calculated and observed wavenumbers (Table V) must be somewhat arbitrary and we make no claim to uniqueness. However, again the force-constant values all are physically reasonable and, in addition to providing a description of the normal modes in MV^+ , they provide an indication of the way in which the chemical bonding has changed from that in MV^{2+} . This change is illustrated in Figure 2. The nature of the bonding in MV^+ , thus suggests that an electron added to MV^{2+} goes to a molecular orbital which has strong bonding character in the inter-ring region.

In Table VI the observed and calculated wavenumber values for MV^{2+} and MV^{+} are compared in full. In ad-

dition to the points made above, it may be seen that a surprisingly large change in the CH_3 symmetric deformation accompanies the transformation from MV^{2+} to MV^{+} . Since this motion is essentially uncoupled from the rest of the molecular motion (see Tables III and V), it is not at all clear what causes this effect.

In conclusion, we offer this admittedly crude approximation to a description of the normal modes of vibration in methylviologen and its radical ion as an aid to the interpretation of experimental spectra. While we recognize fully its defects, the description seems to us to be very much better than anything else we have seen!

Radiolysis of Concentrated Solutions. 2. Pulse and γ -Radiolysis Studies of Direct and Indirect Effects in Lithium Iodide Solutions

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In the preceding study of the radiolysis of concentrated aqueous LiCl solutions (ref 6), one of the hypotheses used to explain the apparent inefficacy of Cl_2^- formation by the direct effect was that molecular chlorine, not detectable by spectrophotometry, could be formed during the early stages of water radiolysis. Such an hypothesis is confirmed here for pulse and γ -radiolysis of concentrated aqueous neutral LiI solutions. Indeed, it is shown that, 10 ns after the pulse, molecular iodine, detected as I_3^- , is formed with a yield that increases with the LiI concentration. The experimental results yields values of 4.8 and 7.3 respectively for the indirect and direct effects of total oxidation $G_{I_2^-} + 2G_{I_3^-}$. This last high value is discussed.

I. Introduction

The research that has been made during these past 10 years on the radiolysis of concentrated solutions of halide ions has led to results that are difficult to interpret. However, the phenomena were thought to be simple enough to provide unequivocal information concerning the primary events of water radiolysis and those following the direct absorption of energy by the solute (direct effect). Thus, according to the basic hypothesis concerning the indirect effect, an increase of the concentration would initially allow capture of the oxidizing entities in order to give rise to the radical-ion species X_2^- according to

$$X^- + OH \rightarrow X + OH^-$$
(I)

$$X + X^{-} \rightarrow X_{2}^{-} \tag{II}$$

But considering the high concentrations necessary for a complete capture, the contribution due to direct effect should start to appear thus adding its own production of X_2^- (reactions III and II):

$$X^- \rightarrow X + e^-$$
 (III)

In total, the X_2^- yield would be

$$G_{\mathbf{X}_2^-} = f_{\mathbf{X}^-}G_{\mathbf{d}} + (1 - f_{\mathbf{X}^-})G_{\mathbf{i}}$$
 (A)

where f_{X^-} is the ratio of the energy directly absorbed by the solute X⁻ to the total energy absorbed by the solution. To a first approximation f_{X^-} is the electron fraction of X⁻. $G_{\rm d}$ is the yield of the direct effect expressed in molecules formed per 100 eV absorbed by the solute. It is assumed to be independent of [X⁻]. $G_{\rm i}$ is the maximum yield of the indirect effect, vis. H₂O; in this case it equals to the primary yield of water decomposition $G_{-\rm H_2O}$.

In relation to these simple hypotheses, pulse radiolysis studies have led to amazingly low values of G_{X_2} . For their analysis of the results found by Anbar and Thomas concerning neutral Cl⁻ solutions up to only 3 M,¹ Sawai and Hamill² have used their semiempirical method of extrapolation to calculate a maximum value $G_{Cl_2} = 3.9$, which is far inferior to the yield of water decomposition, G_{-H_2O} ~ 5. In their pulse radiolysis experiments of neutral LiCl solutions, Woods et al.³ have observed a maximum at 3.35 for [Cl⁻] = 9 M; this yield even decreases for the highest concentrations, down to 2.8 for [Cl⁻] = 14 M.

