

CHROM. 9939

ESTIMATION OF POLARITY OF SOLIDS BY GAS CHROMATOGRAPHY

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(First received November 10th, 1975; revised manuscript received February 2nd, 1977)

SUMMARY

An understanding of the nature and acidity of solids is important, both for gas chromatographers and for catalyst technologists. In this paper, an attempt has been made to correlate polarity with some gas chromatographic parameters by means of thermodynamic factors. A mathematical correlation between the variation of Gibbs free energy of adsorption and the number of methylene groups in an homologous series has been developed. The relationship is rectilinear, and the slope of the line gives an indication of the polarity of the solid. Results are presented for alumina, Chromosorb and Porasil.

INTRODUCTION

Several works have been published on the estimation of the polarity of the stationary phase in gas-liquid chromatography (GLC), and Rohrschneider¹ (among others in this field) has suggested a scale of polarity, with squalane at 0 and 3,3'-oxydipionitrile at 100. Solids, however, have so far been neglected in this respect, and we describe an attempt to correlate the polarities of solids with some gas chromatographic parameters. The polarity can give an indication of the activity of a solid, and, if the proposed method can be generalised, it will be useful in the field of catalysis.

EXPERIMENTAL

An Acrograph Hi-Fi 600 D gas chromatograph was used, with hydrogen as carrier gas and as fuel for the flame; the hydrogen was drawn from a cylinder, and Deoxo catalyst was placed in the carrier-gas line to remove any oxygen, and a molecular sieve was used to remove moisture. The solids tested were packed separately in copper tubes (each 5 ft. × 0.125 in.) in the conventional way. *n*-Alkanes (C₅-C₉) were used as solutes, chromatographic-grade samples being obtained from the

Phillips Petroleum Company (Bartlesville, Okla., U.S.A.). Retention times were noted with use of a stop-watch capable of measurement to within 0.2 sec, and the oven housing of the column was equipped with a relay so that the temperature fluctuations did not exceed $\pm 1^\circ$. The solute samples were injected with a syringe from Precision Sampling Corp. (Baton Rouge, La., U.S.A.).

THEORY

Sawyer and Brookman² deduced that the partial molar free energy of adsorption ($\overline{\Delta G}$) for one molecule of vapour at one atmosphere pressure was given by

$$-Rt \ln V_g^T = 11.33T + \overline{\Delta G} \quad (1)$$

in which V_g^T is the specific retention volume at temperature T .

In a homologous series of the type $(\text{CH}_3)_m(\text{CH}_2)_nX$, where X represents a functional group, the partial molar free energy of adsorption for a single molecule can be expressed, according to the additivity rule, by

$$G = m\overline{\Delta G}(\text{CH}_3) + n\overline{\Delta G}(\text{CH}_2) + \overline{\Delta G}(X) \quad (2)$$

All the terms on the right-hand side of eqn. 2 remain constant as we pass from one homologue to another, except n , so that

$$\overline{\Delta G} = n\overline{\Delta G}(\text{CH}_2) + C$$

where C is a constant. Eqns. 1 and 2 show that

$$-4.58T \log V_g^T = n\overline{\Delta G}(\text{CH}_2) + C \quad (3)$$

This is the equation of a straight line, and the slope of the graph of $(-4.58 T \log V_g^T)$ against n will give an indication of the polarity of the adsorbent.

RESULTS AND DISCUSSION

Although it has been a matter of controversy^{3,4} for some time, the principle behind the additivity rule is that each structural element or group contributes its part to the total retention. In a more detailed additivity rule, however, identical structural elements are differentiated with respect to their intra-molecular environment, the consideration of environment being limited to a certain distance from the structural unit. In practice, this is not so, and the contribution of a structural element or group to the total retention is a function of the total intra-molecular environment, the contributions of identical structural elements within different molecules being basically different and possessing a character as unique as the molecules themselves.

