

CHEMISTRY

ELASTIC VISCOUS OLEATE SYSTEMS CONTAINING KCl. XI ¹⁾

Influence of aliphatic and aromatic hydrocarbons on the elastic behaviour of the 1.2 % oleate system.

BY

H. G. BUNGENBERG DE JONG, W. A. LOEVEN* AND W. W. H. WEIJZEN* ²⁾

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1. *Introduction and Methods.*

Preliminary investigations about the action of some hydrocarbons on the elastic oleate system, have already been performed in the parts VII and X of this series.

To get some insight into the relation between the structure of the hydrocarbon and its action on the elastic behaviour of the oleate system, we deal with 1) the homologous series of the alkanes, 2) isomeres of *n*-octane, 3) introduction of a double or a triple bond in *n*-octane, 4) benzene and alkylbenzenes, 5) *o*-, *m*- and *p*-xylenes, in the present investigation (performed at 15°) ³⁾.

We used the original method with the exactly half filled vessels of approximately 500 ml capacity (Pyrex vessels varying between 496 and 505 ml). This method is described in detail in part VI of this series. The hydrocarbons were added with the dripping pipette, described elsewhere ⁴⁾, the dropweight of each hydrocarbon being determined by weighing 10 drops. As the maximal quantity which was added, changed the degree of filling of the vessels only 0,13 %, no corrections for the increase in volume were necessary.

For the exciting of the rotational oscillation, we used the contrivance described in part VII. As none of us could perform the difficult measurements of the decrement, we had to content ourselves with the change

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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), Parts VII—X in these Proceedings 53, 7, 109, 233, 743 (1950).

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³⁾ We are much indebted to the Koninklijke/Shell Laboratorium, Amsterdam, which sent us the pure hydrocarbons used in our experiments.

⁴⁾ H. G. BUNGENBERG DE JONG and L. J. DE HEER, these Proceedings 52, 783 (1949).

in n , caused by the addition of hydrocarbons, as an approximate measure for the change in $1/A$ (part VII, section 3).

As an oleate preparation we used Na oleate, neutral powder, from BAKER ⁵⁾ (for remarks on this preparation see part X). All experiments were made with one and the same mixture out of the contents of 5 flasks.

The idea was, to measure the influence of the hydrocarbons at the KCl concentration of minimum damping, as at this concentration, maximum information is obtained (part VII, section 5).

For the above mixture this KCl concentration lies very near 1.05 N, but at the beginning of the experiments we did not know yet that the contents of individual flasks of Na oleate, bearing the same lot number, may show differences (part X, section 4). At a preliminary experiment on the position of this KCl concentration of minimum damping, on which occasion we used one flask, we found approximately 1.2 N.

Therefore several series of measurements have been performed at a KCl concentration of 1.2 N, that is at a concentration somewhat higher than that corresponding to the minimum damping of the blank oleate system. This detail is of importance for the discussion of the results. The series with the isomeres of octane, octene and octyn, however, were performed at 1.05 N KCl. The aromatic hydrocarbons were also investigated at 0.6 N KCl, that is at a KCl concentration markedly lower than that corresponding to the minimum damping of the blank oleate system.

The elastic systems used in the experiments always contained 1.2 % oleate and 0.05 N KOH. These are prepared from a stock oleate solution (24 g per liter) containing 0.1 N KOH.

For obtaining the elastic system, one volume of this stock solution is vigorously shaken, in a large flask, with one volume of a KCl solution. A quantity, sufficient to fill a series of 7 exactly half filled 500 ml vessels, is obtained according to this receipt:

1000 ml oleate stock solution + 1000 ml KCl x N (e.g. for 1.2 N KCl $x = 2.4$; for 0.6 N KCl $x = 1.2$).

2. *The homologous series of the n-alkanes from n-pentane up to and including n-undecane.*

The alkanes mentioned in the title, were investigated in two consecutive series, the first (table I) comprising *n*-pentane, *n*-hexane, *n*-heptane and *n*-octane, the second (table II) *n*-octane, *n*-nonane, *n*-decane and *n*-undecane.

The results of both series have been united in fig. 1 ⁶⁾. This gives no difficulties for the plotting of the upper graph, representing G as a function of the concentration of the alkanes, because the mean G values of the

⁵⁾ A generous gift of Na oleate from The Rockefeller Foundation provided the means for the experiments described in this paper.

⁶⁾ Some G and n values, provided with a question mark in the tables are obviously erroneous and have not been used in the plotting of fig. 1.

TABLE I. Influence of pentane, hexane, heptane and octane on the elastic behaviour of the 1.2 % oleate system at 1.2 N KCl and at 15°. Conc. = concentration of the hydrocarbon in millimoles/l; G = shear modulus in dyne/cm²; n = maximum number of observable oscillations through the telescope. Values of the blank $G = 49.1$ and $n = 66.7$

<i>n</i> -pentane			<i>n</i> -hexane			<i>n</i> -heptane			<i>n</i> -octane		
conc.	G	n	conc.	G	n	conc.	G	n	conc.	G	n
2.39	49.4	65.7	2.34	49.8	66.1	2.09	47.1	66.0	2.06	45.6?	69.7
4.79	50.5	65.7	4.68	50.6	65.0	4.17	45.8	70.3	2.89	45.5	75.4
9.58	50.4	62.1	9.36	45.7	67.1	8.34	41.0	66.0	4.12	44.4	71.7
14.4	48.2	59.8	14.0	40.1	71.1	12.5	34.3	29.5	6.60	40.4	62.2
19.2	45.9	61.7	18.7	37.3?	52.0	16.7	—	4.3	8.25	36.1	28.2?
23.9	44.2	79.5	23.4	29.1	21.4				9.48	33.7	26.1
			28.1	—	5.8						

