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Affinity coefficients of the Polanyi/Dubinin adsorption isotherm equations
A review with compilations and correlations

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Abstract

A historical review presents the assumptions and approximations made in the Polanyi and Dubinin adsorption theories, which have defined the affinity coefficient β and proposed parameters to calculate it. A previous compilation of experimental β [Wood GO. Activated carbon adsorption capacities for vapors. Carbon 1992;30:593–599] for gases and vapors on activated carbons has been supplemented to more than double the available database. Experimental affinity coefficients reported and calculated for water vapor have also been compiled. For water vapor at relative humidity >50% on normal industrial (unacidified) activated carbons, 0.1 is a good average value of the affinity coefficient relative to that of benzene. Direct correlations of experimental affinity coefficients (other than for water) with molecular parachor, molar polarizability, and molar volume were successful (β standard deviations of 0.09, 0.12, and 0.12, respectively). Power functions with exponents less than unity (0.9, 0.75, and 0.9, respectively) provided slightly better fits of predictions to experimental values (standard deviations of 0.08, 0.10, and 0.11, respectively). Any of these correlations can be used. Listed advantages of using molar polarization make it the correlation parameter of preference. Correlation of β with critical temperature was largely unsuccessful. No obvious effects of adsorbate polarity, adsorbent molecular sieve properties, or form of the Dubinin equations were detected for β and its correlations.

Keywords: A. Activated carbon; C. Adsorption; D. Affinity coefficients

1. Historical background

The Potential Theory of (physical) Adsorption was introduced by Polanyi [1]. It defines an adsorption potential (adsorption energy) which is thermodynamically equal to the (negative value of the) free energy of change of a substance from the bulk liquid to the adsorbed state [2]. If the vapor pressure p_{sat} of the bulk material (not adsorbed) is taken as the reference state pressure and the adsorbed equilibrium pressure is p, both taken at temperature T and for ideal gas constant R, the adsorption potential is $\varepsilon = RT \ln(p_{sat}/p)$. The Potential Theory of Adsorption states that the amount q of a given adsorbate that is adsorbed on a given adsorbent under equilibrium conditions is some function of the adsorption potential:

$$q = f[\varepsilon] = f[RT \ln(p_{sat}/p)] \quad (1)$$

Differences in applications of the theory come from selections of this function. Polanyi and others (e.g., Dubinin) [3] have also shown experimentally that this relationship is temperature invariant for a given adsorbent–adsorbate system. Therefore, at all temperatures when the adsorption capacity of a substance is plotted against the adsorption potential, all the data should fall on the same adsorption potential plot (q vs. ε or $f[\varepsilon]$).

Polanyi [4] added the observation that for a fixed adsorption volume (volume of condensed liquid-like substance), adsorption potentials ε_i for different substances are related by constants β_i:

$$\varepsilon_1/\beta_1 = \varepsilon_2/\beta_2 = \varepsilon_3/\beta_3 = \varepsilon_{reference}/\beta_{reference} \quad (2)$$

The β are called 'affinity coefficients,' 'similarity coefficients,' or 'relative differential molar works of adsorption.' Often benzene is taken as the reference com-

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pound, $\beta_{benzene} = 1$ is assumed, and the benzene adsorption potential curve is the 'characteristic curve'. The relationship of Eq. (2) leads to the idea that plots of adsorption capacity vs. adsorption potential for different vapors produce different curves that can be coalesced into one 'correlation curve' by dividing ε by the appropriate affinity coefficients. The β are scaling divisors.

Kadlec [5] suggested and Stoeckli and Morel demonstrated [6] that β can be identified with ratios of differential adsorption potentials. The differential adsorption potential is the average excess adsorption energy of molecules in micropores minus those on the open graphic surface.

Separate scaling factors are needed for the maximum adsorption capacity. According to the Theory of Volume Filling of Micropores of Dubinin et al. [7] there is a fixed volume of micropores W_o (cm^3 per gram carbon) that is filled to a capacity W for any chemical at a given value of ε_1/β_1. The original form of this relationship, the Dubinin-Radushkevich (DR) equation, is:

$$W = W_o \exp[-(\{RT/\beta E_o\} \ln\{p_{sat}/p\})^2] \quad (3)$$

where E_o is the characteristic adsorption energy for the reference vapor; $E = \beta E_o$ is the adsorption energy of another chemical. The Gurvitsch [8] rule states that the maximum capacity W_v in gravimetric or molar units can be related to W_o by the normal liquid density d_L (g/cm^3) or the normal liquid molar volume V_M (cm^3/mole) of the chemical, respectively:

$$\text{Maximum capacity (grams vapor/gram carbon) } W_v = W_o d_L \quad (4)$$

$$\text{Maximum capacity (moles vapor/gram carbon) } W_v = W_o/V_M \quad (5)$$

where $V_M = M_w/d_L$ for molecular weight M_w. Below the maximum capacity the actual adsorbed capacity can likewise be expressed in gravimetric or molar units. The liquid density or molar volume becomes a scaling factor that helps coalesce adsorption isotherms into the correlation curve. Although this capacity scaling factor may coincidently be the same as or proportional to the one for the adsorption energy (e.g., molar volume), it is assumed to be independent of β. This assumption of the potential theory is important in determining how β is obtained experimentally (see later descriptions). Capacity scaling factors are not within the scope of this paper.

2. Predictions of affinity coefficients

The goal of much previous work and this paper has been to predict affinity coefficients. Polanyi [4] and Berenyi [9] assumed that for a nonpolar adsorbent, such as activated carbon, adsorption forces are due to dispersion (London potential) forces. Polarizabilities and ionization potentials of the molecule and the surface contribute to the adsorption potential, according to the London Theory [10–12]. Dubinin and Sawerina [12] took ionization potentials for the same adsorbent to be the same and for most adsorbates to be similar, so that using a reference substance cancels out their influences on β. Affinity coefficients can, therefore, be approximated by ratios of molecular polarizabilities or molar polarizabilities, P_e:

$$\beta = P_e/P_{e\ reference} \quad (6)$$

Dubinin and Timofeyev [13] pointed out that according to Debye [14] 'the polarizability of the molecules depends neither on their constant dipole moment nor on the temperature, and for polar as well as non-polar molecules it is made up additively from the polarizabilities of the atoms.'

According to London the polarizabilities of molecules are approximately proportional to square roots of the attraction constants a_i of the van der Waals equation [10–12]. One difficulty in using this is that such constants are not available for many substances.

Also not having very many molecular polarizability values available in 1946, Dubinin and Timofeyev [13] made the further approximation that polarizability of a molecule varies directly as its molecular volume, or as the molar volume V_m of the adsorbate in the liquid state:

$$\beta = V_m/V_{m\ reference} \quad (7)$$

In a test of Eqs. (6) and (7) and other predictive equations mentioned above with 19 chemicals, they found the best agreements with experimental affinity coefficients were with Eq. (7). Formic and acetic acids needed adjustments for molecular associations in the liquid state.

