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Absorption and Fluorescence Properties of Cyanine Dyes

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The absorption and fluorescence properties of a variety of cyanine dyes in dimethyl sulfoxide solutions have been determined. The wavelengths of the absorption and fluorescence maxima and the fluorescence quantum yield relative to sodium fluorescein have been measured. The results are discussed in relation to the molecular structure.

During the course of our research to evaluate indicator substances that could be used in the study of the retinal and choroïdal circulation in the eye, a substantial amount of data was obtained regarding cyanine and merocyanine (or polymethine) dyes. Although the polymethine dyes are widely used as photographic sensitizers, in dye lasers, as saturable absorbers for passively Q-switching lasers, and as molecular probes of membrane potential, there does not appear to be a compilation of the spectral data of these compounds in the literature. In fact, very little has been published regarding fluorescence properties at wavelengths longer than 700 nm. We have correlated the spectral properties of the polymethine dyes with their molecular structure in order to predict the wavelengths of maximum absorption and fluorescence and to roughly estimate the fluorescence quantum yield.

Experimental Section

A Beckman DK-2 spectrometer was used to measure the absorption spectra. A schematic of the fluorescence apparatus is shown in Figure 1. Note that because our work was ultimately for ophthalmic applications, the fluorescence was detected in a direction parallel to the excitation light instead of the usual 90° configuration. A 75-W xenon lamp was used as the excitation source, and the output was filtered by a SPEX Model 1670 monochromator; the slit width was 2.5 mm (10 nm band-pass). The excitation light was focused on the sample cell (1-cm cuvette) by a 30-cm spherical mirror. The fluorescence from the sample was coupled out through a 5-cm diameter hole in the center of the mirror, modulated by a mechanical chopper, and focused on the slit (0.5 mm, 5 nm band-pass) of a Perkin-Elmer Model 83 monochromator. The fluorescence detector was an RCA 4832 photomultiplier tube (PMT) which has a rather flat response from 400 to 850 nm. (For wavelengths longer than 850 nm, an RCA C31004A PMT was used.) The PMT output was preamplified and phase-sensitive detected at the modulation frequency using a lock-in amplifier. The lock-in output was then chart recorded.

All measurements were made at ambient conditions without extensive temperature regulation or solvent degassing. The dyes were obtained from several manufacturers (see Table I) and were used without further purification.

The fluorescence quantum yield of the cyanine dyes was measured relative to sodium fluorescein in distilled water. The optimum fluorescein concentration for the 1-cm cuvette was 0.1 g/L (2.7×10^{-4} M). The quantum yields have been corrected for the spectral response of the apparatus components.

Results and Discussion

The spectral results are summarized in Table I according to the basic molecular structure. λ_{abs} refers to the wavelength at which the absorption was found to be a maximum. The excitation wavelength (λ_{ex}) refers to the actual wavelength setting of the source monochromator which produces the maximum sample fluorescence. Note that λ_{ex} was not corrected for the spectral variations of the source, and since the intensity of the xenon lamp varied with wavelength, λ_{ex} did not necessarily coincide with λ_{abs} .

Although we were primarily interested in aqueous solutions for the ophthalmic applications, the majority of the dyes were not sufficiently soluble in water. In order to compare the results from a variety of dyes, dimethyl sulfoxide (Me_2SO) was used since most of the dyes were readily soluble in it. Studies of the concentration dependence of fluorescence in Me_2SO for several dyes indicated the maximum fluorescence occurred at approximately 0.1 g/L. This concentration was used in all of the fluorescence measurements reported in Table I.

As mentioned above, the fluorescence quantum yield has been corrected for the spectral response of the apparatus. However, the majority of the dyes are rather impure (3) and, therefore, the quantum yields should be considered for general trends rather than for comparing individual dyes. For example, it is evident from Table I that dyes possessing the 4,4'- or 2,2'-quino structure and the merocyanines generally have low

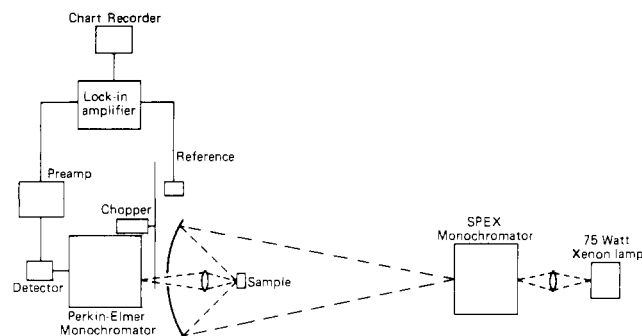


Figure 1. Schematic of apparatus used in measuring fluorescence spectra.

