954 *J. Chem. Eng. Data* **2001,** *46,* 954−958

Adsorption Equilibria of Toluene on Polymeric Adsorbents

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Adsorption equilibria of toluene on various polymeric adsorbents were obtained by a static volumetric technique. The polymeric adsorbents used were Ambersorb 600 (Rohm and Haas Co.), Sp 850 (Mitsubishi Chemical Co.), and Dowex Optipore V493 (Dow Chemical Co.). The equilibrium measurements were done at 273.15, 298.15, 323.15, and 348.15 K and pressures up to 2.95 kPa for toluene. The experimental data of Ambersorb 600 were correlated by the Unilan equation and the Dubinin−Astakhov (D−A) equation was used to correlate experimental data of Sp 850 and Dowex Optipore V493. The isosteric heat of adsorption was calculated. It was found that the values of isosteric heat of adsorption varied with surface loading.

Introduction

Volatile organic compounds (VOCs) are among the most common air pollutants emitted from chemical, petrochemical, and allied industries. VOCs are among the main sources of photochemical reaction in the atmosphere leading to various environmental hazards. However, VOCs have good commercial value. Increasing environmental awareness has led to stringent regulations to control VOCs emissions. In these circumstances, it becomes mandatory for each VOCs emitting industry or facility to opt for proper VOCs control measures. There are many techniques available to control VOCs emission (destruction-based and recovery-based) with many advantages and limitations.[1]

Adsorption is the most effective method of controlling VOCs emission. The design of adsorptive separation and purification processes requires primarily the knowledge of thermodynamic data on the adsorption equilibrium for the adsorption system of interest. For practical applications, the adsorption equilibria must be known over a broad range of operation temperature. This information is used to calculate the operation time of a specific concentration level and to derive optimum size of adsorbers and operating conditions. Moreover, the isotherm of pure species is fundamental information for the dynamic simulation of adsorbers.[2]

Recently, some interest has focused on the potential application of polymeric adsorbents for separation and purification problems. One clear advantage of polymers is the ability to control their pore structure and internal surface area by varying the polymerization conditions. Moreover, one of the main advantages of polymeric adsorbents is that the adsorption can occur by weak adsorption affinity in opposition to other well-known adsorbents such as activated carbons. Therefore, it is expected that the polymeric adsorbents are useful for treating solvent vapors by pressure swing adsorption.[3]

Table 1. Physical Properties of the Polymeric Adsorbents

polymeric adsorbents	Ambersorb 600	Sp 850	Dowex Optipore V493
physical form	black, spheres	brown, spheres	orange, spheres
mean particle diameter (mm)	0.65	0.25	0.56
BET surface area ($m^2 \cdot g^{-1}$)	580	1000	1100
bulk density ($g \cdot cm^{-3}$)	0.54	0.67	0.34
total pore volume ($cm^3 \cdot g^{-1}$)	0.60	1.20	1.16

In this study, toluene was considered as an adsorbate. As potential adsorbents for VOCs treatment, three polymeric adsorbents were selected: Ambersorb 600, Dowex Optipore V493, and Sp 850.

Experimental Section

Materials. The polymeric adsorbents, Ambersorb 600, Sp 850, and Dowex Optipore V493, were chosen as adsorbents. Ambersorb 600 was supplied by Rohm and Haas Co., Dowex Optipore V493 by Dow Chemical Co., and Sp 850 by Mitsubishi Chemical Co. The physical properties are tabulated in Table 1, which are values from manufacturer reports.

Prior to measurement, the adsorbents were kept in a drying vacuum oven at 393 K for more than 24 h to remove impurities. Toluene was obtained from J. T.Baker Inc. and the purity of this material was 99.99%.

Apparatus and Procedure. The adsorption apparatus in Figure 1 is based on the static volumetric method. The total amount of vapor introduced and recovered in the system after equilibrium are determined by appropriate pressure, volume, and temperature measurements. The pressure was recorded using a Baratron absolute pressure transducer (MKS type 270D) ranging from 0 to 133.33 kPa with an accuracy of 0.05%.