Since the direct effect was not taken into account, the first interpretations assumed that the oxidizing species were not captured in their totality by CI^- . It is known⁴ that the oxidation of CI^- by 'OH does not take place in a neutral medium, and that, according to a two-step mechanism, it

M. Anbar and J. K. Thomas, J. Phys. Chem., 68, 3829 (1964).
 T. Sawai and W. H. Hamill, J. Phys. Chem., 74, 3914 (1970).
 R. J. Woods, B. Lesigne, L. Gilles, C. Ferradini, and J. Pucheault,

 ⁽⁴⁾ A. O. Allen, "The Radiation Chemistry of Water and Aqueous

⁽⁴⁾ A. O. Allen, "The Radiation Chemistry of Water and Aqueous Solutions", Van Nostrand, New York, 1961, p 63.

requires the presence of H^+ ions, so that we have the overall reaction

$$Cl^- + OH + H^+ \rightarrow Cl + H_2O$$
 (I')

Contrary to other authors^{1,5} who assume that the acidity produced in the spurs together with OH formation (H_2O^+) + $H_2O \rightarrow OH + H_3O^+$) is enough to produce reaction I', Sawai and Hamill² do not think such a process to be efficient. According to them, G_{Cl_2} would be entirely due to the reaction with the OH ionic precursor:

$$Cl^- + H_2O^+ \rightarrow Cl + H_2O$$
 (IV)

which implies $G_{H_2O^+} = 3.9$. The remaining OH radicals would be those which did not have H_2O^+ as a precursor, that is to say those which would derive from the deexcitation by homolytic rupture of H_2O , with a corresponding yield of about 0.8 ($G_{-H_2O} = 4.7$). According to this hypothesis the maximum value for G_{Cl_2} should be approaching $G_{-H_{2}O}$ when the OH radicals would be in their turn oxidizing Cl^- in acid medium. But this is not the case. Using the same method as mentioned above, Khorana and Hamill⁷ can only obtain a maximum of 3.8 in a 0.05 M HClO₄ solution. The experimental results of Kim and Hamill⁷ (0.1 M HClO₄) increase only up to 3.2 for $[Cl^{-}] =$ 1.8 M. With higher concentrations of LiCl, in a 0.1 M HCl medium, Pucheault et al.⁶ have found a maximum of 3.6 for $[Cl^{-}] = 5$ M, and for the highest concentrations the decrease is similar to that already observed in a neutral medium.³

Another quite different interpretation is that these low values could be accounted for by the poor efficiency of the direct effect causing the yield to fall subsequently due to the gradual absorption of radiation energy by the solute. In their analysis of the decrease occurring for the highest concentrations in neutral medium³ and above all in acid medium,⁶ according to eq A, Pucheault et al. have been led to attribute the values $G_i = 4.7 \pm 0.3$, $G_d \simeq 0$, to the yields for the indirect and direct effects. If the value of $G_{\rm i}$ is consistent with $G_{-{\rm H_2O}}$, the inefficiency of the direct effect is difficult to admit. Hence the hypothesis of compensation by a concomitant yield of molecular $Cl_2^{6,7}$ has been put forward. But the spectrophotometrical observation of Cl₂ was not possible by pulse radiolysis, consequently, it was interesting to undertake similar research with I^- ions, in which I_2 would be easily measured as I_3^- . Here again the values obtained for G_{I_2} are much lower than G_{-H_2O} , and parallel formation of iodine has already been observed, $2G_{I_3} + G_{I_2}$ increasing then to 4.8 for [I⁻] = 1.8 M.⁷ The purpose of this work is to extend these studies to higher LiI concentrations in order to determine the intervention of an eventual direct effect in such an oxidation.

