ASSOCIATION CONSTANTS OF SOLUTIONS OF SOME ALCOHOLS IN INACTIVE SOLVENTS

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Experimental data obtained by infrared spectroscopy (Konopka, Pędzisz and Jurewicz, *Acta Phys. Polon.*, A **40**, 751 (1971) are utilized for determining the association constants of solutions of primary, secondary and tertiary butyl, amyl, hexyl and heptyl alcohols in CCl_4 and C_6H_{14} by the method of Mecke and Kempter. The ratio of the absorbed intensity of the polymer band to that of the monomer band in the examined alcohol solutions is presented as a function of degree of association α. The results obtained are plotted in graphs and a discussion of them is given.

1. Introduction

As spectroscopic studies have shown (Errer and Mollet 1935, Hilbert *et al.* 1935, Pimentel and McCellan 1960), alcohol molecules become associated through hydrogen bonds in which the hydroxyl groups of the alcohol molecules partake. In order to study the association processes in substances forming hydrogen bonds use is often made of infrared spectroscopy (Mecke 1950, Smith and Creitz 1951) or dielectric measurements (Małecki and Dopierała 1969).

In the absorption infrared spectrum of alcohols in the liquid phase there appears a broad absorption band in the vicinity of 3400 cm^{-1} due to the vibrational frequency of the OH group bound by the hydrogen bond in associates of various numerical force (polymers). When the alcohol is diluted more and more in the inactive solvent, an absorption band lying in the region od 3620 cm^{-1} becomes developed. This band corresponds to the vibrational frequency of the OH group of unbounded molecules (monomer). This process is associated with a simultaneous decrease in absorbed intensity of the polymer band and a shift of this band towards the higher frequencies. Experimental data achieved by infrared spectroscopic measurements make it possible to contribute new knowledge to the studies on the course of the association process in alcohol solutions as a function of alcohol concentration in the solvent.

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Mecke and Kempter (1940), Coggeshall and Saier (1951), Liddel and Becker (1957), Inskeep, Kelliher, McMahon and Somers (1958), Dunken and Fritzeche (1964), and other researchers employed infrared spectroscopy in studies on the association process in alcohols, determining the association constants in the examined substances.

Results of research by infrared spectroscopy have been already published (Konopka, Pędzisz and Jurewicz 1971). Using these data, association constants were calculated by the method of Mecke and Kempter for solutions of primary, secondary and tertiary butyl, amyl, hexyl and heptyl alcohols in carbon tetrachloride and in hexane.

2. Results of calculations

According to Ramsay's 3rd method (1952), the integral intensity A_{11} of a monomer band can be determined from the equation

$$A_{10} = \frac{A'}{cl} = A_{11} \left\{ 1 - \frac{1}{2!2} \ln \left(\frac{I_{0\nu}}{I_\nu} \right)_{max} + \frac{3}{3!8} \left[\ln \left(\frac{I_{0\nu}}{I_\nu} \right)_{max} \right]^2 - ... \right\}$$

where A' is the area under the absorption curve, c is alcohol concentration, l is absorption layer thickness, $I_{0\nu \, max}$ is the intensity of infrared radiation falling on the absorbing layer, $I_{\nu \, max}$ is the intensity of infrared radiation transmitted through the absorbing layer calculated at band maximum.

TABLE I

Values of association constants and integral intensities for the examined solutions of alcohol in carbon tetrachloride and in hexane

