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The Activities of Methyl Orange and Homologs in Aqueous Solutions

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The mean activity coefficients of Methyl Orange (MO), Ethyl Orange (EO), Propyl Orange (PO), and Butyl Orange (BO) in aqueous solutions ranging in concentration from 10^{-3} to 10^{-2} mol kg^{-1} have been determined by means of isopiestic measurements at 50 and 60 °C respectively. It has been found that the mean activity coefficients of MO being the largest, and those of BO, the smallest. The coefficients have been found to decrease with an increase in the dye concentration. The examination of the results by Milicéivic treatment suggests that MO, EO, and PO are present as a monomer or a dimer, while BO exists as a trimer at 60 °C.

Most of the anionic dyes are sodium salts of aromatic sulfonic acids. In aqueous solutions, they have been known to be dissociated completely and to be capable of intermolecular interactions through the hydrophobic groups of the dyes.[1–3] Consequently, the mean activity coefficients of such dyes in aqueous solutions may be governed by the hydrophobic groups in the dye anions.

Since there have been few reports on the mean activity coefficients from the above-mentioned point of view, it seemed that it might be worthwhile to examine the mean activity coefficients of the dyes with various alkyl groups in the dye molecules.

In this paper, the mean activity coefficients of Methyl Orange and its homologs, such as Ethyl Orange, Propyl Orange, and Butyl Orange, in aqueous solutions will be determined by means of isopiestic measurements, and the results will be examined by Milicéivic treatment.

Experimental

Materials. Methyl Orange (MO), Ethyl Orange (EO), Propyl Orange (PO), and Butyl Orange (BO) were used in this experiment. The MO was prepared by coupling diazotized sulfanilic acid with *N*,*N*-dimethylaniline in a weakly acetic acid solution; it was recrystallized three times from water. The EO, supplied by the British Drug House Co., was of a reagent grade; it was isolated by column chromatography on activated alumina and then further purified by recrystallization from ethanol. The PO was synthesized from sulfanilic acid and *N*,*N*-di-*n*-propylaniline by procedures similar to those used for MO; it was then purified in a manner similar to that used for EO. The BO, supplied by the Eastman Kodak Co., was also of a reagent grade; it was purified by procedures to those used for EO.

Vapor-pressure Osmotic Measurements. The vapor-pressure osmometry may also be applicable to the examination of the physical properties of such electrolyte solutions as a dye solution. All the vapor-pressure osmotic measurements were carried out at 50 and 60±0.1 °C[4] using a Hitachi molecular-weight apparatus, Model 115. The difference in electrical resistance of a pair of matched thermistors is measured when a drop of a dye solution on one thermistor and a drop of water on the other thermistor evaporate isothermally in a closed compartment saturated with water vapor. From this value, the resistance difference when water drops are placed on both thermistors is subtracted; the resulting value, ΔR, is known to be dependent linearly upon the osmotic concentration of the dye solution:[5,6]

$$\Delta Rk = -\ln(p/p_0) = \nu\phi m_2/m_1 \tag{1}$$

where k is a constant dependent on the temperature of the solution and the instrumental characteristics; p and p_0 are the partial pressures of the solvent over the solution and over the pure solvent; ν is the number of the particles into which the solute dissociates; ϕ is the osmotic coefficient, and m_2 and m_1 are the solute and solvent molarities respectively. Urea was used in order to determine the numerical values of k,[7,8] so the ϕ values could be obtained by means of Eq. 1.

The evaluation of the mean activity coefficient of an electrolyte can be made as follows.[9] The Gibbs-Duhem equation is applied to the derivation of the interrelation between the osmotic coefficient and the mean activity coefficient, $\gamma_\pm$.

$$\mathrm{d}\ln\gamma_\pm = \mathrm{d}\phi + (\phi-1)\mathrm{d}\ln m_2 \tag{2}$$

$$\ln\gamma_\pm = (\phi-1) + \int_0^m(\phi-1)\mathrm{d}\ln m_2 \tag{3}$$

The integration can be carried out graphically from the plot of $(1-\phi)m_2^{-1}$ *vs.* m_2.

