

CAPILLARY EFFECTS AND INFORMATION CONCERNING ADSORBENT PORE STRUCTURES

3. REFINEMENT OF THE THEORY OF CAPILLARY VAPORIZATION FROM ADSORBENT MESOPORES

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A thermodynamic theory of capillary vaporization which can be used for determining the distribution of adsorbent mesopores over pore radii has been developed in our earlier papers [1, 2]. Three different methods were used in determining distributions from this equation. Method I was based on the classical Kelvin equation. Method II followed the work of Broekhoff and de Boer [3, 4], with account taken of the effect of the mesopore adsorption field on the adsorption layer depth and the liquid meniscus curvature. Method III was an extension of method II, account being taken of the effect of the surface tension on the meniscus curvature [1, 2]. In each case, calculations from the experimental data were based on an equivalent cylindrical-pore model adsorbent and were carried out by either the Dollimore-Heal exact method [5] or the Dubinin approximation method [2, 6]. The relation between t , the mean statistical adsorption layer depth, and p/p_s , the relative pressure, was obtained from the Harkins-Jura adsorption isotherm

$$\lg (p_s/p) = \frac{C}{t^2} - D(t) \quad (1)$$

C being a constant and $D(t)$ a correction term, either constant or only weakly t -dependent [3, 4], determined by the nature of the adsorption system.

The thermodynamic theory of capillary vaporization [3, 4] leads to two basic equations for the cylindrical-pore model adsorbent:

$$RT \ln (p_s/p) - F(t) = \frac{\sigma v}{r - t} \quad \text{for } t = t_e \quad (2)$$

$$r - t_e = \frac{2\sigma v}{RT \ln (p_s/p)} + \frac{2}{(r - t_e) RT \ln (p_s/p)} \int_{t_e}^r (r - t) F(t) dt \quad (3)$$

where

$$F(t) = 2,303RT \left[\frac{C}{t^2} - D(t) \right] \quad (4)$$

is a function defined in terms of the t -curve equation (1). Here σ is the surface tension and v the molar volume of the liquid, and t_e is the statistical mean depth of the adsorbed layer in the adsorbent mesopore of radius r . Equations (2) and (3) contain three independent variables, p/p_s , t_e , and r . By computer solution of these equations, it is possible to determine the depth of the adsorbed layer, t_e , and the radius r of the pores exposed through capillary vaporization, at any value of the relative pressure.

If Eq. (3) is cut off with the first term on the right, one has the solution of the classical problem in the form of the Kelvin equation. The second term appearing on the right-hand side of Eq. (3) can therefore be looked on as a correction term for the approximation in question here. Similar conclusions apply to Eqs. (2) and (3) of the treatment by method III given in [1].

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TABLE 1. Parameters for Capillary Vaporization at High p/p_s and for Various Sorption Systems

Sorption system	p/p_s	Method I		Method II		Method III	
		$r, \text{\AA}$	$t_e, \text{\AA}$	$r, \text{\AA}$	$t_e, \text{\AA}$	$r, \text{\AA}$	$t_e, \text{\AA}$
Nitrogen—mineral and charcoal sorbents	0,98	500	39	566	56	572	56
Benzene—charcoal sorbents	0,96	555	40	742	54	751	54
Benzene—silica sorbents	0,94	363	23	872	32	881	32

As the value of p/p_s approaches unity, t_e approaches t , and the correction term of Eq. (3) approaches zero. At p/p_s values close to unity, e.g., 0.96–0.98, pore radii calculated by method I should therefore be almost identical with pore radii calculated by method II. The differences in exposed pore radii calculated by methods I, II, and III are especially marked in the following systems at high relative equilibrium pressures: N_2 —mineral and charcoal adsorbents at 78°K ($D = 0,1682 \exp[-0,1137t]$ and $C = 16,11$); benzene—charcoal sorbents at 293°K ($C = 22,23$ and $D = -0,0035$); and benzene—silica sorbents ($C = 5,924$ and $D = -0,0156$) [7] (Table 1). These differences are particularly marked in the last of these three systems. Methods II and III give identical mesopore adsorbed layer depths, and pore radii which differ only insignificantly. Adsorption layer depths calculated by methods II and III are usually considerably greater than those calculated by method I.