Vaskovsky [15] proposed that affinity coefficients be approximated by ratios of parachors Ω. Parachors can be calculated from molecular volumes and surface tensions γ measured on pure liquids:

$$\Omega = V_m \gamma^{1/4} \quad (8)$$

They can also be calculated as sums of Sugden increments for atoms and groups of atoms [16]. Therefore, according to Vaskovsky:

$$\beta = \Omega/\Omega_{reference} \quad (9)$$

Dubinin and coworkers [17] tested Eq. (9) and found it to predict β better than Eq. (7) for all eight of the substances tested. Unlike liquid molar volume, but like molecular polarizability, parachor is a temperature-invariant property. However, according to Stoeckli and Houriet [18] dipole moments of polar molecules may not be accounted for in calculating affinity coefficients from parachors.

Reucroft et al. [19] compared experimental affinity

coefficients with those calculated from polarizabilities and parachors. Deviations from experimental values upon using parachors were greater than when using polarizations, especially for polar compounds. They obtained better agreement using polarizabilities when the reference compound used was of a similar polarity. However, attempts to improve the agreements by incorporating dipole moments in the β calculations were unsuccessful.

Golovoy and Braslaw [20] compared affinity coefficients obtained experimentally with those calculated using polarizabilities (polarizations), molar volumes, and molecular parachors. They used three reference compounds of differing polarities. Although the polarization method seemed to give slightly better results, no differences among the three methods could be statistically established. They found that use of a reference compound of similar polarity did not necessarily give more accurate predictions.

Noll et al. [21] also did a comparison of molar volume, molecular parachor, and polarization methods. They concluded that the use of a reference compound of similar polarity does improve the agreements of calculated affinity coefficients with experimental ones. After doing so the three parametric methods produced agreements of similar accuracies.

Wood [22] focused on correlations using molar polarizations (polarizabilities). Using 123 experimental affinity coefficients, he demonstrated that the best correlation of experimental β^2 values was with P_e to the 1.8 power, i.e.:

$$\beta^2=(P_e/P_{e\,\text{reference}})^{1.8} \text{ and } \beta=(P_e/P_{e\,\text{reference}})^{0.9} \quad (10)$$

He used β^2 values for correlations since the former are obtained directly from slopes of experimental DR plots and are used, instead of β, to calculate adsorption capacities with the DR equation. A 'floating' reference was used for each set of data: (1) to reduce possible excessive influence of errors in measurements done with the reference substance, (2) to eliminate the effect of arbitrary selection of the reference substance (often different in different data sets) and defining its $\beta=1$, and (3) to compensate for effects of activated carbon differences. Once the correlation functionality is established using the floating reference method, one reference compound (e.g., benzene) can be selected and its value of P_e used in Eq. (10).

Duisterwinkel [23] used square roots of Wood's 123 tabulated experimental β^2 to compare correlations with molecular parachors and molar polarizations. Only 114 compounds could be compared using parachors, since for 9 inorganic gases parachors could not be calculated (missing Sudgen increments). He first assumed simple proportionalities between affinity coefficients β and the two parameters and concluded that the correlation with parachor was significantly better than with polarization. When he used a 0.81 power of P_e, but not a floating reference, he obtained an improved correlation for β, but not significantly better (equal standard deviations) than with parachors.

3. Coalescing factors

A related approach to coalescing adsorption potential curves into a common correlation curve is the use of 'coalescing factors,' k°_i [24]. These empirical multipliers of molar volumes were introduced upon recognition that molar volumes alone would not suffice, particularly for gases. Mehta and Danner [24] published a table of coalescing factors for several gases on activated carbon. These values, varying from 1.00 (the selected reference for each data set) to 1.19, were calculated from various data sources. They can be related to affinity coefficients by:

$$\beta=(k^\circ_i V_M)/(k^\circ_i V_M)_{\text{reference}} \quad (11)$$

However, the molar volume of the condensed, adsorbed phase of a gas (a substance that is normally above its boiling point or critical temperature) is temperature and pressure dependent. Therefore, the debate is at which conditions the molar volume should be calculated and how: (1) at the adsorption pressure [p in Eq. (1)], (2) at the normal boiling point [for a pressure-independent molar volume], or (3) extrapolated from below the critical temperature? [24] Tien [25] used the latter approach with the modified Rackett equation and developed additional experimental coalescing factors for 14 chemicals, including some liquids, on five activated carbons. These are given in Table 1 along with affinity coefficients calculated by Eq. (11) for those substances with known liquid densities at 20–25°C.

4. Water affinity coefficients

Water adsorption on activated carbon is a special case. The Polanyi/Dubinin theories and equations are based on adsorption forces due to non-specific dispersion interactions, which are small for the small molecule H_2O (relatively low polarizability). Stoeckli and Lavanchy [26] have shown quantitatively from carbon immersion studies that the enhanced adsorption of water (above that due to dispersion forces) is due to the oxygen content of the carbon surface. Specific interactions of water molecules with oxygenated surface species and with other water molecules increase at higher water vapor concentrations (higher relative humidities).

As a result, water on activated carbon seems to exhibit Brunauer [27] Type V isotherms, instead of the Type I obtained with organic compounds. Significant loadings ($W/W_o>0.1$) do not occur until $p/p_{sat}>0.4$–0.5 (relative humidity RH>40–50%) for ordinarily activated carbons [28]. With specially oxidized carbons more adsorption will occur at lower RHs [29]. Nevertheless, Stoeckli et al. [30] have shown that the potential theory can also be used to fit a variety of water Type V adsorption isotherms. The more

Table 1
Coalescing factors from Tien [25] and affinity coefficients calculated from them

Adsorbent	Adsorbate	Coalescing factor	Molecular weight	Liquid density at 20–25°C	Calculated β
BPL 2026-54	Methyl mercaptan	1.0 (ref)	48.11	0.8665	1.00 (ref)
	Ethyl mercaptan	0.92	62.14	0.8315	1.24
	n-Propyl mercaptan	1.1	76.16	0.8411	1.79
BPL 2026-54	Carbonyl sulfide	1.0 (ref)			
	Sulfur dioxide	1.1			
	Hydrogen sulfide	1			
BPL Sample	Ethyl ether	1.0 (ref)	74.12	0.7138	1.00 (ref)
Stock No. 2	Carbon tetrachloride	0.9	153.82	1.5940	0.84
	Ethylene oxide	1	44.05	0.8821	0.48
	Ethyl chloride	0.97	64.51	0.8902	0.68
Columbia 1	Acetylene	1.0 (ref)			
Carbon	Carbon dioxide	1.12			
BPL	Carbon disulfide	1.0 (ref)	76.13	1.261	0.52
	Benzene	1.3	78.11	0.8765	1.00 (ref)
	Carbonyl sulfide	1.3			

general form of Eq. (3), the Dubinin–Astakhov (DA) equation [31], is required:

$$W = W_o \exp[-(\{RT/\beta E_o\} \ln\{p_{sat}/p\})^n] \quad (12)$$

where optimum values of the exponent n for water have been shown to vary at least from 1.9 to 7.7, depending on the type of activated carbon [30].

