CHEMISTRY

ELASTIC VISCOUS OLEATE SYSTEMS CONTAINING KCl. XII [1])

1) *Influence of the terms of the homologous series of the alkylbenzenes on the elastic behaviour of the 1.2 % oleate system*
2) *Complications in the use of $G - n$ diagrams for the discussion of the results obtained with the terms of homologous series of alkanes and of alkylbenzenes*

BY

H. G. BUNGENBERG DE JONG, W. A. LOEVEN AND H. J. VERHAGEN * [2])

1. *Introduction.*

In part XI of this series the influence of a number of hydrocarbons (e.g. alkanes, benzene and alkylbenzenes) on the elastic behaviour of the KCl containing oleate system has been investigated.

The results have been discussed from the point of view that the total action is the resultant of two oppositely directed component actions, a KCl-demanding one (D) and a KCl-sparing one (S). We found that D is relatively enforced with regard to S by:

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

For the action of the first hydrocarbon additions there are accordingly two possibilities: a KCl-sparing total action $(D < S)$ and a KCl-demanding total action $(D > S)$.

In the homologous series of the n-alkanes these two possibilities do occur (at 1.2 N KCl pentane and hexane exert a KCl-sparing total action, heptane and the higher homologues exert a KCl-demanding total action). The few terms of the homologous series of the n-alkylbenzenes which had been investigated, (toluene, ethylbenzene, n-propylbenzene) all exerted a KCl-sparing total action at the first additions (even at 0.6 N KCl, which normality according to the above point 3, is favourable for a preponderance of D above S).

The occurrence of a KCl-demanding total action $(D \rangle S)$ of an alkyl-benzene at the first additions, must be expected if the carbon side chain is sufficiently lengthened (see the above point 2). The present communication deals with the action of the terms, ethylbenzene up to and including n-heptylbenzene [3]), at three different KCl concentrations, with the aim to control that the above three points also hold for the higher homologues and to investigate if there exist terms which, at the first addition, exert a KCl-demanding total action.

Besides the present communication deals with $G - n$ diagrams for the plotting of the results obtained with the homologous series of the n-alkanes and the n-alkylbenzenes. These kind of diagrams proved useful at the discussion of the results obtained with the homologous series of the n-primary alcohols (part VIII) and the n-fatty acid anions (part IX), but in the case of the n-alkanes they will appear to lead to quite erroneous conclusions. The aim of the further experiments will be to explain this failure of the method of $G - n$ diagrams.

2. *Influence of ethylbenzene up to and including n-heptylbenzene at three KCl concentrations.*

The experiments with the above-mentioned alkylbenzenes were performed in quite the same way (rotational oscillation, 15°, exactly half filled spheres of approximately 500 ml capacity, H_2 marking) as is described in detail in part XI of this series. The mixture of the contents of five flasks of Na-oleate from BAKER [4]) which was used for the experiments showed a minimum damping at 1.08 N KCl. The experiments were therefore performed at this KCl concentration and at a concentration lower (0.6 N) and higher (1.5 N) than 1.08 N. The three elastic systems were made from the same stock oleate solution and were investigated simultaneously to make the results as much comparable as possible (thus 18 vessels were used at the same time, 6 for the system at 0.6 N, 6 for the system at 1.08 N and 6 for the system at 1.5 N).

The obtained results have been represented in the figures 1, 2 and 3. For some unknown reason the experimental errors are larger than usual. Compare the somewhat irregular position of the experimentally determined points. This is for instance very pronounced with the n curves at 0.6 N KCl for ethylbenzene and n-propylbenzene. Here the experimentally determined points suggest the presence of an additional minimum in the n curves. As nothing of this kind had been found for ethylbenzene and n-propylbenzene at 0.6 N in the experiments described in part XI of this series, we believe that the irregular position is only due to experi-

mental errors. For this reason the n curves for ethylbenzene and n-propyl-benzene have been drawn as simple as possible in fig. 1. The position of the G point in fig. 2 for the highest n-propylbenzene concentration, which would suggest an intersection of the curves for n-propylbenzene and n-butylbenzene is also to be mistrusted, because here, the large damping necessitated a relative large and therefore uncertain correction of the period.

