# The Activities of Sodium Salts of 1-Amino-4-alkylaminoanthraquinone-2-sulfonic Acid in Aqueous Solutions

Masaru MITSUISHI* and Yuzoh YAMAGUCHI
*Faculty of Textile Science and Technology, Shinshu University, Tokida, Ueda 386*

(Received May 30, 1980)

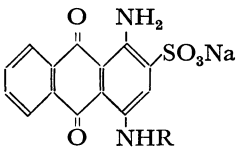
The mean activity coefficients of sodium salts of 1-amino-4-alkylaminoanthraquinone-2-sulfonic acid (alk= Me(MAS), Et, *n*-Pr, or *n*-Bu (*n*-BAS)) in aqueous solutions ranging in concentration from $10^{-3}$ to $10^{-2}$ mol kg$^{-1}$ have been determined by means of isopiestic measurements at 50 and 60 °C respectively. It has been found that the mean activity coefficients of these dyes are much smaller than unity, the coefficients of MAS being the largest, and those of *n*-BAS, the smallest. The coefficients have been found to decrease with an increase in the dye concentration. An examination of the results obtained by Milicéivic treatment suggests that the MAS exists as dimer or trimers, and the other dyes, as tetramers, at 60 °C.

In a previous paper,[1] we have reported on the mean activity coefficients of such azo-acid dyes as Methyl Orange and its homologs in aqueous solutions, and on the effects of the hydrophobic groups on the activity coefficients. The derivatives of sodium salts of 1-aminoanthraquinone-2-sulfonic acid also belong to the acid dye class. The behavior of aminoanthraquinone acid dyes in aqueous solutions is known to be different from that of azo-acid dyes; *e.g.*, the aqueous solutions of sodium salts of 1-amino-4-alkylaminoanthraquinone-2-sulfonic acid (alk=Me, Et, *n*-Pr, or *n*-Bu) have been found to have their critical concentration for dimer formation at from 1 to $4\times10^{-3}$ mol kg$^{-1}$, and the critical concentrations have been found to decrease with an increase in the alkyl groups in the dye molecules.[2] The mean activities of these dyes are supposed to be influenced strongly by dimerization; however, there have been few reports on the mean activities of sodium salts of 1-amino-4-alkylaminoanthraquinone-2-sulfonic acid. Therefore, it would seem valuable to examine the mean activities of these dyes.

In this paper, the mean activity coefficients of sodium salts of 1-amino-4-alkylaminoanthraquinone-2-sulfonic acid (alk=Me, Et, *n*-Pr, or *n*-Bu) in aqueous solutions will be determined by means of isopiestic measurements, and the results will be examined by means of a Milicéivic treatment in order to obtain information on the association of these dyes.

## Experimental

*Materials.* The sodium salts of 1-amino-4-alkylaminoanthraquinone-2-sulfonic acid (AAS) used in this experiment were as follows;




R: $CH_3$ (MAS)
R: $C_2H_5$ (EAS)
R: *n*-$C_3H_7$ (*n*-PAS)
R: *n*-$C_4H_9$ (*n*-BAS)

These dyes were prepared as follows. 1-Amino-4-bromoanthraquinone-2-sulfonic acid (50 g) was refluxed with the corresponding alkylamine (10 g) for 8 h in the presence of copper(II) sulfate and sodium carbonate. The product was isolated by column chromatography on activated alumina, and then purified by recrystallization from ethanol.

*Vapor-pressure Osmotic Measurements.* The vapor-pressure osmotic measurements were carried out by the procedures described in the previous paper[1] at 50 and 60 °C. The measured resistance difference, $\Delta R$, is dependent upon the osmotic concentration of the dye solution according to Eq. 1:[3]

$$\Delta R\,k = -\ln(p/p_0) = \nu\phi m_2/m_1, \quad (1)$$

where $k$ is the constant[4] 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 solvent; $\nu$ is the number of the particles into which the dye dissociates; $\phi$ is the osmotic coefficients, and $m_2$ and $m_1$ are the solute and solvent molalities respectively.

The evaluation of the mean activity coefficients ($\gamma_\pm$) of the dye from the $\phi$ values can be made by means of Eq. 2:

$$\ln\gamma_\pm = (\phi-1) + \int_0^m (\phi-1)d\ln m_2. \quad (2)$$

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

## Results and Discussion

*Measured Resistance Differences.* The measured resistance differences, $\Delta R$, of MAS, EAS, *n*-PAS, and *n*-BAS 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 $\Delta R$ values of MAS solutions are the largest, while those of *n*-BAS are the smallest. All of the $\Delta R$ values of the dye solutions are smaller than twice the $\Delta R$ values of urea solutions.

