

Magneto Optical Rotatory Dispersion Studies of Simple Electrolyte Solutions

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The m.o.r.d. of concentrated aqueous solutions of LiCl, NaCl, KCl, CsCl have been measured in the wavelength range 350-650 nm. The changes in rotation with wavelength are fitted to a one-term Drude equation and the constants of this equation calculated by the Biot-Lowry, the Yang-Doty, and the Heller methods, the last two methods yielding equivalent results. The problems associated with the calculation of the rotation due to the solute are discussed and the results interpreted in terms of the known behaviour of the solutes studied.

In recent years there has been a revival of interest in the chemical applications of the Faraday effect^{1, 2} especially its variation with wavelength (magneto optical rotatory dispersion, m.o.r.d.).^{3, 4} In particular, studies have been made of the m.o.r.d. of compounds in the regions of their electronic absorption bands along with the related measurements of magnetic circular dichroism (m.c.d.). In the regions of optical absorption it is generally agreed that the m.c.d. method is slightly easier to use and interpret than the m.o.r.d. method just as was found to be so for c.d. and o.r.d. of optically active compounds. Many studies have thus involved the measurement of m.c.d. of compounds possessing chromophores in fairly accessible regions of the spectrum and such measurements yield valuable information concerning electronic energy levels and their population.^{3, 4} Nevertheless, there are a great many compounds whose absorption bands are completely inaccessible and it is for such compounds that the Faraday effect can only be studied by the m.o.r.d. method.

Investigations were carried out on aqueous solutions using a wide variety of experimental techniques.^{5, 6} It was thought that a systematic study of the m.o.r.d. of concentrated electrolyte solutions might provide additional information concerning the nature of such solutions. In this paper are presented the results of studies on solutions of LiCl, NaCl, KCl and CsCl.

EXPERIMENTAL

The m.o.r.d. apparatus was built from a Bellingham and Stanley model A polarimeter which was fitted with a Faraday cell modulated at 360 Hz and phase sensitive detecting system incorporating an IP 28 photomultiplier. A Hilger Uvispek spectrophotometer was modified to act as a monochromator to which could be attached a second monochromating device. The light source was a 150 W, 20 V quartz-iodine lamp fitted in the lamp-housing of the Uvispek. Angular rotations could be estimated to 0.002°. Two permanent magnets (nominal flux density 0.5 T with their fields in opposite directions) were placed between the polariser and analyser. The pole pieces contained a hole of about 9 mm diameter through which light from the monochromator passed. Each magnet could accommodate a 10 mm spectrophotometer cell between its pole pieces. The use of two magnets in this manner⁷ allows solvent and cell compensation to be made at the same time as the solution is being measured if this is required. In this work, however, only one of the magnets was used and

separate measurements of cell rotation and solvent rotation were made. This enabled a regular check to be made of instrument stability and in any case the simultaneous cell and solvent compensation is only valid for dilute solutions. Magnetic rotations after measurement were expressed in terms of $\text{deg cm}^{-1} \text{T}^{-1}$ and were counted as positive when magnetic lines of force in the same direction as the light beam produced dextro-rotations in the sample. Measurements were made in the wavelength range 350-650 nm at intervals of 50 nm.

All solutions were made up by volume and their densities interpolated from data in the International Critical Tables.

RESULTS

One of the most comprehensive collections of magnetic rotation data is that of de Malleman.⁸ Much of this data refer to a wavelength of 578 nm and the measurements made with visual detection of the polarimetric null-point. To compare the present work with the earlier work it was necessary to interpolate our results at 578 nm and at solute concentrations corresponding to those given in ref. (8). The comparison is given in table 1; the agreement is quite good.

TABLE 1.—COMPARISON OF MAGNETIC ROTATIONS AT 578 nm

solute	concentration/ mol dm^{-3}	rotation (at 578 nm)/ $\text{deg. cm}^{-1} \text{T}^{-1}$ ref. (8)	this work
LiCl	1.61	2.42	2.42
NaCl	1.35	2.50	2.52
KCl	1.07	2.34	2.40
CsCl	0.91	2.20	2.19

Since it is the whole solution which provides the measured rotation in m.o.r.d. (unlike o.r.d. where it is the solute only) it is appropriate to calculate specific rotations as being a property of the solution as a whole. (The question of the rotation due to the solute alone and the problems associated with its calculation are discussed later). The specific rotation $[\alpha]_s$ is defined as

$$[\alpha]_s = \theta_s / ld \quad (1)$$

where θ_s is the solution rotation in a magnetic flux density of one T (10 000 G), l is the path-length of the solution expressed in m and d is the density of the solution expressed as kg m^{-3} . Thus the units of $[\alpha]_s$ as defined above are $\text{deg m}^2 \text{kg}^{-1} \text{T}^{-1}$.

