The Influence of the Solvent on Reaction Velocity

XXIII. The Alkaline Hydrolysis of Ethyl Acetate in Dimethyl Sulphoxide-Water Mixtures

EERO TOMMILA and MAIJA-LEENA MURTO

Department of Chemistry, University of Helsinki, Helsinki, Finland

The rate of alkaline hydrolysis of carboxylic esters usually decreases with decreasing water concentration in mixtures of water and an organic solvent. In contrast to this, the rate of alkaline hydrolysis of ethyl acetate in dimethyl sulphoxide-water mixtures increases with increasing dimethyl sulphoxide concentration, the enhancement being especially pronounced at high dimethyl sulphoxide concentrations. This increase is attributed to an increased activity of the hydroxide ion caused by its reduced solvation in the presence of dimethyl sulphoxide. The relation between the dielectric constant of the solvent and the rate constant, the variation of ΔG^*, ΔH^* and $T\Delta S^*$ with solvent composition and the specific effect of water on the reaction are discussed.

The hydrolysis of carboxylic esters in mixed solvents has been treated in a number of papers of this series. These studies have now been extended to mixtures of dimethyl sulphoxide (DMSO) and water, and both alkaline and acid hydrolyses have been investigated. In the present paper the results of a study of the alkaline hydrolysis of ethyl acetate are reported.

EXPERIMENTAL

Reagent grade ethyl acetate was carefully distilled. Dimethyl sulphoxide (Nitroglycerin AB, Gyttorp, Sweden) was distilled at reduced pressure (b.p. 71—72°/8 mm) and crystallised from the melt until its melting point was at least 18.50°. The melting point of pure dimethyl sulphoxide, which is very hygroscopic, is reported to be 18.52—18.55°.[1,2] Freshly distilled water was used in the preparation of solvents.

Because kinetic constants are very sensitive to variations in the composition of the solvent, each solvent mixture was prepared in a quantity sufficient for all the experiments with this composition. Equal volumes (5 ml) of 0.1 M ester and 0.1 M NaOH solutions were mixed in the reaction vessel. The initial concentration of each reactant was thus 0.05 M. In the preparation of the solvent mixtures, a measured volume of water or measured volumes of a sodium hydroxide stock solution and water were made up to 200 ml with DMSO in a volumetric flask. The percentage by weight of DMSO in each mixture

was determined separately. Owing to the volatility of ethyl acetate, a slightly more con-
centrated solution than 0.1 M was first prepared, the concentration of the ester deter-
mined by total hydrolysis, and then adjusted to the correct level with the solvent.

The reaction vessels and kinetic method were those used in previous investigations of
the alkaline hydrolysis of ethyl acetate.[3],[4] Cresol red was used as indicator in the titra-
tions. In many cases the runs were made in duplicate. The second-order rate law was
obeyed in all cases.

The temperature of the electrically regulated water thermostats remained constant
within $\pm$ 0.02°. The experiments at 0° were conducted in an insulated vessel which con-
tained crushed ice and water. The thermometers were checked against a thermometer
calibrated at the U.S. Bureau of Standards.

RESULTS

Table 1 gives the mean values of the rate constants k corrected for the ther-
mal expansion of the solvent (Table 2) and the values of the parameters A
and E of the Arrhenius equation $k = Ae^{-E/RT}$, k and A being expressed in 1
mole^{-1}sec^{-1}. The Arrhenius equation was obeyed within the limits of experi-
mental error in every case. The table contains also the values of the activa-
tion entropy ΔS^* calculated from the equation

$$A = e \frac{kT}{h} e^{\Delta S^*/R}$$

and the values of the free enthalpy of activation ΔG^* calculated from the
equation $\Delta G^* = \Delta H^* - T\Delta S^*$, where the enthalpy of activation $\Delta H^* = E - RT$.
The results for the reaction in pure water are in a good agreement with previ-
ously reported values.[4]

The results may be summarized as follows:

(1) Addition of DMSO to the solvent causes an increase in the reaction
velocity. The enhancement is only gradual at first, but when the mole fraction
of DMSO becomes greater than 0.28 (water in the solvent less than 400 ml/l),

Table 1. The alkaline hydrolysis of ethyl acetate in DMSO-water mixtures. Initial con-
centration a of the ester and NaOH was 0.050 mole/l except in the mixtures which con-
tained water 155 ml/l or 100 ml/l, in which a was 0.043 and 0.005 mole/l, respectively.
ε is the dielectric constant at 25°. The data for pure water are taken from Ref.[4], the dielec-
tric constants from Ref.[30]