Subsequently, Stoeckli et al. [32] showed that an overall Type IV water adsorption isotherm can be described as the sum of contributions of a Type I isotherm and a Type V isotherm. The former, dominant at low RHs where interactions with oxygenated (acid) sites occur, was fit to the DA equation with $n = 1$–1.6; the latter, dominant at high RHs where pore filling occurs, was fit to the DA equation with $n = 2.6$–3.8.

In these two papers both adsorption energies E for water and E_o for a reference vapor, benzene, were reported. Since these are related by $E = \beta_{H2O} E_o$, affinity coefficients for water β_{H2O} relative to benzene can be calculated for several activated carbons. The first three sections of Table 2 show the results of such calculations for 16 activated carbons at 25°C.

Matsumura et al. [33] reported relative adsorption efficiencies for benzene, methanol, and water on two activated carbons, untreated and treated to remove hydrophilic surface sites. Data were fit to the linearized DR equation:

$$\ln W = \ln W_o - [(RT/\beta E_o) \ln(p_{sat}/p)]^2 \quad (13)$$

and relative β were derived from reciprocal square root ratios of slopes of log W vs. $[\ln(p_{sat}/p)]^2$. Matsumura used base 10 logarithms instead of ln W; this affected the values of the slopes, but not the ratios. When the results are adjusted to be relative to benzene on the same carbon, the values listed in Table 2 are obtained, varying 0.15–0.19 for activated carbons.

Barton [34] similarly obtained adsorption energies $E = \beta E_o$ from slopes of the linearized DR equation in two regions, RH>20% and RH<20%. Values for water and cyclohexane on variously oxidized BPL carbon have been divided to calculate the β given in Table 2. The numbers attached to the BPL names in Table 2 are hours of oxidation.

Tamon and Okazaki [35] reported linearized DR slopes for 11 chemicals, including water, on a Calgon activated carbon and three increasingly oxidized samples of it. Partial pressures of water shown in a graph at the 50°C measurement conditions correspond to relative pressures of 0.012–0.093. Ratios of the DR benzene slopes to those of water have been used to calculate β^2 and, therefore, β (Table 2).

A group at the U.S. Army [36,37] working with a group at the University of Virginia [38–40] has measured adsorption isotherms of vapors, including water at 25–100°C, on BPL activated carbon. We have analyzed these data in two regimes, >50% RH and <40% RH. and obtained slopes of linearized DR plots. The DR plots were bimodal (apparently two different slopes), as also observed by Barton [34]. Using hexane as a reference, we have calculated β values for water from the DR slopes, as described previously, with the results given in Table 2.

Doong and Yang [41] reported β for water and three organic compounds referenced to benzene on two carbons. Reucroft [42] reported a value relative to chloroform on BPL. Pacheco [43] obtained DR plot slopes of water on BPL and another carbon. We have calculated a β from Pacheco's data using the reference Army data for hexane

Table 2
Affinity Coefficients for Water Vapor on Activated Carbons Reported by or Calculated from Various Sources

Activated Carbon	p/p_{sat} Range	DA exponent	Water βE kJ/mol	Reference E_o kJ/mol	Calculated β	Reference Chemical	Reference β[b]	Calculated β vs Benzene	Citation
CMS	≥0.1	4.20	1.86	26.2	0.071	Benzene	1.00	0.071	30
U-03B	≥0.1	4.68	1.37	21.1	0.065	Benzene	1.00	0.065	30
U-03N	≥0.1	2.67	0.87	16.9	0.051	Benzene	1.00	0.051	30
U-02	≥0.1	2.32	1.19	20.0	0.060	Benzene	1.00	0.060	30
N-125	≥0.1	4.22	1.17	16.8	0.070	Benzene	1.00	0.070	30
DCG-5	≥0.1	1.87	1.79	21.2	0.084	Benzene	1.00	0.084	30
PLW	≥0.1	6.46	2.18	23.9	0.091	Benzene	1.00	0.091	30
PLWK	≥0.1	7.55	2.27	22.9	0.099	Benzene	1.00	0.099	30
ALCA	≥0.1	7.67	2.23	19.4	0.115	Benzene	1.00	0.115	30
MAC-V	≥0.1	3.28	2.39	27.1	0.088	Benzene	1.00	0.088	30
MSC-VR	≥0.1	4.61	1.89	27.1	0.070	Benzene	1.00	0.070	30
			Average and Range		0.08±0.02				
D5-O	Entire	3.16	1.70	21.2	0.080	Benzene	1.00	0.080	32
D5-A	Entire	3.14	1.64	20.5	0.080	Benzene	1.00	0.080	32
CEP-800	Entire	2.70	2.20	21.8	0.100	Benzene	1.00	0.100	32
LOP-3	Entire	3.22	1.56	32.4	0.048	Benzene	1.00	0.048	32
CMA	Entire	2.60	0.97	23.6	0.041	Benzene	1.00	0.041	32
			Average and Range		0.07±0.03				
D5-O[a]	Entire	1.00	5.19	21.2	0.24	Benzene	1.00	0.24	32
D5-A[a]	Entire	1.00	4.75	20.5	0.23	Benzene	1.00	0.23	32
CEP-800[a]	Entire	1.00	7.00	21.8	0.32	Benzene	1.00	0.32	32
LOP-3[a]	Entire	1.00	5.50	32.4	0.17	Benzene	1.00	0.17	32
CMA[a]	Entire	1.62	8.02	23.6	0.34	Benzene	1.00	0.34	32
			Average and Range		0.26±0.09				
PCB	0.2–0.6	2			0.19	Benzene	1.00	0.19	33
Y-25	0.2–0.6	2			0.19	Benzene	1.00	0.19	33
PCB treated	0.2–0.6	2			0.15	Benzene	1.00	0.15	33
Y-25 treated	0.2–0.6	2			0.16	Benzene	1.00	0.16	33
			Average and Range		0.17±0.02				
BPL, 0.5	<0.2	2	6.77	17.4	0.39	Cyclohexane	1.04	0.41	34
BPL, 1	<0.2	2	7.97	14.6	0.55	Cyclohexane	1.04	0.57	34
BPL, 2	<0.2	2	7.31	15.6	0.47	Cyclohexane	1.04	0.49	34
BPL, 4	<0.2	2	8.48	15.2	0.56	Cyclohexane	1.04	0.58	34
BPL, 7	<0.2	2	6.29	19.0	0.33	Cyclohexane	1.04	0.34	34
			Average and Range		0.46±0.13				
BPL, 0.5	> 0.2	2	2.17	17.4	0.12	Cyclohexane	1.04	0.12	34
BPL, 1	> 0.2	2	2.66	14.6	0.18	Cyclohexane	1.04	0.19	34
BPL, 2	> 0.2	2	2.48	15.6	0.16	Cyclohexane	1.04	0.17	34
BPL, 4	> 0.2	2	2.65	15.2	0.17	Cyclohexane	1.04	0.18	34
BPL, 7	> 0.2	2	2.74	19.0	0.11	Cyclohexane	1.04	0.11	34
			Average and Range		0.15±0.04				
AC	0.01–0.09	2	9.62	18.2	0.53	Benzene	1.00	0.53	35
AC-OX1	0.01–0.09	2	8.42	17.1	0.49	Benzene	1.00	0.49	35
AC-OX2	0.01–0.09	2	8.01	16.4	0.49	Benzene	1.00	0.49	35
AC-OX3	0.01–0.09	2	8.48	14.7	0.58	Benzene	1.00		
	0.58	35							
			Average and Range		0.52±0.06				
BPL	<0.4	2	3.65	23.2	0.16	Hexane	1.33	0.21	36,38
BPL	>0.5	2	1.52	23.2	0.066	Hexane	1.33	0.087	36,38
Shirasagi S		2			0.063	Benzene	1.00	0.063	41
Hg I-780		2			0.059	Benzene	1.00	0.059	41
BPL	High pressure	2	1.85	26.5	0.070	Chloroform	0.88	0.061	42
BPL	≥0.5	2	1.62	23.2	0.070	Hexane	1.33	0.093	43
4 Carbons	0.3–0.7	2.0–2.8		19.2–22.4	0.063	Benzene	1.00	0.063	28,44