TABLE II. Influence of octane, nonane, decane and undecane on the elastic behaviour of the 1.2 % oleate system at 1.2 N KCl and at 15°. Conc. = concentration of the hydrocarbon in millimoles/l; G = shear modulus in dyne/cm²; n = maximum number of observable oscillations through the telescope. Values of the blank $G = 48.9$ and $n = 70.6$

<i>n</i> -octane			<i>n</i> -nonane			<i>n</i> -decane			<i>n</i> -undecane		
conc.	G	n	conc.	G	n	conc.	G	n	conc.	G	n
2.89	45.7	80.3	1.95	46.8	79.7	1.47	47.7	77.4	1.04	47.6	75.9
5.77	41.7	71.3	3.50	44.0	75.7	2.21	45.0	75.9	1.74	45.1	78.1
7.42	39.0	55.1	4.67	42.3	69.8	2.94	43.9	71.6	2.43	43.6	70.0
9.07	34.7	32.1	5.84	40.0	56.5	4.78	40.4	58.2	3.47	41.7	59.7
10.3	30.5	13.6	7.00	38.0	42.5	5.89	38.2	41.9	4.86	41.2?	53.6?
			8.17	30.9	20.6	7.36	27.5	11.3	5.91	35.3	27.1

blanks are practically the same in the tables I and II. The two experiments with *n*-octane, give a further justification: the experimentally determined points are lying reasonably close to the one curve which is drawn through them.

The mean values for n , however, are differing somewhat for both series, and therefore we have used in the lower graph of fig. 1 the values $100 n/n_0$, in which n_0 represents the n value of the blank. Now, the experimentally determined points for the two series with *n*-octane lie also close to one and same curve.

A first glance at fig. 1 reveals that the terms of the series of the *n*-alkanes exert their action at very different concentrations, an alkane being the more active when its carbon chain is longer. We will return to this in section 3.

Next, considering the shape of the G and n curves in fig. 1, we perceive

that the investigated alkanes fall apart in two groups: I *n*-undecane, *n*-decane, *n*-nonane, *n*-octane and *n*-heptane, of which the G curves at once go into a downward direction, II *n*-hexane and *n*-pentane, of which the G curves first proceed upwards to a maximum and thereafter proceed downwards.

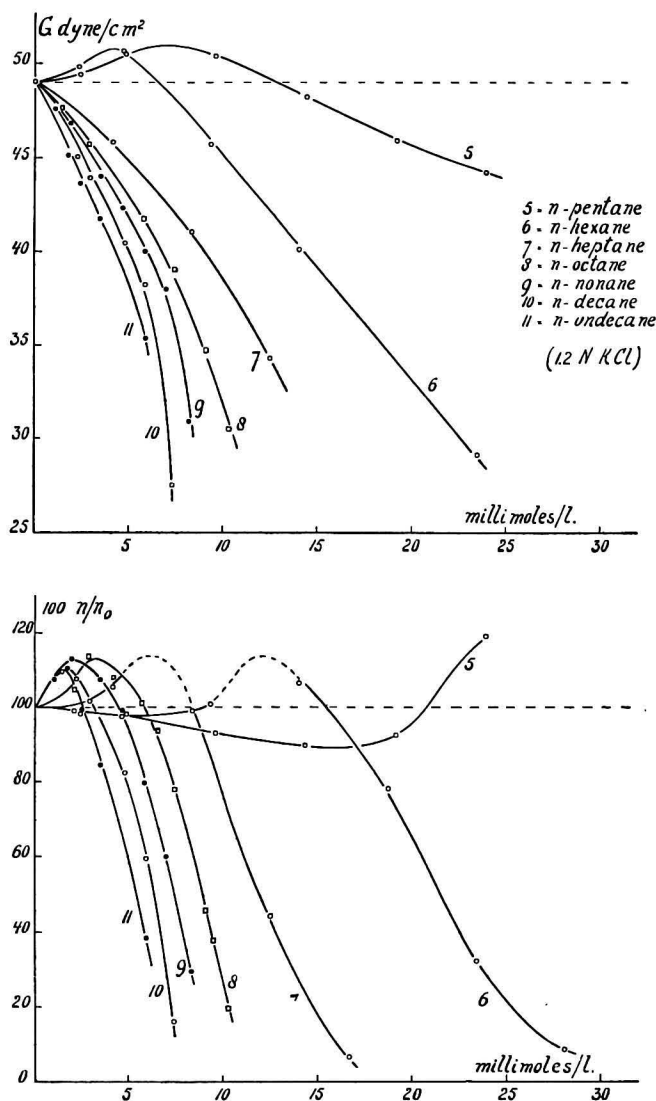


Fig. 1

Likewise, the shape of the n curves gives rise to a distinction of the same groups. For the hydrocarbons of group I these curves are proceeding upwards to a maximum and there after definitely downwards. For the hydrocarbons of group II they are first proceeding to a minimum, then to a maximum and thereafter definitely downwards (the pentane

concentration has obviously not been taken high enough to realise the n curve in its whole).