*Osmotic Coefficients.* The osmotic coefficients, $\phi$, of MAS, EAS, *n*-PAS, and *n*-BAS solutions ragning in concentration from $10^{-3}$ to $10^{-2}$ mol kg$^{-1}$ were obtained from $\Delta R$ values in Figs. 1 and 2 by means of Eq. 1; they are given in Table 1. The $\phi$ values of all four kinds of dyes may be seen to be much smaller than unity. The $\phi$ values of the MAS solutions are the largest, while those of the *n*-BAS solutions are the smallest. In Fig. 3, the $\phi$ values of the MAS and *n*-BAS solutions at 50 °C are plotted against $m_2$. Since the $\phi$ values of these dye solutions were found to decrease monotonically with an increase in $m_2$, no evidence for the presence of Iyer's critical concentrations of the dimerization of these dyes was found. The $\phi$ values given in Table 1 strongly suggest that the aqueous solutions of the AAS deviate from the ideal.

Table 1. Osmotic coefficients of sodium salts of 1-amino-4-alkylaminoanthraquinone-2-sulfonic acid at 50 and 60 °C

| $10^3\ m_2$ / mol kg$^{-1}$ | MAS | | EAS | | PAS | | BAS | |
|---|---|---|---|---|---|---|---|---|
| | 50° C | 60 °C | 50 °C | 60 °C | 50 °C | 60 °C | 50 °C | 60 °C |
| 1.0 | 0.818 | 0.941 | 0.798 | 0.833 | 0.833 | 0.833 | 0.719 | 0.877 |
| 2.0 | 0.748 | 0.820 | 0.709 | 0.739 | 0.729 | 0.739 | 0.659 | 0.766 |
| 3.0 | 0.705 | 0.779 | 0.679 | 0.717 | 0.672 | 0.717 | 0.632 | 0.735 |
| 4.0 | 0.684 | 0.746 | 0.659 | 0.692 | 0.654 | 0.692 | 0.619 | 0.699 |
| 5.0 | 0.671 | 0.736 | 0.643 | 0.693 | 0.639 | 0.688 | 0.611 | 0.688 |
| 6.0 | 0.662 | 0.717 | 0.635 | 0.681 | 0.629 | 0.685 | 0.605 | 0.681 |
| 7.0 | 0.653 | 0.710 | 0.630 | 0.672 | 0.622 | 0.672 | 0.602 | 0.668 |
| 8.0 | 0.649 | 0.705 | 0.624 | 0.669 | 0.616 | 0.672 | 0.592 | 0.662 |
| 9.0 | 0.643 | 0.696 | 0.621 | 0.663 | 0.612 | 0.666 | 0.594 | 0.654 |

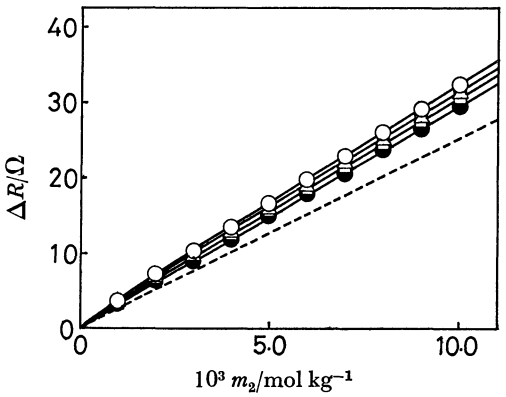



Fig. 1. Measured resistance differences of solutions of sodium salts of 1-amino-4-alkylaminoanthraquinone-2-sulfonic acid at 50 °C.
○: MAS, △: EAS, □: *n*-PAS, ●: *n*-BAS, ---: urea.

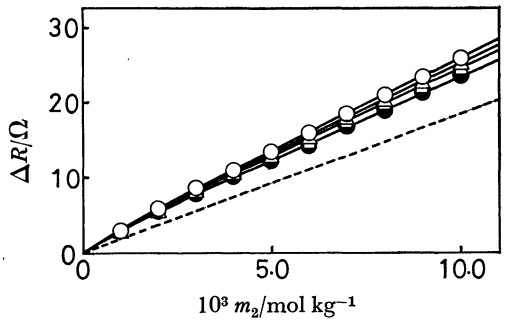



Fig. 2. Measured resistance differences of solutions of sodium salts of 1-amino-4-alkylaminoanthraquinone-2-sulfonic acid at 60 °C.
○: MAS, △: EAS, □: *n*-PAS, ●: *n*-BAS, ---: urea.