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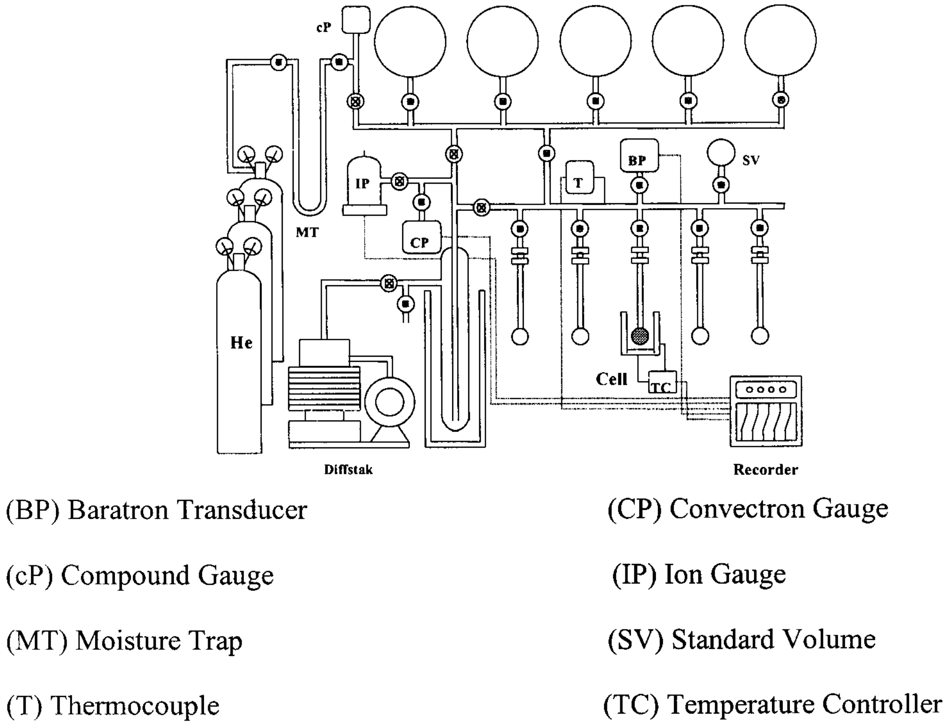

Figure 1. Schematic diagram of adsorption apparatus.

Table 2. Adsorption Isotherm Data for Toluene on Ambersorb 600

273.15 K		298.15 K		323.15 K		348.15 K	
P	*N*	*P*	*N*	*P*	*N*	*P*	*N*
kPa	mol·kg^{-1}	kPa	mol·kg^{-1}	kPa	mol·kg^{-1}	kPa	mol·kg^{-1}
0.007	1.050	0.002	0.179	0.004	0.381	0.009	0.191
0.010	1.180	0.003	0.440	0.008	0.643	0.014	0.320
0.011	1.288	0.005	0.778	0.023	0.962	0.030	0.635
0.022	1.419	0.019	1.142	0.037	1.043	0.078	0.877
0.035	1.519	0.072	1.288	0.236	1.252	0.127	0.944
0.084	1.637	0.153	1.386	0.296	1.307	0.407	1.101
0.113	1.708	0.217	1.470	0.656	1.417	0.600	1.134
0.127	1.712	0.355	1.562	0.873	1.438	0.688	1.168
0.224	1.812	0.598	1.679	1.162	1.511	1.058	1.209
0.276	1.861	0.995	1.704	1.507	1.527	1.069	1.230
0.361	1.959	1.397	1.788	1.959	1.583	1.339	1.243
0.417	1.977	1.699	1.849	2.511	1.638	1.353	1.265
0.470	2.024					1.777	1.288
0.494	2.043					1.824	1.320
0.573	2.161					2.123	1.344
						2.171	1.319
						2.428	1.343
						2.631	1.358

During the adsorption, the reaction cell was put in a water bath, which was maintained by the refrigeration circulator (Haake type F3) with a precision of ±0.02 K.

To eliminate traces of pollutants, the adsorbents were kept in a drying oven at 393 K for 24 h. Prior to the introduction in the reaction cell, the mass of the adsorbent was weighted with an accuracy of ±10 mg after regeneration at 393 K at high vacuum for 13 h. An oil diffusion pump coupled to a mechanical vacuum pump (Edward type Diffstak 63/150M) provided a vacuum down to 10^{-3} Pa. The pressure was monitored by both an ion gauge and a convectron gauge with a vacuum gauge controller (Granville-Philips type 307). The volume of the reaction cell was determined by expansion of helium gas at the experimental temperature. Details of the equipment and the operating procedures used are described in the previous publications of Yun and Choi.[4,5]