The results of the experiments could first be discussed on the same lines (using the expressions: "actions according to type A, type B or type C") as are given in detail for the series of the n-alkanes in part XI (section 2) of this series, but we will at once switch over to a discussion
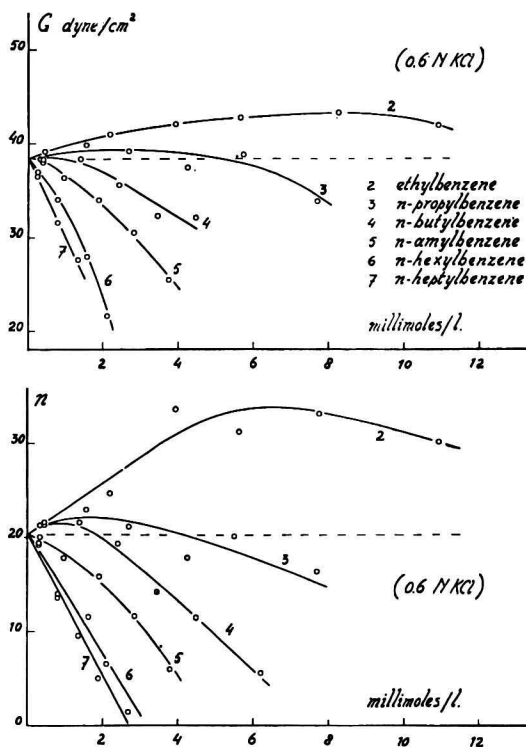

Fig. 1

from the point of view that the total action is the resultant of a KCl-sparing component action (S) and a KCl-demanding component action (D).

From this point of view type A means $D < S$ and type C means $D > S$, whereas type B means exact compensation of the two component actions (thus $D = S$). It has already been discussed in part X (section 6) that it is extremely unlikely that type B will be realized at a whole range of concentrations of the added substance and at a whole range of KCl concentrations.

When we now consider in fig. 1 the influence of the first amounts which were added, we perceive that both G and n increase with ethylbenzene

and n-propylbenzene and both decrease with n-amylbenzene, n-hexylbenzene and n-heptylbenzene.

At the KCl concentration which is used (0.6 N), a concentration lower than that corresponding to the minimum damping of the blank, this means that for ethylbenzene and n-propylbenzene $D < S$, whereas for n-amylbenzene, n-hexylbenzene and n-heptylbenzene it means either $D = S$ or $D > S$. But already n-butylbenzene shows an action (at the first additions G is not increased) which forbids the conclusion $D < S$. Therefore here too we must conclude $D = S$ or $D > S$.

From the distinct spreading of the curves for n-butylbenzene, n-amylbenzene, n-hexylbenzene and n-heptylbenzene we must on the other hand conclude that they can't all four correspond to $D = S$. Therefore we come to the conclusion that it can only be n-butylbenzene which approximately corresponds to $D = S$, whereas for the higher homologues we have $D > S$.

Our expectation (see Introduction) that for the first additions of an alkylbenzene D will preponderate at last over S when the carbon side chain is sufficiently lenghtened, is therefore confirmed by the experiment.

If we take into consideration that in fig. 1 the G curve of n-butylbenzene goes into a downward direction at further additions, we must conclude (in accordance with point 1 of the Introduction) that the approximate compensation of the two component actions $(D = S)$ gives place to a preponderance of the KCl-demanding component action (thus $D = S \rightarrow D > S$).

This relative enforcement of the D component is also present with ethylbenzene and n-propylbenzene, and is indicated by the downward direction of the G curves after the passing of a maximum (in part XI the course of the G curves for these two terms could be followed much further than here; distinct maxima were obtained for both terms, as well as for toluene). We therefore find an illustration of point 1 of the Introduction, and we must conclude that at 0.6 N KCl and at a sufficient hydrocarbon concentration all terms of the n-alkylbenzenes will show a total KCl-demanding action (thus $D > S$).

The next survey summarizes the above discussions:

KCL conc.	hydrocarbon conc.	toluene	ethyl-benzene	n-propyl-benzene	n-butyl-benzene	n-amyl-benzene	n-hexyl-benzene	n-heptyl-benzene
0.6 N	small ↓ increasingly larger	$D < S$	$D < S$	$D < S$	$\mathbf{D = S}$	$D > S$	$D > S$	$D > S$
		$D < S$	$D < S$	$\mathbf{D = S}$	$D > S$	$D > S$	$D > S$	$D > S$
		$D < S$	$\mathbf{D = S}$	$D > S$	$D > S$	$D > S$	$D > S$	$D > S$
		$\mathbf{D = S}$	$D > S$	$D > S$	$D > S$	$D > S$	$D > S$	$D > S$
		$D > S$	$D > S$	$D > S$	$D > S$	$D > S$	$D > S$	$D > S$

We now turn to the results obtained at 1.08 N KCl (see fig. 2). At the first addition of all the investigated alkylbenzenes the G curves go into

an upward direction and the n curves into a downward direction. As 1.08 N KCl represents the KCl concentration of minimum damping of the blank, this means that for all terms of the homologous series is valid: $D < S$.

