ELASTIC VISCOUS OLEATE SYSTEMS CONTAINING KCl. VIII [1]

a. *Influence of the n. primary alcohols $C_1—C_6$ on the elastic behaviour of the 0.6 % oleate system.*

b. *The use of $G — \lambda$, $G — 1/\Lambda$ and $G — n$ diagrams in discussing the results obtained with the homologous series of the alcohols.*

BY

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1. *Introduction.*

Section 2 deals with the action of aliphatic alcohols $C_1 — C_6$ on the 0.6 % oleate system, an investigation wholly analogous to that on the 1.2 % oleate system in Part VI. We will then compare the results obtained with the 0.6 % and the 1.2 % systems, which comparison seemed of importance in connection with the findings in Part III that the damping in the 0.6 % system shows quite another character than in the 1.2 % system.

In the next sections we will consider the question if there exist specific differences between the various alcohols, with regard to the nature of the action excerted on the elastic properties of the oleate system by the alcohol molecules bound to the oleate.

2. *Influence of the first six terms of the n. primary alcohols on the elastic behaviour of the 0.6 % oleate system at the KCl concentration of minimum damping.*

The oleate system used for the following experiments had the composition 0.6 g oleate per 100 ml 1.43 N KCl + 0.12 N KOH, which electrolyte composition corresponds to the minimum damping of the elastic oscillations. [2] We used exactly half filled spheres of nominally 500 ml and followed the same method as described in detail in Part VI of this series (cf. ibid. section 1 and 3). [3] For exciting the rotational

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[1] Part I has appeared in these Proceedings **51**, 1197 (1948), Parts II—VI in these proceedings **52**, 15, 99, 363, 377, 465 (1949), Part VII in these Proceedings **53**, 7 (1950).

[2] As our stock of Na oleinicum medicinale pur. pulv. Merck was nearly exhausted and could not possibly be replenished, we decided to use for the experiments in this section the large volume of the oleate system, which had already served in previous experiments (on the dependence of T and Λ on R, see Part III, section 3, of this series).

[3] In one respect we deviated from this method for investigating the influence of ethanol and methanol. These alcohols exert their full influence at concentrations

oscillation we made use of the contrivance described in Part VII of this series.

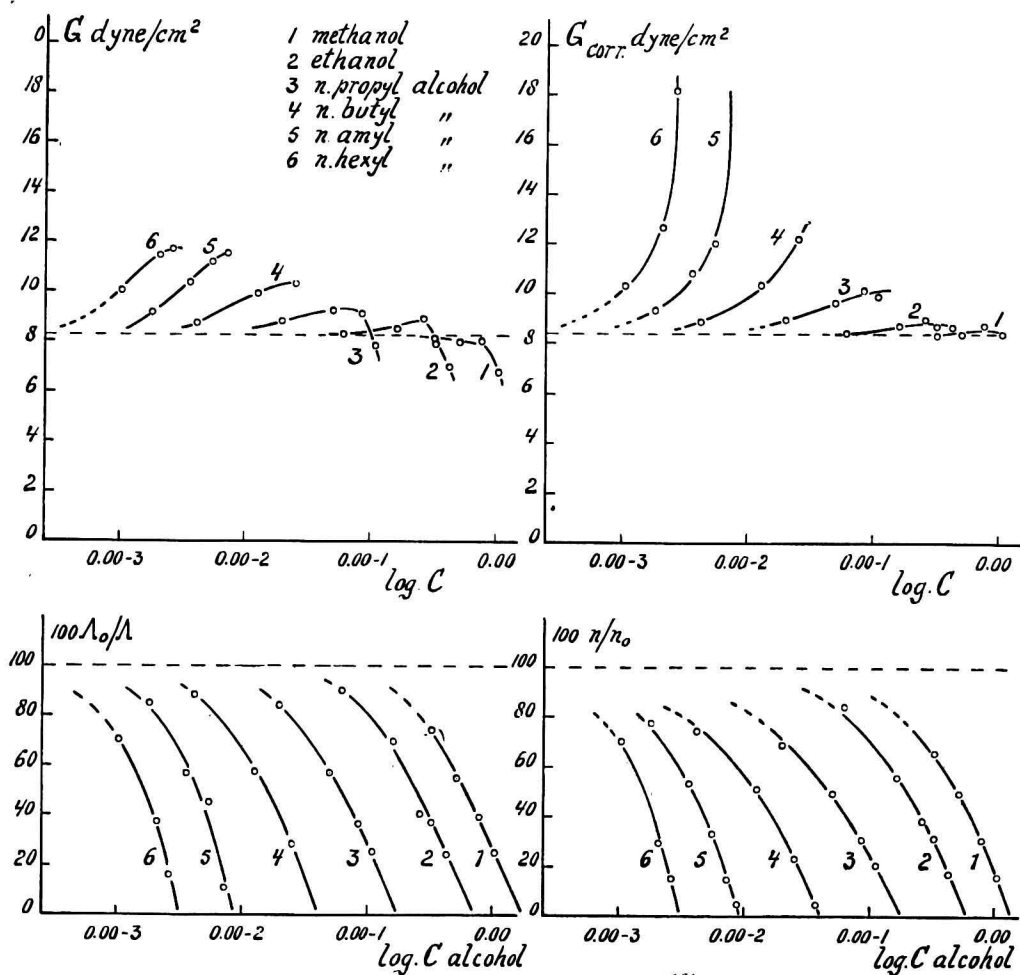The results have been given in Table I, and in fig. 1. In this figure