Table 3. Adsorption Isotherm Data for Toluene on Sp 850

273.15 K		298.15 K		323.15 K		348.15 K	
P	*N*	*P*	*N*	*P*	*N*	*P*	*N*
kPa	mol·kg^{-1}	kPa	mol·kg^{-1}	kPa	mol·kg^{-1}	kPa	mol·kg^{-1}
0.005	0.478	0.020	0.364	0.028	0.246	0.051	0.137
0.008	0.483	0.024	0.426	0.080	0.499	0.160	0.321
0.015	0.913	0.039	0.603	0.200	0.890	0.190	0.412
0.018	0.981	0.059	0.838	0.365	1.132	0.315	0.495
0.026	1.208	0.072	0.905	0.396	1.251	0.463	0.663
0.035	1.467	0.097	1.126	0.617	1.545	0.584	0.713
0.047	1.648	0.122	1.241	0.893	1.848	0.649	0.793
0.064	2.012	0.173	1.537	0.989	1.867	0.896	0.905
0.090	2.300	0.312	2.040	1.226	2.188	0.910	0.944
0.102	2.524	0.362	2.188	1.369	2.199	1.123	1.049
0.147	2.974	0.521	2.641	1.605	2.489	1.256	1.085
0.148	3.012	0.576	2.766	1.793	2.539	1.388	1.168
0.176	3.213	0.781	3.264	1.949	2.763	1.596	1.234
0.203	3.442	0.815	3.338	2.213	2.834	1.764	1.315
0.230	3.663	1.084	3.887	2.363	3.071	2.100	1.443
0.268	3.793	1.104	3.932	2.628	3.092	2.229	1.477
0.288	4.028	1.379	4.507	2.695	3.273	2.525	1.591
0.313	4.238	1.383	4.564			2.725	1.647
0.341	4.444	1.637	5.100			2.951	1.728
0.365	4.629	1.681	5.196				
0.406	4.975	1.829	5.632				
0.483	6.166	1.895	5.733				

Results and Discussion

The adsorption data of toluene on polymeric adsorbents were obtained at 273.15, 298.15, 323.15, and 348.15 K and pressures up to 2.95 kPa. The data are presented in Tables 2−4 and graphically represented in Figures 2−4. In these figures, experimental data were fitted by solid lines.

The adsorption isotherms of toluene on Ambersorb 600 and Dowex Optipore V493 show a Langmuir adsorption isotherm classified as type-I according to Brunauer et al.,[6] while the adsorption isotherms of toluene on Sp-850 look closer to type-Π. The two types are characterized by higher attractive forces between the adsorbate and the adsorbent than between the molecules of the adsorbate in the bulk state.[6]

Table 4. Adsorption Isotherm Data for Toluene on Dowex Optipore V493

273.15 K		298.15 K		323.15 K		348.15 K	
P	*N*	*P*	*N*	*P*	*N*	*P*	*N*
kPa	mol·kg^{-1}	kPa	mol·kg^{-1}	kPa	mol·kg^{-1}	kPa	mol·kg^{-1}
0.008	0.292	0.010	0.321	0.008	0.253	0.022	0.223
0.013	0.564	0.019	0.724	0.017	0.476	0.024	0.289
0.017	0.858	0.031	1.221	0.021	0.565	0.058	0.543
0.020	1.156	0.052	2.056	0.031	0.714	0.063	0.648
0.023	1.453	0.083	2.702	0.059	1.180	0.120	0.990
0.028	1.770	0.165	3.555	0.108	1.780	0.126	1.034
0.031	2.062	0.248	3.912	0.152	2.281	0.230	1.485
0.035	2.342	0.372	4.471	0.212	2.458	0.239	1.501
0.040	2.642	0.487	4.732	0.331	3.025	0.445	2.014
0.048	3.051	0.645	4.964	0.423	3.176	0.447	2.053
0.054	3.385	0.873	5.324	0.681	3.776	0.779	2.494
0.062	3.549	0.972	5.471	0.909	3.968	1.251	2.876
0.092	4.080	1.154	5.607	1.291	4.407	1.748	3.265
0.162	4.764	1.592	5.961	1.769	4.643	2.329	3.513
0.354	5.555	1.747	6.058	2.023	4.878	2.819	3.862
		1.809	6.110				