Apart from ethylbenzene (and possibly n-propylbenzene) the G curves attain a maximum after which they go into a downward direction. This means (compare the diagrams of fig. 2 in part XI) that with increasing hydrocarbon concentration a transition in the type of action $(A \to B \to C)$ or in the new manner of expression, a transition from $D < S$ to $D > S$ occurs. In connection with the relative position of the G curves in fig. 2 we conclude that the transition $(D = S)$ takes place at lower hydrocarbon concentrations when the length of the aliphatic carbon chain is increased. A discussion of the relative position of the n curves in fig. 2 leads to the same conclusion. Whereas at low hydrocarbon concentrations n always decreases, we find at higher concentrations a tendency of the n curves to take a horizontal or even an upward course (the latter for instance with n-amylbenzene).

This change of direction is accompanied by a reversal in the succession of the n curves.

At small hydrocarbon concentrations the curve for ethylbenzene lies at the top, followed by n-propylbenzene and further downwards by the curves of the following hydrocarbons (crowded together). But after the change in direction the curve for n-hexylbenzene is the top one and the curve for ethylbenzene (not showing a change in direction) is the undermost. It is obvious that the concentrations of the hydrocarbons at which the change in direction takes place will be lower when the carbon side chain is longer. These regularities can be explained by a transition of $D < S$ to $D > S$ (a succession of the diagrams 2, 3, 6 and 9 in fig. 2 of part XI). We must expect here that the n curve after attaining a minimum goes upwards to a maximum and thereafter definitively goes into a downward direction. This whole succession is realised with heptylbenzene, though here the maximum is only indicated by the S shape of the curve. For the other terms there are not enough experimentally determined points to show the maximum and the following downward course of the n curves.

The next survey (in which we also incorporate toluene, which is investigated in part XI) summarizes the above discussions:

KCl conc.	hydrocarbon conc.	toluene	ethyl-benzene	n-propyl-benzene	n-butyl-benzene	n-amyl-benzene	n-hexyl-benzene	n-heptyl-benzene
	small	$D < S$	$D < S$	$D < S$	$D < S$	$D < S$	$D < S$	$D < S$
1.08 N		$D < S$	$D < S$	$D < S$	$D < S$	$D < S$	$D < S$	$\mathbf{D = S}$
		$D < S$	$D < S$	$D < S$	$D < S$	$D < S$	$\mathbf{D = S}$	$D > S$
		$D < S$	$D < S$	$D < S$	$D < S$	$\mathbf{D = S}$	$D > S$	$D > S$
	increasingly larger	$D < S$	$D < S$	$D < S$	$\mathbf{D = S}$	$D > S$	$D > S$	$D > S$

If we compare this survey with the preceding one, valid for 0.6 N KCl, we perceive the same general character. Only the oblique bar formed by the symbols $D = S$ is displaced considerably to the right, which is in accordance with point 3 mentioned in the Introduction.

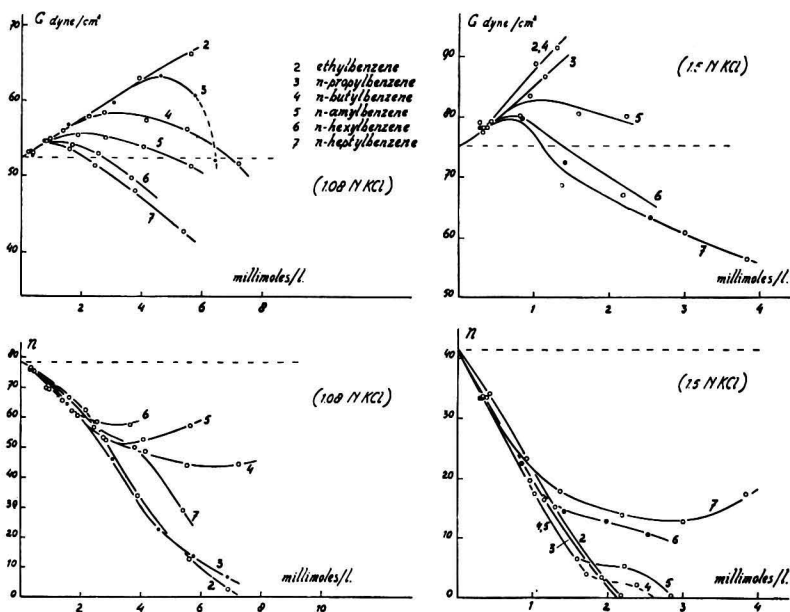The results obtained at 1.5 N KCl (compare fig. 3) show a great simil-

Fig. 2—3

arity [5]) with those obtained at 1.08 N (see fig. 2) and therefore we will not repeat the analogous reasonings (in this case we have to consider the diagrams 3, 6 and 9 in fig. 2 of part XI).