With these additivity rules in mind, we decided to study the nature of the interaction of n -alkanes on the surface. We considered that the contribution towards the free energy of adsorption of one methylene group remained the same, irrespective

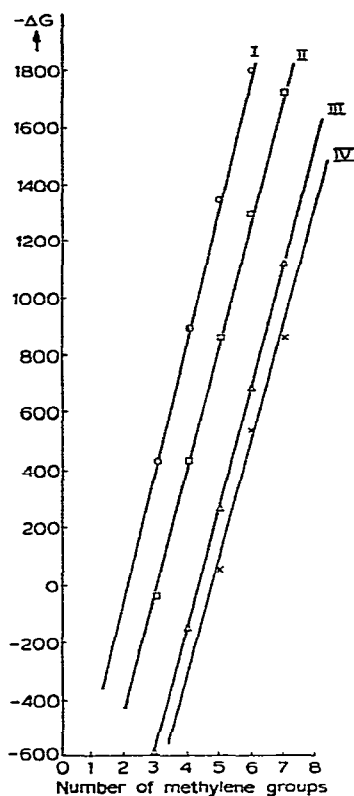


Fig. 1. Variation in free energy of adsorption with number of methylene groups of *n*-alkanes on Porasil D. Temperature: I = 70°; II = 100°; III = 130°; IV = 160°.

of the size of the *n*-alkane to which it belonged. It might be thought that the intra-molecular position and environment around any methylene group remains the same irrespective of its placing in the molecule in an homologous series of *n*-alkanes. The terminal methyl groups have, however, not been considered, as since the difference between one homologue to the next is only a methylene group, the end-groups are immaterial. We suggest that the contribution of a methylene group to the free energy of adsorption of a molecule depends not only on its intra-molecular position, but also on the nature of the surface over which adsorption is taking place. Thus, the properties of the surface should be reflected in the free energy of adsorption of methylene groups. To confirm this view, we studied the retention parameters of *n*-alkanes on three adsorbents, the natures of two of which can be changed by heating or by modification with inorganic salts. The change in the nature of the adsorbent was well reflected in the free energy of adsorption of a methylene group, despite the fact that *n*-alkanes are regarded as being spherically symmetrical and non-specific and not expected to be affected by any type of specificity on a surface⁵. Mathur *et al.*⁶ have shown that the retention of *n*-alkanes can be affected by the mechanism of induced polarity.

EFFECT OF TEMPERATURE

Porasil D (Waters Assoc., Milford, Mass., U.S.A.) was packed in a copper tube, and the retention behaviour of the *n*-alkanes was studied at temperatures of 70, 100, 130 and 160°, and the free energies of adsorption were plotted against the number of methylene groups at all the temperatures (Fig. 1). It can be seen that the slope of the graph does not change with temperature, although the intercept varies. Since specific physical or chemical properties do not change as a result of variation in temperature from 70° to 160°, we conclude that temperature has no effect on the slope of the graph if the other properties of the solid remain unaltered.

STUDIES ON ALUMINA

Active alumina (Hewlett-Packard, Avondale, Pa., U.S.A.) was chosen as the test substance. Initially, it was packed as such in a column and the retention behaviour of the *n*-alkanes was studied. As shown in Fig. 2, the graph of free energy of adsorption against number of methylene groups was rectilinear. Next, the active alumina was impregnated with aqueous sodium sulphate solution, dried and then heated to

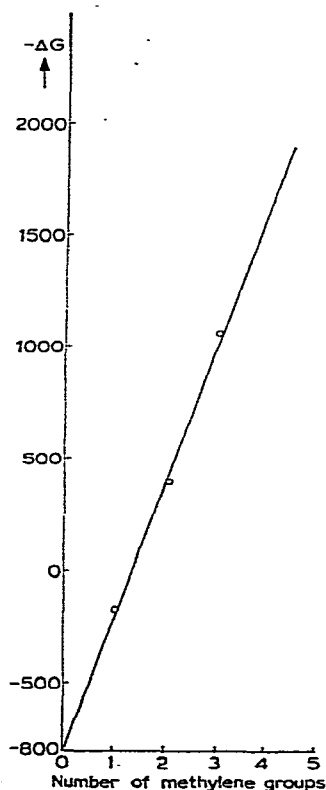


Fig. 2. Variation in free energy of adsorption with number of methylene groups of *n*-alkanes on untreated alumina. Temperature: 100°.

300°. The retention of the *n*-alkanes on this material was studied at temperatures of 150, 160, 180 and 200°; at all four temperatures, the graph was rectilinear, and each graph had almost the same slope (Fig. 3). However, the intercept on the abscissa varied with temperature, just as it had done for the Porasil.