[a] Type I isotherm assumed. All others Type V.
[b] Experimental values taken from Wood [22].

on BPL. Lodewyckx [28,44] reported an average $\beta=0.063$ for water referenced to benzene for five activated carbons. All these values and ranges are also listed in Table 2.

In the next to last column of Table 2 the β values for water are adjusted to benzene reference where the original reference was not benzene. One observation we make from Table 2 is that the calculated adsorption energy and β for water depend on the portion of the isotherm selected for fitting to the DR or DA equation. This is shown graphically in Fig. 1 where midpoints of fit ranges are used. This is a crude plot since ranges used are often wide. An extrapolated average value for water at RH above 50% is $\beta=0.1$.

Stoeckli and Lavanchy [26] have reported an extrapolated value of $\beta=0.052\pm0.007$ for carbon of zero oxygen content. This is the lower limit of β due to dispersion interactions only. For typical industrial activated carbons of typical surface oxygen content, $\beta=0.1$ (Fig. 1) is a practical value. However, it must be recognized as an empirical value when used in the Dubinin equations, which fundamentally do not include specific interactions (e.g., polar attraction and/or hydrogen bonding).

Although this paper is only concerned with gas–solid interactions, it is useful to make some comparisons here with results from aqueous solution studies. Greenback [45] reported coalescing factors for organic compounds and water with a reference of heptane. The average water coalescing factor was $k^{\circ}_{i}=0.28$. From Eq. (11) this is equivalent to $\beta=0.034$ relative to heptane ($\beta=1.48$) [22] or 0.051 relative to benzene. The latter is similar to Table 2 values obtained from water vapor/activated carbon studies at high relative humidities. Organic chemical β, similarly calculated relative to benzene, ranged from 0.43 for ethyl acetate to 0.77 for 1-pentanol; these values are smaller than vapor phase results [22]. They correlated well with molar polarizability (what Greenback calls 'refractive index,' actually the Lorenz–Lorenz function of refractive index, multiplied by molar volume).

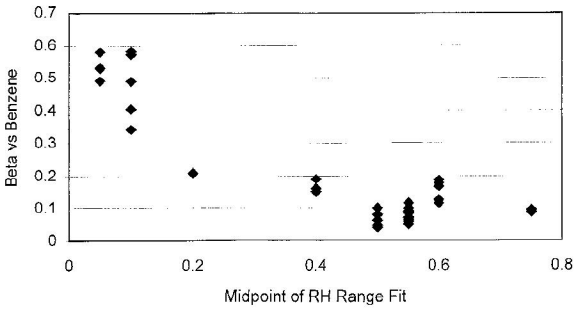

Fig. 1. Affinity coefficients of water on activated carbons as a function of the midpoints of the relative humidity regions used to fit measured adsorption isotherms to the Dubinin-Astakhov equation.

5. Affinity coefficients for other chemicals

Doong and Yang [46] published DA fittings of adsorption data from various sources, mostly for light hydrocarbon gases. With BPL carbon they observed a temperature dependence of the adsorption energy, but this did not affect the calculated affinity coefficient (averages from adsorption energy ratios are given in Table 3).

Tamon and Okazaki [35] also made measurements on three oxidized samples of the Calgon activated carbon. These results are not given in Table 3; those for the original activated carbon are. The β value for ammonia is unusually high, likely due to reactions with acidic surface oxides [35].

Kawazoe et al. [47] measured adsorption isotherms for 28 chemicals on a molecular sieving carbon, MSC-5A. Their adsorption energies from the DA equation were used to calculate β listed in Table 3.

Lee and Reucroft [48,49] studied vapor adsorption on coal- and wood-based chemically activated carbons. The phosphoric acid-activated wood carbon results give abnormally high and variable β. The variously potassium hydroxide-activated coal carbons give β relative to carbon tetrachloride that show no obvious trends with increasing degree of activation (580–1605 m^3/g BET surface areas) and decreasing adsorption energy. The β for the latter five carbons were averaged and are reported in Table 3.

Paulsen et al. [50] reported DA fits for three gases and vapors on an activated coconut carbon. Adsorption energies calculated at different temperatures were averaged for the results in Table 3.

Suzuki and Sakoda [51] reported DA adsorption energies for two 'ordinary' activated carbons and two carbon molecular sieves: MSC-5A and MSC-7A. The results in Table 3 seem to indicate no sieving effects on β; however, the range of molecular sizes is small.

The results of Lu et al. [52] show a trend of slightly increasing β among the three carbons with respect to degree of activation: They reported micropore volumes of 0.27, 0.38, and 0.50 cm^3/g for PA, BPL, and Columbia, respectively.

Matsumura et al. [33] compared methanol and water adsorption with benzene on two original and two deoxygenated activated carbons. The treated carbons gave slightly lower β values (0.43 and 0.46 for methanol relative to benzene on the same carbon) than the original carbons and are not included in Table 3.

Bhatia and Shethna [53] cited data for activated carbon from two sources, obtained β_{calc} from parachor ratios, and calculated characteristic energies multiplied by pore half-widths: $k=rE_o=r\beta_{exp}E/\beta_{calc}$. We have back-calculated original experimental $r\beta_{exp}E$ from tabulated values and have used ratios to get the β_{exp} results listed in Table 3.

Lavanchy et al. [54] and Stoeckli et al. [55] reported characteristic energies for four chemicals on one carbon. These E_o were calculated from experimental adsorption energies $\beta_{exp}E$ using values of β from ratios of parachors.