Fig. 1

which correspond to an increase in volume of the elastic system of one or several per cent., which again necessitates a number of corrections (because of changes in the degree of filling, in the oleate concentration and in the KCl + KOH concentration).

The necessity of applying all these corrections was made redundant by the use of an auxillary mixture, which apart from a relatively large, known alcohol content, had the same composition as the elastic system as regards the oleate, the KCl and the KOH concentration. First a certain volume of this auxillary mixture was added to the oleate system, the contents of the vessel thoroughly mixed and by removing then a same volume as had been added, the degree of filling, the oleate, KCl and KOH concentrations have not been altered and we have only introduced a certain known quantity of alcohol.

TABLE I

Influence of n. primary alcohols on the elastic behaviour of the 0.6 % oleate system at the KCl concentration of minimum damping (at 15°)

Alcohol	conc. moles/l	log. conc.	G dyne/cm²	G corr. for Λ	$100\ G/G_0$	Λ	n	$100\ \Lambda_0/\Lambda$	$100\ n/n_0$
	blank	$-\infty$	8.22	8.35	100	0.758	19.6	100	100
	0.321	0.51−1	8.11	8.35	100.0	1.026	12.9	73.9	65.8
methanol	0.517	0.71−1	8.01	8.42	100.8	1.378	9.7	55.0	49.5
	0.775	0.89−1	8.00	8.75	104.8	1.928	6.0	39.3	30.6
	1.034	0.01	(6.78)	(8.31)	(99.5)	2.98	3.3	25.5	16.8
	blank	$-\infty$	8.24	8.36	100	0.751	19.6	100	100
	0.0617	0.79−2	8.31	8.46	101.2	0.835	16.5	89.9	84.2
ethanol	0.164	0.21−1	8.50	8.74	104.5	1.073	11.0	70.0	56.1
	0.266	0.42−1	8.89	9.03	108.0	1.851	7.5	40.6	38.3
	0.327	0.51−1	7.91	8.71	104.2	1.991	6.2	37.7	31.6
	0.429	0.63−1	(6.99)	(8.64)	(103.3)	3.05	3.4	24.6	17.3
	blank	$-\infty$	8.31	8.43	100	0.762	19.5	100	100
n. propyl	0.0200	0.30−2	8.78	8.96	106.3	0.906	13.5	84.1	69.2
alcohol	0.0501	0.70−2	9.21	9.64	114.3	1.338	9.7	57.0	49.7
	0.0852	0.93−2	9.12	10.14	120.3	2.096	6.0	36.4	30.8
	0.110	0.04−1	(7.84)	(9.87)	(117.1)	3.012	4.0	25.3	20.5
	blank	$-\infty$	8.28	8.40	100	0.762	19.6	100	100
n. butyl	0.00417	0.62−3	8.69	8.85	105.3	0.862	14.6	88.4	74.5
alcohol	0.0125	0.10−2	9.89	10.33	123.0	1.324	10.0	57.6	51.0
	0.0250	0.40−2	(10.32)	(12.18)	(145.0)	2.674	4.5	28.5	23.0
	0.0375	0.57−2	—	—	—	—	1.0	—	5.1
	blank	$-\infty$	8.25	8.37	100	0.765	19.7	100	100
	0.00182	0.26−3	9.14	9.32	111.4	0.905	15.2	84.5	77.2
n. amyl	0.00364	0.56−3	10.35	10.83	129.4	1.339	10.5	57.1	53.3
alcohol	0.00546	0.74−3	11.17	12.00	143.4	1.702	6.5	44.9	33.0
	0.00728	0.86−3	(11.53)	(25.4)	(303.5)	6.89	3.0	11.1	15.2
	0.00850	0.94−3	—	—	—	—	1.0	—	5.1
	blank	$-\infty$	8.27	8.39	100	0.759	19.6	100	100
n. hexyl	0.00105	0.02−3	10.06	10.36	123.5	1.077	13.8	70.5	70.4
alcohol	0.00210	0.32−3	11.42	12.65	150.8	2.050	5.8	37.0	29.6
	0.00263	0.42−3	(11.68)	(18.2)	(217.2)	4.70	3.0	16.1	15.3

mean value of the blanks: $G_0 = 8,38$; $\Lambda_0 = 0.760$; $n_0 = 19.6$.

we give two representations of the functional relation between G and the logarithm of the alcohol concentration, which differ in the way G has been calculated from the experimental data (we shall return to this below). In figure 1 we give further $1/\Lambda$ and n in per cent. of the blank values.