II. Experimental Section

The accelerator used for pulse radiolysis was a Febetron 707 which had been modified in order to produce 1.8-MeV electrons in a 10-ns pulse;^{3,8} the doses delivered were several tens of Gray for each pulse. The γ rays were provided by a 60 Co source (400 Ci); the dose rate was 4 \times $10^{18} \text{ eV cm}^{-3} \text{ h}^{-1}$. In both cases, pulse radiolysis and γ radiolysis, the electronic concentrations of the irradiated



Figure 1. $\epsilon_{I_3^-}$ with respect to LiI concentrations, from 10^{-1} to 7 M: (1) 10^{-1} M; (2) 1 M; (3) 2 M; (4) 3 M; (5) 4 M; (6) 5 M; (7) 6 M; (8) 7 M.

solutions have been taken into account for the measures of the doses actually absorbed.

Triply distilled water with a resistivity of $10^6 \Omega \text{ cm}^{-1}$ was used for the preparation of the solutions. Impurities from concentrated LiI were destroyed by γ preirradiations. Irradiations were performed either in the presence of nitrogen to avoid the oxygen effect or in the presence of N₂O to replace the hydrated electrons by OH radicals.

In pulse radiolysis experiments I_2^- was measured by its specific absorption at 720 nm. A standardization for 10⁻² M LiI solution (G = 2.7) has given a value for $\epsilon = 3900 \text{ M}^{-1}$ cm⁻¹ consistent with those mentioned in the literature.⁹ This value is independent on the $[I^-]$ concentration (see section V).

Some authors have proved that, on the contrary, the molar extinction coefficients of I_3^- were function of $[I^-]$, following the formation of more condensed ions, in particular $I_4^{2-.10,11}$ Figure 1 shows the absorption spectra obtained by comparing, for the same quantity of added iodine $(3.5 \times 10^{-5} \text{ M})$, the optical densities measured in LiI solutions of different concentrations to those obtained with a 10⁻¹ M KI solution. It appears that the maximum absorption shifts slightly toward longer wavelengths while the corresponding values of ϵ increase from 26800 to 38600 M^{-1} cm⁻¹ when the concentration of I⁻ increases from 10^{-1} to 7 M. In all cases, the equilibrium $I_2 + I^- \rightleftharpoons I_3^-$ (K = 768) is shifted to the right.

For analysis of the hydrogen produced during the γ irradiations of LiI solutions, gas chromatography was used on a 5 A molecular sieve with argon as the carrier gas.

III. Initial Formation of I₂⁻

The $G_{L^{-}}$ values have been determined by pulse radiolysis following the absorption at 720 nm measured immediately after the pulse (~ 10 ns) in solutions of variable concentrations in LiI, at their natural pH, under a nitrogen atmosphere and in the presence of $10^{-2}~M~NO_3^-$ in order to scavenge the solvated electrons. Figure 2 shows these values as a function of f_{I} . It appears that G_{I_2} increases from 2.7 ($\sim G_{OH}$) up to a maximum of about 3.8 for [I⁻]

⁽⁵⁾ G. G. Jayson, B. Parsons, and A. J. Swallow, J. Chem. Soc., Far-(6) J. Pucheault, C. Ferradini, R. Julien, A. Deysine, L. Gilles, and M.

 ⁽⁷⁾ S. Khorana and W. H. Hamill, J. Phys. Chem., 75, 3081 (1971); K.
 J. Kim and W. H. Hamill, J. Phys. Chem., 75, 3081 (1971); K.

⁽⁸⁾ B. Lesigne and R. Sauneuf, Rev. Sci. Instrum., 47, 1063 (1976).

⁽⁹⁾ J. H. Baxendale, P. Sharpe, and M. D. Ward, Int. J. Radiat. Phys.

<sup>Chem., 7, 587 (1975).
(10) M. Davies and E. Gwynne, J. Am. Chem. Soc., 73, 1842 (1951).
(11) E. E. Genser and R. E. Conmick, J. Chem. Phys., 58, 3 (1973).</sup>



Figure 2. The dependence of yields on electronic fraction f_{I^-} in pulse radiolysis: (O) $G_{I_2^{-1}}$; (Δ) $G_{e_{00}^{-1}}$.