Water in the solvent				$10^2 k$, 1 mole^{-1}sec.$^{-1}$				E cal	log A	ΔS^* E.U.	ΔG^* cal
ml/l	wt.%	x_w	ε	0.00°	15.00°	25.00°	40.00°				
1000	100.0	1.000	78.54	1.86	5.74	11.1	27.2	11 400	7.398	−26.7	18 760
900	88.9	0.972	78.2	2.17	6.48	12.4	30.4	11 210	7.311	−27.1	18 740
800	77.6	0.938	77.7	2.42	7.07	13.5	32.1	11 010	7.194	−27.6	18 650
600	56.5	0.850	76.2	2.63	8.14	15.4	36.6	11 180	7.375	−26.8	18 570
400	36.8	0.716	72.3	3.35	10.1	20.1	52.2	11 680	7.865	−24.5	18 400
300	27.3	0.632	68.4			26.3					
200	18.1	0.490	63.7	7.33	24.9	50.0	134	12 320	8.726	−20.6	17 870
155	14.3	0.418	61.2	9.21	29.6	64.7	170	12 450	8.921	−19.7	17 730
100	9.1	0.302	57.8			100.0					

Table 2. Temperature expansion coefficients of DMSO-water mixtures. Calculated from pycnometric measurements. The values for 50° obtained by extrapolation.

H_2O ml/l	0°	15°	25°	40°	50°
1000	0.998	0.999	1.001	1.006	1.010
900	0.996	0.999	1.002	1.008	1.012
800	0.993	0.998	1.002	1.009	1.014
700	0.990	0.997	1.002	1.010	1.016
600	0.988	0.996	1.003	1.012	1.019
400	0.983	0.995	1.003	1.016	1.025
200	0.978	0.994	1.004	1.020	1.031
0	0.973	0.992	1.004	1.022	1.034

the rise is very steep (Fig. 1). As the solubility of sodium hydroxide in mixtures containing less water than 100 ml/l is very poor, the experiments could not be extended to solvents of lower water concentration. For the sake of comparison, also the curve for acetone-water mixtures [4] is given in Fig. 1. It is seen that the rate constant decreases with increasing acetone concentration.

(2) In solvent mixtures containing water in concentrations varying from about 25 to 5 moles (from 400 to 100 ml) per litre, $\log k$ is a linear function of $\log [H_2O]$, the slope of the plot being -1.20 at 25° (Fig. 2). Supposing that this linearity continues up to nearly water-free solvents, we *e.g.* obtain $k = 1300$ and $k/k_w = 12\ 000$ for $[H_2O] = 0.1$. The plot of $\log k$ against x_{DMSO} is practically linear when x_{DMSO} is greater than 0.25 (Fig. 3). The plot of $\log k$ *vs.* $\log [DMSO]$ reveals nothing of special interest.

(3) The curves plotting the Arrhenius parameters E and $\log A$ as functions of solvent composition (Fig. 4) have the same form as the curves for the alkaline
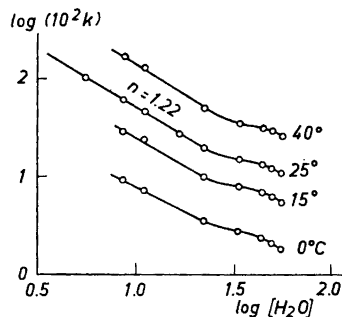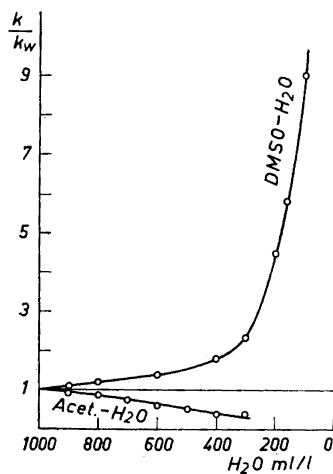

Fig. 1. Variation of k/k_w with solvent composition.
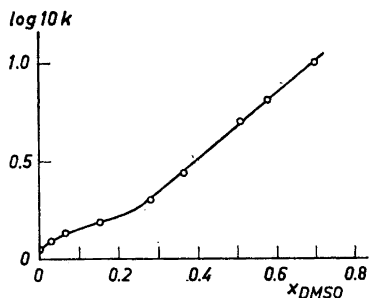
Fig. 2. Plot of $\log k$ against $\log [H_2O]$.

