating of the entire glass apparatus, the constrictions at *O* and *P* were sealed after all cut-offs had been raised. Bulb *F* was broken, and the ethylamine transferred completely to *K* by cooling the latter in liquid air with J_1 open. The portion *G* was then removed by sealing off at *Q* and the pieces of glass from the broken bulb *F* were collected and weighed in order to obtain the total weight of ethylamine introduced into the system. Cut-off J_2 was then lowered, and the vapour pressure of ethylamine, present in excess, read on *L* whilst *K* was immersed in melting ice. By closing J_2 and opening J_3 some ethylamine was removed and condensed in one of the bulbs *M*. This removal was continued until the pressure fell just below saturation, whereupon *M* was sealed off and broken under excess of standard hydrochloric acid. After back-titration

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* Part II, *J.*, 1946, **446**.

with sodium hydroxide, the weight of ethylamine thus removed, and hence the amount left in the system, could be calculated. This procedure was repeated, known weights of amine being removed in a sealed tube after each pressure reading until the pressure fell to a few mm. The bulb K was then heated to 150°, and the residual ethylamine collected and titrated.

Owing to the high vapour pressure of ethylamine and the comparatively large volume of connecting tubing between the bulb K and manometer L, it could not be assumed that all the ethylamine in the system was actually adsorbed by the gel in K. This " dead-space " correction was determined directly by performing a " blank " run in which the gel was replaced by an equal volume of mercury, and a graph was constructed showing the weight of amine in the dead space at a given pressure. The high vapour pressure of ethylamine also resulted in mercury being forced through the sintered discs in the cut-offs, and subsequently blocking the apparatus. This difficulty was largely overcome by providing sumps into which the mercury so displaced could drain and from which it could be returned, *via* a tap, to the cut-off reservoir.

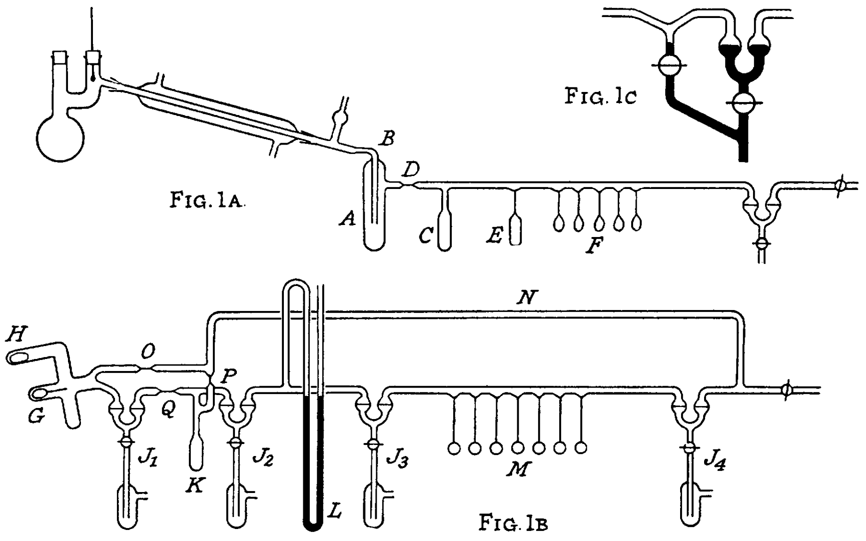


FIG. 1A.

FIG. 1C

FIG. 1B

This device is illustrated in Fig. 1c. No great accuracy is claimed for the experimental method, owing to the high dead-space correction and to the cumulative effect of titration errors, and unfortunately no ascending points can be determined.

Vapour-pressure and Surface-tension Measurements.—No vapour-pressure data are recorded in the literature for the higher amines, and direct manometric measurements were therefore made on purified samples. After preliminary drying and fractionation, the amine was, as with ethylamine, distilled from sodium and finally condensed in a small bulb attached to a mercury manometer, which was sealed off and immersed in a thermostat, and the saturation pressure was read directly by means of the cathetometer.

No literature value could be found for the surface tension of *tert.*-butylamine or *n*-heptylamine. Data for these substances were obtained by the capillary-rise method, by distillation *in vacuo* into a U-tube with capillary limbs of about 0·05 and 0·2 mm. diameter, in which a differential capillary rise of 10—20 mm. could be obtained. The apparatus was calibrated with water and benzene.

The physical constants required in order to calculate the pore radius from the Kelvin equation are the density (d), surface tension (γ) and vapour pressure (v. p.). The values chosen from the literature, together with those determined in the present research, are collected in Table 1.