Alcohol	Solvent							
	CCl$_4$				C$_6$H$_{14}$			
	K $1 \cdot mol^{-1}$	K^P $1 \cdot mol^{-1}$	$A_{11} \times 10^4$ $1 \cdot mol^{-1}$ cm^{-2}	$A_{11}^P \times 10^4$ $1 \cdot mol^{-1}$ cm^{-2}	K $1 \cdot mol^{-1}$	K^P $1 \cdot mol^{-1}$	$A_{11} \times 10^4$ $1 \cdot mol^{-1}$ cm^{-2}	$A_{11}^P \times 10^4$ $1 \cdot mol^{-1}$ cm^{-2}
butyl:								
primary	1.50	1.35	3.40	3.30	3.51	3.63	2.80	2.70
secondary	0.70	0.72	3.20	3.24	2.01	2.20	2.20	2.35
tertiary	1.03	1.10	2.60	2.80	1.67	1.41	2.10	1.95
amyl	0.93	1.04	4.10	4.02	3.20	3.12	3.10	3.00
hexyl	1.04	1.03	3.80	3.70	2.70	2.60	2.90	2.75
heptyl	0.85	0.95	3.90	3.98	2.04	2.20	2.75	2.89

The values of integral intensity A_{11} are obtained by plotting A_{10} as a function of $\ln (I_{0\nu}/I_\nu)_{max}$ and extrapolating $\ln(I_{0\nu}/I_\nu)_{max}$ to zero. The extrapolated values of integral intensity A_{11} for primary, secondary and tertiary butyl, amyl, hexyl and heptyl alcohols dissolved in carbon tetrachloride and hexane are gathered in Table I.

Some interesting information is provided by the graphs illustrating the ratio E_2/E_1 as a function of α (Figs 1 and 2). $E_2 = \dfrac{1}{cl} \displaystyle\int \left(1 - \dfrac{I}{I_0}\right) dv$ defines the value of the absorbed intensity of the polymer band. The area under the curve of the absorption band is a measure of this intensity. E_1 denotes the corresponding value of absorbed intensity of the monomer band in the alcohol solution. The degree of association $\alpha = A_{10}/A_{11}$ defines the degree of association of the alcohol determined for a given concentration c of alcohol in solvent.

As seen in Figs 1 and 2, the points corresponding to the various alcohols in a given solvent can be described by a mutual straight line. This would mean that the association
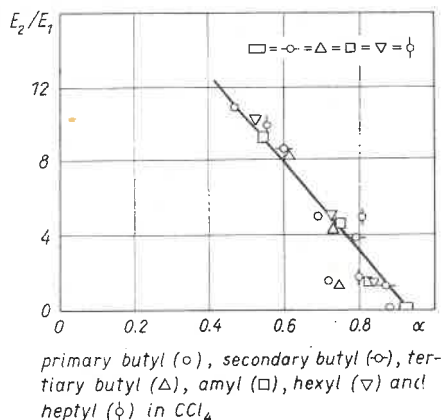

primary butyl (○), secondary butyl (⟨○⟩), tertiary butyl (△), amyl (□), hexyl (▽) and heptyl (φ) in CCl_4

Fig. 1. E_2/E_1 against α for solutions of the alcohols

primary butyl (●), secondary butyl (⟨●⟩), tertiary butyl (▲), amyl (■), hexyl (▼) and heptyl (φ) in C_6H_{14}
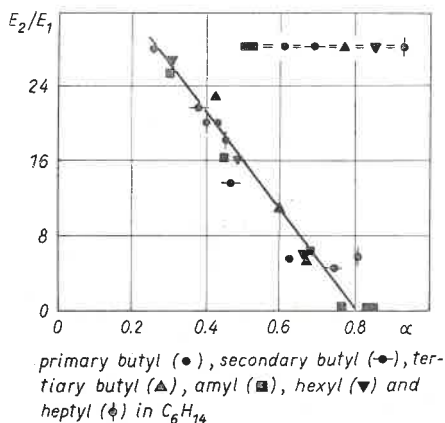
Fig. 2. E_2/E_1 against α for solutions of the alcohols

processes in all of the examined alcohols in a given solvent proceed in a similar manner and that these processes depend on the type of solvent, but not on the length of the alcohol chain very much.