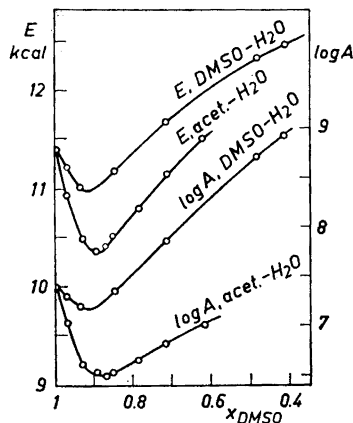Fig. 3. Plot of log k against the mole fraction of DMSO, 25°.

Fig. 4. Variations of E and log A with solvent composition.

hydrolysis of ethyl acetate in acetone-water and dioxan-water mixtures and in aqueous mixtures of ethanol and higher alcohols.[4] E and A are always higher in DMSO-water than in acetone-water mixtures of equal water concentration. The minimum in the curves is deeper for acetone-water than for DMSO-water mixtures.

(4) The reaction rate increases with decreasing dielectric constant of the solvent, whereas the reverse is true for mixtures of water with acetone, dioxan, or alcohols.

DISCUSSION

Reaction rate. During the last few years many reactions have been reported to be accelerated by dimethyl sulphoxide.[5] The uncatalysed hydrolysis of benzyl chloride is retarded by dimethyl sulphoxide, but to a much lesser extent than by acetone or dioxan.[6] J. Murto[7] found that the rate of the reaction $MeI + OH^- \rightarrow MeOH + I^-$ in DMSO-water mixtures increases very rapidly with increasing DMSO concentration, the rate in DMSO being $10^6 - 10^7$ times the rate in water. Also the reaction $MeI + MeO^- \rightarrow MeOMe + I^-$ in methanol and the reaction $MeI + EtO^- \rightarrow MeOEt + I^-$ in ethanol are enormously accelerated by DMSO.[7] The effect of DMSO on the alkaline hydrolysis of esters has not been investigated previously. With a few exceptions at very high water concentrations,[4,8] the rates of alkaline hydrolysis of esters decrease with decreasing water concentration in acetone-water, dioxan-water and alcohol-water mixtures.

The observed acceleration of a base-catalysed hydrolysis reaction is most naturally explained by attributing it to an increase in the activity of the hydroxide ion.[5,7] According to prevailing theories,[9,10] the first and rate-determing step in alkaline ester hydrolysis is the addition of the hydroxide ion to the carbonyl carbon, after which a rapid reaction with water follows. Thus, if the activity of the hydroxide ion is increased, the reaction rate must

increase. The very low solubilities of alkali metal hydroxides in dimethyl sulphoxide and other polar aprotic solvents and the results of polarographic investigations, conductance measurements, and other studies [2,5] have shown that the hydroxide ion is poorly solvated and consequently very active in these solvents. It appears that bulky dipoles with charges on large atoms such as carbon, sulphur, nitrogen, and oxygen cannot fit closely around small anions [11]. Increased reactivities of anions have in general been ascribed to a reduction in the degree of anion solvation.[5,7,11-13]

A large heat evolution on mixing DMSO with water [1,14] and the maxima in viscosity isotherms [14-17] suggest that there is strong association of the two liquids which may be attributed to hydrogen bonding. The dimethyl sulphoxide molecule may exist in the forms I and II [14,18]

$$\underset{I}{\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\diagdown}}\!\!\!S=O} \qquad\qquad \underset{II}{\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\diagdown}}\!\!\!\overset{+}{S}-O^-}$$

in which the negatively charged oxygen should be capable of forming hydrogen bonds with the water molecules. Also spectral evidence of strong hydrogen bonding between water and sulphoxides has been reported.[19,20] It may be taken to be established that hydrogen bonding is stronger between water and dimethyl sulphoxide than between two water molecules.[21] The higher rates in DMSO-water mixtures suggest that the DMSO-water interaction significantly reduces the concentration of "free" water available for the solvation of hydroxide ions. The curve representing the rate constant as a function of solvent composition (Fig. 1) begins to rise rapidly when the mole fraction of DMSO exceeds a value of about 0.28. This is somewhat below the point ($x_{DMSO} = 0.35$) where the heat of mixing is a maximum,[1,14] where the viscosity exhibits a maximum, and where a rather abrupt decrease in the partial molar volume of water and a corresponding increase in that of DMSO take place.[1] Thus, when the ratio of water molecules to DMSO molecules is 2:1 or less, the reaction rate increases very rapidly with increasing DMSO concentration. Already when the mole fraction of DMSO is 0.3, most of the water is probably bound to DMSO as

