*Infrared Spectra and Rotational Isomerism of Some Long-chain n-Alkoxy Ethanols**

By T. K. K. SRINIVASAN, C. I. JOSE and A. B. BISWAS

(Received May 14, 1964)

In connection with a program on water evaporation control, the infrared spectra of a series of alkoxy ethanols, $CH_3(CH_2)_nO-CH_2-CH_2-OH$, where $n=13$, 15, 17, 19 and 21, have been investigated in various physical states. These studies show that the ethanols exhibit rotational isomerism and that the changes in the spectra can be related to definite geometrical arrangements of the molecule.

The alkoxy ethanols have a long chain of CH_2 groups as well as an OCH_2CH_2OH group. As a liquid or in solution, molecules containing long CH_2 chains give a large number of absorption bands because of the various conformations possible by rotation around the single bonds.(1) These sometimes show up as broad bands on account of overlapping. In the crystalline state, on the other hand, only a single rotational species is usually accommodated, and the absorption pattern is considerably simplified.(2) In polyethylene(3) and certain other long-chain compounds(4,5) additional bands appear as a result of the specific molecular arrangement of the CH_2 chain (orthorhombic) in the crystal favorable for intermolecular coupling. The $(O-CH_2-CH_2-O)$ group can be considered to take up independently a gauche or trans configuration by rotation around the single bonds. However, the presence of a hydroxyl group suitably

---

* Communication No. 591 from the National Chemical Laboratory, Poona-8, India.

1) S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, New York (1954).

2) N. Sheppard, *Advances Spectroscopy*, **1**, 288 (1959).

3) S. Krimm, C. Y. Liang and G. B. B. M. Sutherland, *J. Chem. Phys.*, **25**, 549 (1956).

4) D. Chapman, *J. Chem. Soc.*, **1957**, 4489.

5) R. G. Snyder, *J. Mol. Spectroscopy*, **4**, 411 (1960); **7**, 116 (1961).

located for intramolecular hydrogen bonding⁶⁾ with ether oxygen can be expected to influence the type of configuration taken by the molecule.

It is known that the compounds of the type X–CH_2–CH_2–X give four rocking modes, two each corresponding to the gauche (A and B) and trans (A_u and B_g) configurations with C_2 and C_{2h} symmetries respectively, in the $1000\ cm^{-1}\sim700\ cm^{-1}$ region. While both the gauche modes are active, only the A_u trans mode is active in the infrared region. Though these modes are sensitive to changes in the remaining part of the molecule, they have been found useful in identifying rotational isomers of a large number of compounds.⁷,⁸⁾ Indirect evidence can also be obtained regarding the configuration of the (O–CH_2–CH_2–O) group by studies of the hydroxyl group attached to one of its CH_2 groups.

In the present study, the infrared spectra of alkoxy ethanols have been discussed and the configurations of the (O–CH_2–CH_2–O) group investigated in solution as well as in the liquid and solid states by analysis of the CH_2 rocking modes in the $1000\ cm^{-1}\sim700\ cm^{-1}$ region and of the hydroxyl stretching bands.

Experimental

The spectra were obtained either with a Perkin-Elmer model 221 instrument, equipped with an NaCl prism, or a Grubb Parsons model S3, with an LiF prism.

The preparation and purity of the alkoxy ethanols have been reported elsewhere.⁹⁾ A heating cell was constructed to obtain the spectra of solid and liquid films (Fig. 1) between sodium chloride plates at a few relevant temperatures. The reproducibility of the spectra upon repeated heatings or coolings of the substances was checked in situ; little variation in position and intensity was observed. The temperature during a run, as measured with a calibrated copper-constantan thermocouple, was maintained within ±1°C.

The spectra of solutions of octa-decoxy-ethanol (ODE) in carbon tetrachloride and carbon disulfide are also given (Fig. 1) to show their similarity with that of the liquid. The spectra of these compounds in carbon tetrachloride were studied particularly, using a variable path cell, in the hydroxyl-stretching region in order to elucidate the nature of the internal hydrogen bonding and of the rotational isomerism of these molecules.

Results and Discussion

Since the absorption characteristics of the different alkoxy ethanols are alike, the discussion will center upon ODE.