Surface-area Measurements.—The surface area of the gel was determined by a modification of the standard Brunauer–Emmett–Teller (B.E.T.) method, oxygen being used instead of nitrogen, in the apparatus described by Gregg and Sing (*J. Phys. Coll. Chem.*, 1951, **55**, 592). From the slope and intercept of the B.E.T. plot the monolayer capacity V_m was found to be 39·5 c.c. (N.T.P.) of oxygen per g., and the constant c of the B.E.T. equation had the value 42·2.

The calculated surface area will depend on the value taken for the cross-sectional area of the oxygen molecule. Molecular areas are usually calculated from the liquid density by means of an equation of the type $\sigma^2 = F(M/Nd)^{2/3}$. Livingston (*J. Amer. Chem. Soc.*, 1944, **66**, 571) tabulates values of F for different types of packing. The value 1·260 for square close-packing

TABLE 1.

Substance	Temp.	d^t_4	γ (dynes/cm.)	V. p. (mm. Hg)
Ethylamine	0°	0·7056 ^{a}	22·68 ^{b}	369·9 ^{c}
n-Propylamine	0	0·7382 ^{d}	25·14 ^{d}	94·9 *
n-Butylamine	25	0·7369 ^{d}	23·74 ^{d}	95·7 *
n-Amylamine	25	0·7498 ^{d}	24·66 ^{d}	31·8 *
n-Hexylamine	25	0·7618 ^{d}	25·85 ^{d}	9·69 *
n-Heptylamine	35	0·7635 ^{d}	25·96 *	6·46 *
Ethylenediamine	25	0·8938 ^{d}	41·42 ^{d}	13·42 ^{f}
tert.-Butylamine	0	0·7137 ^{e}	31·32 *	116·2 *
*cyclo*Hexylamine	25	0·8629 ^{d}	31·19 ^{d}	9·46 *
Pyridine	25	0·9779 ^{g}	36·48 ^{h}	20·18 ^{i}

* Personal measurements. (*a*) Swift, *J. Amer. Chem. Soc.*, 1942, **64**, 115. (*b*) Swift and Calkins, *ibid.*, 1943, **65**, 2145. (*c*) Pohland and Mehl, *Z. physikal. Chem.*, 1933, **164**, *A*, 45. (*d*) Vogel, *J.*, 1948, 1825. (*e*) Rudnew, *Bull. Soc. chim.*, 1880, **33**, 297. (*f*) Stull, *Ind. Eng. Chem.*, 1947, **39**, 518. (*g*) Walden, Audrieth, and Birr, *Z. physikal. Chem.*, 1932, **160**, *A*, 337. (*h*) Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, New York, 1950. (*i*) Van der Meulen and Mann, *J. Amer. Chem. Soc.*, 1931, **53**, 451.

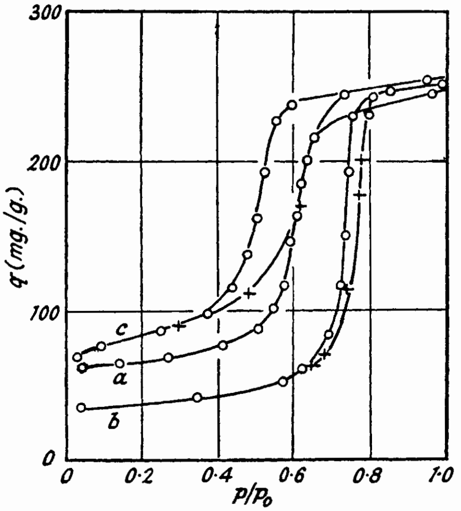
TABLE 2.