Table 1 gives the measured resistance differences, ΔR, of urea solutions at 50 and 60 °C respectively. The numerical values of k are also shown in Table 1.

Table 1. Measured resistance differences, ΔR, and constants, k, of urea solutions at 50 and 60 °C

$10^{-3}\,m_2$ / mol kg^{-1}	50 °C		60 °C	
	ΔR / Ω	$10^{-6}\,k$ / Ω^{-1}	ΔR / Ω	$10^{-6}\,k$ / Ω^{-1}
2.0	5.2	6.92	3.6	9.99
4.0	9.9	7.27	7.6	9.47
6.0	15.2	7.10	11.4	9.47
8.0	19.6	7.34	14.9	9.67
10.0	24.7	7.28	18.4	9.77
Mean		7.18		9.67

Results and Discussion

Measured Resistance Differences. The measured resistance differences, ΔR, of MO, EO, PO, and BO solutions at 50 and 60 °C are plotted against m_2 in Figs. 1 and 2 respectively. From Figs. 1 and 2 it may be seen that the plots of urea solutions are almost linear, while the plots of the dye solutions display slight downward curvatures. It is noteworthy that the ΔR values of MO solutions are the largest, while those of BO solutions are the smallest. All of the ΔR values of the dye solutions are smaller than twice the ΔR values of urea solutions.

Osmotic Coefficients. The osmotic coefficients, ϕ, of MO, EO, PO, and BO solutions ranging in concentration from 10^{-3} to 10^{-2} mol kg^{-1} were obtained from the ΔR values given in Figs. 1 and 2 by means of Eq. 1;

Table 2. Osmotic coefficients of Methyl Organge, Ethyl Orange, Propyl Orange, and Butyl Orange aqueous solutions at 50 and 60 °C

$\frac{10^{-3}\,m_2}{\text{mol kg}^{-1}}$	Methyl Orange		Ethyl Orange		Propyl Orange		Butyl Orange	
	50 °C	60 °C	50 °C	60 °C	50 °C	60 °C	50 °C	60 °C
1.0	0.918	0.994	0.918	0.994	0.878	0.994	0.858	0.914
2.0	0.888	0.941	0.858	0.927	0.818	0.927	0.768	0.779
3.0	0.858	0.932	0.818	0.925	0.792	0.896	0.719	0.744
4.0	0.848	0.914	0.798	0.868	0.768	0.856	0.694	0.705
5.0	0.854	0.908	0.782	0.855	0.758	0.849	0.687	0.693
6.0	0.853	0.900	0.772	0.842	0.748	0.838	0.672	0.685
7.0	0.830	0.895	0.761	0.825	0.747	0.818	0.664	0.672
8.0	0.823	0.894	0.756	0.816	0.736	0.810	0.656	0.665
9.0	0.821	0.884	0.750	0.806	0.730	0.797	0.652	0.657
10.0	0.822	0.881	0.747	0.798	0.729	0.793	0.649	0.656

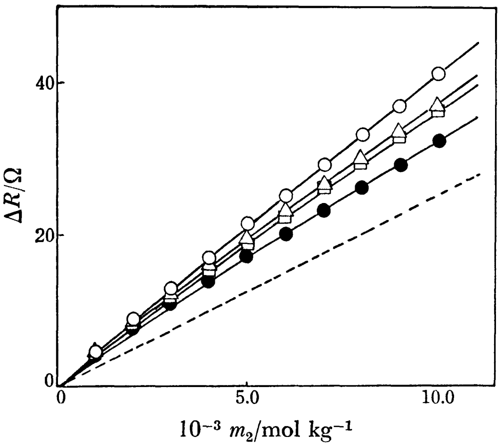

Fig. 1. Measured resistance differences of solutions of Methyl Orange and its homologs at 50 °C.
○: Methyl Orange, △: Ethyl Orange, □: Propyl Orange, ●: Butyl Orange, ----: urea.