TABLE 2.—CHARACTERISATION OF SPECIFIC ROTATION—CONCENTRATION GRAPHS

wavelength/nm	350	400	450	500	550	600
LiCl solution						
$[\alpha]_0 / \text{deg m}^2 \text{kg}^{-1} \text{T}^{-1}$	0.685	0.500	0.380	0.300	0.245	0.205
$10^2 x / u' *$	2.06	1.28	0.88	0.62	0.48	0.40
NaCl solution						
$[\alpha]_0 / \text{deg m}^2 \text{kg}^{-1} \text{T}^{-1}$	0.690	0.504	0.385	0.305	0.249	0.207
$10^2 x / u'$	4.07	2.70	1.87	1.37	1.17	0.97
KCl solution						
$[\alpha]_0 / \text{deg m}^2 \text{kg}^{-1} \text{T}^{-1}$	0.690	0.500	0.382	0.306	0.248	0.206
$10^2 x / u'$	2.50	1.63	1.00	0.50	0.60	0.45
CsCl solution						
$[\alpha]_0 / \text{deg m}^2 \text{kg}^{-1} \text{T}^{-1}$	0.650	0.486	0.365	0.285	0.232	0.189
$10^2 x / u'$	-1.22	-1.08	-0.84	-0.64	-0.54	-0.42

* $u' = \text{deg m}^2 \text{kg}^{-1} \text{T}^{-1} (\text{mol dm}^{-3})^{-1}$.

The variation of $[\alpha]_s$ as a function of the solute concentration was linear for all four solutes at the wavelengths studied, i.e., $[\alpha]_s = [\alpha]_0 + xc$. The intercepts at zero concentration ($[\alpha]_0$) and the gradients of the graphs (x) are given in table 2.

DISCUSSION

THE VARIATION OF $[\alpha]_s$ WITH CONCENTRATION

For LiCl, NaCl, and KCl the change of $[\alpha]_s$ with concentration is positive. For CsCl solutions, however, the values of $[\alpha]_s$ decreased with increasing concentration of solute. The gradients (x) of all the CsCl graphs were negative, in contrast to the other three solutes. The values of the specific rotation at zero concentration, $[\alpha]_0$, might be expected to be the same for all four solutes. While the values for LiCl, NaCl and KCl are fairly close to each other the values for CsCl are significantly different (table 2 and fig. 1).

Large univalent ions such as Cs^+ and I^- have entropies of hydration which are more positive than would be expected and from such values it can be deduced^{9, 10} that such ions cause a breakdown in the structure of the solvent water. The effect is probably also present with other ions in aqueous solutions but it is often overshadowed by the strong orienting effect of the ion upon water molecules close to the ion arising from a higher charge to size ratio. Schoolery and Alder¹¹ concluded from n.m.r. studies that the principal effect of large univalent ions was to break down the water structure. It is apparent from a comparison of table 2 data and also fig. 1 that the

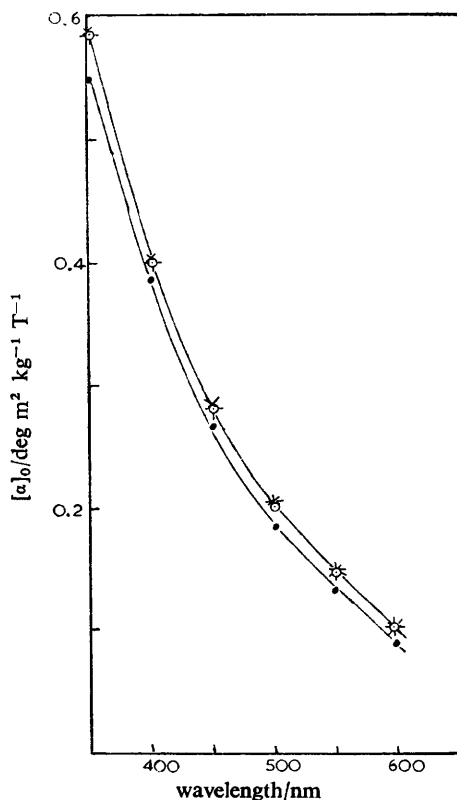


FIG. 1.—Specific rotations at infinite dilution. ○, LiCl; ×, NaCl; +, KCl; ●, CsCl.

