The Magneto-optic Rotations of Some Two-component Liquid Systems.

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The work now described consists of the application of several mixture rules to two-component liquid systems in which the magnetic rotation of each component can be directly determined. The systems studied include an ideal system, a "pseudo-ideal" system, and two non-ideal systems. Each rotation recorded is the mean of 12 values determined at four magnetic field strengths, at each of which the direction of the field was reversed. Non-ideal systems are best described by the apparent molar volume rule.

MEASUREMENTS of magneto-optic rotations are of interest in analysis and in the determination of molecular structure. The determination of the magnetic rotation of pure liquids is a simple matter, but in order to find the rotations of solids dissolved in liquid solutions, it is necessary to develop a satisfactory mixture rule. In the work now described several mixture rules were applied to two-component liquid systems in which the magnetic rotation of each component can be directly determined.

The earliest mixture rule for interpreting the magnetic rotation of two component systems was that of Verdet (*Ann. Chim. Phys.*, 1858, **52**, 129) who concluded that each component of a mixture behaves as if it alone were present in the total volume of the mixture. This rule remained unchallenged for many years, and it was not until 1928 that its validity was questioned by Schönrock (*Z. Physik*, 1928, **46**, 314; 1932, **78**, 707), who pointed out that the contribution of a component of a mixture to the total rotation was dependent on the volume of that component present, and that additivity of rotations was dependent on the additivity of volumes. Scharf (*Ann. Physik*, 1932, **13**, 377) modified Schönrock's rule since he found that it did not hold for solutions where there was appreciable volume change on mixing.

In this work five mixture rules have been examined. δ_{i} is the Verdet constant of a solution calculated according to Schönrock's rule: $\delta_{i} = \delta_1 q_1/s_1 + \delta_2 q_2/s_2$, where δ_{i}, δ_1, and δ_2 are the Verdet constants of the mixture, component 1, and component 2, respectively. The concentrations, q_1 and q_2, of the components are expressed in g./c.c., and s_1 and s_2 are their corresponding densities in the pure state. δ_{ii}, δ_{iii}, δ_{iv} are calculated according to volume-fraction rules $\delta_{ii} = \delta_1 V_1{}^f + \delta_2 V_2{}^f$, where $V_1{}^f$ and $V_2{}^f$ are volume fractions calculated from mole-fractions, N_1 and N_2, *e.g.*, $V_1{}^f = N_1V_1/(N_1V_1 + N_2V_2)$, where V_1 and V_2 are the molar volumes of the components. δ_{ii} is calculated by taking V_1 and V_2 as the molar volumes of pure components, δ_{iii} by using the partial molar volumes of the components, obtained from the plot of the total volume of one mole of mixture, $(N_1M_1 + N_2M_2)/d_4^{25}$, against N_2 by Lewis and Randall's intercept method ("Thermodynamics," McGraw Hill, New York, 1923, p. 38), and δ_{iv} by taking V_1, the molar volume of the solvent, as that of the pure liquid, whilst V_2 is taken as the apparent molar volume, ϕ_2, $\phi_2 = (V - n_1V_1)/n_2$; δ_{v} is calculated according to Waring, Hyman, and Steingiser's mole-fraction rule (*J. Amer. Chem. Soc.*, 1938, **60**, 2294), $\delta_{v} = \delta_1 N_1 + \delta_2 N_2$.

EXPERIMENTAL

Apparatus.—The coil was built according to the specifications of Foehr and Fenske (*Ind. Eng. Chem.*, 1949, **41**, 1956); a battery selector switch was incorporated and this gave four main values of field strength. A network of four high-vacuum switches (Sunvic F105/5M) was used to reverse the direction of the current. The current source consisted of four heavy-duty Exide batteries, and the current strength was measured to 0·01 amp. by using a Cambridge T pattern, unipivot galvanometer. The rotations were read to 0·01° on a Bellingham and Stanley Class A polarimeter. A sodium light source was used throughout all the experiments. The heat developed when current passed through the coil was considerable, and it was necessary to have two water cooling systems. Water at 24·5° was passed through a cooling annulus incorporated in the coil; and water at 25° was passed through a specially adapted water-jacketed polarimeter cell which fitted in the core of the coil and held the sample under test. The temperature of the water was measured immediately before and after passing through the jacket.

Magnetic rotations were measured at 4 main values of field strength, corresponding to 4 battery selector switch positions. At each main value of field strength, 12 readings of the magnetic rotation of the sample were taken, 6 for each direction of the current through the coil. In all, 48 readings were taken for each sample and these were averaged, and from the average result was subtracted the rotation of the cell end-plates. Knowing the value of the field strength per amp., and the length of sample, the magnetic rotation was converted into a Verdet constant.