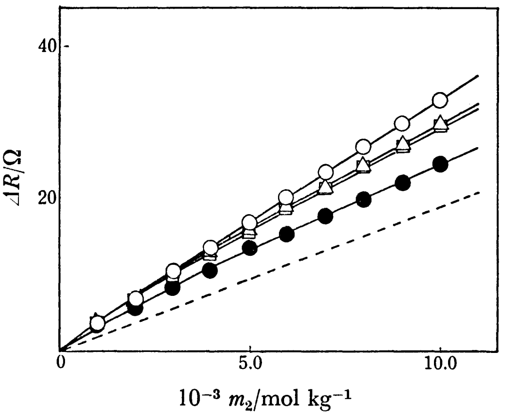

Fig. 2. Measured resistance differences of solutions of Methyl Orange and its homologs at 60 °C.
○: Methyl Orange, △: Ethyl Orange, □: Propyl Orange, ●: Butyl Orange, ----: urea.

they are shown in Table 2. All of the ϕ values of the four dyes are seen to be much smaller than unity. The ϕ values of the MO solution are the largest, while those of the BO solution are the smallest. These results strongly suggest that the aqueous solutions of these dyes deviate from the ideal.

Determination of Mean Activity Coefficients. The determination of the mean activity coefficients, $\gamma_\pm$, was made as follows. The $(1-\phi)m^{-1}$ at 50 °C was plotted against m_2 as is shown in Fig. 3. After the plot has been extrapolated to zero concentration, the area under the curve was measured and the $\gamma_\pm$ values were calculated according to Eq. 3. The $\gamma_\pm$ values of MO, EO, PO, and BO at 50 and 60 °C are shown in Table 3. These values are comparable to those of C. I. Direct Blue 1.[10,11] In Table 3 it may be seen that the $\gamma_\pm$ values are much smaller than unity and decrease with an increase in the chain length of the alkyl groups in the dye molecules. These results strongly suggest that the mean activity coefficients are influenced by the hydrophobic parts of the dye molecules: *i.e.*, the differences in the $\gamma_\pm$ values among these four dyes are attributable to the association of the dye anions.

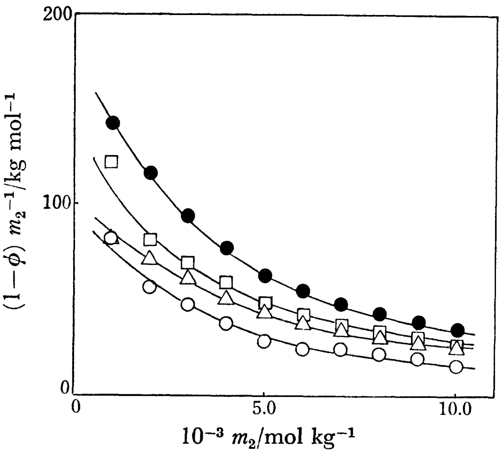

Fig. 3. Plots of $(1-\phi)m_2^{-1}$ against m_2.
○: Methyl Orange, △: Ethyl Orange, □: Propyl Orange, ●: Butyl Orange.

Examinations of Results by Milicěivic Treatment. Since these dyes are known to dissociate completely in aqueous solutions, and since the ionic strengths of these solutions are small, the Debye-Hückel limiting law may be supposed to hold. The relation between the mean activity, $a_\pm$, and the mean association number of the dye anions, n, can be derived from the Debye-Hückel limiting law:[12]

$$\log a_\pm = \log m_2 - \frac{1}{n+1}\log n - Anm_2\sqrt{\frac{1+n}{2}} \tag{4}$$

where;