Table I. Spectral Properties of Cyanine Dyes in Me₂SO, 0.1 g/L

| Manufr. no. | n | R | X | R' | Y | Z | λ _{abs} , nm | λ _{e.x.} , nm | λ _{fl} , nm | Fluores quantum yield ^a | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|--|--------------------------------|--|---------|------------------------|-----------------------|------------------------|----------------------|------------------------------------|--------------------------|------------|---|--|-----------------|----|---|-----------------------|------------------------|----------------------|------------------------------------|-------|--------------------------|---|--|--------------------------------|----|---------|--|-----|-----|-----|------|--------------|---|--|--------------------------------|----|---------|------------------------|-----|-----|-----|-------|---------|---|--|-----------------|--|---------|--|-----|-----|-----|------|---------|---|--|--|-------------------------------------|---------|--|-----|-----|-----|------|
| | | | | | | | | | | | Manufr. no. ^b | n | X | R ^c | R' | Y | Z | λ _{abs} , nm | λ _{e.x.} , nm | λ _{fl} , nm | Fluores quantum yield ^a | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| <div style="display: flex; justify-content: space-around; align-items: flex-start;"> <div style="text-align: center;"> <p>I</p> </div> <div style="text-align: center;"> <p>II</p> </div> <div style="text-align: center;"> <p>III</p> </div> <div style="text-align: center;"> <p>IV</p> </div> <div style="text-align: center;"> <p>V</p> </div> <div style="text-align: center;"> <p>VI</p> </div> <div style="text-align: center;"> <p>VII</p> </div> <div style="text-align: center;"> <p>VIII</p> </div> <div style="text-align: center;"> <p>IX</p> </div> <div style="text-align: center;"> <p>X</p> </div> </div> | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| <p>I. 2,2'-Indocarbocyanine</p> <table border="1"> <tbody> <tr> <td>NK-1639</td> <td>1</td> <td>(CH₂)₃SO₃⁻</td> <td></td> <td></td> <td></td> <td></td> <td>550</td> <td>470</td> <td>600</td> <td>0.19</td> </tr> <tr> <td>NK-1751</td> <td>1</td> <td>(CH₂)₃SO₃Na</td> <td>I⁻</td> <td></td> <td></td> <td></td> <td>550</td> <td>530</td> <td>580</td> <td>0.25</td> </tr> <tr> <td>NK-1405</td> <td>3</td> <td>CH₂COO⁻</td> <td></td> <td></td> <td></td> <td></td> <td>760</td> <td>730</td> <td>790</td> <td>0.25</td> </tr> <tr> <td>NK-1404</td> <td>3</td> <td>CH₂CH=CH₂</td> <td>Br⁻</td> <td></td> <td></td> <td></td> <td>760</td> <td>730</td> <td>790</td> <td>0.26</td> </tr> <tr> <td>NK-1967</td> <td>3</td> <td>(CH₂)₃SO₃⁻</td> <td></td> <td></td> <td></td> <td></td> <td>740</td> <td>735</td> <td>795</td> <td>0.28</td> </tr> </tbody> </table> | | | | | | | | | | | | NK-1639 | 1 | (CH ₂) ₃ SO ₃ ⁻ | | | | | 550 | 470 | 600 | 0.19 | NK-1751 | 1 | (CH ₂) ₃ SO ₃ Na | I ⁻ | | | | 550 | 530 | 580 | 0.25 | NK-1405 | 3 | CH ₂ COO ⁻ | | | | | 760 | 730 | 790 | 0.25 | NK-1404 | 3 | CH ₂ CH=CH ₂ | Br ⁻ | | | | 760 | 730 | 790 | 0.26 | NK-1967 | 3 | (CH ₂) ₃ SO ₃ ⁻ | | | | | 740 | 735 | 795 | 0.28 |