In the CH stretching region strong bands at $2925\ cm^{-1}$ and $2850\ cm^{-1}$ are observed in both the solid and liquid states; they are ascribed to the CH stretching modes of the CH_2 and CH_3 groups.¹⁰⁾ The additional band at 2958 cm^{-1} observed in the solid state is grouped with a similar sharpening and doubling of the bands near $1110\ cm^{-1}$ and $1060\ cm^{-1}$ observed on liquid-solid transformation.

The absorption bands at 1466 (S) and 1376∼1379 (W) observed in the solid and liquid states are assigned to the CH deformation of the CH_2 and CH_3 groups.¹⁰⁾ The band at $1471\ cm^{-1}$, which appears as a shoulder in the solid state and which is observed as a separate band in the compound $CH_3(CH_2)_{17}(O\text{–}CH_2\text{–}CH_2)_2OH$ is assigned to the CH deformation mode of the CH_2 groups adjacent to oxygen. The absorption bands in the $1416\sim1403\ cm^{-1}$ region are similar to those observed for normal higher alcohols at $1412\ cm^{-1}$; they are ascribed to the C–O stretching or O–H deformation modes.¹⁰⁾

The $1360\ cm^{-1}\sim1150\ cm^{-1}$ region in the spectra of the solid alkoxy ethanols features a band progression of irregular intensity, varying from medium to weak. In the liquid state, they broaden out completely, as is observed in other long-chain compounds; they are ascribed to the CH_2 wagging modes. Below $1150\ cm^{-1}$ strong broad bands at $1117\ cm^{-1}$ and $1056\ cm^{-1}$ are observed in the liquid state. The band near $1050\ cm^{-1}$ is characteristic of a primary alcohol¹⁰⁾ and is considered to arise either from an OH deformation or C–O stretching mode. However, normal vibration calculations and the analysis of *n*-paraffin spectra indicate skeletal modes of hydrocarbon chains (C–C stretching) in the $1050\ cm^{-1}\sim950\ cm^{-1}$ region.¹¹⁾ The observed enhanced intensity of the band at $1058\ cm^{-1}$ is, therefore, due to the overlapping of both the C–O stretching or O–H deformation and the skeletal modes. The band progression from $1050\ cm^{-1}$ to $950\ cm^{-1}$ would correspond to the various C–C skeletal modes.¹²⁾

In a large number of ethers, a band at about $1120\ cm^{-1}$ is noticed; in dimethyl ether this has been ascribed to an antisymmetric C–O–C stretching vibration. Hence, the band at $1117\ cm^{-1}$ may be assigned to a C–O–C stretching mode. In the solid state, the two

---

6) S. Mizushima, T. Shimanouchi, T. Miyazawa, K. Abe and M. Yasumi, *J. Chem. Phys.*, **19**, 1477 (1951).

7) A. Miyake, *J. Am. Chem. Soc.*, **82**, 3040 (1960).

8) J. K. Brown, N. Sheppard and D. M. Simpson, *Phil. Trans.*, **A247**, 35 (1954).

9) A. V. Deo, N. R. Sanjana, S. B. Kulkarni, M. K. Gharpurey and A. B. Biswas, *Nature*, **187**, 870 (1960).

10) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons., New York (1958).

11) R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta*, 19, 85, 117 (1963).

12) M. Tasumi, T. Shimanouchi, A. Watanabe and R. Goto, ibid., **20**, 629 (1964).

