J. Pharm. Pharmac., 1968, **20**, 934–940 Received July 15, 1968

The optical rotatory dispersion of some *N*-decyl-*N*-*N*-dimethylalanine salts and their critical micelle concentrations

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The optically active salts of *N*-decyl-*NN*-dimethylalanine are shown to have anomalous optical rotatory dispersion curves and to not be fully ionized in aqueous solution. The position of the peak in the 225 to 230 mμ region varies with concentration of the surfactant as does the molecular rotation at a given wavelength. The positions of the peaks and the molecular rotations at these low wavelengths are pH sensitive. The change in molecular rotation with concentration enables the critical micelle concentrations of L and D *N*-decyl-*NN*-dimethylalanine hydrobromides to be determined by optical rotatory dispersion measurements, the results agreeing well with the values calculated from the literature. The change in rotation on micelle formation appears to be due to a change in the degree of ionization of these weak acids, a fact which is confirmed by pH measurements on these solutions.

OPTICALLY active betaines have been reported by Beckett, Kirk & Virji (1967) to have optical rotatory dispersion (ORD) curves of the "plain type" over the range they examined; however, plain curves are not to be expected for these amino-acids derivatives (Gaffield, 1964; Jennings, Klyne & Scopes, 1965; Cymerman Craig & Roy, 1964). Some optically active *N*-decyl-*NN*-dimethylalanine hydrobromides and hydrochlorides have been made, and further investigations of their ORD characteristics are reported here.

The critical micelle concentration (CMC) of β-D-octyl glucoside has been measured by ORD (Mukerjee, Perrin & Witzke, unpublished), and the rotation at a given wavelength was found to be enhanced by a small but significant amount by micelle formation. Analysis of the plain dispersion curve of the glucoside by a single-term Drude equation (Drude, 1906), showed that on micelle formation the wavelength of maximum absorption was not significantly changed but that the "rotatory power" term was changed by a mere 8%. The change was thus considered to be due to the high concentration of glucoside head groups found at the micelle surface rather than any significant conformational restraint at this surface.

A CMC of slightly less than 1×10^{-2}M at 22° for *N*-decyl-*NN*-dimethylalanine hydrobromides can be calculated from the data of Beckett & others (1967) and the possibility of detecting this micelle formation by ORD is now reported.

Experimental

Materials. 1 Bromodecane (Eastman Organic Chemicals, Rochester, N.Y.), D-Alanine M.A. (Mann Research Labs., New York, N.Y., L-Alanine (Aldrich Chemical Co., Milwaukee, Wis.), palladium 30% on charcoal (Engelhard Industries, Inc., Newark, N.J.) were used as supplied by the manufacturer. All other chemicals were laboratory reagents. Doubly distilled water was used. Any pH adjustment was made using a Beckman Research pH meter and the pH against concentration plot was obtained from measurements made at 25 ± 0·02°.

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PREPARATION OF THE BETAINES

The optically active alanines were methylated by a slight modification of the method of Bowman & Stroud (1950). Alanine (25 g) was dissolved in water (1 litre) and palladium on charcoal (10 g of 30%) and aqueous formaldehyde (100 ml; 37%) were added. This mixture was hydrogenated under three atmospheres pressure until the theoretical quantity of hydrogen was taken up (2 hr). The mixture was then heated until boiling and filtered, and the catalyst extracted with hot water (200 ml) and the aqueous solution evaporated to dryness at 60°. After addition of the theoretical quantity of hydrochloric acid, the residue was re-evaporated twice from water to remove any paraformaldehyde. The residue was then dissolved in methanol and again evaporated to dryness. This dimethylalanine hydrochloride was then dissolved in more methanol and converted to *N*-decyl-*NN*-dimethylalanine hydrobromide or hydrochloride by the method of Beckett & others (1967). Each crystallization from anhydrous acetone was checked by melting point, optical rotatary dispersion, and nuclear magnetic resonance spectra. At least five recrystallizations were necessary to remove an optically more active impurity (probably unchanged dimethylalanine). The products were dried overnight at 50°. The yields were 1 to 5%.

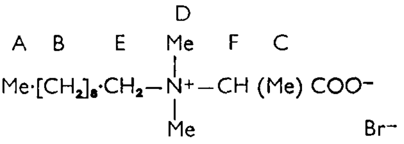
ANALYSIS OF DECYL BETAINES

Compound	Carbon		Hydrogen		Nitrogen		$[\alpha]_D^{22}$	m.p. °C
	Found	Theor.	Found	Theor.	Found	Theor.		
L (bromide)	53·0	53·2	9·6	9·5	4·1	4·1	−10·4	90–91
D (bromide)	53·1	53·2	9·5	9·5	4·1	4·1	10·4	92–93
D (chloride)	61·1	61·3	11·0	11·0	4·8	4·8	12·0	94–95

$[\alpha]_D^{22}$ were measured using 1% aqueous solutions.