We miss in this fig. 1 a graph for $100\ \lambda/\lambda_0$, because it is not possible

to calculate a relaxation time from the experimental data. Cf. Part III of this series in which it was shown, that the 1.2 % and the 0.6 % oleate system differ as regards the functional relation between the logarithmic decrement Λ and the radius of the sphere R (in the 1.2 % system Λ is proportional to R; in the 0.6 % system Λ is independent of R). The quantitative relationships found in Part III gave strong support to the conception that the oscillations in the 0.6 % oleate system are damped in consequence of slipping along the boundary of the glass vessel. This case has been dealt with theoretically by J. M. BURGERS [4]). In a subsequent publication of the same author [5]) it was shown that in the case of slipping along the wall instead of the usual one quite another correction of the period had to be applied for calculating G, as the former holds good only in the case of damping as a consequence of relaxation. He further pointed out, that there are certain indications in our experiments that, besides the supposed slipping relaxation too may play a rôle.

Since then we have made direct observations of the oscillations of very small air bubbles in the 0.6 % oleate system in the immediate vicinity of the glass wall and came to the surprising conclusion that no slipping along the glass wall could be detected. [6]) We could not but come to the conclusion, that the explanation why in the 0.6% oleate system Λ is independent of R has not yet been given.

Returning to the question how we are to calculate G in the present experiments, we must certainly not apply the correction given theoretically by BURGERS, as slipping along the wall is absent. We may follow two different ways:

a. use the uncorrected T values themselves, which gives the G values depicted in the upper left graph in fig. 1;

b. apply the usual correction, $T_{corr} = T/\sqrt{1 + (\Lambda/2\pi)^2}$, before calculating G, which gives the G values depicted in the upper right graph in fig. 1.

We will now compare the results laid down in fig. 1 with the analogous results obtained in Part VI with the 1.2 % oleate system. For this purpose the corresponding figure is once more inserted here as fig. 2 (see also Table II). [7])

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[4]) J. M. BURGERS, these Proceedings, **51**, 1211 (1948).

[5]) J. M. BURGERS, these Proceedings, **52**, 113 (1949).

[6]) We hope to return to these experiments in a later communication in this series.

[7]) Fig. 2 given here differs from fig. 2 given in Part VI by the course of the ends to the right of the G curves in particular for methanol and ethanol (in Part VI markedly bent upwards, here slightly bent downwards).

This difference results from omitting here an extra correction of T which we thought in Part VI to be necessary for highly damped oscillations (reduction of T to the isochronous level, compare Part VII, section 4). This correction we now

We may now first ask if their are any indications which point to a totally different character of the damping in the 0.6 % and the 1.2 % system. On comparing the analogous graphs (referring to $1/\Lambda$ and n) we see for both systems the same characteristics. All alcohols decrease
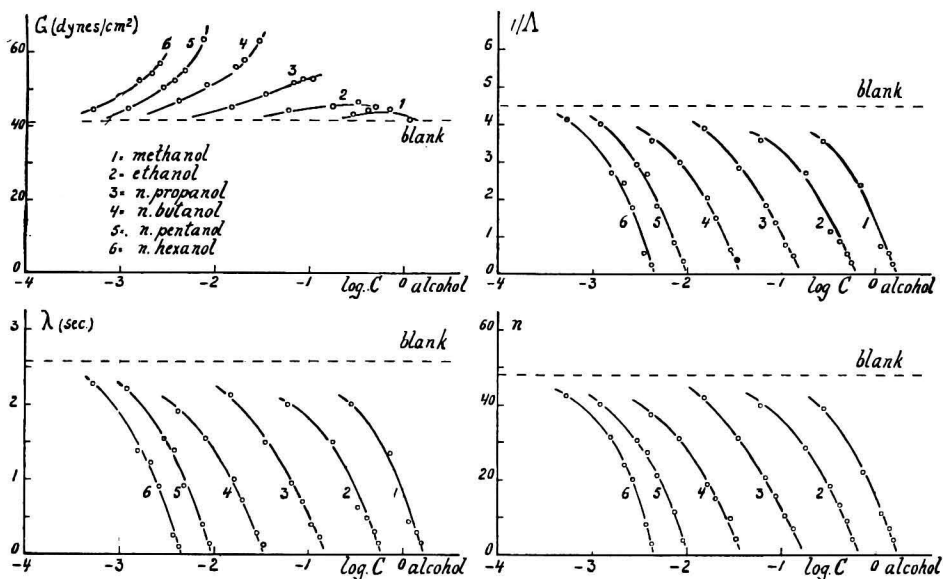

Fig. 2

these quantities and this decreasing action is becoming greater in a highly considerable measure every time the alcohol is lengthened with one carbon atom. In Table III we give for the 0.6% and the 1.2% system (taken from a table in Part VI, section 3) the logarithms of the alcohol concentrations corresponding to a decrease of $1/\Lambda$ and n down to 50 % of their original value.