3. Calculation of association constants by the Mecke-Kempter method

Mecke and Kempter (1940) derived a formula for calculating the association constant by assuming that in a solution of alcohol there may be chain-like associates of various numbers of molecules, for which the constant remains invariant independently of the alcohol concentration in the solution. Namely,

$$K' = \frac{1-\sqrt{\alpha'}}{c\alpha'} = \frac{1 - \sqrt{\dfrac{\varepsilon_{10}}{\varepsilon_{11}}}}{c \cdot \dfrac{\varepsilon_{10}}{\varepsilon_{11}}} \tag{1}$$

where K' is the association constant, c is alcohol concentration in mols per liter solution, $\alpha' = \varepsilon_{00}/\varepsilon_{11}$ is the degree of association of the alcohol. ε_{10} defines the maximum value of extinction coefficient of the monomer band measured in the alcohol solution. ε_{11} is the maximum value of extinction coefficient of the monomer band for an infinitely diluted solution of alcohol in the same solvent, or the value calculated from the equation given by Mecke and Kempter,

$$\varepsilon_{10}c = \frac{\varepsilon_{11}}{K'} - \frac{\sqrt{\varepsilon_{11}}}{K'}\sqrt{\varepsilon_{10}}. \tag{2}$$

Apart from the value of ε_{11}, this equation also enables us to determine the association constant K'.

It seems wiser to substitute in Eqs (1) and (2) the quantity ε_{10} by A_{10} and ε_{11} by A_{11}, namely,

$$K = \frac{1-\sqrt{\alpha}}{c \cdot \alpha} = \frac{1 - \sqrt{\dfrac{A_{10}}{A_{11}}}}{c \cdot \dfrac{A_{10}}{A_{11}}} \tag{1a}$$

$$A_{10} \cdot c = \frac{A_{11}}{K} - \frac{\sqrt{A_{11}}}{K} \cdot \sqrt{A_{10}}. \tag{2a}$$

In determining the values of the association constants K of the examined alcohols and their solutions use was made of both equations (1a) and (2a). According to the assumptions of the theory of Mecke and Kempter, the obtained values of K should not depend on the equation, (1a) or (2a), from which they are determined.

Figures 3 and 4 show the association constant K of the examined solutions as a function of alcohol concentration in the solution. It is seen that the values of association constant K for the range of concentrations investigated are essentially independent of concentration. The values of K presented in Figs 3 and 4 were obtained by the use of Eq. (1a).
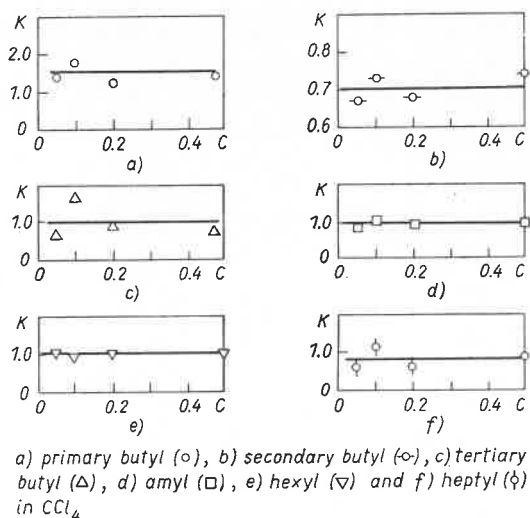
a) primary butyl (o), b) secondary butyl (o-), c) tertiary
butyl (△), d) amyl (□), e) hexyl (▽) and f) heptyl (φ)
in CCl_4