NMR SPECTRA

Nuclear magnetic resonance spectra were obtained using a Varian Model A60A. A typical spectrum gave the following values:



$$\mathrm{Me{\cdot}[CH_2]_8{\cdot}CH_2{-}\overset{\overset{\large Me}{|}}{\underset{\underset{\large Me}{|}}{N^+}}{-}CH\,(Me)\,COO^-}\qquad \mathrm{Br^-}$$

(*N*-Decyl-*NN*-dimethylalanine hydrobromide) A, τ 9·14; B, τ 8·70; C, τ 8·44; D, τ 6·88, 6·84; E τ~6·5; F, τ 5·88; DOH, τ 5·42. A small trace of unreacted dimethylalanine was easily detectable on nmr integration. The D- and L-forms gave identical spectra.

MEASUREMENT OF OPTICAL ROTATORY DISPERSION

A Cary Model 60 spectropolarimeter (Applied Physics Corporation, Monrovia, California) was used. The measurements were made in either 2 or 5 cm cells taped to the cell carriage to aid reproducibility.

The concentrations for preliminary investigations were expressed as weight in volume and the scans made until the limits of the system and the instrument were reached. For the CMC determination, the concentrations were expressed as weight in weight and all solutions were scanned from 250 mμ until the peak in the region of 225–232 mμ was clearly defined. In all instances the opposite enantiomorph gave mirror image curves.

Results and discussion

(*a*) *General.* Fig. 1 shows scans of concentrations of *N*-decyl-*NN*-dimethyl-L-alanine hydrobromide above and below the CMC. This was estimated to be approximately $1{\cdot}0 \times 10^{-2}$ M from the data of Beckett & others (1967). Anomalous curves were obtained, the peak probably being the start of a Cotton effect around the carboxyl chromophore which has an absorption band in the region of 215 to 210 mμ (Schellman, 1960). The $1{\cdot}42 \times 10^{-2}$M solution had a peak at 229·5 mμ and a specific rotation, [α], of 256·0 at this peak, whereas the $2{\cdot}85 \times 10^{-3}$M solution had a peak at 228 mμ and a [α] of 283·4. The full significance of the peak shift and change in specific rotation on micelle formation will be discussed below. Fig. 2A shows a more detailed scan in the region of the rotational peak. At higher pH values the peak was shifted down to 226·5 mμ and at the acid pH it was shifted to 230·5 mμ, all the changes being reversible. These shifts suggest that there is a change in molecular species in moving the aqueous solution (pH 2·03) to more acid or more alkaline conditions. The nitrogen of the betaine is quaternary and so is always positively charged, leaving the betaine hydrobromide to behave as a monobasic acid. Fig. 2A suggests the acid to be only partially ionized; this is contrary to the finding of Beckett & others (1967). Similar observations were made with solutions of concentrations below the CMC and pH measurements on these solutions suggested a pK_a in the region of

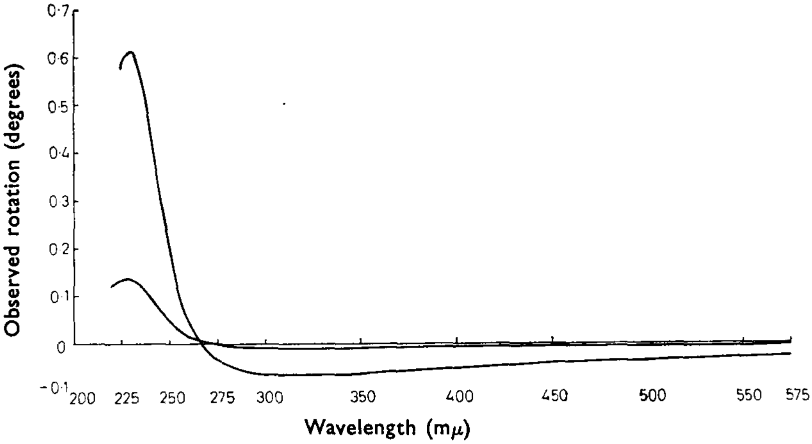


FIG. 1. ORD scan of L-decyl betaine hydrobromide. Upper curve concentration is $1{\cdot}42 \times 10^{-2}$ M and the lower concentration is $2{\cdot}85 \times 10^{-3}$ M. A 5 cm cell was used.