m.o.r.d. of CsCl is of different character to that of the other alkali-metal chlorides. It is also known that caesium chloride (and rubidium chloride) are incompletely dissociated even in dilute solution^{12, 13} and this may also contribute to the different m.o.r.d. results for CsCl as well as the disordering effect upon the solvent water of a large cation.

THE VARIATION OF $[\alpha]_s$ WITH WAVELENGTH

The simplest mathematical representation of normal o.r.d. for optically active compounds at wavelengths distant from an absorption band is the one-term Drude equation,¹⁴

$$[\alpha]_s = K/(\lambda^2 - \lambda_0^2) \quad (2)$$

where λ is the wavelength of measurement, λ_0 is the wavelength of an absorption band, and K is the rotation dispersion constant, a parameter related to the rotational strength of the electronic transition. It is of interest to test the simple one-term Drude equation for our m.o.r.d. results and calculate the constants K and λ_0 and evaluate the influence of solute concentration upon their values.

It is not often realised that there are several methods of evaluation of these constants which may not yield identical values. Three methods will be considered here, namely, the Biot-Lowry method,^{15, 16} the Yang-Doty method¹⁷ and the Heller method.¹⁸ The Biot-Lowry method^{15, 16} rearranges the one-term Drude equation in the form

$$\frac{1}{[\alpha]_s} = \frac{\lambda^2}{K} - \frac{\lambda_0^2}{K} \quad (3)$$

and hence a plot of $1/[\alpha]_s$ against λ^2 should be linear and have a gradient of $1/K$ and an intercept of $-\lambda_0^2/K$ which allows evaluation of K and λ_0 .

The Yang-Doty method¹⁷ arranges the Drude equation in the form

$$\lambda^2[\alpha]_s = \lambda_0^2[\alpha]_s + K \quad (4)$$

and a plot of $\lambda^2[\alpha]_s$ against $[\alpha]_s$ should have a gradient of λ_0^2 and an intercept of K .

The Heller method¹⁸ arranges the Drude equation as

$$\frac{1}{[\alpha]_s \lambda^2} = \frac{1}{K} - \frac{\lambda_0^2}{K} \left(\frac{1}{\lambda^2} \right) \quad (5)$$

and a plot of $1/[\alpha]_s \lambda^2$ against $1/\lambda^2$ should be linear and have a gradient of $-\lambda_0^2/K$ and an intercept of $1/K$.

The applicability of the one-term Drude equation was tested for the solution specific rotations at the various concentrations of solute using the above three methods of evaluation. The m.o.r.d. data did in fact give quite good linear plots. Their gradients and intercepts, however, were calculated by linear regression analysis using a Sumlock Statistician calculator. In addition to the calculated values of K and λ_0 the mathematical analysis gave the correlation coefficients (r) for the data as they applied to eqn (3), (4), and (5). The results of these calculations are presented in table 3.

It can be seen from table 3 that the correlation coefficients (r) for the Yang-Doty method and the Heller method for a given solution are marginally less than those for the Lowry method for the same solution. Nevertheless, the values obtained from the Yang-Doty and Heller methods are indicative of an acceptable linearity for the data when analysed by these two methods. In practice this means that the Yang-Doty and Heller methods of evaluation are slightly more rigorous tests than the Lowry

