The value, -406.50 ± 0.33 kcal·mole^{-1}, for the heat of combustion of liquid 1,3-dioxolane is in close agreement with the value, -406.4 ± 0.9 kcal·mole^{-1}, reported by Fletcher *et al.*[5] Skuratov *et al.*[8] have reported the value -407.6 kcal·mole^{-1}.

Kankaanperä measured the free energy difference between the liquid 2,4-dimethyl-1,3-dioxolanes[3] and assuming that $\Delta S = 0$ for these isomers, we can estimate that $\Delta H° = \Delta G° = -0.36$ kcal·mole^{-1}, the *cis* form being the more stable. Now it is possible to evaluate the heats of formation of both liquid isomers since the experimental result can be expressed as follows:

$$-100.58 = 0.671 \cdot \Delta H_f°(\mathrm{l}, cis) + 0.329[\Delta H_f°(\mathrm{l}, cis) + 0.36]$$

Thus $-\Delta H_f°(\mathrm{l}, cis) = 100.70$ and $-\Delta H_f°(\mathrm{l}, trans) = 100.34$ kcal·mole^{-1}.

Using a previously proposed bond-bond interaction scheme for aliphatic oxygen compounds,[9] we can write:

1,3-Dioxolane: $\Delta H_f°(\mathrm{g}) = 3\Delta H_a°(\mathrm{C, g}) + 6\Delta H_a°(\mathrm{H, g}) + 2\Delta H_a°(\mathrm{O, g}) - \sum E_b - 2\Gamma_{\mathrm{COC}} - \Delta_{\mathrm{OCO}} + [S]$

2-Me-1,3-d.: $\Delta H_f°(\mathrm{g}) = 4\Delta H_a°(\mathrm{C, g}) + 8\Delta H_a°(\mathrm{H, g}) + 2\Delta H_a°(\mathrm{O, g}) - \sum E_b - 4\Gamma_{\mathrm{CCO}} - 2\Gamma_{\mathrm{COC}} - \Gamma_{\mathrm{OCO}} - \Delta_{\mathrm{OCO}} + [S]$

cis-2,4-diMe: $\Delta H_f°(\mathrm{g}) = 5\Delta H_a°(\mathrm{C, g}) + 10\Delta H_a°(\mathrm{H, g}) + 2\Delta H_a°(\mathrm{O, g}) - \sum E_b - 5\Gamma_{\mathrm{CCO}} - 2\Gamma_{\mathrm{COC}} - \Gamma_{\mathrm{OCO}} - \Gamma_{\mathrm{CCC}} - \Delta_{\mathrm{OCO}} - \Delta_{\mathrm{CCO}} - S_{15}^{\mathrm{HH}} + [S]$

By substituting the experimental heats of formation and the heats of atomization of the elements, the bond energies (E_b) and the values of the group increments given in Ref. 9 in the above equations, the values 6.67, 5.46 and 6.72 kcal·mole^{-1} are obtained for the apparent strain $[S]$[10] of the 1,3-dioxolane ring in these compounds, respectively. On average $[S] = 6.3$ kcal·mole^{-1}.

These and other data for "oxanes" will be discussed in detail in a paper which deals with bond-bond interactions of "oxanes".[11]

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Mesomorphous Phases in Systems of Water-Nonionic Emulsifier-Hydrocarbon

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Our work on the influence of mesomorphous phases on the stability of emulsions showed the existence of a large region with a mesomorphous phase possessing a lamellar structure in the system water—nonionic emulsifier—*p*-xylene and gave also convincing evidence of the stabilizing action on the emulsion by the presence of this phase.[1] Since these results appeared to make a contribution to the understanding of hitherto unexplained behaviour of emulsions, we found further investigations along these lines to be of general value. The results of these investigations have confirmed the hypothesis of stabilizing influence of the mesomorphous phases.[2]

The investigations have included phase equilibria in three component systems: water—nonylphenol nona-ethylene glycol ether—*p*-xylene (Fig. 1 A), water—nonylphenol di-ethylene glycol ether—p-xylene (Fig. 1 B) and water—nonylphenol nona-ethylene glycol ether—hexadecane (Fig. 1 C). The emulsifiers were commercial and contain consequently each a distribution of the number of ethylene glycol ether groups, but contain less than 0.01 % of foreign substances, when carefully purified from polyglycols.