$$\underset{\displaystyle \,}{\overset{\displaystyle H_2O}{|}}$$

2:1 complexes, e.g. $Me_2S=O\cdots\cdots H-O-H$, and at higher mole fractions the amount of "free" water decreases rapidly with increasing DMSO concentration. Evidence for the existence of such complexes is provided by the above properties of the mixtures. This implies that the solvation of hydroxide ions is especially reduced in this range of mixtures.

The values of ΔG^*, ΔH^*, and ΔS^*. The free enthalpy of activation, ΔG^*, upon which the rate constant depends according to the formula

$$k = \mathbf{k}T/\mathbf{h} \text{ exp. } (-\Delta G^*/RT)$$

decreases smoothly with increasing DMSO concentration, reflecting the increase in reaction velocity (Fig. 5). Greater variations are found in the values of
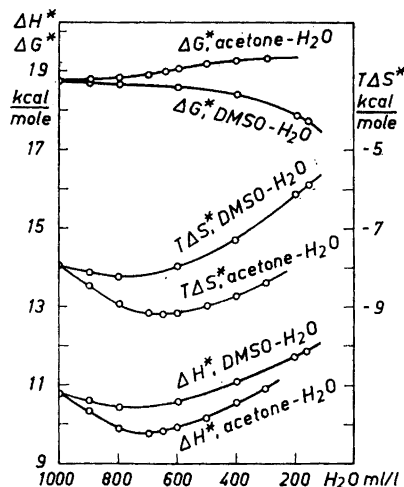
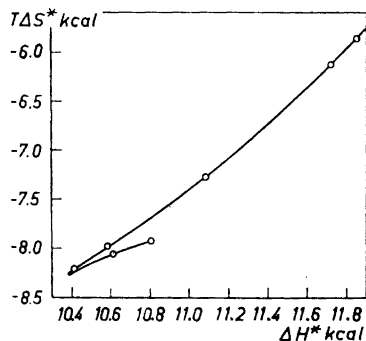Fig. 5. Variation of ΔH^*, $T\Delta S^*$ and ΔG^* with solvent composition, 25°.

Fig. 6. Plot of $T\Delta S^*$ against ΔH^*.

ΔH^* and ΔS^*, which pass through shallow minima at about $x_w = 0.9$. It is known that the ΔH^* and ΔG^* curves often are much more complicated than the curves in Fig. 5, although ΔG^* changes quite smoothly (e.g. Refs.[22,23]). The effects of changes in ΔH^* and ΔS^* a gradual change in solvent composition introduces largely compensate one another, so that no signs of a minimum are evident in the ΔG^* curve. ΔH^* and ΔS^* (or E and A) decrease and increase simultaneously. In Fig. 6 $T\Delta S^*$ is plotted against ΔH^*; the minimum seen in Fig. 5 divides the curve in two approximately linear parts. Linear relationships between ΔH^* and $T\Delta S^*$ have been observed in many cases and have often been discussed.[4,24]

The forms of the curves which plot ΔH^* and $T\Delta S^*$ as functions of solvent composition have been attributed to changes in the solvation of the reactants and the transition state as the composition of the solvent is gradually varied.[4] The orientation of the solvent molecules round the solute particles involves an increase of order in the reacting system (in which we include also the surrounding solvent molecules), and thus solvation lowers the entropy of the system. Solvation is a spontaneous process, and so its $\Delta G = \Delta H - T\Delta S < 0$. Since $\Delta S < 0$, also $\Delta H < 0$, i.e. the potential energy of the solvated state is less than that of the unsolvated state. In an aqueous solvent mixture the water molecules have a specific attraction for the hydrophilic part and the organic molecules a specific attraction for the alkyl or other groups of a solute. Thus a variation in the composition of the solvent leads in general to changes in the solvation of the solute particles, i.e. in a reaction system in the solvation of the reactants and the transition complex.