In part VII of this series (in section 5) it was discussed how one can conclude from experiments on the influence of an added organic substance, performed at constant KCl concentration, to the type of action (A , B or C) which this substance would exhibit on the position of the G and $1/\Lambda$ (or λ or n) curves, in graphs representing G and $1/\Lambda$ (or λ or n) as functions of the KCl concentration (type A , a shift in the direction of smaller, type C , a shift in the direction of higher KCl concentrations and type B , no shift in either direction). A scheme was given, being repro-

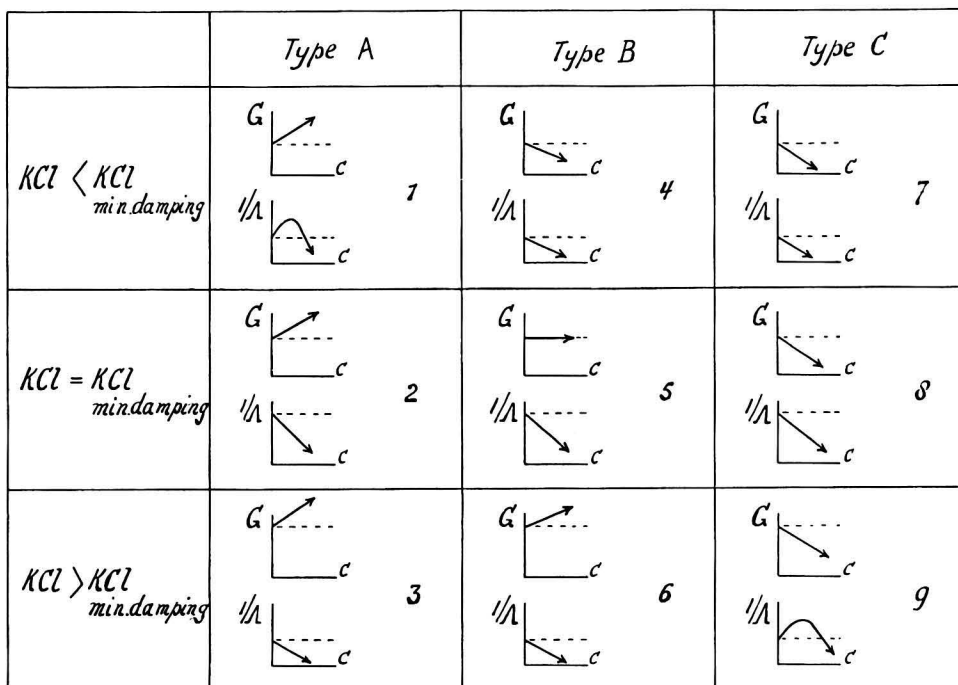


Fig. 2

duced here as fig. 2. From this one can read for KCl concentrations lower than, equal to or higher than that corresponding to the KCl concentration of minimum damping, the sign of the change of G and of $1/\Lambda$, λ or n if the added substance shows the type of action A , B or C .

Applying this to the present experiments with added hydrocarbons we must bear in mind that these have been performed at 1.2 N KCl, that is at a concentration somewhat higher than that corresponding to the KCl concentration of minimum damping of the blank. From the nine diagrams of fig. 2 we must therefore only consider the diagrams 3, 6 and 9.

The results of the experiments with octane, nonane, decane and undecane correspond to diagram 9, from which we conclude that the above alkanes $C_8 - C_{11}$ typically follow the action type C .

The results obtained with pentane and hexane give more complicated G and n curves, which do not correspond to one of the diagrams 3, 6 and 9 in fig. 2. They can, however, be considered as to be composed of the G and n curves from the diagrams 6 and 9, or from the diagrams 3, 6 and 9, linked together in the above mentioned succession.

This would mean, that hexane and pentane show a transition in the type of action at increasing hydrocarbon concentration, namely $B \rightarrow C$, or $A \rightarrow B \rightarrow C$. As to hexane we need not ponder much which of the two is more probable, because in part X we have found by the direct method, that both at 1.05 N and 1.7 N KCl, hexane shows the transition in type $A \rightarrow B \rightarrow C$, at increasing hexane concentration. Therefore, at 1.2 N KCl it must show the same transition.

As to pentane, we have no such direct indications in favour of one of the two possibilities, but here too we must conclude to $A \rightarrow B \rightarrow C$ on the ground of regularities, exhibited by fig. 8 of part X of this series. In this figure, which gives the shifts of three characteristic points of the n - C_{KCl} curve at the addition of a number of organic substances, we perceive that going from hexane to heptane, the initial shift, resulting from the action type A , in the transition $A \rightarrow B \rightarrow C$, diminishes (at 1.7 N KCl) or even disappears, leaving only the transition $B \rightarrow C$ (at 1.05 N KCl). We therefore may conclude with high probability, that the transition $A \rightarrow B \rightarrow C$ which exists at 1.2 N for hexane, will also hold for pentane, and further that the initial action resulting from the action type A in the transition $A \rightarrow B \rightarrow C$ will be more pronounced in pentane than in hexane. This latter expectation is confirmed by the experiment, the n curve for pentane in fig. 1 showing a deeper minimum than the n curve for hexane.

Now when we consider in fig. 1, the results obtained with heptane, we find that the course of the n curve (proceeding nearly horizontally before it mounts to the maximum) lies between the courses of the n -curves for the higher alkanes (proceeding at once upwards to the maximum) and the courses of the n curves for the hexane and pentane (proceeding at once downwards to the minimum).

Heptane may therefore be considered as a substance standing very near to one which at small concentrations shows type B and which at further increase of the concentration shows the transition in type $B \rightarrow C$ (in accordance with the findings in part X for heptane at the KCl concentration corresponding to the minimum damping of the blank).

We have therefore indicated in the survey below, which summarizes the above discussions, the type of action exhibited by heptane at the first additions, with " B ".

We will end this section by remarking that this survey (valid for 1.2 N KCl) on the action of alkanes gives only two of the three variables that are involved. Next to the length of the carbon chain and

to the concentration of the alkane, the action type still depends on the KCl concentration (— or probably better — on the internal structure of the elastic system, this structure being a function of the KCl concentration). The experiments with hexane and heptane in part X of this series allow to conclude that the centre column (with at the top "B") of the survey is displaced to the right at increasing KCl concentration, and to the left at decreasing KCl concentration.

