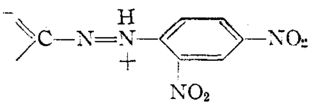


TABLE II

SPECTRA OF 2,4-DINITROPHENYLHYDRAZINE AND ITS DERIVATIVES IN ALCOHOLIC POTASSIUM HYDROXIDE SOLUTION

Compound	$\lambda_{max.}$[a] (mμ)	$\epsilon_{max.}$[a]	$\Delta\lambda_{max.}$[c]
2,4-Dinitrophenylhydrazine	395?[b]	2,600	43?
Formaldehyde DNPH	410?[b]	5,000	61?
Acetaldehyde DNPH	425	16,200	69
Crotonaldehyde DNPH	451	29,900	74
Benzaldehyde DNPH	467	33,000	89
p-Hydroxybenzaldehyde DNPH	482	32,300	87
Chalcone DNPH	516	24,600	121

[a] Solution in 0.12 *N* alcoholic potassium hydroxide. [b] Broad maximum with uncertain peak. [c] $\Delta\lambda_{max.} = \lambda_{max.}$ (alkaline solution) − $\lambda_{max.}$ (neutral solution).

The colors of solutions of dinitrophenylhydrazones are usually greatly changed by the addition of alkali and we have studied the absorption spectra of several of the derivatives in alcoholic potassium hydroxide solution. The results are given in Table II. In every case $\lambda_{max.}$ in neutral solution was shifted toward the visible by adding alkali. A somewhat greater shift was observed for the more unsaturated compounds. No consistent effect on $\epsilon_{max.}$ was found. In some cases $\epsilon_{max.}$ was considerably increased, in others it was lowered to one-third or less of its original value.

Summary

The absorption spectra of some 2,4-dinitrophenylhydrazones have been studied and related to the structure of the corresponding carbonyl compounds.

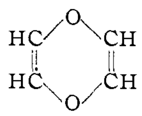
CAMBRIDGE, MASS. RECEIVED OCTOBER 23, 1945

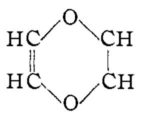
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MOUNT HOLYOKE COLLEGE]

The Ultraviolet Absorption Spectra of Dioxadiene and Dioxene

BY LUCY W. PICKETT AND ELIZABETH SHEFFIELD

The present study of the ultraviolet absorption spectra of dioxadiene (also called *p*-dioxin) and dioxene (or 2,3-dihydro-*p*-dioxin) is in continuation of an extensive investigation of the absorption spectra of unsaturated hydrocarbons in this Laboratory.[1] This study has included both acyclic and cyclic alkenes and dienes and has been extended to certain heterocyclic compounds such as furan[2] which may be considered as related to hydrocarbons by the substitution of oxygen for a methylene group. Dioxadiene and dioxene may thus be compared with 1,4-cyclohexadiene and cyclohexene, respectively.





Both compounds were first prepared by Summerbell and co-workers[3] whose reports of their preparation and properties are the only record of them so far found in the literature with the exception of a study[4] of their configuration by electron diffraction. Dioxadiene in particular is of especial interest for spectral studies because of its high degree of symmetry and the comparatively small number of atoms present in the molecule. Its spectrum is very distinct, showing five electronic transitions with well marked vibrational patterns.

Experimental

Preparation and Purification of Compounds[5]

Dioxene was prepared from 2,3-dichlorodioxane by the method reported by Summerbell[3] and purified by fractional distillation through a 40-cm. Fenske column in an atmosphere of nitrogen. The fraction used in the measurements boiled at 94.1° at 760 mm., and its physical constants (d^{20}_4 1.0836, n^{20}_D 1.4372) agreed with those of Summerbell.

Dioxadiene was similarly prepared from 2,3,5,6-tetrachlorodioxane. The preparation of the latter is of interest because of the number of stereoisomers as well as position isomers which can be formed when dioxane is chlorinated. A number of these have been isolated. Butler and Cretcher[6] obtained two symmetrical tetrachlorodioxanes melting, respectively, at 59–60° and 143–144°. Christ and Summerbell[7] reported symmetrical isomers melting at 143 and 70°. A 101°[8] isomer has also been reported. In the present work, mixtures were separated by fractional distillation to yield products melting at 143–144, 70 and 58–59° as well as liquid unsymmetrical isomers. The structures of the different products were ascertained by an identification of the products of hydrolysis. The solid products mentioned here are three of the five theoretically possible stereoisomers of symmetrical tetrachlorodioxane.

