

CHAPTER IV

CONCLUSIONS AND SUMMARY

Analysis of the reaction products showed that as the water concentration of the aqueous alcohol increased, there was less methyl n-butyl ether formed. The finding of less ether is in accord with the work of Bird, Hughes and Ingold²¹ who studied the uncatalyzed reaction of n-butyl bromide in alcohol-water mixtures containing 0.0 to 45 weight per cent water, inclusive. (Their work included a determination of the ether directly and of the alcohol by difference.)

The kinetics of solvolysis appear to be first-order in both hydroxide ion and butyl bromide within experimental error over the ranges investigated (see figures 5, 6, 7, 8 and 9). There was some indication that the first-order specific rates dropped slightly and that the rates tended to "level off" after about 600 minutes for runs 2-3 and 4-7, and after about 1000 minutes for runs 5-6.

Plots of per cent reaction (t_0, t_1, t_2, t_3, t_4) versus time-- the time taken directly from the log C versus t graphs-- show very nearly the same curvature for both hydroxide ion and for butyl bromide.

The least squares computations gave the following estimates of the total specific solvolysis rates:

25% methanol-75% water

$$k_{(\text{OH}^-)} = \frac{-2.681 - \ln(a-x)}{t_{\text{min.}}}; \quad k_{(\text{BuBr})} = \frac{-2.784 - \ln(b-x)}{t_{\text{min.}}};$$

50% methanol-water

$$k_{(\text{OH}^-)} = \frac{-2.080 - \ln(a-x)}{t_{\text{min.}}}; \quad k_{(\text{BuBr})} = \frac{-2.363 - \ln(b-x)}{t_{\text{min.}}};$$

75% methanol-25% water

$$k_{(\text{OH}^-)} = \frac{-1.941 - \ln(a-x)}{t_{\text{min.}}}; \quad k_{(\text{BuBr})} = \frac{-2.344 - \ln(b-x)}{t_{\text{min.}}};$$

Up to about fifty per cent reaction, the values ($t_{\frac{1}{4}}$, $t_{\frac{1}{2}}$, $t_{\frac{3}{4}}$) calculated from the least squares equations and those taken from the graphs (in the latter case, assuming ideal behaviour, i.e., linearity throughout the entire reaction for the plot of $\log C$ versus t) agree fairly well in hydroxide ion for all runs and, in butyl bromide for the 50-50 and 75-25 runs (% methanol-% water).

Several mechanisms for the total solvolysis of the alkyl halide (BuBr) in aqueous alcohol were proposed.

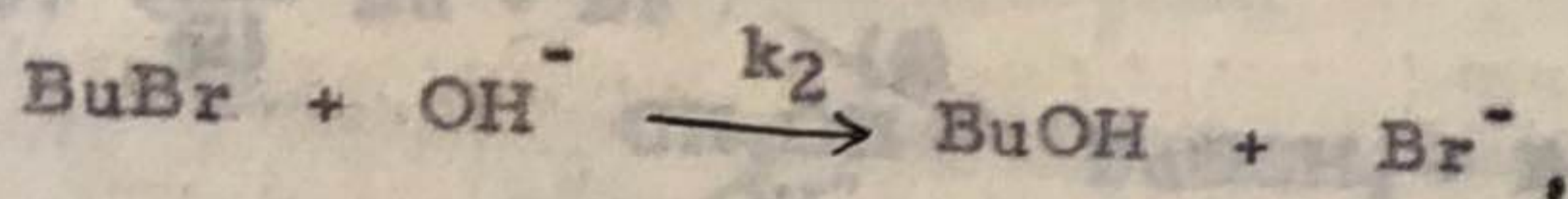
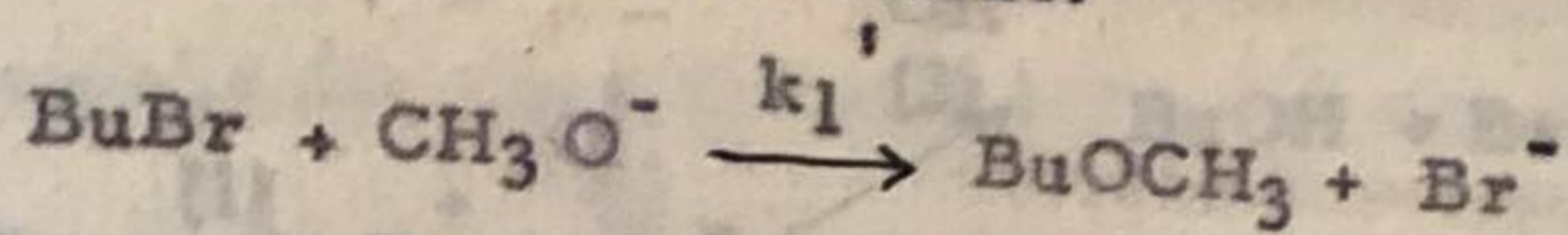
Values were calculated to test the mechanisms which