| NK-1639 | 1 | (CH ₂) ₃ SO ₃ ⁻ | | | | | 550 | 470 | 600 | 0.19 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| NK-1751 | 1 | (CH ₂) ₃ SO ₃ Na | I ⁻ | | | | 550 | 530 | 580 | 0.25 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| NK-1405 | 3 | CH ₂ COO ⁻ | | | | | 760 | 730 | 790 | 0.25 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| NK-1404 | 3 | CH ₂ CH=CH ₂ | Br ⁻ | | | | 760 | 730 | 790 | 0.26 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| NK-1967 | 3 | (CH ₂) ₃ SO ₃ ⁻ | | | | | 740 | 735 | 795 | 0.28 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| <p>II. 2,2'-Indo-4,5,4',5'-dibenzocarbocyanine</p> <table border="1"> <tbody> <tr> <td>NK-1841</td> <td>2</td> <td>(CH₂)₄SO₃⁻</td> <td></td> <td></td> <td></td> <td></td> <td>680</td> <td>685</td> <td>720</td> <td>0.36</td> </tr> <tr> <td>H.W.D. Indocyanine Green</td> <td>3</td> <td>(CH₂)₄SO₃⁻</td> <td>I⁻</td> <td></td> <td></td> <td></td> <td>795</td> <td>765</td> <td>835</td> <td>0.13</td> </tr> <tr> <td>East. IR-125</td> <td>3</td> <td>(CH₂)₄SO₃Na</td> <td></td> <td></td> <td></td> <td></td> <td>795</td> <td>765</td> <td>835</td> <td>0.13</td> </tr> </tbody> </table> | | | | | | | | | | | | NK-1841 | 2 | (CH ₂) ₄ SO ₃ ⁻ | | | | | 680 | 685 | 720 | 0.36 | H.W.D. Indocyanine Green | 3 | (CH ₂) ₄ SO ₃ ⁻ | I ⁻ | | | | 795 | 765 | 835 | 0.13 | East. IR-125 | 3 | (CH ₂) ₄ SO ₃ Na | | | | | 795 | 765 | 835 | 0.13 | | | | | | | | | | | | | | | | | | | | | | |
| NK-1841 | 2 | (CH ₂) ₄ SO ₃ ⁻ | | | | | 680 | 685 | 720 | 0.36 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| H.W.D. Indocyanine Green | 3 | (CH ₂) ₄ SO ₃ ⁻ | I ⁻ | | | | 795 | 765 | 835 | 0.13 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| East. IR-125 | 3 | (CH ₂) ₄ SO ₃ Na | | | | | 795 | 765 | 835 | 0.13 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| <p>III. 2,2'-Thiacarbocyanine</p> <table border="1"> <tbody> <tr> <td>NK-442</td> <td>1</td> <td>Me</td> <td>p-ASA</td> <td></td> <td></td> <td></td> <td>560</td> <td>550</td> <td>595</td> <td>0.018</td> </tr> <tr> <td>NK-1839</td> <td>2</td> <td>(CH₂)₃SO₃⁻</td> <td></td> <td>Me</td> <td>4,4'-Me</td> <td></td> <td>660</td> <td>665</td> <td>695</td> <td>0.23</td> </tr> <tr> <td>NK-156</td> <td>2</td> <td>Et</td> <td>EtSO₄⁻</td> <td>Et</td> <td>4,4'-Me</td> <td>8-(3-Et-4-Me-thiazole)</td> <td>610</td> <td>580</td> <td>640</td> <td>0.042</td> </tr> </tbody> </table> | | | | | | | | | | | | NK-442 | 1 | Me | p-ASA | | | | 560 | 550 | 595 | 0.018 | NK-1839 | 2 | (CH ₂) ₃ SO ₃ ⁻ | | Me | 4,4'-Me | | 660 | 665 | 695 | 0.23 | NK-156 | 2 | Et | EtSO ₄ ⁻ | Et | 4,4'-Me | 8-(3-Et-4-Me-thiazole) | 610 | 580 | 640 | 0.042 | | | | | | | | | | | | | | | | | | | | | | |