The dioxadiene used in the present work was prepared from the isomer melting at 58–59°, while Summerbell and Umhoefer[3] obtained their product from the isomer melting at 143°. The physical constants of the material used,

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(1) E. P. Carr and H. Stücklen, *J. Chem. Phys.*, **4**, 760 (1936); **6**, 55 (1938); E. P. Carr, L. Pickett and H. Stücklen, *Rev. Mod. Phys.*, **14**, 260 (1942).

(2) L. Pickett, *J. Chem. Phys.*, **8**, 293 (1940).

(3) R. K. Summerbell and L. N. Bauer, THIS JOURNAL, **57**, 2364 1935); R. K. Summerbell and R. R. Umhoefer, *ibid.*, **61**, 3020 (1939).

(4) J. Y. Beach, *J. Chem. Phys.*, **9**, 54 (1941).

(5) The synthesis and purification of these compounds were carried out under the direction of Dr. Mary L. Sherrill. The authors are also indebted to Miss Jean Lamont for the preparation and preliminary studies of dioxene and 1,4-cyclohexadiene.

(6) C. L. Butler and L. H. Cretcher, THIS JOURNAL, **54**, 2987 (1932).

(7) R. Christ and R. K. Summerbell, *ibid.*, **55**, 4547 (1933).

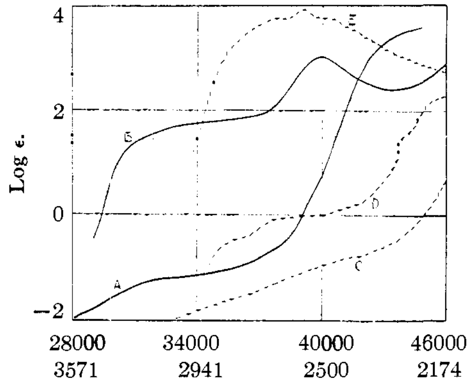
(8) W. Baker, *J. Chem. Soc.*, 2666 (1932).

after fractionation in nitrogen atmosphere (b. p. 74.6° at 743.2 mm., $n^{20}D$ 1.4350) agree with that of the preparation from the other isomer. Further proof of its structure was obtained when it was chlorinated to yield a white crystalline product melting at 141–142° and proved by mixed melting points to be the known symmetrical tetrachlorodioxane. It was the intention of the authors to prepare the dioxadiene also from the isomer of tetrachlorodioxane melting at 143° but the work was interrupted by the war. Spectral measurements made of three independent preparations of both dioxene and dioxadiene showed substantial agreement. The data presented below represent measurements made immediately after the final distillation of the samples considered the most pure.

The 1,4-cyclohexadiene used for comparison was prepared by the dehydration of 1,4-cyclohexandiol. The 1,3-cyclohexadiene which was simultaneously formed was successfully removed by treatment with maleic anhydride but traces of benzene remained which could not be removed even by careful fractional distillation. The curve is presented for comparison only since it is uncertain in the region of the absorption of benzene.

Measurements of Absorption Spectra

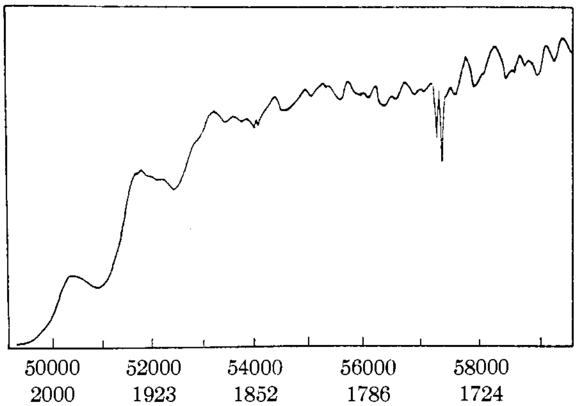
The absorption spectrum of dioxadiene in vapor phase was measured in the region between 30,000 and 62,000 cm.$^{-1}$, while dioxene vapor was studied between 42,000 and 62,000 cm.$^{-1}$. Measurements of both compounds in hexane solution were made in the region covered by the quartz spectrograph. The technique employed, using quartz and fluorite prism spectrographs, has been discussed in previous publications.[1,2]



(Top figures, 1/λ, cm. $^{-1}$; lower figures, λ, Å.)