*Determinations of Mean Activity Coefficients.* The determinations of the mean activity coeeficients, $\gamma_\pm$, was done as follows. The $(1-\phi)m_2^{-1}$ value at 50 °C was plotted against $m_2$, as shown in Fig. 4. After the plots had been extrapolated to zero concentration, the area under the curve was measured and the $\gamma_\pm$ values were calculated according to Eq. 2. The $\gamma_\pm$ values of MAS, EAS, *n*-PAS, and *n*-BAS at 50 and 60 °C are shown in Table 2. In Table 2 it can be seen that the $\gamma_\pm$ values are much smaller than unity and that they decrease with an increase in the chain length of the alkyl groups in the dye molecules.

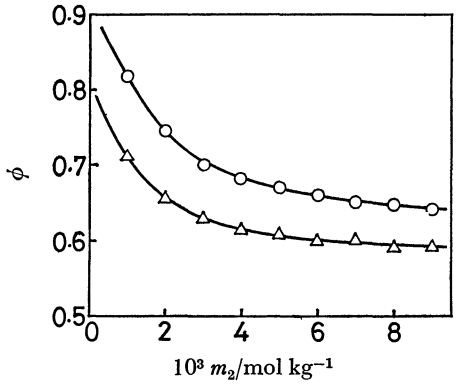



Fig. 3. Osmotic coefficients of solutions of MAS and *n*-BAS at 50 °C.
○: MAS, △: *n*-BAS.

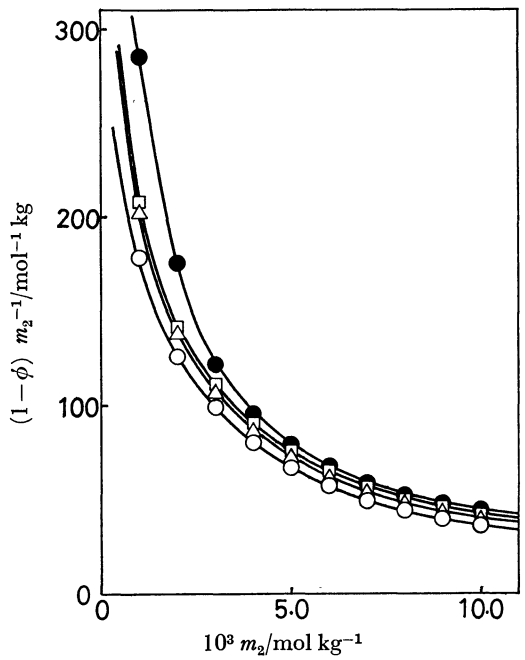



Fig. 4. Plots of $(1-\phi)\ m_2^{-1}$ against $m_2$.
○: MAS, △: EAS, □: *n*-PAS, ●: *n*-BAS.

Generally, the $\gamma_\pm$ values of the AAS dyes seem to be less than those of Methyl Orange and its homologs reported in the previous paper.[1] These $\gamma_\pm$ values

Table 2. Mean activity coefficients of sodium salts of 1-amino-4-alkylaminoanthraquinone-2-sulfonic acid at 50 and 60 °C

| $10^3\ m_2$ / mol kg$^{-1}$ | MAS | | EAS | | PAS | | BAS | |
|---|---|---|---|---|---|---|---|---|
| | 50 °C | 60 °C | 50 °C | 60 °C | 50 °C | 60 °C | 50 °C | 60 °C |
| 1.0 | 0.676 | 0.839 | 0.647 | 0.703 | 0.646 | 0.703 | 0.540 | 0.760 |
| 2.0 | 0.593 | 0.677 | 0.532 | 0.551 | 0.550 | 0.551 | 0.459 | 0.598 |
| 3.0 | 0.508 | 0.607 | 0.477 | 0.525 | 0.470 | 0.525 | 0.422 | 0.532 |
| 4.0 | 0.478 | 0.553 | 0.452 | 0.477 | 0.447 | 0.480 | 0.406 | 0.494 |
| 5.0 | 0.462 | 0.542 | 0.429 | 0.488 | 0.427 | 0.473 | 0.395 | 0.473 |
| 6.0 | 0.451 | 0.526 | 0.418 | 0.472 | 0.414 | 0.481 | 0.387 | 0.476 |
| 7.0 | 0.434 | 0.502 | 0.420 | 0.453 | 0.405 | 0.449 | 0.386 | 0.454 |
| 8.0 | 0.433 | 0.523 | 0.403 | 0.454 | 0.397 | 0.458 | 0.375 | 0.449 |
| 9.0 | 0.416 | 0.484 | 0.372 | 0.448 | 0.349 | 0.445 | 0.369 | 0.436 |