Table 3
Supplemental values of affinity coefficients on activated carbons calculated from various sources

Compound	Activated carbon	DA exponent	βE kJ/mol	Experimental β vs. reference	Molar polarizability	Liquid molar volume	Parachor	Citation
Methane	Nuxit AC	2.02	3.954	0.71	6.541		73.2	46
Ethylene	Nuxit AC	1.86	4.386	0.79	10.726		101.2	46
Ethane	Nuxit AC	1.89	4.456	0.80	11.225		112.2	46
Propylene	Nuxit AC	1.89	5.547	1.00	15.791	81.884	140.2	46
Propane[a]	Nuxit AC	1.85	5.568	1.00	15.967	88.092	151.2	46
Methane	BPL	1.55–1.93	3.52–4.12	0.81	6.541		73.2	46
Ethylene[a]	BPL	1.48–1.75	4.05–5.35	1.00	10.726		101.2	46
Ethane	BPL	1.56–1.79	4.17–5.78	1.05	11.225		112.2	46
Ethylene	Carbon mol sieve	2.68	6.740	0.59	10.726		101.2	46
Ethane	Carbon mol sieve	2.85	6.670	0.58	11.225		112.2	46
Propylene	Carbon mol sieve	2.78	8.410	0.73	15.791	81.884	140.2	46
Propane	Carbon mol sieve	3.02	7.81	0.68	15.967	88.092	151.2	46
Methanol	Carbon mol sieve	1.81	4.651	0.40	8.236	40.485	82.2	46
Acetone	Carbon mol sieve	2.00	9.774	0.85	16.177	73.528	162.0	46
Hexane	Carbon mol sieve	1.62	14.968	1.30	29.898	130.486	271.0	46
Benzene[a]	Carbon mol sieve	1.78	11.52	1.00	26.274	89.116	206.1	46
Cyclohexane	CAL AC	2	18.73	1.03	27.735	108.105	240.1	35
Benzene[a]	CAL AC	2	18.23	1.00	26.274	89.116	206.1	35
Methanol	CAL AC	2	8.06	0.44	8.236	40.485	82.2	35
Ethanol	CAL AC	2	10.55	0.58	12.922	58.368	121.2	35
2-Propanol	CAL AC	2	12.57	0.69	17.623	76.512	166.2	35
2-Butanol	CAL AC	2	15.75	0.86	22.177	91.926	205.2	35
Acetone	CAL AC	2	13.21	0.72	16.177	73.528	162.0	35
Acetonitrile	CAL AC	2	9.85	0.54	11.069	52.246	121.9	35
Sulfur Dioxide	CAL AC	2	12.64	0.69	10.090		88.2	35
Ammonia	CAL AC	2	17.28	0.95	5.460	25.609	63.8	35
1-Hexanol	BPL	2	24.55	1.04	31.636	125.590	280.0	37
2-Hexanol	BPL	2	22.22	0.94	31.321	125.236	280.0	37
DMMP[b]	BPL	2	17.90	0.76	28.181	108.300		36, 38
Hexane[a]	BPL	2	23.59	1.00	29.898	130.486	271.0	36, 38
Heptane	BPL	2	27.86	1.18	34.552	146.556	307.2	36, 38
Nonane	BPL	2	32.80	1.39	43.846	178.635	385.2	36, 38
R-113[b]	BPL	2	18.22	0.77	26.166	116.875	249.6	39
Dichloromethane	BPL	2	14.43	0.61	16.338	64.021	147.6	39
R-123[b]	BPL	2	18.61	0.79	20.911	103.192	212.4	36
R-11[b]	BPL	2	15.90	0.67	21.241	91.700	193.4	36
R-134[b]	BPL	2	13.72	0.58	11.225		146.6	36
Toluene	BPL	2	22.49	0.95	31.054	106.287	245.6	36
R-22[b]	BPL	2	13.99	0.59	11.521		127.6	36
R-318	BPL	2	16.28	0.69	18.197		236.4	36
1-Butanol	BPL	2	18.29	0.78	22.154	91.529	205.2	40
1-Propanol	BPL	2	15.55	0.66	17.529	74.798	166.2	40
Ethanol	BPL	2	11.21	0.47	12.922	58.368	121.2	40
Ethanol	BPL	2	12.84	0.54	12.922	58.368	121.2	36
Methanol	BPL	2	10.15	0.43	8.236	40.485	82.2	40
Acetone	BPL	2	15.48	0.66	16.177	73.528	162.0	36
Cyanogen Chloride	BPL	2	14.85	0.63	11.326	51.405	120.1	36
Perfluorocyclo-hexane	BPL	2	19.27	0.82	27.735		240.1	36
Ammonia	BPL	2	7.28	0.31	5.460	25.609	63.8	36
Nitrogen	Carbon mol sieve	2.6	11.72	0.41	4.390		50.0	47
Carbon Dioxide	Carbon mol sieve	2.3	11.30	0.39	7.344		91.2	47
Oxygen	Carbon mol sieve	2.3	9.21	0.32	3.989		40.0	47
Hydrogen	Carbon mol sieve	2.5	5.44	0.19	2.029		34.2	47
Neon	Carbon mol sieve	3.0	4.06	0.14	0.998			47
Argon	Carbon mol sieve	2.9	10.04	0.35	4.140			47
Krypton	Carbon mol sieve	2.8	11.30	0.39	6.267			47