were proposed, and plots of the values (e. g.,

$\frac{\Delta x / \Delta t}{(b-x)}$ versus $(a-x)$; $\frac{\Delta x / \Delta t}{(b-x)_{\text{avg.}}}$ versus $(a-x)$, and so on)

were not rectilinear as predicted by theory.

A second proposed mechanism considered the following competing substitution reactions:



since: $\text{CH}_3\text{OH} + \text{OH}^- \rightleftharpoons \text{CH}_3\text{O}^- + \text{H}_2\text{O}$. The relationship for the rate of formation of bromide ion with time, t , and $x = (\text{Br}^-)_t$ is:

$$d(x)/dt = k_1 (\text{BuBr})(\text{CH}_3\text{O}^-) + k_2 (\text{BuBr})(\text{OH}^-)$$

$$d(x)/dt = k_1 (\text{BuBr}) + k_2 (\text{BuBr})(\text{OH}^-), \text{ where}$$

$k_1 (\text{CH}_3\text{O}^-) = k_1$. Using $(\text{BuBr})_0 = b$ and $(\text{OH}^-)_0 = a$, this rate will be:

$$d(x)/dt = k_1 (b-x) + k_2 (b-x)(a-x)$$

$$\frac{d(x)/dt}{(b-x)} = k_1 + k_2 (a-x), \text{ in which the terms in paren-}$$

theses represent concentrations in moles per liter. If the

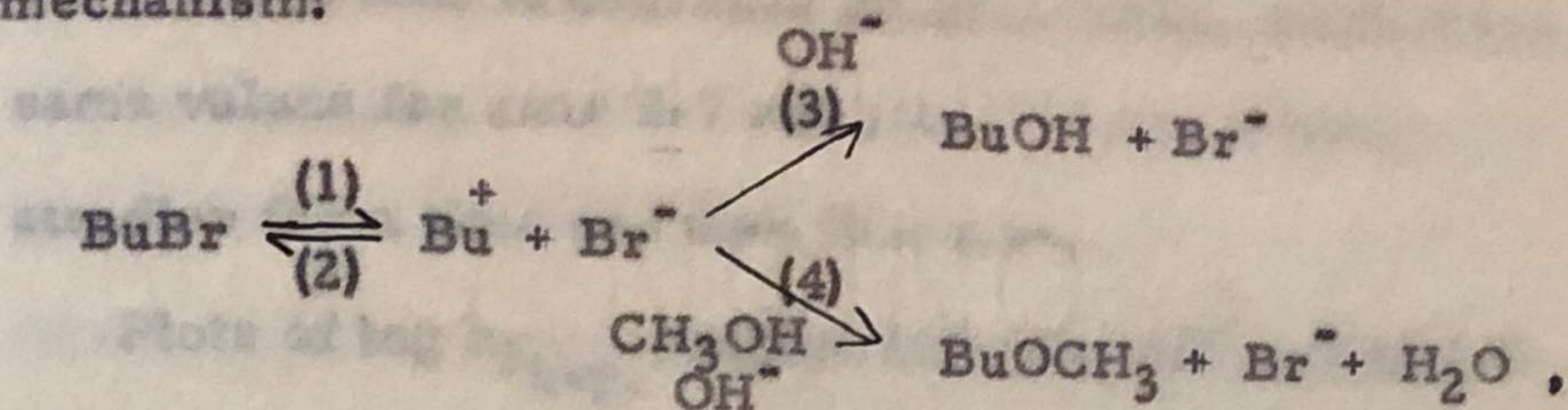
plot of $\frac{d(x)/dt}{(b-x)}$ versus $(a-x)$ were linear, the slope would

equal k_2 and the intercept would be k_1 . The plot of these coordinates was not linear.