We conclude that at 1.5 N KCl all alkylbenzenes which are investigated exert a KCl-sparing total action at the first additions (thus $D < S$), and that at increase of the hydrocarbon concentration a transition into a KCl-demanding total action (thus $D > S$) occurs for n-amylbenzene, n-hexylbenzene and n-heptylbenzene. From the deflecting to the right of the n curve for n-butylbenzene one may not conclude to this transition because of reasons still to be mentioned in section 5.

We have the impression that at 1.5 N KCl the transition from $D < S$ into $D > S$ is somewhat more difficult than at 1.08 N KCl (deflection of the n curves to the right takes place at proportionally smaller values of n than at 1.08 N KCl). The results at 1.5 N KCl may therefore be represented schematically by the following survey:

---

[5]) A difference is that the G curve for n-butylbenzene is situated at the left of the G curve for n-propylbenzene, but this may be the result of an experimental error. The sequence of the corresponding n curves (before butylbenzene deflects to the right) is quite normal.

KCl conc.	hydrocarbon conc.	toluene	ethyl-benzene	n-propyl-benzene	n-butyl-benzene	n-amyl-benzene	n-hexyl-benzene	n-heptyl-benzene
	small	$D < S$	$D < S$	$D < S$	$D < S$	$D < S$	$D < S$	$D < S$
	$\downarrow$	$D < S$	$D < S$	$D < S$	$D < S$	$D < S$	$D < S$	$D < S$
1.5 N		$D < S$	$D < S$	$D < S$	$D < S$	$D < S$	$D < S$	**$D = S$**
		$D < S$	$D < S$	$D < S$	$D < S$	$D < S$	**$D = S$**	$D > S$
	increasingly larger	$D < S$	$D < S$	$D < S$	$D < S$	**$D = S$**	$D > S$	$D > S$

Comparing the three above surveys (at 0.6 N, 1.08 N and 1.5 N KCl), we may state that the results laid down in this section strongly support the hypothesis that the total action is the resultant of two component actions (D and S), and that they confirm the three factors mentioned in the Introduction which relatively enforce D with regard to S.

3. The displacement of the maximum of the n-C_{KCl} curve by added alkylbenzenes.

The n graphs of the figs 1, 2 and 3 allow to read for the blank or for a given concentration of added hydrocarbons the values of n at 0.6 N, 1.08 N and 1.5 N KCl. Therefore three points of the corresponding n-C_{KCl} curve are known. Though this is not enough to draw this n-C_{KCl} curve with certainty, it nevertheless suffices to sketch its position approximately. This has been done in fig. 4 for a number of hydrocarbon concentrations (the numbers added to the individual curves give the hydrocarbon concentration in millimoles/l) [6]). Through the maxima of the n-C_{KCl} curves dotted curves have been drawn which therefore represent the displacement of the maxima by the added hydrocarbons. The latter curves have been united in fig. 5A, from which their relative position can be discerned.

In this figure the curve representing the displacement of the maximum by benzene (calculated from the data represented in fig. 2 of part X), is also drawn [7]).

---

[6]) The blank curves in fig. 4 have been arbitrary sketched in the following way (using the mean values of n at 0.6, 1.08 and 1.5 N KCl): a straight line was drawn through $n = 20.3$ at 0.6 N KCl and $n = 0$ at 0.47 N KCl; similarly one through $n = 41.5$ at 1.5 N KCl and $n = 0$ at 1.77 N KCl. The two straight lines were united at the top by a curve through $n = 78.4$ at 1.08 N KCl. The remaining curves were constructed in a similar way by drawing straight lines through the values of n (read from the graphs of the fig. 1, 2 and 3), parallel to the corresponding ones of the blank, and uniting them at the top by a curve.

[7]) From fig. 2 in part X we read for the positions of the maxima of the n curves expressed in N KCl the values 1.10; 1.04; 0.82; 0.70 and 0.55, whereas the values of n at these maxima amounted to 61, 58, 54, 47,5 and 34. The maximum of the blank n curve and the value of n at this maximum were 1.08 N KCl and 78.4 respectively, in the present experiments. For the plotting of the curve for benzene in fig. 5 A, we have therefore multiplicated the above mentioned values of the KCl concentrations by 1.08/1.10 and those of the n values by 78.4/61.

