Extent of Hydration of Ethers in Aqueous Solution

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The extent of hydration of ethers in aqueous solution was determined by means of the deviation of fluidities measured at different concentrations from those calculated by the Kendall equation. For dioxane, ethylene glycol dimethyl ether, and diethylene glycol dimethyl ether, this deviation went through a maximum at compositions corresponding to 2.03 ± 0.05 water molecules per ether linkage, indicating that the highest hydration of each ether oxygen is with two water molecules. At those compositions, the calculated fluidities were between 2.1 and 3.5 times greater than those measured.

THE PURPOSE of this work is to ascertain how many molecules of water are associated with each ether linkage in water-ether mixtures at room temperature. The extent of hydration of ether bonds is of current theoretical interest in physicochemical studies of nonionic surfactant solutions, particularly as it affects the hydrodynamic volume of the micelles (*1, 2, 3, 8*). Nonionic surfactants are based largely on long-chain alcohols or alkyl phenols into which a hydrophilic part, consisting of (—CH_2-CH_2-O—) repeat units, is incorporated by the addition of ethylene oxide (EO).

The model compounds chosen were dioxane, ethylene glycol dimethyl ether, and diethylene glycol dimethyl ether, because extensive data on their aqueous solutions at 25° C. exist in the literature, covering the whole range of concentration (*4, 9, 10, 11, 12*).

Association in a binary liquid system can usually be detected by the deviation of the experimental values of an intensive property of the solutions from the additive values of the property, calculated by linear interpolation between the two values of that property of the two pure components as a function of composition. The stoichiometric composition of a complex formed between the two components is often that composition at which this deviation reaches a maximum. Among properties very sensitive to association is the fluidity, ϕ. Fluidity is the reciprocal of the viscosity.

The Kendall equation (*7*)

$$\log \phi_{12} = x_1 \log \phi_1 + x_2 \log \phi_2 \qquad (1)$$

where x represents mole fraction and subscripts 1 and 2 refer to the two components, is obeyed by ideal or nearly ideal solutions (*5*), if the fluidities of the two pure liquids are of the same order of magnitude (*6*). Association between the two liquid components causes the observed fluidity of their mixtures to be smaller than that calculated by Equation 1 (*5, 6*).

The effect of association on the deviation of the experimentally observed from the calculated values is much larger for fluidity than for most other properties. For instance, in the system water-dioxane, the maximum deviation in fluidity is somewhat larger than the experimental fluidity itself: It amounts to 108% of the latter. By contrast, the maximum deviation of the refractive index and of the density amounts to only 3% of the experimentally observed values (*10*).

EXPERIMENTAL

A few viscosity and density measurements were made for each of the three systems to supplement the values reported in the literature, in order to determine accurately the composition corresponding to the maximum deviation in fluidity. The three ethers were purified as previously described (*10, 11, 12*). The mixtures were prepared in 100-gram batches by weighing out the two liquids to the nearest milligram.

Densities were determined at 25.00° ± 0.01° C. with a Sprengel-Ostwald pycnometer of 25-ml. capacity. Duplicate measurements were identical within ±0.00003 gram per ml. or better. Viscosities were measured at the same temperature with a Cannon-Fenske viscometer, which had the flow time of 286.4 seconds for water. The kinetic energy correction was too small to be taken into account. Duplicate measurements, made on fresh portions of the solutions, agreed within 0.1 second.

RESULTS

The differences between calculated (Equation 1) and experimental fluidities as a function of molar composition are plotted in Figure 1 for the three binary systems. Each curve has only one maximum, but the three maxima are pronounced. When referred to the same standard values for the viscosity of water as used in (*4, 9, 11, 12*), respectively, the present experimental viscosities agree with the values obtained by interpolation of the published experimental viscosities as a function of composition within 0.1%, except for one point. As can be seen from Table I, the compositions at which the difference between the calculated and experimental fluidities reaches a maximum correspond closely to a ratio of two water molecules per ether link. This then represents the extent to which ethers can be hydrated. Evidently, each ether oxygen forms two hydrogen bonds with hydrogen atoms belonging to different water molecules.

DISCUSSION

Studies of nonionic surfactant solutions by means of vapor pressure measurements or the combination of light scattering and viscosity show that the degree of hydration of the micelles increased with increasing ethylene oxide chain length (*3*). For polyoxyethylated hexadecyl alcohols, the hydration increased from 2.0 water molecules per ethyl-