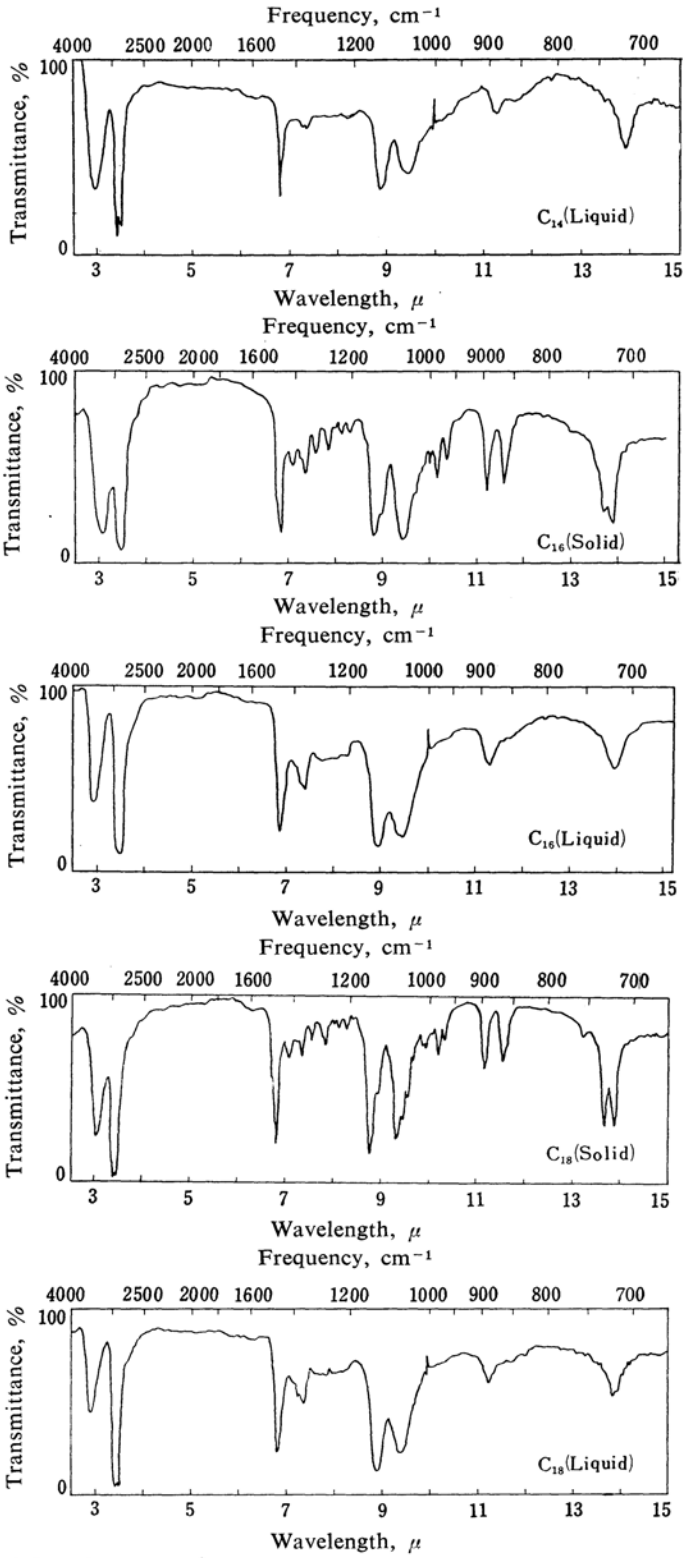
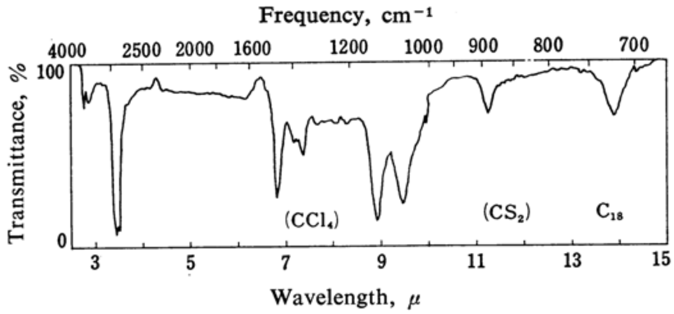
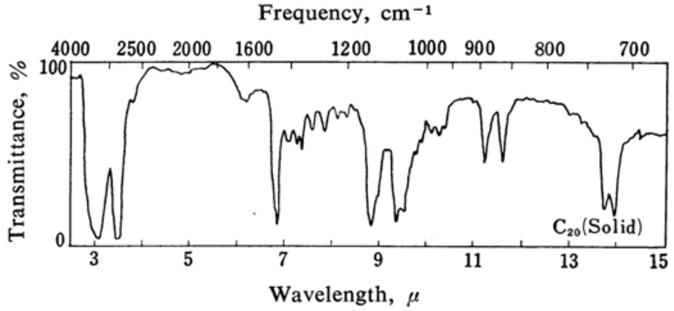
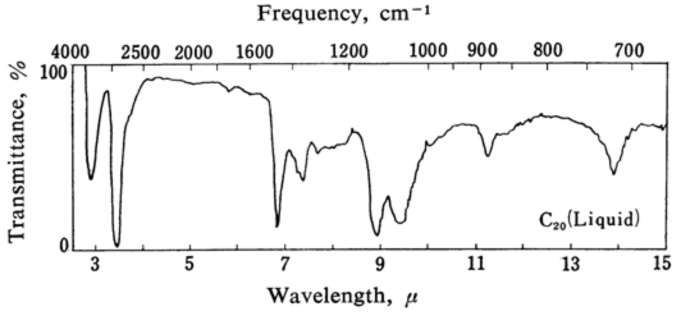


