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 selena) 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)$(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, and (Al, Cr)$(NO_3)_3 \cdot 9H_2O$, 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 idealy 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: $Ni(NO_3)_2 \cdot 6H_2O$, BDH (England), Laboratory Reagent; $Mg(NO_3)_2 \cdot 6H_2O$, BDH (India), Analytical Reagent; $Fe(NO_3)_3 \cdot 6H_2O$, Riedel (Germany), Guaranteed Reagent; $Mn(NO_3)_2 \cdot 6H_2O$, Riedel (Germany), Guaranteed Reagent; $Cr(NO_3)_3 \cdot 9H_2O$, Ortanal (Italy), Analytical Reagent; $Al(NO_3)_3 \cdot 9H_2O$, E. Merck (Germany), Guaranteed Reagent; $FeCl_3 \cdot 6H_2O$, 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 $Mg(NO_3)_2 \cdot 6H_2O$ 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 cm^3) 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

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

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

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

Table I. Densities and Equivalent Volumes for Some Molten Hydrated Salts

Temp, °C	Density, g cm^{-3}	Equiv vol, cm^3 equiv^{-1}
	$Ni(NO_3)_2 \cdot 6H_2O$, 56.8 °C (56.7 °C)[a]	
43.0	1.7894	81.26
47.5	1.7819	81.60
52.6	1.7772	81.81
58.0	1.7725	82.03
62.9	1.7678	82.25
68.0	1.7631	82.47
73.4	1.7585	82.68
78.5	1.7528	82.95
	$Fe(NO_3)_3 \cdot 6H_2O$, 35.0 °C (35 °C)	
42.1	1.6177	72.12
44.9	1.6148	72.25
47.5	1.6120	72.37
51.5	1.6076	72.57
57.6	1.6010	72.87
62.3	1.5958	73.11
68.5	1.5889	73.43
75.5	1.5813	73.78
81.5	1.5767	73.99
	$Mn(NO_3)_2 \cdot 6H_2O$, 26.0 °C (25.8 °C)	
30.9	1.8122	79.20
36.1	1.8062	79.46
41.1	1.8013	79.67
45.9	1.7964	79.89
50.8	1.7916	80.11
57.7	1.7848	80.41
65.6	1.7762	80.80
71.4	1.7709	81.04
78.3	1.7639	81.36
	$Mg(NO_3)_2 \cdot 6H_2O$, 94.8 °C (95 °C)	
96.8	1.5294	83.82
99.7	1.5268	83.97
104.7	1.5225	84.20
110.0	1.5191	84.39
114.5	1.5157	84.58
120.0	1.5097	84.92
125.0	1.5055	85.15
131.0	1.4940	85.81
	$Cr(NO_3)_3 \cdot 9H_2O$, 36.9 °C (37 °C)	
31.7	1.7000	78.47
36.3	1.6958	78.66
38.5	1.6939	78.75
40.4	1.6920	78.84
45.5	1.6872	79.06
50.5	1.6823	79.30
55.1	1.6773	79.53
60.0	1.6728	79.75
64.0	1.6687	79.94
68.9	1.6638	80.18
74.7	1.6580	80.46
80.8	1.6522	80.74
87.0	1.6450	81.09
	$Al(NO_3)_3 \cdot 9H_2O$, 69.6 °C (70 °C)	
40.6	1.5563	80.35
47.1	1.5517	80.58
51.2	1.5489	80.73
56.1	1.5461	80.88
60.8	1.5429	81.05
66.2	1.5388	81.26
75.0	1.5334	81.55
86.1	1.5253	81.98
	$FeCl_3 \cdot 6H_2O$, 36.9 °C (37 °C)	
33.0	1.6456	54.75
37.6	1.6364	55.06
40.9	1.6301	55.27
44.0	1.6248	55.45
50.2	1.6124	55.88
55.5	1.6021	56.24
61.0	1.5953	56.48
64.5	1.5892	56.69
68.1	1.5821	56.95
70.4	1.5784	57.08
74.5	1.5709	57.35
76.9	1.5668	57.50
79.1	1.5631	57.64
82.0	1.5577	57.84

[a] Values in parentheses are the literature (*16*) melting temperatures.