Fig. 3. Association constant K against concentration c of the alcohols

a) primary butyl (●), b) secondary butyl (●-), c) tertiary
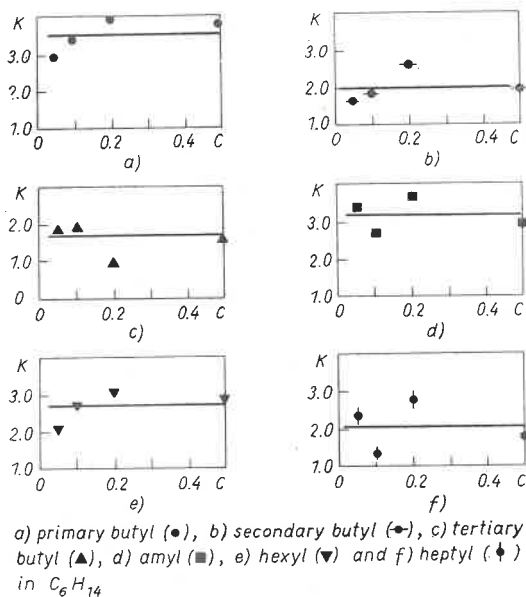butyl (▲), d) amyl (■), e) hexyl (▼) and f) heptyl (◆)
in $C_6 H_{14}$

Fig. 4. Association constant K against concentration of the alcohols

Using Eq. (2a), the dependence of $A_{10}c$ on $\sqrt{A_{10}}$ was plotted for the examined alcohol solutions (Figs 5 and 6). As is seen, this dependence is describable by a straight line. Hence, resorting to the value extrapolated for $\sqrt{A_{10}} \to 0$ and the straight line's slope we are able to find the association constant K and the integral intensity A_{11}.

The values of K and A_{11} obtained by means of Eq. (2a) are presented in Table I, where they are denoted by K^P and A_{11}^P in order to differentiate them from the values of K
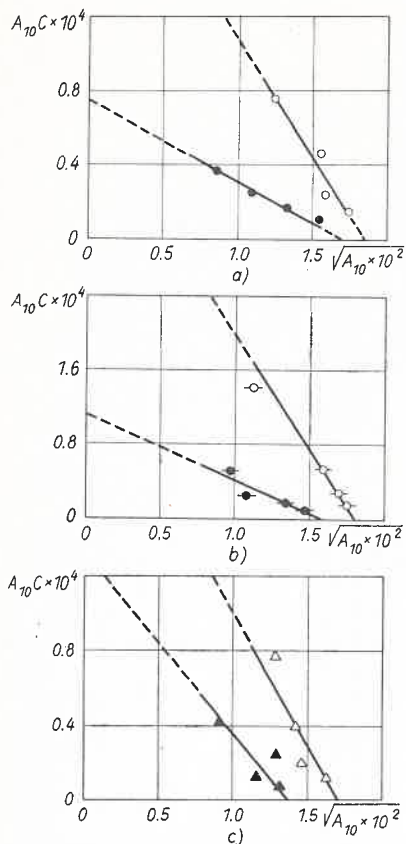
a) primary butyl in CCl_4 (○) and in C_6H_{14} (◐),
b) secondary butyl in CCl_4 (o‑) and in C_6H_{14} (◐‑),
c) tertiary butyl in CCl_4 (△) and in C_6H_{14} (▲),

Fig. 5
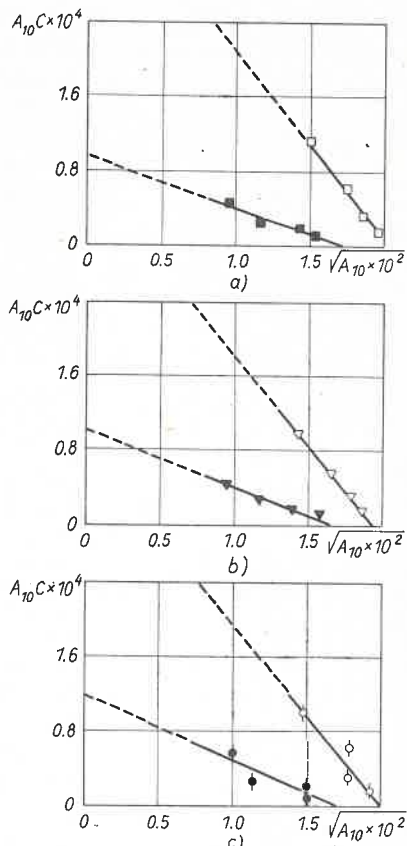
a) amyl in CCl_4 (□) and in C_6H_{14} (■),
b) hexyl in CCl_4 (▽) and in C_6H_{14} (▼),
c) heptyl in CCl_4 (◊) and in C_6H_{14} (♦)