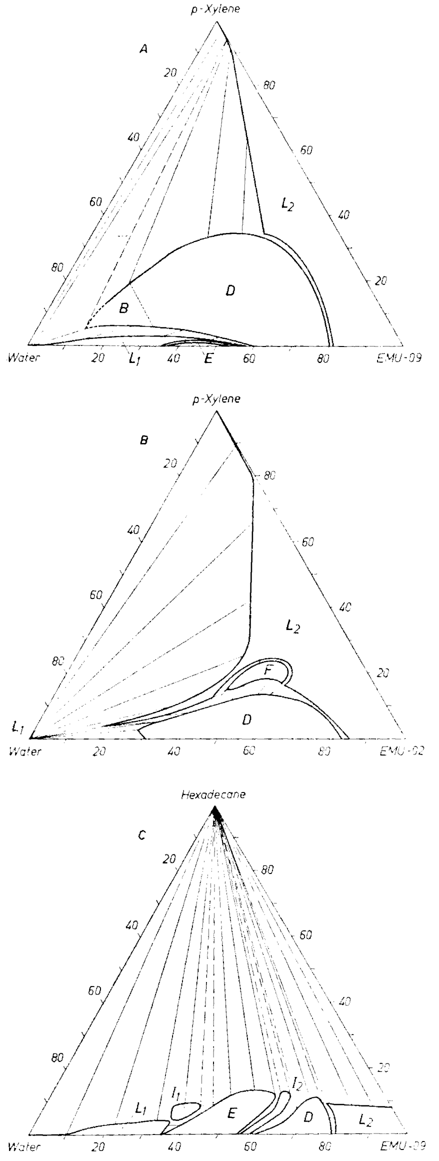

Fig. 1. Phase diagrams for the three component systems:

A. Water—nonylphenol nona-ethylene glycol ether (EMU-09)—p-xylene at 20°C.
B. Water—nonylphenol di-ethylene glycol ether (EMU-02)—p-xylene at 20°C.
C. Water—nonylphenol nona-ethylene glycol ether (EMU-09)—hexadecane at 20°C.

As shown by the figures the systems contain several mesomorphous phases in addition to the solution. The regions for the different phases were determined by means of visual observation of the phase changes at the addition of one component and by means of centrifugal separation followed by determination of the composition of the phases. Different mesomorphous phases were identified and characterized by their texture under the microscope with crossed nicols and by means of their X-ray diffraction pattern.[3,4]

X-Ray investigations showed that the mesomorphous phase in region E (Figs. 1 A and C) has a two-dimensional hexagonal structure with long hexagonally disposed rod-shaped aggregates, consisting of amphiphile molecules oriented with the hydrophilic groups outwards to the water.[4,5] The mesophase in region F (Fig. 1 B) has also a two-dimensional hexagonal structure and is built up of long rod-shaped aggregates consisting of an aqueous core surrounded by amphiphile molecules oriented with the hydrocarbon chains facing outwards.[4] The mesomorphous phase D and B has a lamellar structure with alternating water and amphiphile layers.[4,6] The phases in regions I_1 and I_2 are optically isotropic and X-ray diffraction data indicate cubic structures similar to those previously reported.[7]

A comparison of Figs. 1 A and 1 B shows the changes of phase equilibria when the hydrophilic character of the emulsifier molecule is reduced, when the mean number of the ethylene glycol ether groups of the molecule is being reduced from nine to two. The concentration of the onset of the solubilizing of water in the L_2 region is increased, the size of the D-phase area is reduced to a high degree, the B-phase, the micellar solution L_1 and the hexagonal phase E have disappeared. All these changes can easily be referred to the reduced hydrophilic properties due to shortened ethylene glycol ether chain.

The differences of the phase behaviour when the polarizable p-xylene is being replaced by hexadecane (Figs. 1 A and 1 C) is even more pronounced. The L_2 area is reduced to a small region, where the emulsifier dissolves the hydrocarbon, and the area of the D-phase is also reduced to a high degree. The E-phase is able to solubilize considerably more hexadecane than *p*-xylene. The continuous L_1 region in Fig. 1 A is transformed into three isotropic phases; one liquid and two viscous isotropic ones (I_1 and I_2) in Fig. 1 C.

The reason for this markedly changed phase behaviour is partly to find in the difference of the polarizability of the hydrocarbon which has an influence on the site of the molecules in the micells as shown by NMR investigations.[8] This would explain the change in L_1 area when *p*-xylene is replaced by hexadecane, but could scarcely explain the excess solubility of the hexadecane in the E-phase. This behaviour is considered to have a close connection with the packing of the xylene molecules and the benzene part of the emulsifier, a fact that may favour a lamellar structure.

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Bacterial Carotenoids XXVIII*

C_{50}-Carotenoids

4. Stereochemistry of the Terminal Double Bonds of *Dehydrogenans*-P439

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A year ago we reported on the structure determination of dehydrogenans-P439 (*1*).[1] The configuration around the terminal double bond was not established and was arbitrarily chosen as *trans* between the two largest substituents. Support for the *trans*-configuration is now obtained from the aldehyde signal in the PMR-spectrum of P439-dialdehyde (*2*), compared with data recently reported for related *cis* and *trans* α,β-unsaturated aldehydes (Table 1, p. 1058).

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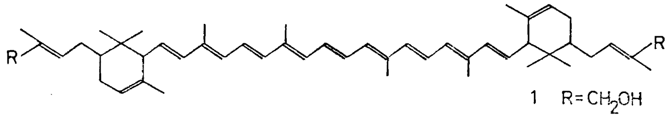

1 $R=CH_2OH$
2 $R=CHO$