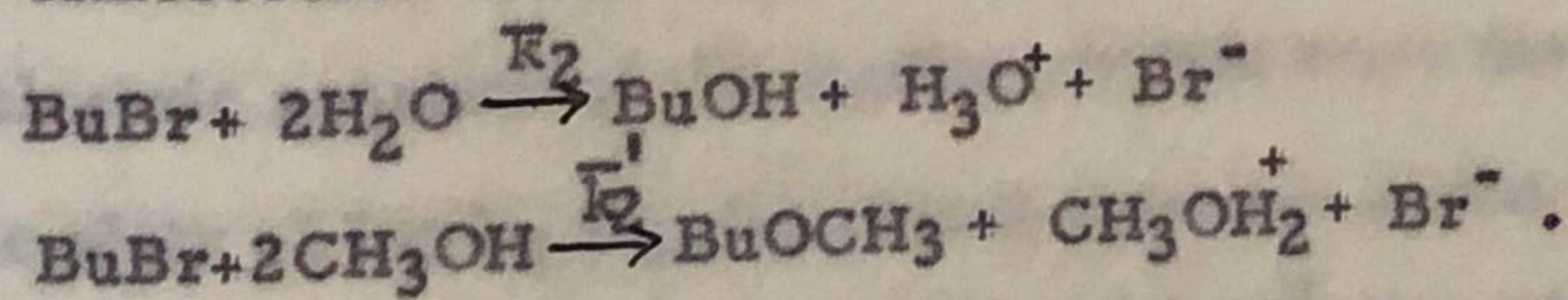
Although the rate constants were calculated by several methods, they were inconstant. Therefore, it is quite certain that these values do not represent good estimates of the true specific reaction rate constants for the solvolyses

studied.

If we think of the reaction measured as (4) in the S_N1 mechanism:



addition of water to the solvent may favor the competing substitution (3) considering $k_2 \ll k_3$, and k_4 small, which are reasonable assumptions. However, the amount of n-butyl alcohol (BuOH) formed was negligible or small for the higher weight per cent methanol solutions. Because both butyl alcohol and methyl n-butyl ether (BuOCH₃) were recovered as products, it is apparent that either both k_3 and k_4 are operating by the S_N1 mechanism or that the mechanism may be S_N2 ; in the latter case, the rate may be partially specified by the rate constants \bar{k}_2 and \bar{k}_2' in the bimolecular mechanism:



It is conceivable that as the ionizing power of the solvent increases (i.e., as water is added), a change in mechanism may occur. Perhaps the bimolecular (S_N2) mechanism is overcome at some point by the unimolecular (S_N1) one when the more "active" solvent, water, is added to the "less

active" solvent, methanol. Some indication of this possibility is given by the $k_{1(a-x)}$ and $k_{1(b-x)}$ values for run 5 which tend to decrease progressively, while these same values for runs 4-7 and runs 2-3 are slightly steadier for a time and then decrease.

Plots of $\log k_{1\text{avg.}}$ versus $1/D$ and $1/D^2$, where D is the dielectric constant of the solvent at 50°C. , ---the k values calculated by the method of least squares---are noticeably parabolic, contrary to expected behaviour (see figures 10 and 11). For these graphs, a maximum is found in the vicinity of 40-60 % methanol-water. "Anomalous" behaviour of the methanol-water system has been observed in other ways.

Much of the published data supports the idea that *n*-butyl bromide reacts via mechanism B (i.e., S_N2) in water and in aqueous alcohol solvents. The rate constants for the solvolysis should have increased directly as did the dielectric constant of the medium if this were the case. The plots of $\log k_2$ (k_2 calculated from the strict second-order rate equation) versus $1/D$ and $1/D^2$ show this behaviour (see figures 10 and 12). Plots of $\log k$ versus mole fraction of water illustrate similar effects for both estimates, $k_{1\text{avg.}}$ and k_2 , (see figure 13).