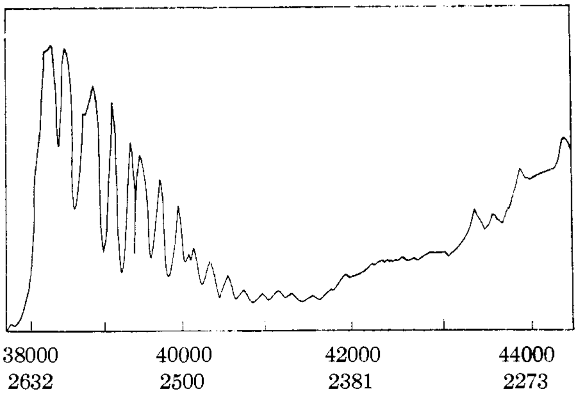
Fig. 1.—Ultraviolet absorption curves of hexane solutions of A, dioxene; B, dioxadiene; in comparison with C, cyclohexene; D. 1,4-cyclohexadiene; E, 1,3-cyclohexadiene.

The absorption curves of hexane solutions of dioxadiene and dioxene are shown in Fig. 1 in comparison with those of cyclohexene,[9] 1,3-cyclohexadiene,[10] and 1,4-cyclohexadiene. The positions and relative intensities of the bands in the vapor spectra are shown by the peaks in the microphotometer record tracings presented as Fig. 2–4. The wave numbers of the stronger absorption bands of the five band systems are listed in Table I, together with the separations from the first strong band of each series.



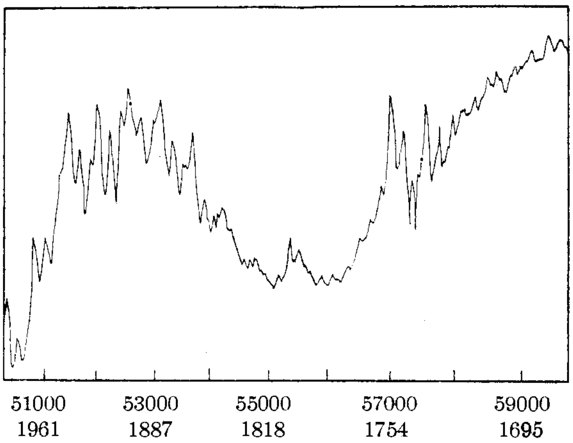
(Top figures, 1/λ, cm. $^{-1}$; lower figures, λ, Å.)

Fig. 2.—Microphotometer record of far ultraviolet absorption spectrum of dioxene vapor.



(Top figures, 1/λ, cm. $^{-1}$; lower figures, λ, Å.)

Fig. 3.—Microphotometer record of absorption spectra of dioxadiene vapor showing second and part of third band systems.



(Top figures, 1/λ, cm. $^{-1}$; lower figures, λ, Å.)

Fig. 4.—Microphotometer record of absorption spectra of dioxadiene vapor showing fourth and fifth band systems.

Discussion of Results

Dioxene.—Dioxene shows low intensity absorption in the longer wave length region, which is displaced toward the visible and somewhat more intense than that of cyclohexene, followed by a steep rise in the curve to a stepout near 43,000 cm.$^{-1}$ on which are indistinct fused bands. This is followed by another sharp increase in ab-

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[9] H. Stücklen, H. Thayer and P. Willis, THIS JOURNAL, **62**, 1717 (1940).

[10] V. Henri and L. Pickett, *J. Chem. Phys.*, **7**, 439 (1939).