As the concentrations of the added hydrocarbons are no independent variables in this figure, the relative positions of the curves represent specific differences in action between the individual hydrocarbons. In
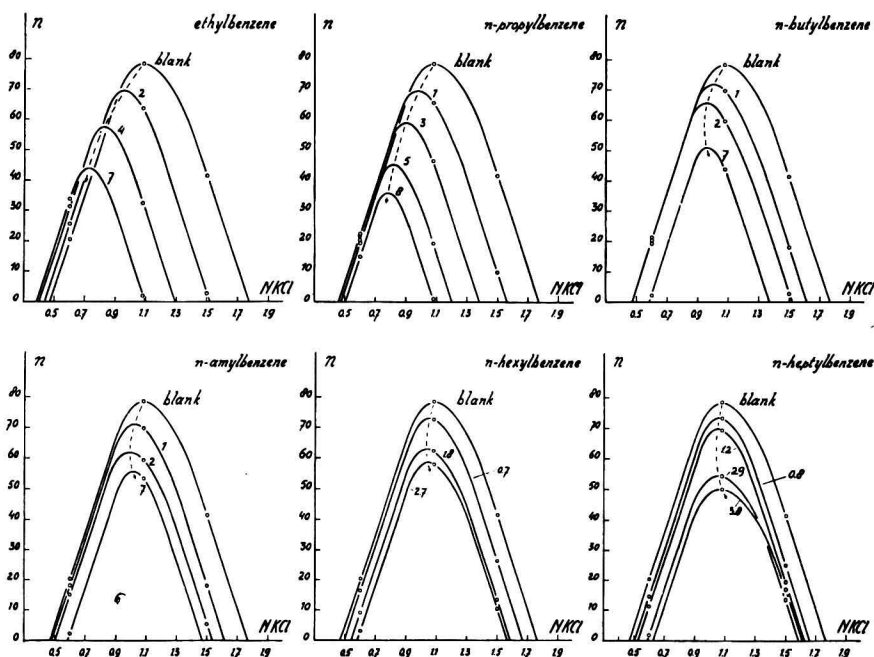

Fig. 4

the sequence from left to right we easily recognize point 2 of the Introduction: increase of the length of the carbon side chain relatively enforces the KCl-demanding component action (D) with regard to the KCl-sparing component action (S).

Point 1 of the Introduction finds its expression in the bent character of each of the curves (D is relatively enforced with regard to S by increase of the hydrocarbon concentration), though point 3 of the Introduction also steps in here. This factor (lowering of the KCl concentration relatively enforces D with regard to S), will hardly play a part in the shape of the curves for n-amylbenzene, n-hexylbenzene and n-heptylbenzene, for these substances do not bring about considerable shifts either to smaller or to larger KCl concentrations.

When the carbon side chain is shortened, this factor becomes more and more of importance. This may explain why the curvature of the curves is greatest for benzene (no side chain) and diminishes with increasing length of the side chain.

In fig. 5B we have plotted the positions of the maxima of the n curves (expressed in N KCl) as functions of the concentration of the alkylbenzenes. The sequence of the terms of the homologous series is quite the same as in fig. 5A. This is to be expected because in the KCl-water

medium the considered alkylbenzenes are practically insoluble. For in this case the specific differences in action of the successive terms must also express themselves in the succession of the curves (compare part
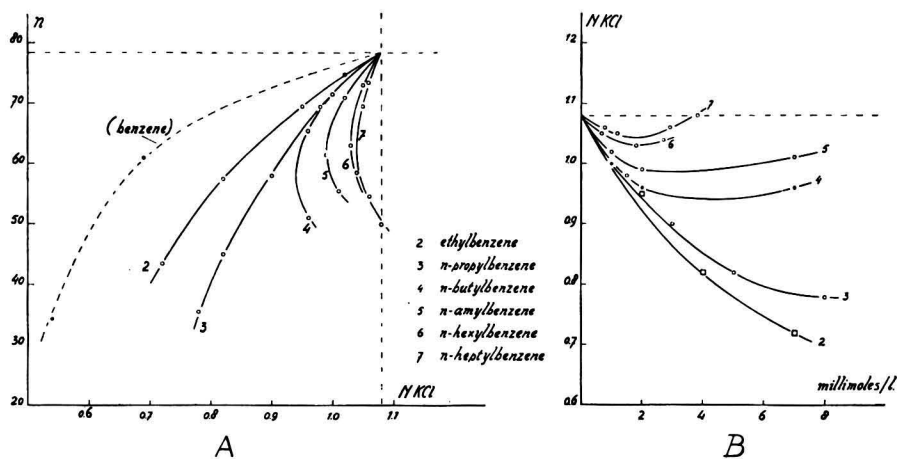

Fig. 5

VIII, section 3). As benzene, however, is already slightly soluble, this may no longer hold for this substance. Indeed if we had designed, in fig. 5*B*, the curve for benzene, it would not lie entirely to the left of the other curves, but would cross them.