It is concluded that the solvolysis of n-butyl bromide in methanol-water mixtures (of 25, 50 and 75 weight % water) at 50° C., and in the presence of equimolar sodium hydroxide probably is of an intermediate (viz., fractional) kinetic order for which a mechanism must be found. If other criteria find that butyl bromide reacts via mechanism B (i.e., S_N2) in aqueous methanol, second-order rate constants (k_2) are probably fair estimates of the total solvolysis.

The correlation data of Grunwald, Jones and Winstein is supported by the linearity of the plot of $\log k$ for butyl bromide versus $\log k_0$ (for tertiary butyl chloride at 25° C.) in acetone-water, ethanol-water and methanol-water systems.

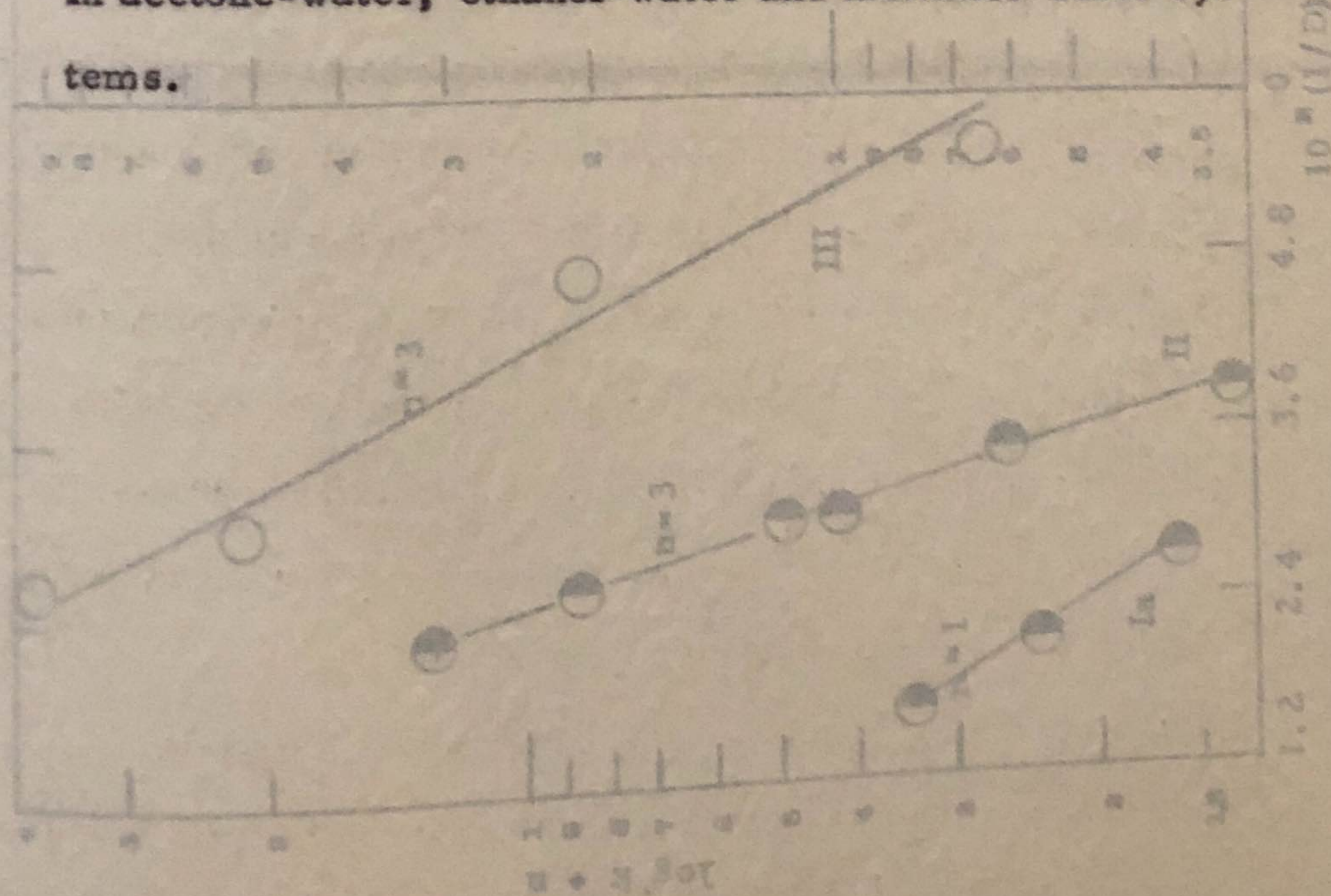


Fig. 10. Plot of $\log k$ versus $1/D$ for n-Butyl bromide (D is the dielectric constant).