Concentration of the alkane	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
small ↓ increasingly larger	A ↓ A ↓ B ↓ C	A ↓ B ↓ C ↓ C	"B" ↓ C ↓ C ↓ C	⏟ C ↓ C ↓ C ↓ C			

3. *Discussion of the results obtained with the n-alkanes from the point of view that the total action is the resultant of two action components, a KCl-sparing one and a KCl-demanding one.*

In part X of this series the transitions in the type of action shown by hexane and heptane, led to the hypothesis that what we have called the type of action (*A* or *B* or *C*) is the resultant of two components acting in opposite directions (having type *A* and type *C* if one of the two preponderates over the other, type *B* when they compensate each other exactly).

BOOIJ and collaborators investigated the influence of organic substances on the shift of the coacervation limit (which as a rule, lies at a slightly higher concentration than the right footpoint of the *n* curve). With the *n*-alkanes ⁷⁾ he obtained transitions in the sign of the KCl shift, which follow the same general rules as were found at the investigation about the influence of the alkanes on the elastic behaviour of the oleate system (at lower KCl concentrations) i.e. transitions as a result of the concentration of the alkane and, at constant concentration, as a result of the number of carbon atoms of the alkane. BOOIJ too, considered the total KCl shift as the resultant of two component shifts acting in opposite directions, and drew up a hypothesis to explain the existence of component actions and their mechanism.

We have the strong conviction that similar considerations (the component actions being the result of the actions of the molecules taken up by the oleate micelles at essentially different places) will also be useful in the explanation of the influence of organic substances on the elastic behaviour of the oleate system, though probably, a superstructure of micelles is a complicating factor here.

⁷⁾ H. L. BOOIJ, J. C. LYCKLAMA and C. J. VOGELSANG, these Proceedings 53, 407—413 (1950).

It will be very convenient for the future work both of BOOIJ and collaborators working on the coacervation limit, and of us working on the elastic behaviour, to have expressions for the sign of the total action and that of the component actions. These expressions must be as neutral as possible and must therefore not contain elements borrowed from hypotheses about the mechanism of the actions on coacervates or on the elastic systems.

In concerted discussion with BOOIJ we propose the terms "*KCl-sparing*" and "*KCl-demanding*".

These terms will characterize the nature of the total action of an organic substance (and even may be used elliptically for the characterization of the substance at a given concentration of its own and of the KCl on hand) and the nature of the component actions of which the total action is the resultant.

Applying this to the action of the alkanes on the elastic behaviour at 1.2 N KCl, pentane and hexane exert a KCl-sparing action at low concentrations of these hydrocarbons and a KCl-demanding action at higher concentrations. The higher alkanes (octane up to and including undecane) exert a KCl-demanding action, independent of their concentration.

In applying the hypothesis of the action type (*A, B, C*) as being a resultant of oppositely directed component actions, the results obtained with the alkanes at 1.2 N KCl may be formulated as indicated in the survey below, in which the symbols *S* and *D* are used as to denote the KCl-sparing and KCl-demanding component actions.

Concentration of the hydrocarbon	C_5	C_6	C_7	C_8 C_9 C_{10} C_{11}
small	$D < S$	$D < S$	$D = S$	$D > S$
↓	$D < S$	$D = S$	$D > S$	$D > S$
increasingly	$D = S$	$D > S$	$D > S$	$D > S$
larger	$D > S$	$D > S$	$D > S$	$D > S$

At decrease of the KCl concentration the oblique bar formed in the survey by the symbols $D = S$ is displaced to the left, and at increase of the KCl concentration it is displaced to the right.

We now come back to the remark made in section 2 that the alkanes exert their action at very different concentrations, an alkane being the more "active" when its carbon chain is longer (compare the succession of the *G* and *n* curves in fig. 1).

In part VI of this series we have met with an analogous rule for the homologous series of the *n*-primary alcohols ($C_1 - C_6$) and the fatty acid anions ($C_7 - C_{11}$), but the resemblance with the succession of the alkanes of fig. 1 is only superficial. In the case of the alcohols and the

fatty acid anions — these being soluble in the soap free KCl solution — the series of “increasing activity” of the alcohols 6>5>4>3>2>1 or of the fatty acid anions 11>10>9>8 brings practically only to expression that the distribution of the added molecules (or anions) between oleate micelles and medium shows an important shift in favour of the micelles when the carbon chain is lengthened (compare part VIII, section 3).

With the hydrocarbons we have quite another situation. As these are practically insoluble in the soap free KCl solution, a distribution equilibrium between hydrocarbon molecules being present free in the medium and molecules taken up by the oleate micelles, can be practically neglected. By approximation we may consider the added hydrocarbon (expressed in the tables and in fig. 1 as a “concentration”) as being wholly taken up in the oleate micelles. But this means that the different location of the G and n curves in fig. 1 directly brings to expression specific differences in action between the successive terms of the homologous series of the n -alkanes.

The hypothesis of the total action being the resultant of two oppositely directed component actions may shed some light on the marked spreading of the curves in fig. 1. One must assume (see already part X, section 6) that the hydrocarbon molecules are taken up simultaneously by the oleate micelle at two essentially different places, and that dependent on the occupied place, the hydrocarbon molecules exert a KCl-sparing or a KCl-demanding action. Calling these places within the oleate micelle S -places and D -places, the marked spreading of the curves in fig. 1 may for the greater part be caused by a change in the distribution between S - and D -places of the alkane molecules which are taken up, this being a result of the lengthening of the carbon chain of the alkane.

