53. *Simultaneous Adsorption from Dilute Aqueous Solutions.*

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The object of this investigation was to determine, in certain cases, the relative adsorbability of two different solutes from a solution containing both. It has been found that for certain of the investigated systems, the curve relating adsorption to equilibrium concentration is inflected, and this appears to be the first reported instance of such curves with pairs of substances in dilute solution. In all cases investigated, a mutual displacement effect is apparent.

At the concentrations employed, it was found that Traube's rule was obeyed in the adsorption of acetone, of methyl ethyl ketone, and of methyl *n*-propyl ketone from aqueous solution.

Adsorption from some binary liquid systems has been found to give S-shaped isothermals (Flörow, *Kolloid-Z.*, 1925, **36**, 215; Pawlow, *ibid.*, p. 217; Ostwald and Schulze, *ibid.*, p. 289; Bartell and Sloan, *J. Amer. Chem. Soc.*, 1929, **51**, 1637, 1643; Bartell, Scheffler, and Sloan, *ibid.*, 1931, **53**, 2501; Rao, *J. Physical Chem.*, 1932, **36**, 616). In the present work, isothermals of the same shape have been obtained with ternary systems consisting of dilute aqueous solutions containing phenol and a ketone, or aniline and a ketone, the adsorbent being sugar-charcoal. Since, in the present experiments, the concentration of a solute never exceeds 0·50 g.-mol./l., the adsorption of the water may probably be regarded as constant. The equation of Markham and Benton (*J. Amer. Chem. Soc.*, 1931, **53**, 503), if applicable to the present systems, would give, for a given equilibrium concentration of ketone, a hyperbolic isothermal for the adsorption of the phenol or aniline; however, the isothermals obtained are not of this form.

Experimental.

All the substances used were carefully purified before use. The adsorbent was one uniform sample of finely powdered sugar-charcoal, which had been quartered, thoroughly mixed, dried at 130° for 12 hours, and thereafter preserved in a vacuum desiccator over calcium chloride; the ash from 5 g. was not weighable. Phenol was estimated by the Landolt–Koppeschaar method (*Ber.*, 1871, **4**, 770; *Z. anal. Chem.*, 1876, **15**, 233), aniline by that of Vaubel (*J. pr. Chem.*, 1877, **15**, 237), and acetone by that of Messinger (*Ber.*, 1888, **21**, 3366); in estimations of methyl ethyl ketone and methyl *n*-propyl ketone, it was found necessary to use 2N-alkali with 20 minutes' standing. In solutions containing both phenol and ketone, the former was removed as *s*-tribromophenol before estimation of the ketone; aniline was likewise removed as *s*-tribromoaniline.

Each system was prepared by taking 1·000 g. of the charcoal and 100·0 c.c. of standard aqueous solution in a sealed bottle, which was then immersed in a thermostat at 25·0° and agitated until equilibrium had been attained. After about 20 hours, an aliquot portion of the supernatant liquid, free from charcoal, was removed for analysis.

That true equilibrium had been established was proved by trial experiments in which the time of agitation was varied. It was found that, with the same initial concentration of ketone and of phenol or aniline, the same equilibrium concentrations were obtained in whichever order the solutions were added to the charcoal or whether both ketone and phenol or aniline were added together in the same solution.

The results obtained for the adsorption of phenol from its dilute aqueous solution are shown in Fig. 1, wherein $v(c_0 - c)/m$ is plotted against c, c_0 being the initial concentration in g.-mol./l. of the phenol or aniline in the solution used in the experiment, and c its equilibrium concentration, when v c.c. of solution are treated with m g. of adsorbent. The adsorption of aniline is similarly represented in Fig. 1, and that of each of the ketones in Fig. 2, which thus conform with Traube's rule (*Annalen*, 1891, **265**, 27). It has been considered unnecessary to tabulate the results obtained, since, owing to the nature of sugar-charcoal, they could not be exactly reproduced except with the sample here used.

The adsorptions, $v(c_0 - c)/m$, are respectively represented closely by the following functions at the concentrations used in the experiments:

Phenol, $6{\cdot}25\ c^{0{\cdot}57}$ — Aniline, $9{\cdot}09\ c^{0{\cdot}48}$

Acetone, $0{\cdot}955\ c^{0{\cdot}55}$ — Methyl *n*-propyl ketone, $0{\cdot}922\ c^{0{\cdot}36}$

Methyl ethyl ketone, $0{\cdot}745\ c^{0{\cdot}43}$

The adsorption of the ketones from solutions containing also phenol at initial concentration 0·0530 g.-mol./l. is shown in Fig. 3, and that of the ketones from ketone–aniline solutions, wherein the aniline was initially at concentration 0·0496, in Fig. 4. In both these figures, c_0 and c refer to the ketone concentration. It will be noted that these curves are not S-shaped.

