

Correlations among Parameters of Dubinin–Radushkevich and Langmuir–Freundlich Isotherms for Adsorption from Binary Liquid Mixtures on Solids

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The dependences among the optimized parameters of Dubinin–Radushkevich and Langmuir–Freundlich isotherms, lately proposed for single gas adsorption (M. Jaroniec and A. W. Marczewski, *J. Colloid Interface Sci.* **101**, 280 (1984)), are extended to adsorption from binary liquid mixtures on solids. Moreover, new relationships among the parameters of the above equations are proposed for describing the liquid/solid adsorption systems. Some considerations concerning the choice of the adsorption capacity are also presented and illustrated by model calculations. The theoretical conclusions are compared with experimental data analysis. A satisfactory correlation among the experimental and calculated parameters of Dubinin–Radushkevich and Langmuir–Freundlich isotherms is observed. © 1987 Academic Press, Inc.

In the literature a great number of theoretical isotherms have been proposed to describe the adsorption process from gas and liquid phases on solid surfaces (1, 2). Many authors, upon investigation of the utility of these isotherms for interpreting the adsorption data, have stated that different equations frequently describe the same experimental isotherm quite well. Such convergence was observed in the case of gas adsorption (2, 3), adsorption from dilute aqueous solutions (4–7), and adsorption from liquid mixtures of nonelectrolytes (8–10). However, it should be noted that this resemblance of different theoretical isotherms does not generally persist over the whole pressure and concentration region but is only limited to a definite range. Some investigators motivated by the above observations have made attempts to find relationships among the parameters of different isotherm equations. Dubinin *et al.* (11–13) defined the dependence

among the parameters of Dubinin–Astakhov and Langmuir–Freundlich isotherms (2). Next, Jaroniec and Marczewski (14), applying the different methods, have obtained more general relationships among the Dubinin–Astakhov and generalized Langmuir equations (15). Using these relationships it is possible to calculate the parameters of a Dubinin–Astakhov isotherm and its special forms by means of the generalized Langmuir isotherm parameters and vice versa.

In this paper we extend the method proposed by Jaroniec and Marczewski (14) to adsorption from binary liquid mixtures on solids. However, our considerations are limited to two isotherm equations, i.e., Dubinin–Radushkevich and Langmuir–Freundlich isotherms. Moreover, a new method of calculating the relationship between the parameters of these equations is presented. We also discuss the problem of the choice of adsorption capacity and illustrate its implications through the results of model calculations. The theoretical conclusions are examined by using the

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experimental data of adsorption from binary liquid mixtures on silica gel and activated carbon.

THEORETICAL

The isotherms considered in this paper, i.e., Dubinin-Radushkevich (DR) and Langmuir-Freundlich (LF) ones, belong to two different groups of isotherm equations (2). The first is the special case of the Dubinin-Astakhov (DA) equation (16) and may be written in the following form for adsorption from binary liquid mixtures on solids,

$$x_1^s = n_1^s/n_m^s = \exp\{-B[\ln(x_{12}^1/\alpha)]^2\} \quad [1]$$

for $x_{12}^1 \leq \alpha$,

where $x_{12}^1 = x_1^1/x_2^1$ and $x_1^1 + x_2^1 = 1$. In the above x_1^s is the mole fraction of the first component in the adsorption space, n_1^s is the adsorbed amount of first component in the adsorption space expressed in millimoles per gram, n_m^s is the total number of moles in the adsorption space (adsorption capacity) expressed in the same units as n_1^s , x_i^1 ($i = 1, 2$) is the mole fraction of the i th component in the bulk phase, B is the structural parameter determining the width of the quasi-Gaussian energy distribution corresponding to Eq. [1] (2), whereas, α determines the position of this distribution on the energy axis and is connected with the characteristic adsorption energy.

The Langmuir-Freundlich isotherm is the special case of the generalized Langmuir (GL) equation (10); it may be written as

$$x_1^s = (\bar{K}_{12}x_{12}^1)^m / [1 + (\bar{K}_{12}x_{12}^1)^m] \quad [2]$$

In the above \bar{K}_{12} is the Langmuir-type constant and m is the heterogeneity parameter characterizing the width of the symmetrical one-peak energy distribution relating to Eq. [2]. Details concerning the physical meaning of the parameters appearing in Eqs. [1] and [2] are given in the review by Jaroniec (2).