$$a_\pm = \gamma_\pm m_2 \tag{5}$$

TABLE 3. MEAN ACTIVITY COEFFICIENTS OF METHYL ORANGE, ETHYL ORANGE, PROPYL ORANGE, AND BUTYL ORANGE AT 50 AND 60 °C

$10^{-1}\ m_2$ / mol kg^{-1}	Methyl Orange		Ethyl Orange		Propyl Orange		Butyl Orange	
	50 °C	60 °C	50 °C	60 °C	50 °C	60 °C	50 °C	60 °C
1.0	0.850	0.960	0.838	0.945	0.771	0.934	0.743	0.795
2.0	0.776	0.879	0.737	0.846	0.666	0.831	0.601	0.623
3.0	0.722	0.858	0.664	0.800	0.627	0.773	0.527	0.555
4.0	0.702	0.826	0.632	0.740	0.582	0.716	0.485	0.507
5.0	0.691	0.807	0.603	0.723	0.569	0.719	0.484	0.484
6.0	0.683	0.793	0.591	0.712	0.543	0.694	0.460	0.481
7.0	0.684	0.807	0.568	0.671	0.559	0.658	0.452	0.459
8.0	0.684	0.792	0.563	0.662	0.538	0.658	0.438	0.453
9.0	0.674	0.761	0.548	0.623	0.518	0.616	0.431	0.433

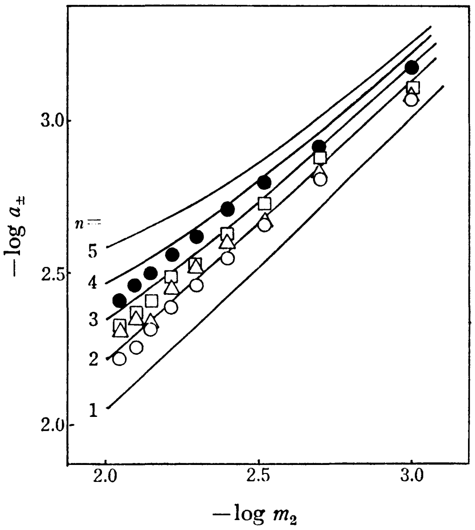

Fig. 4. Mean activities of Methyl Orange and its homologs at 50 °C.

○: Methyl Orange, △: Ethyl Orange, □: Propyl Orange, ●: Butyl Orange.

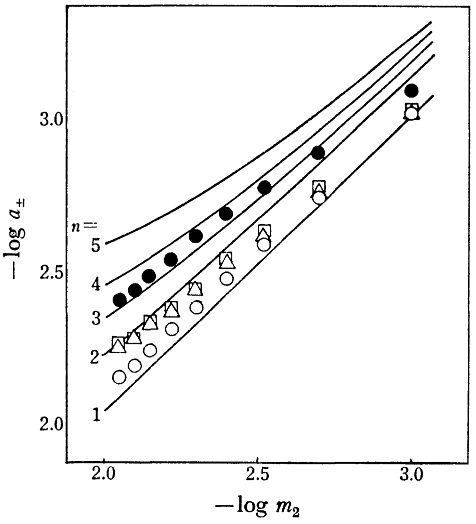

Fig. 5. Mean activities of Methyl Orange and its homologs at 60 °C.

○: Methyl Orange, △: Ethyl Orange, □: Propyl Orange, ●: Butyl Orange.

Also, if the electronic charge and the gas constant are taken as 4.80×10^{-10} esu and 8.31×10^{-7} erg °C mol^{-1} ($1\ \text{erg}=1\times10^{-7}$ J) respectively,

$$A = 1.825\times10^{6}\left(\frac{\rho_0}{D_0{}^3T^3}\right)^{1/2} \tag{6}$$

where D_0 and ρ_0 are the dielectric constant and the density of the solvent at a temperature, T, respectively.

The mean activities of MO, EO, PO, and BO at 50 and 60 °C are plotted against log m_2 in Figs. 4 and 5 respectively. The solid lines in Figs. 4 and 5 are theoretical lines drawn according to Eq. 4. In Fig. 4, the plots for MO and EO are seen to be close to the dimer line ($n=2$), the plots for PO, close to the trimer line ($n=3$), and the plots for close to the tetramer line ($n=4$). These results indicate that the MO and EO dye anions are present as dimers, the PO anions, as trimers, and the BO dye anions, as tetramers, on the average, at 50 °C. From Fig. 5, MO, EO, and PO are seen to exist as monomers or dimers, and BO, as trimers, at 60 °C.

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8) Since a very dilute urea solution is known to behave ideally, the urea can be used as the reference solute ($\nu=1$ and $\phi=1$).[7]

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