TABLE 3.—MAGNETO OPTICAL DISPERSION CONSTANTS FOR THE DRUDE EQUATION

		LiCl solution							
concentration/mol dm ⁻³		0.13	0.27	0.54	1.08	1.62	2.16	3.24	4.32
Lowry method	r^*	0.998	0.966	0.998	0.998	0.998	0.999	0.999	0.998
	$10^{10} K/u$ †	6.61	6.57	6.53	6.53	6.70	6.87	7.01	6.99
	λ_0/nm	171	175	182	182	182	175	180	187
Yang and Doty method	r	0.968	0.966	0.965	0.984	0.998	0.988	0.985	0.971
	$10^{10} K/u$	6.74	6.72	6.71	6.88	7.05	6.96	7.12	7.15
	λ_0/nm	157	161	166	159	159	167	170	174
Heller method	r	0.993	0.958	0.954	0.974	0.997	0.981	0.973	0.949
	$10^{10} K/u$	6.74	6.62	6.61	6.89	7.07	6.96	7.13	7.16
	λ_0/nm	158	166	171	158	156	168	170	174
		NaCl solution							
concentration/mol dm ⁻³		0.17	0.67	1.33	2.00	2.66	3.33		
Lowry method	r	1.000	1.000	1.000	1.000	0.999	0.998		
	$10^{10} K/u$	7.02	7.12	7.36	7.56	7.46	7.46		
	λ_0/nm	147	154	155	157	177	187		
Yang and Doty method	r	0.998	0.977	0.977	0.967	0.985	0.975		
	$10^{10} K/u$	7.04	7.30	7.38	7.48	7.54	7.64		
	λ_0/nm	147	145	154	162	168	175		
Heller method	r	0.998	0.948	0.995	0.974	0.972	0.953		
	$10^{10} K/u$	7.04	7.30	7.38	7.42	7.58	7.64		
	λ_0/nm	146	145	153	165	167	175		
		KCl solution							
concentration/mol dm ⁻³		0.40	0.81	1.61	2.42	3.22	4.03		
Lowry method	r	1.000	0.997	1.000	0.999	0.999	1.000		
	$10^{10} K/u$	6.98	6.94	7.10	7.24	7.28	7.18		
	λ_0/nm	150	175	161	161	171	172		
Yang and Doty method	r	0.999	0.992	0.992	0.996	0.987	0.993		
	$10^{10} K/u$	7.00	7.04	7.14	7.16	7.38	7.23		
	λ_0/nm	150	167	157	163	163	167		
Heller method	r	0.988	0.948	0.987	0.994	0.980	0.989		
	$10^{10} K/u$	7.00	7.12	7.14	7.16	7.38	7.22		
	λ_0/nm	150	159	158	163	163	168		
		CsCl solution							
concentration/mol dm ⁻³		1.19	1.78	2.37	3.56	4.75	5.93		
Lowry method	r	0.994	0.998	1.000	0.999	1.000	1.000		
	$10^{10} K/u$	5.68	5.90	6.07	6.20	5.72	5.39		
	λ_0/nm	201 ?	179	162	136	169	178		
Yang and Doty method	r	0.950	0.955	0.990	0.979	0.996	0.992		
	$10^{10} K/u$	5.98	6.08	6.10	6.12	5.73	5.46		
	λ_0/nm	178	163	169	146	167	171		
Heller method	r	0.950	0.931	0.990	0.974	0.997	0.989		
	$10^{10} K/u$	5.99	6.09	6.11	6.14	5.74	5.47		
	λ_0/nm	177	163	159	144	163	170		

* r = correlation coefficient; † u = deg m⁴ kg⁻¹ T⁻¹.

method as to the fit of the data to the one-term Drude equation. The correlation by all three methods is acceptable enough to validate the applicability of the one-term Drude equation to the electrolyte solutions in the wavelength range 350-650 nm.

The values of the dispersion constant, K (table 3), show the equivalence of the Yang-Doty method and the Heller method, while the Biot-Lowry method in most cases gave slightly lower values. The variation of K with solute concentration for the Biot-Lowry method and the Yang-Doty method are plotted in fig. 2(a) and 2(b). The slightly different behaviour shown by CsCl may be due to enhanced structure breaking of the solvent by this solute or its incomplete dissociation,^{12, 13} or a combination of both. The position of the LiCl curve is seen to be anomalous with respect to NaCl, KCl, and CsCl, which may be due to factors arising from the very small size of the Li^+ ion.

There does not seem to be any simple interpretation of the λ_0 except that the values are what might be expected for absorption maxima for the solutions of the type studied.

