excess of water is zero. The Gibbsian surface excess will be proportional to the difference between the area under the concentration curve and the area of the rectangle $a$-$b_0$-0-$s$. For this case it is easy to see that, even though there is a surface *layer* of solute (positive adsorption at the interface), the Gibbsian *surface excess* may be positive, zero or negative depending on the concentrations in the double layer region below the interface. It is also plausible that changes in the bulk concentration will change the concentrations in this region, and thus change the surface excess, even though only slight changes occur in the outer ionic layer. Thus the apparent paradox of a surface deficiency and yet a surface tension less than that of water is readily understandable.

Actually the argument may be reversed. A surface deficiency along with a low surface tension, *i. e.*, a Type III surface tension–concentration curve, suggests a state of affairs such as illustrated in Fig. 1. Also, because only electrostatic forces seem likely to be of sufficiently long range to produce such an effect, a result of this type strongly suggests that much or all of the material actually in the physical surface is present in the form of ions.

Because of the paradox of a low surface tension and a negative surface excess, McBain and Mills[1] have concluded that the Gibbs equation is a limiting law, similar to the ideal gas law. They suggest that additional terms should be included to take account of such factors as molecular orientation, submerged electrical double layer, free electrical charges and perhaps others. It is well known that free electrical charges, introduced by *external means*, do necessitate a different treatment. However, the great generality of the thermodynamic derivation of the Gibbs equation[9] makes it apparent that all these phenomena, if of spontaneous origin, are within the scope of the equation. Thus one may conclude that the Gibbs equation in its usual form is valid for solutions of paraffin-chain salts just as for other two-component solutions.

The recently reported[1] measurements of the Gibbs surface excess for a typical paraffin-chain salt indicate a surface excess in the concentration region where the Gibbs equation predicts a surface deficiency. The significant measurements are those done by the microtome method of McBain. The data, if substantiated, will imply serious added complications for the problem. However, it might be pointed out that because of two factors, one, the great depth of the surface region as compared to almost any other type of solution, and two, the fact that establishment of equilibrium between the surface and the underlying solution is a slow process,[8] it is probable that this type of solution represents about the most difficult possible case for an experimental verification of the adsorption equation.

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[9] See, for example, Gibbs, "Collected Works," Vol. I, p. 219 ff.; Guggenheim, "Modern Thermodynamics," p. 160 ff.; Guggenheim, *J. Chem. Phys.*, **4**, 689 (1936).

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## Reaction between Maleic Anhydride and the Isomers of Piperylene

BY RICHARD F. ROBEY, CHARLES E. MORRELL AND HERBERT K. WIESE

In recent studies on the quantitative aspect of the reaction between maleic anhydride and piperylene (pentadiene-1,3), we have observed what is apparently an important difference in the rates of reaction of the isomers of this diolefin with the anhydride. The observation was made on piperylene from two different sources, namely, gas oil cracking and dehydrochlorination of dichloropentane, when the diolefin, which had been concentrated and subsequently purified, was analyzed using maleic anhydride as reagent. In the analysis the samples were vaporized under reduced pressure, blended with hydrogen gas in known proportions to prevent condensation at room temperature, and submitted to analysis for conjugated dienes in the vapor phase.[1] It was found that although the initial rate of absorption was rapid, the reaction stopped short of the quantitative figure, some 18% in one case and 35% in the other. The high purity of the diolefin is evidenced in each case by an index of refraction ($n^{20}$D 1.4309) which agrees with the best value in the literature,[2] and by its reaction with two moles of hydrogen per mole, within experimental error, on catalytic hydrogenation.

In lieu of any better explanation, we have ascribed the incomplete absorptions to the presence of both *cis* and *trans* isomers of piperylene which apparently present somewhat different chemical behavior toward maleic anhydride. As

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[1] Tropsch and Mattox, *Ind. Eng. Chem., Anal. Ed.*, **6**, 104 (1934).
[2] Farmer and Warren, *J. Chem. Soc.*, 3221 (1931).

far as we have been able to tell, the isomers have never been separated heretofore. In isolating the non-reactive component, samples of purified piperylene were vaporized in a stream of hydrogen and the mixture passed through molten maleic anhydride, the small quantity of hydrocarbon remaining with the effluent gas being condensed and examined.

Piperylene from both sources yielded a condensate which had the same index of refraction, *viz.*, 1.4321, and exhibited only an extremely slow and incomplete reaction with maleic anhydride. The normal corrected boiling point of the substance, as determined in a micro-Cottrell apparatus, was 43.8° as compared to 41.9° of the original purified piperylene. On the basis of the higher boiling point and index, it would appear that the unreactive form is the *cis* isomer, although Provost[3] has reported the boiling points of the *cis* and *trans* forms as 39 and 42.5°, respectively, from distillation data.