= 7 M. This maximum is still far from the accepted values for G_{-H_20} . This difference here again can be attributed to a certain inefficiency of the direct effect. If we apply the formalism quoted above with $G_i = 4.8$, eq A of the line tangent to the experimental curve gives $G_d = 2.2$ (extrapolation for $f_{\Gamma} \rightarrow 1$).

Figure 2 shows also the values of $G_{e_{aq}}$ determined from the increase in the formation of I_2^- when irradiation takes place under an N₂O atmosphere instead of N₂. The variations of $G_{e_{a0}}$ appear to be similar to those of G_{I_2} .

The inefficiency of the direct effect can be compensated for by the formation of I_3^- . This has been studied both by measuring the iodine produced by γ irradiations and by examining the initial spectra obtained by pulse radiolysis in the range of I_3^- absorption.

IV. γ Radiolysis

The products I_3^- and H_2 , measured in γ -irradiated LiI solutions, appear in all cases to be proportional to the dose. Figure 3 shows that the corresponding yields increase with increasing concentrations of I⁻.

On curve 1 of Figure are plotted $G_{N_2}(I_3^{-})$ and $G(H_2)$ measured after irradiation in an N₂ atmosphere. They look almost equal, which is consistent with the final balance between oxidized and reduced species. They increase regularly from about 0.45 at the lowest concentrations to 1.2 at $[I^-] = 7.75$ M. The reaction mechanism is well-known for dilute solutions:^{12,13}

$$OH + I^{-} \rightarrow I + OH^{-} \tag{1}$$

$$I + I^- \rightleftharpoons I_2^-$$
 (2)

$$I_2^- + I_2^- \rightarrow I_3^- + I^-$$
 (3)

$$e_{ao}^{-} + H_2 O_2 \rightarrow OH + OH^{-}$$
(4)

$$\mathbf{e}_{ac}^{-} + \mathbf{I}_{3}^{-} \rightarrow \mathbf{I}_{2}^{-} + \mathbf{I}^{-} \tag{5}$$

$$H + I_3^- \rightarrow I_2^- + I^- + H^+$$
 (6)

It follows that, for dilute solutions, the yields are

$$G_{\rm N_2}({\rm I_3}^-) = G_{{\rm H_2O_2}} + \frac{1}{2}(G_{\rm OH} - G_{{\rm e_{sq}}^-} - G_{\rm H}) = G_{{\rm H_2}} = 0.45$$

according to the experimental results. When concentrated I⁻ is used, it reacts in spurs and $G_{\rm H_2O_2}$, $G_{\rm OH}$, and $G_{\rm H}$ become negligible before $G_{\rm I_2^{-14,15}}$ In this case the yield is

$$G_{N_2}(I_3^-) = \frac{1}{2}G_{I_2}^- - \frac{1}{2}G_{e_{aq}}^-$$
 (B)



Figure 3. Effect of LiI concentrations on yield in γ radiolysis: (•) $G_{N_2O}(I_3^-)$; (O) $G_{N_2}(I_3^-)$; (*) G_{H_2} .



Figure 4. Initial spectra for two LiI concentrations in an N_2 atmosphere, in pulse radiolysis: (1) 10^{-1} M (2) 6 M.

On curve 2 of Figure 3 are plotted the yields of $G_{\rm N_2O}(\rm I_3^{-1})$ measured after irradiation in an N₂O atmosphere. At low concentrations in I⁻, the yield is equal to 1.75. It rapidly increases with [I⁻], then less rapidly up to 4.1 at [I⁻] = 7.75 M. In an N₂O atmosphere, H₂O₂ is no longer reduced by e_{aq}⁻, but, on the contrary, reduces I₂⁻ and I₃⁻ according to reactions 7 and 8 which replace reactions 4 and 5.

$$I_2^- + H_2O_2 \rightarrow 2I^- + 2 H^+ + O_2^-$$
 (7)