For the 0.6 % and the 1.2 % oleate systems are the absolute values of the logarithms of the concentrations for each alcohol of the same order of magnitude. The same applies for the mean logarithmic differences

consider as erroneous, for the example given in Part VII was a slightly damped oscillation, and correction factors following from this example may not be applied to strongly damped oscillations (in which the isochronous level is reached proportionally sooner). Therefore all values of G in Table II (and also in Table I) have been recalculated from the experimental T values themselves (of course corrected in the usual way for Λ). Still for the highest damped oscillations (e.g. n below 6) a correction of the kind used in Part VI is probably necessary, the omitting of which may be the cause of the slightly bent downward ends of the G curves for methanol and ethanol. Therefore these downwards bent ends of the curves in fig. 1 and 2 must possibly be considered as not exact, but they come nearer to the true course of the curves than the markedly bent upward ends of the curves in fig. 2 of Part VI.

TABLE II

Influence of n. primary alcohols on the elastic behaviour of the 1.2 % oleate system at approximately the KCl concentration of minimum damping (at 15°)

Alcohol	Conc. moles/l	log. conc.	G dyne/cm²	Λ	$1/\Lambda$	λ sec.	n
methanol	blank	$-\infty$	40.8	0.222	4.50	2.56	48.2
	0.28	0.45 − 1	42.5	0.279	3.58	1.99	39.1
	0.73	0.86 − 1	43.9	0.415	2.41	1.33	22.0
	1.15	0.06	40.9	1.31	0.76	0.42	11.0
	1.42	0.15	(39.4)	1.755	0.57	0.31	7.0
	1.56	0.19	(38.8)	3.64	0.27	0.15	4.0
ethanol	blank	$-\infty$	41.1	0.219	4.57	2.60	48.1
	0.061	0.79 − 2	44.1	0.277	3.61	1.99	39.8
	0.181	0.26 − 1	44.8	0.368	2.72	1.50	28.3
	0.33	0.52 − 1	45.6	0.859	1.16	0.63	18.2
	0.416	0.62 − 1	43.7	1.12	0.89	0.47	13.2
	0.503	0.70 − 1	44.7	1.78	0.56	0.31	9.0
	0.506	0.75 − 1	(42.6)	3.20	0.31	0.16	4.0
n. propyl alcohol	blank	$-\infty$	40.5	0.222	4.50	2.57	48.0
	0.0153	0.18 − 2	44.5	0.255	3.92	2.13	42.1
	0.0357	0.55 − 2	47.8	0.350	2.86	1.49	31.1
	0.069	0.84 − 2	50.9	0.540	1.85	0.94	20.4
	0.086	0.93 − 2	51.8	0.715	1.40	0.70	15.4
	0.110	0.04 − 1	51.8	1.26	0.79	0.39	10.5
	0.136	0.13 − 1	(58.2)	1.92	0.52	0.24	6.8
n. butyl alcohol	blank	$-\infty$	40.6	0.222	4.50	2.57	47.9
	0.00414	0.62 − 3	46.1	0.280	3.57	1.91	37.6
	0.0083	0.92 − 3	50.6	0.332	3.01	1.54	31.0
	0.0166	0.22 − 2	55.1	0.491	2.04	0.99	18.7
	0.0207	0.32 − 2	57.0	0.670	1.49	0.72	15.0
	0.0289	0.46 − 2	62.2	1.59	0.63	0.28	9.7
	0.0328	0.52 − 2	(67.4)	3.04	0.33	0.13	4.0
n. amyl alcohol	blank	$-\infty$	40.8	0.220	4.55	2.60	47.8
	0.00119	0.08 − 3	44.1	0.249	4.02	2.21	40.2
	0.00298	0.47 − 3	49.7	0.338	2.96	1.54	30.5
	0.00382	0.58 − 3	51.2	0.369	2.71	1.38	26.9
	0.00476	0.68 − 3	53.9	0.549	1.82	0.91	21.2
	0.0074	0.87 − 3	62.2	1.185	0.84	0.39	11.6
	0.0092	0.96 − 3	(65.7)	2.95	0.34	0.15	4.0
n. hexyl alcohol	blank	$-\infty$	41.2	0.224	4.46	2.54	47.9
	0.00052	0.72 − 4	44.2	0.241	4.15	2.28	42.4
	0.00157	0.20 − 3	51.7	0.367	2.72	1.38	31.5
	0.00217	0.34 − 3	53.5	0.407	2.46	1.23	23.8
	0.00262	0.42 − 3	56.2	0.561	1.78	0.87	20.1
	0.00374	0.57 − 3	(64.8)	1.89	0.53	0.24	8.0
	0.00426	0.63 − 3	—	4.03	0.25	0.10	3.0

mean values of the blanks: $G_0 = 40.8$; $\Lambda_0 = 0,222$; $\lambda_0 = 2,57$; $n_0 = 48,0$

TABLE III

Logarithms of the alcohol concentrations corresponding to a decrease of $1/\Lambda$ and n down to 50% of their original value.