TABLE I

WAVE NUMBERS IN CM.$^{-1}$ OF BANDS OBSERVED TOGETHER WITH SEPARATION FROM FIRST STRONG BAND

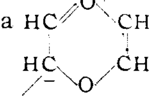
I		II		III		IV		V	
1/λ	Δ 1/λ	1/λ	Δ 1/λ	1/λ	Δ 1/λ	1/λ	Δ 1/λ	1/λ	Δ 1/λ
		37,800	−500			49,860	−460		
		38,135	−165			50,180[a]	−140	56,840	−160
30,860	0	38,300	0	43,450	0	50,320	0	57,000	0
30,950	90							57,220	220
31,040	180	38,530	230	43,650	200	50,540	220		
31,135	275								
31,180	320	38,750	450						
		38,825	525	43,950	500	50,840	520	57,550	550
31,370	510	38,900	600						
31,700	840	39,140	840	44,165	715	51,080	760	57,770	770
31,890	1030	39,370[a]	1070	44,425	975	51,380	1060	57,960	960
32,020	1160	39,550	1250	44,740	1290	51,510	1190	58,110	1110
		39,760	1460	44,940	1490	51,710	1390	58,330	1330
						51,880	1560	58,510	1510
		39,990	1690	45,090	1640	52,040	1720	58,620	1620
32,660	1800							58,700	1700
		40,200	1900	45,270	1820	52,260	1940	58,900	1900
32,900	2040	40,370	2070	45,600	2150	52,460	2140	59,180	2180
33,220	2360	40,580	2280					59,410	2410
33,380	2520	40,780	2480	45,840	2390	52,580	2260	59,600	2600
33,500	2640	40,980	2680	46,150	2700	52,830	2510	59,790[a]	2790
						53,020	2700	59,980	2980
						53,160	2840		
						53,360	3040		
						53,700	3380		
						53,920	3600		
						55,180	4860		
						55,340	5020		

[a] Poor region for observation.

sorption near 50,000 cm.$^{-1}$ where there are three diffuse bands, the first of which is at 50,500 cm.$^{-1}$, showing separations of 1410 and 1380 cm.$^{-1}$. These are familiar as characteristic vibrational frequencies of doubly bonded carbon atoms in an excited state. The diffuse bands are followed by a number of narrow bands with separations around 450 cm.$^{-1}$ especially prominent. There is evidence of another group of bands near 57,000 cm.$^{-1}$.

The diffuse character of the dioxene spectrum as compared with that of dioxadiene is easily explained on the basis of the low symmetry of the former. Because of this fact, many more vibrational as well as electronic transitions are allowed and so there is much overlapping of bands. No attempt at vibrational analysis was made for this reason.

Dioxadiene.—The spectrum of dioxadiene contrasts more sharply with that of 1,4-cyclohexadiene. The first broad stepout shown in solution is of lower frequency and greater intensity and there is a band at 40,000 cm.$^{-1}$ which corresponds rather to the more intense band of 1,3-cyclohexadiene. This similarity with the conjugated diene may be evidence to support the suggestion of Beach[4] that the formula



contributes to the molecular structure to a considerable extent.

More exact information is available from a consideration of the vapor spectra. Five band systems are clearly marked in the region studied and, with the exception of the first, have patterns of sharp bands. In addition to the bands listed in Table I, the use of higher pressures brought out additional bands complicating the pattern.

The first band system beginning at 30,860 cm.$^{-1}$ corresponds to the first broad stepout observed in solution and is characterized by indistinct but narrow bands of low intensity with no one of these noticeably stronger than the others. This system is believed to be due to a forbidden transition. The second band system is of higher intensity than the first and corresponds in frequency with the band in the solution spectrum. The first and most intense band is at 38,300 cm.$^{-1}$ and is interpreted as a 0–0 transition: lower frequency bands were well marked at higher pressures, doubtless representing transitions from higher vibrational levels of the normal molecule. The first band was so broad that measurements made from its apparent center cause uncertainty as to the vibrational frequencies.

The third, fourth and fifth systems seem to be superimposed on a broad presumably structureless band with the third system on its upward slope and the fourth at its peak. The third system begins at 43,450 cm.$^{-1}$ and seems to consist of doublets with the first member of each pair the stronger. This system was photographed by both instruments as it is within the range of each. The fourth band system is the most intense one observed and begins at 50,300 cm.$^{-1}$. The individual bands were sharp and clearly marked. The first four bands while distinct are of lower intensity than the others, although this may be due to the superposition referred to. A fifth system begins at 57,000 cm.$^{-1}$ and is of lower intensity than the record indicates as the intensity of the hydrogen lamp used as light source is lower in this region. In all of the systems except the first, separations of 550 and 220 cm.$^{-1}$ are very apparent and it is possible to account for many of the bands on the basis of these frequencies alone.