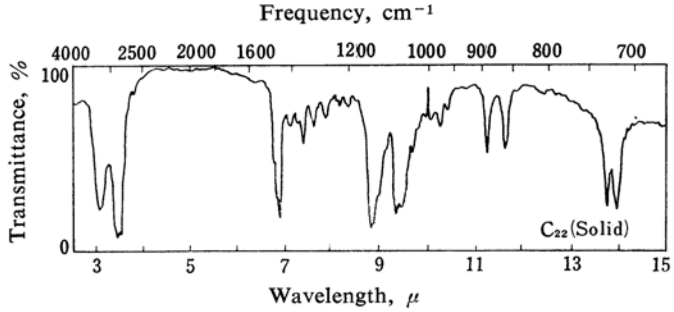
Fig. 1. Infrared spectra of

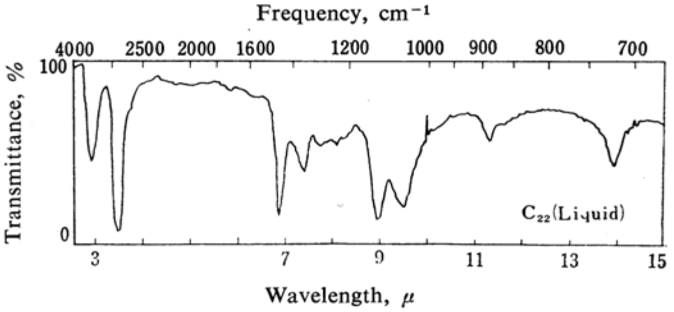
$CH_3(CH_2)_{13}$-O-CH_2-CH_2-OH : C_{14} (liquid)
$CH_3(CH_2)_{15}$-O-CH_2-CH_2-OH : C_{16} (solid) ; C_{16} (liquid)
$CH_3(CH_2)_{17}$-O-CH_2-CH_2-OH : C_{18} (solid) ; C_{18} (liquid)











$CH_3(CH_2)_{17}$-O-CH_2-CH_2-OH : C_{18} (solution)
$CH_3(CH_2)_{19}$-O-CH_2-CH_2-OH : C_{20} (solid) ; C_{20} (liquid)
$CH_3(CH_2)_{21}$-O-CH_2-CH_2-OH : C_{22} (solid) ; C_{22} (liquid)

bands in the liquid are found doubled and sharpend at 1117 cm^{-1} and 1137 cm^{-1} and at 1058 cm^{-1} and 1071 cm^{-1} respectively. The sharpening and doubling of bands on liquid-solid transformation observed in this region and also in the CH stretching region (see above) appears to be due to an imposed symmetry in the crystalline state or to changes due to hydrogen bonding rather than to rotational isomerism. The splitting of bands due to intermolecular effects[5] has so far been established only for CH_2 chains among long-chain compounds. However, a similar doubling and sharpening of bands observed in the case of $CH_3(CH_2)_{17}(O–CH_2–CH_2)_2OH$, in which the splitting of the CH_2 rocking at 720 cm^{-1} is absent (see below), indicates that they are not connected with the intermolecular interaction of the long sequence of CH_2 groups.