Oleate concentr.		n.hexyl alcohol	n.amyl alcohol	n.butyl alcohol	n.propyl alcohol	ethanol	methanol
0.6 %	$1/\Lambda$	$0.23-3$	$0.67-3$	$0.21-2$	$0.80-2$	$0.39-1$	$0.78-1$
	n	$0.20-3$	$0.58-3$	$0.11-2$	$0.69-2$	$0.31-1$	$0.70-1$
	mean logarithmic difference	0.41		0.54	0.59	0.61	0.39
1.2 %	$1/\Lambda$	$0.32-3$	$0.63-3$	$0.15-2$	$0.74-2$	$0.34-1$	$0.85-1$
	n	$0.35-3$	$0.64-3$	$0.12-2$	$0.73-2$	$0.37-1$	$0.84-1$
	mean logarithmic difference	0.30		0.50	0.60	0.62	0.49

which in both cases (at least when going from methanol to amyl alcohol) correspond to ratios of approximately 3 or 4.

All this gives us a strong conviction that the damping in the 0.6 % oleate system is also a consequence of relaxation, though by a unknown circumstance Λ is independent of R, so that a relaxation time λ cannot be calculated.

We are strengthtened in this conviction if we now turn to a comparison of the G graphs of fig. 1 with the G graph of fig. 2. We observe that there is a striking similarity (viz. all the alcohols increase G only, though with methanol this is so slight that it comes in the order of the experimental errors) only if we now take the G graph in fig. 1 to the right. As already stated above, this latter graph represents G as computed from T after applying the usual correction for Λ, viz. that correction which was also applied for calculating the G values in fig. 2. The drooping ends of the G curves upper left in fig. 1 we therefore consider to be the result only of non correcting the period before computing G. In this connection it may be mentioned that the G curves for methanol and ethanol in fig. 2 would also show such downward bent curls intersecting the blank level, if G was calculated from the uncorrected T values.

3. *$G - \lambda$, $G - 1/\Lambda$ and $G - n$ diagrams, an alternative method of representing graphically the experimental results obtained with the homologous series of the alcohols.*

In studying the action of organic substances on the elastic properties of the oleate system at constant KCl concentration, one must make a difference between the gross concentration of the organic substances at which a certain effect is obtained, and the action per bound molecule of the organic substance.

If we consider the hydrocarbons — which are on the whole practically insoluble in water — all molecules added will be taken up by the oleate micelles. The different positions of the curves, obtained with a number of hydrocarbons (see fig. 5 in Part VII) then indicate differences in the action of the hydrocarbon molecules bound to the oleate micelles.

If we compare, however, the lower terms of the homologous series of the n-primary alcohols — these being soluble in water — this no longer holds.

In this case only part of the added alcohol molecules are bound to the oleate micelles, the other part being left free in the medium and constituting a true equilibrium concentration characteristic for the distribution of the alcohol molecules between micelles and medium. If the quantity of bound molecules is small in comparison with the total quantity of molecules added (the latter representing the gross concentration), the different positions of the curves (laid out as a function of the gross concentration) will in the first place give information about the distribution of the alcohol molecules between micelles and medium.

And indeed, if we compare the terms $C_1 - C_5$, we find values of 3 to 4 (compare section 2) for the ratios of the gross concentrations of two successive terms needed to reach a same change in λ (or $1/\Lambda$ or n). This is reminiscent of values occurring in TRAUBE's rule. This shows that even for C_5 the bound molecules are only a small fraction of the total amount of molecules added, or in other words: From C_1 up tot C_5 the gross concentrations represent practically equilibrium concentrations.

Therefore if we consider the figures 1 and 2 and deduce from them a series of "increasing activity" of the alcohols: 6>5>4>3>2>1, it must be well understood that this series indicates only that the ease with which the alcohols are taken up by the oleate micelles increases rapidly from right to left every time the carbon chain in lengthtened with one carbon atom. Therefore graphs of the kind of fig. 1 and 2, in which G or λ or $1/\Lambda$ or n are plotted as functions of the alcohol concentrations, cannot give expression to possible differences in the nature of the action exerted by the bound molecules of the various alcohols.

For the latter purpose we must evidently look for a graphical representation of the experimental results, in which the concentrations of the various alcohols are no longer used. Now the measurements always give two kinds of quantities: a. G, the elastic shear modulus, and b. quantities which refer to the damping (λ, Λ, n). This circumstance opens the possibility of representing the experimental results by diagrams in which these two kinds of quantities are used as ordinates and abscissa.