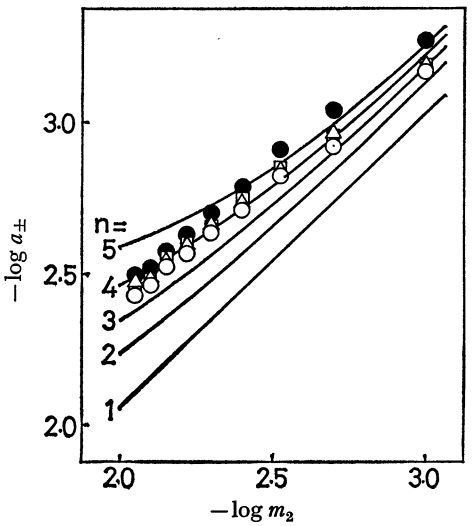



Fig. 5. Mean activities of sodium salts of 1-amino-4-alkylaminoanthraquinone-2-sulfonic acid at 50 °C.
○: MAS, △: EAS, □: *n*-PAS, ●: *n*-BAS.

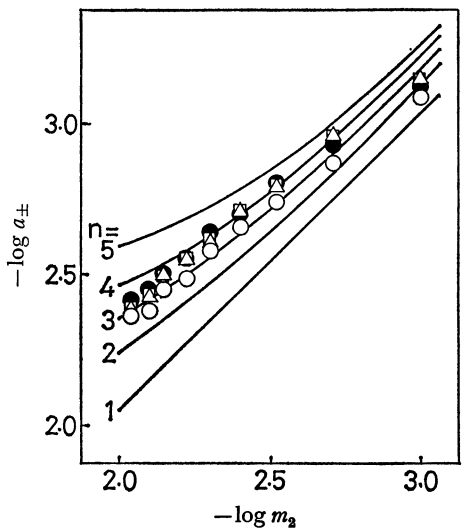



Fig. 6. Mean activities of sodium salts of 1-amino-4-alkylaminoanthraquinone-2-sulfonic acid at 60 °C.
○: MAS, △: EAS, □: *n*-PAS, ●: *n*-BAS.

strongly suggest that the $\gamma_\pm$ values of the AAS dyes are also dependent on the hydrophobic parts of the dye molecules; *i.e.*, the differences in the $\gamma_\pm$ values among these dyes are due to the association of the dye anions.

*Examination of Results Obtained by Milicéivic Treatment.* Since these dyes are known to dissociate completely, and since the ionic strengths of these solutions are small, the Debye-Hückel limiting law can also hold.

The relation between the mean activity, $a_\pm$, and the mean association number of the dye anions, $n$, was given by Milicéivic as:[5]

$$\log a_\pm = \log m_2 - \frac{1}{n+1}\log n - A n m_2 \sqrt{\frac{1+n}{2}}, \qquad (3)$$

where $A$ is the constant and where the numerical values at 50 and 60 °C are 0.5320 and 0.5425 respectively.

The mean activities of MAS, EAS, *n*-PAS, and *n*-BAS at 50 and 60 °C are plotted against $\log m_2$ in Figs. 5 and 6 respectively. The solid lines in Figs. 5 and 6 are Milicéivic lines drawn according to Eq. 3.

In Fig. 5 the plots of MAS, EAS, and *n*-PAS are seen to be close to the trimer ($n$=3) and tetramer ($n$=4) curves. The plots of *n*-BAS are close to the pentamer ($n$=5) curves. The results suggest that MAS, EAS, *n*-PAS dye anions are present as trimers or tetramers, and n-BAS dye anions, as tetramers, on the average usually, at 50 °C. From Fig. 6, MAS dye anions are seen to exist as dimers or trimers, and EAS, *n*-PAS, and *n*-BAS, as tetramers, at 60 °C. These results also suggest that there is no evidence for the presence of Iyer's critical concentration of the dimerization of these dyes. The quantities of the dye association become larger with an increase in the number of alkyl groups in the dye molecules.

## References

1) M. Mitsuishi and Y. Yamaguchi, *Bull. Chem. Soc. Jpn.*, **52**, 3496 (1979).
2) S. R. Sivaraja Iyer and G. S. Singh, *J. Soc. Dyers Colour.*, **89**, 128 (1973).
3) I. Porigoric and I. J. Gal, *Trans. Faraday Soc.*, **68**, 1093 (1972).
4) Urea was used in order to determine the numerical values of $k$,[3] and the $k$ values at 50 and 60 °C are $71.8\times10^{-6}$ and $9.67\times10^{-6}\ \Omega^{-1}$ respectively.[1]
5) M. Milicéivic and G. Eigen, *Helv. Chim. Acta.*, **44**, 1039 (1964).