In this line of thought a small length of the carbon chain is much in favour of occupying the S -places. The KCl-demanding component action therefore prevails at small concentrations of the alkane. At higher concentrations the S -places cannot take up much more alkane molecules and now the D -places become more and more occupied. This gives an explanation of the reverse in total action type ($A \rightarrow B \rightarrow C$) shown by pentane and hexane.

Alkanes with long hydrocarbon chains will on the contrary favour the D -places, that is at all concentrations the KCl-demanding component action is larger than the KCl-sparing component action; they only show the total action type C .

4. *Isomers of octane. Introduction of a double and of a triple bond in n -octane.*

In connection with the fact that these experiments (table III, fig. 3) have been performed at 1.05 N KCl, i.e. at the KCl concentration corresponding to the minimum damping of the blank, here the n curve of n -octane at once takes a course in a downward direction, whereas in

TABLE III. Influence of some octanes, of transoctene-4 and octyne-4 on the elastic behaviour of the 1.2 % oleate system at 1.05 N KCl and at 15°. Conc. = concentration of the hydrocarbon in millimoles/l; G = shear modulus in dyne/cm²; n = maximum number of observable oscillations through the telescope.

n-octane			trans-octene-4			octyne-4		
conc.	G	n	conc.	G	n	conc.	G	n
blank	47.8	75.8	blank	48.0	76.3	blank	47.8	76.0
2.89	46.0	68.7	2.09	48.0	69.5	2.44	49.1	62.4
4.54	42.8	59.7	4.19	45.8	61.6	3.90	51.3	54.4
6.18	39.1	41.6	5.86	44.2	50.7	6.82	49.5	49.5
7.42	34.2	29.5	7.54	39.5	35.8	9.75	46.9	59.7
8.25	30.0	16.2	9.22	34.3	23.5			
9.48	25.9	10.5	11.3	24.1	10.6			
11.5	—	2.0						

2,5-dimethylhexane			3,4-dimethylhexane			3-methyl-3-ethylpentane		
conc.	G	n	conc.	G	n	conc.	G	n
blank	47.9	76.3	blank	48.2	76.1	blank	47.4?	76.2
1.88	45.9	68.3	2.07	46.2	71.5	1.65	47.4	74.2
3.75	42.7	59.7	4.54	43.1	63.7	4.96	44.1	64.5
5.63	39.9	43.6	6.20	41.3	46.6	7.45	40.8	47.6
7.50	34.8	23.6	8.26	36.5	28.4	9.93	35.1	31.5

Mean values of the blanks $G_0 = 47.9$ $n = 76.1$

fig. 1 (experiments performed at 1.2 N KCl) the n curve at first mounts to a maximum before it definitely takes its course in a downward direction (compare the diagrams 8 and 9 in fig. 2).

It appears from fig. 3A that the four octanes which are investigated all follow the action type C , but that their actions are not identical. We will not comment upon this, but only mention that analogous differences in the influence on the displacement of the coacervation limit, do occur⁸).

A distinct influence results from the introduction of a double bond. In fig. 3B, the curves for trans-octene-4 show a course which indicates that at small concentrations type B is followed and at larger concentrations type C (a succession of the diagrams 5 and 8 in fig. 2).

The introduction of a triple bond in n -octane has a still larger effect. The course of the G and n curves for octyne-4 must be interpreted as a succession of the types $A \rightarrow B \rightarrow C$. In the scheme of fig. 2 we have the following succession of diagrams: $2 \rightarrow 3 \rightarrow 6 \rightarrow 9$.

The switching over from diagram $2 \rightarrow 3$ follows from the displacement of the G and n curves as a result of the type of action A . After

⁸) H. L. BOOIJ, J. C. LYCKLAMA and C. J. VOGELSANG, these Proceedings 53, 407–413 (1950).

this displacement the KCl concentration of 1.05 N is a KCl concentration higher than that corresponding to the minimum of the displaced curve.

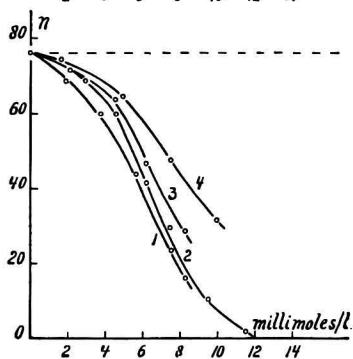
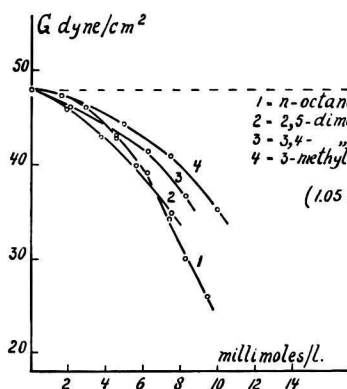


Fig. 3 A

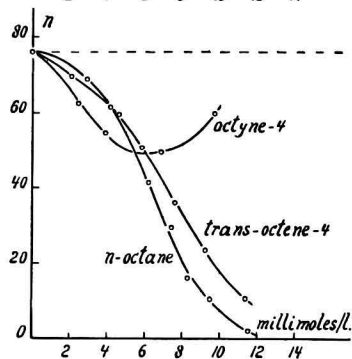
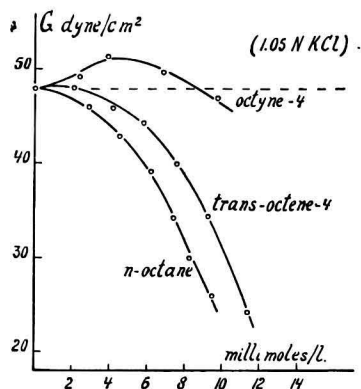


Fig. 3 B

From the point of view of the total action type being a resultant of component actions, we may conclude that the introduction of a double bond and still more that of a triple bond in an alkane, relatively enforces the KCl-sparing component action with regard to the KCl-demanding component action. An analogous conclusion was reached by BOOIJ and collaborators⁹⁾ in studying the shift of the coacervation limit.