In such diagrams we can plot the actually determined values of G and of λ (or of $1/\Lambda$ or of n) as such, or expressed in percents of the blank G and λ (or $1/\Lambda$ or n) values. The latter method will be followed here, as it is to advantage in view of comparison of the results obtained with the 0.6 % and the 1.2 % oleate systeni.

Fig. 3 gives the results for the 0.6 % oleate system, using the data of table I. In these graphs we see the curves going upwards to the left. They all take their origin at the point with an ordinate 100 and an abscissa 100. This point therefore represents the blank oleate system.
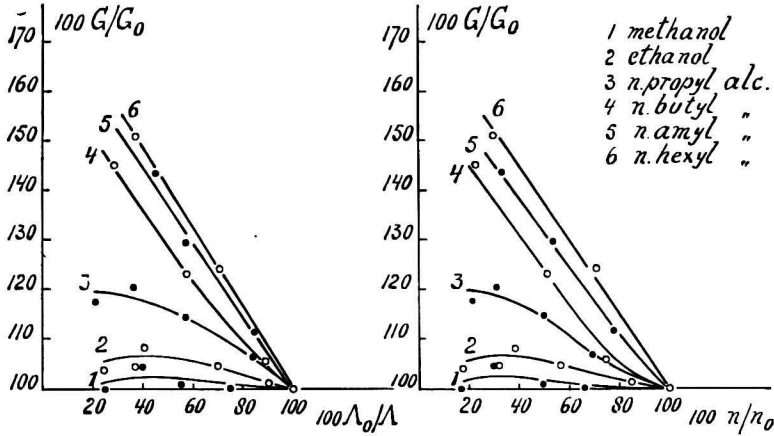

Fig. 3

We observe that their are six different curves each representing the measuring points of one of the n primary alcohols. The increase in G at the same decrease of $1/\Lambda$ or of n is seen to diminish in the order

$$6 > 5 > 4 > 3 > 2 > 1 \qquad (0.6 \text{ % oleate at } 1.43 \text{ N KCl})$$

In the same way we have laid out in fig. 4 the results obtained with the 1.2 % oleate system (data of Table II, expressed in per cents of the corresponding blanks). The graphs are fairly similar to those of fig. 3.
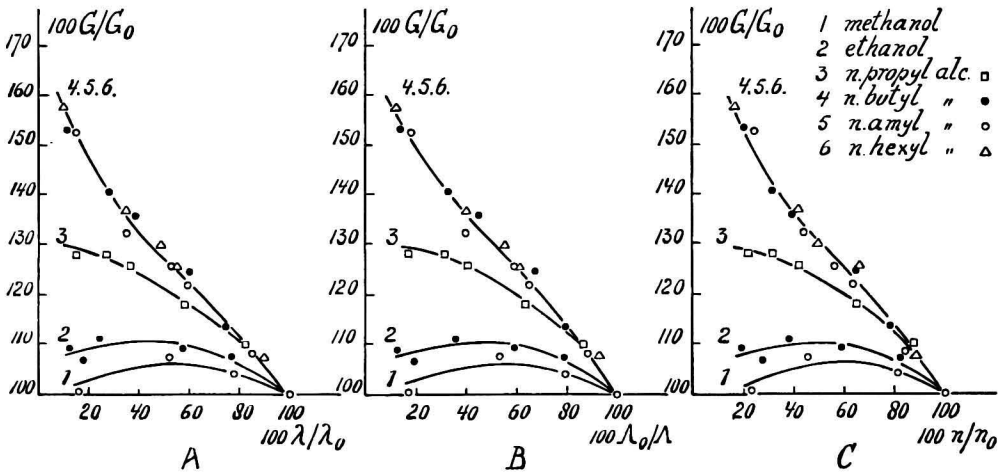

Fig. 4

The position of the curves in this percentual representation is not very much different, though the absolute values of G, $1/\Lambda$ and n are very different in the 0.6 and 1.2 % oleate systems. The sequence of the curves is in principle the same:

$$6,\ 5,\ 4 > 3 > 2 > 1 \qquad (1.2\ \%\ \text{oleate at } 1.52\ N\ KCl).$$

The expected spreading of the curves for 6, 5 and 4 does not find expression here, probably because by some unknown reason [8]) these curves are lying so close together here, that their distance is of the same order of magnitude as the experimental error.