THE CALCULATION OF SOLUTE ROTATION

The calculation of the contribution from the dissolved solute to the total rotation of concentrated solutions is not straight-forward. The simple subtraction of the water rotation from the rotation of the solution is not valid for concentrated solutions. The magnetic rotation of the solution is measured on a given volume of solution in the light beam and the presence of solute molecules displaces solvent molecules which would have occupied that volume in the pure solvent.

A simple volume displacement correction¹⁹ means that the solute rotation would be $\theta_s - (d_s - w)\theta_0/d_0$, where θ_0 is the rotation of the pure solvent, d_s and d_0 are the densities of solution and pure solvent respectively (g cm^{-3}), and w is the solute concentration expressed in g cm^{-3} . Thus if c is the concentration of solute expressed as mol m^{-3} , the molar solute rotation corrected for volume displacement, Φ_d will be given by

$$\Phi_d = \frac{\theta_s - (d_s - w)\theta_0/d_0}{c} \quad (6)$$

An alternative approach is to consider that the "free water" in the solution, i.e., that not used in solvation, is measurable by means of the water activity, a_1 . This would give the molar solute rotation corrected for rotation of free water, Φ_a , as

$$\Phi_a = \frac{\theta_s - \theta_0 a_1}{c} \quad (7)$$

Although Φ_d provides a function corrected for volume displacement of solvent by solute it does not take account of any changes in solvent properties (such as structural properties) produced by the presence of the solute. Φ_a on the other hand while possibly accounting for such changes does not include a correction for the volume of solvent displaced. A better approximation to the true solute rotation is probably achieved by a combination of the two corrections discussed above. The water not used in solvation is thus compared with pure water via the water activity of the solution, so that the effective molar solute rotation Φ_{eff} is given by

$$\Phi_{\text{eff}} = \frac{\theta_s - (d_s - w)a_1\theta_0/d_0}{c} \quad (8)$$

This function should now correct for both displacement of solvent by solute and the structural effects of the solute upon the solvent, and yet should still include a contribution from the primary hydration shell to the rotation of the solute.

Values of the functions Φ_d , Φ_a , and Φ_{eff} were calculated using water activity data from Robinson and Stokes.²⁰ If θ_s and θ_o are in $\text{deg m}^{-1} \text{ T}^{-1}$ and c is in mol m^{-3} , the units of the above three functions are $\text{deg m}^2 \text{ mol}^{-1} \text{ T}^{-1}$. The variation of Φ_d , Φ_a , and Φ_{eff} with concentration for NaCl or KCl is very slight indicating an independence of molar magnetic rotation (however calculated) upon concentration of solute. Graphs of Φ_d , Φ_a , Φ_{eff} against solute molarity were plotted and found to be linear, i.e., $\Phi = \Phi^0 + zc$. The gradients (z) and the corresponding intercepts Φ_d^0 , Φ_a^0 , Φ_{eff}^0 are given in table 4. For LiCl and CsCl the variations of molar rotation are in

TABLE 4.—CHARACTERISATION OF MOLAR ROTATION—CONCENTRATION GRAPHS

wavelength/nm	350	400	450	500	550	600
LiCl						
Φ_d^0/u *	0.058	—	0.029	0.023	0.018	0.015
$10^3 z_d/u' \dagger$	0.0	—	0.0	0.0	0.0	0.0
Φ_a^0/u	0.072	—	0.038	0.030	0.024	0.020
$10^3 z_a/u'$	4.2	—	2.0	1.6	1.4	1.2
Φ_{eff}^0/u	0.076	—	0.042	0.032	0.025	0.022
$10^3 z_{eff}/u'$	4.2	—	1.6	1.6	1.4	1.0
NaCl						
values of z_d , z_a , z_{eff} were zero at the various wavelengths						
Φ_d^0/u	0.081	0.057	0.044	0.035	0.026	0.021
Φ_a^0/u	0.098	0.069	0.053	0.042	0.032	0.024
Φ_{eff}^0/u	0.109	0.077	0.058	0.046	0.037	0.028
KCl						
values of z_d , z_a , z_{eff} were zero at the various wavelengths						
Φ_d^0/u	0.076	0.056	0.038	0.034	0.025	0.021
Φ_a^0/u	0.076	0.056	0.040	0.033	0.024	—
Φ_{eff}^0/u	0.096	0.069	0.050	0.042	0.031	0.026
CsCl						
Φ_d^0/u	0.102	0.071	0.048	0.039	0.032	—
$10^3 z_d/u'$	−2.4	−1.4	−0.4	−0.4	−0.6	—
Φ_a^0/u	0.093	0.065	0.044	0.036	0.028	—
$10^3 z_a/u'$	−1.4	−0.6	0.0	−0.4	0.0	—
Φ_{eff}^0/u	0.118	0.086	0.058	0.048	0.038	—
$10^3 z_{eff}/u'$	−1.6	−1.4	0.0	−0.6	−0.4	—