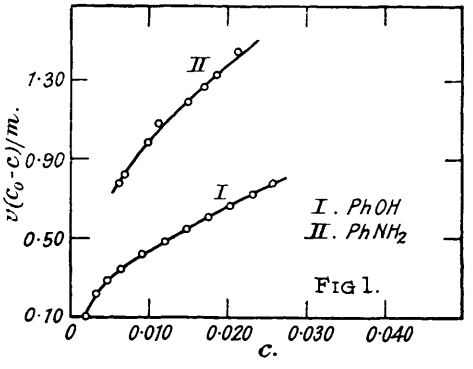

FIG 1.

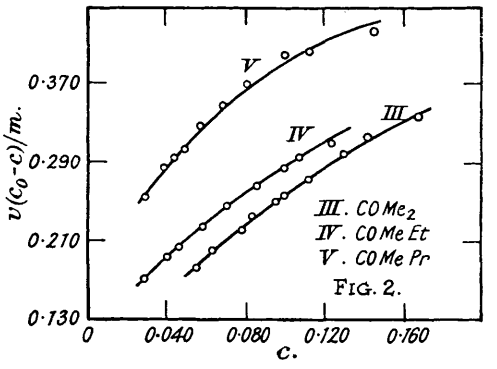

FIG. 2.

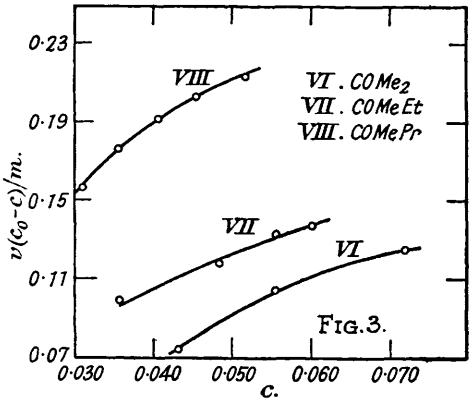

FIG.3.

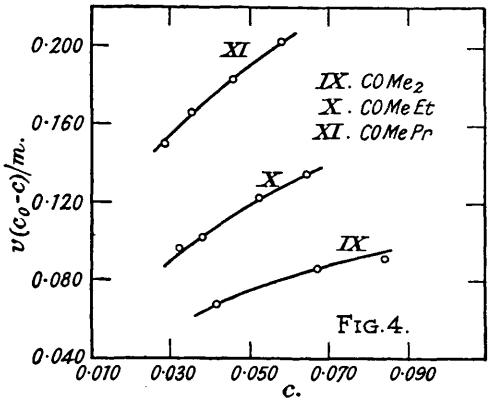

FIG.4.

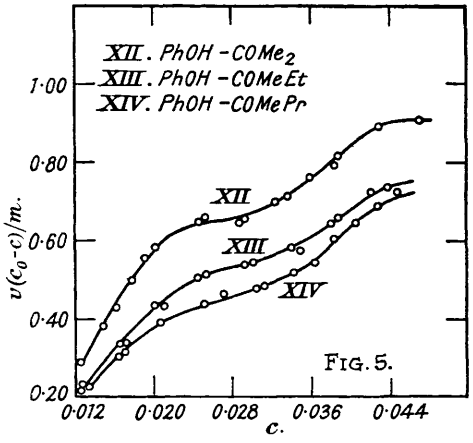

FIG.5.

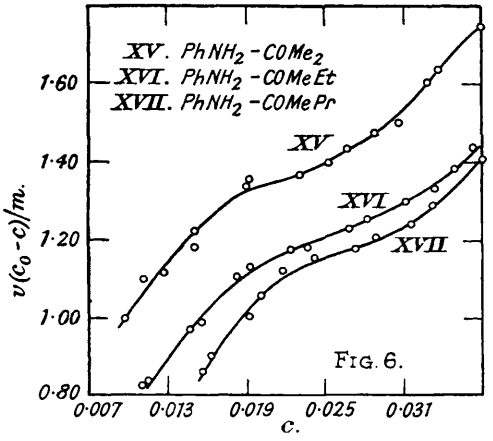

FIG. 6.

The adsorption of phenol from phenol–ketone solutions containing the ketone initially at concentration 0·217 g.-mol./l. is represented in Fig. 5, and of aniline from aniline–ketone solutions of initial ketone concentration 0·206 in Fig. 6.

That the adsorption of the ketones is depressed by phenol or aniline is seen on comparing Fig. 3 or Fig. 4 respectively with Fig. 2. Likewise, the depressing effect of ketone on the adsorption of phenol or aniline is shown by a comparison of Fig. 5 or Fig. 6 with Fig. 1. The

S-shape of curves XII—XVII may be variously explained, *e.g.*, by the assumption that the adsorbed substances combine together, or that an additional layer is formed on an originally unimolecular layer, but the present experiments do not permit of decision in this respect.

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