Table II. Coefficients of Linear Density/Equivalent Volume–Temperature Equations

			ρ(g cm^{-3}) = $\alpha - \beta t$			V(cm^3 equiv^{-1}) = $A + Bt$		
Salt	Temp range, °C	Data points	α	$10^3\beta$	10^2 SE	A	10^2B	SE
$Ni(NO_3)_2 \cdot 6H_2O$	43–78	8	1.8296	0.978	0.10	79.39	4.53	0.04
$Fe(NO_3)_3 \cdot 6H_2O$	42–81	9	1.6624	1.066	0.05	70.07	4.87	0.02
$Mn(NO_3)_2 \cdot 6H_2O$	31–78	9	1.8430	1.012	0.03	77.80	4.54	0.01
$Mg(NO_3)_2 \cdot 6H_2O$	96–131	8	1.6234	0.958	0.22	78.62	5.32	0.12
$Cr(NO_3)_3 \cdot 9H_2O$	32–87	13	1.7320	0.991	0.03	76.93	4.73	0.02
$Al(NO_3)_3 \cdot 9H_2O$	41–86	8	1.5837	0.675	0.03	78.90	3.56	0.01
$FeCl_3 \cdot 6H_2O$	33–82	14	1.7025	1.767	0.09	52.72	6.21	0.03

Table III. Equivalent Volumes and Expansion Coefficients of Certain Molten Hydrated Salts at 75 °C

Salt	Cation radius, Å	Equiv vol, cm^3 equiv^{-1}	N_{H_2O}[b]	$10^4\alpha$, deg^{-1}
$Ca(NO_3)_2 \cdot 4H_2O$[a]	0.99	69.17	2	4.71
$Cd(NO_3)_2 \cdot 4H_2O$[a]	0.97	68.22	2	4.76
$Fe(NO_3)_3 \cdot 6H_2O$	0.67	73.72	2	6.61
$Mg(NO_3)_2 \cdot 6H_2O$	0.65	82.61	3	6.34
$Ni(NO_3)_2 \cdot 6H_2O$	0.78	82.79	3	5.57
$Mn(NO_3)_2 \cdot 6H_2O$	0.80	81.20	3	5.59
$Cr(NO_3)_3 \cdot 9H_2O$	0.65	80.48	3	5.58
$Al(NO_3)_3 \cdot 9H_2O$	0.50	81.57	3	4.36
$FeCl_3 \cdot 6H_2O$	0.67	57.38	2	9.24

[a] Values adopted from ref 7. [b] Per cationic charge.

to the cation radii. It is interesting to note that the salts having equal number of moles of water per equivalent of the cationic charges have almost equal equivalent volumes. Much lower values for the equivalent volume of ferric chloride hexahydrate when seen in comparison with the nearly constant equivalent volumes for nitrates lead one to conclude that in hydrated melts also the structure is predominantly controlled by the space and the packing requirements of the anions (Cl^- being smaller than NO_3^-); a finding very much similar to that reported for anhydrous melts (*10*).

Glossary

ρ density, g cm^{-3}

V_e volume of the melt, cm^3/equiv of NO_3^-

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Liquid Heat Capacity of *tert*-Butyl Alcohol, Isobutyl Alcohol, and Isopropyl Alcohol at High Temperature

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Liquid isobaric heat capacities of *tert*-butyl alcohol, isobutyl alcohol, and isopropyl alcohol were measured in a flow calorimeter at temperatures ranging between the normal boiling point and a reduced temperature of 0.93–0.97. Pressures up to the critical pressure were studied. Heat capacities were found to increase with temperature but, for the alcohols studied, inflection points were found at temperatures of about $T_r = 0.65$ and 0.85; within this reduced temperature range the C_p–T curve was concave to the temperature axis. This behavior has not been observed in nonpolar compounds such as hydrocarbons or is it noted for liquid water or ammonia.