The field strength of the coil was determined by measurement of the magnetic rotation of carefully purified substances whose Verdet constants are reported in the literature, *e.g.*, water, benzene, and carbon disulphide. The average value of field strength was found to be 163·10 ± 0·05 gauss/cm. amp., or 164·6 ± 0·30 gauss/cm. amp. according to Waring and Custer's new absolute values of the Verdet constants of water and benzene (*ibid.*, 1952, **74**, 2506; 1952, **74**, 5726). The former value was used to calculate the Verdet constant of the solutions.

Densities were determined in a Perkin-type pycnometer, and refractive indices were measured on an Abbé refractometer at 25°. The length of the polarimeter cell was measured with a Cambridge measuring machine.

Materials.—The water used was of conductivity standard. " AnalaR " benzene was further purified by fractional distillation and fractional freezing. The portion used for standardisation of the field strength had n_{D}^{25} 1·4977, d_4^{25} 0·8735, in close agreement with values given by Timmermans (" Physico-Chemical Constants of Pure Organic Compounds," Elsevier, London, 1950, p. 145). " AnalaR " carbon disulphide was fractionally distilled and had n_{D}^{25} 1·6237, d_4^{25} 1·2555.

Commercial ethyl bromide was purified by shaking it with concentrated sulphuric acid, followed by 10% sodium carbonate solution, and then with distilled water. The ethyl bromide was dried ($MgSO_4$) and fractionally distilled through a 46 cm. × 17 mm. fractionating column packed with Dixon gauze. The reflux ratio used was 25 : 1 and the boil-up rate 320 ml./hr. Only the middle fraction was collected and the values of $n_{\mathrm{D}}^{15\cdot1}$ and $d_4^{15\cdot1}$ were 1·4276 and 1·4704 respectively, in close agreement with values given by Timmermans (*op. cit.*, p. 233). Ethyl iodide was also purified by fractional distillation at the same reflux ratio and boil-up rate; the values of n_{D}^{15} and d_4^{25} were 1·5168 and 1·9232 respectively. " AnalaR " pyridine was dried (KOH pellets) and then fractionally distilled; the middle fraction was collected and the values of n_{D}^{25} and d_4^{25} were 1·5071 and 0·9779 respectively.

Absolute ethanol was dehydrated according to a method described by Vogel (" Practica Organic Chemistry," Longmans Green, London, 1948, method 1, p. 165) and the values of n_{D}^{2} and d_4^{25} were 1·3592 and 0·7851 respectively. Nicotine, 95% (B.D.H.), was purified by a series of vacuum fractional distillations in a specially constructed, almost joint-free apparatus, and the fraction which boiled at 115°/12 mm. was collected. It was immediately sealed into ampoules under dry nitrogen, and the values of n_{D}^{25}, d_4^{25}, and $-[\alpha]_{\mathrm{D}}^{25}$ were respectively 1·5250, 1·0042, and 168·54°.

Results.—The mixture rules have been used to calculate the Verdet constant of solutions belonging to the five following liquid–liquid systems: (1) ethyl bromide–ethyl iodide, an ideal system; (2) pyridine–ethanol, a " pseudo-ideal " system; (3) nicotine–ethanol; (4) pyridine–water, a non-ideal system; (5) sulphuric acid–water, a non-ideal system.

(1) *Ethyl bromide–ethyl iodide system.* Table 1 shows the results for this system. In this table, N_2 is the mole-fraction of ethyl iodide. The Verdet constants are in units of minutes of angle/cm. gauss. The graph of the total volume of one mole of mixture plotted against the mole-fraction of ethyl bromide (N_1) is a linear curve (Fig. 1) showing that there is no volume contraction or expansion on mixing. The density of the mixtures plotted against the mole-fraction of ethyl bromide is shown in Fig. 2. There is a slight curve as required theoretically if Fig. 1 is linear with a finite slope. The average divergence between the Verdet constant of