The yield for dilute solutions is then

$$G_{N_2O}(I_3^-) = \frac{1}{2}(G_{OH} + G_{e_{aa}^-} - G_H) - G_{H_2O_2}$$

that is 1.75 according to the values commonly accepted for radical and molecular yields ($G_{\rm OH} = 2.75$; $G_{\rm e_{qq}} = 2.7$; $G_{\rm H} = 0.55$; $G_{\rm H_2O_2} = 0.7$). The rapid increase with [I⁻] corresponds to the disappearance of $G_{\rm H_2O_2}$ in favor of $G_{\rm I_2}$; the yield is then

$$G_{\rm N_2O}({\rm I_3}^-) = \frac{1}{2}G_{{\rm I_2}^-} + \frac{1}{2}G_{{\rm e_{aa}}^-}$$
 (C)

When comparing (B) and (C) we obtain

$$G_{N_2}(I_3^-) + G_{N_2O}(I_3^-) = G_{I_2^-}$$

This balanced equation is far from being experimentally verified. For example, at $[I^-] = 7$ M, the sum of the two yields measured after γ radiolysis is equal to 5.4, while the determination of $G_{I_2^-}$ in pulse radiolysis (see Figure 2) lead to a value of only 3.7. It would seem that, 10 ns after the electron pulse, formation of molecular iodine already occurs and can be found again in the final balance.

⁽¹²⁾ M. Anbar, D. Meyerstein, and P. Neta, J. Phys. Chem., 68, 2967 (1964).

⁽¹³⁾ J. H. Baxendale, P. L. T. Bevan, and D. A. Stott, *Trans. Faraday Soc.*, 64, 2389 (1968).

⁽¹⁴⁾ E. Hayon, Trans. Faraday Soc., 61, 723 (1965).

⁽¹⁵⁾ E. Peled, D. Meisel, and G. Czapski, J. Phys. Chem., 76, 25 (1972).



Figure 5. Variation of optical density with LII concentrations in an N₂ atmosphere at two wavelengths: (1) OD_{370} (2) $OD_{720} \times 3.55$.

V. Initial Spectra in Pulse Radiolysis

Figure 4 shows the spectra obtained 10 ns after a 1.26 $\times 10^{17}$ eV cm⁻³ pulse in 0.1 and 6 M LiI solutions in an N₂ atmosphere. The spectrum corresponding to [I⁻] = 0.1 M is similar to the one attributed to I₂⁻ in the literature,⁹ with two maxima at 370 and 720 nm with a ratio of

$$OD_{370}/OD_{720} = \epsilon_{370}^{I_0}/\epsilon_{720}^{I_0} = 3.55$$

For 6 M LiI solution, the two maxima are approximately at the same wavelengths but the ratio OD_{370}/OD_{720} has a value of about 5. Such a variation is to be found again in Figure 5 where it appears that for equal doses OD_{370} shifts progressively away from the curve giving $3.55 \times OD_{720}$ when the concentration of I⁻ increases.

Qualitatively, the existence of this variation can corroborate the conclusion of the preceding paragraph:molecular iodine which is already formed 10 ns after the pulse would add its own absorption to the OD measured around 370 nm. But from a quantitative point of view, it remains to be demonstrated that all or part of the phenomenon is not simply due to a variation in the I₂⁻ spectrum. In this respect, besides the results of Figure 5, the optical densities OD_{iso} measured at the isobestic points for the transformation I₂⁻ + I₂⁻ \rightarrow I₃⁻ + I⁻ have been taken into account. At these points $\epsilon_{iso}^{I_2^-} = 1/2\epsilon_{iso}^{I_3^-}$ and the optical densities can be expressed by the formula

$$\begin{aligned} \text{OD}_{\text{iso}} &= \epsilon_{\text{iso}}^{\text{I}_{3}^{-}} ([\text{I}_{3}^{-}] + \frac{1}{2}[\text{I}_{2}^{-}]) \\ \text{OD}_{370} &= \epsilon_{370}^{\text{I}_{2}^{-}}[\text{I}_{3}^{-}] + \epsilon_{370}^{\text{I}_{2}^{-}}[\text{I}_{2}^{-}] \\ \text{OD}_{720} &= \epsilon_{720}^{\text{I}_{2}^{-}}[\text{I}_{2}^{-}] \end{aligned}$$