In a recent paper (*14*), isobaric liquid heat capacities were reported for several hydrocarbons and 1-butanol at temperatures above the normal boiling point. The data for 1-butanol were found to differ qualitatively from those for hydrocarbons in that an inflection point was noted when graphing C_p as a function of temperature. To investigate this phenomenon further, additional experiments have been carried out with three other alcohols and the results are reported in this paper. Data were obtained in the same closed-loop flow calorimeter described earlier (*14*) but the heater was replaced with one having an increased heat transfer area since the alcohols to be studied were expected to have quite large heat capacities, especially at high reduced temperatures. Experimental details are given elsewhere (*7*) and the method of calculating heat capacities from experimental data has been outlined (*14*).

Results

Isobutyl Alcohol. The pressure–temperature field studied is shown in Figure 1. Data were collected at each isobar (12.6, 26.8, and 41.9 bar), and measurements made both for ascending and descending temperatures. The highest reduced temperature attained was 0.93 (234 °C).

The vapor pressure curve of Ambrose and Townsend (*1*) is also shown in Figure 1.

Heat capacities as a funciton of temperature are given in Figure 2 along with the low-temperature results of Counsell et al. (*4*). At low temperatures (20–75 °C), C_p increases with temperature with a positive second derivative. This behavior is similar to that found for hydrocarbons (*14*). At higher temperatures, the C_p–T curves become concave with respect to the temperature axis, but, eventually, there is a second inflection point ($T_r \sim 0.85$) and C_p then increases rapidly as the critical point is approached.

At temperatures below the normal boiling point (108 °C; $T_r = 0.7$), C_p is nearly independent of pressure. At higher temperatures, an increase in pressure reduces C_p in a manner significantly more pronounced than found in hydrocarbon systems.

The dashed line in Figure 2 represents the saturated liquid. This boundary was obtained by cross-plotting C_p as a function of pressure as shown in Figure 3. Isothermal data were then extrapolated to the vapor pressure corresponding to the appropriate temperature.

Smoothed isobaric liquid heat capacities are given in Table I. The uncertainty is believed to be less than 1%.

tert-Butyl Alcohol. Measurements were made at five different isobars (8.4, 12.7, 18.5, 31.8, and 39.5 bar) over a temperature range of 30–219 °C (T_r from 0.6 to 0.97). Experimental results are shown in Figure 4. Agreement with the low-temperature data of Oetting (*10*) is excellent; the maximum deviation is +0.3% at 58 °C.

Over the temperature range of 30–150 °C ($T_r = 0.6$ to $T_r = 0.84$), the C_p vs. T curve is concave to the temperature axis, a behavior similar to that observed for isobutyl alcohol over the same reduced temperature region. The low-temperature inflection point (if there is one) is difficult to locate. Under atmospheric pressure, *tert*-butyl alcohol is a liquid over a very small temperature range ($T_{mp} = 25.5$ °C and $T_b = 82.9$ °C). Oetting made heat capacity measurements of the solid down to 15 K and these results are shown in Figure 5. Solid *tert*-butyl alcohol can exist in two different crystalline forms denoted as crystal I and II. From 110 to 286 K ($T_r = 0.22$ to $T_r = 0.57$) the C_p vs. T curve for crystal II is concave upward, a behavior similar to that observed for hydrocarbons and other polar compounds below their normal boiling points. At 286.14 K a discontinuity occurs in the C_p vs. T curve and the crystal I structure exists from 286.14 to 298.97 K ($T_r = 0.57$ to $T_r = 0.59$). Above this temperature *tert*-butyl alcohol is a liquid and the C_p–T curve is concave to the temperature axis. Note that C_p for crystal II can be extrapolated to $T_r = 0.59$ and joins smoothly with the curve for C_p of