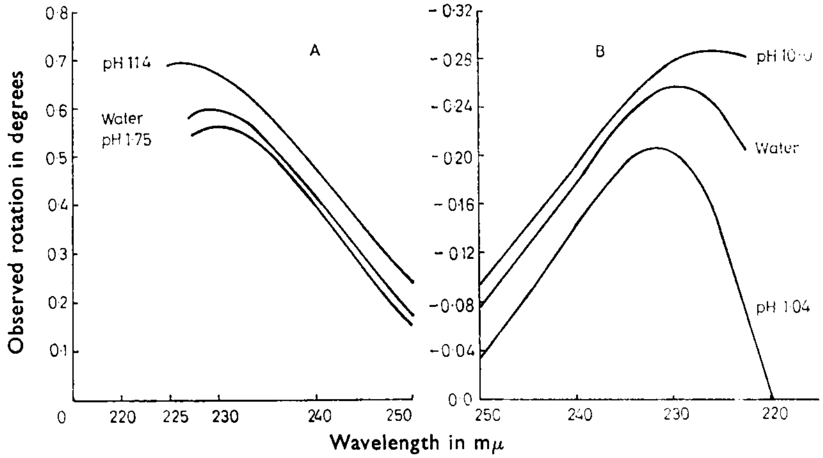


FIG. 2. A. Effect of pH on ORD curve of 1·38 × 10^{-2} M solution of L-decyl betaine hydrobromide. Measurements were made in a 5 cm cell. B. Effect of pH on ORD curve of 1·65 × 10^{-2} M solution of D-decyl betaine hydrochloride. Measurements were made in a 2 cm cell.

2·1 for the acid. When the betaine was in the fully ionized form the rotation was enhanced; this is not to be expected since the $-COO^-$ substituent has a plane of symmetry and decreasing the symmetry of acids by forming the symmetrical $-COO^-$ group decreases the rotation of amino-acids (Schellman, 1960). Fig. 2B shows the scan for *N*-decyl-*NN*-dimethyl-D-alanine hydrochloride, the replacement of the bromide by the chloride allowed scanning to lower wavelengths, but absorption prevented scanning below 205 mμ even with very dilute solutions, and so the second extremity of a Cotton effect was never obtained. The effects of pH change were similar to that observed for the bromide and a pK_a in the region of 2·2 was estimated from pH measurements on dilute solutions. The zero crossover of the pH 1·04 solution is at 219 mμ, in the region expected for a compound having a Cotton effect due to the absorption of the carboxyl group. The steeply ascending positive tail of the ORD curve at wavelengths between 225 and 200 mμ is characteristic of amino-acids having the absolute configuration of the D-series (Cymerman Craig & Roy, 1965).

(*b*) *Critical micelle concentration determination.* The full ORD scan in Fig. 1 suggested a change in rotation on micelle formation, and so the solutions were scanned from 250 mμ down to beyond the peak. A representative sample of the curves for various betaine concentrations is shown in Fig. 3. The CMC was approximately 0·325%, and it can be seen that the peaks at higher concentrations were in the region of 230–230·5 mμ whereas at concentrations below the CMC they were shifted to 228–229 mμ. The specific rotations [α] calculated at any wavelength were lower for concentrations above than for concentrations below the CMC (Fig. 4) where observed rotations are plotted against concentration at a fixed wavelength of 232·5 mμ). The line changes to a smaller slope after the

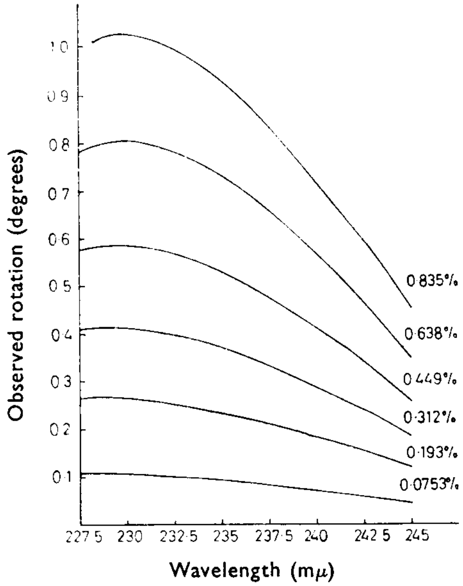


FIG. 3. Effect of concentration on ORD curves of the L-enantiomorph.

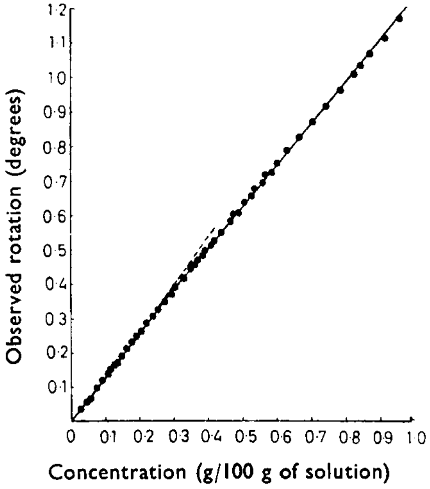


FIG. 4. Plot of observed rotation at 232·5 mμ against concentration for the L-enantiomorph.