Eliminating the unknown concentrations $[I_3^-]$ and $[I_2^-]$ and gathering the terms which are already known (ϵ^{I_3} given Figure 1) or measured (OD) in the expression Y, we obtain

$$Y = \frac{OD_{370} - OD_{iso}\epsilon_{370}^{L_{2}^{-}} / \epsilon_{iso}^{L_{3}^{-}}}{OD_{720}} = \frac{1}{2\epsilon_{720}^{L_{2}^{-}}} (2\epsilon_{370}^{L_{2}^{-}} - \epsilon_{370}^{L_{3}^{-}})$$

If the I₂⁻ spectrum does not vary, particularly if $\epsilon_{370}^{\text{L}_{-}}/\epsilon_{720}^{\text{L}_{-}}$ = 3.55 and $\epsilon_{720}^{\text{L}_{-}}$ = 3900, whatever the concentration of [I⁻], we must obtain

$$Y = 3.55 - \frac{1}{2 \times 3900} \epsilon_{370}^{I_2^-}$$

Actually, the experimental determinations of Y shown in Figure 6 can be placed on a straight line corresponding to this variation with ϵ_{170}^{1} .

The relative increase of OD_{370} with [I⁻] is really due to the presence of a certain quantity of triiodine, I_3^- . This quantity may thus be calculated by

$$OD_{370} - 3.55OD_{720} = \epsilon_{370}^{1}[I_3]$$



Figure 6. Dependence of Y on ϵ_{370}^{13} (see text): (X) experimental points; (--) curve $Y = (OD_{370} - OD_{iso}\epsilon_{370}^{13}/\epsilon_{iso}^{13})/OD_{720}$.



Figure 7. G_{I_3} as a function of LiI concentrations.



Figure 8. The dependence of yields on electronic fraction $f_{1^{-1}}$: (∇) G_{ox} = $G_{1_2^{-1}} + 2G_{1_3^{-1}}$; (O) $G_{e_{1_3^{-1}}} + 2G_{H_2}$.

The corresponding yields G_{I_3} are indicated in Figure 7. It can be seen that they increase rapidly up to 0.93 at $[I^-] = 2$ M, and then more slowly.

VI. Discussion

This work has shown that the oxidation of I^- in the spurs leads to the formation of two species I_2^- and I_3^- . When they appear in the bulk, about 10 ns after the pulse, the ratio of their yields varies considerably with the concentration, while the increase of $[I^-]$ is not very effective concerning the formation of I_2^- , but it favors on the contrary the formation of I_3^- giving a very high yield for total oxidation (see below).

For high concentrations of I⁻, the formation of I_2^- ions, whether produced by direct or indirect effect, occurs very early in the process of spurs evolution which favors the following recombination:

$$I_2^- + I_2^- \rightarrow I^- + I_3^-$$

As I_2^- diffuses less rapidly than OH, we can even understand why G_{I_3} becomes superior to the initial value of $G_{H_2O_2}$. Moreover, if one part of the direct effect interest the ion pairs $(I^{-}Li^{+})$ present at the highest concentrations in LiI, we may think that this also enhances the formation of molecular iodine if the positive ion created by such a direct effect reacts with I⁻, for instance, according to

$$(I^-, Li^+)^+ + I^- \rightarrow Li + I_2 \xrightarrow{+I^-} I_3^-$$

Li atoms ultimately reduce water into H_2 .

Figure 8 shows the total oxidation yield of I⁻, $G_{ox} = G_{I_2}^{-}$ + $2G_{I_3}$, as a function of f_{I} . This indicates that the yield increases from 2.7 ($\simeq G_{OH}$) to almost 4.8, which is consistent with the values observed by some authors for $f_{I^-} \sim$ $0.2.^7$ Then G_{ox} continues to increase being, according to the final balance, approximatively equal to the reduced species yield, $G_{e_{m}} + 2G_{H_2}$. In the end the increase becomes almost linear which proves that the direct effect is far more efficient than the indirect effect. Consequently, if we identify this linear increase with expression A we obtain the following values:

$$G_{\rm i} = 4.8$$
 $G_{\rm d} = 7.3$

This value of G_d is the sum of two processes, one leading to I_2^- (Figure 2), the other leading to I_3^- .