4. *The results obtained with the homologous series of the n-alkylbenzenes and the n-alkanes represented in* $G - n$ *diagrams.*

In the parts VIII and IX of this series we have introduced $G-1/\varLambda, G-\lambda$ and $G-n$ diagrams for the discussion of the results obtained (at constant KCl concentration) with the homologous series of the *n*-primary alcohols and of the fatty acid anions. Supposing that the premises in which this method is based are realised (or approximately realised) one can draw conclusions as to specific differences in action exerted by the molecules bound to the oleate micelles of the successive terms of the homologous series from the sequence of the curves in such diagrams. This method only has its right of existence when the substances are markedly soluble in the KCl-water medium in which the oleate micelles are suspended. For in this case (e.g. the *n*-primary alcohols $C_1 - C_6$; the fatty acid anions $C_7 - C_{11}$) one cannot draw conclusions as to the above-mentioned specific differences from the sequence of the curves representing G or n as functions of the concentrations of the added substances [8]).

In the case of the hydrocarbons we may generally neglect their solu-

---

[8]) This sequence is mainly the expression here of the distribution equilibrium between the molecules being present free in the medium and the molecules taken up by the oleate micelles, which changes considerable from term to term. Compare parts VIII and IX.

bility in the KCl-water medium [9]) and therefore there is no real need to discuss the results with the aid of $G - n$ diagrams. The latter can in principle give no other information here than the graphs representing G or n as functions of the hydrocarbon concentrations already give. Nevertheless we have represented in this way in fig. 6 the results obtained with the alkylbenzenes at 1.08 N KCl (minimum damping of the blank). Starting from the point representing the blank ($G = 52.4$; $n = 78.4$), all curves first proceed upwards to the left, that is to say they exert a KCl-sparing total action ("Type A", compare diagram 2 given in part IX fig. 1). Apart from ethylbenzene, they are bending downwards, that is to say, at increase of the carbon side chain $D < S$ makes place for $D > S$, and this happens so much the sooner when carbon chain is longer.

The shape and the relative position of the curves in the $G - n$ diagram for the n-alkylbenzenes is therefore in the general as we would expect. We will return to this at the end of this section.

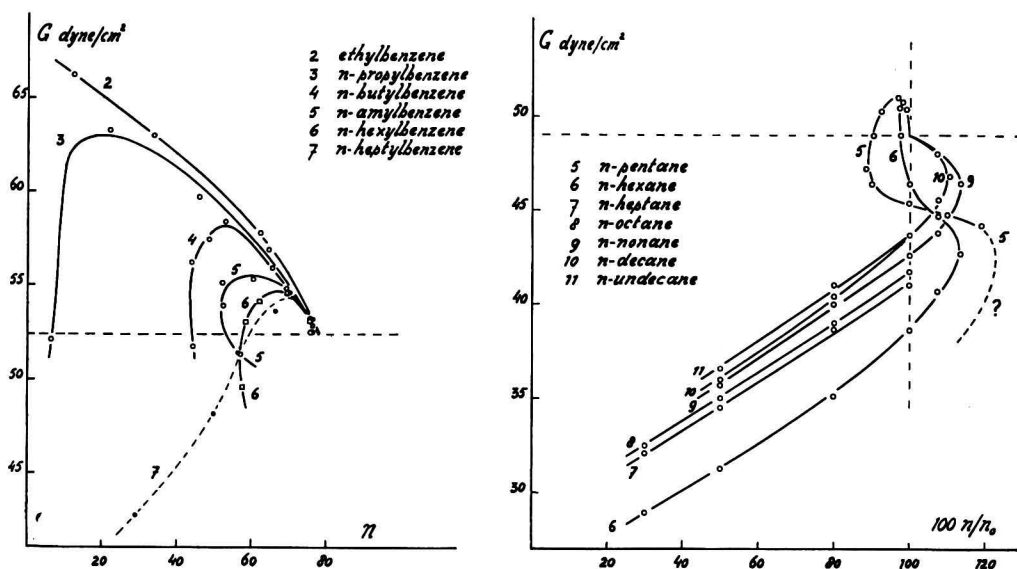In sharp contrast to this stands the $G - n$ diagram of fig. 7, in which

Fig. 6—7

we have plotted the results obtained in part XI (data of tables I and II) with the n-alkanes [10]). We have no objection to the shape of the curves in fig. 7 for each of the alkanes apart. As these experiments have been performed at 1.2 N KCl (KCl $>$ KCl min. damping) we have to consider

[9]) Except the slight solubility of benzene; compare H. L. BOOIJ, these Proceedings **53**, 882 (1950).

[10]) The points on the curves of fig. 7 are not the experimentally determined points themselves, but they represent G values corresponding to a number of arbitrary chosen values of 100 n/n_0 (using the G and n graphs represented in fig. 1 of part XI).

the diagrams 3, 6 and 9 in fig. 2 of part XI. The first additions of pentane and hexane show $D < S$, which at higher concentrations changes into $D > S$. The S shape of the $G - n$ curves for pentane and hexane in fig. 7 is in accordance with this (the shape of the curves can be considered as a succession of the initial courses of the $G - n$ curves which are represented in the diagrams 3, 6 and 9 of the above-mentioned figure in part XI).

