

Adsorption Potential Correlation for Dual-Mode Sorption Systems

INTRODUCTION

The Polanyi or potential theory¹ has, for many years, provided a useful method for correlating adsorption data of gases and vapors on porous solids. To our knowledge, no one has attempted its use for sorption systems, involving glassy polymeric sorbents, which may also be correlated according to the dual-mode concepts.² In its simplest form, the adsorption potential ϵ is visualized as the work of compressing an ideal gas isothermally from the pressure existing in the gas phase p , to the vapor pressure of the liquid, P^0 :

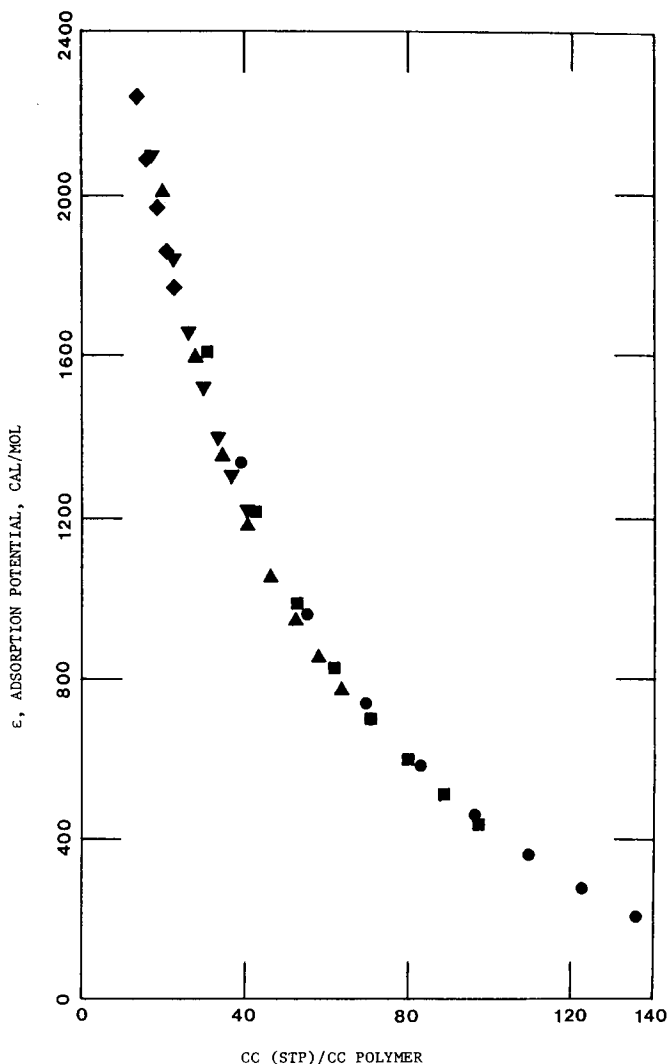


Fig. 1. Adsorption Potential plot for SO_2 ; polyester-polycarbonate system: (●) 0°C; (■) 10°C; (▲) 25°C; (▼) 45°C; (◆) 70°C.

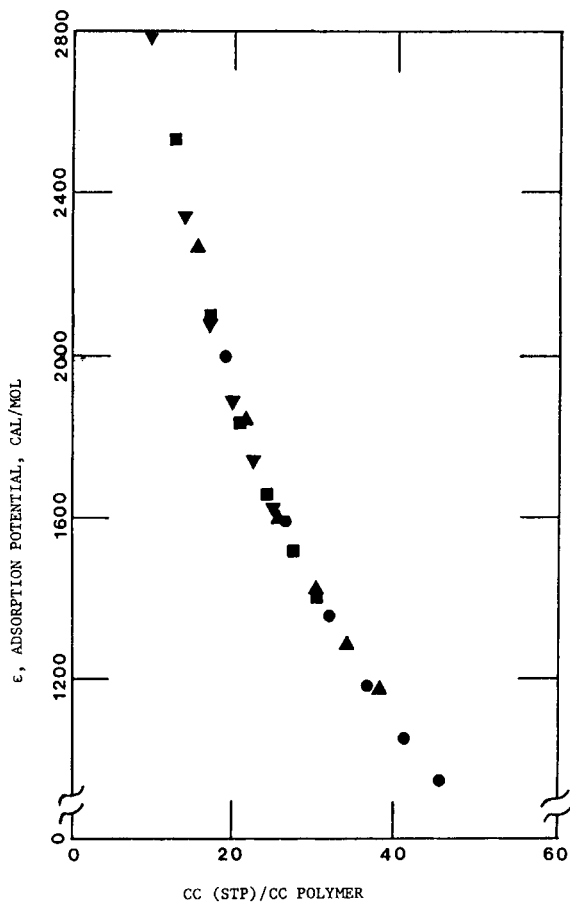


Fig. 2. Adsorption potential plot for SO_2 , Kapton polyimide system (data from Ref. 4): (●) 25°C; (▲) 35°C; (■) 45°C; (▼) 55°C.