As we have seen, the addition of DMSO to the water lowers the degree of the solvation of hydroxide ions. Thus the entropy and enthalpy of a system comprising a hydroxide ion and the surrounding solvent molecules increase

on addition of DMSO. At the same time the solvation of the ester molecules increases and this causes a decrease in entropy and enthalpy. Since the selectivity of an ion must be greater than that of an ester molecule,[25] the entropy and enthalpy of the initial state (hydroxide ion + ester molecule + the surrounding solvent) will with increasing DMSO concentration increase somewhat. The transition state may be solvated by both water and DMSO. As the DMSO concentration is increased, there will be an initial range of composition over which the solvation by water remains practically unchanged but above this range the solvation will decrease continuously because increasing amounts of water will be firmly bound to DMSO and will not be available for solvation. The result is that with increasing concentration of DMSO the solvation of the transition complex increases slightly at first and then decreases continuously as the pyramidal DMSO molecules [18] cannot fit well around the oxygen atoms of the transition state.

Considering all the above facts, the enthalpy and entropy of the initial state (indicated by a single prime) and transition state (indicated by a double prime) can be represented schematically as functions of solvent composition as in Fig. 7, cf. Refs.[22,26] (Since the transition state is a state of greater order
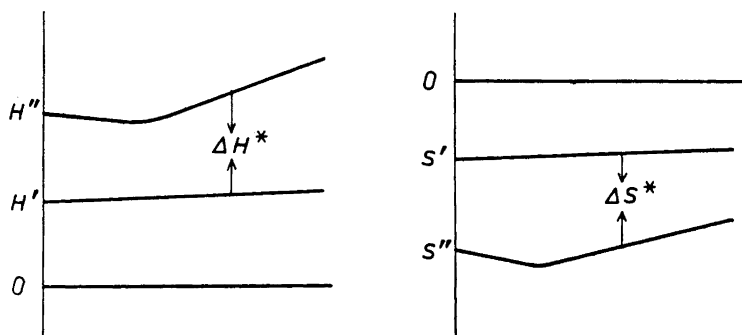

Fig. 7. Schematic representation of solvation effects in DMSO-water mixtures.

than the initial state where the reacting species are apart, its entropy is lower than that of the latter). In drawing the curves it has been supposed that the intramolecular energies and entropies of the reactants and the transition state remain constant, so that only the energies and entropies of interaction between the reacting species and the solvent need be considered. Fig. 7 illustrates the variation of $\Delta H^*(= H'' - H')$ and ΔS^* $(= S'' - S')$, also the appearance of the minima.

As to the difference between DMSO-water mixtures and acetone-water mixtures, the following should be noted. Water is also a reactant in the hydrolysis, and before a water molecule can enter into the reaction, bonds between it and other solvent molecules must presumably be broken. As judged from the heats of mixing,[27,28] (Table 3), the bonds are much weaker between water and acetone than between water and DMSO, and thus the water molecules are more freely available for reaction, and also for solvation in acetone-water

Table 3. The heats of mixing (ΔH) at 25° (cal/mole).[1,27,28]

x_w	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
DMSO-water	−130	−260	−380	−500	−618	−708	−690	−540	−362
Acetone-water	−11	−25	−42	−60	−83	−122	−172	−188	−160

mixtures than in DMSO-water mixtures. The effect of this factor should be significant especially at low water concentrations. Further, the transition state will be more easily solvated by acetone than by DMSO, because the planar acetone molecules fit better around the transition state than the pyramidal DMSO molecules. Accordingly, replacing DMSO by acetone causes a lowering of the H''- and S''-curves in Fig. 7 and, since changes in the positions of the H'- and S'-curves are of a minor importance, also a lowering of the values of ΔH^* and $\Delta S,^*$ which is in agreement with the experimental results.

The relation between the rate constant and the dielectric constant of the solvent. The rate of base-catalysed hydrolysis of esters increases with increasing dielectric constant, ε, in mixtures of acetone, dioxan or various alcohols with water, the plot of log k vs. $1/\varepsilon$ being approximately linear over a wide range of mixtures.[4] In DMSO-water mixtures the reaction rate increases with decreasing dielectric constant. The plot of log k vs. $1/\varepsilon$ is a straight line for mixtures that contain less water than 850 ml/l, but its slope is positive, *i.e.* opposite in sign to the slope for the first-named solvent mixtures (Fig. 8).
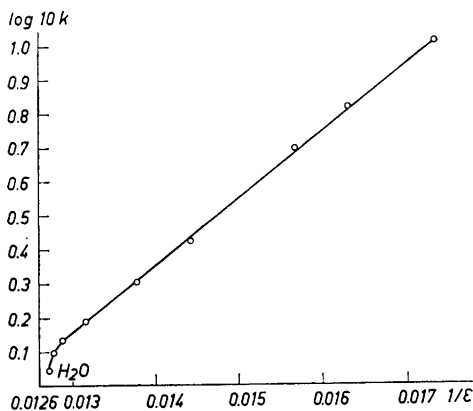
Fig. 8. Plot of log k against $1/\varepsilon$, 25°.