* $u = \text{deg m}^2 \text{ mol}^{-1} \text{ T}^{-1}$; $\dagger u' = \text{deg m}^2 \text{ mol}^{-1} \text{ T}^{-1} (\text{mol dm}^{-3})^{-1}$.

opposite directions, that is the values of Φ_a and Φ_{eff} for LiCl increase with concentration, while the values of Φ_d , Φ_a and Φ_{eff} for CsCl decrease slightly with concentration. This means that either (6), (7) and (8) are not compensating for the solvent rotation, or that other chemical complications are present which are not accounted for in these equations. For LiCl the very strong solute–solvent interaction arising from the small size of the cation may be responsible and for CsCl the incomplete dissociation of the solute^{12, 13} may be responsible.

The values of Φ_d^0 , Φ_a^0 , Φ_{eff}^0 (table 4) for LiCl, NaCl and CsCl are in the same order as the cationic sizes. The values for KCl, however, are out of order (being closest to the NaCl values) and there does not seem to be a simple explanation for this.

Thus it can be seen that the m.o.r.d. method provides an interesting comparison of

simple electrolytes in concentrated solution. Further investigations are in progress with electrolytes which are known to possess greater complexity. It is hoped that the technique will provide further information concerning the structure and forces involved in such systems. The method should also be applicable to the study of ion-pairs, micellar systems, liquid crystals, and solute-solvent interactions in bio-polymer systems.

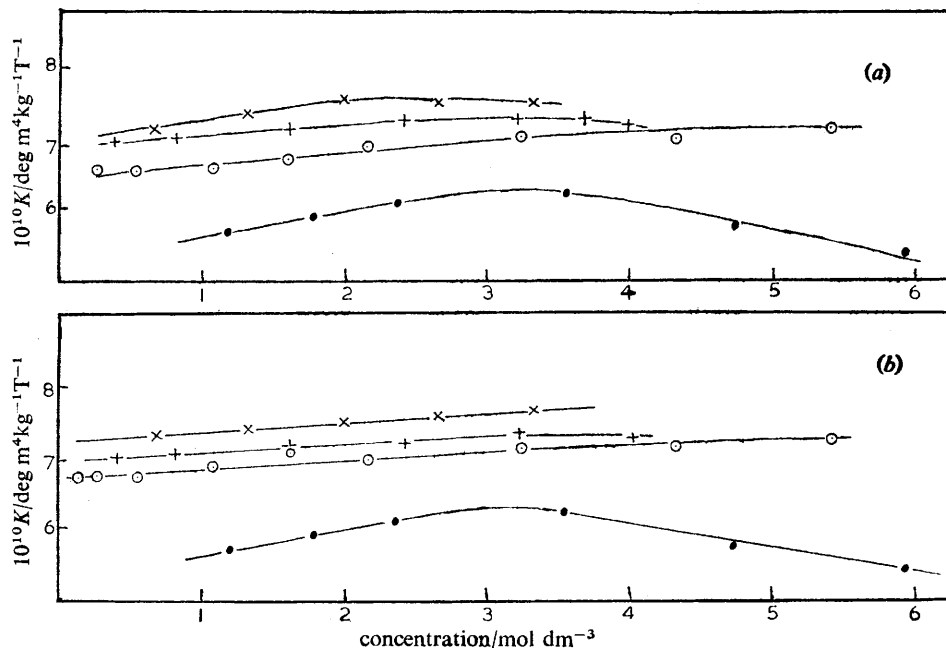


FIG. 2.—Dispersion constants for the one-term Drude equation. \circ , LiCl; \times , NaCl; $+$, KCl; \bullet , CsCl. (a) Biot-Lowry method, (b) Yang-Doty method.

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