TABLE 1. *Ethyl bromide–ethyl iodide system.*

N_2	$10^4\delta_{\mathrm{D}}^{25}$	d_4^{25}	n_{D}^{25}	N_2	$10^4\delta_{\mathrm{D}}^{25}$	d_4^{25}	n_{D}^{25}	N_2	$10^4\delta_{\mathrm{D}}^{25}$	d_4^{25}	n_{D}^{25}
(EtI)	293·0	1·9232	1·5100	0·5741	247·3	1·7302	1·4760	0·1243	197·5	1·5125	1·4335
0·9349	286·3	1·8944	1·5043	0·4372	231·0	1·6645	1·4600	0·0612	190·1	1·4813	1·4272
0·8089	272·3	1·8395	1·4940	0·2785	214·5	1·5874	1·4470	(EtBr)	182·8	1·4490	1·4211
0·7250	262·7	1·7997	1·4862	0·1642	201·6	1·5313	1·4365				

Average divergence × 10^4: $\delta_{\mathrm{i}} \pm 0{\cdot}74$; $\delta_{\mathrm{ii}} \pm 0{\cdot}74$; $\delta_{\mathrm{iii}} \pm 0{\cdot}74$.

the solutions calculated according to the mixture rules and the experimentally determined Verdet constant δ^{25}_{D} is shown.

(2) *Pyridine–ethanol system* (see Table 2). Recently Griffiths (*J.*, 1952, 1327) has found that the density–concentration curves are smooth and do not show any marked discontinuities. Blackburn and Kipling (*Nature*, **1953**, **171**, 174) have found that this system is " pseudo-ideal," since the total and partial vapour pressures at room temperature approximate closely to the behaviour required by Raoult's law. The partial molar volumes of pyridine and ethanol, used to calculate the Verdet constants according to the partial molar volume mixture rule, were determined by the intercept method from the graph of the total volume of one mole of mixture plotted against the mole-fraction of pyridine.

TABLE 2. *Pyridine–ethanol system.*

N_2	$10^4\delta^{25}_{\text{D}}$	d^{25}_4	n^{25}_{D}	N_2	$10^4\delta^{25}_{\text{D}}$	d^{25}_4	n^{25}_{D}	N_2	$10^4\delta^{25}_{\text{D}}$	d^{25}_4	n^{25}_{D}
(C_5H_5N)	255·4	0·9779	1·5071	0·7408	225·9	0·9418	1·4786	0·2349	154·0	0·8471	1·4053
0·8880	243·2	0·9622	1·4950	0·5229	197·9	0·9054	1·4509	0·1264	135·6	0·8193	1·3855
0·8635	237·3	0·9564	1·4900	0·3061	165·8	0·8605	1·4171	(EtOH)	113·1	0·7851	1·3592

Average divergence $\times 10^4$: δ_{i} ±1·77; δ_{ii} ±1·25; δ_{iii} ±1·27; δ_{iv} ±0·6; δ_{v} ±1·00.

FIG. 1.

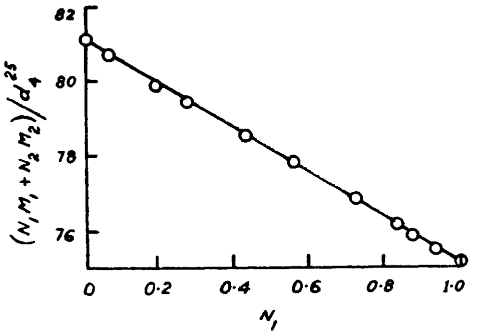
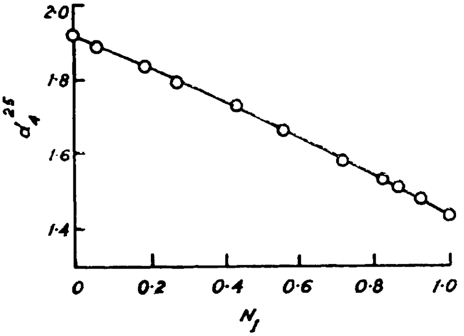


FIG. 2.



(3) *Nicotine–ethanol system* (see Table 3). The Verdet constant of pure nicotine has been determined by Lowry and Allsopp (*J.*, 1932, 1617). The plot of $(N_1M_1 + N_2M_2)/d^{25}_4$ was a straight line, and so the partial molar volumes were equal to the molar volumes of the pure components.