| NK-442 | 1 | Me | p-ASA | | | | 560 | 550 | 595 | 0.018 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| NK-1839 | 2 | (CH ₂) ₃ SO ₃ ⁻ | | Me | 4,4'-Me | | 660 | 665 | 695 | 0.23 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| NK-156 | 2 | Et | EtSO ₄ ⁻ | Et | 4,4'-Me | 8-(3-Et-4-Me-thiazole) | 610 | 580 | 640 | 0.042 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| <p>IV. 2,2'-Thiacarbocyanine</p> <table border="1"> <tbody> <tr> <td>G.S.G-1740</td> <td>1</td> <td>Et</td> <td>Br⁻</td> <td>Et</td> <td></td> <td>9-Me</td> <td>550</td> <td>500</td> <td>595</td> <td>0.006</td> </tr> <tr> <td>NK-1638</td> <td>1</td> <td>Et</td> <td>EtSO₄⁻</td> <td>Et</td> <td></td> <td></td> <td>565</td> <td>560</td> <td>590</td> <td>0.14</td> </tr> <tr> <td>East. 7663</td> <td>2</td> <td>Et</td> <td>I⁻</td> <td>Et</td> <td></td> <td></td> <td>660</td> <td>650</td> <td>695</td> <td>0.73</td> </tr> <tr> <td>NK-1838</td> <td>2</td> <td>(CH₂)₃SO₃⁻</td> <td></td> <td>(CH₂)₃SO₃Na</td> <td>6,6'-Me</td> <td></td> <td>660</td> <td>665</td> <td>700</td> <td>0.65</td> </tr> <tr> <td>NK-1893</td> <td>2</td> <td>C₂H₄COO⁻</td> <td></td> <td>C₂H₄COONa</td> <td>6,6'-Me</td> <td></td> <td>650</td> <td>650</td> <td>685</td> <td>0.19</td> </tr> </tbody> </table> | | | | | | | | | | | | G.S.G-1740 | 1 | Et | Br ⁻ | Et | | 9-Me | 550 | 500 | 595 | 0.006 | NK-1638 | 1 | Et | EtSO ₄ ⁻ | Et | | | 565 | 560 | 590 | 0.14 | East. 7663 | 2 | Et | I ⁻ | Et | | | 660 | 650 | 695 | 0.73 | NK-1838 | 2 | (CH ₂) ₃ SO ₃ ⁻ | | (CH ₂) ₃ SO ₃ Na | 6,6'-Me | | 660 | 665 | 700 | 0.65 | NK-1893 | 2 | C ₂ H ₄ COO ⁻ | | C ₂ H ₄ COONa | 6,6'-Me | | 650 | 650 | 685 | 0.19 |
| G.S.G-1740 | 1 | Et | Br ⁻ | Et | | 9-Me | 550 | 500 | 595 | 0.006 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| NK-1638 | 1 | Et | EtSO ₄ ⁻ | Et | | | 565 | 560 | 590 | 0.14 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| East. 7663 | 2 | Et | I ⁻ | Et | | | 660 | 650 | 695 | 0.73 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| NK-1838 | 2 | (CH ₂) ₃ SO ₃ ⁻ | | (CH ₂) ₃ SO ₃ Na | 6,6'-Me | | 660 | 665 | 700 | 0.65 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| NK-1893 | 2 | C ₂ H ₄ COO ⁻ | | C ₂ H ₄ COONa | 6,6'-Me | | 650 | 650 | 685 | 0.19 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |