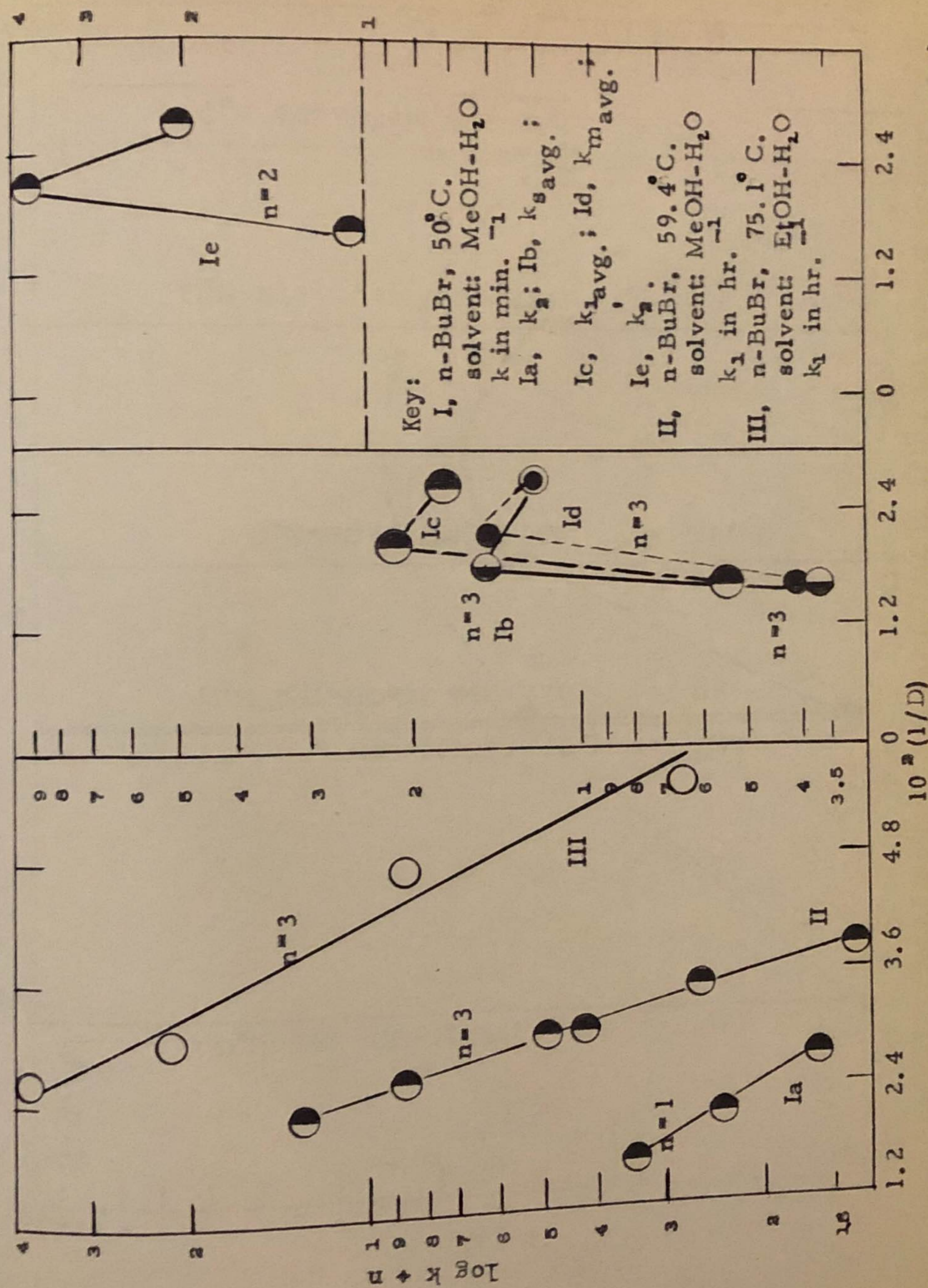


Fig. 10. Plot of $\log k$ versus $1/D$ for n-Butyl bromide (D is the Dielectric constant).