It would thus appear that the Broekhoff and de Boer theory of capillary vaporization is not entirely satisfactory for work at high values of the relative equilibrium pressure. Let us now consider the factors responsible for this breakdown in the case of the benzene—silica sorbent systems where the differences are most pronounced. Here integration of (3) gives an equation of the form

$$r = \frac{9,142}{\lg(p_s/p)} + t_e + \frac{10,85 \left[\frac{r}{t_0} - 1 - \ln \frac{r}{t_e} \right]}{(r - t_e) \lg(p_s/p)} + \frac{0,0156(r - t_e)}{\lg(p_s/p)} \quad (5)$$

The third and fourth terms of this equation can be considered as corrections to the Kelvin equation, itself given by the first term. The values of these correction terms can be estimated by using the parameter values appearing in the calculations on the capillary vaporization of benzene by method II, i.e., $p/p_s = 0,94$, $t_e = 32 \text{\AA}$, and $r = 872 \text{\AA}$ (Table 1). Substitution of the results obtained back into (5) gives, in round figures,

$$r = 340 + 32 + 23 + 488 = 883 \text{\AA}$$

The sum of the values of the correction terms, 511 \AA , is considerably greater than the pore radius calculated from the Kelvin equation, a quantity of the order of 370 \AA . Some 95% of this correction arises from the last term of Eq. (5), a quantity directly proportional to the D member of the t -curve equation (1). Since this term has the opposite sign for N_2 —mineral sorbent systems, the difference between pore radii calculated by methods I and II is much less there. Thus, it can be concluded that breakdown in the t -curve equation accounts for the fact that incorrect results are obtained by the Broekhoff—de Boer theory.

Refinement of the Theory of Capillary Vaporization from Mesopore Adsorbents. Elimination of these deficiencies requires the use of a more rational t -curve equation. Analysis showed that it would be well to modify the term in D which, if constant, is one of the parameters of Eq. (1). In principle, this can be done by introducing a second parameter in the form of a t -exponential into the first term of Eq. (1). One then obtains a Halsey-type equation [8] for the t -curve,

$$\ln \frac{p_s}{p} = \frac{K}{t^m} \quad (6)$$

in which the curve parameters are K and m . For setting up comparisons with experimental data, it is useful to cast this last relation into linear form:

$$\ln \ln(p_s/p) = \ln K - m \ln t \quad (7)$$

TABLE 2. Depths of Adsorbed Layers, Measured and Calculated through Eq. (6), for the General de Boer-Linens t-Curve (N₂, 78°K)

p/p _s	t, Å		Δ, %	p/p _s	t, Å		Δ, %
	meas.	calc.			meas.	calc.	
0.10	3.68	3.75	+1.90	0.60	7.36	7.34	-0.24
0.20	4.36	4.40	+0.92	0.70	8.57	8.62	+0.57
0.30	5.01	5.01	0	0.80	10.57	10.63	+0.52
0.40	5.71	5.66	-0.92	0.86	12.75	12.65	-0.75
0.50	6.50	6.41	-1.42	0.90	14.94	14.84	-0.60

Thirty measured values of the adsorption of N₂ on nonporous mineral adsorbents, at 78°K and relative equilibrium pressures ranging from 0.08 to 0.90, have been reported in [4]. In the Broekhoff-de Boer theory these data would be described by two Harkins-Jura isotherms, each applying to a particular p/p_s interval. One of these equations would contain a variable D(t) parameter [3, 4]. Each of the 30 points fell close to a single straight line corresponding to Eq. (7) with the parameter values K = 44.54 and m = 2.241, t being expressed in Å.

Comparison showed that the agreement between measured t-values and values calculated through Eq. (6) was good over the entire range of relative pressures, and especially good at the higher pressures (Table 2). This, of course, makes for more trustworthy extrapolation to higher p/p_s values. It is to be noted that the integral in the second term of Eq. (3) is to be evaluated over the interval from t_e to r, and the t-curve equation entering into the expression for F(t) is naturally applicable over this range.

Equation (6) gives an equally good description of the t-curve for other systems, the benzene-hydrated nonporous silica system at 293°K, for example. Here calculations were based on the 0.04-0.96 interval of relative pressures on the isotherm for benzene adsorption on quartz powders with 6.0 m²/g specific surface area at 293°K [9]. Adsorption isotherms cannot be determined with high accuracy for sorbents with such high specific surface areas. Thus, although Eq. (7) is applicable over the entire range of p/p_s values, departures from the experimental values can be as high as 10-13% at certain points on the isotherm. This effect is compensated for by the almost complete absence of capillary condensation in the interstices between the roughly dispersed quartz particles. Determined graphically, the values of the parameters of Eq. (6) for this system proved to be K = 5.61 and m = 1.435, t being measured in Å.