Table 3. Continued

Compound	Activated carbon	DA exponent	βE kJ/mol	Experimental β vs. reference	Molar polarizability	Liquid molar volume	Parachor	Citation
Xenon	Carbon mol sieve	2.8	14.23	0.49	10.202			47
Methane	Carbon mol sieve	2.8	13.39	0.46	6.541		73.2	47
Ethylene	Carbon mol sieve	3.0	15.48	0.54	10.726		101.2	47
Ethane	Carbon mol sieve	2.9	16.74	0.58	11.225		112.2	47
Propylene	Carbon mol sieve	3.0	21.34	0.74	15.791	81.884	140.2	47
n-Butane	Carbon mol sieve	2.9	23.43	0.81	20.624	100.415	190.2	47
n-Hexane	Carbon mol sieve	2.8	30.55	1.06	29.898	130.486	271.0	47
Benzene[a]	Carbon mol sieve	3.1	28.87	1.00	26.274	89.116	206.1	47
Ethyl Acetate	Carbon mol sieve	3.1	27.62	0.96	22.267	97.867	216.0	47
p-Xylene	Carbon mol sieve	3.3	37.66	1.30	36.005	123.298	282.4	47
Trichlorethylene	Carbon mol sieve	3.2	31.38	1.09	25.369	89.735	212.8	47
Tetrahydrofuran	Carbon mol sieve	3.0	24.27	0.84	19.876	81.095	184.5	47
Dichloromethane	Carbon mol sieve	3.0	20.92	0.72	16.338	64.021	147.6	47
Cyclohexane	Carbon mol sieve	2.8	25.11	0.87	27.735	108.105	240.1	47
Acetone	Carbon mol sieve	2.8	20.92	0.72	16.177	73.528	162.0	47
Carbon Disulfide	Carbon mol sieve	2.6	20.92	0.72	21.494	60.694	147.4	47
Methanol	Carbon mol sieve	2.7	10.88	0.38	8.236	40.485	82.2	47
Ethanol	Carbon mol sieve	2.7	17.16	0.59	12.922	58.368	121.2	47
1-Butanol	Carbon mol sieve	2.6	25.53	0.88	22.154	91.529	205.2	47
Acetic Acid	Carbon mol sieve	3.0	20.92	0.72	13.008	57.234	138.0	47
Pyridine	Carbon mol sieve	3.0	28.45	0.99	24.074	80.558	196.7	47
Benzene[a]	Shirasagi S	2		1.00	26.274	89.116	206.1	41
Acetone	Shirasagi S	2		0.86	16.177	73.528	162.0	41
Toluene	Shirasagi S	2		1.36	31.054	106.287	245.6	41
Methanol	Shirasagi S	2		0.40	8.236	40.485	82.2	41
Benzene[a]	HG I-780	2		1.00	26.274	89.116	206.1	41
Acetone	HG I-780	2		0.85	16.177	73.528	162.0	41
Methanol	HG I-780	2		0.36	8.236	40.485	82.2	41
Chloroform[a]	BPL	2	26.5	1.00	21.462	80.488	184.8	56
Phosgene	BPL	2	24.1	0.91	18.391	72.104	132.4	56
Cyanogen Chloride	BPL	2	16.9	0.64	11.326	51.405	120.1	57
Hydrogen Cyanide	BPL	2	10.8	0.41	6.370	39.311	82.9	57
Carbon Tetrachloride[a]	BPL	2	18.2–25.8	1.00	26.435	96.499	219.7	48
Acetone	BPL	2	15.5–19.4	0.81	16.177	73.528	162.0	48
Ammonia	BPL	2	6.8–10.2	0.38	5.460	25.609	63.8	49
Hydrogen Sulfide	BPL	2	9.24–13.46	0.50	9.750		82.4	49
m-Xylene[a]	Coconut BS	2.0	32.2	1.00	35.962	122.854	284.2	50
MIBK[b]	Coconut BS	2.4	28.0	0.87	30.179	123.456	278.7	50
Argon	Coconut BS	2.4	6.2	0.19	4.140			50
Ethane[a]	Carbon C	2.03	12.3	1.00	11.225		112.2	51
Ethylene	Carbon C	1.98	11.7	0.95	10.726		101.2	51
Xenon	Carbon C	1.90	10.9	0.89	10.202			51
Ethane[a]	Carbon D	1.91	11.5	1.00	11.225		112.2	51
Ethylene	Carbon D	1.98	11.9	1.03	10.726		101.2	51
Xenon	Carbon D	1.93	11.0	0.96	10.202			51
Ethane[a]	MSC-5A	2.45	16.0	1.00	11.225		112.2	51
Ethylene	MSC-5A	2.53	15.6	0.98	10.726		101.2	51
Xenon	MSC-5A	2.30	14.0	0.88	10.202			51
Ethane[a]	MSC-7A	2.17	14.1	1.00	11.225		112.2	51
Ethylene	MSC-7A	2.16	13.7	0.97	10.726		101.2	51
Xenon	MSC-7A	2.11	12.7	0.90	10.202			51
n-Butane[a]	BPL	2	18.3	1.00	20.624	100.415	190.2	52
Propane	BPL	2	14.8	0.81	15.967	88.092	151.2	52

Table 3. Continued

Compound	Activated carbon	DA exponent	βE kJ/mol	Experimental β vs. reference	Molar polarizability	Liquid molar volume	Parachor	Citation
Ethane	BPL	2	12.3	0.67	11.225		112.2	52
n-Butane[a]	Columbia	2	17.1	1.00	20.624	100.415	190.2	52
Propane	Columbia	2	14.5	0.85	15.967	88.092	151.2	52
Ethane	Columbia	2	12.1	0.71	11.225		112.2	52
n-Butane[a]	PA	2	23.3	1.00	20.624	100.415	190.2	52
Propane	PA	2	17.0	0.73	15.967	88.092	151.2	52
Ethane	PA	2	12.8	0.55	11.225		112.2	52
Benzene[a]	Calgon PCB	2		1.00	26.274	89.116	206.1	33
Methanol	Calgon PCB	2		0.50	8.236	40.485	82.2	33
Benzene[a]	Y-25	2		1.00	26.274	89.116	206.1	33
Methanol	Y-25	2		0.58	8.236	40.485	82.2	33
Benzene[a]	AC			1.00	26.274	89.116	206.1	53
Hexane	AC			1.08	29.898	130.486	271.0	53
n-Pentane[a]	AC			1.00	25.278	115.219	231.0	53
Pyridine	AC			0.75	24.074	80.558	196.7	53
Argon	AC			0.26	4.140			53
Carbon monoxide	AC			0.24	5.279		61.6	53
Benzene[a]	U-02	2	17.00	1.00	26.274	89.116	206.1	55
1,2,-Dichloro-ethane	U-02	2	14.23	0.84	21.316	80.123	188.5	55
Carbon tetrachloride	U-02	2	15.51	1.03	26.435	96.499	219.7	54
Chlorobenzene	U-02	2	18.39	1.08	31.150	101.791	244.3	54
Benzene[a]	Ajax 976	2		1.00	26.274	89.116	206.1	58
Propane	Ajax 976	2		0.68	15.967	88.092	151.2	58

[a] Reference compound in a set.

[b] DMMP=Dimethyl methylphosphonate; R-113=1,1,1-Trichlorotrifluoroethane; R-123=2,2-Dichloro-1,1,1-trifluoroethane; R-11=Trichlorofluoromethane; R-134=1,1,2,2-Tetrafluoroethane; R-22=Chlorodifluoromethane; R-318=Perfluorocyclobutane.

We have calculated the original adsorption energies and experimental affinity coefficients and also put them in Table 3.

Chiou and Reucroft [56,57] reported affinity coefficients for phosgene, cyanogen chloride, and hydrogen cyanide relative to chloroform on BPL carbon.

Ahmadpour and Do [58] reported characteristic adsorption energies E_o for propane ($\beta=0.8$ assumed) and benzene ($\beta=1.0$) calculated for an activated carbon and further burned-off samples of it. They fit measured isotherms to the DR, the DA, and the Dubinin-Stoeckli [59] equations. The latter is a generalization of the DR equation for non-homogeneous carbon. Calculated ratios of DR adsorption energies $0.8E_o$ for propane and E_o for benzene yield propane β values ranging from 0.64 to 0.75, with no apparent trend with percent burn-off (Table 4). The average 0.68 is also listed in Table 3.

Note: The DA column of Table 1 of Ref [58]. seems to erroneously list adsorption energies, not characteristic adsorption energies with $\beta=0.8$ assumed. In two cases n of the DA equation are close to 2.0, which should yield adsorption energies similar to the ones from the DR fits. They are too low by a factor of 0.8.

Recognizing this error, we can make other observations and conclusions from Tables 1 and 2 of Reference [58]. DA data fits yield a β average of 0.66 with ranges of 0.60–0.74 and $n=1.70$–2.25; DS fits yield a β average of 0.67 with range of 0.63–0.77 (Table 4). Adsorption energy ratios among the models for each carbon were close to unity, DA/DR and DA/DS both averaging 0.99 with ranges of 0.95–1.04 and 0.97–1.02, respectively. Again, there were no trends with burn-off. These observations indicate that values of β are not sensitive to burn-off or to which potential model is chosen.