$$\epsilon = RT \ln P^0/p$$

A plot of the potential of a given sorbate vs. some measure of the amount adsorbed defines the "characteristic" curve for the sorbate-sorbent system. The characteristic curve is capable, in many cases, of representing the adsorption equilibria over a reasonable temperature range. Modifications of the simple theory to include use of fugacities and other corrections have also been used.¹

DISCUSSION

While correlating recent sorption data of SO_2 on a film of polyester-polycarbonate, the adsorption potential plot was found to give a good representation of the data over the experimental range of 0–70°C³ (Fig. 1). Data from the literature for SO_2 -Kapton polyimide,⁴ H_2O -polyacrylonitrile (PAN),⁵ C_3H_8 -polystyrene, and C_3H_8 -polycarbonate⁶ have also been shown to correlate nicely by the simple potential plots as shown in the accompanying Figures 2–4.

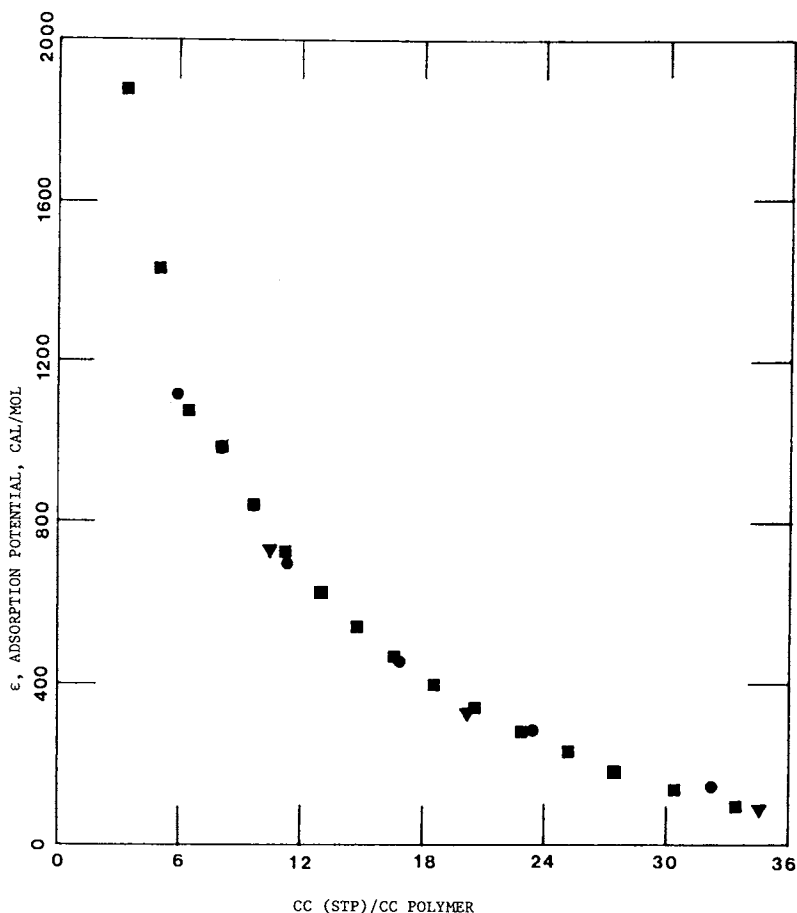


Fig. 3. Adsorption potential plot for water vapor, polyacrylonitrile (PAN) system (data from Ref. 5): (∇) 20°C; (\bullet) 30°C; (\blacksquare) 50°C.

