

Such a high energy suggests that undissociated uranyl nitrate, perhaps unlike most other nitrates, may exist in covalent rather than ion-pair form. Indeed, the mere fact that the properties in question are most highly developed for the very large uranyl ion would seem to rule out any explanation in terms of ion-pairs alone.

As the title of our note made clear, we consider *f*-shell covalency a possibility rather than a certainty, and we hope that further evidence will be forthcoming from other lines of approach. For the present, the conclusion reached will depend on the relative weight given to different lines of argument, and in spite of Katzin's comments we still favour our original suggestion.

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### Mode of Action of Specific Solvents for Bituminous Coals

It has been reported<sup>1</sup> that conditions of solution such as coal/solvent ratio and successive treatment with solvent have a considerable influence on the yield of extract obtained when coals of low rank are treated with specific solvents<sup>2</sup>. Further work has shown that these effects, and others since observed, can largely be ascribed to mechanical causes, and they will therefore not be discussed in detail. Four points of interest have, however, come to light.

(1) Mechanical shaking, although desirable in order to increase the *rate* of solution, has a markedly adverse effect on the yield of soluble material which can be obtained in a single treatment.

(2) By appropriate methods a maximum yield of soluble matter can be obtained, which depends only upon the type of coal, the solvent and the temperature of treatment. This limiting yield may be reached by extended treatment (successive extraction) in spite of the adverse effect of shaking mentioned in note (1).

(3) With the lowest-rank coals (the internal colloidal structure of which is readily accessible to liquids), and one or two of the best solvents, the concentration of dissolved material appears to be the same both in the solvent imbibed into the micropores and in the bulk solution outside the coal particles. This, however, is only strictly true under ideal conditions of mechanical treatment. It is considered to represent the fundamental primary equilibrium.

(4) An important departure from the behaviour described in note (3) is observed when the bulk solution concentration exceeds a certain value, for example, approximately 8 gm./100 c.c. in the case of ethylene diamine; the concentration in the bulk solution then appears to increase at the expense of that in the micropores, and in consequence the recoverable extract or apparent yield increases. This effect is ascribed to aggregation of the soluble units in the bulk solution. Evidence of such aggregation is shown independently by the tendency of strong solutions rapidly to form surface skins and to throw down sludge, whereas dilute solutions are stable almost indefinitely.

The function of the solvent in reversing the effect of ageing has already been pointed out<sup>2</sup>. If imbibed

solvent can loosen up the colloidal structure of the solid sufficiently, it is probable that controlling factors more akin to equilibrium solubility come into play. Up to a volume imbibition ratio of approximately 2, whether the (specific) solvent or the coal is varied, extraction yield shows a striking proportionality to the imbibition ratio. But the greater the imbibition the greater become the differences between the yields obtained with different solvents at a given swelling-level; scatter increases, and a departure from the average linear proportionality is also observed at very high imbibition ratios. In this upper range, it is probable (and supported by independent evidence) that the yield of extract is determined chiefly by the size distribution of colloidal units in the coal in relation to the largest unit which is appreciably soluble (in the equilibrium sense); in the lower range, on the contrary, a large measure of control must be exerted by difficulties of disengagement, that is, by what may be termed a micellar sieve mechanism.

The temperature coefficient of extraction yield varies to a limited extent with the rank of coal. The property found most suitable for characterizing rank in this connexion is the amount of solvent imbibed at room temperature. When the volume imbibition ratio exceeds unity, the value of the temperature coefficient ceases to change further with rank. This observation is probably to be explained in terms of a coefficient fundamentally independent of rank but nevertheless influenced by a barrier to solution imposed by the sieve mechanism mentioned in the previous paragraph. It is probable that the constant value of the temperature coefficient can be used, on the lines indicated by Brønsted<sup>3</sup>, Schulz<sup>4</sup> and Gee<sup>5</sup>, to deduce a size distribution for the unit particles of soluble material. The form of the relation between extraction yield (in ethylene diamine) and temperature, for a number of coals with which the imbibition ratio exceeds unity, indicates, if interpreted in this way, a modal size which is constant over a considerable range of rank; but in the present state of knowledge it is impossible to calculate the absolute magnitude of this parameter. The value of the modal size is of interest in connexion with estimates of the average colloidal unit size derived from porosity and heat of wetting (internal surface) measurements by Bangham<sup>6</sup> and co-workers, of crystallite sizes derived by Riley<sup>7</sup> and co-workers, and of molecular weights determined by cryoscopic methods<sup>8</sup>.

A fuller account of this work will be published elsewhere.

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<sup>1</sup> Dryden, I. G. C., *Nature*, **162**, 959 (1948); **163**, 141 (1949).

<sup>2</sup> [*Nature*, **166**, 561 (1950).]

<sup>3</sup> Brønsted, J. N., *C. R. Lab. Carlsberg*, Sér. chim., **22**, 99 (1938).

<sup>4</sup> Schulz, G. V., *Z. phys. Chem.*, **A**, **179**, 321 (1937).

<sup>5</sup> Gee, G., *Ann. Rep. Chem. Soc.*, **39**, 7 (1942).

<sup>6</sup> Bangham, D. H., Franklin, R. E., Hirst, W., and Maggs, F. A. P., *Fuel*, **28**, 231 (1949).

<sup>7</sup> Blayden, H. E., Gibson, J., and Riley, H. L., "The Ultrafine Structure of Coals and Coke", 176 (Brit. Coal Util. Res. Assoc., 1944).

<sup>8</sup> For example, see: Asbury, R. S., *Indust. Eng. Chem.*, **28**, 687 (1936); Kuznetsov, M. I., *Khim. Tver. Topl.*, **6**, 515 (1935); *Fuel*, **16**, 114 (1937). Biggs, B. S., *J. Amer. Chem. Soc.*, **58**, 484, 1020 (1936).