As we stated previously, many authors reported that both the above equations, i.e., DR (or DA) and LF, might be successfully used to interpret the same experimental data (2-10). This problem was first considered for gas adsorption by Dubinin *et al.* (11-13) who compared the LF and DA isotherms by performing suitable numerical studies. They found that both isotherms have similar courses over the range of moderate pressures. It means that in this range the LF and DA equations similarly describe the adsorption systems. Recently Jaroniec and Marczewski (14) compared the courses of two general isotherm equations, i.e., DA and GL. Their considerations were based on the so-called ϕ -function (15), which for adsorption from binary solutions may be defined as

$$\phi_1 = \partial \ln n_1^s / \partial \ln x_{12}^1. \quad [3]$$

The mathematical analysis of the dependences ϕ_1 vs $\ln x_{12}^1$, ϕ_2^1 vs $\ln n_1^s$, and ϕ_1 vs n_1^s allows us to formulate the following inequalities for the DR and LF parameters:

$$B \leq m^2/8 \quad \text{or} \quad m \geq (8B)^{1/2} \quad [4]$$

$$\ln \alpha \geq 2/m - \ln \bar{K}_{12} \quad \text{or} \quad \ln \bar{K}_{12} \geq (2B)^{-1/2} - \ln \alpha \quad [5]$$

$$\ln n_{m,DR}^s \geq \ln n_{m,LF}^s + (0.5 - \ln 2)$$

$$\text{or} \quad \ln n_{m,LF}^s \leq \ln n_{m,DR}^s - (0.5 - \ln 2). \quad [6]$$

A relationship similar to Eq. [6] was obtained by Cerofolini (17) for DR- and BET-optimized adsorption capacities:

$$\ln n_{m,DR}^s \approx \ln n_{m,BET}^s - 0.2.$$

For adsorption systems with a well-defined adsorption capacity (e.g., volume of micropores in zeolites or activated carbons), the parameter n_m^s cannot be a free optimized parameter but has a definite physical meaning and should be independent of the type of isotherm equation. Thus, Eqs. [4]-[6] have an approximate character and therefore we propose new alternative relationships. We assume that the mean values of ϕ -functions for DR and LF

isotherms within an experimental range of surface concentrations (a, a') are equal, i.e.,

$$\bar{\phi}_1^{\text{DR}} = \bar{\phi}_1^{\text{LF}} = (a' - a)^{-1} \int_a^{a'} \phi_1 dx_1^s, \quad [7]$$

where a and a' are the minimum and maximum values of the mole fraction x_1^s obtained from the excess adsorption isotherm. Both isotherms intersect at a mean surface concentration \bar{a} . The analysis of Eq. [7] leads to the following dependence between the heterogeneity parameters B and m :

$$\begin{aligned} m/\sqrt{B} = & \frac{\sqrt{\pi}[\text{erf}(\sqrt{-\ln a}) - \text{erf}(\sqrt{-\ln a'})]}{(a' - a)[1 - (a + a')/2]} \\ & - \frac{2(a\sqrt{-\ln a} - a'\sqrt{-\ln a'})}{(a' - a)[1 - (a + a')/2]}. \quad [8] \end{aligned}$$

However, for the parameters \bar{K}_{12} and α we get

$$\ln \alpha + \ln \bar{K}_{12} = [(-\ln \bar{a})/B]^{1/2} + (1/m)\ln[\bar{a}/(1 - \bar{a})], \quad [9]$$

where $\bar{a} = (a + a')/2$ and erf denotes the well-known probability integral (18).