5. Benzene, toluene, ethylbenzene, *n*-propylbenzene and the three xylenes.

The experiments have been performed at 1.2 N KCl (table IV, fig. 4) and at 0.6 N KCl (table V, fig. 5).

We will first discuss the results obtained with benzene, toluene, ethylbenzene and *n*-propylbenzene.

The results at 1.2 N KCl (fig. 4A) show that all four follow type A (compare diagram 3 in fig. 2). There is a distinct spreading of the curves. The concentration of the hydrocarbon which is needed to give a same

⁹⁾ H. L. BOOIJ, J. C. LYCKLAMA and C. J. VOGELSANG, these Proceedings 53, 407—413 (1950).

TABLE IV. Influence of some aromatic hydrocarbons on the elastic behaviour of the 1.2 % oleate system at 1.20 N KCl and at 15°. Conc. = concentration of the hydrocarbon in millimoles/l; G = shear modulus in dyne/cm²; n = maximum of observable oscillations though the telescope.

benzene			toluene			ethylbenzene			<i>n</i> -propylbenzene		
conc.	G	n	conc.	G	n	conc.	G	n	conc.	G	n
blank	47.5	67.2	blank	48.0	67.3	blank	47.8	67.4	blank	47.9	67.2
2.35	51.0	53.6	1.95	51.5	50.0	1.17	51.3	60.3	1.04	51.7	53.3
3.92	54.3	48.3	3.25	57.9	33.6	2.34	56.2	40.4	2.08	56.7	34.2
6.27	61.2	33.1	3.90	61.3	28.3	2.92	59.7	33.8	2.60	59.7	24.2
7.84	63.7	23.5	4.55	63.2	23.0	3.50	60.5	24.7	3.13	62.6	19.7
9.4	65.5	13.7	5.20	64.4	16.2	4.10	61.0	16.7	3.65	—	11.2
11.0	—	5.8	6.5	—	6.8	5.26	—	7.0	4.17	—	5.7

<i>o</i> -xylene			<i>m</i> -xylene			<i>p</i> -xylene		
conc.	G	n	conc.	G	n	conc.	G	n
blank	47.6	67.4	blank	47.7	67.4	blank	47.5	67.3
1.82	54.1	48.3	1.74	54.3	48.3	1.74	54.5	48.1
3.04	62.9	25.9	2.90	58.6	30.6	2.90	57.1	31.2
3.64	67.0	19.7	3.48	61.2	21.4	3.48	60.2	21.6
4.25	—	10.0	4.06	—	13.2	4.06	—	14.3
4.86	—	5.5	4.64	—	6.3	4.64	—	6.8
5.46	—	coac.	5.22	—	1.0	5.22	—	3.0

Mean values of the blanks $G_0 = 47.7$ $n_0 = 67.3$

increase of G , or a same decrease in n , diminishes in the order: benzene > toluene > ethylbenzene > *n*-propylbenzene.

The results at 0.6 N KCl (fig. 5A) show that all four hydrocarbons begin to follow type *A* (compare diagram 1 of fig. 2). At increasing hydrocarbon concentration, however, a transition in the type of action occurs because G passes a maximum and further on decreases. It seems probable that we have a succession of the diagrams 1 → 5 → 8 or 1 → 5 → 9 of fig. 2 here, which means that at increasing hydrocarbon concentration the type of action changes from *A* → *B* → *C*. Just as at 1.2 N KCl, here too we perceive the sequence: benzene > toluene > ethylbenzene > propylbenzene at small concentrations. The relative positions of the G and n curves of benzene and toluene do not allow to conclude for which of the two hydrocarbons the transition *A* → *B* → *C* occurs earlier. However, it is clear that this transition occurs at smaller and smaller concentrations in the sequence: toluene > ethylbenzene > *n*-propylbenzene.

We could now proceed to discuss the results from the point of view that the total action is the resultant of a KCl-sparing and a KCl-demanding component action. But this would only be an analogous repetition of the discussions in section 4 for the *n*-alkanes. We therefore give at once, in the survey below, the results to which this discussion leads.

KCl concentration	hydrocarbon concentration	benzene	toluene	ethylbenzene	n-propylbenzene
0.6 N	small ↓ increasingly larger	$D < S$	$D < S$	$D < S$	$D < S$
		$D < S$	$D < S$	$D < S$	$D = S$
		$D < S$	$D < S$	$D = S$	$D > S$
		$D = S$	$D = S$	$D > S$	$D > S$
		$D > S$	$D > S$	$D > S$	$D > S$
1.2 N	at all concentrations investigated . . .	$D < S$	$D < S$	$D < S$	$D < S$