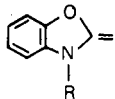
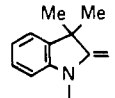
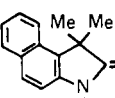
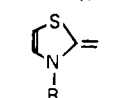
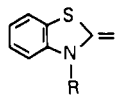
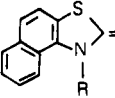
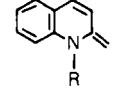
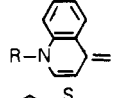
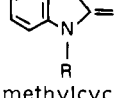
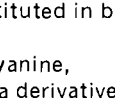
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|---|---|--|--------------------------------|--|-----|-----|-----|--------|--|
| NK-1666 | 3 | Et | Br ⁻ | Et | 750 | 765 | 810 | 0.36 | |
| NK-126 | 3 | Et | I ⁻ | Et | 760 | 765 | 810 | 0.38 | |
| NK-1407 | 3 | C ₂ H ₄ COOH (CH ₂) ₃ SO ₃ ⁻ | Br ⁻ | C ₂ H ₄ COOH (CH ₂) ₃ SO ₃ Na | 780 | 765 | 815 | 0.34 | |
| NK-1975 | 3 | (CH ₂) ₃ SO ₃ ⁻ | | | 765 | 765 | 815 | 0.28 | |
| V. 2,2'-Thia-4,5,4',5'-dibenzocarbocyanine | | | | | | | | | |
| G.S.G-1645 | 1 | Et | I ⁻ | Et | 585 | 550 | 620 | 0.011 | |
| G.S.G-2905 | 1 | Me | Br ⁻ | Me | 585 | 550 | 620 | 0.011 | |
| NK-2075 | 1 | (CH ₂) ₃ SO ₃ ⁻ | | | 605 | 605 | 630 | 0.25 | |
| NK-460 | 2 | Et | <i>p</i> -TSA | Et | 690 | 680 | 720 | 0.38 | |
| NK-1158 | 3 | Et | <i>p</i> -TSA | Et | 820 | 765 | 855 | 0.17 | |
| NK-1528 ^d | 3 | Et | EtSO ₄ ⁻ | Et | 810 | 765 | 850 | 0.16 | |
| NK-1978 | 3 | (CH ₂) ₃ SO ₃ ⁻ | | (CH ₂) ₃ SO ₃ Na | 810 | 765 | 855 | 0.13 | |
| NK-427 | 3 | Et | I ⁻ | Et | 825 | 765 | 855 | 0.16 | |
| VI. 2,2'-Oxocarbocyanine | | | | | | | | | |
| G.S.G-1745 | 1 | Et | I ⁻ | Et | 490 | 465 | 515 | 0.093 | |
| G.S.G-1730 | 1 | Et | <i>p</i> -TSA | Et | 525 | 465 | 560 | 0.24 | |
| East. 11808 | 1 | (CH ₂) ₇ CH ₃ | <i>p</i> -TSA | (CH ₂) ₇ CH ₃ 4,5,4',5'-Bzo ₂ | 495 | 465 | 515 | 0.17 | |
| NK-1952 | 1 | (CH ₂) ₃ SO ₃ ⁻ | | (CH ₂) ₃ SO ₃ Na 5,5'-Ph ₂ | 510 | 465 | 535 | 0.071 | |
| NK-2073 | 1 | (CH ₂) ₃ SO ₃ ⁻ | | (CH ₂) ₃ SO ₃ H 5-ph-4,5'-Bzo | 475 | 465 | 540 | 0.23 | |
| East. 11219 | 2 | Et | I ⁻ | Et | 585 | 585 | 620 | 0.87 | |
| NK-1511 | 3 | Et | I ⁻ | Et | 680 | 620 | 740 | 0.63 | |
| VII. 2,2'-Quinocarbocyanine | | | | | | | | | |
| East. 7851 | 0 | Et | I ⁻ | Et | 530 | 580 | 645 | <0.001 | |
| G.S.G-1700 | 1 | Et | I ⁻ | Et | 615 | 580 | 650 | 0.004 | |
| NK-179 | 1 | Et | EtSO ₄ ⁻ | Et | 615 | 580 | 650 | 0.004 | |
| East. 9618 | 2 | Et | I ⁻ | Et | 720 | 690 | 760 | 0.005 | |
| NK-1150 | 2 | Et | Br ⁻ | Et | 690 | 650 | 740 | 0.006 | |
| NK-197 | 2 | Et | Br ⁻ | Et | 690 | 650 | 735 | 0.006 | |
| NK-1143 | 2 | Et | <i>p</i> -TSA | Et | 710 | 695 | 740 | 0.007 | |
| NK-123 | 3 | Et | I ⁻ | Et | 820 | 825 | 865 | 0.035 | |
| VIII. 4,4'-Quinocarbocyanine | | | | | | | | | |
| East. 1334 | 1 | Et | I ⁻ | Et | 710 | 700 | 735 | 0.036 | |
| NK-171 | 1 | Et | EtSO ₄ ⁻ | Et | 705 | 650 | 740 | 0.029 | |
| NK-2009 | 1 | (CH ₂) ₃ SO ₃ ⁻ | | (CH ₂) ₃ SO ₃ Na | 700 | 710 | 740 | 0.055 | |
| NK-1950 | 2 | Et | Br ⁻ | Et | 780 | 765 | 830 | 0.033 | |
| NK-1255 | 2 | Et | <i>p</i> -TSA | Et | 820 | 765 | 835 | 0.027 | |
| NK-4 | 2 | Et | I ⁻ | Et | 770 | 765 | 835 | 0.001 | |
| NK-471 | 2 | Me | <i>p</i> -TSA | Me | 790 | 765 | 825 | 0.009 | |
| NK-153 | 2 | Et | EtSO ₄ ⁻ | Et | 780 | 765 | 825 | 0.001 | |
| NK-2061 | 2 | (CH ₂) ₃ SO ₃ ⁻ | | (CH ₂) ₃ SO ₃ Na | 810 | 765 | 840 | 0.031 | |
| NK-1949 | 3 | Et | I ⁻ | Et | 865 | 825 | 865 | <0.001 | |
| IX. Dimethylcyclohexene Substituted in Bridge | | | | | | | | | |
| NK-1836 | 0 | Et | I ⁻ | Et | 660 | 620 | 705 | 0.14 | |
| NK-2070 | 0 | (CH ₂) ₃ SO ₃ ⁻ | | (CH ₂) ₃ SO ₃ ⁻ | 650 | 650 | 695 | 0.17 | |
| NK-2237 | 1 | (CH ₂) ₃ SO ₃ ⁻ | | (CH ₂) ₃ SO ₃ ⁻ | 750 | 765 | 815 | 0.28 | |
| NK-2236 | 2 | (CH ₂) ₃ SO ₃ ⁻ | | (CH ₂) ₃ SO ₃ ⁻ | 860 | 825 | 900 | 0.10 | |