Now, we consider the two special cases of Eqs. [8] and [9]. The first case refers to the whole concentration range corresponding to $x_1^s \in (0, 1)$. Then, we obtain

$$B = m^2/(4\pi) \quad [10]$$

and

$$\ln \alpha + \ln \bar{K}_{12} = (2/m)\sqrt{\pi \ln 2}. \quad [11]$$

Equations [10] and [11] show correlations between parameters of the DR and LF equations for the whole concentration region but it is a crude approximation because the DR and LF isotherms show different behaviors at low and high concentrations. These isotherms show similar behaviors in a narrow concentration region, i.e., in the region of point \bar{a} determining the intersection of the DR and LF isotherms. Therefore, equations defining relationships between DR and LF parameters in a narrow region of point \bar{a} are more useful for

interpretation of the experimental adsorption data:

$$B = m^2[-(1 - \bar{a})^2/(4 \ln \bar{a})] \quad [12]$$

$$\ln \alpha + \ln \bar{K}_{12}$$

$$= (1/m)\{\ln[\bar{a}/(1 - \bar{a})] - 2(\ln \bar{a})/(1 - \bar{a})\}. \quad [13]$$

The method proposed earlier by Jaroniec and Marczewski (14) gives more general relationships among the optimized parameters of GL (or LF) and DA (or DR) isotherms (Eqs. [4]–[6]) than the new one presented above (Eqs. [8]–[13]). It formulates limiting conditions and best-fit dependences for GL (or LF) and DA (or DR) parameters over a narrow range of moderate concentrations. However, the new method gives mean values of parameters for both equations over a slightly wider range of concentrations (see Eqs. [12] and [13]). The main difference between these methods consists in the diverse approach to adsorption capacity determination. From the physical point of view the adsorption capacity should be independent of the adsorption model used. However, the mathematical properties of various theoretical isotherm equations lead to different optimized values of n_m^s . In the method of (14) all parameters are treated as being free, whereas our new approach assumes one value for adsorption capacity, which characterizes the adsorption system and may be evaluated from the excess adsorption data.

We will show a comparison of these methods by analyzing the model curves presented in Figs. 1 and 2. In Fig. 1 the relationships ϕ_1 vs n_1^s (parts A and C) and ϕ_1^s vs $\ln n_1^s$ (parts B and D) for LF (the solid lines) and DR (the dashed lines) equations are shown. The LF parameters are the same in all parts of Fig. 1: $m = 0.5$ and $n_{m,\text{LF}}^s = 1$. The values of the DR parameters have been calculated from the LF ones by using Eqs. [4]–[6] (in parts A and B: $n_{m,\text{DR}}^s = 0.8244$ and $B = 0.03125$) and Eqs. [10] and [11] (in parts C and D: $n_{m,\text{DR}}^s = 1$ and $B = 0.01989$). To show clearly the difference in both these methods we compared ϕ -curves

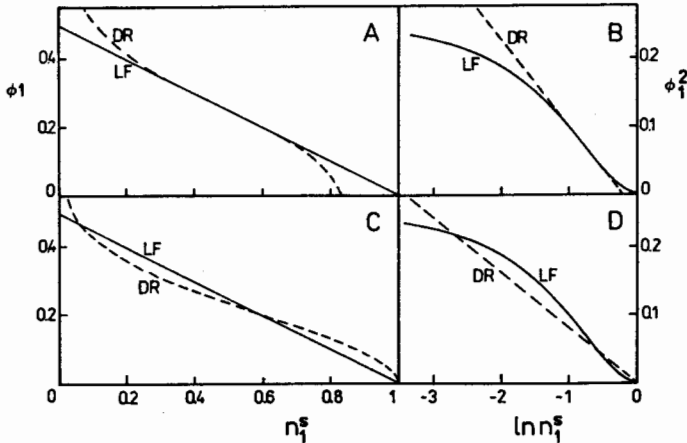


FIG. 1. Dependences ϕ_1 vs n_1^s ((A) and (C)) and ϕ_1^2 vs $\ln n_1^s$ ((B) and (D)) for LF (the solid lines) and DR (the dashed lines) equations. The LF parameters are $m = 0.5$ and $n_{m,LF}^s = 1$. The DR parameters are calculated according to Eqs. [4]–[6] ((A) and (B)) $n_{m,DR}^s = 0.8244$ and $B = 0.03125$) and Eq. [10] ((C) and (D)) $n_{m,DR}^s = 1$ and $B = 0.01989$).

for the parameters calculated according to Eqs. [4]–[6] and Eqs. [10] and [11]; these last equations describe correlations between DR and LF parameters in the whole concentration region. In the case of a narrow concentration region (Eqs. [12] and [13]) our new method gives results similar to those presented in Figs. 1A and 1B; in this region the convergence of DR and LF isotherms is good.