However, evidence contrary to this conclusion can be drawn from Hacskaylo and LeVan [60]. They fit data for light hydrocarbon gases on two carbons to both the DR and DA equations. We have calculated β values in Table 4 from reported adsorption energies βE_o. DA/DR adsorption energy ratios averaged 0.95 and ranged from 0.78 to 1.02. In this case a trend was observed of ratios closer to unity for larger molecules (0.78 for methane to 0.98 for butane with one of the carbons; 0.96 for methane to 1.02 for ethane with the other). One thing these authors did differently from the analysis of Doong and Yang [46] of the same data was to assume constant micropore volumes for each carbon and all gases. The β from the DR fits of this paper were tabulated previously [22].

Table 4
Comparisons of affinity coefficients from various Dubinin equations

Carbon	Chemical	β			n_{DA}	Source
		DR	DS	DA		
Ajax 976	Propane	0.75	0.77	0.74	1.96	58
5% Burn-off	Propane	0.64	0.64	0.66	2.25	58
10% Burn-off	Propane	0.68	0.66	0.64	1.75	58
16% Burn-off	Propane	0.64	0.63	0.60	1.70	58
19% Burn-off	Propane	0.68	0.68	0.67	2.21	58
30% Burn-off	Propane	0.65	0.66	0.63	1.95	58
42% Burn-off	Propane	0.70	0.69	0.67	1.72	58
Average		0.68	0.67	0.66		58
Ajax 976	Benzene[a]	1.00	1.00	1.00		58
Nuxit-A1	Methane	0.68		0.53	1.387	60
Nuxit-A1	Ethylene	0.75		0.69	1.448	60
Nuxit-A1	Ethane	0.78		0.72	1.498	60
Nuxit-A1	Propylene	0.88		0.88	1.443	60
Nuxit-A1	Propane	0.90		0.90	1.490	60
Nuxit-A1	Butane[a]	1.00		1.00	1.435	60
BPL	Methane	0.84		0.79	1.506	60
BPL	Ethylene	0.94		0.93	1.219	60
BPL	Ethane*	1.00		1.00	1.354	60

[a] Reference compound in a data set.

6. Correlations of affinity coefficients

The β values in Tables 1 and 3 plus those in the previously published table [22] have been correlated with molar polarizability, molar volume, molecular parachor, and critical temperature. We chose power functions $\beta = aX^m$ of each parameter, X, with coefficients, a, that defined benzene as the reference, so that $\beta = 1$ for the value of the parameter for benzene. When the reference chemical for a set of data in Tables 1 and 3 was not benzene, we used the appropriate ratio of β for comparison with experimental data. A Sum of the Squares of Deviations analysis resulted in standard deviations for experimental values vs. correlation values. Selected values of power exponents m were used first and then varied until the standard deviation was minimized. This data fitting process is equivalent to the 'floating reference' approach used previously [22]. Numbers of data differed for the three parameters, since some parameter values were not available (e.g. parachors for inert gases or liquid molar volumes for gases). One questionable $\beta = 0.95$ for ammonia (see above) was excluded from all correlations. Figs. 2–5 and Table 5 show the results of these correlations.

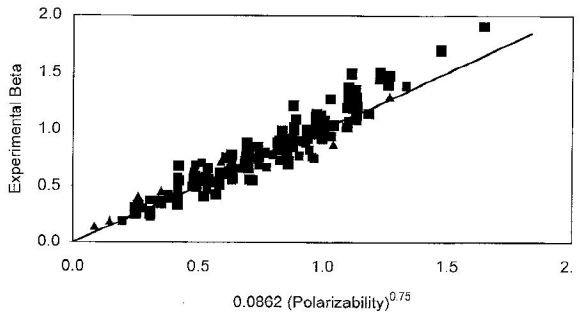

Fig. 2. Comparison of experimental affinity coefficients with those calculated by the optimum molar polarizability correlation. Triangles represent data for carbon molecular sieves. The line is the trend for all the data.

7. Discussions

The best-fit correlations in Table 5 predict that for water vs. benzene $\beta = 0.24$ using molar polarizability, 0.29 using molecular parachor, 0.25 using molar volume, and 1.15

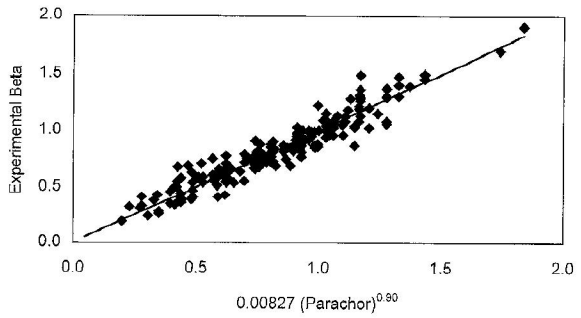

Fig. 3. Comparison of experimental affinity coefficients with those calculated by the optimum molecular parachor correlation. The line is the trend for all the data.

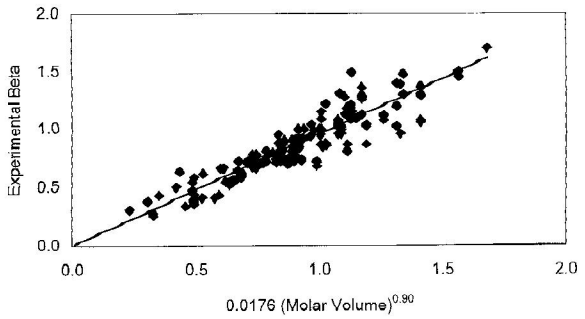

Fig. 4. Comparison of experimental affinity coefficients with those calculated by the optimum molar volume correlation. The line is the trend for all the data.

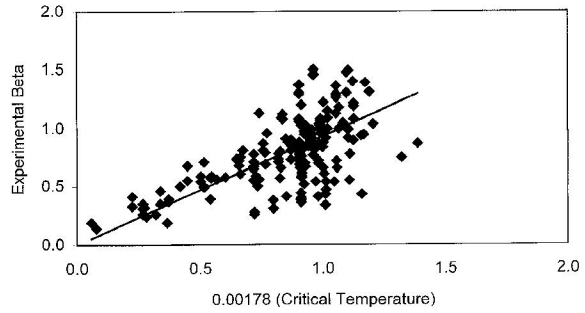

Fig. 5. Comparison of experimental affinity coefficients with those calculated by the critical temperature correlation. The line is the trend for all the data.

using critical temperature. The former three are similar to values reported in Table 2 for $p/p_{sat}<0.5$, but not representative of those at high relative humidity ($\beta=0.1$). Again, the difference is due to specific interactions of water with oxygenated surface sites, not taken into account by the Polanyi/Dubinin theories for nonspecific interactions.