The $G - \lambda$, $G - 1/\Lambda$ and $G - n$ diagrams of fig. 3 and fig. 4 are representations in which the concentration of the alcohols no longer plays any part. They show us that for the successive terms of the homologous series the molecules bound to the oleate have not the same action, *but that a gradual shift in the nature of the action occurs as the carbon chain of the alcohol is lenghtened.* For if the nature of the action was exactly the same, the experimentally determined points of all alcohols would lay on one and the same $G - \lambda$ or $G - 1/\Lambda$ or $G - n$ curve. The next section will show us how to interpretate the figs. 3 and 4:

4. *Interpretation of the G—λ, G—$1/\Lambda$ and G—n diagrams of section 3.*

In Part VI of this series we have investigated the shift of the curves, which represent G and λ (or $1/\Lambda$ or n) as functions of the KCl concentration, by the addition of a number of constant quantities of n. hexylalcohol and of ethanol. In both cases the maximum of the λ (or $1/\Lambda$ or n) curve is displaced downwards and to the left, but in the case of n. hexylalcohol the ratio of the horizontal and the vertical component of this displacement is much larger than in the case of ethanol. Evidently this difference points to a different kind of action of the bound molecules of both alcohols because in the corresponding graphs (see Part VI, fig. 2 and fig. 4) the alcohol concentrations themselves are no variables.

It can be easily shown that there exists a close relation between the magnitude of the above mentioned ratios and the slope of the curves in the $G - \lambda$, $G - 1/\Lambda$ and $G - n$ diagrams of fig. 3 and 4.

For that purpose we consider the schemes A_2, A_1 and B of fig. 5 in which the full drawn curves represent G and λ (or $1/\Lambda$ or n) as functions of the KCl concentration for the blank oleate system and in which the dotted curves represent G and λ (or $1/\Lambda$ or n) as functions of the KCl concentration at certain (see below) constant concentrations of three different substances A_2, A_1 and B.

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[8]) It may be that the crowding together is caused by the circumstance, that in this 1.2 % oleate series the KCl concentration (1.52 N) is somewhat higher than that corresponding with the minimum damping of the blank (1.43 N).

The schemes A_2 and A_1 of fig. 5 relate to two substances of type A. [9]) In these schemes the ratio of the horizontal and the vertical component of the displacement of the maximum of the λ (or $1/\Lambda$ or n) curve has different values. This ratio (ad/dc) is larger in the case of A_2 than in the
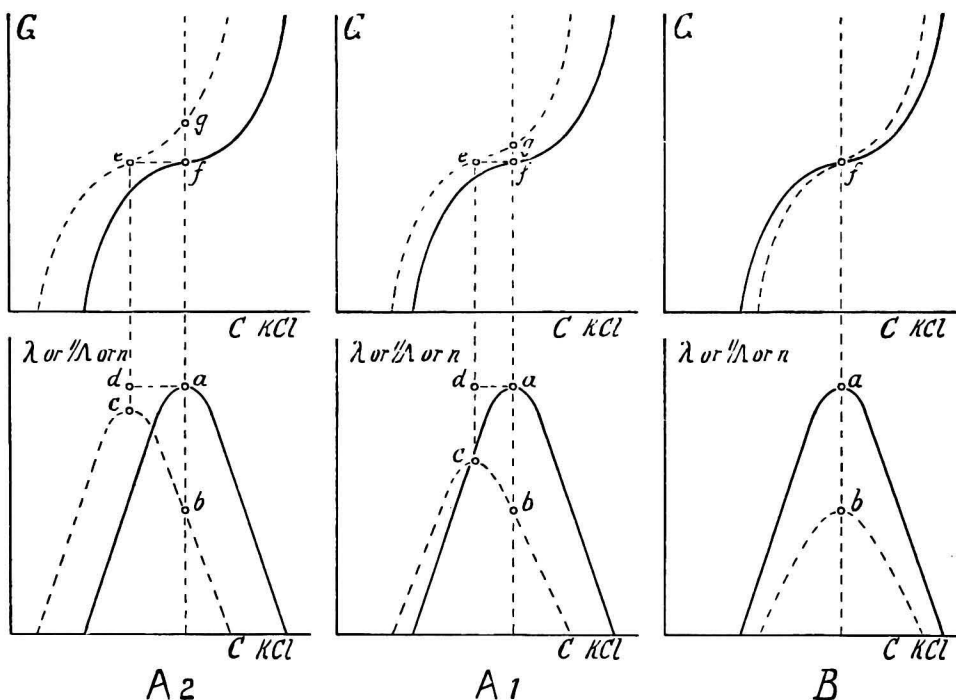

Fig. 5

case of A_1. The third scheme relates to a substance of type B, which is the limiting case of type A as here the horizontal component ad is zero.

In the schemes of fig. 5, we have further considered such concentrations of the substances A_2, A_1 and B, that the displaced λ (or $1/\Lambda$ or n) curve of each passes (with its right side, or with its maximum) through the same point b, which is situated on a vertical line drawn through the maximum a of the λ (or $1/\Lambda$ or n) curve of the blank.

This means, that we only consider such concentrations of the substances A_2, A_1 and B, where the decrease of λ (or $1/\Lambda$ or n), represented by the distance ab, is the same for all three substances.

