## Dipole Moments of Metal Oleates

Banerjee and Palit[1] have reported a value of 0·29 D. for the dipole moment of zinc oleate in contrast to values of 1·20 and 1·66 D. for the oleates of copper and magnesium. A possible reason for this anomaly has been found in the course of an ebullioscopic investigation of the micellar weights of some of the metal soaps in benzene and other solvents.

The dipole moments reported by Banerjee and Palit were evaluated by measuring the molar polarization of the oleates in benzene solution, using a heterodyne beat method. This procedure is based on the fundamental assumption that the solute is either molecularly dispersed or is approaching molecular dispersion in the concentration range in which the polarization measurements are made. Micellar weight data for zinc oleate, however, are shown in the accompanying graph.
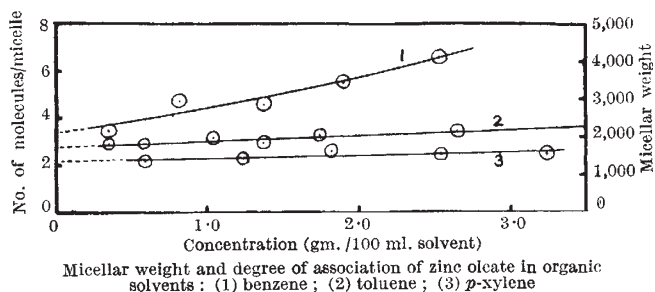
Micellar weight and degree of association of zinc oleate in organic solvents : (1) benzene ; (2) toluene ; (3) p-xylene

These results demonstrate the presence, in all the solutions, of aggregates at concentrations well below those at which Banerjee and Palit made their polarization measurements. Further, the shape of the micellar weight-concentration curves provides no justification for the assumption that extrapolation of the polarization data to infinite dilution is likely to give a reliable value for the polarization of the molecularly dispersed solute. Aggregation was also detected ebullioscopically in solutions of the copper and magnesium compounds ; but, in these cases, the accuracy obtainable did not warrant extrapolation of the micellar weight data to infinite dilution. The fact that aggregation occurs in all these solutions even at low concentrations suggests that the absolute values of the moments reported by Banerjee and Palit may be in error, although there is little reason to doubt that their measurements place the oleates in the correct order of polarity.

It should be noted that Banerjee and Palit's measurements were made at room temperature, whereas the micellar weight measurements now reported are at the boiling points at atmospheric pressure of the respective solvents. However, a comparison of the micellar weights of zinc oleate in benzene (boiling point 80·1° C.) and p-xylene (boiling point 138·4° C.) indicates clearly that, at room temperature in benzene, aggregates even larger than those observed at the boiling point are to be expected. The measured micellar weights are average values, and a high average micellar weight in solution does not therefore exclude the presence of some micelles of smaller size, or even of some molecularly dispersed solute. The measured polarizations are thus mean values for the different sizes of particles present in the solutions. Since the larger aggregates might reasonably be expected to be much less polar, the relatively high polarization values recorded by

Banerjee and Palit provide evidence for the existence in the solutions of some particles considerably smaller than the average and possibly also for a small proportion of the monomeric solute. The ebullioscopic apparatus used in these experiments has been described elsewhere[2].

A. GILMOUR
S. M. NELSON
R. C. PINK

Department of Chemistry,
Queen's University,
Belfast.   Dec. 17.

[1] J. Indian Chem. Soc., 27, 385 (1950).
[2] Nelson and Pink, J. Chem. Soc., 1744 (1952).

Optical Exaltation in Aromatic Compounds

IT is known that the molecular refraction, as defined by Lorenz–Lorentz, of liquid (non-aromatic and non-conjugated) organic compounds may be calculated with fair accuracy by summation of the atomic refractions and the contributions to structural influences which may play a part (for example, olefinic double bonds). For aromatic compounds this additive character of the molecular refraction does not apply. Here the value measured is nearly always greater than the sum of the atomic refractions and contributions due to double bonds.

In determining the molecular refraction, the difficulty is encountered that, under normal conditions (20° C.), most of the aromatic compounds with three or more rings are solids, some of which have a very high melting point. This difficulty may be avoided by dissolving compounds the molecular refraction of which is required in a solvent with a known molecular refraction, determining the refractive index and the density of the solution, and afterwards calculating the molecular refraction of the solution from these results. The molecular refraction of the dissolved substances as a hypothetical liquid is denoted by :

$$R_{M_I} = \frac{R_{M_{I\,II}} - f_{II} \cdot R_{M_{II}}}{f_I}, \qquad (1)$$

where R_{M_I} and $R_{M_{II}}$, $R_{M_{I\,II}}$ are molecular refractions of the dissolved substance, the solvent and the solution respectively ; and f_I and f_{II} are molecular fractions of the dissolved substance and the solvent respectively. The molecular refractions of a number of aromatic compounds in the hypothetical liquid state at 20° C., calculated in this manner, are given in the accompanying table.

With the help of the values of the molecular refractions determined, we derived the corresponding refractometric exaltations (see table). Here the exaltation of an aromatic $C_pH_qO_rN_sS_t$ molecule is defined as :

$$E = R_M - (p.R_C + q.R_H + r.R_O + s.R_N + t.R_S), \quad (2)$$

where R_M is the measured molecular refraction of the compound; R_C, R_H, R_O, R_N and R_S are the atomic refractions of C, H, O, N and S, as derived from non-aromatic compounds. For the atomic refractions we used those which may be calculated from the bond refractions given by Vogel et al.[1]. p, q, r, s and t are the number of C, H, O, N and S atoms.