Thus, it is useful to incorporate the t-curve Eq. (6) into the Broekhoff-de Boer theory of capillary vaporization. This leads to a considerable simplification of the final forms of the various equations. By substituting (6) into (2) and (3), and drawing on the analogy of Eq. (4), one is led to

$$F(t) = RT \frac{K}{t^m} \quad (8)$$

Integration followed by certain algebraic rearrangements gives the following final forms (r and t measured in Å):

$$\ln(p_s/p) - \frac{K}{t_e^m} - \frac{\sigma v}{RT(r - t_e)} = 0 \quad (9)$$

$$r - t_e = \frac{2\sigma v}{RT \ln(p_s/p)} + \frac{2K}{(r - t_e) \ln(p_s/p)} \left[\frac{r^{2-m}}{(1-m)(2-m)} - \frac{r t_e^{1-m}}{1-m} + \frac{t_e^{2-m}}{2-m} \right] \quad (10)$$

Rough calculations show that methods I and II lead to essentially identical r values at high relative pressures. Representative data on benzene-silica sorbent systems in which the difference between pore radii calculated by methods I and II at high relative pressure is greatest (cf. Table 1) are given below. Consider the case for p/p_s = 0.94. For this system, 2σv/RT = 21.05, K = 5.61, m = 1.435. Consider first the results obtained through method I. The Kelvin equation gives the radius of curvature of the spherical meniscus as r_c = 21.05 (ln p_s/p) = 340 Å, while Eq. (6) gives t = 23 Å. The exposed pore radius at p/p_s = 0.94 is then given as r = r_c + t = 363 Å.

Estimation of t_e by method II can be made through Eq. (9) and successive approximation procedures. Since essentially identical pore radii are obtained by methods I and II in the refined theory of capillary vaporization, the correction third term of Eq. (9) was estimated by setting r = 363 Å and t = t_e = 23 Å. Solution

with the resulting value of this correction term gave $t_e = 38 \text{ \AA}$ as a first approximation. Substitution of this value, and $r = 363 \text{ \AA}$, into the third term of Eq. (9) gave 39 \AA as the second approximation for t_e .

Estimation of r by this same method involved substituting $r = 363 \text{ \AA}$ and $t_e = 39 \text{ \AA}$ into the second term correction of Eq. (10). This gave a value of 39.3 \AA or, rounded off, $t_e = 39 \text{ \AA}$ for the correction term, with a pore radius $r = t_e + r_c + \delta = 39 + 340 + 39 = 418 \text{ \AA}$ instead of the 363 \AA obtained by method I. The deviation here was 15.1% instead of the 140% (cm. Table 1) obtained through Eqs. (2) and (3) with $F(t)$ expressed by Eq. (4).

V. I. Ulin has improved the treatment by method III given in [1] by introducing a more exact expression for the relation of the surface tension to radius of curvature of the liquid meniscus. Here the equations analogous to (9) and (10) have the form

$$\ln(p_s/p) - \frac{K}{t^m} - \frac{\sigma_0 v}{RT(r - t_e - \omega)} = 0 \quad (11)$$

$$r - t_e = \frac{2\sigma_0 v}{RT \ln(p_s/p)} + \frac{2K}{(r - t_e) \ln(p_s/p)} \left[\frac{r^{2-m}}{(1-m)(2-m)} - \frac{rt_e^{1-m}}{1-m} + \frac{t_e^{2-m}}{2-m} \right] + 4\omega \left[1 - \frac{K}{(r - t_e) \ln(p_s/p)} \cdot \frac{r^{1-m} - t_e^{-m}}{1-m} \right] \quad (12)$$

σ_0 being the surface tension for the planar liquid surface and ω the Tolman equation parameter, a quantity equal to 3.31 for nitrogen at 78°K and 4.64 for benzene at 293°K. If the surface tension is assumed to be independent of the mean radius of curvature of the meniscus, $\omega = 0$ and Eqs. (11) and (12) reduce to Eqs. (9) and (10) of method II.

CONCLUSIONS

1. The form of the t -curve accounts for differences in mesopore radii calculated by the Broekhoff-de Boer theory and by classical methods, as the relative pressure tends toward unity.
2. Arguments are advanced for the use of a more rational form of t -curve equation, applicable over the entire range of relative equilibrium pressure applying to capillary vaporization from adsorbent mesopores.
3. A refined theory of capillary vaporization based on a new type of t -curve equation is proposed. Calculated and predicted values are almost identical to this theory.

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