Figure 2 presents the excess and individual adsorption isotherms. The adsorption excess was calculated according to the well-known equation

$$n_1^e = n_m^s(x_1^s - x_1^l). \quad [14]$$

The LF parameters used to calculate the solid lines in Fig. 2 are the same as those in Fig. 1. Moreover, we assumed that $\ln \bar{K}_{12} = 3$. The

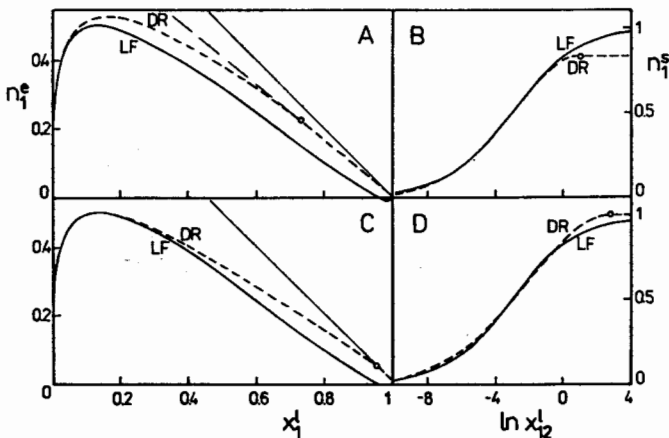


FIG. 2. Excess and individual adsorption isotherms corresponding to the dependences shown in Fig. 1. The LF parameters are the same as in Fig. 1 and $\ln \bar{K}_{12} = 3$. The DR parameters are the same as in Fig. 1 and $\ln \alpha$ was calculated according to Eq. [5] ((A) and (B)) $\ln \alpha = 1$) and Eq. [11] ((C) and (D)) $\ln \alpha = 2.903$). The thin solid and dashed lines are plotted according to the equation $n_1^e = n_m^s x_1^s$.

DR parameters used to calculate the dashed lines in Fig. 2 are also the same as in Fig. 1 and $\ln \alpha$ -values were calculated according to Eq. [5] (in Figs. 2A and 2B, $\ln \alpha = 1.0$) and Eq. [11] (in Figs. 2C and 2D, $\ln \alpha = 2.903$). It ought to be underlined that in the case of the new method the same value of n_m^s is used to calculate the DR and LF isotherms. It follows from Fig. 2 that agreement between the DR and LF isotherms in the whole concentration region is better in the case of the new method (the same value of n_m^s for both isotherms). Of course, the method published previously (14) gives better agreement in the region of moderate concentrations but is not useful to correlate the DR and LF parameters at lower and higher concentrations. It is worthy to note that the parameters obtained by means of Eqs. [10] and [11] fulfill inequalities expressed by Eqs. [4] and [5].

For most experimental adsorption systems we have no possibility to measure the adsorption capacity. In such a case, it is necessary to evaluate its value by using other indirect methods, e.g., those of Everett (19) or Schay and Nagy (20). Let us consider the course of the DR excess isotherms (see Fig. 3). These isotherms were calculated for different values of the parameters B and α . Part A of Fig. 3 presents the DR excess isotherms plotted for

the constant value of $\alpha = 1$ and three different values of $B = 0.1, 0.03,$ and 0.01 . It is evident that all curves, independent on the value of heterogeneity parameter, have a common linear segment for $x_1^1 > [\alpha/(1 + \alpha)]$. This means that the adsorption capacity evaluated according to the Schay method (19) may be considered as the DR capacity. However, this method may only be used for the systems showing a large linear segment, as is illustrated in Fig. 3B, which presents the curves for $B = 0.03$ and $\alpha = 10, 1,$ and 0.1 . Analyzing these curves a general condition may be formulated: the isotherms with the parameter α not exceeding unity have enough large linear segments to make evaluation of the adsorption capacity according to the Schay method possible (19). For other types of isotherms the other thermodynamic methods should be used to evaluate the adsorption capacity.