Table I (Continued)

| Manufr. no. | <i>n</i> | R | X | R' | Y | Z | λ_{abs} , nm | λ_{ex} , nm | λ_{fl} , nm | Fluores quantum yield ^a |
|---|----------|--|---|----|---------|------|-----------------------------|----------------------------|----------------------------|------------------------------------|
| NK-2239 | 1 | (CH ₂) ₃ SO ₃ ⁻ | | | | | 800 | 765 | 855 | 0.12 |
| NK-2238 | 2 | (CH ₂) ₃ SO ₃ ⁻ | | | | | 920 | 825 | 950 | 0.012 |
| IX. Dimethylcyclohexene Substituted in Bridge | | | | | | | | | | |
| G.S. G-1875 | 1 | Et | | | | | 525 | 465 | 575 | 0.006 |
| NK-1149 | 1 | C ₂ H ₄ COOH | | | | | 525 | 465 | 585 | 0.005 |
| NK-756 | 1 | Et | | | 6-MeO | 9-Ph | 560 | 500 | 610 | 0.004 |
| NK-1321 | 2 | Et | | | | | 620 | 560 | 665 | 0.035 |
| NK-1901 | 2 | C ₂ H ₅ COOH | | | | | 640 | 620 | 665 | 0.072 |
| NK-1934 | 2 | (CH ₂) ₃ SO ₃ H | | | | | 640 | 620 | 685 | 0.048 |
| NK-2050 | 2 | C ₂ H ₄ COOH | | | | | 625 | 620 | 660 | 0.053 |
| NK-1943 | 2 | (CH ₂) ₃ SO ₃ H | | | 6,7-Bzo | | 640 | 620 | 685 | 0.097 |
| NK-2015 | 2 | C ₂ H ₄ COOH | | | 6,7-Bzo | | 640 | 620 | 685 | 0.083 |

^a Fluorescence quantum yield is relative to sodium fluorescein. ^b Key: NK, Nippon Kankoh-Shikiso Kenkyusho, Ltd., Okayama, Japan; H.W.D., Hynson, Westcott and Dunning; East., Eastman Chemical; G.S., Gallard-Schlesinger. ^c Key: Me, methyl; Et, ethyl; py, pyridine; Bzo, benzo; Ph, phenyl; Quin, quinoline; MeO, methoxy; *p*-ASA = *p*-anilinesulfonic acid; *p*-TSA = *p*-toluenesulfonic acid. ^d NK-1528 is a 6,7,6',7'-dibenzo compound.