Affinity coefficients for carbon molecular sieves (CMS) did not differ significantly from those of more ordinary activated carbons. Fig. 2, the optimum polarizability

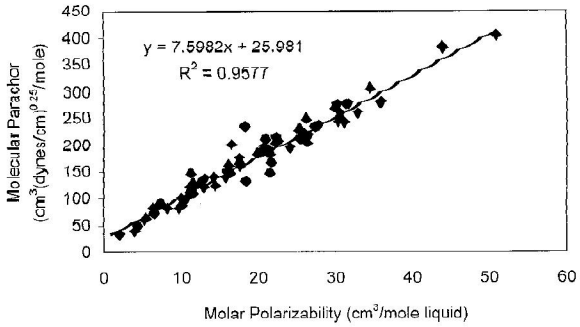

Fig. 6. Correlation of molecular parachor with molar polarizability. The least squares trend line and equation are given on the graph.

correlation, shows CMS as triangles. There seems to be no trend distinguishing ordinary activated carbons from molecular sieve carbons for either small or large molecules.

Molecular parachor was the parameter that produced the best β correlations. Since liquid surface tensions and/or liquid densities are unknown or cannot be measured for many chemicals, molecular parachor is usually calculated from sums of Sugden atomic and structural constants. We have used parachors tabulated in American Chemical Society references or calculated from the Sugden tables in them [61]. However, there are no Sugden constants for less common atoms such as phosphorus and inert gases. Fig. 6 shows a correlation of parachor and the often more available polarizability that can be used in these cases:

$$\text{Parachor} = 26.0 + 7.60\,(\text{Molar Polarizability})$$

Although this is a good overall correlation, it tends to overestimate the parachor (and therefore calculated β) for the smallest molecules (Fig. 6).

Standard deviations reported in Table 5 for correlations with parachor and polarizability are close to those obtained by Duisterwinkel [23] for the original dataset [22] (see previous comments). Using unitary exponents he reported that parachor produced a better correlation (standard

Table 5
Results of affinity coefficient correlations: $\beta = aX^m$

Parameter X	Power m	Coefficient a	Number of data	Standard deviation in β
Molar polarizability	1.00	0.0381	263	0.12
	0.90	0.0528	263	0.11
	0.75[a]	0.0862	263	0.10
Molecular parachor	1.00	0.00485	247	0.09
	0.90[a]	0.00827	247	0.08
Molar volume	1.00	0.0112	203	0.12
	0.90[a]	0.0176	203	0.11
Critical temperature	1.00[a]	0.00178	254	0.24

[a] Power that produced the best fit to data.

deviation of 0.084 vs. 0.11); however, allowing an optimum exponent of 0.81 for polarizability gave 0.084 for polarizability also.

The work of Reucroft [19] has suggested that using parachor to calculate β might not properly account for dipole moments in polar molecules. The analyses of our more extensive database do not indicate any worse correlations of polar compounds than nonpolar ones. Fig. 7 shows comparisons of experimental β for the most polar compounds, alcohols, with those calculated using the best correlations (Table 5) for the complete dataset. Within experimental scatter there are no trends or significant deviations from equivalence using parachor, polarizability, or molar volume parameters.

Polarizability was almost as good as parachor as a parameter for estimating β. There are many advantages that may make it preferable to use the polarizability correlations:

1. Molar polarizabilities can be easily (and preferably) calculated from handbook [62] values of refractive index (n_D), molecular weight (M_w), and liquid density (d_L) by the Lorenz-Lorenz equation:

$$P_e = (M_w/d_L)(n_D^2 - 1)/(n_D^2 + 2)$$

2. Polarizability (polarization) can be measured for atoms and molecules in a fluctuating electric field. A common handbook [62] lists many of these values, which can be converted to molar polarizations by the divisor $0.3964308 \times 10^{-24}$ cm^3.
3. As a third option molar polarizabilities can be calculated from atomic, group, and molecular structure increments [61,63].
4. Unlike molar volume, but like parachor, polarizability is a temperature-, pressure-, and density-invariant (and molecular) property, which is desirable for describing correlation curves and affinity coefficients, which are also assumed to be temperature invariant.

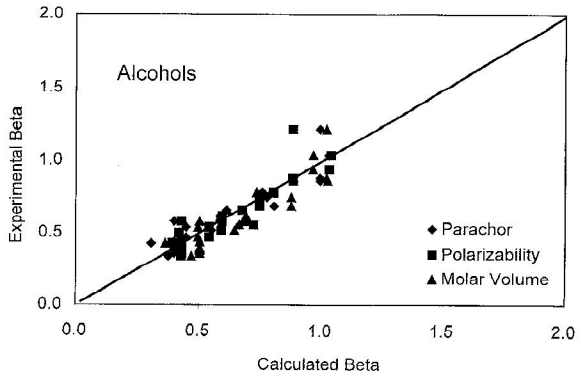

Fig. 7. Comparisons of experimental and calculated affinity coefficients for alcohols.

5. Polarizability has a more fundamental theoretical relation to adsorption potential than molar volume or parachor (see history above).
6. Electronic polarizations include electrostatic as well as dispersion forces.

Molar volume correlations produced standard deviations in β close to those of molar polarization (Table 5). However, 60 fewer experimental β could be used because for these gases, liquid densities at normal temperatures and pressures are not available from handbook references. Although it has been done, it is difficult to calculate densities of condensed, adsorbed phases at temperatures approaching and exceeding critical temperatures.

Critical temperature was not a very useful correlation parameter for β (Table 5) except, possibly, for light gases with $T_c < 390$ °K and $\beta < 0.6$ (Fig. 5).

8. Conclusions

The affinity coefficient β of the Polanyi and Dubinin adsorption theories has had a long history of discussion and analysis. This review and a previous paper [22] provide the most extensive compilation of affinity coefficients available. This compilation has provided an opportunity to review and extend correlations of β with proposed physical parameters.

For water vapor ($p/p_{sat} > 0.5$ and RH > 50%) on unacidified activated carbons 0.1 is a good average value of the affinity coefficient relative to that of benzene. This concentration region is where water loading is significant (> 10% of maximum) and where interference with loading of other gases and vapors is the greatest. This β value is about a factor of 2.5 smaller than is predicted by parachor, polarization, and molar volume correlations from other chemicals.

For other chemicals direct correlations of experimental affinity coefficients with molecular parachor, molar polarization, and molar volume were successful (β standard deviations of 0.09, 0.12, and 0.12, respectively). Power functions with exponents less than unity provided slightly better fits of predictions to experimental values (standard deviations of 0.08, 0.10, and 0.11, respectively). Any of these correlations can be used; however, it is our opinion that the listed advantages of using molar polarization make it the correlation parameter of preference. Correlation of β with critical temperature was largely unsuccessful.

Results did not show any effects of adsorbate polarity, adsorbent molecular sieve properties, or form of the Dubinin equations on β and its correlations.

While we have tried to be thorough in this review, there are certainly β values, adsorption energies to calculate them, and references that we have missed or are yet to be published. The author would appreciate hearing about these for a later update.

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