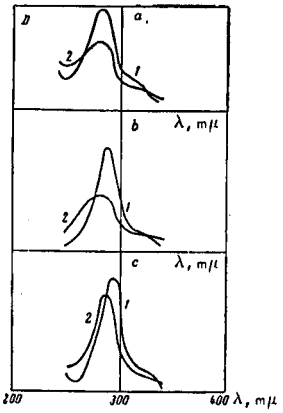

Fig. 3. Ultra-violet absorption spectra of polyamide films dyed with thiazine dyes:
a) thionine; *b*) Azure I; *c*) methylene blue; 1) before illumination; 2) after illumination in the presence of oxygen.

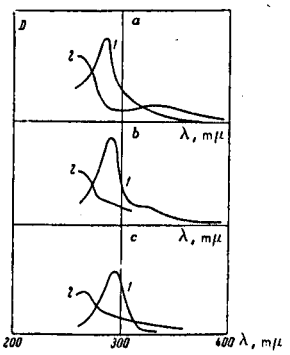

Fig. 4. Ultra-violet absorption spectra of formamide solutions of thiazine dyes.
a) thionine; *b*) Azure I; *c*) methylene blue; 1) before illumination; 2) after illumination.

band of 3,6-diaminoacridine (Fig.5). Obviously, demethylation is involved in this process. In polyamide films, the phenomenon is complicated by a change in the 3,6-diaminoacridine, caused by the illumination of samples from which oxygen has been excluded; this is the subject of further investigation.

Thus, a combination of dyes with poly(acrylic acid) and poly(methacrylic acid) is not essential for photochemical demethylation and, in addition, it may apparently be assumed that photo-demethylation is not restricted to thiazine dyes.

In conclusion the authors express their thanks to M.V. Savost'yanova and A.T.Vartanyan for much valuable advice.

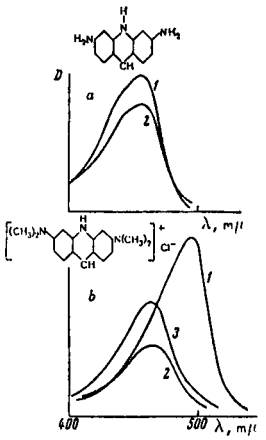

Fig. 5. Absorption spectra:
a) 3, 6-diaminoacridine in formamide solution; *b*) rhoduline orange in formamide solution; 1) before illumination; 2) after illumination in the presence of oxygen; 3) after illumination in the absence of oxygen.

SUMMARY

As a result of irradiation with visible light, the absorption spectra of methylene blue and Azure I in amide media (formamide and polyamide films) shift towards shorter wavelengths. This is ascribed to the demethylation of the dye molecules.

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POTENTIALS OF SOME ION-EXCHANGE MEMBRANES

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If two solutions of potassium chloride of different concentrations are separated by a membrane, the relative mobilities of the K^+ and Cl^- ions and their transport numbers change in comparison with their transport numbers in the free solution. In consequence of this change, a membrane potential arises[1,2]. In the present work, the authors have determined the potentials of some cation-exchange membranes†.

† The membranes were obtained from the Institute of Plastics.

EXPERIMENTAL

The membrane potentials were calculated from the electromotive force E_{exp} of the cell‡:

(-)Ag, AgCl|0.02 N KCl|membrane|0.01 N KCl|AgCl, Ag(+) (1)

The electromotive force of the cell may be expressed by the formula

$$E_{exp} = \frac{RT}{F} \ln \frac{\gamma_1 c_1}{\gamma_2 c_2} + E_M = E_{conc} + E_M, \quad (2)$$

where the potential of the membrane is given by

$$E_M = \frac{RT}{F} \frac{U-V}{U+V} \ln \frac{\gamma_1 c_1}{\gamma_2 c_2},$$

and U and V are, respectively, the mobilities of the cation K^+ and the anion Cl^- in the membrane; c_1 and c_2 are the concentrations of the KCl solutions on the two sides of the membrane ($c_1 > c_2$); and γ_1 and γ_2 are the corresponding activity coefficients.

Substituting the value of E_M in Eqn. (2) and rearranging, we obtain

$$E_{exp} = \frac{2U}{U+V} \frac{RT}{F} \ln \frac{\gamma_1 c_1}{\gamma_2 c_2}, \quad (3)$$

where $U/(U + V) = n_{K^+}$ is the transport number of the cation K^+ for transfer through the membrane.

Taking $n_{K^+} = 1$ for an ideally permeable cation-exchange membrane, we obtain from (3)

$$E_{theor} = 0.1182 \log \frac{\gamma_1 c_1}{\gamma_2 c_2} \text{ (at } 25°). \quad (4)$$

An actual cation-exchange membrane is characterised by the difference

$$\Delta E = E_{theor} - E_{exp}; \quad (5)$$

E_{theor} was determined from (4).

The Table gives the potentials of some membranes, E_M, calculated from (2), the values of ΔE, and the transport numbers, determined from the relation

$$n_{K^+} = \frac{E_{exp}}{E_{theor}}. \quad (6)$$

It follows from the Table that E_{conc} = 16.89 for E_{theor} = = 33.78 mV.

Potentials of some cation--exchange membrances at 25°.

Membranes	E_{exp}	ΔE	E_M	n_{K^+}
DPU	33.40	0.38	16.51	0.99
DKB-10	30.90	2.88	14.01	0.91
DPB	33.40	0.38	16.51	0.99
DKU-101	30.60	3.18	13.71	0.90
DKU-100	32.70	1.08	15.81	0.97
DKU-104	30.20	3.58	13.31	0.89

‡ The measurements were carried out by the method described by Grigorov *et al.* [1].

The data given are evidence of a parallelism between changes in the membrane potentials, E_M, and the membrane transport numbers.

For DPU, DPB, and DKU-100 membranes, the observed values of the potential are extremely close to the theoretical values, which shows the high permeability of these membranes for cations.

SUMMARY

The membrane potentials of several cation-exchange membranes have been calculated from the e.m.f. of the cell:

(-)Ag, AgCl|0.02 N KCl|membrane|0.01 N KCl|AgCl, Ag(+).

A parallelism between membrane potentials and transport numbers has been established.

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PROPERTIES OF THE DIMETHYLFORMAMIDE–WATER SYSTEM. II. VAPOUR PRESSURE AND OSMOTIC PRESSURE OF AQUEOUS SOLUTIONS

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In spite of the great practical importance of the separation of dimethylformamide–water mixtures and of the preparation of dry dimethylformamide, the literature offers very little information on the vapour–liquid equilibrium of this system. Measurements of the vapour pressure of solutions, over a wide range of temperatures and pressures, offer, in addition, much information on the thermodynamic properties of both components. In a previous article[1] we reported the results of our thermochemical studies and showed that under suitable conditions dimethylformamide can form hydrates of composition $HCON(CH_3)_2 \cdot nH_2O$, where $n = 2-4$. We also tabulated the relative partial enthalpies of the dimethylformamide–water system over the concentration range from 28% to the pure solvent. Earlier, on the basis of ultrasonic studies combined with viscometric, dilatometric, and refractometric measurements, we had shown[2,3] that no dimethylformamide hydrates exist at temperatures higher than 50°–60°.

The present work is devoted to a detailed study of the liquid–vapour equilibrium at 760 mm pressure as well as various reduced pressures, and to the evaluation of some thermodynamic characteristics of the dimethylformamide–water system.