In order to proceed further with theoretical deductions from the above results, the symmetry of dioxadiene should be considered. The assumption that the molecule is planar is most reasonable and was made in the electron diffraction studies. The normal molecule would therefore have three twofold axes, three planes and a center of symmetry and thus belong to the class D_{2h} or V_h. From an application of selection rules[11] it may be shown that electronic changes from a totally symmetrical ground state (A_{1g}) are allowed to states of symmetry B_{1u}, B_{2u}, and B_{3u}, corresponding to changes of electric moment in the z, y, and x directions, respectively. The z direction for this molecule may be taken as the line joining the oxygen atoms, the x direction as perpendicular to the molecular plane.

The first band system probably represents a forbidden transition, either of a symmetry type other than that given above or a transition involving a change of multiplicity, *i. e.*, from a singlet to a triplet state. In the former case a vibrational change must occur of a species which will combine with that of the electronic change to give a product which is allowed. If, for example, the electronic change is to a B_{3g} state, one quantum of a B_{2u} vibration in conjunction would give a product B_{1u} which is permitted. The last four band systems seem to be of sufficiently high intensity to be classified as allowed transitions and may be either charge-transfer (N → V)[12] or Rydberg transitions.

Note.—Dr. R. S. Mulliken in a private communication has predicted the N → V electronic transitions of this molecule by considering the excitation of unsaturation electrons of the carbon and oxygen atoms to antibonding orbitals. Four of the eight possible excited states might fall within the range of observation since their estimated term values are between 4.8 and 7.5 e. v. These are of types B_{1u}, B_{3g}, B_{3g} and B_{1u} respectively; the first and last transitions would be allowed, while the second and third could occur if accompanied by one quantum of a B_{2u} vibration because of the neighboring allowed transition of the same polarization.

The observed results are not inconsistent with the prediction except for the first system which cannot be accounted for in this way. This leaves a singlet-triplet transition as the most probable way of explaining the bands although the question of impurity cannot be ruled out of consideration.

An application of the selection rules to vibrational changes would lead to the expectation that series of totally symmetrical or A_{1g} vibrations would appear as most prominent in the allowed transitions. A consideration of the numbers of possible modes of vibration of each species, first for the dioxadiene ring of six atoms exclusive of hydrogen, and then for the molecule of ten atoms, is shown in Table II. Of the five possible A_{1g} vibrations, one (the C-H stretching) may be above 2500 cm.$^{-1}$ in the excited molecule, the others are to be expected below 1700 cm.$^{-1}$, with the ring vibrations the more strongly excited and depending on the electronic excitation for their relative intensities.

A consideration of the vibrational frequencies observed shows that there is present in each band system except the first, a frequency near 220 cm.$^{-1}$ which is especially prominent. It is customary to attribute low frequency vibrations to out of plane or torsional motions and such modes of vibration are obviously not totally symmetrical. Such a vibration might belong to the B_{2g} species and thus could combine with electronic states of species B_{1u} to give a product of type B_{3u}. Although such a transition is possible, it would not be expected to give such an intense band. Other possibilities are a transition from an activated vibrational level of the lower electronic state or that it represents two quanta of a 110 cm.$^{-1}$ frequency. Vibrational frequencies of approximately 100 cm.$^{-1}$ have been observed in such molecules as cyclopentene and 1,3-cyclohexadiene[1] in which the symmetry is lower and therefore imposes less restriction.

A second frequency prominent in all systems is around 550 cm.$^{-1}$ and is thought to represent a totally symmetrical vibration. This may be related to one of the degenerate modes of vibration of type E^{+g} prominent in the benzene spectrum whose frequency in the normal state is 606 cm.$^{-1}$ and in the first excited state 520 cm.$^{-1}$. This

TABLE II

VIBRATIONS OF DIOXADIENE

Symmetry type	Number of vibrations of ring	Number of vibrations of molecule	Selection rules Infrared	Raman
A_{1g}	3	5		p
A_{1u}	1	2		
B_{1g}	0	1		dp
B_{1u}	2	4	Active M_z	
B_{2g}	1	2		dp
B_{2u}	2	4	Active M_y	
B_{3g}	2	4		dp
B_{3u}	1	2	Active M_x	

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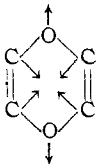
[11] H. Sponer and E. Teller, *Rev. Mod. Phys.*, **13**, 76 (1941); Kohlrausch, "Der Smekel-Raman Effekt," Julius Springer, Berlin, 1938, p. 43.