Fig. 6

Fig. 5. Dependence of $A_{10}c$ on $\sqrt{A_{10}}$ for solutions of the alcohols

Fig. 6. Dependence of $A_{10}c$ on $\sqrt{A_{10}}$ for solutions of the alcohols

and A_{11} obtained from Eq. (1a) and the earlier mentioned method of Ramsay. The value of K for a given alcohol, given in Table I, is the mean value obtained from calculations of the association constant as a function of the examined alcohol's concentration in the solution (Figs 3 and 4).

Figures 7 and 8 illustrate the dependence of the value of $\varepsilon_{10}c$ on $\sqrt{\varepsilon_{10}}$ for the solutions of hexyl alcohol in carbon tetrachloride (Fig. 7) and in hexane (Fig. 8) in accord with the equation given by Mecke and Kempter in the form (2). It is distinctly seen that the obtained points no not satisfy the equation for a straight line. Therefore, application of Eqs (1) and (2) in the form stipulated by Mecke and Kempter for determining association constants of alcohols would appear to be futile. A similar deviation of analogous points from the straight line was also found by Dunken and Fritzsche (1964) for a solution of propyl

alcohol in CCl$_4$. Comparing the data obtained by means of our modified equations (1a) and (2a) with values obtained from Eqs (1) and (2) for the exemplary hexyl alcohol solutions in CCl$_4$ and C$_6$H$_{14}$ we find that use of the integral intensity of the absorption
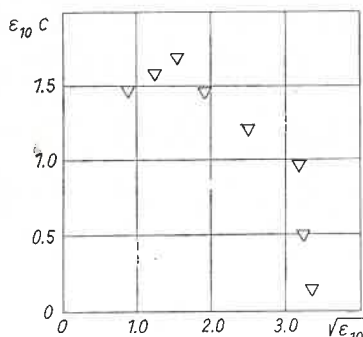

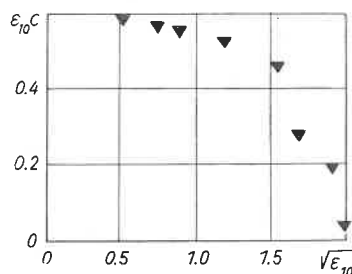Fig. 7. Dependence of $\varepsilon_{10}c$ on $\sqrt{\varepsilon_{10}}$ for a solution of hexyl alcohol in CCl$_4$

Fig. 8. Dependence of $\varepsilon_{10}c$ on $\sqrt{\varepsilon_{10}}$ for a solution of hexyl alcohol in C$_6$H$_{14}$

band for determining the association constants of alcohols gives better results than the use of the maximum extinction coefficient for this purpose.

4. Discussion

Integral intensity of a band seems to be a better measure of absorption than the extinction coefficient ε_{max} calculated at the absorption band peak, for the former takes account of the entire area under the absorption curve. The association constants calculated with the use of integral intensity, therefore, give a better portrayal of the association process occurring in alcohol solutions than that presented by association constants calculated on the basis of maximum extinction coefficients. It seems, however, that it must also be remembered that the points marking out the dependence of association constant K on concentration in Figs 3 and 4 show in some cases rather large scattering round the straight line representing the independence of association constant K on concentration. This probably stems from the inaccuracy of the Mecke-Kempter model which assumes that the association constant is independent of concentration and numerical force of the chain-like associate.

The plots also show that there is a difference between the association states of alcohols, which depends on the type of solvent used. For the solutions of alcohols

in CCl_4 the calculated association constants K are smaller than those for the solutions in C_6H_{14}. On the other hand, the course of the association process of alcohol solutions was not found to depend on the number of carbons in the chain.

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