The shape of the $G - n$ curves for the higher alkanes in fig. 7 (in order not to overcrowd the figure, we have only drawn the complete course for nonane and decane) is in accordance with diagram 9 of the above-mentioned fig. 2 in part XI, because the higher alkanes at once show $D > S$.

Therefore when the shape of the $G - n$ curves for each of the terms of the n-alkanes is considered apart, they are quite as one would expect. But, what is most remarkable, the succession of the curves in the bundle proceeding downwards to the left is in sharp contradiction with our expectations. In this bundle the curve for undecane is the top one and that for hexane (or probably pentane) is the undermost. One would therefore conclude from this succession that the preponderance of D over S is greatest with hexane (pentane) and least with undecane (thus undecane would stand nearest to a substance showing $D = S$). But this conclusion is quite erroneous. The total KCl-demanding action is just greatest with undecane and decreases with the shortening of the carbon chain (see part XI).

The method of the $G - n$ diagrams, which was useful in the case of the n-primary alcohols (part VIII) and of the fatty acid anions (part IX) and does not lead to conclusions which are in principle erroneous in the case of the n-alkylbenzenes, utterly fails in the case of the n-alkanes.

To shed some light on the question why this method fails here, we have investigated the influence of increasing concentrations of n-undecane on the curves which represent G and n as functions of the KCl concentration (using just as in part X the simplified method of half filled 110 ml vessels). The results have been represented in fig. 8, which confirms that n-undecane exerts a powerful KCl-demanding action (the G and n curves are shifted into the direction of higher KCl concentrations). The compound nature of the total action is still visible in the displacement of the right footpoint of the n curve. The first addition (1.13 millimoles/l) shifts this footpoint to the left (thus $D < S$) and at higher concentrations (2.26 millimoles/l and higher) brings about shifts to the right (thus $D < S \to D = S \to D > S$).

The maximum and the left footpoint of the n curve, however, is already shifted to the right at the first addition (thus $D > S$), in accordance with point 3 mentioned in the Introduction. We further perceive that the course which is followed by the maximum of the n curve, when this curve is shifted to the right at increasing concentrations of n-undecane, is a curve with a minimum.

Thus the ratio of the vertical and horizontal components of the displacement of the maximum of the n curve does not remain approximately constant at all but even changes its sign at increase of the n-undecane
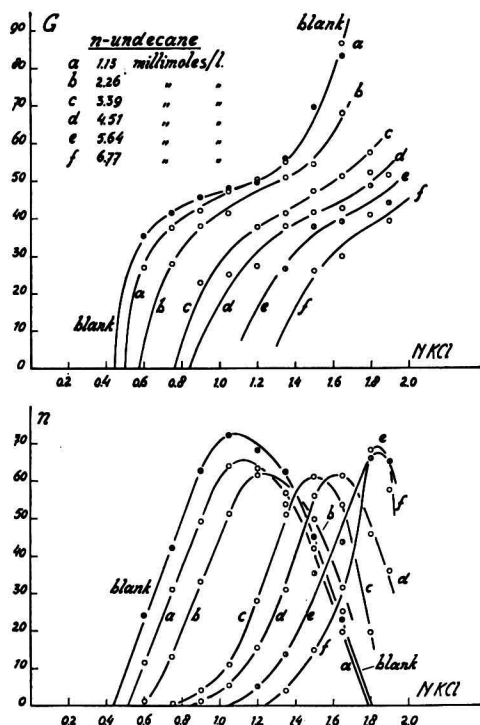

Fig. 8

concentration. Compare the next survey which gives the KCl concentrations corresponding to the maxima of the n curves, the values of n and of G at these maxima.

Conc. n-undecane millimoles/l	blank	1.13	2.26	3.39	4.51	5.64	6.77
KCl conc. moles/l corresp. to max. of the n curves	1.08	1.14	1.23	1.50	1.62	1.83?	1.83?
n at the max. of the n curves .	72	65.5	61.5	61	61.5	67	68,5
G at the max. of the n curves .	48.5	48.5	48	47	44	43	39?

We further observe that the values of G, corresponding to the maxima of the n curves do not remain constant, but decrease at increase of the n-undecane concentration.

However, the method of using $G - n$ diagrams for the discussion of the results with the successive terms of a homologous series, resides on the assumptions that the above-mentioned ratio remains constant and that the value of G on the shifted G curves which correspond to the maxima of the shifted n curves retains its original value.

It therefore seems likely that the failure of the method of $G - n$ diagrams when applied to the homologous series of the n-alkanes [11]) resides in the large deviations from the above assumptions.

We now return to the $G - n$ diagram for the alkylbenzenes which is given in fig. 6. One may wonder why in this diagram the succession of the curves is as one would expect. For, the above-mentioned ratio is not constant in the case of the n-alkylbenzenes too (compare the bent character of the curves in fig. 5A.