Ethylamine (0°)													
q (mg./g.)...	245	237	232	232	205	182	110	76	62	47	40	38	
p/p_0	0·95	0·85	0·77	0·70	0·68	0·66	0·63	0·52	0·42	0·26	0·16	0·03	
n-*Propylamine* (0°)													
q (mg./g.)...	238	235	226	209	152	124	87	59	51	68	96	147	224
p/p_0	0·99	0·76	0·64	0·61	0·59	0·57	0·47	0·11	0·02	0·28	0·53	0·64	0·69
q (mg./g.)...	235												
p/p_0	0·80												
n-*Butylamine* (25°)													
q (mg./g.)...	258	243	230	206	183	150	120	102	94	74	67	65	92
p/p_0	0·99	0·62	0·61	0·59	0·58	0·55	0·52	0·47	0·44	0·18	0·06	0·02	0·43
q (mg./g.)...	114	152	244										
p/p_0	0·52	0·67	0·74										
n-*Amylamine* (25°)													
q (mg./g.)...	246	236	231	190	160	140	116	104	100	87	78	71	
p/p_0	0·90	0·57	0·56	0·52	0·50	0·48	0·44	0·40	0·35	0·25	0·09	0·03	
n-*Hexylamine* (25°)													
q (mg./g.)...	254	247	241	232	210	150	110	101	88	81	99	106	129
p/p_0	0·95	0·75	0·59	0·49	0·47	0·44	0·37	0·30	0·16	0·06	0·31	0·39	0·47
q (mg./g.)...	209	239	256										
p/p_0	0·59	0·69	0·98										
n-*Heptylamine* (35°)													
q (mg./g.)...	256	248	246	238	225	193	186	135	116	103	94		
p/p_0	0·96	0·58	0·47	0·43	0·40	0·38	0·38	0·33	0·27	0·15	0·03		
Ethylenediamine (25°)													
q (mg./g.)...	307	300	296	287	283	253	256	185	130	109	102	82	66
p/p_0	0·97	0·88	0·76	0·61	0·56	0·53	0·52	0·49	0·43	0·40	0·39	0·32	0·19
q (mg./g.)...	59	54	67	77	104								
p/p_0	0·12	0·05	0·23	0·32	0·44								
tert.-*Butylamine* (0°)													
q (mg./g.)...	236	231	221	201	159	121	97	73	53	58	43	78	119
p/p_0	1·0	0·80	0·59	0·57	0·55	0·52	0·48	0·40	0·17	0·09	0·01	0·43	0·55
cyclo*Hexylamine* (25°)													
q (mg./g.)...	286	284	275	266	244	190	145	120	98	92	82	73	70
p/p_0	0·99	0·77	0·51	0·46	0·44	0·42	0·46	0·36	0·30	0·27	0·18	0·04	0·03
Pyridine (25°)													
q (mg./g.)...	325	319	309	314	305	280	225	155	113	81	63		
p/p_0	1·0	0·89	0·74	0·82	0·66	0·54	0·49	0·44	0·36	0·18	0·03		
Oxygen (90·3° K)													
Vol. (c.c. N.T.P./g.) ...	27·9	34·1	38·5	41·0	47·0	51·3	58·7	68·7					
p/p_0	0·038	0·081	0·126	0·155	0·226	0·278	0·356	0·445					

makes the above equation correspond to the relation $\sigma = 1{\cdot}33 \times 10^{-8}\ (M/d)^{1/3}$, which was used previously in this work and is retained throughout the present paper. The value 1·091 for hexagonal close-packing gives the relation used by Emmett and Brunauer (*ibid.*, 1937, **59**, 1553) upon which most of the surface-area values determined by the B.E.T. method are based. These two relations give 16·3 and 14·1 Å², respectively, for oxygen, whence the surface area of the gel is either 175 or 151 sq. m. per g.

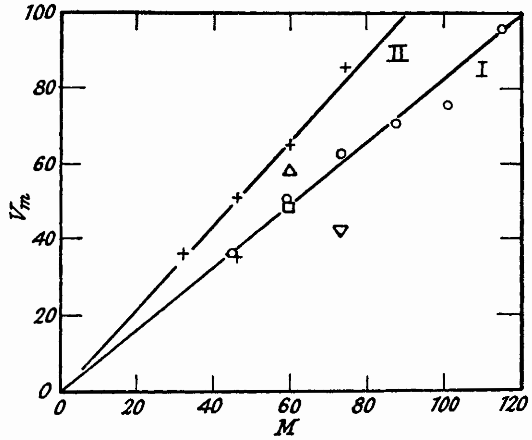
Results.—The experimental data are recorded in Table 2, which gives the amount adsorbed (q) in mg./g. of gel at various relative pressures (p/p_0). The gel used here was the remainder of the batch prepared by Broad and Foster in 1938 and used by them in Part II (*loc. cit.*). In Fig. 2 isothermals of ethyl alcohol determined in 1938 and in 1949 (present work) are compared. The marked shift due to ageing of the gel indicates an increase in pore radius and a decrease in surface area, the saturation volume remaining unchanged. A typical isothermal for the amines is also shown in Fig. 2. The isothermals have the same features as those of the alcohols and all show large reproducible hysteresis loops. Comparative data are summarised in Table 3.

FIG. 2.



Adsorption points + ; *Desorption points* ○.
(*a*) EtOH, 1939; (*b*) EtOH, 1949;
(*c*) n-*Amylamine*.