The active alumina was modified in three different ways in an attempt to change its specificity. The modes of modification were (i) heating to 950° and subsequently cooling in a desiccator, (ii) impregnating with sodium sulphate solution and then heating to 950°, and (iii) impregnating with copper sulphate solution and heating to 950°. Ghosh *et al.*⁷ studied the interaction between sodium sulphate or copper sulphate and active alumina as a result of heating the impregnated mass to 950°; they observed that copper sulphate was deposited in the pores of the alumina, almost completely blocking the narrower pores and thereby reducing the surface area from 44 to 7.2 m²/g. Sodium sulphate, on the other hand, reacted with the alumina to form a new compound with an entirely different texture, surface and surface properties.

All three solids were packed in chromatographic columns and the retention times for *n*-alkanes were measured. Graphs of $\overline{\Delta G}$ against the number of methylene

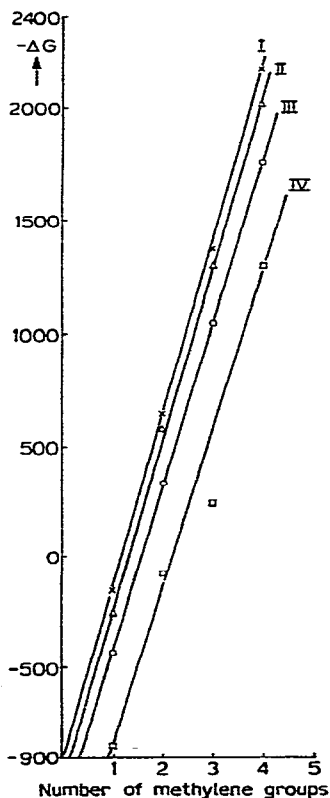


Fig. 3. Variation in free energy of adsorption with number of methylene groups of *n*-alkanes on Na₂SO₄-modified alumina heated at 300°. Temperature: I = 150°; II = 160°; III = 180°; IV = 200°.

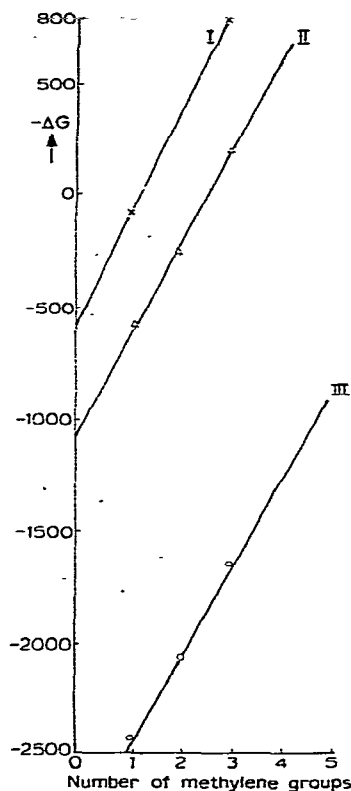


Fig. 4. Variation in free energy of adsorption with number of methylene groups of *n*-alkanes at 100°. Sorbent: I = alumina heated to 950°; II = Na₂SO₄-modified alumina heated to 950°; III = CuSO₄-modified alumina heated to 950°.

groups are shown in Fig. 4. The slope for the untreated alumina was 608.28, whereas for the alumina heated to 950°, the slope was 446.68. Alumina modified with copper sulphate gave a slope of 384.59, and for that modified with sodium sulphate the slope was 400.03. The values in Table I show that the heat of adsorption (ΔH) for propane, *n*-butane and *n*-pentane on untreated alumina and on the three modified aluminas varied in the same way, despite wide variations in the average pore radius.

TABLE I

EFFECT OF HEATING AND SALT MODIFICATION ON HEAT OF ADSORPTION OF *n*-ALKANES

Adsorbent	Average pore radius (Å)	Heat of adsorption (kcal/mole)		
		Propane	<i>n</i> -Butane	<i>n</i> -Pentane
Untreated alumina	32	3.8	5.5	6.8
Alumina heated to 950°	133	2.2	3.5	4.5
Alumina-CuSO ₄ heated to 950°	761	1.6	2.7	3.5
Alumina-Na ₂ SO ₄ heated to 950°	81	2.1	3.3	4.2

CONCLUSIONS

The slope of the graph of partial molar free energy of adsorption against the number of methylene groups provides a good estimate of the polarity of a solid; it can be successfully utilized for estimating the activity of catalysts. The sorbate molecules should be carefully selected, bearing in mind the parameters of the test solid.

ACKNOWLEDGEMENTS

We thank Dr. S. Varma and Dr. K. M. Verma for their keen interest and constant encouragement.

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