For each equilibrium datum, rigorous assessments were performed and correlated by several pure species equilibrium models. The isotherm equations used in this study were the Langmuir,[7] Unilan,[7] Toth[7], Dubinin−Radushkevich (D−R),[8] and Dubinin−Astakhov (D−A).[8] The mathematical forms of these models are as follows:

Langmuir

$$N = \frac{mbP}{1 + bP} \tag{1}$$

Unilan

$$N = \frac{m}{2s} \ln\left[\frac{c + P\exp(+s)}{c + P\exp(-s)}\right] \tag{2}$$

Toth

$$N = \frac{mP}{(b + p^t)^{1/t}} \tag{3}$$

D−R

$$W = W^0 \exp\left[-\left(\frac{\epsilon}{\beta E^0}\right)^2\right] \tag{4}$$

D−A

$$W = W^0 \exp\left[-\left(\frac{\epsilon}{\beta E^0}\right)^r\right] \tag{5}$$

where N is the amount adsorbed, P is the equilibrium pressure, and b, m, c, s, and t are isotherm parameters.

To find the isotherm parameters for each adsorption system, two parameter estimation techniques were applied. These methods include a least-squared fitting method, which correlated the Langmuir, D−R, and D−A equations, and the so-called Nelder−Mead simplex pattern search algorithm,[9] which correlated the Toth and the Unilan equations. In addition, the following objective functions were used in this work,

$$\min \sum_j (N_j^{\text{obs}} - N_j^{\text{cal}})^2 \tag{6}$$

where N_j^{obs} are the experimental data of the adsorbed amount and N_j^{cal} are the correlation results. Besides, the deviation parameter on the adsorbed amount, D, was utilized to compare the correlation results with experimental data,

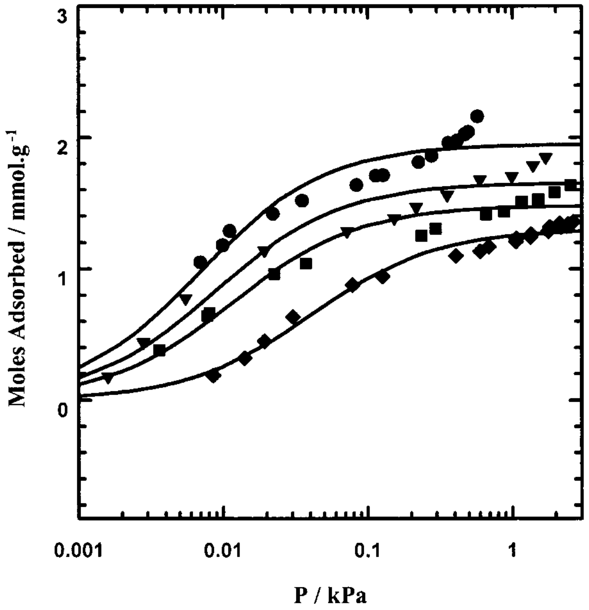

Figure 2. Measured and fitted isotherms for toluene adsorption onto Ambersorb-600 at various temperatures: ●, 273 K; ▼, 298 K; ■, 323 K; ◆, 348 K; —, Unilan equation.

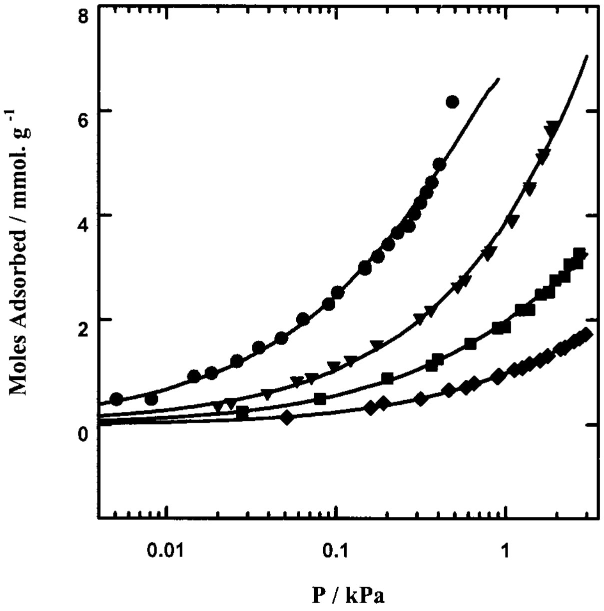

Figure 3. Measured and fitted isotherms for toluene adsorption onto Sp-850 at various temperatures: ●, 273 K; ▼, 298 K; ■, 323 K; ◆, 348 K; —, D−A equation.

$$D = \frac{1}{k}\sum_i^k \left|\frac{N_i^{\text{obs}} - N_i^{\text{cal}}}{N_i^{\text{obs}}}\right| \tag{7}$$

where k is the number of data.