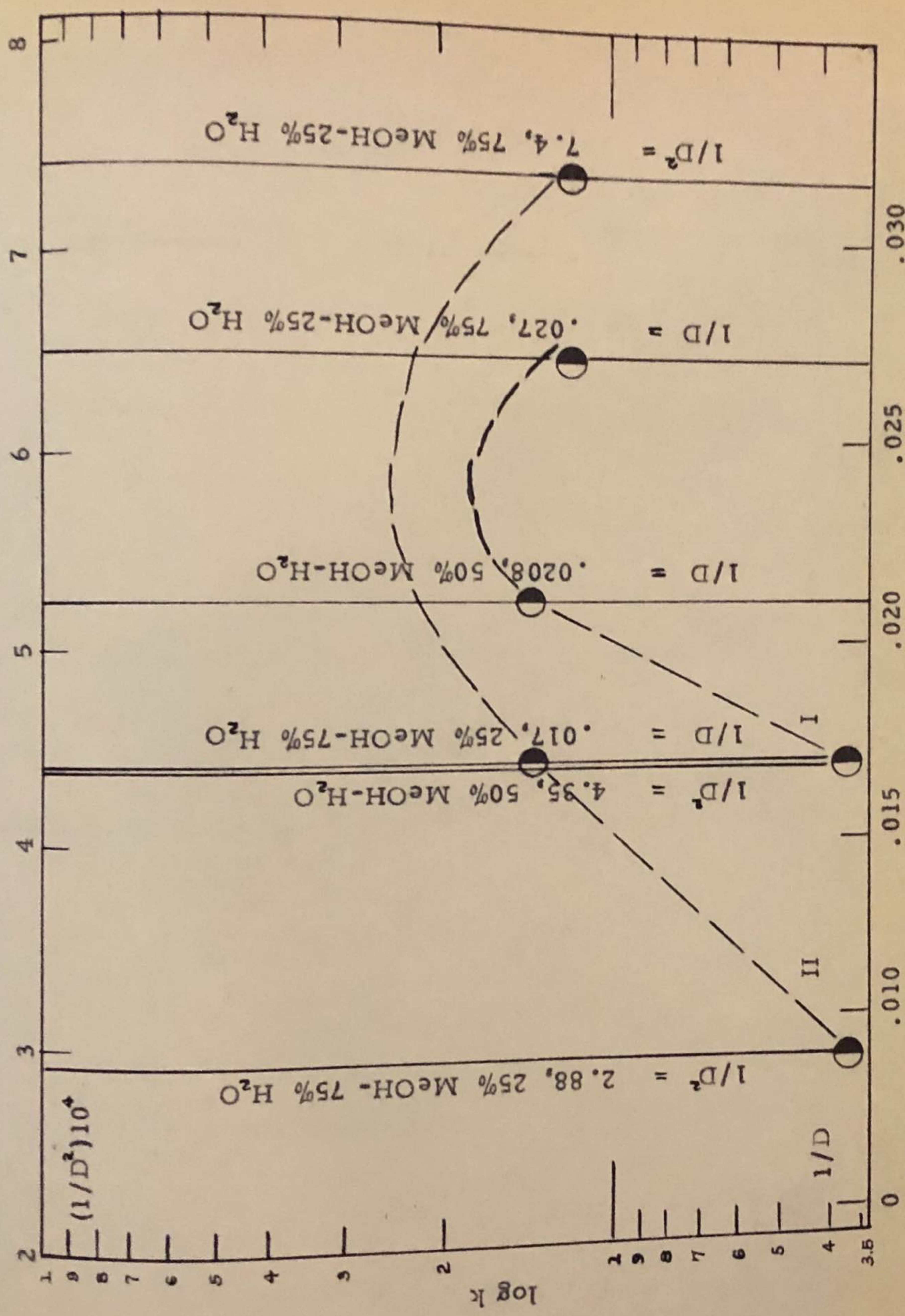


Fig. 11. Plot of $\log k_{s,avg}$ versus I, $1/D$; II, $1/D^2$, for n-Butyl bromide, 50° C.