RESULTS AND DISCUSSION

In order to examine the effectiveness of Eqs. [1]–[13] the experimental data of binary solutions on silica gel and activated carbon were used (21–23). The systems are collected in Table I. All excess adsorption isotherms were interpreted by means of the following linear forms of Eqs. [1] and [2]:

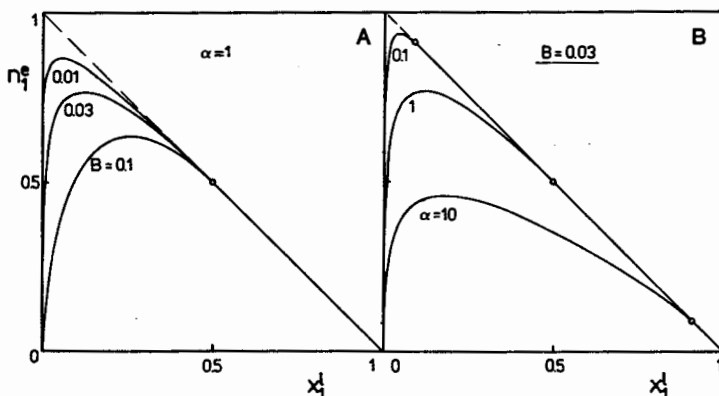


FIG. 3. Excess adsorption isotherms calculated according to Eqs. [1] and [14] for $n_m^s = 1$ and (A) $\alpha = 1$ and $B = 0.1, 0.03, 0.01$ and (B) $B = 0.03$ and $\alpha = 10, 1, 0.1$.

TABLE I
Experimental Adsorption Systems Studied

Code	Adsorbate	Adsorbent	Temp (K)	Ref
A	Benzene(1) + cyclohexane(2)	Silica gel	298	21
B	Toluene(1) + cyclohexane(2)	Silica gel	298	21
C	<i>p</i> -Xylene(1) + cyclohexane(2)	Silica gel	298	21
D	Methyl ethyl ketone(1) + benzene(2)	Silica gel	298	22
E	Diethyl ketone(1) + benzene(2)	Silica gel	298	22
F	Benzene(1) + cyclohexane(2)	Activated carbon	303	23
G	Benzene(1) + ethyl acetate(2)	Activated carbon	303	23
H	Ethyl acetate(1) + cyclohexane(2)	Activated carbon	303	23

$$\sqrt{-\ln x_1^s} = B \ln \alpha - B \ln x_{12}^1 \quad [15]$$

$$\ln x_{12}^s = m \ln \bar{K}_{12} + m \ln x_{12}^1. \quad [16]$$

In the case of systems A–E the adsorption capacity for the LF equation was found numerically by using Eq. [16] (21, 22), whereas, the DR adsorption capacity was evaluated according to the Schay method (20) (see Table II). However, for systems F–H we applied values of n_m^s measured experimentally by the authors of the data (23). In Fig. 4 the linear de-

pendence given by Eq. [15] is shown for all experimental systems studied. A good correlation among the experimental points and theoretical lines is observed. It indicates that the DR isotherm describes well the experimental data over a wide concentration region. The usefulness of the LF equation for interpreting the experimental systems studied was presented in our previous papers (21, 22).

In Table II the values of DR-optimized parameters obtained from Eq. [15] and LF-optimized parameters obtained from Eq. [16] are

TABLE II

Comparison of the DR and LF Parameters Obtained from Experimental Data by Using Eqs. [1] and [2], Respectively, and Calculated by Applying Eqs. [4]–[6] (Systems A–E) and [8] and [9] (Systems F–H) for the Experimental Systems Summarized in Table I