The value of G_d (7.3) is really very high. We may notice in this respect that the ionization potential of I^- (5 eV) is much lower than that of water. Moreover, the mechanism mentioned above which involves direct effect on ions pairs is energetically very favorable, since one single ionization would be enough to create the two equivalents necessary for the molecular iodine formation.

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Phases and Interfacial Tensions of Aqueous/Hydrocarbon Systems Containing Low-Equivalent-Weight Organic Salts

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Miscibility diagrams for systems containing a hydrocarbon, water, a low-equivalent-weight organic salt, an alcohol, and, in some cases, an inorganic salt do not undergo a sharp discontinuous transition as the equivalent weight of the organic electrolyte is increased into the surfactant range, where micellar and other aggregates are known to form. Three-phase regions are found with compounds of low degrees of alkyl substitution ("protosurfactant") as they are with surfactants. Scans of phase volumes as the concentration of one component is changed are qualitatively similar for the two, although the concentration range over which the middle phase (sometimes characterized as a microemulsion with surfactants) persists is wider for the protosurfactant systems investigated here than is usual with surfactants. Low interfacial tensions (IFT) are observed; values are ultralow (of the order of 10^{-3} dyn/cm) in some cases between adjacent phases (lower vs. middle or middle vs. upper). These low tensions, the sharpness of transitions between two and three phases with compositional changes, and observations of opalescence imply that the postulation of proximity to critical end points suggested to correlate such properties of surfactant systems is also applicable here.

In recent years, we have investigated the solubilization of hydrocarbons in water by a variety of organic salts, used both with and without alcohols.¹⁻⁷ Most of the organic salts were low-molecular-weight alkylbenzenesulfonates, carboxylates, and salicylates. These are in the class re-ferred to as "hydrotropes",⁸⁻¹³ substances which enhance the solubility in water of compounds normally only slightly soluble. One of our motivations has been in elucidation of the chemistry of enhanced oil recovery by micellar flooding. The systems in micellar flooding are extremely complex; at least five classes of components-water, hydrocarbon, surfactant, cosurfactant (usually an alcohol), and inorganic salt—are involved, and several of them may be mixtures of many compounds. The criterion usually

(10) McKee, R. H. U.S. Patent 2 308 564, 1943.
(11) McKee, R. H. Ind. Eng. Chem. 1946, 38, 382.
(12) Migita, N.; Nakano, J.; Hirai, S.; Taktsuka, C. Sen'i Gakkaishi 1956. 12. 632

⁽¹⁾ Ho, P. C.; Ho, C.-H.; Kraus, K. A. J. Chem. Eng. Data 1979, 24, 115

Ho, P. C.; Ogden, S. B. J. Chem. Eng. Data 1979, 24, 234.
 Ho, P. C.; Kraus, K. A. J. Colloid Interface Sci. 1979, 70, 537.
 Ho, P. C.; Burnette, R. G.; Lietzke, M. H. J. Chem. Eng. Data 1980, 25, 41.

⁽⁵⁾ Ho, P. C.; Kraus, K. A. J. Chem. Eng. Data 1980, 25, 132.

 ⁽⁶⁾ Ho, P. C.; Kraus, K. A. Soc. Pet. Eng. J. 1982, 22, 363.
 (7) Ho, P. C. J. Phys. Chem. 1981, 85, 1445.

 ⁽⁸⁾ Hofmeister, F. Arch. Exp. Pathol. Pharmakol. 1888, 25, 1.
 (9) Neuberg, C. Biochem. Z. 1916, 76, 107.

⁽¹³⁾ Rath, H. Tenside 1965, 2, 1.