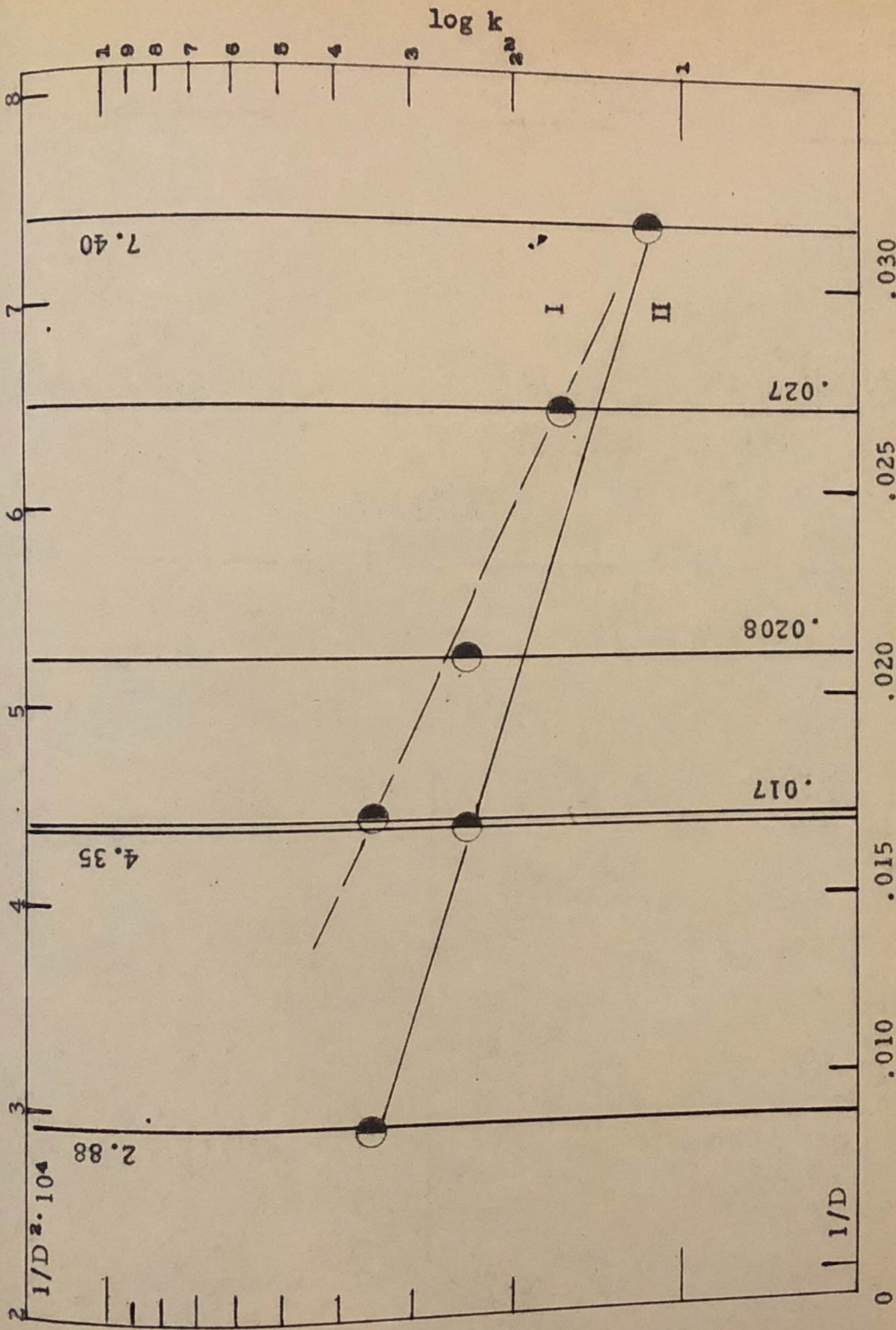


Fig. 12. Plot: $\log k_{avg}$ versus $1/D$; I, $1/D_2$, (n-Butyl bromide, 50°C.).