FIG. 3.



+ *Alcohols*, 1936. ○ *Amines*, 1949.
△ iso*Propyl alcohol*. ▽ tert.-*Butylamine*.
□ *Ethylenediamine*.

TABLE 3.

1	2	3	4	5	6	7	8	9	10	11	12
	t	q_s (mg./g.)	V_s (mm.³/g.)	V_m (mg./g.)	V_m/q_s (%)	V_m/M (m.-moles/g.)	$10^{19} V_m\sigma^2/M$	p_i/p_0	r (Å)	$r + 2\sigma$ (Å)	V_h/V_m
Et·NH$_2$	0°	246	314	36	15	0·80	22·65	0·66	31	42	—
Pr^n·NH$_2$	0	238	322	50	21	0·85	27·95	0·58	32	44	1·7
Bu^n·NH$_2$	25	252	342	64	25	0·87	32·98	0·58	34	46	1·5
n-C$_5$H$_{11}$·NH$_2$	25	248	331	70	28	0·80	33·82	0·51	35	48	1·5
n-C$_6$H$_{13}$·NH$_2$	25	256	336	76	30	0·75	34·52	0·46	35	49	1·4
n-C$_7$H$_{15}$·NH$_2$	35	256	335	96	37	0·83	41·65	0·39	32	46	—
(CH$_2$·NH$_2$)$_2$ ...	25	310	347	49	16	0·82	24·02	0·51	33·5	45	1·5
Bu^t·NH$_2$	0	237	332	42	18	0·57	22·08	0·55	32	46	1·9
C$_6$H$_{11}$·NH$_2$ ...	25	284	329	68	24	0·69	28·05	0·43	34	47	1·4
C$_5$H$_5$N	25	328	330	58	18	0·73	24·15	0·48	34	45	—
H$_2$O	25	328	329	36	11	2·0	24·38	0·73	34	41	2·5
EtOH	25	252	321	35	14	0·76	20·31	0·74	34	44	1·6

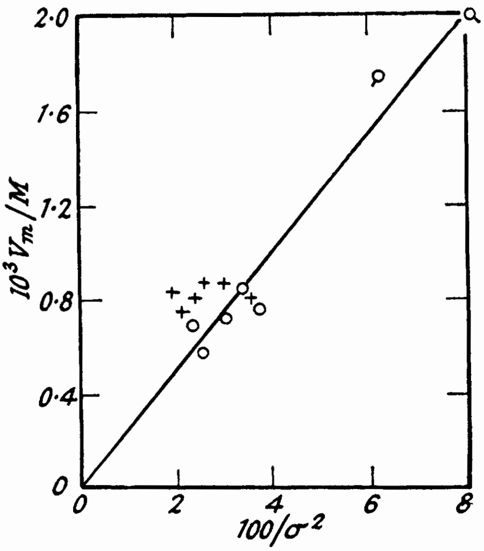
DISCUSSION

Saturation Volumes.—The amounts (q_s) held at saturation are recorded in col. 3 of Table 3. The corresponding volumes (V_s), calculated from the normal liquid density, are approximately constant and show maximum deviations of ±5% from the mean value 330 mm.³/g.

Monolayer Capacity.—Col. 5 gives the amounts (V_m) required to form a complete monolayer, estimated, as in Part II, by the " point A " method. For the straight-chain amines, V_m is clearly proportional to the molecular weight as shown by the approximate constancy of the values of V_m/M in col 7. In Fig. 3, curve I, V_m for these amines is plotted against M, and curve II shows the corresponding relation for the alcohols investigated in Part I. The difference in slope is due to the ageing of the gel, and since the 1949 point for ethyl alcohol falls exactly on curve I it is reasonable to suppose that if both the alcohols and the amines had been examined on the same sample of gel, the two curves would coincide. It is noteworthy that, just as the point for *iso*propyl alcohol falls below curve II, so also does that for *tert.*-butylamine fall below curve I. Further, the point for ethylenediamine falls exactly on the latter curve. The low V_m/M values for all the other substances except water indicate that these points, which have been omitted from Fig. 3, would fall well below curve I.

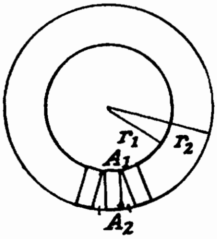
In Part I it was assumed that the constancy of V_m/M indicated a definite orientation, similar to that of the long-chain fatty acids on water, with a cross-sectional area of the order 20 Å² per molecule, independent of the length. On this basis, the slope (0·82) of curve I corresponds to a surface area of 99 sq. m. per g., which is considerably lower than either of the values derived by the B.E.T. method from the oxygen isothermal. In order to obtain agreement with the lower of the last two values it would be necessary to assume a sectional area of at least 30 Å² per molecule.