The 950 cm^{-1}～800 cm^{-1} Region. — In this region considerable changes are observed in the spectra of alkoxy ethanols. In the liquid state or in solution, only a band of medium intensity is observed at 889 cm^{-1}. This is in good agreement with that observed by Chalkowsky[13] for the lower liquid homologues at 892 cm^{-1}. In the solid state, on the other hand, two sharp bands of almost equal intensity (medium) at 864 cm^{-1} and 892 cm^{-1} are observed, in addition to a weak band at 962 cm^{-1}. From the measurement of the areas under the bands during the liquid-solid transformation, it was found that the band at 864 cm^{-1} developed at the expense of that at 889 cm^{-1}. The development of the band at 864 cm^{-1} at the expense of that at 889 cm^{-1} during crystallization may be explained as the conversion of one of the rotational isomer into another. The assignment of the bands to the two rotational isomers was made by comparison with disubstituted ethanes, particularly ethylene glycol, its derivatives and polymers. It has been shown by theoretical calculations[14] that in disubstituted ethanes the CH_2 rocking frequencies increase in the order A_u(trans)< B(gauche)<A(gauche)<B_g(trans), so that the gauche mode frequencies lie between those of the trans modes. This has been well established in the case of the simple disubstituted ethanes $X–CH_2–CH_2–Y$, where X and Y are CH_3, Cl, Br, SCN, etc. Miyake[7] recently assigned CH_2 rocking modes of the $(O–CH_2–CH_2–O)$ group in ethylene glycol, its derivatives and polymers on the above basis. He found that the A_u type mode of the $(O–CH_2–CH_2–O)$ group occurs near 850 cm^{-1}, which is about 100 cm^{-1} higher than in compounds where the two oxygens are replaced by other atoms, and that the spacing between the two A and B gauche forms is approximately 20 cm^{-1}. In the present case, therefore, the bands 864 cm^{-1} and 964 cm^{-1} are assigned to the CH_2 trans modes A_u and B_g of the $(O–CH_2–CH_2–O)$ group respectively and the band at 889 cm^{-1}, to the two gauche modes coalesced into one. A single band for a gauche mode has also been observed at 895 cm^{-1} for polyethylene terephthalate.[15] The formation of the cis species with a higher symmetry, C_{2v}, may be a possible explanation for a single CH_2 rocking mode for the gauche form.[16]

The above assignment indicates that the $(O–CH_2–CH_2–O)$ group in alkoxy ethanols has a predominantly gauche configuration in a liquid or in solution, while in the crystalline state both the gauche and trans forms are present in approximately equal numbers. The presence of the gauche configuration in solution is supported by observations in the hydroxyl-stretching region. In the case of polyethylene glycol, it has been concluded by Miyake[7] that a gauche configuration is predominant in the melt, while both the gauche and trans forms exist in the solid state. In contrast, Davison,[17] and Kuroda and Kubo,[18] on the basis of a different assignment of the CH_2 rocking modes, have arrived at a complete gauche configuration in the solid state. Recently Miyazawa[19] has made calculations for the infrared frequencies and molecular conformations of various polymers by a normal coordinate treatment and compared the results with the observed results. In the case of polyethylene glycol these studies have shown that the most likely structural model consists of trans-gauche-trans (TGT) conformations of the $(O–CH_2–CH_2–O)$ group. Further recent X-Ray diffraction studies[20] of the long-chain alcohols with an odd number of carbon atoms have shown that both trans and gauche configurations of the OH group are present in the crystalline state.

The 730 cm^{-1}～720 cm^{-1} Region.—The bands in this region are attributed to the methylene rocking modes of the long hydrocarbon chain. The band at 719 cm^{-1} in the liquid state splits into two bands, at 729 cm^{-1} and 719 cm^{-1}, of almost equal intensity in the solid state, as observed in the case of polyethylene[3] and certain long-chain compounds. Chapman[4] has shown that the presence of two bands of the

---

[13] N. Chalkowsky, R. H. Martin and R. Van Nechal, *Bull. Soc. Chem. Belges.*, **65**, 458 (1956).

[14] L. Nakagawa and S. Mizushima, This Bulletin, **28**, 589 (1955).

[15] A. Miyake, *J. Polymer Sci.*, **38**, 486 (1959).

[16] Y. Kuroda and M. Kubo, ibid., **26**, 323 (1957).

[17] W. H. T. Davison, *J. Chem. Soc.*, **1955**, 3270.

[18] Y. Kuroda and M. Kubo, *J. Polymer Sci.*, **36**, 453 (1959).

[19] T. Miyazawa, K. Fukushima and Y. Ideguchi, *J. Chem. Phys.*, **37**, 2764 (1962).