[12] R. S. Mulliken, *J. Chem. Phys.*, **7**, 20, 121, 339 (1939).

vibration, which is represented below, would be totally symmetrical for the molecule of dioxadiene.



The band separation occurring near 750 cm.$^{-1}$ in the different systems may represent a combination of the vibrations described above, although it is reasonable to expect a ring vibration similar to the "breathing" vibration prominent in the benzene spectrum. Bands are present in all systems which probably represent two quanta of the 550 cm.$^{-1}$ vibration. The next prominent band is found separated by about 1150 cm.$^{-1}$ from the band assigned as 0–0 band in the allowed transitions and is thought to be due to a symmetrical ring vibration. There are a number of bands in the region 1200–1600 cm.$^{-1}$ but only one of these, 1460 cm.$^{-1}$ in the second system, is of outstanding intensity. An intense band is present in each system near 1700 cm.$^{-1}$ Its prominence suggests a fundamental vibration but the value seems surprisingly high for an excited state frequency. The bands are so placed that they could represent a combination of the 1150 and 550 cm.$^{-1}$ frequencies if the potential energy curves happened to be in a position to favor this transition.

The other bands are of lower intensity and can be accounted for as combinations or overtones and the C–H stretching vibration. There seems to be very little change in fundamental frequencies in the different band systems; differences of 20 cm.$^{-1}$ are not believed to be significant in general although the error of measurement differs in different regions of the spectrum. The small changes in frequency and short progressions indicate that the structure of the ring is not greatly changed by the electronic excitations.

The conclusions above must necessarily be of a tentative nature. A study of the Raman spectra of dioxadiene would be valuable as a test of the assignments since totally symmetrical vibrations of the normal molecule would appear as polarized lines and those of the B_g classes as depolarized lines. They would not be found in the infrared spectra. The Raman spectrum of 1,4-cyclohexadiene was measured by Kohlrausch and Seka[13] who observed frequencies of 400, 706, 987, 1196, 1676 and 3032 cm.$^{-1}$, together with others attributed to 1,3-cyclohexadiene which was present as impurity.

Acknowledgment.—The authors wish to make grateful acknowledgment to Dr. Emma P. Carr and Dr. Mary L. Sherrill for their interest and assistance throughout the work, and to Dr. R. S. Mulliken for helpful suggestions.

Summary

The ultraviolet absorption spectra of dioxene and dioxadiene have been measured up to wave numbers of 62,000 cm.$^{-1}$ Five separate band systems have been observed for dioxadiene and vibrational separations measured. Possible interpretations of the data are given on the basis of the symmetry of the molecule.

(13) K. W. Kohlrausch and R. Seka, *Ber.*, **68**, 528 (1935).

South Hadley, Mass. Received August 27, 1945

[Contribution from the Department of Chemistry, University of Chicago]

Structure of Soap Micelles Indicated by X-Rays and the Theory of Molecular Orientation. I. Aqueous Solutions[1]

By William D. Harkins, Richard W. Mattoon and Myron L. Corrin

I. General Structure of Soap Micelles.—Soap solutions and those of many other detergents exhibit an extremely interesting structure, which is revealed by a combination of X-ray data with the theory of orientation of molecules in surfaces. The manifold uses of soap in life and industry are dependent in part upon this structure and in part upon the behavior of the molecules whose structure is responsible for that of the soap solutions. In the present work the principal attention has been focused upon the soaps themselves, that is, upon the alkali salts of the *n*-long paraffin chain (fatty) acids.

On account of the extreme insolubility of long paraffin chains in water, it is to be expected that the alkali salts of the high fatty acids should not exhibit a large molecular solubility, although the presence of the highly polar —COO^-A^+ groups should increase the solubility greatly above that of the acids, which are much more soluble than the paraffins of equal chain length. However, it is found that at room temperature potassium laurate (12 carbon atoms) gives a clear solution at concentrations somewhat above 35%, and potassium myristate (14 carbon atoms) above 26%. These extremely high values may be taken to indicate that solid soap may reduce its free energy by going into solution in some other form than that of single molecules. It is found that in general most of the soap dissolved is present as

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(1) The work reported in this paper was done in connection with the Government Research Program on Synthetic Rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.