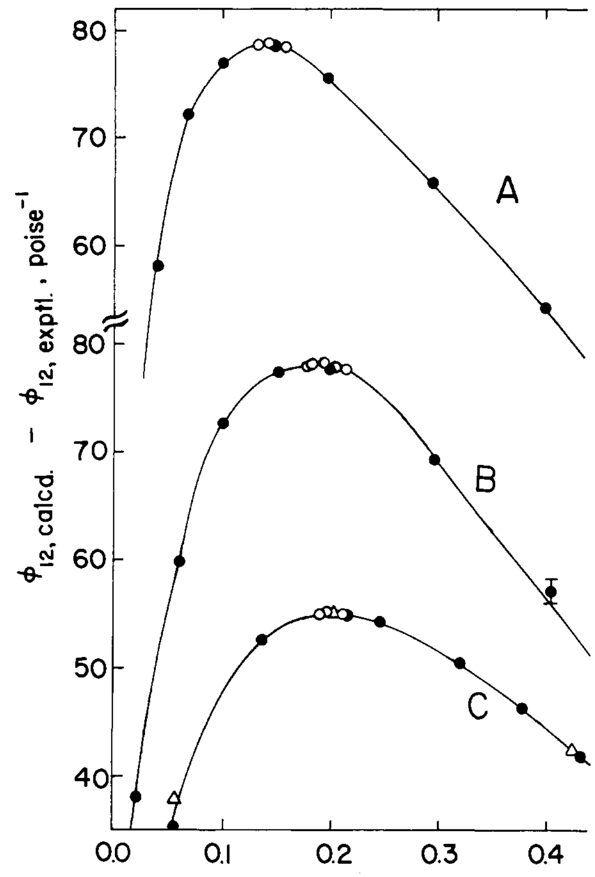

Figure 1. Difference between calculated and experimental fluidities of water-ether systems as a function of composition

○ Present work

A. Component 2, diethylene glycol dimethyl ether
● From (12)

B. Component 2, ethylene glycol dimethyl ether
● From (11)

C. Component 2, dioxane
● From (9)
△ From (4)

Table I. Composition and Fluidity of Aqueous Ether Solutions at the Point of Maximum Deviation in Fluidity

Component 2	x_2	x_1/x_2E[a]	$\phi_{12\,exptl}$, Poise^{-1}	$\phi_{12\,calcd}$,[b] Poise^{-1}	Dev.,[c] %
Dioxane	0.201	1.988	50.88[d]	105.90	108
Ethylene glycol dimethyl ether	0.193	2.091	50.47[e]	128.72	155
Diethylene glycol dimethyl ether	0.142	2.014	31.45[e]	110.27	251

[a] E is number of ether oxygens per molecule. [b] Calculated by Equation 1. [c] Deviation = 100 $(\phi_{12\,calcd.} - \phi_{12\,exptl.})/\phi_{12\,exptl.}$. [d] Based on viscosity of 0.008903 poise for water, to conform with (*9*). [e] Based on viscosity of 0.008940 poise for water, to conform with (*11, 12*).

ene oxide group for hexadecyl alcohol.7 EO to 5.7 for hexadecyl alcohol.21 EO (*2, 3*). The explanation of Elworthy and Macfarlane (*3*) that the increase in micellar hydration with higher ethylene oxide chain length is due to trapping of water within the mesh of polyoxyethylene chains is consistent with the present data on model ethers: Since two is the maximum number of water molecules that can be bound to each ether linkage by secondary valence forces, the excess water must be held by the micelle in a different manner.

LITERATURE CITED

(1) Becher, P., *J. Colloid Sci.* **16**, 49 (1961).
(2) Elworthy, P.H., McDonald, C., *Kolloid Z. Z. Polymere* **195**, 16 (1964).
(3) Elworthy, P.H., Macfarlane, C.B., *J. Chem. Soc.* **1964**, 311.
(4) Geddes, J.A., *J. Am. Chem. Soc.* **55**, 4832 (1933).
(5) Glasstone, S., "Textbook of Physical Chemistry," 2nd ed., p. 500, Van Nostrand, New York, 1951.
(6) Hatschek, E., "The Viscosity of Liquids," Chap. IX, Van Nostrand, New York, 1928.
(7) Kendall, J., *Medd. K. Vetenskapsakad. Nobelinst.* **2**, No. 25, 1 (1913); *C.A.* **7**, 2714 (1913).
(8) Kushner, L.M., Hubbard, W.D., *J. Phys. Chem.* **58**, 1163 (1954).
(9) Lind, J.E., Jr., Fuoss, R.M., *Ibid.*, **65**, 999 (1961).
(10) Schott, H., J. CHEM. ENG. DATA **6**, 19 (1961).
(11) Wallace, W.J., Mathews, A.L., *Ibid.*, **8**, 496 (1963).
(12) *Ibid.*, **9**, 267 (1964).

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Ultraviolet and Infrared Spectra of Some Nitroindoles and Nitroindole-3-carboxaldehydes

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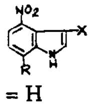
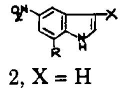
IN CONNECTION with recent synthetic studies in the indole field (*3-7*), a number of nitroindole-3-carboxaldehydes have been prepared (*3,4,6,7*) (Table II, 4a-7c) by the Vilsmeier reaction, involving formylation of the precursor nitroindoles (*5*) (1a-3c) prepared via the Fischer indole synthesis. In view of the usefulness of spectral data, particularly in the ultraviolet region, in structural studies (*9*) concerning the location of the nitro group in nitroindoles, the ultraviolet and infrared data which have been obtained are recorded (Tables I and II). The data in Table I supplement ultraviolet data recently summarized for nitro-3-acylindoles (*9,10*).



1, X = H
4, X = CHO



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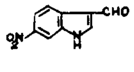
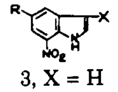
5, X = CHO



6



3, X = H
7, X = CHO

Nitroindoles, X = H:
1a, 2a, 3a, R = H
1b, 2b, 3b, R = CH_3
3c, R = OCH_3

Nitroindole-3-carboxaldehydes, X = CHO:
4a, 5a, 7a, R = H
4b, 5b, 7b, R = CH_3
7c, R = OCH_3
and 6

The data in Table I show that replacement of a hydrogen (4a, 5a) by a methyl group (4b, 5b) in the 7-position of 4-