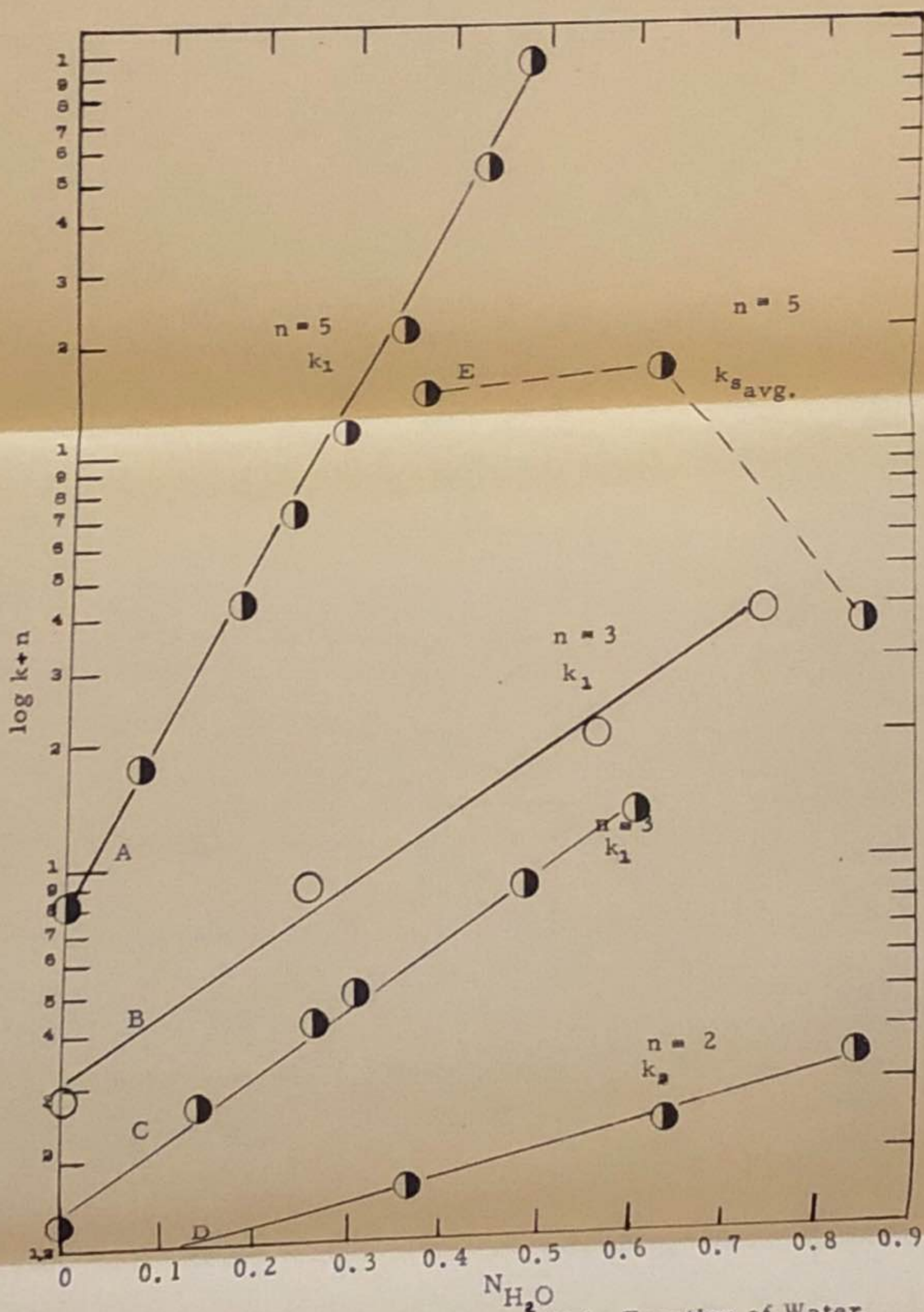


Fig. 13. Plot of $\log k$ versus Mole Fraction of Water, N_{H_2O} , for: A, t-BuCl, 25°C.; n-BuBr, B, 75.1°C.; C, 59.4°C.; D, 50°C.; E, 50°C. Solvents: \circ , H_2O -EtOH; \bullet , H_2O -MeOH. (A, sec.⁻¹; B, C, hr.⁻¹; D, E, min.⁻¹)