According to Laidler,[29] the slope of the plot of ln k against $1/\varepsilon$ for an ion(A)-dipole(B) reaction with net charge $z_B e = 0$ is given by the equation

$$\frac{\mathrm{d}\ln k}{\mathrm{d}(1/\varepsilon)} = \frac{1}{kT}\left[\frac{z_A^2 e^2}{2}\left(\frac{1}{r_A} - \frac{1}{r_*}\right) + \frac{3}{4}\left(\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_*^2}{r_*^3}\right)\right]$$

where k is the Boltzmann constant and the μ's and r's are the dipole moments and radii of the reactants and the transition complex, respectively. In all cases $r_* > r_A$, so that if the terms involving $z_A^2 e^2$ predominate the slope would be positive, i.e. the reaction rate would decrease with increasing dielectric constant. This does indeed appear to be very often the case. However, if μ_*^2/r_*^3 is large, an acceleration is to be expected with increasing dielectric constant. This is in general the case in the hydrolysis of esters and other carbonyl compounds. Laidler supposes that large values of μ_* arise here from an ionization of the carbonyl group in the transition state. In DMSO-water mixtures the reverse is true. Here the hydroxide ion is poorly solvated and r_A is small. Furthermore, r_A decreases with decreasing dielectric constant. It is further possible that, because the DMSO molecules can fit around the carbonyl oxygen only with difficulty, the ionization of the carbonyl group is less complete, the transition state less polar and the term μ_*^2/r_*^3 smaller in DMSO-water mixtures, than in the other solvents. These factors together lead to a positive slope of the plot of ln k against $1/\varepsilon$. However, the value of the slope is so large (about 195) that if the normal values of the radii and dipole moments are employed, the equation would give a negative value for the radius of the transition state. The large value of the slope is probably chiefly a consequence of the fact that the solvation of the hydroxide ion decreases gradually with increasing concentration of DMSO.

The role of water. Laidler and Landskroener [31] have assumed that the rate-governing step in the alkaline hydrolysis consists of a simultaneous attack of a hydroxide ion on the carbonyl and of a water molecule on the ether oxygen. Support for this hypothesis is provided by the very low frequency factor values and the relation between water concentration and rate constant. Although the variation in the reaction rate caused by changes in solvent composition in DMSO-water mixtures is opposite to that in other mixed solvents, there is no evidence that the reaction mechanism is essentially different in these cases. No case of ester hydrolysis where the activity of the attacking hydroxide ion varies greatly with solvent composition has been investigated previously, and it is interesting to note that as in other solvents, the reaction is kinetically of first order in both hydroxide ion and ester also in DMSO-water mixtures. Since water is a reactant, a decrease in its concentration no doubt tends to retard the reaction; nevertheless the reaction is accelerated, but this is entirely brought about by DMSO.

If the activity of the hydroxide ions remains approximately constant despite variations in the relative amounts of the components in a mixed solvent, the water participation order n, defined by the relation $k_{exp.} = k[H_2O]^n$ or log $k_{exp.} = n$ log $[H_2O] +$ log k can be calculated.[22] The plot is linear for the alkaline hydrolysis of ethyl acetate in acetone-water mixtures in the range from pure water to a water concentration of 400 ml/l, and in dioxan-water mixtures over the range of water concentration from 950 to 430 ml/l; in the former case $n = 1.0$ and in the latter case $n = 0.9$. Linear plots of different slopes have been reported for a number of other esters.[32-34] If we assume that the activity of hydroxide ions in DMSO-water mixtures is proportional to the mth power of the molar water concentration and that the water participation order is n, we may write $k_{exp.} = k[H_2O]^{m+n}$. If n has the same value as in

acetone-water and dioxan-water mixtures, namely 1, we obtain $k_{exp.} = [H_2O]^{m+1}$. We see from Fig. 2 that $m + 1 = -1.20$, and thus $m = -2.20$ or the activity of hydroxide ions is proportional to about $1/[H_2O]^2$ in the range where the plot is linear.