CMC (0·325%) and the specific rotation calculated from the slope changes from a value of 259·6 below to one of 232·0 above CMC. A similar plot for the D-enantiomorph gives [α] values of —262·0 and —232·0 respectively and the same CMC. To emphasize the change in rotation on micelle formation, a deviation plot is shown in Fig. 5. The slope of the line below the CMC was calculated and the theoretical rotation for any concentration = slope × concentration, and the deviations observed from

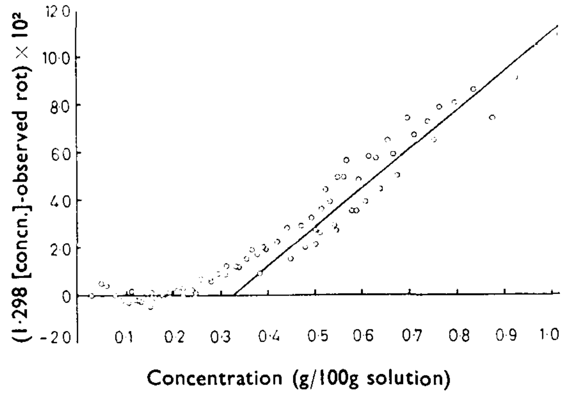


FIG. 5. Deviation plot showing the CMC for the L-compound.

this theoretical rotation are plotted against concentration in the diagram. The figure clearly shows a break in the region of the CMC and contains points from two different preparations of the betaine. The curvature near the CMC which was also observed with the octyl glucoside lends support to arguments against the phase separation model for micellar systems (Mukerjee, 1967).

The decrease in rotation and the shift of the peak to higher wavelength on micelle formation when compared with the shifts due to pH changes, suggest that the rotational changes are due to the change in degree of ionization of the betaine on micelle formation. The betaines are apparently less ionized in the micellar form and this change masks any head group concentration effects that may be present. That the change in rotation on micelle formation is due to a change in the apparent dissociation constant of the weak acid is confirmed by the plot of pH against log concentration shown in Fig. 6. A break occurs at the CMC and slope is diminished on micelle formation confirming that the betaine is less ionized when in the micellar form.

These surfactants probably form micelles with the polar head groups containing both the positive and negative charges exposed to water and the hydrocarbon chains forming an almost spheroidal core. The primary driving force for micelle formation is the tendency of the hydrocarbon portion of the monomer to associate with itself rather than to remain in close proximity to water. This "hydrophobic" bonding must overcome the repulsion forces in the ionic head groups of the ionic detergents. The surface of the betaine must always have a net positive charge due to the quaternary nitrogen and the fact that not all the carboxylic acid groups are ionized; however, the outer periphery of the micelle is negatively charged, being well orientated for capture of the hydrogen ions. This effect may be minimized by orientation of the negatively charged carboxyl group towards the positively charged nitrogen closer to the hydrocarbon core. If two adjacent carboxyl groups on the micelle surface are charged, then they will be repelled as far away from each other as possible, and

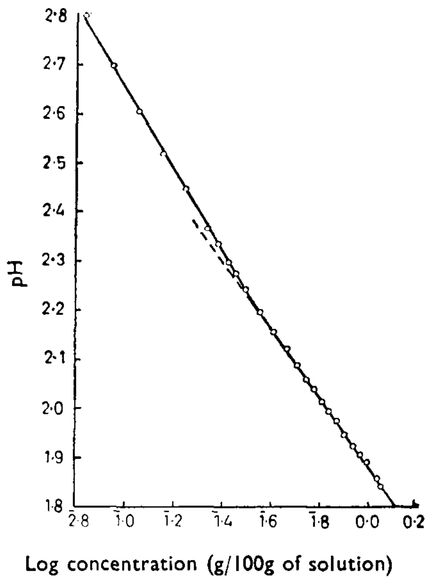


FIG. 6. Plot of pH against log concentration for the L-salt showing a break at the CMC.

micelle formation, or micelle stability, will be enhanced if one of the carboxyl groups captures a hydrogen atom and becomes uncharged, giving a possible reason for change in degree of ionization of the betaine on micelle formation. The lack of electrostatic theory for such systems, and the lack of further knowledge of the properties of the betaine micelles as well as the uncertainties of the glass electrode in such systems, makes further interpretation of the pH-log concentration plot impossible at this stage.

The authors would like to thank Mr. Robert Sandmann for obtaining the NMR spectra and Dr. Philip Hart for many helpful discussions.

This work resulted in a 1968 Lunsford Richardson Award for undergraduate research in an American School of Pharmacy being given to Miss Bonkoski.

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