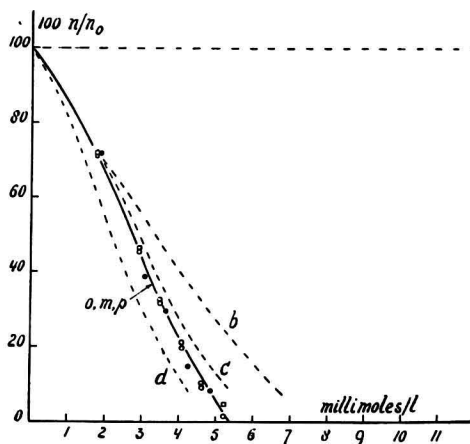
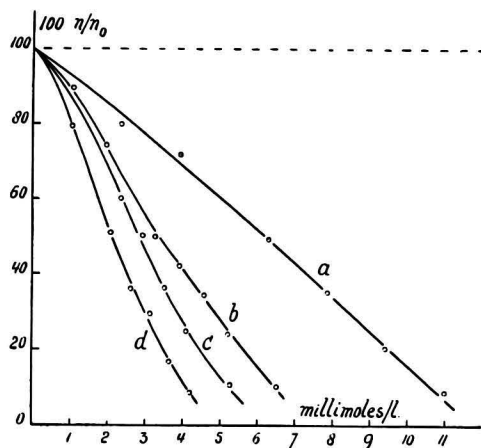
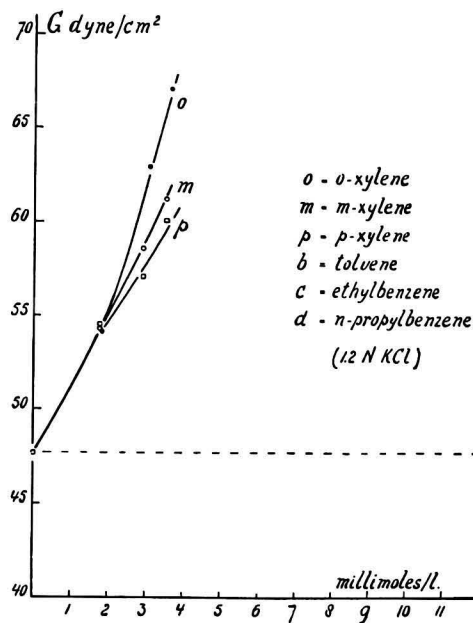
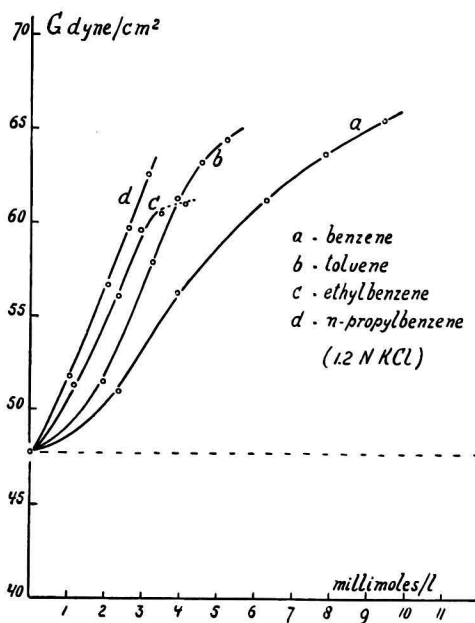


Fig. 4 A

Fig. 4 B

TABLE V. Influence of some aromatic hydrocarbons on the elastic behaviour of the 1.2 % oleate system at 0.6 N KCl and at 15°. Conc. = concentration of the hydrocarbon in millimoles/l; G = shear modulus in dyne/cm²; n = maximum number of observable oscillations though the telescope.

benzene			toluene			ethylbenzene			<i>n</i> -propylbenzene		
conc.	G	n	conc.	G	n	conc.	G	n	conc.	G	n
blank	31.3	22.1	blank	31.5	21.9	blank	31.3	22.1	blank	31.2	21.8
1.57	33.3	25.6	0.65	32.7	26.0	0.59	32.5	25.4	0.52	32.3	25.3
3.92	34.8	31.6	1.95	33.9	29.4	1.75	34.4	30.9	1.56	33.6	29.1
10.2	38.6	46.2	6.5	38.9	45.2	5.26	36.9	36.3	4.17	33.9	28.1
13.3	40.9	53.8	8.4	40.2	47.6	6.4	36.5	37.5	4.7	32.7	25.8
17.2	40.9?	53.8	11.0	40.3	50.6	7.6	36.2	38.3	6.3	31.7	21.6
23.5	45.6	50.0	16.2	41.1	49.2	11.7	34.6	30.7	8.9	26.7	15.3
35.3	30.3	7.9	26.0	38.8	47.1	15.8	32.0	26.1	11.5	19.3	8.3
39.2	—	5.0	39.0	11.9	6.9	21.6	18.2	10.6	15.6	—	1.0

<i>o</i> -xylene			<i>m</i> -xylene			<i>p</i> -xylene		
conc.	G	n	conc.	G	n	conc.	G	n
blank	31.3	22.0	blank	31.1	21.8	blank	30.9	21.8
0.61	31.9	25.8	0.58	32.6	25.6	0.58	32.8	26.2
1.82	34.2	30.3	1.74	34.2	29.8	1.74	34.2	29.6
5.46	38.8	47.3	5.22	38.5	43.8	5.22	37.8	43.2
6.7	38.5	47.6	6.4	37.7	44.3	6.4	37.8	43.7
7.9	38.1	43.8	7.5	37.4	41.5	7.5	37.7	40.3
12.1	38.7	42.2	11.6	37.8	39.7	11.6	38.5	40.2
18.2	33.9	34.2	17.4	32.2	30.6	17.4	34.2	32.4
27.3	—	6.5	26.1	13.5	6.4	26.1	19.3	9.9

Mean values of the blanks $G_0 = 31.2$ $n_0 = 21.9$

By comparing this survey with the analogous one in section 3 for the homologous series of the alkanes we perceive that here too the same three variables work in exactly the same direction as with the *n*-alkanes, viz. *D* is relatively favoured to *S* by:

1. increase of the hydrocarbon concentration,
2. increase of the length of the carbon chain,¹⁰⁾
3. lowering of the KCl concentration.