For the toluene−Ambersorb 600 system, the Unilan equation was employed because the Unilan equation showed the minimum value of the average deviation parameter (D). On the other hand, for the toluene−Sp 850 and toluene−Dowex Optipore V493 systems, the D−A equation to show the minimum value of the average deviation parameter was employed.

The Unilan equation is based on a uniform distribution of energies of adsorption with the Langmuir equation for the local isotherm.[7] The correlation by the Unilan equation

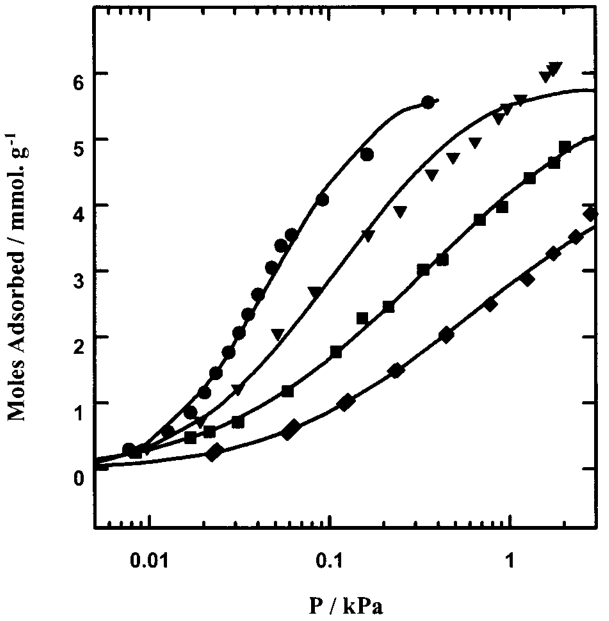

Figure 4. Measured and fitted isotherms for toluene adsorption onto Dowex optipore V493 at various temperatures: ●, 273 K; ▼, 298 K; ■, 323 K; ◆, 348 K; —, D−A equation.

Table 5. Unilan Equation Parameters for Toluene on Ambersorb-600

T / K	m / mol·kg^{-1}	c / kPa	s	100 × D
273.15	1.951	0.007	0.0014	5.87
298.15	1.655	0.009	0.0015	11.26
323.15	1.483	0.012	0.0010	6.49
348.15	1.303	0.041	−0.0041	5.25

has two advantages. The first one is that the Unilan equation contains only three parameters and gives analytical expressions for the amount adsorbed. Second, this model reduces to Henry's law at pressures approaching zero. Thus, it provides a good fit for adsorption data at low pressure,[7]

$$H = \lim_{P\to 0}\frac{N}{P} = \lim_{P\to 0}\frac{\mathrm{d}N}{\mathrm{d}P} = \frac{m}{c}\,\frac{\sinh(s)}{s} \tag{8}$$

where H is Henry's constant.

In eq 2, m is the maximum adsorbed amount corresponding to a complete monolayer coverage, c is related to the adsorption affinity, and the parameter s characterizes the heterogeneity of the system. The larger this parameter is, the more heterogeneous is the system. If $s = 0$, the Unilan equation reduces to the classical Langmuir equation as in this limit the range of energy distribution is zero.[8]

It has been reported that the D−A equation has found utility in interpreting adsorption by capillary condensation or pore filling.[10,11] In eq 5, W is the specific volume of adsorbate condensed in micropores at temperature T and P^*/P (P^* is the equilibrium saturation vapor pressure at T) is relative pressure, W^0 is the limiting specific volume of the adsorbed space, which equals the micropore volume, N is the moles adsorbed at equilibrium, $\epsilon(=\Delta G = RT\ln(P^*/P))$ is the adsorption potential, the parameter r describes the surface heterogeneity, E^0 is the characteristic energy of the reference adsorbate, and β is the affinity coefficient.[8] For the nonpolar and weakly polar adsorbates, the adsorption interaction is strongly dependent on the polarizability of the molecules. Because the polarizability of a molecule is approximately proportional to the molar volume of the saturated liquid, the affinity coefficient can be expressed as[12]

$$\beta = V^0/V^0_{\mathrm{ref}} \tag{9}$$

where V^0 is the saturated liquid molar volume and V^0_{ref} is the saturated liquid molar volume of the reference vapor.