[20] A. Watanabe, This Bulletin, **36**, 336 (1963).

same intensity indicates an orthorhombic packing of the CH_2 chains, while both the hexagonal and triclinic packing give rise to a single band in this region. Using this criterion, the long CH_2 chain in alkoxy ethanols would be expected to have an orthorhombic packing (orthorhombic sub-cell). It is interesting to note that the compound $CH_3(CH_2)_{17}(O\text{-}CH_2\text{-}CH_2)_2OH$ shows only a single band[21] at 729 cm^{-1} in the solid state, while the absorption pattern in the 950~800 cm^{-1} regions remains similar to that of the alkoxy ethanols.

Solution Spectra.—ODE (Fig. 2) in a dilute carbon tetrachloride solution (0.005 M~0.01 M) shows a strong band at 3600 cm^{-1} and a weak band at 3636 cm^{-1}. These, as in the methoxy ethanol reported on by Flett[22] and by Kuhn[23], would correspond to monomer units of the intramolecularly bonded gauche, and trans or nonbonded gauche, forms respectively. At higher concentrations until the solubility limit at about 0.5 M is reached, a dimer band at 3480±10 cm^{-1} is observed which increases in intensity with the concentration at the expense of the band at 3600 cm^{-1}.* at 0.1 M, in addition to the dimer and monomer bands at 3484 cm^{-1} and 3636 cm^{-1} respectively. In the liquid state ODE shows only the broad dimer band at 3465 cm^{-1}. The ODA (octadecanol) shows, on the other hand, a broad polymer band at 3350 cm^{-1} in the liquid and bands at 3270 cm^{-1} and 3230 cm^{-1} in the solid state.[24]

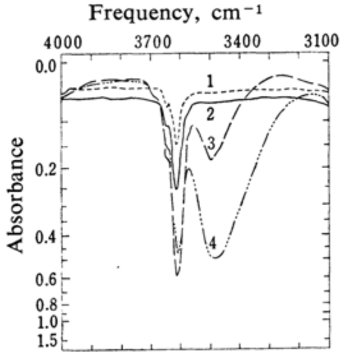


Fig. 2. Octadecoxy ethanol (ODE) in carbon tetrachloride.

1 ------ 0.005 M (3 mm. path length)
2 —— 0.01 M (3 mm. path length)
3 - - - 0.1 M (1 mm. path length)
4 -·-·- 0.5 M (0.2 mm. path length)

During solidification the band at 3465 cm^{-1} in ODE is slowly shifted to lower frequencies; in the crystalline solid, it is located as a strong broad band at 3260 cm^{-1}. The dimer formation of alkoxy ethanols in the liquid state, in contrast to higher polymers by normal long chain alcohols in the liquid state and even in solution, supports the earlier conclusion that, in the liquid state, the alkoxy ethanols exist predominantly in gauche configuration.

Summary

The infrared spectra of *n*-alkoxy ethanols $CH_3(CH_2)_nO\text{-}CH_2\text{-}CH_2\text{-}OH$ with $n=13$, 15, 17, 19 and 21 have been obtained in the solid and liquid states as well as in solution. From a study of the CH_2 rocking modes of the $(O\text{-}CH_2\text{-}CH_2\text{-}O)$ group at 893 cm^{-1} and 864 cm^{-1} during liquid-solid transformation and from the solution spectra in the hydroxyl-stretching region, it has been shown that this group exists predominantly in a gauche configuration in liquids or in solution, while both gauche and trans configurations are present in the solid state.

The authors are grateful to Professor Sanichiro Mizushima and Drs. Ichiro Nakagawa and Mitsuo Tasumi of the University of Tokyo, Japan, for their valuable comments and for communicating results on the infrared spectra of normal higher alcohols prior to publication.

We are also grateful to Dr. (Miss) S. B. Kulkarni for supplying the purified compounds used in the present studies.

National Chemical Laboratory
Poona-8, India

---

[21] Unpublished work.

[22] M. ST. C. Flett, *Spectrochim. Acta*, **10**, 21 (1957).

[23] M. Kuhn, W. Lüttke and R. Mecke, *Z. Anal. Chem.*, **170**, 106 (1959).

* The octadecanol (ODA) on the other hand shows a polymer band 3363 cm^{-1}.

[24] M. M. Davies, *J. Chem. Phys.*, **8**, 577 (1940).