System	LF parameters						DR parameters					
	Optimized			Calculated			Optimized			Calculated		
	n_m^s	m	$\ln R_{12}$	n_m^s	m	$\ln R_{12}$	n_m^s	B	$\ln \alpha$	n_m^s	B	$\ln \alpha$
A	2.38	0.95	1.97	2.30	0.75	1.77	1.90 ^a	0.070	0.9	1.96	0.113	0.1
B	1.32	0.91	2.64	1.33	0.90	2.42	1.10 ^a	0.101	-0.2	1.09	0.104	-0.4
C	1.19	0.81	3.03	1.04	0.86	3.33	0.86 ^a	0.092	-1.0	0.98	0.082	-0.6
D	1.80	0.52	5.50	1.94	0.37	5.31	1.60 ^a	0.017	0.1	1.48	0.034	-1.6
E	1.40	0.50	5.26	1.46	0.42	5.06	1.20 ^a	0.022	-0.3	1.15	0.031	-1.3
F	4.89 ^b	0.72	1.30	—	0.68	1.16	4.89 ^b	0.038	3.1	—	0.042	2.7
G	5.22 ^b	0.86	0.60	—	0.84	0.55	5.22 ^b	0.058	2.9	—	0.061	2.8
H	4.62 ^b	0.71	0.75	—	0.67	0.52	4.62 ^b	0.037	3.8	—	0.042	3.3

Note. n_m^s [mmole/g]—values optimized by using Eq. [16] (21, 22).

^a Values evaluated according to Schay method (20).

^b Values obtained experimentally (23).

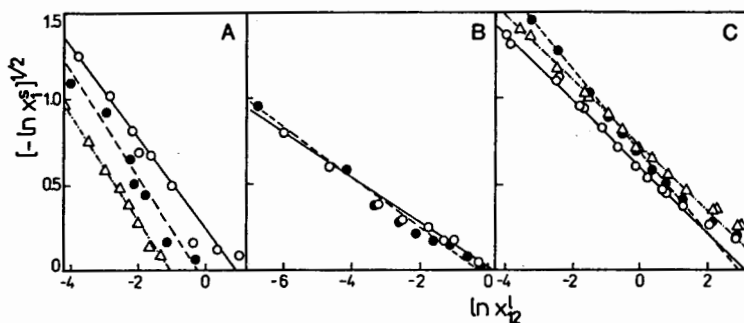


FIG. 4. Linear dependencies plotted according to Eq. [15] for the systems (A) A (O), B (●), C (Δ); (B) D (O), E (●); and (C) F (O), G (●), H (Δ) summarized in Table I. The values of adsorption parameters are given in Table II.

summarized. These DR and LF parameters were used to estimate the LF and DR parameters, respectively, by using Eqs. [4]–[6] (systems A–E) and Eqs. [8] and [9] (systems F–H). The calculated parameters are also summarized in Table II and compared with the DR- and LF-optimized parameters. Generally, it may be stated that the calculated values of both DR and LF equations are similar to those obtained from experimental data. Small deviations are only observed for certain systems. For the systems B and C (n_m^s value was obtained by the optimization procedure) and F–H (n_m^s values were measured experimentally) a satisfactory agreement between the optimized and calculated parameters is observed. Besides, the agreement between optimized and calculated values of $\ln \bar{K}_{12}$ is satisfactory for all systems studied. However, a considerable divergence was found in the case of systems A, D, and E for the parameters B , m , and especially $\ln \alpha$, which might be caused by experimental errors (see Figs. 4A and 4B). Additionally, greater discrepancies observed for $\ln \alpha$ -values result from extrapolative methods for their estimation. Generally, both methods used to evaluate the DR and LF parameters give satisfactory results and may be useful for predicting these parameters.

CONCLUSIONS

The proposed equations [8] and [9] and their special cases, Eqs. [10]–[13], give mean

values of the DR and LF parameters and therefore these equations are more useful to correlate the above parameters over a wide concentration region than what was proposed previously (14). The main difference in the present and previous (14) methods consists in the adsorption capacity determination; previously, this capacity was determined by an optimization procedure according to DR and LF equations (14), whereas, in the present treatment it was assumed to be constant for both isotherm equations according to its physical meaning. Generally, it may be stated that the optimized and calculated values of the DR and LF parameters are similar and that both methods give satisfactory results. In the case of adsorption systems with known values of adsorption capacity the present method is recommended.

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