Table II. Correlation of Absorption and Fluorescence Wavelengths with Molecular Structure for Cyanine Dyes in Me₂SO

| Nuclei | <i>n</i> ^a | λ_{abs} , ^b nm | λ_{fl} , ^b nm |
|--|--|--|---|
|  | 1 | 490 | 515 |
| | 2 | 585 | 620 |
| | 3 | 680 | 740 |
|  | 1 | 550 | 590 |
| | 2 | 650 | 690 |
| | 3 | 750 | 790 |
|  | 1 | 570 | 610 |
| | 2 | 680 | 720 |
| | 3 | 795 | 835 |
|  | 1 | 560 | 595 |
| | 2 | 660 | 695 |
| | 3 | 760 | 795 |
|  | 1 | 560 | 590 |
| | 2 | 660 | 690 |
| | 3 | 765 | 810 |
|  | 1 | 600 | 630 |
| | 2 | 700 | 740 |
| | 3 | 815 | 855 |
|  | 0 | 530 | 550 |
| | 1 | 615 | 650 |
| | 2 | 720 | 760 |
|  | 3 | 820 | 865 |
| | 1 | 705 | 740 |
| | 2 | 790 | 840 |
|  | 3 | 865 | 940 |
| | 0 | 650 | 700 |
| | 1 | 750 | 810 |
|  | 2 | 860 | 900 |
| | with dimethylcyclohexene substituted in bridge | | |
| Merocyanine, 2-thia derivatives | 1 | 530 | 590 |
| | 2 | 640 | 675 |
| | 3 | 750 | 760 |

^a *n* refers to the length of the cyanine bridge (see Table I). ^b The listed wavelengths are average values derived from the results in Table I. λ_{abs} and λ_{fl} for individual dyes will generally be within 20 nm of the average values.

fluorescence quantum yields, while the other dye structures have quantum yields ranging from roughly 0.1 to 0.5.

It is obvious from the results in Table I that a correlation exists between the length of the cyanine bridge and the wavelengths of maximum absorption and fluorescence, i.e., the longer the bridge, the longer the wavelength. (It should be emphasized that the presence of impurities in the sample was found to have a negligible effect on the wavelengths of the absorption and fluorescence maxima.) The correlation between the molecular structure and the wavelength of the absorption maximum has been known for some time (1, 2), and it was expected that the wavelength of the fluorescence maximum would exhibit a similar correlation. The fluorescence maxima for various nuclei are listed in Table II. The length of the cyanine bridge largely determines the wavelength, and for each -CH=CH group the

wavelength increases by roughly 100 nm. However, there is a practical limit to the length of the straight-chain chromophore since the stability of the molecule is greatly reduced for $n > 3$. Thus, a long wavelength requires substitution of a chemical group in the bridge to increase the stability of the long cyanine chain. An example of such a stabilization is the use of dimethylcyclohexene as the bridge substituent. It should be noted that substitution on the bridge (as opposed to in the bridge for stabilization) generally decreases the wavelength and the fluorescence quantum yield; e.g., compare G-1645 and G-2905 with NK-2075 in Table I.

The heterocyclic nuclei also affect the wavelength, but to a lesser degree than the chromophore length. The oxa derivatives are at shorter wavelengths than the corresponding thia (and seleno) derivatives, and substitution of a benzene group on the

nuclei at the 4,5 position increases the wavelength by 20–40 nm.

In summary, the spectral properties of a wide range of cyanine dyes have been measured. The absorption and fluorescence maxima of the dyes were found to correlate rather well with the molecular structure, and the fluorescence quantum yield can be roughly estimated on the basis of the molecular structure.