TABLE 3. *Nicotine–ethanol system.*

N_2	$10^4\delta^{25}_{\text{D}}$	d^{25}_4	n^{25}_{D}	N_2	$10^4\delta^{25}_{\text{D}}$	d^{25}_4	n^{25}_{D}	N_2	$10^4\delta^{25}_{\text{D}}$	d^{25}_4	n^{25}_{D}
($C_{10}H_{14}N_2$)	228·8	1·0042	1·5250	0·4512	192·4	0·9419	1·4761	0·1274	145·6	0·8546	1·4120
0·8918	224·4	0·9971	1·5208	0·2602	170·2	0·9015	1·4447	0·1131	142·2	0·8479	1·4048
0·6142	208·2	0·9697	1·4993	0·1768	156·2	0·8741	1·4210	(EtOH)	113·1	0·7851	1·3592

Average divergence $\times 10^4$: δ_{i} ±1·21; δ_{ii} ±1·34; δ_{iv} ±1·05; δ_{v} ±20·5

TABLE 4. *Pyridine–water system.*

N_2	$10^4\delta^{25}_{\text{D}}$	$10^4\delta_{\text{i}}$	$10^4\delta_{\text{ii}}$	$10^4\delta_{\text{iii}}$	$10^4\delta_{\text{iv}}$	$10^4\delta_{\text{v}}$	d^{25}_4	n^{25}_{D}
(C_5H_5N)	255·4	—	—	—	—	—	0·9779	1·5071
0·8941	250·9	252·8	252·1	252·8	252·1	242·5	0·9803	1·5031
0·6628	241·7	244·7	242·8	243·2	242·5	213·4	0·9892	1·4920
0·4816	230·3	234·7	231·0	232·5	230·7	190·9	0·9974	1·4782
0·3731	222·2	225·2	221·5	220·7	220·7	177·6	1·0010	1·4640
0·2875	209·3	214·8	210·9	211·2	210·0	166·6	1·0028	1·4491
0·2600	205·3	210·4	206·7	207·5	206·0	163·2	1·0032	1·4432
0·1909	196·0	198·3	194·9	195·3	194·2	154·4	1·0038	1·4295
0·0883	168·8	173·6	168·4	167·2	165·5	141·9	1·0025	1·3880
0·0539	154·8	157·3	155·9	154·8	155·1	137·5	1·0016	1·3690
(H_2O)	130·8	—	—	—	—	—	0·9971	1·3323
Average divergence		±1·8	±1·3	±1·3	±1·0	±32·4		

(4) *Pyridine–water system* (see Table 4). Griffiths (*loc. cit.*) has shown that the density–concentration curve is smooth, and this agrees with our results. This system is non-ideal, and

the average divergences show clearly that the apparent molar volume mixture rule is the best one for calculating the Verdet constant of the solutions. There appears to be little advantage in using partial molar volumes in place of molar volumes; the Schönrock and the Waring mixture rule are unsatisfactory when the systems are non-ideal.

(5) *Sulphuric acid–water system* (see Table 5). Perkin (*J.*, 1893, **63**, 57) determined the magnetic rotation of sulphuric acid in water and found that the rotations of the mixtures were less than the sum of those of the constituents. The difference was considerable for small dilutions, but diminished as the amount of water increased. The molar volume of sulphuric acid was calculated from the density of pure sulphuric acid as determined by Gillespie and Wasif (*J.*, 1953, 215). The partial molar volumes and apparent molar volumes were determined as previously described.

TABLE 5. *Sulphuric acid–water system.*

N_2	$10^4\delta_D^{25}$	d_4^{25}	n_D^{25}	N_2	$10^4\delta_D^{25}$	d_4^{25}	n_D^{25}
(H_2O)	130·8	0·9971	—	0·2883	120·5	1·5715	1·4150
0·0302	130·4	1·0970	1·3491	0·4953	114·6	1·7598	1·4347
0·0753	128·6	1·2218	1·3691	(98% H_2SO_4)	103·6	1·8310	—
0·1483	127·9	1·3772	1·3915	(H_2SO_4)	—	1·8269	—

Average divergence $\times 10^4$: $\delta_i = \pm 4{\cdot}4$; $\delta_{ii} = \pm 3{\cdot}7$; $\delta_{iii} = \pm 2{\cdot}9$; $\delta_{iv} = \pm 2{\cdot}2$; $\delta_v = \pm 1{\cdot}5$.

Conclusion.—The magnetic rotations of the ideal and " pseudo-ideal " systems are described within the limits of experimental error (mean standard deviation of each recorded determination = 0·4%), by any one of the mixture rules. Non-ideal systems are best described by the apparent molar volume rule, δ_{iv}. The partial molar volume rule, δ_{iii}, does not give such good agreement with the experimental results and this may be due to errors in the graphical determination of the partial molar volumes. The Schönrock and the mole-fraction rule show large errors when applied to some of the systems.

It is fortunate that the apparent molar volume mixture rule, δ_{iv}, describes accurately the experimental rotation of non-ideal systems since this is the simplest rule to apply to systems containing solid solutes.

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