Finally, it is believed that the observations mentioned here are of interest not only as a means of isolating what is believed to be *cis*-piperylene, but also from the standpoint of the selectivity of the Diels–Alder condensation in general.

The writers wish to acknowledge the coöperation of Mr. A. L. Ward of the United Gas Improvement Company, who originally called their attention to the discrepancies in the analysis for piperylene in cracked $C_5$ fractions and to the possibility of the presence of close boiling *cis*- and *trans*-configurations. This work has been done on cracked $C_5$ fractions furnished by Mr. Ward, and on pure piperylene samples supplied by Messrs. E. R. Gilliland and H. E. Buc.

[3] Provost, *Compt. rend.*, **182**, 1475 (1926).

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# The Activity Coefficients of Sodium and Potassium Fluorides at 25° from Isopiestic Vapor Pressure Measurements

BY R. A. ROBINSON[1]

It is known as a result of freezing point determinations[2] that the order of the activity coefficients of the alkali metal fluorides is the reverse of that which holds for the other three halides. The equation developed by Scatchard[3] predicts that the activity coefficients of the alkali metal fluorides should increase with increasing atomic number of the cation, although quantitative agreement with the freezing point results requires a larger radius for the fluoride ion than that obtained from crystallographic data. Scatchard's theory is therefore supported by data at the freezing point. It is of some interest to ascertain whether this reversal in order is also to be found at higher temperatures, and for this purpose isopiestic measurements have been made at 25° on sodium and potassium fluoride. Stock solutions were prepared from Baker C. P. material and the concentrations determined by analysis. The solutions were equilibrated with solutions of potassium chloride with the results given in Table I.

TABLE I

MOLALITIES OF SOLUTIONS OF POTASSIUM CHLORIDE AND SODIUM OR POTASSIUM FLUORIDE WHICH ARE ISOPIESTIC AT 25°

Sodium Fluoride

| $m_{KCl}$ | $m_{NaF}$ | $m_{KCl}$ | $m_{NaF}$ |
|---|---|---|---|
| 0.1554 | 0.1562 | 0.6765 | 0.6896 |
| .2490 | .2504 | .7874 | .8088 |
| .4047 | .4097 | .8518 | .8734 |
| .5616 | .5728 | .8908 | .9124 |
| .5774 | .5870 | .9106 | .9356 |

Potassium Fluoride

| $m_{KCl}$ | $m_{KF}$ | $m_{KCl}$ | $m_{KF}$ |
|---|---|---|---|
| 0.1612 | 0.1598 | 2.245 | 2.086 |
| .3254 | .3221 | 2.484 | 2.290 |
| .7544 | .7353 | 3.112 | 2.823 |
| .9904 | .9572 | 3.188 | 2.873 |
| 1.084 | 1.049 | 3.761 | 3.354 |
| 1.383 | 1.316 | 3.918 | 3.497 |
| 1.568 | 1.480 | 3.982 | 3.526 |
| 1.941 | 1.815 | 4.580 | 4.006 |
| 2.108 | 1.964 | 4.81 | 4.183 |

TABLE II

OSMOTIC AND ACTIVITY COEFFICIENTS OF SODIUM AND POTASSIUM FLUORIDE AT 25°

| $m$ | $\varphi_{NaF}$ | $\gamma_{NaF}$ | $m$ | $\varphi_{NaF}$ | $\gamma_{NaF}$ |
|---|---|---|---|---|---|
| 0.1 | 0.923 | 0.764 | 0.5 | 0.888 | 0.631 |
| .2 | .909 | .708 | .7 | .880 | .602 |
| .3 | .899 | .675 | 1.0 | .873 | .572 |

| $m$ | $\varphi_{KF}$ | $\gamma_{KF}$ | $m$ | $\varphi_{KF}$ | $\gamma_{KF}$ |
|---|---|---|---|---|---|
| 0.1 | 0.929 | 0.774 | 1.5 | 0.958 | 0.649 |
| .2 | .920 | .727 | 2.0 | .987 | .663 |
| .3 | .917 | .701 | 2.5 | 1.021 | .684 |
| .5 | .917 | .672 | 3.0 | 1.054 | .713 |
| .7 | .922 | .657 | 3.5 | 1.091 | .748 |
| 1.0 | .934 | .649 | 4.0 | 1.130 | .790 |

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[1] Sterling Fellow, Yale University, 1940.

[2] Karagunis, Hawkinson and Damköhler, *Z. physik. Chem.*, **151A** 433 (1930).

[3] Scatchard, *Chem. Rev.*, **19**, 309 (1936).