[9]) In Part VI we have already discerned three types of organic substances A, B and C, characterised by the direction of the horizontal component of the shift of the maximum of the λ (or $1/\Lambda$ or n) curve. Having type A when the horizontal component of this shift shows towards smaller KCl concentrations, type C, when it shows to the opposite direction and B when the horizontal component is zero.

We now direct our attention to the upper graphs which show the displacement of the G-curves. For this displacement two things are characteristic (cf Part VI and Part VII);

a. that the inflexion point situated on the G curve always corresponds to the maximum of the λ (or $1/\Lambda$ or n) curve, independent whether we consider the blank (points f and a) or the shifted curves (points e and c),

b. that the shift of the inflexion point on the G curve consist of an horizontal component fe only, which (see under *a*) is just as large as the horizontal component ad of the displacement of the maximum of the λ (or $1/\Lambda$ or n) curve.

It may now be read from the figure, that the distance fg, that is the increase of G at the KCl concentration of minimum damping of the blank, is correlated with the ratio ad/dc.

This increase of G is larger for substance A_2 than for substance A_1, and the ratio ad/dc is indeed larger for A_2 than for A_1. For substance B the increase of G is zero (the points g and f are coinciding in this case) and the ratio ad/dc is here also zero (the points d and a coincide).

The above reasonings open the possibility to use the results of a much simpler form of experimentation — in which the influence of added organic substances at only one KCl concentration, namely the concentration of minimum damping of the blank are determined — to arrange a number of substances A_1, A_2 A_3 etc. into a series in which the ratio of the horizontal and the vertical component of the displacement of the maximum of the λ (or $1/\Lambda$ or n) curve increases.

One procedure to use these results consists of reading from interpolation graphs, at which concentration a certain decrease (e.g. of 50 per cent.) of λ (or $1/\Lambda$ or n) is attained with each of the alcohols, and after that to read on analogous G- interpolation graphs, which G values correspond with these concentrations for each of the alcohols.

If the above procedure will have any real significance, we must find of course the same arrangement of the substances A_1, A_2, A_3, A_4, etc. if we choose for comparison other (constant) values of the decrease in λ (or $1/\Lambda$ or n).

A still simpler procedure consists of laying out the actual experimental results in a $G - \lambda$ diagram (or in a $G - 1/\Lambda$ or in a $G - n$ diagram). For in these diagrams we have at once a representation of all increases in G at all decreases in λ, (or in $1/\Lambda$ or in n). The interpretation of these diagrams is then very simple, provided we obtain a bundle of non intersecting curves: The order of increasing steepness of the curves will be the order in which the ratio of the horizontal and vertical component of the displacement increases.

Applying this to the diagrams of fig. 3 and 4, we may conclude that

the alcohols $C_1 - C_6$ may be arranged in one continuous series:

$$6 > 5 > 4 > 3 > 2 > 1$$

in which from right to left the ratio of the horizontal and vertical component of the displacement of the maximum of the λ (or $1/\Lambda$ or n) curve increases.

Summary.

1. In connection with the divergent character of the damping in the 1.2% oleate system (Λ is proportional to R) and in the 0.6% oleate system (Λ is independent of R) — compare Part III of this series — the influence of the first six terms of the n. primary alcohols has been investigated on the elastic behaviour of the 0.6 % oleate system at the KCl concentration of minimum damping. The influence on G, $1/\Lambda$ and n is quite the same as in the case of the 1.2 % oleate system.

2. The results mentioned sub 1., combined with the finding that any slipping along the glass wall could not be observed, lead to the conclusion of the non validity of the interpretation (slipping along the boundary of the glass vessel) as was accepted in Part III of this series for: Λ is independent of R, characteristic of the 0.6 % oleate system.

3. Graphs in which G or λ or $1/\Lambda$ or n are plotted as functions of the alcohol concentrations (compare figures 1 and 2) bring mainly to epxression the differences between the successive terms of the homologous series with regard to the distribution of the alcohol molecules between oleate micelles and medium.

The alcohols may be arranged in the order $6 > 5 > 4 > 3 > 2 > 1$, in which from right to left the above distribution strongly shifts in favour of the oleate micelles.

4. $G - \lambda$, $G - 1/\Lambda$ and $G - n$ diagrams, being representations in which the concentration of the alcohols no longer plays any part, inform us on the nature of the action of the alcohol molecules bound to the oleate micelles. The graphs obtained (compare fig. 3 and 4) show that this action is not the same for the successive terms of the homologous series, but that a gradual shift occurs as the carbon chain of the alcohol is lengthened.

5. The gradual shift sub 4. consists of a change in the ratio of the horizontal and vertical component of the displacement of the maximum of the λ, $1/\Lambda$ or n curves (in the graphs representing λ, $1/\Lambda$ and n as functions of the KCl concentration). The alcohols may be arranged in the order $6 > 5 > 4 > 3 > 2 > 1$, in which from right to left the above ratio increases.

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