Though on first acquaintance with the action of hydrocarbons on the elastic behaviour in part VII, the results seemed to indicate an essential difference between aliphatic and aromatic hydrocarbons (at the KCl concentration of minimum damping of the blank: heptane follows type *C*, benzene and toluene follow type *A*), this first impression was erroneous. From the results of the present investigation we cannot but conclude that there is only a gradual difference between aliphatic and aromatic hydrocarbons.

¹⁰⁾ See also H. L. BOOIJ, C. J. VOGELSAMG and J. C. LYCKLAMA, these Proceedings 53, 882 (1950).

The results with the three xylenes (fig. 4B and fig. 5B) show that an alteration in the relative position of the two methyl groups does not bring about a large difference in action.

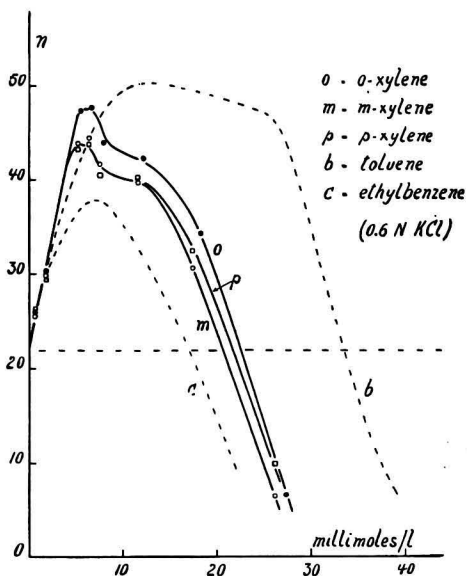
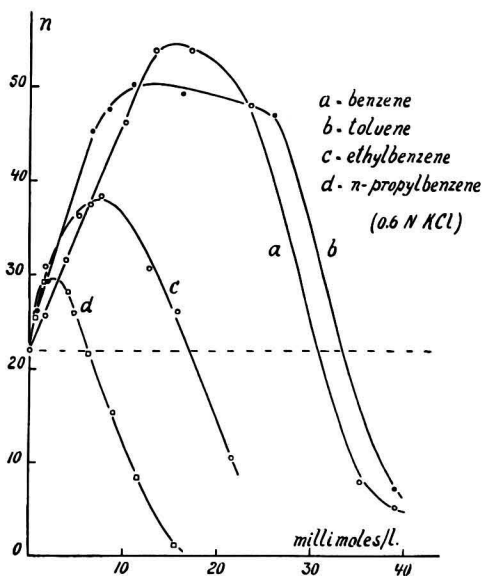
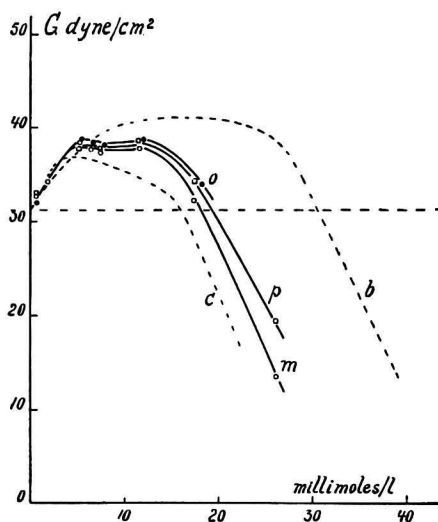
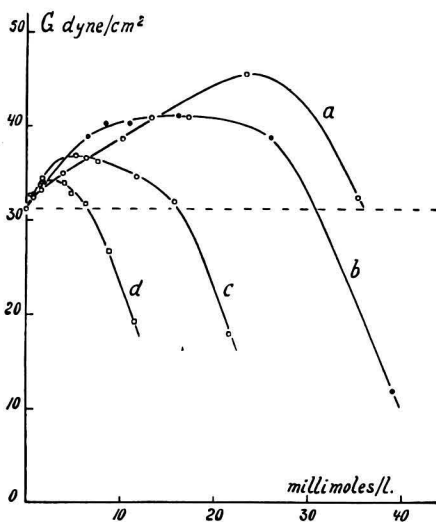


Fig. 5 A

Fig. 5 B

Summary.

1. An investigation has been made about the influence on the elastic behaviour of the 1.2% oleate system by a number of hydrocarbons (*n*-pentane up to and including *n*-undecane, four isomers of octane, trans octene-4, octyne-4, benzene, toluene, ethylbenzene, *n*-propylbenzene and the three xylenes).

2. The type of action shown by *n*-alkanes and *n*-alkylbenzenes depends on:
 1. the length of the carbon chain (or: of the side chain),
 2. the concentration of the hydrocarbon,
 3. the KCl concentration.
3. The results, discussed from the point of view that the total action type is the resultant of a KCl-sparing and a KCl-demanding component action, allow to conclude that there is no essential but only a gradual difference between the action of aliphatic and aromatic hydrocarbons.
4. The KCl-demanding component action is relatively enforced with regard to the KCl-sparing component action by:
 1. increase of the hydrocarbon concentration,
 2. increase of the length of the carbon (side) chain,
 3. lowering of the KCl concentration.
5. Introduction of a double bond, and still more that of a triple bond in *n*-octane relatively enforces the KCl-sparing component action with regard to the KCl-demanding one.
6. The four isomers of octane which are investigated show actions which differ quantitatively. Though differences between the three xylenes are also present, they are here but relatively small.

*Department of Medical Chemistry,
University of Leiden.*