Actual experimental data for these latter systems were not available to the present authors, and the points were generated from the reported dual-mode parameters. The solubility coefficient of the H_2O -PAN system was also concentration-dependent. For consistency the points shown for the SO_2 -(polyester-polycarbonate) system were also calculated from dual-mode parameters, although the actual experimental data correlated equally well. For reasons not clear at the present time, the data for an intermediate isotherm, 40°C (not shown), for the H_2O -PAN system did not fit well on the characteristic curve even though the dual-mode parameters were apparently consistent with the other isotherms. All the systems shown here involve vapors at subcritical temperatures being sorbed by polymeric films. An attempt was made to correlate the data for the CO_2 -poly(ethylene terephthalate) (PET) system,⁷ even though only one isotherm was below the critical temperature. The correlation in this case was poor. Perhaps the problem of the "vapor pressure" at supercritical temperatures was the main factor. Attempts were made to use "logical" extrapolations of vapor pressure data past the critical temperature. In all of the correlation attempts, the use of fugacities as calculated from various equations of state instead of pressures made no noticeable improvement.

The adsorption potential theory, while giving no insight to the mechanism, offers the ability

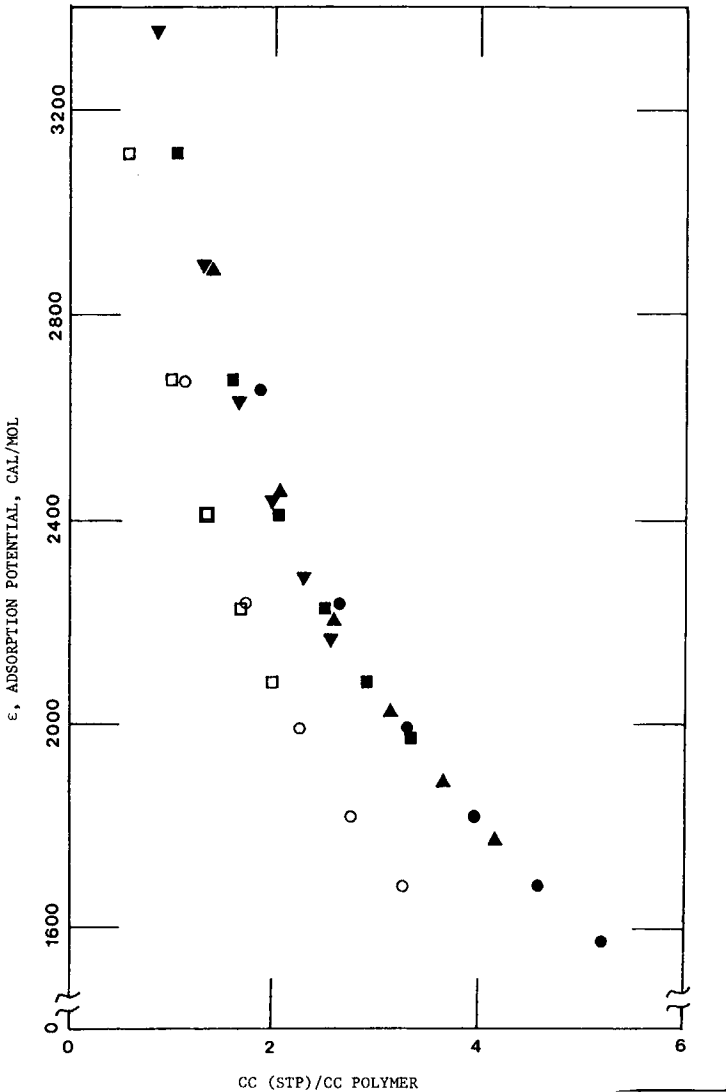


Fig. 4. Adsorption potential plots for propane sorption on polystyrene and polycarbonate (data from Ref. 6). C_3H_8 -polystyrene: (○) 30°C; (□) 50°C. C_3H_8 -polycarbonate: (●) 30°C; (▲) 40°C; (■) 50°C; (▼) 60°C.

to estimate isotherms over a reasonable temperature range based upon a single-measured isotherm. The simple dual-mode model does not have such predictive capability. It may also prove useful as an additional means of looking at data consistency. The successful application of the potential theory in its simplest form to some vapor-polymer sorption systems indicates that its utility may cover a wider range of applications than previously expected. The preliminary success of the present approach warrants further investigation using more refined concepts of the theory. Such an effort is expected to aid in pinpointing the criteria to be fulfilled for applicability of the potential theory for sorption systems involving polymeric materials.

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