Notes

Use of Amyl Alcohol in the Sodium Diethyl Dithiocarbamate Method for Estimation of Copper

By R. W. Thatcher

Several laboratory workers have experienced some difficulty in securing a sharp separation of the amyl alcohol layer in using the McFarlane[1] method for the determination of copper in organic tissues.

I have found that if isoamyl alcohol (redistilled at 129–131°) is used, this difficulty is avoided and a sharp separation occurs in a very short time even after quite vigorous shaking of the mixture. The amyl alcohol layer is so clear that it is rarely necessary to filter it through paper to remove traces of water before final colorimetric comparison. On the other hand, if normal amyl alcohol (boiling point 138–140°) is used, the separation is slow and the alcohol layer often turbid. This difference is probably due to the greater solubility of normal amyl alcohol in water than that of the iso form.

[1] McFarlane, *Biochem. J.*, **26**, 1022 (1932).

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The System Lead Acetate–Acetic Acid

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The recent discovery by Tarbutton and Vosburgh[1] of a solvate of the composition $Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2$, stable at 25° in contact with lead acetate–acetic acid solutions containing small concentrations of water, made it seem probable that the lower portions of both branches of the previously presented freezing-point curve for the anhydrous binary system[2] corresponded to equilibria metastable with respect to this solvate. A reëxamination of the binary system was therefore undertaken, with the aid of crystals of the solvate kindly furnished by Dr. Vosburgh.

Pure acetic acid (m. p. 16.62°) was prepared as described in previous papers. Anhydrous lead acetate was made by recrystallizing the trihydrate twice from solution in dilute acetic acid, heating it to 125° for two days, moistening the slightly basic product with anhydrous acetic acid and heating again to 115° for six hours. The resulting substance melted at 204°, and on analysis for lead gave 63.81%, as compared with the calculated 63.71%. The synthetic method described in previous papers was employed, except that solutions of the appropriate concentrations were

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[1] Tarbutton and Vosburgh, This Journal, **54**, 4537 (1932).

[2] Davidson and McAllister, *ibid.*, **52**, 507 (1930).

seeded with minute amounts of the plate-like crystals of the solvate before determining the freezing points. It is remarkable that, although this compound proved to be the stable solid phase throughout a long range of concentrations (12.0 to 36.5 mole per cent. of lead acetate), we have not observed a single instance of its spontaneous separation, without seeding, from anhydrous solutions.[3]

The composition of the solid separating, on seeding, from saturated solutions in this range was determined by filtering it off, drying between porous tiles in a desiccator over sodium hydroxide for twenty hours, and analyzing for lead by means of precipitation as lead sulfate. Three analyses gave a mean value of 66.78 mole per cent. of lead acetate, proving it to be the hemisolvate, $Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2$.

The new freezing point data are tabulated below, and are shown, together with portions of the curves for acetic acid and unsolvated lead acetate as solid phases, in Fig. 1.

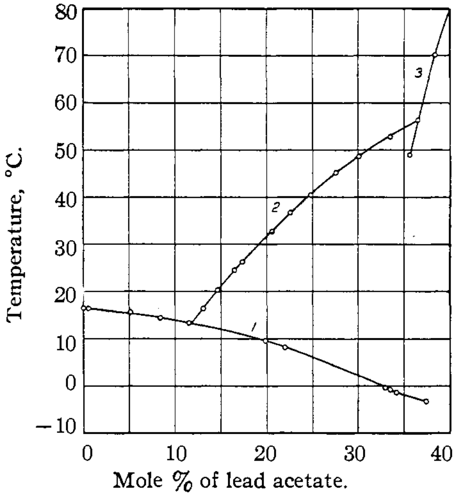

Fig. 1.—System $Pb(C_2H_3O_2)_2$–$HC_2H_3O_2$: 1, $HC_2H_3O_2$ as solid phase; 2, $Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2$ as solid phase; 3, $Pb(C_2H_3O_2)_2$ as solid phase.

$Pb(C_2H_3O_2)_2$, mole %	13.06	14.67	16.55	17.37	20.57	
Temperature, °C.	16.4	20.3	24.5	26.4	32.8	
$Pb(C_2H_3O_2)_2$, mole %	22.60	24.77	27.60	30.23	33.55	36.60
Temperature, °C.	36.7	40.5	45.2	48.7	52.9	56.4

The solubility of the hemisolvate at 25° is 3.35 moles per 1000 g. of solvent, 16.75 mole per cent. or 52.16 weight per cent. This value agrees well with the trend of the solubility data of Tarbutton and Vosburgh for solutions containing small amounts of water. At 56° the compound undergoes transition to unsolvated lead acetate.

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(3) *Cf.* Ref. 1, p. 4542.