FIG. 4.



+ *Normal amines*; ○ O_2; ○ H_2O; ○ *Other compounds.*

FIG. 5.



It was shown by Broad and Foster (*J.*, 1945, 369) that on silica gel the values of V_m/M for the alcohols are not constant but proportional to $1/\sigma^2$, *i.e.*, the quantity $V_m\sigma^2/M$ is constant. This corresponds to the expression $(V_m/M)(M/d)^{2/3}$ suggested by Goldmann and Polanyi (*loc. cit.*) for the covering of a constant surface area. A similar behaviour is shown by the amines on silica gel (Brown and Foster, *J. Phys. Coll. Chem.*, in the press), where it is found that the best curve through the plot of V_m/M against $1/\sigma^2$ is a straight line which also passes through the points for water and oxygen. Fig. 4 shows a similar graph for the substances investigated in the present work on ferric oxide gel. The points for the normal amines naturally lie round a constant value of V_m/M, but the best curve through the other points, including those for oxygen and water, is a straight line of slope $2{\cdot}56 \times 10^{-18}$ mole cm.$^{-2}$, which multiplied by **N** gives a specific surface area of 155 sq. m. The value of σ^2 corresponding to the constant number of moles of the straight-chain amines adsorbed is

31 Å^2, which is therefore the apparent cross-sectional area of these substances when adsorbed on ferric oxide.

The discrepancy between this and the value 20 Å^2 usually found for surface films may be due to the curvature of the surface on which adsorption takes place. Then, considering the rather crude model represented by Fig. 5, in which cylindrical molecules of cross-sectional area A_1 are adsorbed with their *heads* forming a close-packed assembly, it is clear that the *tails* are no longer in contact with one another and, so far as the covering of the adsorbent surface is concerned, the molecules have an effective cross-section A_2 given by $A_2/A_1 = (r_2/r_1)^2$. If r_1 is taken as 35 Å, then, for a molecule 10 Å long, r_2 will be 45 Å and $A_2 = 20(9/7)^2 = 33$ Å^2. Similarly, a molecule 5 Å long would have an effective area of 25 Å^2, so that the observed effective area of 31 Å^2 is quite consistent with this explanation, although the predicted variation with chain length is not observed.

Capillary Radii.—The relative pressures at the point of inflexion of the desorption branch of the hysteresis loop are recorded in col. 9 of Table 3, and the corresponding pore radii, calculated by means of the Kelvin equation, are given in col. 10. Unfortunately, these points of inflexion are much less clearly defined than in the earlier parts of this work, an effect presumably due to ageing of the gel. The radii lie within ±3 Å of the mean value 34 Å and show no significant variation with the size of the adsorbed molecule. A similar conclusion was drawn from the data for the alcohols in Part I, where it was tentatively suggested that there was a tendency for the adsorbed layer to build up to a constant thickness before the advent of capillary condensation. On the other hand, the data of Part II, in which mainly non-polar liquids were examined, supported the view that two adsorbed layers were present before condensation, and the values of $r + 2\sigma$ were reasonably constant, showing variations of ±2 around a mean of 32 Å. The corresponding figures for the amines, recorded in col. 11, show variations of ±4 around a mean of 45 Å, which is slightly less satisfactory but still reasonable.

In the systems investigated in Part II, the amount (V_h) .adsorbed when hysteresis begins is usually rather more than twice the monolayer capacity (V_m), and the ratio V_h/V_m varies from 2·1 to 2·7. The values for the alcohols are significantly lower, *e.g.*, 1·3 for *n*-butyl alcohol, and the figures of col. 12 show clearly that this is true also of the amines. This is most likely a consequence of the very close packing involved in the formation of an oriented monolayer which is not possible with the less polar liquids, and suggests that the second layer of amine or alcohol molecules is not oriented.

In a parallel investigation of these amines on silica gels (Brown and Foster, *loc. cit.*) it has been found that the size of the hysteresis loop decreases as the molecular diameter increases, and on one sample of gel with a Kelvin radius of approx. 15 Å, hysteresis occurs only with the lower amines and is not observed with molecules larger than *n*-butylamine. On the coarser ferric oxide gel used here, little variation is observed in the size of the loop.

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