To this we must remark that the erroneous succession of the $G - n$ curves of the n-alkanes only appears there in fig. 7 where these curves definitely proceed downwards to the left. The relative positions of those parts of the curves (here only visible for two terms, namely n-pentane and n-hexane) which lie above the dotted horizontal line are quite normal.

Now the experimentally accessible points represented in the $G - n$ diagrams of the n-alkylbenzenes lie in general also above the dotted horizontal line in fig. 6.

This at least allows for a partial reconciliation of the at first sight quite opposite cases of the n-alkanes ($G - n$ diagram leads to erroneous conclusions) and of the n-alkylbenzenes ($G - n$ diagram allows right conclusions). So far the $G - n$ curves proceed upwards to the left, i.e. so long as $D < S$, including the eventual bends downwards (transition via $D = S$ to $D > S$), no erroneous conclusions are obtained in either case. When the curves, however, have definitively taken their course in a direction downwards to the left, i.e. when the transition to $D > S$ has been completely accomplished, the succession of the curves leads to erroneous conclusions in the case of the n-alkanes. As the further course of the $G - n$ curves, but for n-heptylbenzene, is not known in the case of the n-alkylbenzenes we cannot make the same statement here. But if we consider, in fig. 6, the position of the curve for n-heptylbenzene relative to the loops of the curves for n-hexylbenzene and n-amylbenzene, it seems likely that if the further course of the $G - n$ curves would be accessible, here too we would obtain quite the same situation as in the $G - n$ diagrams of the n-alkanes, i.e. a succession of the curves also leading to erroneous conclusions.

5. Metastable elastic systems at the coacervation limit.

At just transgressing the coacervation limit, two phase systems (very large coacervate layer + small layer of equilibrium liquid) are obtained,

---

[11]) In part X indications may be found that also for other alkanes similar deviations from the simple assumptions on which the use of the $G - n$ diagrams is based do occur. Compare fig. 4 in part X, in which n-hexane causes the maximum of the n curve to shift in a similar way (curve with a minimum!) as is the case with n-undecane in the present fig. 8. See also the survey in section 5 of part X where there are indications that the values of G corresponding to the maxima of the n curves also decrease in the case of n-hexane and n-heptane.

which are transformed to clear elastic systems by agitation or shaking. The latter, however, are metastable and when they are at rest sooner or later turbidity develops, i.e. coacervate drops are formed which gradually coalesce to form the coacervate layer anew.

Such metastable elastic systems were formed in a very pronounced way with the system lying on the dotted part of the n curve for n-butylbenzene in fig. 3 by wheeling round the vessels before applying the electrolytic H_2-mark (see part X, section 3). The metastable character of these systems forbids to draw conclusions from the shape of this n curve analogous to the conclusion drawn from the similar shaped curves for the higher homologues (where the elastic system are stable).

Summary.

1. The influence of added n-alkylbenzenes (from ethylbenzene up to and including n-heptylbenzene) has been investigated on the elastic behaviour of the oleate system at three KCl concentrations.

2. The results support the hypothesis that the total action of hydrocarbon is the resultant of a KCl-demanding (D) and a KCl-sparing (S) component action. They also confirm that D is relatively enforced with regard to S by increase of the hydrocarbon concentration, by increase of the length of the carbon (side) chain and by lowering of the KCl concentration.

3. The expectation that at sufficient length of the carbon side chain D might at once preponderate over S has been confirmed at 0.6 N KCl. At small concentrations ethylbenzene and n-propylbenzene show $D < S$; n-amylbenzene, n-hexylbenzene and n-heptylbenzene show $D > S$, whereas n-butylbenzene here just stands at the transition $D = S$.

4. The method to discuss the experimental results obtained with a homologous series with the aid of $G - n$ diagrams and which proved useful in the case of the n-primary alcohols (part VIII) and the fatty acid anions (part IX) does not lead to erroneous conclusions in the case of the n-alkylbenzenes for the experimentally accessible G and n values. This method, however, utterly fails in the case of the n-alkanes.

5. An investigation has been made about the influence of increasing concentrations of n-undecane on the curves representing G and n as functions of the KCl concentration. The results show that the simple assumptions on which the method of the $G - n$ diagrams is based are not fulfilled here. The failure of this method in the procuring of correct conclusions in the case of the n-alkanes is ascribed to this.

7. At just transgressing the coacervation limit, two phase systems (very large coacervate layer + small layer of equilibrium liquid) are obtained, which by agitation (or shaking) are transformed into clear elastic systems. The latter, however, are metastable and when they are at rest sooner or later coacervation sets in anew.

Department of Medical Chemistry,
University of Leiden.