REFERENCES

1. Kenttämaa, J. and Lindberg, J. J. *Suomen Kemistilehti* **B 33** (1960) 32, 98.
2. Schläfer, H. L. and Schaffernicht, W. *Angew. Chem.* **72** (1960) 618.
3. Tommila, E. and Koivisto, A. *Suomen Kemistilehti* **B 20** (1947) 54.
4. Tommila, E., Koivisto, A., Lyyra, J. P., Antell, K. and Heimo, S. *Ann. Acad. Sci. Fennicae A II* **1952** No. 47.
5. Parker, A. J. *Quart. Rev. (London)* **16** (1962) 163.
6. Tommila, E. and Virtanen, O. *Suomen Kemistilehti* **B 34** (1961) 139.
7. Murto, J. *Suomen Kemistilehti* **B 34** (1961) 92.
8. Anantakrishnan, S. V. and Anantaraman, A. V. *Proc. Indian Acad. Sci.* **49 A** (1959) 86, 174.
9. Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, Chapter XIV, G. Bell and Sons Ltd. London 1953.
10. Hine, J. *Physical Organic Chemistry*, 2nd Ed. Chapter 12, McGraw-Hill Book Company, New York 1962.
11. Miller, J. and Parker, A. J. *J. Am. Chem. Soc.* **83** (1961) 117.
12. Winstein, S., Savedoff, L. G., Smith, S., Stevens, I. D. R. and Gall, J. S. *Tetrahedron Letters* **9** (1960) 24.
13. Parker, A. J. *J. Chem. Soc.* **1961** 1328.
14. Cowie, J. M. G. and Toporowski, P. M. *Can. J. Chem.* **39** (1961) 2240.
15. Nitroglycerin AB, Gyttorp, Sweden. *Dimetylsulfoxid. Teknisk information*, 1957.
16. Lindberg, J. J. and Laurén, R. *Finska Kemistsamfundets Meddelanden — Suomen Kemistiseuran Tiedonantoja* **71** (1962) 37.
17. LeBel, R. G. and Goring, D. A. I. *J. Chem. Eng. Data* **7** (1962) 100.
18. Bastiansen, O. and Viervoll, H. *Acta Chem. Scand.* **2** (1948) 702.
19. Tamres, U. and Searless, S. *J. Am. Chem. Soc.* **81** (1959) 2100.
20. Salonen, A. *Ann. Acad. Sci. Fennicae A VI* **1961** No. 14.
21. Fuchs, R., McCrary, G. E. and Bloomfield, J. J. *J. Am. Chem. Soc.* **83** (1961) 4281.
22. Tommila, E., Tiilikainen, M. and Voipio, A. *Ann. Acad. Sci. Fennicae A II* **1953** No. 65.
23. Tommila, E., Paakkala, E., Virtanen, U. K., Erva, A. and Varila, S. *Ann. Acad. Sci. Fennicae A II* **1959** No. 91.
24. Fairclough, R. A. and Hinshelwood, C. N. *J. Chem. Soc.* **1937** 358; Blackadder, S. and Hinshelwood, C. *Ibid.* **1958** 2728; Venkataraman, H. S. and Hinshelwood, C. *Ibid.* **1960** 4977, 4986.
25. Kirkwood, J. G. *J. Chem. Phys.* **2** (1934) 351.
26. Hyne, J. B. *J. Am. Chem. Soc.* **82** (1960) 5129.
27. Landolt-Börnstein, *Physikalisch-Chemische Tabellen, Erg. I*, 852 (1927).
28. Kister, A. T. and Waldman, D. C. *J. Phys. Chem.* **62** (1958) 245.
29. Laidler, K. J. *Suomen Kemistilehti* **A 33** (1960) 44.
30. Lindberg, J. J. and Kenttämaa, J. *Suomen Kemistilehti* **B 33** (1960) 104.
31. Laidler, K. J. and Landskroener, P. A. *Trans. Faraday Soc.* **52** (1956) 200.
32. Tommila, E. *Suomen Kemistilehti* **B 25** (1952) 37.
33. Tommila, E., Takanen, L. and Salonen, K. *Suomen Kemistilehti* **B 31** (1958) 37.
34. Tommila, E. and Hietala, S. *Acta Chem. Scand.* **8** (1954) 257.