The isotherm parameters for the Unilan equation and D−A equation are given in Tables 5 and 6. The isosteric heat of adsorption (q_{st}) can be calculated by the Clausius−Clapeyron equation for adsorption,[13]

$$\frac{q_{st}}{RT^2} = \left[\frac{\partial \ln P}{\partial T}\right]_N \tag{10}$$

where P is the pressure, T is the temperature, and R is the gas constant.

The isosteric heat is a measure of the interaction between adsorbate molecules and adsorbent lattice atoms and may be used as a measure of the energetic heterogeneity of a solid surface. Usually, the isosteric heat curve varies with the surface loading. This phenomenon has been well understood that the adsorbent for adsorptive separation usually has an energetic heterogeneous surface.[13] According to the ideal Langmuir model, the heat of adsorption should be independent of coverage but this requirement is seldom fulfilled in real systems because the effects of surface heterogeneity and adsorbate−adorbate interaction are generally significant. Information concerning the magnitude of the heat of adsorption and its variation with coverage can provide useful information concerning the nature of the surface and the adsorbed phase.[14]

As shown in Figure 5, the isosteric heat of adsorption varied with the surface loading for toluene. This result indicates that the polymeric adsorbents used have an energetically heterogeneous surface.

Conclusions

Adsorption equilibria of toluene on the various polymeric adsorbents were investigated. The adsorption equilibrium

Table 6. Dubinin−Astakhov Equation Parameters and Physical Properties of Toluene on Sp-850 and Dowex Optipore V493

adsorbent	T / K	W^0 / cm^3·kg^{-1}	E / kJ·mol^{-1}	r	β	V^0 / cm^3·mol^{-1}	100 × D
Sp-850	273.15	688.0	5.053	1.175	1.192	104.1	4.41
	298.15	845.3	4.571	1.039	1.190	106.8	4.10
	323.15	563.7	6.979	1.296	1.187	109.8	2.51
	348.15	420.2	8.270	1.438	1.184	113.0	2.31
Dowex Optipore xsV493	273.15	588.6	7.557	3.169	1.192	104.1	5.46
	298.15	612.3	10.225	2.866	1.190	106.8	4.21
	323.15	592.7	12.071	2.335	1.187	109.8	2.40
	348.15	492.0	13.875	2.532	1.184	113.0	3.20

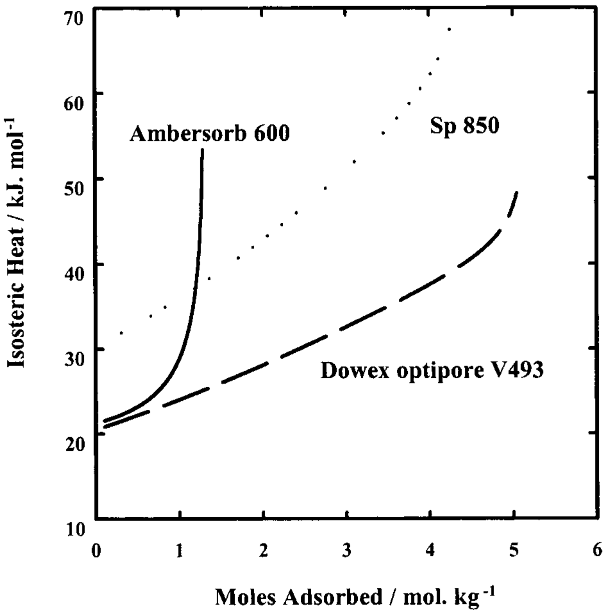

Figure 5. Isosteric heat of adsorption with respect to surface loading.

data were obtained for the pure vapors at 273.15, 298.15, 323.15, and 348.15 K and pressures up to 2.95 kPa. The experimental equilibrium data of toluene on Ambersorb 600 were well correlated by the Unilan equation. For toluene on Sp 850 and Dowex Optipore V493, the Dubinin–Astakhov equation was employed. By the Clausius–Clapeyron equation, the isosteric heat of adsorption was derived. The values of isosteric heat of adsorption varied with surface coverage and this result implies that the polymeric adsorbents used have an energetically heterogeneous surface.

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Received for review August 25, 2000. Accepted April 24, 2001.

JE000282I