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Volumetric Properties of Some Single Molten Hydrated Salts

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Densities of molten (Mg, Ni, Mn)(NO₃)₂·6H₂O, Fe(NO₃)₃·6H₂O, FeCl₃·6H₂O, and (Al, Cr)(NO₃)₃·9H₂O, from temperatures far above their melting points to well below into the supercooled region, were measured. In all cases the density and the equivalent volume varied linearly with the temperature, over the range of investigation. The equivalent volumes appear to be governed by the number of molecules of water of hydration per equivalent of cationic charge.

Low liquidus temperatures, strong supercooling, and glass-forming tendencies generally exhibited by hydrated melts have given them an exclusive status in the field of solvents for carrying out low-temperature studies, e.g., the molecular and ionic relaxation processes in the long time domain (2, 5, 8, 9, 12), as glassy matrices for trapping and studying the subsequent reactions of radiolysis products (8), and as a media for low-temperature electrochemical (14) and spectroscopic investigations (1, 3). Thus, any study aimed at obtaining information about the fundamental properties of such systems is expected to be beneficial for a better understanding of these systems, at least indirectly.

Precise density data are required for an adequate interpretation of certain other experimental parameters, such as equivalent conductivity, molar refraction, etc. Its variation with temperature and composition can yield information regarding the changes taking place in the melt structure. In molten binary nitrate mixtures the additivity of volumes has been reported by various workers (10, 13). For molten mixtures containing tetrahydrates of calcium and cadmium nitrates and monovalent nitrates, the additivity of volumes has also been reported by Braunstein et al. (4) and Jain (7). Moynihan et al. (11) has shown through ¹H NMR studies that the molten mixtures of tetrahydrates of calcium and cadmium nitrate behave ideally over the entire composition range. Thus, it appears that the principle of additivity provides a useful basis for estimating the equivalent volumes of the mixtures in such systems from the limited density data. These considerations prompted this study regarding the density measurements in certain single molten hydrated salts of bi/trivalent metal nitrates and chloride.

Experimental Section

The source and the quality grade of the salts used in this study are the following: Ni(NO₃)₂·6H₂O, BDH (England), Laboratory Reagent; Mg(NO₃)₂·6H₂O, BDH (India), Analytical Reagent; Fe(NO₃)₃·6H₂O, Riedel (Germany), Guaranteed Reagent; Mn(NO₃)₂·6H₂O, Riedel (Germany), Guaranteed Reagent; Cr(NO₃)₃·9H₂O, Ortonal (Italy), Analytical Reagent; Al(NO₃)₃·9H₂O, E. Merck (Germany), Guaranteed Reagent; FeCl₃·6H₂O, BDH (India), Laboratory Reagent.

The melting temperatures of these salts, determined by the cooling curve method, are included in Table I. Agreement between the experimentally measured liquidus temperatures and those reported in literature (16) leads one to believe that the salts were of the stoichiometric composition as reported by the manufacturers. This, however, was verified in the case of Mg(NO₃)₂·6H₂O by the EDTA titrimetric method; ferric and nickel salts were verified by standard gravimetric methods (15). Repeated cross checks established the water content in these salts within ±0.02 of the stoichiometric value.

The salts were fused in small flasks (ca. 100 cm³) provided with air-tight ground-glass stoppers and were maintained at 60–70 °C for a few hours after fusion. The dilatometer originally designed by Husband (6) was modified so as to allow a direct measurement of the volume of a known amount of the melt. The details regarding the dilatometer, its calibration and measuring technique, etc., were similar to those reported earlier (7).

Results and discussion

The density and equivalent volume data for all the salts investigated in this study are recorded in Table I. The variation of density and the equivalent volume with temperature could be expressed by linear equations of the type

$$\rho(\text{g cm}^{-3}) = \alpha - \beta t (\text{°C})$$

$$V_e(\text{cm}^3 \text{equiv}^{-1}) = A + Bt (\text{°C})$$

The coefficients α , β , and A , B are the characteristic of the melt; these are presented in Table II. Table III includes the equivalent volumes, the expansion coefficients (at 75 °C), and the crystallographic radii (16) of the cations. The results indicate that the volume per gram equivalent of nitrate ion is almost insensitive